POSSE HERRERA RUIZ

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
No. 14-042046- -00000-0000
Fecha: 2014-02-27 15:19:28 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 125

1000 2013

CHAMBERS

-Top Ranked Chambers Latin America 2012
-Firma Colombiana del año 2011
-Firma Colombiana del año 2010

Industria y Comercio
SUPERINTENDENCIA

DELEGATURA DE NUEVAS CREACIONES

SOLICITUD
FASE NACIONAL -PCT

21. EXPEDIENTE No. _____

54. TITULO: PROCEDIMIENTO DE FABRICACIÓN DE UN CATALIZADOR QUE COMPRENDE UNA ZEOLITA MODIFICADA CON FÓSFORO Y USO DE DICHA ZEOLITA

51. CLASIFICACION INTERNACIONAL:

B01J 29/40 (2006.01) **B01J 29/85 (2006.01)**
B01J 37/10 (2006.01) **B01J 37/28 (2006.01)**
C07C 1/20 (2006.01)

71. SOLICITANTE:

1. TOTAL RESEARCH & TECHNOLOGY FELUY

DOMICILIO:

1. Zone Industrielle C, B-7181 Seneffe BELGICA

74. APODERADO: HELENA CAMARGO WILLIAMSON

22. BOGOTÁ D.C., FEBRERO 27 DE 2014

Industria y Comercio
SUPERINTENDENCIA

el adhesivo de radicación

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DIRECCIÓN DE NUEVAS CREACIONES
SOLICITUD FASE NACIONAL –PCT

1	TIPO DE SOLICITUD	[X] Patente de invención [X] Capítulo I	[ ] Patente de Modelo de Utilidad [ ] Capitulo II

2 DATOS SOLICITUD INTERNACIONAL PCT (86)

Solicitud Internacional No.	PCT/EP2012/064580	Fecha	25/07/2012
Publicación Internacional No.	WO 2013/017497 A1	Fecha	07/02/2013

3 TÍTULO DE LA INVENCIÓN (200 caracteres o espacios máximos)

PROCEDIMIENTO DE FABRICACIÓN DE UN CATALIZADOR QUE COMPRENDE UNA ZEOLITA MODIFICADA CON FÓSFORO Y USO DE DICHA ZEOLITA

4 CLASIFICACIÓN INTERNACIONAL (CIP)

B01J 29/40 (2006.01) ***B01J 29/85*** (2006.01) ***B01J 37/10*** (2006.01) ***B01J 37/28*** (2006.01) ***C07C 1/20*** (2006.01)

SOLICITANTE (S) Esta persona también es inventor. Para datos adicionales utilizar hoja de información complementaria

	APELLIDOS O RAZÓN SOCIAL	NOMBRE	IDENTIFICACIÓN	TIPO
1	TOTAL RESEARCH & TECHNOLOGY FELUY			

6 DATOS DEL SOLICITANTE

DIRECCIÓN	Zone Industrielle C,	No. TELÉFONO	
CIUDAD	SENEFFE	CORREO ELECTRÓNICO	
DEPARTAMENTO/ESTADO		NACIONALIDAD O LUGAR DE CONSTITUCIÓN	BELGICA
PAÍS DE RESIDENCIA	BELGICA		

7 INVENTOR (ES) Para datos adicionales utilizar hoja de información complementaria

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1. NESTERENKO	1. Nikolai	1. RUSIA
2. MINOUX	2. Delphine	2. FRANCIA
3. ADAM	3. Cindy	3. BELGICA
4. DATH	4. Jean-Pierre	4. BELGICA

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4. BELGICA		4. Beloeil	4. Rue d'Ath, 53, B-7970

OTRO(S) SOLICITANTE(S) Y/O (OTRO(S)) INVENTOR(ES)

[ ] Los demás solicitantes y/o (demás) inventores se indican en una hoja a continuación.

9 [ ] **REPRESENTANTE LEGAL** [X] **APODERADO**

APELLIDOS	NOMBRES	IDENTIFICACIÓN
CAMARGO WILLIAMSON	HELENA	C.C 35.455.268 Bta. T.P 76985

DIRECCIÓN	CARRERA 7 Nº 71 – 52, TORRE A, PISO 5	No. TELÉFONO	3257300
CIUDAD	BOGOTÁ	CORREO ELECTRÓNICO	helena.camargo@phrlegal.com
PAÍS	COLOMBIA	No. RADICACIÓN DE PROTOCOLO DE PODER GENERAL	PODER PROT. 13 144198

72

10	DECLARACIONES DE PRIORIDAD ☒ SI ☐ NO			
	(33) PAÍS DE ORIGEN	CÓDIGO PAÍS	(31) NÚMERO	(32) FECHA (AAAA/MM/DD)
	1. COMUNIDAD EUROPEA		11176391.8	03/08/2011

11 DECLARACIÓN SOBRE USO DE RECURSOS GENÉTICOS O BIOLÓGICOS

Declaro que el objeto de la presente solicitud de patente fue obtenido a partir de recursos genéticos o biológicos de los que cualquiera de los países miembros de la Comunidad Andina es país de origen.

☐ SI ☒ NO

Nota: En caso afirmativo deberá anexar copia del contrato de acceso de recursos genéticos o productos derivados, o certificado o número de registro, expedido por la Autoridad competente.

12 DECLARACIÓN SOBRE USO DE CONOCIMIENTOS TRADICIONALES

Declaro que el objeto de la presente solicitud de patente fue obtenido a partir de conocimientos tradicionales de comunidades indígenas, afroamericanas o locales de países miembros de la Comunidad Andina.

☐ SI ☒ NO

Nota: En caso afirmativo deberá anexar la licencia o autorización de uso de conocimiento tradicional, o certificado, o número de registro expedido por la Autoridad competente.

13 REDUCCIÓN DE TASAS

Declaro que carezco de medios económicos para presentar la solicitud de patente.

☐ SI ☒ NO

Nota: En caso de ser persona natural y carecer de medios económicos, y por lo tanto, aplique la reducción de tasas a que se refiere la resolución vigente en tarifas, debe firmar la presente solicitud bajo la gravedad de juramento.

Micro, pequeñas y medianas empresas ☐
Universidades públicas o privadas ☐
Entidades sin ánimo de lucro ☐

Debe aportar los documentos que se indican en el numeral 17 de anexos

14 AUTORIZACIÓN DE NOTIFICACIÓN EN LÍNEA ☒ SI ☐ NO

Manifiesto que he leído y entendido perfectamente los términos y condiciones de uso de medios electrónicos para las notificaciones en línea a través de Internet de los actos administrativos proferidos por la Superintendencia de Industria y Comercio que deben ser notificados personalmente y, en consecuencia, autorizo el servicio de notificación a través de internet.

15	COMPROBANTE DE PAGO O PAGO ELECTRÓNICO	N°	Fecha

16 FIRMA DEL SOLICITANTE, DEL APODERADO O DEL REPRESENTANTE LEGAL

Junto a cada firma, indicar el nombre del firmante y su calidad (si tal calidad no es obvia al leer el petitorio)

HELENA CAMARGO WILLIAMSON

17 ANEXOS

Documentación Técnica
Solicitud Internacional en castellano

1. ☒ Descripción — N° de folios:
2. ☒ Reivindicaciones — N° Reivindicaciones:
3. ☒ Dibujos y/o figuras — N° folios:
4. ☒ Resumen.
5. ☐ Certificado de depósito de material biológico si fuera el caso.
6. ☐ Listado de secuencias de nucleótidos y/o aminoácidos en forma digital si fuera el caso.
7. ☐ Arte final 12 x 12.
8. ☐ Anexo formato digital.

Documentación Jurídica

9. ☒ Poderes, si fuera el caso, PODER PROT. 13 144198
10. ☐ Documento que legalmente pruebe la cesión del inventor al solicitante o a su causante.
11. ☐ Copia del contrato de acceso de recursos genéticos o productos derivados, certificado o número de registro, si fuera el caso.
12. ☐ Copia de la licencia o autorización de Conocimientos Tradicionales, certificado o número de registro, si fuera el caso.
13. **Reducción de tasas**

Micro, pequeñas o medinas empresas

☐ Copia simple de la declaración de renta del año inmediatamente anterior, o en su defecto prueba documental idónea.

☐ Documento de constancia de cumplimiento con lo establecido en la ley 905 de 2004.

Universidades públicas o privadas

☐ Copia acto de reconocimiento institucional emitido por el Ministerio de Educación

Entidades sin ánimo de lucro

☐ Copia de registro vigente en Cámara de comercio.
☐ Hoja de información complementaria.
☐ Otros, especificar

14. ☒ Comprobante de pago de la tasa de presentación de la solicitud.
15. ☐ Comprobante de pago por reivindicación de prioridad.
16. ☐ Comprobante de pago de la tasa por concepto de excedente de palabras en la publicación.
17. ☐ Comprobante de pago por reivindicación adicional a 10.

PROCEDIMIENTO DE FABRICACIÓN DE UN CATALIZADOR QUE COMPRENDE UNA ZEOLITA MODIFICADA CON FÓSFORO Y USO DE DICHA ZEOLITA

[Campo de la invención]

La presente invención se refiere a un procedimiento de fabricación de un catalizador que comprende una zeolita modificada con fósforo y al uso de dicha zeolita. Esta zeolita modificada es de interés en procedimientos en los que dicha zeolita funciona en presencia de vapor a alta temperatura. A modo de ejemplo puede citarse,

la deshidratación de alcohol para convertir al menos un alcohol en la correspondiente olefina,

el craqueo de olefinas C4+ (conocido también como PCO, procedimiento de conversión de olefinas) para crear una mezcla de etileno y propileno,

el craqueo de metanol y dimetiléter (conocido también como MTO) para producir olefinas ligeras tales como etileno y propileno, así como hidrocarburos pesados tales como butenos, la alquilación de aromáticos con alcoholes, a modo de ejemplo, alquilación de benceno o tolueno con metanol, etanol o propanol.

[Antecedentes de la invención]

Un catalizador eficaz es clave en la industrialización de la deshidratación de alcoholes, así como en los otros procedimientos anteriores. Uno de los primeros catalizadores empleados para la deshidratación de etanol era alúmina. Este catalizador es relativamente barato pero necesita una baja velocidad espacial, una alta temperatura de reacción y produce mucho etano, que es necesario separar. Las zeolitas, particularmente las zeolitas fosfatadas, resuelven un problema con la

actividad del catalizador y proporcionan una fracción de etileno que está relacionada con la calidad del polímero. Las zeolitas, particularmente las zeolitas fosfatadas, resuelven un problema con la actividad del catalizador. Se conocen catalizadores que comprenden una zeolita modificada con fósforo (la zeolita modificada con fósforo se denomina también zeolita-P). Las siguientes técnicas anteriores han descrito diversos procedimientos para fabricar dichos catalizadores.

El documento US 2006 106270 se refiere al uso de un sistema catalítico de doble función en la zona de reacción de síntesis de hidrocarburos de un procedimiento de oxigenado a propileno (OTP) que funciona a temperaturas relativamente altas, preferentemente con un diluyente de vapor y usa una tecnología de reactor de lecho móvil. El sistema catalítico de doble función comprende un tamiz molecular que tiene capacidad de doble función dispersado en una matriz de alúmina modificada con fósforo que contiene aniones fósforo y/o aluminio inestables. Se explica que el efecto de estabilización hidrotérmica que se observa cuando se utiliza esta matriz de alúmina modificada con fósforo está provocado por la migración o dispersión de los aniones fósforo y/o aluminio de esta matriz hacia el tamiz molecular unido. Estos aniones están disponibles entonces para reparar, hibridar y/o estabilizar la estructura básica del tamiz molecular frente al mecanismo de desaluminación bien conocido de destrucción o modificación de la estructura básica del tamiz molecular que se induce por exposición a vapor a temperaturas correspondientes a aquellas usadas en la zona de reacción OTP y en la zona de regeneración.

El documento US 5.231.064 se refiere a un catalizador fluido que comprende arcilla y una zeolita, al menos una de las cuales se ha tratado con un compuesto que contiene fósforo, por ejemplo, dihidrogenofosfato de amonio o

ácido fosfórico, y que se seca por pulverización a un bajo pH, preferentemente menor de aproximadamente 3. Se considera que dichos catalizadores presentan un desgaste ventajosamente reducido.

El documento EP 511013 A2 proporciona un procedimiento mejorado para la producción de olefinas C2-C5 a partir de materias primas olefínicas o parafínicas superiores o de olefina y parafina mixta. De acuerdo con esta técnica anterior, los materiales de alimentación de hidrocarburos se ponen en contacto con un catalizador ZSM-5 particular a temperaturas elevadas, una alta velocidad espacial y una baja presión parcial de hidrocarburo para producir olefinas inferiores. Los catalizadores se tratan con vapor antes de usarlos en la conversión de hidrocarburos. El procedimiento preferido es calentar el catalizador de 500 a 700 ºC, preferentemente de 550 a 600 ºC de 1 a 5 atmósferas, preferentemente de 1,5 a 3 atmósferas de vapor durante 1 a 48 horas, preferentemente de 15 a 30 horas. El componente catalítico activo es ZSM-5 que contiene fósforo que tiene una relación superficial Si/Al en el intervalo de 20-60. Preferentemente, el fósforo se añade a la ZSM-5 formada por impregnación de la ZSM-5 con un compuesto de fósforo de acuerdo con los procedimientos descritos, por ejemplo, en la patente de Estados Unidos 3.972.832. Menos preferentemente, el compuesto de fósforo puede añadirse a la mezcla multicomponente a partir de la cual se forma el catalizador. El compuesto de fósforo se añade en una cantidad suficiente para proporcionar una composición de ZSM-5 final que tiene un 0,1-10 % en peso de fósforo, preferentemente un 1-3 % en peso.

La ZSM-5 que contiene fósforo preferentemente se combina con aglutinantes o matrices conocidas tales como sílice, caolín, bentonita de calcio, alúmina, aluminato de sílice y similares. La ZSM-5 generalmente comprende un 1-

50 % en peso de la composición de catalizador, preferentemente un 5-30 % en peso y lo más preferentemente un 10-25 % en peso. No se introducen metales tales como Ca en el catalizador. El contenido de ZSM-5 está por debajo del 50 %, no hay etapa de prevaporización.

El documento EP 568 913 A2 describe un procedimiento para preparar un catalizador basado en ZSM-5 adaptado para usarlo en la conversión catalítica de metanol o dimetiléter en olefinas ligeras, que comprende las siguientes etapas consecutivas:

- mezclar un catalizador basado en zeolita ZSM-5 con sol de sílice y una solución de nitrato de amonio,
- amasar, moldear, secar y calcinar la mezcla,
- intercambiar la zeolita modificada con una solución de HCl a 70-90 ºC,
- secar y calcinar la zeolita modificada con H,
- impregnar la zeolita modificada con H con ácido fosfórico a presión reducida,
- secar y calcinar la zeolita modificada con P,
- impregnar la zeolita modificada con P con una solución de elementos de tierras raras a presión reducida,
- secar y calcinar la zeolita modificada con P-tierras raras,
- tratar hidrotérmicamente la zeolita modificada con P-tierras raras a 500-600 ºC con vapor de agua, y
- calcinar la zeolita modificada.

El documento WO 03 020667 se refiere a un procedimiento de fabricación de olefinas, particularmente etileno y propileno, a partir de una alimentación oxigenada, que comprende poner en contacto una alimentación oxigenada con al

menos dos catalizadores de zeolita diferentes para formar una composición de olefina, en la que uno primero de los catalizadores de zeolita contiene un tamiz molecular ZSM-5 y uno segundo de los catalizadores de zeolita contiene un tamiz molecular de zeolita seleccionado entre el grupo que consiste en ZSM-22, ZSM-23, ZSM-35, ZSM-48 y mezclas de los mismos. La ZSM-5 puede estar no modificada, modificada con fósforo, modificada con vapor que tiene un volumen de microporos reducido a no menos del 50 % de el de la ZSM-5 no vaporizada, o diversas mezclas de las mismas. De acuerdo con una realización, la zeolita se modifica con un compuesto que contiene fósforo para controlar la reducción en el volumen de poros. Como alternativa, la zeolita se vaporiza, y el compuesto de fósforo se añade antes o después de la vaporización. La cantidad de fósforo, según se mide en una base elemental, es del 0,05 % en peso al 20 % en peso, y preferentemente es del 1 % en peso al 10 % en peso, basado en el peso del tamiz molecular de zeolita. Preferentemente, la relación atómica de fósforo a la estructura básica de aluminio (es decir, en la estructura básica de la zeolita) no es mayor que 4:1 y más preferentemente que 2:1 a 4:1. La incorporación de un modificador de fósforo en el catalizador de la invención se consigue, de acuerdo con una realización, poniendo en contacto el tamiz molecular de zeolita ya sea en solitario o la zeolita en combinación con un aglutinante con una solución de un compuesto de fósforo apropiado. La zeolita sólida o el catalizador de zeolita se separa de la solución de fósforo, se seca y se calcina. En algunos casos, el fósforo añadido se convierte en su forma óxido en tales condiciones. El contacto con el compuesto que contiene fósforo generalmente se realiza a una temperatura de 25 °C a 125 °C durante un tiempo de 15 minutos a 20 horas. La concentración del fósforo en la zeolita puede ser del 0,01 % en peso al 30 % en peso. Esta técnica

anterior desvela una P-ZSM-5 no formulada.

El documento WO 2009 022990 A1 describe una composición catalítica para deshidratación de un alcohol para preparar un alqueno. La composición catalítica comprende un catalizador y un agente modificador que es ácido fosfórico, ácido sulfúrico o trióxido de tungsteno, o un derivado de los mismos. No hay aglutinante.

El documento EP 2348004 A1 se refiere a la deshidratación de etanol para fabricar etileno y la conversión de metanol para fabricar una mezcla de olefinas (MTO). El catalizador se prepara por el siguiente procedimiento: se vaporiza una ZSM-5, se introduce P poniendo en contacto la zeolita vaporizada con una solución de H_3PO_4 en condiciones de reflujo, la zeolita modificada con P se extruye con un aglutinante, se introduce calcio y el catalizador resultante se vaporiza dos horas a 600 °C. Esta técnica anterior desvela una P-ZSM-5 formulada, donde al menos una parte del fósforo se introdujo en la zeolita antes de la etapa de formulación.

El documento WO 2009-098262 A1 se refiere a la deshidratación de etanol para fabricar etileno. El catalizador se prepara mediante el siguiente procedimiento: se vaporiza una ZSM-5, se introduce P poniendo en contacto la zeolita vaporizada con una solución de H_3PO_4 en condiciones de reflujo, la zeolita modificada con P se extruye con un aglutinante, no habiendo vaporización final. No hay introducción de calcio.

El documento EP 2082802 A1 se refiere a diversos procedimientos petroquímicos, aunque no se cita la deshidratación de alcoholes para fabricar una olefina que tiene el mismo número de átomos de carbono que el alcohol. Entre los procedimientos citados están el craqueo de olefinas y la conversión de

oxigenados, por ejemplo metanol para fabricar una mezcla de etileno, propileno, butenos y diversos hidrocarburos. El catalizador se fabrica por el siguiente procedimiento: se vaporiza una ZSM-5, la zeolita vaporizada se extruye con un aglutinante, se introduce P poniendo en contacto la zeolita vaporizada con una solución de H_3PO_4 en condiciones de reflujo, se introduce calcio en forma de silicato metálico y el catalizador resultante se vaporiza dos horas a 600 °C.

El documento US 4.356.338 se refiere a la aromatización de hidrocarburos, aunque no se cita la deshidratación de alcoholes para fabricar una olefina que tiene el mismo número de átomos de carbono que el alcohol. La zeolita (ZSM-5) puede combinarse con un aglutinante y se trata mediante un componente que contiene P o vapor, o tanto vapor como componente que contiene P. No se introducen metales tales como Ca en el catalizador. Dicho catalizador tiene una coquización reducida.

Se ha descubierto ahora un nuevo procedimiento para fabricar zeolitas modificadas con P.

[Breve descripción de la invención]

La presente invención se refiere, en una primera realización, a un procedimiento para fabricar una zeolita modificada con fósforo que comprende las siguientes etapas, en este orden,

a) proporcionar una zeolita que comprenda al menos un anillo de diez miembros en la estructura, vaporizando opcionalmente dicha zeolita,

b) mezclar dicha zeolita de la etapa a) con al menos un componente seleccionado entre uno o más aglutinantes y aditivos de conformación, conformando después dicha mezcla,

c) realizar opcionalmente un intercambio de iones,

d) vaporizar opcionalmente el catalizador conformado, opcionalmente antes de la etapa c), al menos entre dicha vaporización de la etapa d) y la vaporización de la etapa a) una es obligatoria,

e) introducir fósforo en el catalizador para introducir al menos un 0,1 % en peso de fósforo, realizándose dicha introducción por impregnación en seco o deposición química en fase vapor,

f) introducir opcionalmente un metal, opcionalmente de forma simultánea con la etapa e),

g) lavar opcionalmente el catalizador,

h) calcinar opcionalmente el catalizador,

i) vaporizar el catalizador, denominada también etapa de equilibrado.

La presente invención se refiere, en una segunda realización, a un procedimiento para fabricar una zeolita modificada con fósforo que comprende las siguientes etapas, en este orden,

a) proporcionar una zeolita que comprende al menos un anillo de diez miembros en la estructura, vaporizando opcionalmente dicha zeolita,

b) mezclar dicha zeolita de la etapa a) con al menos un componente seleccionado entre uno o más aglutinantes y aditivos de conformación, conformando después dicha mezcla,

c) realizar opcionalmente un intercambio de iones,

d) vaporizar opcionalmente el catalizador conformado, opcionalmente antes de la etapa c), al menos entre dicha vaporización de la etapa d) y la vaporización de la etapa a) una es obligatoria,

e) introducir fósforo en el catalizador para introducir al menos un 0,1 % en peso de fósforo,

f) introducir opcionalmente un metal, opcionalmente de forma simultánea con la etapa e),

g) lavar opcionalmente el catalizador,

h) calcinar opcionalmente el catalizador,

i) vaporizar el catalizador, denominada también etapa de equilibrado, a una intensidad de vaporización (X) de al menos aproximadamente 2.

La "intensidad de vaporización (X)" descrita anteriormente es una definición importante, medible y crítica de las condiciones de tratamiento para las etapas d) que son útiles en la presente invención.

"Aproximadamente" significa que podría estar ligeramente por debajo de 2. Como se explicará más adelante, la intensidad describe condiciones de vaporización para conseguir desaluminación.

La cuestión es que los resultados de la vaporización son una función de la naturaleza del catalizador (tipo de zeolita, tipo de aglutinante, relación Si/Al, tamaño de cristal, cristalinidad, defectos de la estructura, la presencia de contaminantes ocluidos, etc.) así como de las condiciones del tratamiento usado. Queda claro que la intensidad mínima no es un valor absoluto, considerando los parámetros anteriores puede variar de un catalizador a otro. El experto en la materia puede determinar fácilmente la intensidad mínima. Para asegurarse, a modo ejemplo, puede ampliar la duración del tratamiento y/o aumentar la temperatura. Los parámetros críticos para el tratamiento incluyen principalmente presión parcial de vapor, temperatura y duración del tratamiento. Si los objetos del tratamiento fueran de una naturaleza similar, el efecto del tratamiento sería una función únicamente de la "intensidad de la vaporización".

Una vaporización o un tratamiento hidrotérmico de la zeolita por encima de

500 °C conduce a una desaluminación de la estructura básica. Un grado de desaluminación puede medirse mediante RMN de ^{27}Al, ^{29}Si MAS, por medición de acidez (como TPD NH_3) o por cualquier otro medio, bien conocido en la técnica anterior. Una tasa de desaluminación se define principalmente por los parámetros mencionados anteriormente, en concreto presión parcial de vapor, temperatura y duración del tratamiento.

Por lo tanto, la "intensidad de la vaporización (X)" se define como una relación de las tasas de desaluminación entre una condición experimental y una condición convencional.

La vaporización realizada a 600 °C en 100 % de vapor a presión atmosférica durante 2 horas se selecciona como una condición convencional para la presente invención.

La tasa de desaluminación (V) para el catalizador de la invención se da mediante la ecuación:

$$V \div Const \times P(H_2O)\,\hat{}\,1{,}5 \times t_{vap} / EXP\,(-0{,}03 \times T_{vap}),$$

donde P (H_2O) - presión parcial de vapor (P/Patm); T_{vap} - temperatura de vaporización en °C; t_{vap} - tiempo en horas (duración) del tratamiento y ÷ significa proporcional.

X (intensidad de vaporización) = $V_{condición\ experimental}/V_{condición\ convencional}$

Esta ecuación es válida para un intervalo de vaporización de 500 °C a 760 °C.

Por lo tanto, el valor de la intensidad de vaporización podría conseguirse incluso a una menor temperatura respecto a la usada en la condición convencional, pero para un mayor tiempo de duración.

La temperatura de 625 °C proporciona una intensidad de vapor aproximadamente 2 veces mayor que la condición convencional a igual tiempo de

presión parcial de vapor y duración del tratamiento.

Si la temperatura de la etapa de equilibrado está por encima de 760 ºC (fuera del intervalo), la duración de la vaporización es de al menos 0,1 horas y la presión parcial de vapor es de al menos 0,01 bar (1 kPa).

Ventajosamente, en la segunda realización, la temperatura de la etapa de equilibrado está en el intervalo de 625 a 870 ºC.

En una realización la zeolita conformada (o tamiz molecular) de la etapa b) contiene menos de 1000 ppm en peso de sodio, menos de 1000 ppm en peso de potasio y menos de 1000 ppm en peso de hierro.

En una realización, la zeolita conformada (o tamiz molecular) de la etapa b) contiene menos de 1000 ppm en peso de sodio.

En una realización la zeolita conformada (o tamiz molecular) de la etapa b) contiene menos de 100 ppm en peso de sodio.

En una realización la zeolita conformada (o tamiz molecular) de la etapa b) contiene menos de 100 ppm en peso de sodio, menos de 100 ppm en peso de potasio y menos de 500 ppm en peso de hierro.

La presente invención se refiere también al uso del catalizador preparado de acuerdo con el procedimiento anterior en procedimientos en los que dicho catalizador funciona en presencia de vapor a alta temperatura. "Alta temperatura" significa por encima de 300 ºC y hasta 800 ºC. A modo de ejemplo, puede citarse la deshidratación de alcohol para convertir al menos un alcohol en la olefina correspondiente, el craqueo de la olefina para fabricar olefinas más ligeras, el MTO y la alquilación de los aromáticos mediante alcoholes con olefinas y/o alcoholes, produciendo dicho procedimiento, a modo de ejemplo, para-xileno, etilbencenos y cumeno.

[Descripción detallada de la invención]

Respecto a la zeolita de la etapa a) que contiene al menos un anillo de 10 miembros en la estructura, pueden citarse los silicatos cristalinos. A modo de ejemplo, el MFI (ZSM-5, silicalita-1, boralita C, TS-1), MEL (ZSM-11, silicalita-2, boralita D, TS-2, SSZ-46), FER (Ferrierita, FU-9, ZSM-35), MTT (ZSM-23), MWW (MCM-22, PSH-3, ITQ-1, MCM-49), TON (ZSM-22, Theta-1, NU-10), EUO (ZSM-50, UE-1), MFS (ZSM-57) y ZSM-48 que es una familia de materiales microporosos que consiste en silicio, aluminio, oxígeno y opcionalmente boro.

Las estructuras de zeolita preferidas se seleccionan entre IMF, MTT, FER, MEL, TON, MWW, EUO, MFS.

En una realización, la zeolita es ZSM-5 con una relación atómica Si/Al que varía de 11 a 30, que ha sido preparada sin adición directa de una plantilla orgánica.

En una realización, la zeolita es zeolita MFI con una relación atómica Si/Al que varía de 30 a 200.

Las denominaciones de tres letras "MFI" y "MEL" representan cada una un tipo de estructura de silicato cristalino particular según se establece por la Comisión de Estructuras de la Asociación Internacional de Zeolitas. Los ejemplos de un silicato cristalino de tipo MFI son la zeolita sintética ZSM-5 y silicalita, y otros silicatos cristalinos de tipo MFI conocidos en la técnica. Los ejemplos de un silicato cristalino de la familia MEL son la zeolita ZSM-11 y otros silicatos cristalinos de tipo MEL conocidos en la técnica. Otros ejemplos son boralita D y silicalita-2, como describe la Asociación de Zeolitas Internacional (Atlas of zeolite structure types 1987, Butterworths). Los silicatos cristalinos preferidos tienen poros o canales definidos por diez anillos de oxígeno.

Los silicatos cristalinos son polímeros inorgánicos microporosos basados en una estructura básica de un tetraedro de XO_4 unidos entre sí por compartición de iones oxígeno, donde X puede ser trivalente (por ejemplo Al, B, ...) o tetravalente (por ejemplo Ge, Si, ...). La estructura cristalina de un silicato cristalino se define por el orden específico en el cual una red de unidades tetraédricas están unidas entre sí. El tamaño de las aberturas de poro del silicato cristalino se determina por el número de unidades tetraédricas o, como alternativa, de átomos de oxígeno, requeridos para formar los poros y la naturaleza de los cationes que están presentes en los poros. Poseen una combinación única de las siguientes propiedades: alta área superficial interna; poros uniformes con uno o más tamaños discretos; capacidad de intercambio de iones; buena estabilidad térmica; y capacidad para adsorber compuestos orgánicos. Puesto que los poros de estos silicatos cristalinos son de un tamaño similar a muchas moléculas orgánicas de interés práctico, controlan la entrada y salida de reactivos y productos, dando como resultado una selectividad particular en las reacciones catalíticas. Los silicatos cristalinos con estructura MFI poseen un sistema de poros de intersección bidireccional con los siguientes diámetros de poro: un canal recto a lo largo de [010]: 0,53-0,56 nm y un canal sinusoidal a lo largo de [100]: 0,51-0,55 nm. Los silicatos cristalinos con la estructura MEL poseen un sistema de poros recto de intersección bidireccional con canales rectos a lo largo de [100] que tienen diámetros de poro de 0,53-0,54 nm.

En una realización, la zeolita se pretrata con vapor. El pretratamiento se realiza en el intervalo de 420 a 870 °C, más preferentemente en el intervalo de 480 a 800 °C. La presión parcial de agua puede variar de 13 a 100 kPa. La atmósfera de vapor preferentemente contiene del 5 al 100 % en volumen de vapor,

con del 0 al 95 % en volumen de un gas, preferentemente nitrógeno o aire. El tratamiento con vapor preferentemente se realiza durante un periodo de 0,01 a 200 horas, más preferentemente de 0,05 a 50 horas, aún más preferentemente durante al menos 0,1 horas y, de una manera preferida, de 0,1 a 50 horas y, de una manera más preferida aún, de 0,5 a 50 horas y aún más preferido de 1 a 50 horas.

El tratamiento con vapor tiende a reducir la cantidad de aluminio tetraédrico en la estructura básica de silicato cristalino formando alúmina. Preferentemente, la cantidad de Al tetraédrico residual en la zeolita es entre el 60 y el 95 %. Este valor puede estimarse por RMN de ^{27}Al MAS o TPD NH_3. Opcionalmente, dicha alúmina puede retirarse por lixiviado con un ácido.

En una realización, la ZSM-5 con una relación atómica Si/Al que varía de 11 a 30, que ha sido fabricado sin adición directa de una plantilla orgánica, se pretrata con vapor.

Adicionalmente, si durante la preparación de la zeolita se han usado metales alcalinos o alcalinotérreos, el tamiz molecular podría someterse a una etapa de intercambio de iones. Convencionalmente, el intercambio de iones se realiza en soluciones acuosas usando sales de amonio o ácidos inorgánicos.

En una realización, la zeolita se somete a desaluminación, retirándose tanto como aproximadamente un 10 % en peso del aluminio. Tal desaluminación puede realizarse por cualquier técnica convencional conocida por sí misma, pero se realiza ventajosamente por vaporización, opcionalmente seguida de lixiviado. El silicato cristalino que tiene una relación Si/Al de al menos aproximadamente 30 a 200 puede sintetizarse tal cual o puede prepararse por desaluminación de un silicato cristalino con una relación Si/Al inicial menor.

Respecto a la etapa b), y el aglutinante, se selecciona de manera que sea resistente a la temperatura y las otras condiciones empleadas en los procedimientos en los que se usa el catalizador. El aglutinante puede ser un material inorgánico seleccionado entre sílice, zirconia, boratos, alúmina, sílice-alúminas, fosfatos, por ejemplo aluminofosfatos amorfos, fosfatos de calcio, arcillas, óxidos metálicos tales como ZrO_2 y/o metales o geles incluyendo mezclas de sílice y óxidos metálicos.

En una realización, el aglutinante es sustancialmente neutro (inerte) y se selecciona entre un material inorgánico seleccionado entre sílice, alúmina no ácida, aluminofosfatos amorfos, fosfatos metálicos, arcillas o una mezcla de los mismos. La naturaleza neutra del aglutinante permite limitar las reacciones secundarias conduciendo a la formación de oxigenados pesados e hidrocarburos, etano, acetaldehído, etc.

Un aglutinante particularmente preferido para el catalizador de la presente invención comprende sílice. Las proporciones relativas del material de silicato cristalino finamente dividido y el óxido inorgánico del aglutinante pueden variar ampliamente.

Los ejemplos no limitantes de fuentes de silicio incluyen silicatos, sílices precipitadas, por ejemplo, la gama Zeosil disponible en Rhodia, sílices pirógenas, por ejemplo, Aerosil-200 disponible en Degussa Inc., Nueva York, N.Y., compuestos de silicio tales como tetraalquil ortosilicatos, por ejemplo, tetrametil ortosilicato (TMOS) y tetraetilortosilicato (TEOS), sílices coloidales o suspensiones acuosas de los mismos, por ejemplo el sol Ludox-HS-40 disponible en E.I. du Pont de Nemours, Wilmington, Del., ácido silícico, silicato de metal alcalino o cualquier combinación de los mismos.

Otras formas adecuadas de sílice amorfa incluyen sílice en polvo, tal como Ultrasil VN3SP (disponible en el mercado en Degussa).

Otros ejemplos no limitantes de una fuente de sílice sólida adecuada son sílices pirógenas hidrófilas granuladas especiales, sílice mesoporosa de calidad EXP y sílice precipitada de alta área superficial SIPERNAT de Evonik, HiSil 233 EP (disponible en PPG Industries) y Tokusil (disponible en Tokuyama Asia Pacific).

Además, las fuentes de sílice amorfa adecuadas incluyen soles de sílice, que son dispersiones coloidales estables de partículas de sílice amorfa en un medio acuoso o un líquido orgánico, preferentemente agua.

Los ejemplos no limitantes de soles de sílice disponibles en el mercado incluyen aquellos comercializados con los nombres comerciales Nyacol (disponible en Nyacol Nano Technologies, Inc. o PQ Corp.), Nalco (disponible en Nalco Chemical Company), Ultra-Sol (disponible en RESI Inc), Ludox (disponible en W.R. Grace Davison) y NexSil (disponible en NNTI).

Muchos soles de sílice se preparan a partir de silicato sódico e inevitablemente contienen sodio. Sin embargo, se ha descubierto que la presencia de iones sodio puede provocar la sinterización del cuerpo de la sílice a alta temperatura y/o afectar al rendimiento catalítico. Por lo tanto, si se usan soles de sílice que contienen sodio, puede requerirse una etapa de intercambio de iones para reducir o retirar el sodio. Para evitar realizar etapas de intercambio de iones, es conveniente usar soles de sílice que contengan poco o idealmente ninguna traza detectable de sodio y que tengan un valor de pH de menos de 7. Más preferentemente, el sol de sílice usado en el procedimiento es ligeramente ácido con o sin estabilizadores poliméricos. Los ejemplos no limitantes de soles de sílice

que no contienen trazas detectables de sodio incluyen Bindzil 2034DI, Levasil 200, Nalco 1034A, Ultra-Sol 7H o NexSil 20A.

En cualquier caso, la dispersión de sílice preparada con alquilamonio podría ser útil. Los ejemplos no limitantes de soles de sílice de bajo contenido de sodio comerciales estabilizados con amoniaco o cationes alquilamonio incluyen LUDOX TMA (disponible en W.R. Grace Davison) o VP WR 8520 disponible en Evonik.

Los soles de sílice con un contenido de SiO_2 mayor del 30 % e incluso hasta el 50 % en peso, por ejemplo, W1250, W1836, WK341, WK7330 de Evonik son particularmente preferidos.

La fuente de silicio preferida es un sol de sílice o una combinación de sol de sílice con sílice precipitada o pirógena.

Los tipos de soles de sílice usados para formar un catalizador unido para su uso en un procedimiento de deshidratación de alcohol están disponibles en el mercado como acuasoles u organosoles, que contienen partículas de sílice coloidales dispersadas. Por ejemplo, puede usarse silicato sódico como un sol de sílice. Por otro lado, puede usarse también un gel de sílice, sílice pirógena o pirogénica, para proporcionar un aglutinante de sílice en el catalizador de tamiz molecular. El ácido silícico es otra posible fuente de sílice. Ventajosamente, el aglutinante contiene una baja cantidad de sodio, por debajo de 1000 ppm.

Se sabe que las arcillas son esencialmente inertes en un amplio intervalo de condiciones de reacción. Las arcillas adecuadas incluyen productos disponibles en el mercado tales como caolín, caolinita, montmorillonita, atapulgita, saponita y bentonita. Estas arcillas pueden usarse tal cual se extraen en su estado natural, o pueden emplearse también en formas altamente activas, típicamente activadas mediante un procedimiento de tratamiento con ácido. Los proveedores

comerciales de estas arcillas incluyen Thiele Kaolin Company, American Colloidal Co., y otros.

Las arcillas contribuyen a reforzar como un aglutinante que refuerza las propiedades de resistencia a desgaste de las partículas de catalizador, y las arcillas en combinación con los aglutinantes contribuyen a la dureza de las partículas. Las arcillas también empiezan como pequeñas partículas y tienen una mayor densidad, de manera que cuando se combinan con el tamiz molecular y el aglutinante proporcionan partículas más densas, confiriendo las características deseables de mayor densidad.

Las arcillas usadas en este procedimiento para formar un producto endurecido incluyen, aunque sin limitación, caolín, caolinita, montmorillonita, saponita, bentonita y haloisita.

En una realización, el material aglutinante a menudo, en una cierta extensión, es de naturaleza porosa y puede ser eficaz para promover la conversión deseada de etanol a etileno. El aglutinante podría ser una única entidad amorfa, o una combinación de dos o más compuestos amorfos individuales.

En una realización relacionada, el catalizador (zeolita + aglutinante) tiene un volumen de poros entre 30 Å y 1000 Å de al menos 0,25 cc/g, ventajosamente entre 0,25 y 1 cc/g, preferentemente al menos 0,26 cc/g, lo más preferible entre 0,27-0,92 cc/g. "cc" significa cm^3.

En una realización, el material aglutinante posee propiedades ácidas y puede promover también la conversión del etanol.

Al hacer referencia a estos tipos de aglutinantes que pueden usarse, debe observarse que el término sílice-alúmina no significa una mezcla física de sílice y

alúmina sino que se refiere a un material ácido y amorfo que ha sido co-gelificado o co-precipitado. Este término se conoce bien en la técnica y se describe, por ejemplo, en los documentos US-A-3.909.450 B1; US-A-3.274.124 B1 y US-A-4.988.659 B1. En este sentido, es posible formar otros materiales amorfos co-gelificados o co-precipitados que también sean eficaces como materiales aglutinantes o cargas. Estos incluyen sílice-zirconias, sílice-torias, sílice-berilias, sílice-titanias, sílice-alúmina-torias, sílice-alúmina-zirconias, aluminofosfatos, mezclas de éstos y similares.

En otra realización, el catalizador contiene materiales de alúmina tales como oxihidróxido de aluminio, γ-alúmina, boehmita, diáspora y alúminas de transición tales como α-alúmina, β-alúmina, γ-alúmina, δ-alúmina, ε-alúmina, κ-alúmina y ρ-alúmina, trihidróxido de aluminio tal como gibbsita, bayerita, nordstrandita, doyelita y mezclas de los mismos.

Es deseable proporcionar un catalizador que tenga una buena resistencia al aplastamiento. Esto se debe a que en el uso comercial es deseable evitar que el catalizador se rompa en materiales pulverulentos. Tales aglutinantes de óxido se han empleado normalmente solo para fines de mejorar la resistencia al aplastamiento del catalizador.

La composición de catalizador puede prepararse, como se ha indicado anteriormente, por cualquiera de los procedimientos descritos en la técnica. Ventajosamente, sin embargo, las partículas de catalizador se combinan con el material aglutinante inicialmente por mezcla en seco, después en un líquido, preferentemente agua, preferentemente con un plastificante, para producir una pasta.

Como plastificante (aditivo de conformación), puede mencionarse uno que

se descompondrá durante cualquier tratamiento térmico posterior, por ejemplo calcinación. Los materiales adecuados para este fin incluyen, por ejemplo, derivados de celulosa alquilados, hidroxietilcelulosa (HEC), tilosa, alginato amónico, polivinil pirrolidona, glicerol y polietilenglicol.

Además de potenciar las propiedades de resistencia del catalizador, el material aglutinante permite que la cristalita en polvo del tamiz molecular se una en tamaños de partícula más grandes adecuados para procedimientos catalíticos comerciales. La formulación de la mezcla b) puede formarse en una amplia diversidad de formas, incluyendo extruidos, esferas, píldoras y similares.

La pasta mezclada uniformemente puede conformarse posteriormente, por ejemplo mediante secado por pulverización para producir microesferas, granularse o preferentemente por extrusión.

La pasta se extruye después, por ejemplo en una extrusora de pistón, en filamentos, por ejemplo cilíndricos, se seca, se calcina de nuevo y se trocea en trozos de una longitud deseada.

Respecto a las proporciones de la zeolita, el uno o más aglutinantes y aditivos de conformación, ventajosamente la proporción de la zeolita es del 5 al 95 % en peso del catalizador. El catalizador comprende la zeolita y al menos un componente seleccionado entre uno o más aglutinantes y aditivos de conformación. La cantidad de zeolita que está contenida en el catalizador varía más ventajosamente del 15 al 90 por ciento en peso del catalizador total, preferentemente del 20 al 85 por ciento en peso del catalizador.

Una vez que la composición de catalizador de tamiz molecular se ha conformado y está en un estado sustancialmente seco o secado, se realiza ventajosamente un tratamiento con calor, por ejemplo calcinación, para endurecer

y/o activar la composición. Por lo tanto, el tratamiento con calor se realiza preferentemente a una temperatura de al menos 400 °C, durante un periodo de 1 a 48 horas. La calcinación puede realizarse, por ejemplo, en un calcinador rotatorio, un calcinador de lecho fluido o un horno discontinuo.

Respecto al intercambio de iones de la etapa c), el fin es conseguir ventajosamente un tamiz molecular zeolítico formulado con un aglutinante inerte, antes de ponerlo en contacto con un agente de fosfatación, que tiene menos de 1000 ppm en peso de metales alcalinos y alcalinotérreos, Na, K, Fe, así como menos de 200 ppm de elementos redox y nobles tales como Zn, Cr, Rh, Mn, Ni, V, Mo, Co, Cu, Cd, Pt, Pd, Ir, Ru, Re. Esto puede conseguirse mediante una etapa de intercambio de iones opcional conocida por sí misma.

En una realización, el catalizador comprende un tamiz molecular que ha sido tratado para reducir el contenido de metal alcalino a menos de 100 ppm antes o después de la etapa de vaporización d).

Aunque en principio el mezclado con el aglutinante y el intercambio de iones pueden realizarse en cualquier orden, ventajosamente el intercambio de iones se realiza después del conformado pero antes de la introducción de fósforo.

Ventajosamente, la etapa de intercambio de iones se realiza sobre un catalizador calcinado conformado antes o después de la etapa de vaporización d).

Respecto a la vaporización de la etapa d), se conoce también como pre-vaporización por referencia a la vaporización final de la etapa i). El tratamiento se realiza en el intervalo de 420-870 °C, más preferentemente en el intervalo de 480 a 800 °C. La presión parcial de agua puede variar de 13 a 100 kPa. La atmósfera de vapor preferentemente contiene del 5 al 100 % en volumen de vapor, con del 0 al 95 % en volumen de un gas, preferentemente nitrógeno o aire. El tratamiento

con vapor se realiza preferentemente durante un periodo de 0,01 a 200 horas, más preferentemente de 0,05 a 50 horas, aún más preferentemente durante al menos 0,1 horas y, de una manera preferida, de 0,1 a 50 horas y, de una manera aún más preferida, de 0,5 a 50 horas y lo más preferido de 1 a 50 horas.

El tratamiento con vapor tiende a reducir la cantidad de aluminio tetraédrico en la estructura básica de silicato cristalino formando alúmina. Preferentemente, la cantidad de Al tetraédrico residual en la zeolita es entre el 60 y el 95 %. Este valor puede estimarse mediante RMN de ^{27}Al MAS o TPD NH_3.

Respecto a la introducción de P de la etapa e), dicha introducción de fósforo puede realizarse a presión reducida o atmosférica a una temperatura de 10 a 400 °C. Puede proporcionarse una fuente no limitante de fósforo en un medio acuoso o no acuoso.

En una realización, el medio no acuoso se selecciona entre el grupo que contiene etanol, metanol u otros alcoholes.

Las técnicas preferidas son impregnación y deposición química en fase vapor. Dichas técnicas son obligatorias en la primera realización de la invención.

Estas técnicas implican un residuo mínimo a tratar y permiten mantener sustancialmente todo el fósforo en el catalizador.

En una realización, el precursor catalítico se trata mediante una fuente de fósforo inyectado en un flujo de vapor. En este caso, la fosfatación se realiza en condiciones de vaporización moderada con un flujo de vapor que contiene fósforo a 100-400 °C.

En una realización, el fósforo se introduce mediante un tratamiento del precursor catalítico (zeolita + aglutinante) en una solución que contiene una fuente de fósforo a una temperatura de 25-100 °C durante 0,1-96 horas, seguido de

filtración o evaporación.

En una realización, la cantidad de dicha solución ácida que contiene P es ventajosamente entre 2 y 10 litros por kg de zeolita más aglutinante. Un periodo típico es de aproximadamente 0,5 a 24 horas. Ventajosamente, la solución ácida acuosa que contiene la fuente de P tiene un pH de 3, ventajosamente de 2 o menor. Ventajosamente, dicha solución ácida acuosa es ácido fosforoso, una mezcla de ácidos fosforosos y ácido orgánico o inorgánico o mezclas de sales de ácidos fosforosos y ácidos orgánicos o inorgánicos. Los ácidos fosforosos o las sales correspondientes pueden ser de tipo fosfato ($[PO_4]^{3-}$, que es tribásica), fosfito ($[HPO_3]^{2-}$que es dibásica) o hipofosfito ($[H2PO_2]^{-1}$ que es monobásica). Del tipo fosfato pueden usarse también di- o polifosfatos ($[P_nO_{3n+1}]^{(n+2)-}$). El contacto de la zeolita + aglutinante con el componente que contiene P puede realizarse en condiciones de reflujo.

En una realización preferida se usa la técnica de impregnación por humectación incipiente. En este caso, el fósforo se introduce por impregnación usando una cantidad limitada de agua líquida que se somete a un contacto con un catalizador. Este procedimiento se conoce también como impregnación en seco.

La humectación incipiente (HI) o la impregnación por humectación incipiente (IHI) es una técnica usada comúnmente para la síntesis de catalizadores heterogéneos. Típicamente, el precursor (compuestos que contienen fósforo) se disuelve en una solución acuosa u orgánica. El volumen de solución, que se usa para disolver el precursor, es sustancialmente el mismo que el volumen de poros del precursor catalítico que contiene tanto aglutinante como zeolita. Después, la solución que contiene precursor se añade a un precursor catalítico. La acción capilar dirige la solución hacia los poros. El catalizador puede secarse después y

calcinarse para dirigir los componentes volátiles al interior de la solución, depositando el fósforo sobre la superficie del catalizador.

La muestra puede secarse o calcinarse antes de la impregnación. La impregnación podría realizarse a temperatura ambiente o temperatura elevada (30-100 ºC).

La capacidad de adsorción típicamente se mide impregnando la zeolita extruida secada con agua hasta que la zeolita se humedece completamente. El pesaje de la zeolita antes y después de la impregnación da la capacidad de absorción:

$$Capacidad\ de\ absorción\ (\%) = \frac{peso\ tras\ la\ impregnación - peso\ en\ seco}{peso\ en\ seco} * 100$$

En una realización, se usa una solución de H_3PO_4 para la impregnación.

Ventajosamente, se usa una mezcla de H_3PO_4 con sus sales de amonio que proporcionan un pH de la solución acuosa mayor que 2,0 para la impregnación.

En una realización, las fuentes de fósforo son componentes sustancialmente libres de metales, por ejemplo H_3PO_4, fosfatos de amonio o compuestos-P orgánicos. La expresión "sustancialmente libre de metal" significa una proporción de metal que no tiene efecto negativo sobre la introducción de P. A modo de ejemplo, esta proporción puede estar por debajo de 1000 ppm en peso.

La cantidad de fósforo en el catalizador puede ser del 0,5 al 30 % en peso, pero preferentemente del 0,5 al 9 % en peso.

En una realización, la etapa de fosfatación se realiza antes de o simultáneamente con la introducción de óxidos metálicos.

Respecto a la etapa f), la introducción de metal, puede ser de uno o más metales. Ventajosamente, dichos metales se seleccionan entre metales

alcalinotérreos o de tierras raras. El metal alcalinotérreo o de tierras raras M preferentemente se selecciona entre uno o más de: Mg, Ca, Sr, Ba, La, Ce. Más preferentemente, M es un metal alcalinotérreo. Más preferentemente aún, M es Ca. Particularmente en el caso de modificación con P por vaporización y lixiviación, M puede ser un metal de tierras raras tal como La y Ce. Ventajosamente, el metal se introduce en una forma soluble.

El componente que contiene M preferentemente está en forma de un compuesto orgánico, una sal, un hidróxido o un óxido. El compuesto preferentemente está en una forma solubilizada cuando se pone en contacto con el tamiz molecular. Como alternativa, la solución del compuesto que contiene M puede formarse después de poner el contacto el tamiz molecular con dicho compuesto.

Los posibles compuestos que contienen M incluyen compuestos tales como sulfato, formiato, nitrato, acetato, haluros, oxihaluros, oxalato, boratos, carbonatos, hidróxido, óxido y mezclas de los mismos. Puede citarse carbonato de calcio.

Aquellos compuestos que contienen M, que son poco solubles en agua, pueden disolverse para formar una solución bien solubilizada por calentamiento y/o modificando del pH de la solución por adición de ácido fosfórico, acético o nítrico o las sales de amonio correspondientes de dichos ácidos.

Respecto a la etapa g), puede preverse una etapa de lavado. De acuerdo con la presente invención, el catalizador se trata con agua durante un periodo de tiempo de 0,1 a 48 horas, preferentemente durante un periodo de tiempo de aproximadamente 0,5 a 36 horas y, lo más preferentemente, de aproximadamente 1 a 24 horas. El agua estaba a una temperatura entre aproximadamente 20 °C y 180 °C, preferentemente entre aproximadamente 20 y 100 °C y, lo más

preferentemente, entre aproximadamente 25 ºC y 60 ºC. A modo de ejemplo, el agua puede estar a 30 ºC. Después del tratamiento con agua, el catalizador puede secarse a aproximadamente >60 ºC. Opcionalmente, el agua puede contener al menos un sólido disuelto seleccionado entre el grupo que consiste en cloruro de amonio, fosfato de amonio, sulfato de amonio, acetato de amonio, carbonato de amonio, nitrato de amonio y mezclas de los mismos.

Respecto a la etapa h), dicha calcinación puede realizarse en aire o en un gas inerte, típicamente a una temperatura de 350 a 900 ºC durante un periodo de 1 a 48 horas. Opcionalmente, el aire o un gas inerte pueden contener vapor en una concentración del 10 al 90% en volumen.

Respecto a la etapa i), en la primera realización de la invención, esta puede realizarse en el intervalo de 420 a 870 ºC, preferentemente en el intervalo de 480 a 870 ºC, preferentemente de 625 a 870 ºC y más preferentemente de 700 a 800 ºC, aún más preferentemente en el intervalo de 720 a 800 ºC. Como alternativa, puede realizarse en el intervalo de 420 a 600 ºC, preferentemente de 420 a 580 ºC.

En la segunda realización de la invención, esta se realiza por vaporización con una intensidad de vaporización por encima de aproximadamente 2 o, como alternativa, a una temperatura por encima de 625 ºC, preferentemente de 625 a 870 ºC y más preferentemente de 700 a 800 ºC, aún más preferentemente en el intervalo de 720 a 800 ºC. La presión parcial de agua puede variar de 13 a 100 kPa. La atmósfera de vapor preferentemente contiene del 5 al 100 % de un volumen de vapor del 0 al 95 % en volumen de un gas, preferentemente nitrógeno o aire. El tratamiento con vapor se realiza preferentemente durante un periodo de 0,01 a 200 horas, preferentemente de 0,05 a 50 horas, más preferentemente

durante al menos 0,1 horas y de una manera preferida de 0,1 a 50 horas y de una manera más preferida de 0,5 a 50 horas y aún más preferido de 1 a 50 horas.

Respecto al procedimiento de deshidratación para convertir un alcohol en una olefina, este procedimiento se ha descrito en muchas solicitudes de patente. Pueden citarse los documentos WO/2009/098262, WO/2009/098267, WO/2009/098268 y WO 2009/098269, cuyos contenidos se incorporan en la presente solicitud. El alcohol es cualquier alcohol con la condición de que pueda deshidratarse a la olefina correspondiente. Ventajosamente, el alcohol tiene dos o más átomos de carbono. La olefina correspondiente es una olefina que tiene el mismo número de carbonos que el alcohol. A modo de ejemplo, pueden mencionarse alcoholes que tienen de 2 a 10 átomos de carbono. Ventajosamente, la invención es interesante para etanol, propanol, butanol y feniletanol.

Respecto al craqueo de olefinas, más precisamente la presente invención se refiere a un procedimiento para craquear una materia prima de hidrocarburo rica en olefinas que es selectiva hacia olefinas ligeras en el efluente. En particular, las materias primas olefínicas de refinerías o plantas petroquímicas pueden convertirse selectivamente tal como para redistribuir el contenido de olefina de la materia prima en el efluente resultante. Dicho craqueo de una materia prima rica en olefina a menudo se menciona en la siguiente descripción y en las reivindicaciones, como PCO (procedimiento de craqueo de olefina). Respecto a la materia prima de hidrocarburo que contiene una o más olefinas enviadas al reactor PCO, de acuerdo con la presente invención, el craqueo de olefinas se realiza en el sentido de que las olefinas en una corriente de hidrocarburos se craquean en olefinas más ligeras y selectivamente en propileno. La materia prima y el efluente preferentemente tienen sustancialmente el mismo contenido en peso de olefina.

Típicamente, el contenido de olefina del efluente está dentro del ±15 % en peso, más preferentemente ±10 % en peso del contenido de olefina de la materia prima. La materia prima puede comprender cualquier clase de corriente de hidrocarburo que contenga olefina. La materia prima puede comprender típicamente del 10 al 100 % en peso de olefinas y adicionalmente puede alimentarse no diluida o diluida con un diluyente, incluyendo el diluyente opcionalmente un hidrocarburo no olefínico. En particular, la materia prima que contiene olefina puede ser una mezcla de hidrocarburo que contiene olefinas normales y ramificadas en el intervalo de carbono de C_4 a C_{10}, más preferentemente en el intervalo de carbono C_4 a C_6, opcionalmente en una mezcla con parafinas y/o aromáticos normales y ramificados en el intervalo de carbono de C_4 a C_{10}. Típicamente, la corriente que contiene olefina tiene un punto de ebullición de aproximadamente 15 a aproximadamente 180 °C. Con respecto al procedimiento PCO, dicho procedimiento es conocido por sí mismo. Se ha descrito en los documentos EP 1036133, EP 1035915, EP 1036134, EP 1036135, EP 1036136, EP 1036138, EP 1036137, EP 1036139, EP 1194502, EP 1190015, EP 1194500 y EP 1363983, cuyo contenido se incorpora en la presente invención.

Respecto al MTO, dicho procedimiento produce olefinas ligeras tales como etileno y propileno así como hidrocarburos pesados tales como butenos. Dicho procedimiento MTO es la conversión de metanol o dimetiléter por contacto con un tamiz molecular que puede ser una zeolita modificada con P.

Respecto a la alquilación de compuestos aromáticos con olefinas y alcoholes, dicho procedimiento produce, a modo de ejemplo, para-xileno, etilbencenos y cumenos. Se sabe que la alquilación de productos aromáticos, por ejemplo la metilación de tolueno, ocurre sobre un catalizador ácido,

particularmente sobre zeolita o un catalizador de tipo zeolita. En particular, para este procedimiento se han usado catalizadores de zeolita tipo ZSM-5, zeolita Beta y silicaaluminofosfato (SAPO).

Un experto en la materia apreciará también que las olefinas preparadas mediante el procedimiento de deshidratación de la presente invención, a modo de ejemplo, pueden polimerizarse. Cuando la olefina es etileno, a modo de ejemplo, puede

polimerizarse para formar polietilenos,

dimerizarse a buteno y después isomerizarse a isobutano, haciendo reaccionar dicho isobuteno con etanol para producir ETBE,

dimerizarse a butano seguido de reacción con etileno por metátesis para producir propileno;

convertirse en propileno sobre un catalizador metálico, ácido o bifuncional, usado para alquilación de benceno para formar etil-benceno,

dimerizarse a 1-buteno, trimerizarse a 1-hexeno o tetramerizarse a 1-octeno, haciéndose reaccionar adicionalmente dichos comonómeros de alfa-olefina con etileno para producir polietileno

dimerizarse a 1-buteno, dicho 1-buteno se isomeriza a 2-buteno y dicho 2-buteno se convierte adicionalmente con etileno por reacción de metátesis en propileno y dicho propileno puede polimerizarse a polipropileno,

convertirse en óxido de etileno y glicol o

convertirse en cloruro de vinilo.

La presente invención se refiere también a dichos polietilenos, polipropileno, propileno, buteno, hexano, octeno, isobuteno, ETBE, cloruro de vinilo, óxido de etileno y glicol.

Cuando la olefina es propileno, a modo de ejemplo, puede polimerizarse para formar polipropileno, usarse para alquilación de aromáticos, etc...

[Ejemplos]

EJEMPLO 1

Una muestra de zeolita ZSM-5 (Si/Al = 12) en forma de NH_4 (que contenía 250 ppm de Na y sintetizada sin plantilla) se combinó con un aglomerante de sílice en una proporción 80:20 seguido de adición de aditivos de extrusión y conformado. Un contenido de Na final en el catalizador era 320 ppm.

La muestra extruida se secó durante 2 horas a 140 ºC, se calcinó durante 2 horas a 600 ºC seguido de vaporización a 550 ºC durante 6 horas en vapor al 100 %.

El sólido vaporizado se impregnó por humectación incipiente con una solución acuosa de ácido fosfórico para introducir aproximadamente un 3 % en peso de fósforo al catalizador. El sólido impregnado se secó durante 16 horas a 110 ºC.

Después, la muestra fosfatada se impregnó por humectación incipiente con una solución de nitrato de calcio obtenida por disolución de carbonato de calcio para introducir aproximadamente un 1 % en peso de calcio al sólido. El sólido impregnado se secó durante 16 horas a 110 ºC.

El catalizador resultante, que contenía un 2,8 % en peso de fósforo y un 0,8 % de calcio, se vaporizó a 600 ºC durante 2 horas en 100 % de vapor (intensidad de vaporización 1). La muestra se identifica en lo sucesivo en el presente documento como **muestra A.**

El catalizador resultante que contenía aproximadamente un 2,8 % en peso

de fósforo y un 0,8 % de calcio se vaporizó a 750 °C durante 1 hora en 100 % de vapor (intensidad de vaporización 45). La muestra se identifica en lo sucesivo en el presente documento como **muestra B.** El volumen total de poros medido por porosimetría de intrusión de mercurio es de 0,36 cm^3/g.

Los ensayos de catalizador se realizaron sobre 1 ml de granos de catalizador (malla 35-45) cargados en un reactor tubular con un diámetro interno de 11 mm. Una mezcla de 25 % en peso de EtOH/75 % en peso de H_2O se puso en contacto con el catalizador descrito en el ejemplo I en un reactor de lecho fijo a 380 °C, WHSV = 7 h^{-1}, P = 200 kPa absolutos. Los resultados se dan en la Tabla 1 a continuación. Los valores son los porcentajes en peso en una base de carbono.

Ejemplo 2

Una muestra de zeolita ZSM-5 (Si/Al = 12) en forma de NH_4 (que contenía 250 ppm de Na y sintetizada sin plantilla) se combinó con un aglutinante de sílice en una proporción 80:20 seguido de adición de aditivos de extrusión y conformado. Un contenido final de Na en el catalizador era 320 ppm.

La muestra extruida se secó durante 16 horas a 110°°C, se calcinó durante 10 horas a 600 °C seguido de vaporización a 550 °C durante 6 horas en 100 % de vapor.

La zeolita conformada vaporizada se puso después en contacto con una solución acuosa de H_3PO_4 (85% en peso) en condiciones de humectación incipiente. Después, se introdujo 1 g de $CaCO_3$. Después de la agitación durante 30 minutos, el sistema se enfría a temperatura ambiente y el exceso de solución se retira por filtración sin lavado. El sólido recuperado se seca a 110 °C durante 16 horas seguido de vaporización a 600 °C durante 2 horas en 100 % de vapor (intensidad de vaporización 1).

El catalizador resultante contenía aproximadamente un 1,7 % en peso de fósforo y un 0,4 % en peso de calcio. La muestra se identifica en lo sucesivo en el presente documento como **muestra C.**

Los rendimientos del catalizador se evaluaron después en las mismas condiciones operativas descritas anteriormente, usando 1 ml de catalizador (malla 35-45) cargado en un reactor tubular con un diámetro interno de 11 mm. Una mezcla de 25 % EtOH/75 % H_2O se ha procesado sobre el catalizador C, en un reactor de lecho fijo a 380 °C, WHSV = 7 h^{-1}, P = 200 kPa absolutos. Los resultados se dan en la Tabla 1. Los valores son los porcentajes en peso en una base de carbono.

EJEMPLO 3

Una muestra de zeolita ZSM-5 (Si/Al = 12) en forma de NH_4 (que contenía 250 ppm de Na y sintetizada sin plantilla) se combinó con un aglutinante de sílice en una proporción 80:20 seguido de adición de aditivos de extrusión y conformado. Un contenido de Na final en el catalizador era 320 ppm.

La muestra extruida se secó durante 16 horas a 110 °C, se calcinó durante 10 horas a 600 °C, seguido de vaporización a 550 °C durante 6 horas en 100 % de vapor.

Se impregnaron por humectación incipiente 12 g del sólido vaporizado con una solución acuosa que contenía 1,54 g de $NH_4H_2PO_4$. El sólido impregnado se secó durante 16 horas a 110 °C.

Después, la muestra fosfatada se impregnó en húmedo de forma incipiente con una solución de nitrato de calcio obtenida por disolución de 0,3 g de carbonato de calcio en ácido nítrico. El sólido impregnado se secó durante 16 horas a 110 °C seguido de vaporización a 600 °C durante 2 horas en 100 % de vapor (intensidad

de vaporización 1).

El catalizador resultante contenía aproximadamente un 2,54 % en peso de fósforo y un 0,82 % en peso de calcio. La muestra se identifica en lo sucesivo en el presente documento como **muestra D**.

Los rendimientos del catalizador se evaluaron después en las mismas condiciones operativas que las descritas anteriormente usando 1 ml de catalizador (malla 35-45) cargado en un reactor tubular con un diámetro interno de 11 mm. Una mezcla de 25 % en peso EtOH/75 % en peso de H_2O se había procesado sobre el catalizador D, en un reactor de lecho fijo a 380 °C, WHSV = 7 h^{-1}, P = 200 kPa absolutos. Los resultados se dan en la Tabla 1. Los valores son los porcentajes en peso en una base de carbono.

Tabla 1

Muestra	A	B	C	D
P (kPa abs.)	200	200	200	200
T (°C)	380	380	380	380
WHSV (H-1)	7	7	7	7
Conversión EtOH (% en peso CH_2)	99,9	99,8	99,9	99,9

(continuación)

Muestra	A	B	C	D
DEE	0,0	0,0	0,0	0,0
Acetaldehído	0,31	0,17	0,17	0,13
EtOH	0,10	0,20	0,05	0,05
Rendimiento en una base de C (% en peso CH_2)				
CH4	0,00	0,00	0,00	0,00
C2	0,13	0,06	0,11	0,12
C2=	97,9	99,0	97,3	97,4
C3=	0,56	0,07	0,7	0,8
olef C4+	0,86	0,48	1,6	1,4
Desconocido	0,10	0,06	0,07	0,08
Selectividad en una base de C (% en peso CH_2)				
C2=	98,0	99,20	97,4	97,4
Pureza de corte C2 (%)	99,87	99,94	99,88	99,87

EJEMPLO 4

Una muestra de zeolita ZSM-5 (Si/Al = 12) en forma de NH_4 (que contenía 250 ppm de Na y sintetizada sin plantilla) se combinó con un aglutinante que contenía sílice y caolín en una proporción 70:10:20 seguido de adición de aditivos de extrusión y conformado.

La muestra extruida se secó durante 2 horas a 140 °C, se calcinó durante 10 horas a 600 °C seguido de vaporización a 550 °C durante 6 horas en 100 % de vapor.

El sólido vaporizado se impregnó por humectación incipiente con una solución acuosa de ácido fosfórico para introducir aproximadamente el 3 % en peso de fósforo al catalizador. El sólido impregnado se secó durante 16 horas a 110 °C.

Después, la muestra fosfatada se impregnó por humectación incipiente con

una solución de nitrato de calcio obtenida por disolución de carbonato de calcio para introducir aproximadamente un 1 % en peso de calcio al sólido. El sólido impregnado se secó durante 16 horas a 110 °C.

El catalizador resultante, que contenía un 2,94 % en peso de fósforo y un 0,8 % de calcio, se vaporizó a 750 °C durante 2 horas en 100 % de vapor (intensidad de vaporización 90). La muestra se identifica en lo sucesivo en el presente documento como **muestra E**.

EJEMPLO 5

Una muestra de zeolita ZSM-5 (Si/Al = 12) en forma de NH_4 (sintetizada sin plantilla) se calcinó durante 10 horas a 600 °C seguido de vaporización a 550 °C durante 6 horas en 100 % de vapor.

Se impregnaron por humectación incipiente 100 g de sólido vaporizado (impregnación en seco) con una solución acuosa que contenía 9,86 g de ácido fosfórico. El sólido impregnado se secó durante 16 horas a 110 °C.

Después, 16 g de la muestra fosfatada se extruyeron con 4 g de aglutinante de sílice y 0,4 g de $CaCO_3$.

El catalizador resultante se calcinó a 600 °C durante 10 horas seguido de vaporización a 600 °C durante 2 horas en 100 % de vapor (intensidad de vaporización 1). La muestra se identifica en lo sucesivo en el presente documento como **muestra F**.

EJEMPLO 6 (ensayo PCO)

Los ensayos de catalizador se realizaron sobre 0,8 g de granos de catalizador (malla 35-45) cargados en el reactor tubular. La materia prima que no contiene sustancialmente nada de olefina cíclica C4 (~60 %) se sometió a craqueo catalítico en presencia de un catalizador en un reactor de lecho fijo a T_{en} -550 °C,

WHSV = 16 h^{-1}, P = 150 kPa abs.. Los resultados se dan en la Tabla 2. Los valores en la Tabla 2 son el rendimiento catalítico promedio durante 1-10 horas en la corriente, dados en porcentajes en peso sobre una base de carbono.

Los datos dados a continuación ilustran una buena actividad de craqueo y una alta selectividad de la zeolita-P en la conversión de olefinas C4 a propileno y etileno.

Tabla 2

Muestra	E	F
P (kPa abs.)	150	150
T_{en} (°C)	550	550
WHSV (h^{-1})	16	16
Conversión de olefinas C4, %	65,4	65,2
Pureza de C3, %	**94,9**	**96,0**
Rendimiento en base de C, %		
Metano	0,07	0,14
Aromáticos	1,2	1,4
Propano	1,0	0,8
Etileno	3,5	3,4
Propileno	19,5	19,1

REIVINDICACIONES

1. Procedimiento para fabricar una zeolita modificada con fósforo que comprende las siguientes etapas, en este orden,

a) proporcionar una zeolita que comprende al menos un anillo de diez miembros en la estructura, vaporizando opcionalmente dicha zeolita,

b) mezclar dicha zeolita de la etapa a) con al menos un componente seleccionado entre uno o más aglutinantes y aditivos de conformación, conformando después dicha mezcla,

c) realizando opcionalmente un intercambio de iones,

d) vaporizando opcionalmente el catalizador conformado, opcionalmente antes de la etapa c), al menos entre dicha vaporización de la etapa d) y la vaporización de la etapa a) una es obligatoria,

e) introducir fósforo en el catalizador para introducir al menos un 0,1 % en peso de fósforo, realizándose dicha introducción por impregnación en seco o deposición química en fase vapor,

f) introducir opcionalmente un metal, opcionalmente de forma simultánea con la etapa e),

g) lavar opcionalmente el catalizador,

h) calcinar opcionalmente el catalizador,

i) vaporizar el catalizador, denominada también etapa de equilibrado.

2. Procedimiento de acuerdo con la reivindicación 1, en el que la introducción de fósforo de la etapa e) se realiza por humectación incipiente (HI) o impregnación por humectación incipiente (IHI).

3. Procedimiento de acuerdo con la reivindicación 1 o 2, en el que la vaporización de la etapa i) se realiza en el intervalo de 420 a 870 ºC.

4. Procedimiento de acuerdo con la reivindicación 3, en el que la vaporización de la etapa i) se realiza en el intervalo de 480 a 870 ºC.

5. Procedimiento de acuerdo con la reivindicación 4, en el que la vaporización de la etapa i) se realiza en el intervalo de 625 a 870 ºC.

6. Procedimiento de acuerdo con la reivindicación 5, en el que la vaporización de la etapa i) se realiza en el intervalo de 700 a 800 ºC.

7. Procedimiento de acuerdo con la reivindicación 6, en el que la vaporización de la etapa i) se realiza en el intervalo de 720 a 800 ºC.

8. Procedimiento de acuerdo con la reivindicación 3, en el que la vaporización de la etapa i) se realiza en el intervalo de 420 a 600 ºC.

9. Procedimiento de acuerdo con la reivindicación 8, en el que la vaporización de la etapa i) se realiza en el intervalo de 420 a 580 ºC.

10. Procedimiento para fabricar una zeolita modificada con fósforo que comprende las siguientes etapas, en este orden,

a) proporcionar una zeolita que comprende al menos un anillo de diez miembros en la estructura, vaporizando opcionalmente dicha zeolita,

b) mezclar dicha zeolita de la etapa a) con al menos un componente seleccionado entre uno o más aglutinantes y aditivos de conformación, conformando después dicha mezcla,

c) realizar opcionalmente un intercambio de iones,

d) vaporizar opcionalmente el catalizador conformado, opcionalmente antes de la etapa c), al menos entre dicha vaporización de la etapa d) y la vaporización de la etapa a) una es obligatoria,

e) introducir fósforo en el catalizador para introducir al menos un 0,1 % en peso de fósforo,

f) introducir opcionalmente un metal, opcionalmente de forma simultánea con la etapa e),

g) lavar opcionalmente el catalizador,

h) calcinar opcionalmente el catalizador,

i) vaporizar el catalizador, denominada también etapa de equilibrado, a una intensidad de vaporización (X) de al menos aproximadamente 2.

11. Procedimiento de acuerdo con la reivindicación 10, en el que la vaporización de la etapa i) se realiza en el intervalo de 625 a 870 ºC.

12. Procedimiento de acuerdo con la reivindicación 11, en el que la vaporización de la etapa i) se realiza en el intervalo de 700 a 800 ºC.

13. Procedimiento de acuerdo con la reivindicación 12, en el que la vaporización de la etapa i) se realiza en el intervalo de 720 a 800 ºC.

14. Procedimiento de acuerdo con una cualquiera de las reivindicaciones anteriores, en el que la zeolita conformada (o tamiz molecular) de la etapa b) contiene menos de 100 ppm en peso de sodio.

15. Procedimiento de acuerdo con la reivindicación 14, en el que la zeolita conformada (o tamiz molecular) de la etapa b) contiene menos de 100 ppm en peso de sodio, menos de 100 ppm en peso de potasio y menos de 500 ppm en peso de hierro.

16. Procedimiento de acuerdo con una cualquiera de las reivindicaciones 1 a 13, en el que la zeolita conformada (o tamiz molecular) de la etapa b) contiene menos de 1000 ppm en peso de sodio.

17. Procedimiento de acuerdo con la reivindicación 16, en el que la zeolita conformada (o tamiz molecular) de la etapa b) contiene menos de 1000 ppm en peso de sodio, menos de 1000 ppm en peso de potasio y menos de 1000 ppm en peso de hierro.

18. Procedimiento de acuerdo con una cualquiera de las reivindicaciones anteriores, en el que la zeolita es seleccionada entre MFI, MTT, FER, MEL, TON, MWW, EUO, MFS.

19. Procedimiento de acuerdo con la reivindicación 18, en el que la zeolita es ZSM-5 con una relación atómica Si/Al que varía de 11 a 30, que ha sido fabricada sin adición directa de una plantilla orgánica.

20. Procedimiento de acuerdo con la reivindicación 18, en el que la zeolita es MFI con una relación atómica Si/Al que varía de 30 a 200.

21. Procedimiento de acuerdo con una cualquiera de las reivindicaciones anteriores, en el que la cantidad de fósforo en el catalizador es del 0,5 al 30 % en peso.

22. Procedimiento de acuerdo con la reivindicación 21, en el que la cantidad de fósforo en el catalizador es del 0,5 al 9 % en peso.

23. Procedimiento de acuerdo con una cualquiera de las reivindicaciones anteriores, en el que el metal en la etapa f) es un metal alcalinotérreo o metal de tierras raras M preferentemente seleccionado entre uno o más de: Mg, Ca, Sr, Ba, La, Ce.

24. Procedimiento de acuerdo con una cualquiera de las reivindicaciones anteriores, en el que el catalizador (zeolita + aglutinante) tiene un volumen de poros entre 30 Å y 1000 Å de al menos 0,25 cm^3/g.

25. Uso del catalizador fabricado de acuerdo con una cualquiera de las reivindicaciones anteriores, en procedimientos en los que dicho catalizador funciona en presencia de vapor a una temperatura por encima de 300 ºC y hasta 800 ºC.

26. Procedimiento para deshidratar un alcohol para convertir al menos dicho alcohol en la olefina correspondiente que tiene el mismo número de átomos de carbono que el alcohol, en el que dicha deshidratación se realiza en presencia de un catalizador fabricado de acuerdo con una cualquiera de las reivindicaciones 1 a 24.

27. Procedimiento para realizar el craqueo de olefinas para fabricar olefinas más ligeras en el que dicho craqueo se realiza en presencia de un catalizador fabricado de acuerdo con una cualquiera de las reivindicaciones 1 a 24.

28. Procedimiento para realizar el craqueo de metanol o dimetiléter para producir olefinas ligeras tales como etileno y propileno en el que dicho craqueo se realiza en presencia de un catalizador fabricado de acuerdo con una cualquiera de las reivindicaciones 1 a 24.

29. Procedimiento para realizar la alquilación de aromáticos con alcoholes u olefinas, en el que dicha alquilación se realiza en presencia de un catalizador fabricado de acuerdo con una cualquiera de las reivindicaciones 1 a 24.

RESUMEN

La presente invención se refiere, en una primera realización, a un procedimiento para fabricar una zeolita modificada con fósforo que comprende las siguientes etapas, en este orden, a) proporcionar una zeolita que comprende al menos un anillo de diez miembros en la estructura, vaporizando opcionalmente dicha zeolita, b) mezclar dicha zeolita de la etapa a) con al menos un componente seleccionado entre uno o más aglutinantes y aditivos de conformación, conformando después dicha mezcla, c) realizar opcionalmente un intercambio de iones, d) vaporizar opcionalmente el catalizador conformado, opcionalmente antes de la etapa c), al menos entre dicha vaporización de la etapa d) y la vaporización de la etapa a) una es obligatoria, e) introducir fósforo en el catalizador para introducir al menos un 0,1 % en peso de fósforo, realizándose dicha introducción por impregnación en seco o deposición química en fase vapor, f) introducir un metal, opcionalmente de forma simultánea con la etapa e), g) lavar opcionalmente el catalizador, h) calcinar opcionalmente el catalizador, i) vaporizar el catalizador, denominada también etapa de equilibrado. En una segunda realización puede introducirse fósforo por cualquier medio y, en la etapa i), la intensidad de la vaporización (X) es de al menos aproximadamente 2. En dicha segunda realización el catalizador se vaporiza ventajosamente a una temperatura por encima de 625 ºC, preferentemente en el intervalo de 700 a 800 ºC. El metal de la etapa f) es ventajosamente calcio. La presente invención se refiere también al uso de dicho catalizador en la deshidratación de alcohol, el craqueo de olefinas para fabricar olefinas más ligeras, el MTO y la alquilación de aromáticos mediante alcoholes con olefinas y/o alcoholes.

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(54) **Title**: METHOD FOR MAKING A CATALYST COMPRISING A PHOSPHORUS MODIFIED ZEOLITE AND USE OF SAID ZEOLITE

(57) **Abstract**: The present invention relates, in a first embodiment, to a method to make a phosphorus modified zeolite comprising the following steps in this order, a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite, b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture, c) optionally making a ion-exchange, d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory, e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus, said introduction being made by dry impregnation or chemical vapor deposition, f) introducing a metal, optionally simultaneously with step e), g) optionally washing the catalyst, h) optionally calcinating the catalyst, i) steaming the catalyst, also referred to as the equilibration step. In a second embodiment phosphorus can be introduced by any means and at step i) the steaming severity (X) is at least about 2. In said second embodiment the catalyst is advantageously steamed at a temperature above 625°C, preferably in the range 700 to 800°C. The metal of step f) is advantageously Calcium. The present invention also relates to the use said catalyst in the alcohol dehydration, the olefin cracking to make lighter olefins, the MTO and the alkylation of aromatics by alcohols with olefins and/or alcohols.

METHOD FOR MAKING A CATALYST COMPRISING A PHOSPHORUS MODIFIED ZEOLITE AND USE OF SAID ZEOLITE

[Field of the invention]

The present invention relates to a method for making a catalyst comprising a phosphorus modified zeolite and the use of said zeolite. This modified zeolite is of interest in processes wherein said zeolite is operated in presence of steam at high temperature. By way of example one can cite,
the alcohol dehydration to convert at least an alcohol into the corresponding olefin,
the cracking of C4+ olefins (also known as OCP, olefins conversion process) to make a mixture of ethylene and propylene,
the cracking of methanol or dimethylether (also known as MTO) to produce light olefins such as ethylene and propylene as well as heavy hydrocarbons such as butenes,
the alkylation of aromatics by alcohols, by way of example alkylation of benzene or toluene with methanol, ethanol or propanol.

[Background of the invention]

An efficient catalyst is a key in industrialization of dehydration of alcohols as well as in the other above processes. One of the early catalysts employed for the dehydration of ethanol was alumina. This catalyst is relatively cheap but needs low space velocity, high reaction temperature and makes a lot of ethane, which needs to be separated. Zeolites, particularly phosphated zeolites, solve a problem with catalyst activity and provide with ethylene fraction, which is closed to polymer grade. Zeolites, particularly phosphated zeolites, solves a problem with catalyst activity. Catalysts comprising a phosphorus modified zeolite (the phosphorus modified zeolite is also referred as P-zeolite) are known. The following prior arts have described various methods to make said catalysts.

US 2006 106270 relates to the use of a dual-function catalyst system in the hydrocarbon synthesis reaction zone of an oxygenate to propylene (OTP) process that operates at relatively high temperatures preferably with a steam diluent and uses moving bed reactor technology. The dual-functional catalyst system comprises a molecular sieve having dual-function capability dispersed in a phosphorus-modified alumina matrix containing labile phosphorus and/or aluminum anions. It is explained that the hydrothermal stabilization effect that is observed when this phosphorus-modifed alumima matrix is utilized is caused by migration or dispersion of phosphorus and/or aluminum anions from this matrix into the bound molecular sieve. These anions are then available to repair, anneal and/or stabilize the framework of the molecular sieve against the well-known dealumination mechanism of molecular sieve framework destruction or modification that is induced by exposure to steam at temperatures corresponding to those used in the OTP reaction zone and in the regeneration zone.

US 5,231,064 is directed to a fluid catalyst comprising clay and a zeolite, at least one of which has been treated with a phosphorus containing compound, for example ammonium dihydrogen phosphate or phosphoric acid, and which is spray dried at a low pH, preferably lower than about 3. Said catalysts are deemed to advantageously exhibit reduced attrition.

EP 511013 A2 provides an improved process for the production of C2-C5 olefins from higher olefinic or paraffinic or mixed olefin and paraffin feedstocks. In accordance with this prior art, the hydrocarbon feed materials are contacted with a particular ZSM-5 catalyst at elevated temperatures, high space velocity and low hydrocarbon partial pressure to produce lower olefins. The catalysts is treated with steam prior to use in the hydrocarbon conversion. The preferred method is to heat the catalyst at 500 to 700°C, preferably 550 to 600°C, under 1 to 5 atmospheres,

preferably 1.5 to 3 atmospheres steam for 1 to 48 hours, preferably 15 to 30 hours. The active catalyst component is phosphorus-containing ZSM-5 having a surface Si/Al ratio in the range 20-60. Preferably, the phosphorus is added to the formed ZSM-5 as by impregnating the ZSM-5 with a phosphorus compound in accordance with the procedures described, for example, in U.S. Patent 3,972,832. Less preferably, the phosphorus compound can be added to the multicomponent mixture from which the catalyst is formed. The phosphorus compound is added in amount sufficient to provide a final ZSM-5 composition having 0. 1-10 wt.% phosphorus, preferably 1-3 wt.%.

The phosphorus-containing ZSM-5 is preferably combined with known binders or matrices such as silica, kaolin, calcium bentonite, alumina, silica aluminate and the like. The ZSM-5 generally comprises 1-50 wt.% of the catalyst composition, preferably 5-30 wt.% and most preferably 10-25 wt.%. There is no introduction of metals such as Ca in the catalyst. ZSM-5 content is below 50%, there is no presteaming step.

EP 568913 A2 describes a method for preparing a ZSM-5 based catalyst adapted to be used in the catalytic conversion of methanol or dimethyl ether to light olefins, wherein it comprises the following consecutive steps:

- mixing a zeolite ZSM-5 based catalyst with silica sol and ammonium nitrate solution,
- kneading, moulding, drying and calcining the mixture,
- exchanging the modified zeolite with a solution of HCl at 70-90°C,
- drying and calcining the H-modified zeolite,
- impregnating the H-modified zeolite with phosphoric acid under reduced pressure,
- drying and calcining the P-modified zeolite,
- impregnating the P-modified zeolite with a solution of rare earth elements under reduced pressure,
- drying and calcining the P-rare earths-modified zeolite,

- hydrothermally treating the P-rare earths-modified zeolite at 500-600°C with water vapour, and
- calcining the modified zeolite.

WO 03 020667 relates to a process of making olefin, particularly ethylene and propylene, from an oxygenate feed, comprising contacting an oxygenate feed with at least two different zeolite catalysts to form an olefin composition, wherein a first of the zeolite catalysts contains a ZSM-5 molecular sieve and a second of the zeolite catalysts contains a zeolite molecular sieve selected from the group consisting of ZSM-22, ZSM-23, ZSM-35, ZSM-48, and mixtures thereof. The ZSM-5 can be unmodified, phosphorus modified, steam modified having a micropore volume reduced to not less than 50% of that of the unsteamed ZSM-5, or various mixtures thereof. According to one embodiment, the zeolite is modified with a phosphorus containing compound to control reduction in pore volume. Alternatively, the zeolite is steamed, and the phosphorus compound is added prior to or after steaming. The amount of phosphorus, as measured on an elemental basis, is from 0.05 wt.% to 20 wt. %, and preferably is from 1 wt.% to 10 wt.%, based on the weight of the zeolite molecular sieve. Preferably, the atomic ratio of phosphorus to framework aluminum (i.e. in the zeolite framework) is not greater than 4:1 and more preferably from 2:1 to 4:1. Incorporation of a phosphorus modifier into the catalyst of the invention is accomplished, according to one embodiment, by contacting the zeolite molecular sieve either alone or the zeolite in combination with a binder with a solution of an appropriate phosphorus compound. The solid zeolite or zeolite catalyst is separated from the phosphorus solution, dried and calcined. In some cases, the added phosphorus is converted to its oxide form under such conditions. Contact with the phosphorus-containing compound is generally conducted at a temperature from 25°C to 125°C for a time from 15 minutes to 20 hours. The concentration of the phosphorus in the zeolite may be from 0.01 wt.% to 30 wt.%. This prior art discloses a non-formulated P-ZSM-5.

WO 2009 022990 A1 describes a catalyst composition for dehydration of an alcohol to prepare an alkene. The catalyst composition comprises a catalyst and a modifying agent which is phosphoric acid, sulfuric acid or tungsten trioxide, or a derivative thereof. There is no binder.

EP 2348004 A1relates to the dehydration of ethanol to make ethylene and conversion of methanol to make a mixture of olefins (MTO). The catalyst is made by the following process : A ZSM-5 is steamed, P is introduced by contacting the steamed zeolite with an H3PO4 solution under reflux conditions, the P modified zeolite is extruded with a binder, calcium is introduced and the resulting catalyst is steamed two hours at 600°C. This prior art discloses a formulated P-ZSM-5, where at least a part of phosphorous was introduced into zeolite before formulation step.

WO 2009-098262 A1 relates to the dehydration of ethanol to make ethylene. The catalyst is made by the following process : A ZSM-5 is steamed, P is introduced by contacting the steamed zeolite with an H3PO4 solution under reflux conditions, the P modified zeolite is extruded with a binder, there is no final steaming. There is no introduction of calcium.

EP 2082802 A1 relates to various petrochemical processes, the dehydration of alcohols to make an olefin having the same number of carbon atoms as the alcohol is not cited. Among the cited processes are the cracking of olefins and the conversion of oxygenates, e.g. methanol to make a mixture of ethylene, propylene, butenes and various hydrocarbons. The catalyst is made by the following process : A ZSM-5 is steamed, the steamed zeolite is extruded with a binder, P is introduced by contacting the steamed zeolite with an H3PO4 solution under reflux conditions, calcium is introduced in form of metal silicate and the resulting catalyst is steamed two hours at 600°C.

US 4,356,338 relates to the aromatization of hydrocarbon, the dehydration of alcohols to make an olefin having the same number of carbon atoms as the alcohol is not cited. The zeolite (ZSM-5) may be combined with a binder and is treated by a P containing component or steam or both steam and P containing component. There is no introduction of metals such as Ca in the catalyst. The said catalyst has a reduced coking.

It has now been discovered a new process to make P modified zeolites.

[Brief description of the invention]

The present invention relates, in a first embodiment, to a method to make a phosphorus modified zeolite comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory,

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus, said introduction being made by dry impregnation or chemical vapor deposition,

f) optionally introducing a metal, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step.

The present invention relates, in a second embodiment, to a method to make a phosphorus modified zeolite comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory,

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus,

f) optionally introducing a metal, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step, at a steaming severity (X) of at least about 2.

The above-described "steaming severity (X)" is an important, measurable and critical definition of treatment conditions for the steps d) which are useful in the instant invention.

"About" means that it could be slightly under 2. As explained hereunder the severity describes conditions of steaming to achieve a dealumination.

The matter is that the results of the steaming is a function of the nature of catalyst (type of zeolite, type of binder, Si/Al ratio, crystal size, crystallinity, structure defects, the presence of occluded contaminants etc) as well as of conditions of the treatment used. It is clear that the minimum severity is not an absolute value, considering the above parameters it can vary from a catalyst to another. The man skilled in the art can easily determine the minimun severity. To be sure he can, by way of example, extend the duration of treatment and/or increase the temperature.

The critical parameters for the treatment include mainly steam partial pressure, temperature and duration of the treatment. If the objects of the treatment were similar nature the effect of the treatment is only a function of the "steaming severity".

A steaming or a hydrothermal treatment of the zeolite above 500°C leads to a delumination of the framework. A degree of dealumination could be measured by ^{27}Al, ^{29}Si MAS NMR, by acidity measurement (like TPD NH_3) or by any other means, which are well known in the prior art. A rate of the dealumination is defined mainly by mentioned above parameters, namely, steam partial pressure, temperature and duration of the treatment.

Thus, the "steaming severity (X)" is defined as a ratio of the dealumination rates between an experimental condition vs a standard condition.

Steaming performed at 600°C, in 100% of steam at atmospheric pressure during 2h is selected as a standard condition for this invention.

The rate of dealumination (V) for the catalyst of invention is given by equation:

$V \div Const \times P(H_2O)\text{^}1.5 \times t_{st} / EXP(-0.03 \times T_{st})$,

where $P(H_2O)$ – steam partial pressure (P/Patm); T_{st} – steaming temperature in °C; t_{st} – time in hours (duration) of treatment and ÷ means proportional.

X (The steaming severity) = $V_{\text{experimental condition}}/V_{\text{standard condition}}$

This equation is valid in a steaming interval from 500°C to 760°C.

So, the steaming severity value could be achieved even at lower temperature relative to the used in standard condition but for a higher time of duration.

The temperature 625°C provides roughly 2 times higher steam severity vs the standard condition at equal time steam partial pressure and duration of the treatment.

If the temperature of the equilibration step is above 760°C (out of the range), the duration of steaming is at least 0.1 h and the partial pressure of steam is at least 0.01 bar.

Advantageously in the second embodiment the temperature of the equilibration step is in the range 625 to 870°C.

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less that 1000 wppm of sodium, less that 1000 wppm of potassium and less that 1000 wppm of iron.

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less than 1000 wppm of sodium.

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less than 100 wppm of sodium

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less that 100 wppm of sodium, less that 100 wppm of potassium and less that 500 wppm of iron.

The present invention also relates to the use of the catalyst made according to the above method in processes wherein said catalyst is operated in presence of steam at high temperature. "High temperature" means above 300°C and up to 800°C. By way of example one can cite, the alcohol dehydration to convert at least an alcohol into the corresponding olefin, the olefin cracking to make lighter olefins, the MTO and the alkylation of aromatics by alcohols with olefins and/or alcohols, said process producing, by way of example, para-xylene, ethylbenzenes and cumene.

[Detailed description of the invention]

As regards the zeolite of step a) containing at least one 10 members ring into the structure, one can cite the crystalline silicates. It is by way of

example the MFI (ZSM-5, silicalite-1, boralite C, TS-1), MEL (ZSM-11, silicalite-2, boralite D, TS-2, SSZ-46), FER (Ferrierite, FU-9, ZSM-35), MTT (ZSM-23), MWW (MCM-22, PSH-3, ITQ-1, MCM-49), TON (ZSM-22, Theta-1, NU-10), EUO (ZSM-50, EU-1), MFS (ZSM-57) and ZSM-48 family of microporous materials consisting of silicon, aluminium, oxygen and optionally boron.

Preferred zeolite structures are selected from the MFI, MTT, FER, MEL, TON, MWW, EUO, MFS.

In an embodiment, the zeolite is ZSM-5 with Si/Al atomic ratio ranging from 11 to 30, which has been made without direct addition of organic template.

In an embodiment, the zeolite is MFI zeolite with Si/Al atomic ratio ranging from 30 to 200.

The three-letter designations "MFI" and "MEL" each representing a particular crystalline silicate structure type as established by the Structure Commission of the International Zeolite Association. Examples of a crystalline silicate of the MFI type are the synthetic zeolite ZSM-5 and silicalite and other MFI type crystalline silicates known in the art. Examples of a crystalline silicate of the MEL family are the zeolite ZSM-11 and other MEL type crystalline silicates known in the art. Other examples are Boralite D and silicalite-2 as described by the International Zeolite Association (Atlas of zeolite structure types, 1987, Butterworths). The preferred crystalline silicates have pores or channels defined by ten oxygen rings.

Crystalline silicates are microporous crystalline inorganic polymers based on a framework of XO_4 tetrahedra linked to each other by sharing of oxygen ions, where X may be trivalent (*e.g.* Al,B,...) or tetravalent (*e.g.* Ge, Si,...). The crystal structure of a crystalline silicate is defined by the specific order in which a network of tetrahedral units are linked together. The size of the crystalline silicate pore openings is determined by the number of tetrahedral units, or, alternatively, oxygen atoms, required to form the pores and the nature of the cations that are present in

the pores. They possess a unique combination of the following properties: high internal surface area; uniform pores with one or more discrete sizes; ion exchangeability; good thermal stability; and ability to adsorb organic compounds. Since the pores of these crystalline silicates are similar in size to many organic molecules of practical interest, they control the ingress and egress of reactants and products, resulting in particular selectivity in catalytic reactions. Crystalline silicates with the MFI structure possess a bidirectional intersecting pore system with the following pore diameters: a straight channel along [010]:0.53-0.56 nm and a sinusoidal channel along [100]:0.51-0.55 nm. Crystalline silicates with the MEL structure possess a bidirectional intersecting straight pore system with straight channels along [100] having pore diameters of 0.53-0.54 nm.

In an embodiment, the zeolite is pretreated by steam. The pretreatment is performed in the range 420 to 870°C, more preferably in the range 480 to 800°C. The water partial pressure may range from 13 to 100 kPa. The steam atmosphere preferably contains from 5 to 100 vol % steam with from 0 to 95 vol % of a gas, preferably nitrogen or air. The steam treatment is preferably carried out for a period of from 0.01 to 200 hours, more preferably from 0.05 to 50 hours, still more preferably for at least 0.1 hour and in a preferred way from 0,1 to 50 hours and in a more preferred way from 0.5 to 50 hours and still more preferred 1 to 50 hours.

The steam treatment tends to reduce the amount of tetrahedral aluminium in the crystalline silicate framework by forming alumina. Preferably, the amount of residual tetrahedral Al in the zeolite is between 60 to 95%. This value can be estimated by ^{27}Al MAS NMR or TPD NH3. Optionally said alumina can be removed by leaching with an acid.

In an embodiment, the ZSM-5 with Si/Al atomic ratio ranging from 11 to 30, which has been made without direct addition of organic template, is pretreated by steam.

Additionally, if during the preparation of the zeolite alkaline or alkaline earth metals have been used, the molecular sieve might be subjected to an ion-exchange step. Conventionally, ion-exchange is done in aqueous solutions using ammonium salts or inorganic acids.

In an embodiment, the zeolite is subjected to dealumination such as about 10% by weight of the aluminium is removed. Such dealumination can be done by any conventional techniques known per se but is advantageously made by a steaming optionally followed by a leaching. The crystalline silicate having a ratio Si/Al of at least about 30 to 200 can be synthetized as such or it can be prepared by dealumination of a crystalline silicate with lower initial Si/Al ratio.

As regards step b), and the binder, it is selected so as to be resistant to the temperature and other conditions employed in the processes using the catalyst. The binder can be an inorganic material selected from silica, zirconia, borates, alumina, silica-aluminas, phosphates, for example amorphous aluminophosphates, calcium phosphates, clays, metal oxides such as ZrO_2 and/or metals, or gels including mixtures of silica and metal oxides.

In an embodiment, the binder is substantially neutral (inert) and it is selected from inorganic material selected from silica, non-acid alumina, amorphous aluminophosphates, metalphosphates, clays or a mixture of thereof. The neutral nature of the binder allow limiting secondary reactions leading to formation of heavy oxygenates and hydrocarbons, etane, acetaldehyde etc.

A particularly preferred binder for the catalyst of the present invention comprises silica. The relative proportions of the finely divided crystalline silicate material and the inorganic oxide of the binder can vary widely.

Non-limiting examples of silicon sources include silicates, precipitated silicas, for example, Zeosil range available from Rhodia, fumed silicas, for example, Aerosil-200 available from Degussa Inc., New York, N.Y., silicon compounds such as tetraalkyl orthosilicates, for example, tetramethyl orthosilicate (TMOS) and tetraethylorthosilicate (TEOS), colloidal silicas or aqueous suspensions thereof, for example Ludox-HS-40 sol available from E.I. du Pont de Nemours, Wilmington, Del., silicic acid, alkali-metal silicate, or any combination thereof.

Other suitable forms of amorphous silica include silica powders, such as Ultrasil VN3SP (commercially available from Degussa).

Other non-limiting examples of a suitable solid silica source are special granulated hydrophilic fumed silicas, mesoporous silica grade EXP & high surface area precipitated silica SIPERNAT from Evonik, HiSil 233 EP (available from PPG Industries) and Tokusil (available from Tokuyama Asia Pacific).

In addition, suitable amorphous silica sources include silica sols, which are stable colloidal dispersions of amorphous silica particles in an aqueous or organic liquid medium, preferably water.

Non-limiting examples of commercially available silica sols include those sold under the tradenames Nyacol (available from Nyacol Nano Technologies, Inc. or PQ Corp.), Nalco (available from Nalco Chemical Company), Ultra-Sol (available from RESI Inc), Ludox (available from W.R. Grace Davison), NexSil (available from NNTI).

Many silica sols are prepared from sodium silicate and inevitably contain sodium. It is, however, found that the presence of sodium ions can cause sintering of the silica body at high temperature and/or affect catalytic performance. Therefore, if silica sols containing sodium are used, a step of ion exchange may be required in order to reduce or remove sodium. To avoid carrying out ion exchange steps, it is

convenient to use silica sols that contain very little or, ideally, no detectable traces of sodium and have a pH value of less than 7. Most preferably, the silica sol used in the process is slightly acidic with or without polymeric stabilizers. Non limiting examples of silica sols that contain no detectable traces of sodium include Bindzil 2034DI, Levasil 200, Nalco 1034A, Ultra-Sol 7H or NexSil 20A.

In some case, silica dispersion prepared with alkylammonium might be useful. Non-limiting examples of commercially low sodium silica sols stabilized by ammonia or alkylammonium cations include LUDOX TMA (available from W.R. Grace Davison) or VP WR 8520 from Evonik.

The silica sols with higher SiO2 content than 30% and even up to 50wt%, for example W1250, W1836, WK341, WK7330 from Evonik are particularly preferred.

The preferred source of silicon is a silica sol or a combination of silica sol with precipitated or fumed silica.

Types of silica sols used to form a bound catalyst for use in alcohol dehydration process are commercially available as aquasols or organosols containing dispersed colloidal silica particles. For example, sodium silicate can be used as a silica sol. Otherwise, a silica gel, fumed or pyrogenic silica may also be used to provide a silica binder in the molecular sieve catalyst. Silicic acid is another possible source of silica. Advantageously, the binder contains low amount of sodium below 1000 ppm.

Clays are known to be essentially inert under a wide range of reaction conditions. Suitable clays include commercially available products such as kaolin, kaolinite, montmorillonite, attapulgite, saponite, and bentonite. These clays can be used as mined in their natural state, or they may also be employed in highly active

forms, typically activated by an acid treatment procedure. Commercial suppliers of these clays include Thiele Kaolin Company, American Colloidal Co., and others.

Clays contribute to strength as a binder enhancing the attrition resistance properties of the catalyst particles, and clays in combination with binders contribute to the hardness of the particles. Clays also start as small particles and have a higher density, such that when combined with the molecular sieve and binder provide for denser particles, imparting the desirable characteristic of higher density.

Clays are used in this process to form a hardened product include, but are not limited to, kaolin, kaolinite, montmorillonite, saponite, bentonite, and halloysite.

In an embodiment, the binder material is often, to some extent, porous in nature and may be effective to promote the desired conversion of ethanol to ethylene. The binder might be a single amorphous entity, or a blend of two or more individual amorphous compounds.

In a related embodiment, the catalyst (zeolite+binder) has a volume of the pore between 30 Å and 1000 Å of at least 0.25 cc/g, advantageously between 0.25 and 1 cc/g preferably at least 0.26 cc/g, the most preferable between 0.27-0.92 cc/g. "cc" means cm3.

In an embodiment, the binder material possesses acid properties and may also promote conversion of the ethanol.

In referring to these types of binders that may be used, it should be noted that the term silica-alumina does not mean a physical mixture of silica and alumina but means an acidic and amorphous material that has been cogelled or coprecipitated. This term is well known in the art and is described, for example, in US-A-3,909,450 BI; US-A-3,274, 124 B1 and US-A-4,988,659 B I. In this respect, it is possible to form other cogelled or coprecipitated amorphous materials that will also be effective as either binder or filler materials. These include silica-zirconias,

silica-thorias, silica-berylias, silica-titanias, silica-alumina-thofias, silica-alumina-zirconias, alurninophosphates, mixtures of these, and the like.

In another embodiment, catalyst contains alumina materials such as aluminum oxyhydroxide, γ-alumina, boehmite, diaspore, and transitional aluminas such as α-alumina, β-alumina, γ-alumina, δ-alumina, ε-alumina, κ-alumina, and ρ-alumina, aluminum trihydroxide, such as gibbsite, bayerite, nordstrandite, doyelite, and mixtures thereof.

It is desirable to provide a catalyst having a good crush strength. This is because in commercial use, it is desirable to prevent the catalyst from breaking down into powder-like materials. Such oxide binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

The catalyst composition may be prepared, as indicated above, by any of the methods described in the art. Advantageously, however, the catalyst particles are combined with the binder material initially by dry-mixing, then in a liquid, preferably water, preferably with a plasticizer, to yield a paste.

As plasticizer (shaping additive), there may be mentioned one that will be decomposed during any subsequent heat treatment, e.g., calcination. Suitable materials for this purpose include, for example, alkylated cellulose derivatives, hydroxyethylcellulose (HEC), tylose, ammonium alginate, polyvinyl pyrrolidone, glycerol, and polyethylene glycol.

In addition to enhancing the catalyst strength properties, the binder material allows the molecular sieve crystallite powder to be bound into larger particle sizes suitable for commercial catalytic processes. The formulation of the mixture b) may be formed into a wide variety of shapes including extrudates, spheres, pills, and the like.

The uniformly mixed paste may subsequently be shaped, for example by spray drying to yield microspheres, pelletizing or, preferably, by extrusion.

The paste is then extruded, for example in a piston extruder, into strings, for example cylindrical, dried, again calcined, and chopped into pieces of a desired length.

As regards the proportions of the zeolite, the one or more binders and shaping additives, advantageously the proportion of the zeolite is from 5 to 95w% of the catalyst. The catalyst comprises the zeolite and at least a component selected among one or more binders and shaping additives. The amount of zeolite which is contained in the catalyst ranges more advantageously from 15 to 90 weight percent of the total catalyst, preferably 20 to 85 weight percent of the catalyst.

Once the molecular sieve catalyst composition is shaped, and in a substantially dry or dried state, a heat treatment, for example calcination, is advantageously performed to harden and/or activate the composition. Therefore the heat treatment is preferably carried out at a temperature of at least 400°C, for a period of from 1 to 48 hours. Calcination may be carried out, for example, in a rotary calciner, fluid bed calciner, or a batch oven.

As regards the Ion-exchange of step c), purpose is to get advantageously a formulated zeolitic molecular sieve with an inert binder, before subjecting in a contact with a phosphatation agent, having less than 1000 wppm of alkali & alkali-earth metals, Na, K, Fe as well as less than 200 ppm of red-ox & noble elements such as Zn, Cr, Rh, Mn, Ni, V, Mo, Co, Cu, Cd, Pt, Pd, Ir, Ru, Re. This may achieved by an optional back ion-exchange step known per se.

In an embodiment, the catalyst comprises a molecular sieve has been treated to reduce alkali metal content to less than 100 ppm before or after the steaming step d).

Although in principle mixing with the binder and ion exchange may be carried out in any order, advantageously ion exchange is performed after shaping but before phosphorus introduction.

Advantageously, the ion exchange step is performed on shaped calcined catalyst before or after the steaming step d).

As regards the steaming of step d), it is also known as the pre-steaming by reference to the final steaming of step i). The treatment is performed in the range 420 to 870°C, more preferably in the range 480 to 800°C. The water partial pressure may range from 13 to 100 kPa. The steam atmosphere preferably contains from 5 to 100 vol % steam with from 0 to 95 vol % of a gas, preferably nitrogen or air. The steam treatment is preferably carried out for a period of from 0,01 to 200 hours, more preferably from 0,05 to 50 hours, still more preferably for at least 0.1 hour and in a preferred way from 0,1 to 50 hours and in a more preferred way from 0.5 to 50 hours and still more preferred 1 to 50 hours.

The steam treatment tends to reduce the amount of tetrahedral aluminium in the crystalline silicate framework by forming alumina. Preferably, the amount of residual tetrahedral Al in the zeolite is between 60 to 95%. This value can be estimated by ^{27}Al MAS NMR or TPD NH_3.

As regards the introduction of P of step e), said introduction of phosphorus can be performed under reduced or atmospheric pressure at temperature from 10 to 400°C. A non-limiting source of phosphorus can be provided in aqueous or non-aqueous medium.

In an embodiment, the non-aqueous medium is selected from the group containing ethanol, methanol or other alcohols.

The preferred techniques are impregnation and chemical vapour deposition. Said techniques are mandatory in the first embodiment of the invention.

These techniques imply a minimum waste to treat and allow maintaining substantially all phosphorus on the catalyst.

In an embodiment, the catalyst precursor is treated by a source of phosphorus injected into a steam flow. In this case, the phosphatation is performed under mild steaming condition with a steam flow containing phosphorus at 100-400°C.

In an embodiment, the phosphorus is introduced by a treatment of the catalyst precursor (zeolite + binder) in a solution contaning a source of phosphorus at temperature 25-100°C for 0.1-96h followed by filtering or evaporation.

In an embodiment amount of said acid solution containing P is advantageously between 2 and 10 liters per kg of zeolite plus binder. A typical period is around 0.5 to 24 hours. Advantageously the aqueous acid solution containing the source of P has a pH of 3, advantageously 2, or lower. Advantageously said aqueous acid solution is phosphorus acids, a mixture of phosphorus acids and organic or inorganic acid or mixtures of salts of phosphorus acids and organic or inorganic acids. The phosphorus acids or the corresponding salts can be of the phosphate ($[PO_4]^{3-}$, being tribasic), phosphite ($[HPO_3]^{2-}$, being dibasic), or hypophosphite ($[H_2PO_2]^{1-}$, being monobasic), type. Of the phosphate type also di or polyphosphates ($[P_nO_{3n+1}]^{(n+2)-}$) can be used. The contact of the zeolite+binder with the P containing component can be made under reflux conditions.

In a preferred embodiment the incipient wetness impregnation technique is used. In this case the phosphorus is introduced via impregnation using a limited amount of liquid water which is subjected to a contact with catalyst. This method is also known as the dry impregnation.

Incipient wetness (IW) or incipient wetness impregnation (IWI) is a commonly used technique for the synthesis of heterogeneous catalysts. Typically, the precursor (phosphorus-containing compounds) is dissolved in an aqueous or organic solution. The volume of solution, which is used for dissolution of the precursor, is substantially the same as the pore volume of catalyst precursor containing both binder and zeolite . Then the precursor-containing solution is added to a catalyst precursor. Capillary action draws the solution into the pores. The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the phosphorus on the catalyst surface.

The sample before impregnation can be dried or calcined. The impregnation could be performed at room or elevated temperature (30-100°C).

The adsorption capacity is typically measured by impregnating the dried extruded zeolite with water until the zeolite was completely wet. Weighing the zeolite before and after impregnation gives the absorption capacity:

$$Absorption\ capacity(\%) = \frac{weight\ after\ impregantion - dry\ weight}{dry\ weight} * 100$$

In an embodiment, H3PO4 solution is used for impregnation.

Advantageously, a mixture of H3PO4 with their ammonium salts providing a pH of the aqueous solution higher than 2.0 is used for impregnation

In an embodiment, the sources of phosphorus are substantially metal free components, for example H3PO4, ammonium phosphates or organic P-compounds. "substantially metal free" means a metal proportion with has no adverse effect on the P introduction. By way of example this proportion can be below 1000 wppm.

The amount of phosphorus on the catalyst can be from 0.5 to 30 wt%, but preferably from 0.5 to 9 w%.

In an embodiment, the phosphatation step is performed before or simultaneously with introduction of metal oxides.

As regards step f), the introduction of metal, it can be one or more metals. Advantageously said metals are selected among alkaline earth or rare earth metals. The alkaline earth or rare earth metal M is preferably selected from one or more of: Mg, Ca, Sr, Ba, La, Ce. More preferably, M is an alkaline earth metal. Most preferably, M is Ca. Particularly in the case of P-modification via steaming and leaching, M can be a rare earth metal such as La and Ce. Advantageously the metal is introduced in a soluble form.

The M-containing component is preferably in the form of an organic compound, a salt, hydroxide or oxide. The compound is preferably in a solubilized form when bringing it into contact with the molecular sieve. Alternatively, the solution of the M-containing compound can be formed after bringing the molecular sieve in contact with said compound.

Possible M-containing compounds include compounds such as sulphate, formate, nitrate, acetate, halides, oxyhalides, oxalate, borates, carbonate, hydroxide, oxide and mixtures thereof. One can cite calcium carbonate.

Those M-containing compounds, which are poorly water-soluble, can be dissolved to form a well-solubilized solution by heating and/or by modifying the pH of the solution by addition of phosphoric, acetic or nitric acid or corresponding ammonium salts of said acids.

As regards step g), a washing step can be envisaged. In accordance with the present invention, the catalyst is treated with water for a period of time from 0.1 to 48 hours, preferably for a period of time from about 0.5 to 36 hours and most

preferably from about 1 to 24 hours. The water was at a temperature between about 20°C and 180°C, preferably between about 20°C and 100°C and most preferably between about 25°C and 60°C. By way of example the water can be at 30°C. Following the water treatment, the catalyst may be dried at about >60° C. Optionally, the water can contain at least one dissolved solid selected from the group consisting of ammonium chloride, ammonium phosphate, ammonium sulfate, ammonium acetate, ammonium carbonate, ammonium nitrate and mixtures thereof.

As regards step h), said calcination can be made in air or an inert gas, typically at a temperature of from 350 to 900°C for a period of from 1 to 48 hours. Optionally the air or an inert gas may contain steam in concentration from 10 to 90 vol%.

As regards step i), in the first embodiment of the invention it can be performed in the range 420 to 870°C, preferably in the range 480 to 870°C , preferably from 625 to 870°C and more preferably from 700 to 800°C, still more preferably in the range 720 to 800°C. Alternatively it can be performed in the range 420 to 600°C, preferably 420 to 580°C.

In the second embodiment of the invention it is performed by steaming steaming severity above about 2 or alternatively at temperature above 625°C, preferably from 625 to 870°C and more preferably from 700 to 800°C still more preferably in the range 720 to 800°C. The water partial pressure may range from 13 to 100 kPa. The steam atmosphere preferably contains from 5 to 100 vol % steam with from 0 to 95 vol % of a gas, preferably nitrogen or air. The steam treatment is preferably carried out for a period of from 0,01 to 200 hours, preferably from 0,05 to 50 hours, more preferably for at least 0.1 hour and in a preferred way from 0,1 to 50 hours, and in a more preferred way from 0.5 to 50 hours and still more preferred 1 to 50 hours.

As regards the dehydration process to convert an alcohol into an olefin, this process has been described in a lot of patent applications. One can cite WO/2009/098262, WO/2009/098267, WO/2009/098268 and WO 2009/098269, the content of which is incorporated in the present application. The alcohol is any alcohol provided it can be dehydrated to the corresponding olefin. Advantageously the alcohol has two or more carbon atoms. The corresponding olefin is an olefin having the same number of carbons as the alcohol. By way of example mention may be made of alcohols having from 2 to 10 carbon atoms. Advantageously the invention is of interest for ethanol, propanol, butanol and phenylethanol.

As regards the cracking of olefins, more precisely the present invention relates to a process for cracking an olefin-rich hydrocarbon feedstock which is selective towards light olefins in the effluent. In particular, olefinic feedstocks from refineries or petrochemical plants can be converted selectively so as to redistribute the olefin content of the feedstock in the resultant effluent. Said cracking of an olefin-rich feedstock is often referred in the following description and claims as OCP (Olefin Cracking Process). As regards the hydrocarbon feedstock containing one or more olefins sent to the OCP reactor, in accordance with the present invention, cracking of olefins is performed in the sense that olefins in a hydrocarbon stream are cracked into lighter olefins and selectively into propylene. The feedstock and effluent preferably have substantially the same olefin content by weight. Typically, the olefin content of the effluent is within ±15wt%, more preferably ±10wt%, of the olefin content of the feedstock. The feedstock may comprise any kind of olefin-containing hydrocarbon stream. The feedstock may typically comprise from 10 to 100wt% olefins and furthermore may be fed undiluted or diluted by a diluent, the diluent optionally including a non-olefinic hydrocarbon. In particular, the olefin-containing feedstock may be a hydrocarbon mixture containing normal and branched olefins in

the carbon range C_4 to C_{10}, more preferably in the carbon range C_4 to C_6, optionally in a mixture with normal and branched paraffins and/or aromatics in the carbon range C_4 to C_{10}. Typically, the olefin-containing stream has a boiling point of from around -15 to around 180°C. With regards to the OCP process, said process is known per se. It has been described in EP 1036133, EP 1035915, EP 1036134, EP 1036135, EP 1036136, EP 1036138, EP 1036137, EP 1036139, EP 1194502, EP 1190015, EP 1194500 and EP 1363983 the content of which are incorporated in the present invention.

As regards the MTO, said process produces light olefins such as ethylene and propylene as well as heavy hydrocarbons such as butenes. Said MTO process is the conversion of methanol or dimethylether by contact with a molecular sieve which can be a P modified zeolite.

As regards the alkylation of aromatic compounds with olefins and alcohols, said process produces, by way of example, para-xylene, ethylbenzenes and cumene. Alkylation of aromatic, for example, toluene methylation has been known to occur over acidic catalyst, particularly over zeolite or zeolite-type catalyst. In particular, ZSM-5-type zeolite, zeolite Beta and silicaaluminophosphate (SAPO) catalysts have been used for this process.

One skilled in the art will also appreciate that the olefins made by the dehydration process of the present invention can be, by way of example, polymerized. When the olefin is ethylene it can be, by way of example,

polymerized to form polyethylenes,

dimerized to butene and then isomerised to isobutene, said isobutene reacting with ethanol to produce ETBE,

dimerized to butane followed by reacting with ethylene via methatesis to produce propylene;

converted to propylene over metal, acid or bifunctional catalyst,used for alkylation of benzene to form ethyl -benzene,

dimerised to 1-butene, trimerised to 1-hexene or tetramerised to 1-octene, said alpha-olefins comonomers are further reacted with ethylene to produce polyethylene

dimerised to 1-butene, said 1-butene is isomerised to 2-butene and said 2-butene is further converted with ethylene by metathesis reaction into propylene and said propylene can be polymerised to polypropylene,

converted to ethylene oxide and glycol or

converted to vinyl chloride.

The present invention relates also to said polyethylenes, polypropylene, propylene, butene, hexane, octene, isobutene, ETBE, vinyl chloride, ethylene oxide and glycol.

When the olefin is propylene it can be, by way of example,

polymerized to form polypropylene,

used for alkylation of aromatics etc.....

[Examples]

EXAMPLE 1

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (contained 250 ppm of Na & synthesized without template) was blended with a silica binder in a ratio 80:20 followed by addition of extrusion additives and shaping. A final Na content in the catalyst was 320 ppm.

The extruded sample was dried for 2h at 140°C, calcined for 2h at 600°C followed by steaming at 550°C for 6h in 100% steam.

Steamed solid was incipient wetness impregnated with an aqueous solution of phosphoric acid to introduce about 3wt% of phosphorus to the catalyst. The impregnated solid was dried for 16h at 110°C.

Then, the phosphated sample was incipient wetness impregnated with a solution of calcium nitrate obtained by dissolution of calcium carbonate to introduce about1wt% of calcium to the solid. The impregnated solid was dried for 16h at 110°C.

Resulted catalyst containing 2.8wt% of phosphorus and 0.8 % of calcium was steamed at 600°C for 2h in 100% of steam (steaming severity 1). The sample is hereinafter identified as **sample A.**

Resulted catalyst containing about 2.8wt% of phosphorus and 0.8 % of calcium was steamed at 750°C for 1h in 100% of steam (steaming severity 45). The sample is hereinafter identified as **sample B.** Total pore volume measured by mercury intrusion porosimetry is 0.36 cm3/g.

Catalyst tests were performed on 1 ml of catalyst grains (35-45 meshes) loaded in a tubular reactor with internal diameter 11mm. A mixture 25wt%EthOH/75wt% H_2O was subjected to a contact with catalyst described in the example I in a fixed bed reactor at 380°C, WHSV = $7h^{-1}$ P=2 bara. The results are given in table 1 hereunder. The values are the weight percents on carbon basis.

Example 2

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (containing 250 ppm of Na & synthesized without template) was blended with a silica binder in a ratio 80:20 followed by addition of extrusion additives and shaping. A final Na content in the catalyst was 320 ppm.

The extruded sample was dried for 16h at 110°C, calcined for 10h at 600°C followed by steaming at 550°C for 6h in 100% steam.

Steamed shaped zeolite was then contacted with an aqueous solution of H_3PO_4 (85%wt) under conditions of incipent wetness. Then 1 g of $CaCO_3$ was introduced. After stirring during 30min, the system is cooled down at room temperature and the excess of solution is removed by filtration without washing. The recovered solid is dried at 110°C for 16h followed by steaming at 600°C for 2h in 100% of steam (steaming severity 1)..

Resulted catalyst contained about 1.7wt% of phosphorus and 0.4wt% of calcium. The sample is hereinafter identified as **sample C**

The performances of the catalyst were then evaluated under the same operating conditions as described above, using 1 ml of catalyst (35-45 mesh) loaded in a tubular reactor with internal diameter 11mm. A mixture of 25wt%EtOH/75wt% H_2O has been processed on catalyst C, in a fixed bed reactor at 380°C, WHSV = $7h^{-1}$ P=2 bara. The results are given in table 1. The values are the weight percents on carbon basis.

EXAMPLE 3

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (containing 250 ppm of Na & synthesized without template) was blended with a silica binder in a ratio 80:20 followed by addition of extrusion additives and shaping. A final Na content in the catalyst was 320 ppm.

The extruded sample was dried for 16h at 110°C, calcined for 10h at 600°C followed by steaming at 550°C for 6h in 100% steam.

12g of steamed solid was incipient wetness impregnated with an aqueous solution containing 1.54g of NH4H2PO4. The impregnated solid was dried for 16h at 110°C.

Then, the phosphated sample was incipient wetness impregnated with a solution of calcium nitrate obtained by dissolution of 0.3g calcium carbonate in nitric acid. The impregnated solid was dried for 16h at 110°C followed by steaming at 600°C for 2h in 100% of steam (steaming severity 1).

Resulted catalyst contained about 2.54wt% of phosphorus and 0.82wt% of calcium. The sample is hereinafter identified as **sample D.**

The performances of the catalyst were then evaluated under the same operating conditions as described above, using 1 ml of catalyst (35-45 mesh) loaded in a tubular reactor with internal diameter 11mm. A mixture of 25wt%EtOH/75wt% H_2O has been processed on catalyst D, in a fixed bed reactor at 380°C, WHSV = $7h^{-1}$ P=2 bara. The results are given in table 1. The values are the weight percents on carbon basis.

Table 1

Sample	A	B	C	D
P (bara)	2	2	2	2
T (°C)	380	380	380	380
WHSV (H-1)	7	7	7	7
EtOH conversion (% wt CH2)	99.9	99.8	99.9	99.9
DEE	0.0	0.0	0.0	0.0
Acetaldyde	0.31	0.17	0.17	0.13
EtOH	0.10	0.20	0.05	0.05
Yield on C-basis (%wt CH2)				
CH4	0.00	0.00	0.00	0.00
C2	0.13	0.06	0.11	0.12
C2=	97.9	99.0	97.3	97.4
C3=	0.56	0.07	0.7	0.8
C4+ olef	0.86	0.48	1.6	1.4
Unknown	0.10	0.06	0.07	0.08
Selectivity on C-basis (%wt CH2)				
C2=	98.0	99.20	97.4	97.4
C2's cut purity (%)	99.87	99.94	99.88	99.87

EXAMPLE 4

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (contained 250 ppm of Na & synthesized without template) was blended with a binder containing silica and kaolin in a ratio 70:10:20 followed by addition of extrusion additives and shaping.

The extruded sample was dried for 2h at 140°C, calcined for 10h at 600°C followed by steaming at 550°C for 6h in 100% steam.

Steamed solid was incipient wetness impregnated with an aqueous solution of phosphoric acid to introduce about 3wt% of phosphorus to the catalyst. The impregnated solid was dried for 16h at 110°C.

Then, the phosphated sample was incipient wetness impregnated with a solution of calcium nitrate obtained by dissolution of calcium carbonate to introduce about 1wt% of calcium to the solid. The impregnated solid was dried for 16h at 110oC.

Resulted catalyst containing 2.94wt% of phosphorus and 0.8 % of calcium was steamed at 750°C for 2h in 100% of steam (steaming severity 90). The sample is hereinafter identified as **sample E.**

EXAMPLE 5

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (synthesized without template) was calcined for 10h at 600°C followed by steaming at 550°C for 6h in 100% steam.

100g of steamed solid was incipient wetness impregnated (dry impregnated) with an aqueous solution containing 9.86g of phosphoric acid. The impregnated solid was dried for 16h at 110°C.

Then, 16g of the phosphated sample was extruded with 4g of silica binder and 0.4g of $CaCO_3$.

The resulted catalyst was calcined at 600°C for 10h followed by steaming at 600oC for 2h in 100% of steam (steaming severity 1). The sample is hereinafter identified as **sample F.**

EXAMPLE 6 (OCP test)

Catalyst tests were performed on 0.8g of catalyst grains (35-45 meshes) loaded in the tubular reactor. The feedstock which contains substantially non cyclic olefins C4 (~60%) was subjected to catalytic cracking in the presence of catalyst in a fixed bed reactor at T_{in}-550°C, WHSV= 16h^{-1}, P=1.5 bara. The results are in table

2. The values in the table 2 are the average catalyst performance for 1-10 hours-on-stream given in weight percents on carbon basis.

The data given below illustrate good cracking activity and high selectivity of the P-zeolite in C4 olefins conversion to propylene and ethylene.

Table 2

Sample	E	F
P (bara)	1.5	1.5
T_{in} (°C)	550	550
WHSV (h^{-1})	16	16
C4 olefins conversion, %	65.4	65.2
Purity C3's, %	94.9	96.0
Yield on C-basis, %		
Methane	0.07	0.14
Aromatics	1.2	1.4
Propane	1.0	0.8
Ethylene	3.5	3.4
Propylene	19.5	19.1

CLAIMS

1 Method to make a phosphorus modified zeolite comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory,

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus, said introduction being made by dry impregnation or chemical vapor deposition,

f) optionally introducing a metal, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step.

2 Method according to claim 1 wherein the phosphorus introduction of step e) is made by incipient wetness (IW) or incipient wetness impregnation (IWI).

3 Method according to claim 1 or 2 wherein the steaming of step i) is performed in the range 420 to 870°C.

4 Method according to claim 3 wherein the steaming of step i) is performed in the range 480 to 870°C.

5 Method according to claim 4 wherein the steaming of step i) is performed in the range 625 to 870°C.

6 Method according to claim 5 wherein the steaming of step i) is performed in the range 700 to 800°C.

7 Method according to claim 6 wherein the steaming of step i) is performed in the range 720 to 800°C.

8 Method according to claim 3 wherein the steaming of step i) is performed in the range 420 to 600°C.

9 Method according to claim 8 wherein the steaming of step i) is performed in the range 420 to 580°C.

10 Method to make a phosphorus modified zeolite comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory,

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus,

f) optionally introducing a metal, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step, at a steaming severity (X) of at least about 2.

11 Method according to claim 10 wherein the steaming of step i) is performed in the range 625 to 870°C.

12 Method according to claim 11 wherein the steaming of step i) is performed in the range 700 to 800°C.

13 Method according to claim 12 wherein the steaming of step i) is performed in the range 720 to 800°C.

14 Method according to any one of the preceding claims wherein the shaped zeolite (or molecular sieve) of step b) contains less than 100 wppm of sodium.

15 Method according to claim 14 wherein the shaped zeolite (or molecular sieve) of step b) contains less than 100 wppm of sodium, less than 100 wppm of potassium and less than 500 wppm of iron.

16 Method according to any one of claims 1 to 13 wherein the shaped zeolite (or molecular sieve) of step b) contains less than 1000 wppm of sodium.

17 Method according to claim 16 wherein the shaped zeolite (or molecular sieve) of step b) contains less than 1000 wppm of sodium, less than 1000 wppm of potassium and less than 1000 wppm of iron.

18 Method according to any one of the preceding claims wherein the zeolite is selected from the MFI, MTT, FER, MEL, TON, MWW, EUO, MFS.

19 Method according to claim 18 wherein the zeolite is ZSM-5 with Si/Al atomic ratio ranging from 11 to 30, which has been made without direct addition of organic template.

20 Method according to claim 18 wherein the zeolite is MFI with Si/Al atomic ratio ranging from 30 to 200.

21 Method according to any one of the preceding claims wherein the amount of phosphorus on the catalyst is from 0.5 to 30 wt%.

22 Method according to claim 21 wherein the amount of phosphorus on the catalyst is from 0.5 to 9 w%.

23 Method according to any one of the preceding claims wherein the metal at step f) is an alkaline earth or rare earth metal M preferably selected from one or more of: Mg, Ca, Sr, Ba, La, Ce.

24 Method according to any one of the preceding claims wherein the catalyst (zeolite+binder) has a volume of the pores between 30 Å and 1000 Å of at least 0.25 cc/g.

25 Use of the catalyst made according to any one of the preceding claims in processes wherein said catalyst is operated in the presence of steam at temperature above 300°C and up to 800°C.

26 Process to dehydrate an alcohol to convert at least said alcohol into the corresponding olefin having the same number of carbon atoms as the alcohol wherein said dehydration is made in the presence of a catalyst made according to any one of claims 1 to24.

27 Process to make cracking of olefins to make lighter olefins wherein said cracking is made in the presence of a catalyst made according to any one of claims 1 to24.

28 Process to make cracking of methanol or dimethylether to produce light olefins such as ethylene and propylene wherein said cracking is made in the presence of a catalyst made according to any one of claims 1 to24.

29 Process to make alkylation of aromatics by alcohols or olefins wherein said alkylation is made in the presence of a catalyst made according to any one of claims 1 to24.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/064580

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J29/40 B01J29/85 B01J37/10 B01J37/28 C07C1/20
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 348 004 A1 (TOTAL PETROCHEMICALS RES FELUY [BE]) 27 July 2011 (2011-07-27) claims; examples	1-29
X	WO 2009/098262 A1 (TOTAL PETROCHEMICALS RES FELUY [BE]; MINOUX DELPHINE [BE]; NESTERENKO) 13 August 2009 (2009-08-13) claims; examples	1-29
X	EP 2 082 802 A1 (TOTAL PETROCHEMICALS RES FELUY [BE]) 29 July 2009 (2009-07-29) claims; examples	1-29
X	EP 0 511 013 A2 (ARCO CHEM TECH [US] ARCO CHEM TECH [DE]; ARCO CHEM TECH [US]) 28 October 1992 (1992-10-28) cited in the application claims; examples	1-29

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 November 2012	27/11/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schoofs, Bart

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/064580

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 356 338 A (YOUNG LEWIS B) 26 October 1982 (1982-10-26) cited in the application claims; examples -----	1-29

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/064580

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2348004 A1	27-07-2011	AR 080012 A1	07-03-2012
		CA 2787548 A1	28-07-2011
		EP 2348004 A1	27-07-2011
		EP 2528880 A1	05-12-2012
		EP 2528881 A1	05-12-2012
		KR 20120106996 A	27-09-2012
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US 4356338 A	26-10-1982	NONE	

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DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:		**PCT/EP2012/064580**
International filing date:		**25 July 2012 (25.07.2012)**
Document type:		**Certified copy of priority document**
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	Number:	**11176391.8**
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Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-*bis*)

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Bescheinigung	Certificate	Attestation
Die angehefteten Unterlagen stimmen mit der als ursprünglich eingereicht geltenden Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.	The attached documents are exact copies of the text in which the European patent application described on the following page is deemed to have been filed.	Les documents joints à la présente attestation sont conformes au texte, considéré comme initialement déposé, de la demande de brevet européen qui est spécifiée à la page suivante.

Patentanmeldung Nr.	**Patent application No.**	**Demande de brevet n°**
	11176391.8 / EP11176391	

The organization code and number of your priority application, to be used for filing abroad under the Paris Convention, is EP11176391.

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le President de l'Office européen des brevets
p.o.

R.C. van Dijk

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Anmeldung Nr:
Application no.: 11176391.8
Demande no :

Anmeldetag:
Date of filing: 03.08.11
Date de dépôt :

Anmelder / Applicant(s) / Demandeur(s):

Total Petrochemicals Research Feluy
Zone Industrielle C
7181 Seneffe (Feluy)/BE

Bezeichnung der Erfindung / Title of the invention / Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

METHOD FOR MAKING A CATALYST COMPRISING A PHOSPHORUS MODIFIED ZEOLITE AND USE OF SAID ZEOLITE

In Anspruch genommene Priorität(en) / Priority(Priorities) claimed / Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen / State/Date/File no. / Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation / International Patent Classification / Classification internationale de brevets:

B01J29/00

Am Anmeldetag benannte Vertragstaaten / Contracting States designated at date of filing / Etats contractants désignées lors du dépôt:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

METHOD FOR MAKING A CATALYST COMPRISING A PHOSPHORUS MODIFIED ZEOLITE AND USE OF SAID ZEOLITE

[Field of the invention]

The present invention relates to a method for making a catalyst comprising a phosphorus modified zeolite and the use of said zeolite. This modified zeolite is of interest in processes wherein said zeolite is operated in presence of steam at high temperature. By way of example one can cite,
the alcohol dehydration to convert at least an alcohol into the corresponding olefin,
the cracking of C4+ olefins (also known as OCP, olefins conversion process) to make a mixture of ethylene and propylene,
the cracking of methanol or dimethylether (also known as MTO) to produce light olefins such as ethylene and propylene as well as heavy hydrocarbons such as butenes,
the alkylation of aromatics by alcohols, by way of example alkylation of benzene or toluene with methanol, ethanol or propanol.

[Background of the invention]

An efficient catalyst is a key in industrialization of dehydration of alcohols as well as in the other above processes. One of the early catalysts employed for the dehydration of ethanol was alumina. This catalyst is relatively cheap but needs low space velocity, high reaction temperature and makes a lot of ethane, which needs to be separated. Zeolites, particularly phosphated zeolites, solve a problem with catalyst activity and provide with ethylene fraction, which is closed to polymer grade. Zeolites, particularly phosphated zeolites, solves a problem with catalyst activity. Catalysts comprising a phosphorus modified zeolite (the phosphorus modified zeolite is also referred as P-zeolite) are known. The following prior arts have described various methods to make said catalysts.

US 2006 106270 relates to the use of a dual-function catalyst system in the hydrocarbon synthesis reaction zone of an oxygenate to propylene (OTP) process that operates at relatively high temperatures preferably with a steam diluent and uses moving bed reactor technology. The dual-functional catalyst system comprises a molecular sieve having dual-function capability dispersed in a phosphorus-modified alumina matrix containing labile phosphorus and/or aluminum anions. It is explained that the hydrothermal stabilization effect that is observed when this phosphorus-modifed alumima matrix is utilized is caused by migration or dispersion of phosphorus and/or aluminum anions from this matrix into the bound molecular sieve. These anions are then available to repair, anneal and/or stabilize the framework of the molecular sieve against the well-known dealumination mechanism of molecular sieve framework destruction or modification that is induced by exposure to steam at temperatures corresponding to those used in the OTP reaction zone and in the regeneration zone.

US 4,356,338 discloses a method for decreasing catalyst coking and extending the usable catalyst life by pre-treatment of the catalyst with steam and/or a phosphorus-containing compound. Pretreatment may be accomplished by the impregnation of the catalyst or of the catalyst/binder combination with a phosphorus containing compound to deposit approximately 4 wt.% of phosphorus thereon, and preferably from about 2% to about 15% by weight of phosphorus, based on the weight of the catalyst or catalyst/binder matrix being treated.

US 5,231,064 is directed to a fluid catalyst comprising clay and a zeolite, at least one of which has been treated with a phosphorus containing compound, for example ammonium dihydrogen phosphate or phosphoric acid, and which is spray dried at a low pH, preferably lower than about 3. Said catalysts are deemed to advantageously exhibit reduced attrition.

EP 511013 A2 provides an improved process for the production of C2-C5 olefins from higher olefinic or paraffinic or mixed olefin and paraffin feedstocks. In accordance with this prior art, the hydrocarbon feed materials are contacted with a particular ZSM-5 catalyst at elevated temperatures, high space velocity and low hydrocarbon partial pressure to produce lower olefins. The catalysts is treated with steam prior to use in the hydrocarbon conversion. The active catalyst component is phosphorus-containing ZSM-5 having a surface Si/Al ratio in the range 20-60. Preferably, the phosphorus is added to the formed ZSM-5 as by impregnating the ZSM-5 with a phosphorus compound in accordance with the procedures described, for example, in U.S. Patent 3,972,832. Less preferably, the phosphorus compound can be added to the multicomponent mixture from which the catalyst is formed. The phosphorus compound is added in amount sufficient to provide a final ZSM-5 composition having 0. 1-10 wt.% phosphorus, preferably 1-3 wt.%.

The phosphorus-containing ZSM-5 is preferably combined with known binders or matrices such as silica, kaolin, calcium bentonite, alumina, silica aluminate and the like. The ZSM-5 generally comprises 1-50 wt.% of the catalyst composition, preferably 5-30 wt.% and most preferably 10-25 wt.%.

EP 568913 A2 describes a method for preparing a ZSM-5 based catalyst adapted to be used in the catalytic conversion of methanol or dimethyl ether to light olefins, wherein it comprises the following consecutive steps:

- mixing a zeolite ZSM-5 based catalyst with silica sol and ammonium nitrate solution,
- kneading, moulding, drying and calcining the mixture,
- exchanging the modified zeolite with a solution of HCl at 70-90°C,
- drying and calcining the H-modified zeolite,
- impregnating the H-modified zeolite with phosphoric acid under reduced pressure,
- drying and calcining the P-modified zeolite,

- impregnating the P-modified zeolite with a solution of rare earth elements under reduced pressure,
- drying and calcining the P-rare earths-modified zeolite,
- hydrothermally treating the P-rare earths-modified zeolite at 500-600°C with water vapour, and
- calcining the modified zeolite.

WO 03 020667 relates to a process of making olefin, particularly ethylene and propylene, from an oxygenate feed, comprising contacting an oxygenate feed with at least two different zeolite catalysts to form an olefin composition, wherein a first of the zeolite catalysts contains a ZSM-5 molecular sieve and a second of the zeolite catalysts contains a zeolite molecular sieve selected from the group consisting of ZSM-22, ZSM-23, ZSM-35, ZSM-48, and mixtures thereof. The ZSM-5 can be unmodified, phosphorus modified, steam modified having a micropore volume reduced to not less than 50% of that of the unsteamed ZSM-5, or various mixtures thereof. According to one embodiment, the zeolite is modified with a phosphorus containing compound to control reduction in pore volume. Alternatively, the zeolite is steamed, and the phosphorus compound is added prior to or after steaming. The amount of phosphorus, as measured on an elemental basis, is from 0.05 wt.% to 20 wt. %, and preferably is from 1 wt.% to 10 wt.%, based on the weight of the zeolite molecular sieve. Preferably, the atomic ratio of phosphorus to framework aluminum (i.e. in the zeolite framework) is not greater than 4:1 and more preferably from 2:1 to 4:1. Incorporation of a phosphorus modifier into the catalyst of the invention is accomplished, according to one embodiment, by contacting the zeolite molecular sieve either alone or the zeolite in combination with a binder with a solution of an appropriate phosphorus compound. The solid zeolite or zeolite catalyst is separated from the phosphorus solution, dried and calcined. In some cases, the added phosphorus is converted to its oxide form under such conditions. Contact with the phosphorus-containing compound is generally conducted at a temperature from 25°C to 125°C for a time from 15

minutes to 20 hours. The concentration of the phosphorus in the zeolite may be from 0.01 wt.% to 30 wt.%. This prior art discloses a non-formulated P-ZSM-5.

WO 2009 022990 A1 describes a catalyst composition for dehydration of an alcohol to prepare an alkene. The catalyst composition comprises a catalyst and a modifying agent which is phosphoric acid, sulfuric acid or tungsten trioxide, or a derivative thereof. There is no binder.

It has now been discovered a new process to make P modified zeolites.

[Brief description of the invention]

The present invention relates, in a first embodiment, to a method to make a phosphorus modified zeolite comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c),

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus,

f) optionally introducing metal oxides, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step.

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less that 1000 wppm of sodium.

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less that 1000 wppm of sodium, less that 1000 wppm of potassium and less that 1000 wppm of iron.

In a second embodiment the phosphorus is introduced in the zeolite prior to the mixing with the binder.

The present invention relates, in a second embodiment, to a method to make a phosphorus modified zeolite comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally making an ion-exchange,

b) optionally steaming said zeolite,

c) introducing phosphorus on the zeolite to introduce at least 0.1 wt% of phosphorus and said introduction is made by dry impregnation,

d) mixing said zeolite of step c) with at least a component selected among one or more binders and shaping additives,

e) shaping said mixture,

f) optionally introducing metal oxides, optionally simultaneously with step d),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step.

In an embodiment the zeolite (or molecular sieve) prior to step c) contains less that 1000 wppm of sodium.

In an embodiment the zeolite (or molecular sieve) prior to step c) contains less that 1000 wppm of sodium, less that 1000 wppm of potassium and less that 1000 wppm of iron.

The present invention also relates to the use of the catalyst made according to the above method in processes wherein said catalyst is operated in presence of

steam at high temperature. "high temperature" means above 300°C and up to 800°C. By way of example one can cite, the alcohol dehydration to convert at least an alcohol into the corresponding olefin, the olefin cracking to make lighter olefins, the MTO and the alkylation of aromatics by alcohols with olefins and/or alcohols, said process producing, by way of example, para-xylene, ethylbenzenes and cumene.

[Detailed description of the invention]

Hereunder are explained the steps of the first embodiment of the invention.

As regards the zeolite of step a) containing at least one 10 members ring into the structure, one can cite the crystalline silicates. It is by way of example the MFI (ZSM-5, silicalite-1, boralite C, TS-1), MEL (ZSM-11, silicalite-2, boralite D, TS-2, SSZ-46), FER (Ferrierite, FU-9, ZSM-35), MTT (ZSM-23), MWW (MCM-22, PSH-3, ITQ-1, MCM-49), TON (ZSM-22, Theta-1, NU-10), EUO (ZSM-50, EU-1), MFS (ZSM-57) and ZSM-48 family of microporous materials consisting of silicon, aluminium, oxygen and optionally boron.

Preferred zeolite structures are selected from the MFI, MTT, FER, MEL, TON, MWW, EUO, MFS.

In an embodiment, the zeolite is ZSM-5 with Si/Al atomic ratio ranging from 11 to 30, which has been made without direct addition of organic template.

In an embodiment, the zeolite is MFI zeolite with Si/Al atomic ratio ranging from 30 to 200.

The three-letter designations "MFI" and "MEL" each representing a particular crystalline silicate structure type as established by the Structure Commission of the International Zeolite Association. Examples of a crystalline silicate of the MFI type are the synthetic zeolite ZSM-5 and silicalite and other MFI type crystalline silicates known in the art. Examples of a crystalline silicate of the

MEL family are the zeolite ZSM-11 and other MEL type crystalline silicates known in the art. Other examples are Boralite D and silicalite-2 as described by the International Zeolite Association (Atlas of zeolite structure types, 1987, Butterworths). The preferred crystalline silicates have pores or channels defined by ten oxygen rings.

Crystalline silicates are microporous crystalline inorganic polymers based on a framework of XO_4 tetrahedra linked to each other by sharing of oxygen ions, where X may be trivalent (*e.g.* Al,B,...) or tetravalent (*e.g.* Ge, Si,...). The crystal structure of a crystalline silicate is defined by the specific order in which a network of tetrahedral units are linked together. The size of the crystalline silicate pore openings is determined by the number of tetrahedral units, or, alternatively, oxygen atoms, required to form the pores and the nature of the cations that are present in the pores. They possess a unique combination of the following properties: high internal surface area; uniform pores with one or more discrete sizes; ion exchangeability; good thermal stability; and ability to adsorb organic compounds. Since the pores of these crystalline silicates are similar in size to many organic molecules of practical interest, they control the ingress and egress of reactants and products, resulting in particular selectivity in catalytic reactions. Crystalline silicates with the MFI structure possess a bidirectional intersecting pore system with the following pore diameters: a straight channel along [010]:0.53-0.56 nm and a sinusoidal channel along [100]:0.51-0.55 nm. Crystalline silicates with the MEL structure possess a bidirectional intersecting straight pore system with straight channels along [100] having pore diameters of 0.53-0.54 nm.

In an embodiment, the zeolite is pretreated by steam. The pretreatment is performed in the range 420 to 870°C, more preferably in the range 480 to 800°C. The water partial pressure may range from 13 to 100 kPa. The steam atmosphere preferably contains from 5 to 100 vol % steam with from 0 to 95 vol % of a gas,

preferably nitrogen or air. The steam treatment is preferably carried out for a period of from 0,01 to 200 hours, more preferably from 0,05 to 50 hours.

The steam treatment tends to reduce the amount of tetrahedral aluminium in the crystalline silicate framework by forming alumina. Preferably, the amount of residual tetrahedral Al in the zeolite is between 60 to 95%. This value can be estimated by ^{27}Al MAS NMR or TPD NH3.

In an embodiment, the ZSM-5 with Si/Al atomic ratio ranging from 11 to 30, which has been made without direct addition of organic template, is pretreated by steam.

Additionally, if during the preparation of the zeolite alkaline or alkaline earth metals have been used, the molecular sieve might be subjected to an ion-exchange step. Conventionally, ion-exchange is done in aqueous solutions using ammonium salts or inorganic acids.

In an embodiment, the zeolite is subjected to dealumination such as about 10% by weight of the aluminium is removed. Such dealumination can be done by any conventional techniques known per se but is advantageously made by a steaming optionally followed by a leaching. The crystalline silicate having a ratio Si/Al of at least about 30 to 200 can be synthetized as such or it can be prepared by dealumination of a crystalline silicate with lower initial Si/Al ratio.

As regards step b), and the binder, it is selected so as to be resistant to the temperature and other conditions employed in the processes using the catalyst. The binder can be an inorganic material selected from silica, metal silicates, zirconia, borates, alumina, silica-aluminas, phosphates, for example amorphous aluminophosphates, calcium phosphates, clays, metal oxides such as ZrO_2 and/or metals, or gels including mixtures of silica and metal oxides.

In an embodiment, the binder is substantially neutral (inert) and it is selected from inorganic material selected from silica, non-acid alumina, amorphous aluminophosphates, metalphosphates, clays or a mixture of thereof. The neutral nature of the binder allow limiting secondary reactions leading to formation of heavy oxygenates and hydrocarbons, etane, acetaldehyde etc.

A particularly preferred binder for the catalyst of the present invention comprises silica. The relative proportions of the finely divided crystalline silicate material and the inorganic oxide of the binder can vary widely.

Non-limiting examples of silicon sources include silicates, precipitated silicas, for example, Zeosil range available from Rhodia, fumed silicas, for example, Aerosil-200 available from Degussa Inc., New York, N.Y., silicon compounds such as tetraalkyl orthosilicates, for example, tetramethyl orthosilicate (TMOS) and tetraethylorthosilicate (TEOS), colloidal silicas or aqueous suspensions thereof, for example Ludox-HS-40 sol available from E.I. du Pont de Nemours, Wilmington, Del., silicic acid, alkali-metal silicate, or any combination thereof.

The preferred source of silicon is a silica sol or a combination of silica sol with precipitated or fumed silica.

Types of silica sols used to form a bound catalyst for use in alcohol dehydration process are commercially available as aquasols or organosols containing dispersed colloidal silica particles. For example, sodium silicate can be used as a silica sol. Otherwise, a silica gel, fumed or pyrogenic silica may also be used to provide a silica binder in the molecular sieve catalyst. Silicic acid is another possible source of silica. Advantageously, the binder contains low amount of sodium below 1000 ppm.

Clays are known to be essentially inert under a wide range of reaction conditions. Suitable clays include commercially available products such as kaolin,

kaolinite, montmorillonite, attapulgite, saponite, and bentonite. These clays can be used as mined in their natural state, or they may also be employed in highly active forms, typically activated by an acid treatment procedure. Commercial suppliers of these clays include Thiele Kaolin Company, American Colloidal Co., and others.

Clays contribute to strength as a binder enhancing the attrition resistance properties of the catalyst particles, and clays in combination with binders contribute to the hardness of the particles. Clays also start as small particles and have a higher density, such that when combined with the molecular sieve and binder provide for denser particles, imparting the desirable characteristic of higher density.

Clays are used in this process to form a hardened product include, but are not limited to, kaolin, kaolinite, montmorillonite, saponite, bentonite, and halloysite.

In an embodiment, the binder material is often, to some extent, porous in nature and may be effective to promote the desired conversion of ethanol to ethylene. The binder might be a single amorphous entity, or a blend of two or more individual amorphous compounds.

In a related embodiment, the catalyst (zeolite+binder) has a volume of the pore between 30 Å and 1000 Å of at least 0.25 cc/g, advantageously between 0.25 and 1 cc/g preferably at least 0.26 cc/g, the most preferable between 0.27-0.92 cc/g.

In an embodiment, the binder material possesses acid properties and may also promote conversion of the ethanol.

In referring to these types of binders that may be used, it should be noted that the term silica-alumina does not mean a physical mixture of silica and alumina but means an acidic and amorphous material that has been cogelled or coprecipitated. This term is well known in the art and is described, for example, in US-A-3,909,450 BI; US-A-3,274, 124 B1 and US-A-4,988,659 B I. In this respect, it is possible to form other cogelled or coprecipitated amorphous materials that will

also be effective as either binder or filler materials. These include silica-zirconias, silica-thorias, silica-berylias, silica-titanias, silica-alumina-thofias, silica-alumina-zirconias, alurninophosphates, mixtures of these, and the like.

In another embodiment, catalyst contains alumina materials such as aluminum oxyhydroxide, γ-alumina, boehmite, diaspore, and transitional aluminas such as α-alumina, β-alumina, γ-alumina, δ-alumina, ε-alumina, κ-alumina, and ρ-alumina, aluminum trihydroxide, such as gibbsite, bayerite, nordstrandite, doyelite, and mixtures thereof.

It is desirable to provide a catalyst having a good crush strength. This is because in commercial use, it is desirable to prevent the catalyst from breaking down into powder-like materials. Such oxide binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

The catalyst composition may be prepared, as indicated above, by any of the methods described in the art. Advantageously, however, the catalyst particles are combined with the binder material initially by dry-mixing, then in a liquid, preferably water, preferably with a plasticizer, to yield a paste.

As plasticizer (shaping additive), there may be mentioned one that will be decomposed during any subsequent heat treatment, e.g., calcination. Suitable materials for this purpose include, for example, alkylated cellulose derivatives, hydroxyethylcellulose (HEC), tylose, ammonium alginate, polyvinyl pyrrolidone, glycerol, and polyethylene glycol.

In addition to enhancing the catalyst strength properties, the binder material allows the molecular sieve crystallite powder to be bound into larger particle sizes suitable for commercial catalytic processes. The formulation of the mixture b) may be formed into a wide variety of shapes including extrudates, spheres, pills, and the like.

The uniformly mixed paste may subsequently be shaped, for example by spray drying to yield microspheres, pelletizing or, preferably, by extrusion.

The paste is then extruded, for example in a piston extruder, into strings, for example cylindrical, dried, again calcined, and chopped into pieces of a desired length.

As regards the proportions of the zeolite, the one or more binders and shaping additives, advantageously the proportion of the zeolite is from 5 to 95w% of the catalyst. The catalyst comprises the zeolite and at least a component selected among one or more binders and shaping additives. The amount of zeolite which is contained in the catalyst ranges more advantageously from 15 to 90 weight percent of the total catalyst, preferably 20 to 85 weight percent of the catalyst.

Once the molecular sieve catalyst composition is shaped, and in a substantially dry or dried state, a heat treatment, for example calcination, is advantageously performed to harden and/or activate the composition. Therefore the heat treatment is preferably carried out at a temperature of at least 400°C, for a period of from 1 to 48 hours. Calcination may be carried out, for example, in a rotary calciner, fluid bed calciner, or a batch oven.

As regards the Ion-exchange of step c), purpose is to get advantageously a formulated zeolitic molecular sieve with an inert binder before subjecting in a contact with a phosphatation agent having less than than 1000 wppm of alkali & alkali-earth metals, Na, K, Fe as well as less than 200 ppm of red-ox & noble elements such as Zn, Cr, Rh, Mn, Ni, V, Mo, Co, Cu, Cd, Pt, Pd, Ir, Ru, Re. This may achieved by an optional back ion-exchange step known per se.

Although in principle mixing with the binder and ion exchange may be carried out in any order, advantageously ion exchange is performed after shaping but before phosphorus introduction.

The ion exchange step is performed on shaped calcined catalyst before or after the steaming step d).

As regards the steaming of step d), it is also known as the pre-steaming by reference to the final steaming of step i). The treatment is performed in the range 420 to 870°C, more preferably in the range 480 to 800°C. The water partial pressure may range from 13 to 100 kPa. The steam atmosphere preferably contains from 5 to 100 vol % steam with from 0 to 95 vol % of a gas, preferably nitrogen or air. The steam treatment is preferably carried out for a period of from 0,01 to 200 hours, more preferably from 0,05 to 50 hours.

The steam treatment tends to reduce the amount of tetrahedral aluminium in the crystalline silicate framework by forming alumina. Preferably, the amount of residual tetrahedral Al in the zeolite is between 60 to 95%. This value can be estimated by ^{27}Al MAS NMR or TPD NH_3.

As regards the introduction of P of step e), said introduction of phosphorus can be performed under reduced or atmospheric pressure at temperature from 10 to 400°C. A non-limiting source of phosphorus can be provided in aqueous or non-aqueous medium.

In an embodiment, the non-aqueous medium is selected from the group containing ethanol, methanol or other alcohols.

The preferred techniques are impregnation and chemical vapour deposition.

These techniques imply a minimum waste to treat and allow maintaining substantially all phosphorus on the catalyst.

In an embodiment, the catalyst precursor is treated by a source of phosphorus injected into a steam flow. In this case, the phosphatation is performed under mild steaming condition with a steam flow containing phosphorus at 100-400°C.

In an embodiment, the phosphorus is introduced by a treatment of the catalyst precursor (zeolite + binder) in a solution contaning a source of phosphorus at temperature 25-100°C for 0.1-96h followed by filtering or evaporation.

In a preferred embodiment the incipient wetness impregnation technique is used. In this case the phosphorus is introduced via impregnation using a limited amount of liquid water which is subjected to a contact with catalyst. This method is also known as the dry impregnation.

Incipient wetness (IW) or incipient wetness impregnation (IWI) is a commonly used technique for the synthesis of heterogeneous catalysts. Typically, the precursor (phosphorus-containing compounds) is dissolved in an aqueous or organic solution. The volume of solution, which is used for dissolution of the precursor, is substantially the same as the pore volume of catalyst precursor containing both binder and zeolite . Then the precursor-containing solution is added to a catalyst precursor. Capillary action draws the solution into the pores. The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the phosphorus on the catalyst surface.
The sample before impregnation can be dried or calcined. The impregnation could be performed at room or elevated temperature (30-100°C).

The adsorption capacity is typically measured by impregnating the dried extruded zeolite with water until the zeolite was completely wet. Weighing the zeolite before and after impregnation gives the absorption capacity:

$$Absorption\ capacity(\%) = \frac{weight\ after\ impregantion - dry\ weight}{dry\ weight} * 100$$

In an embodiment, H3PO4 solution is used for impregnation.

Advantageously, a mixture of H3PO4 with their ammonium salts providing a pH of the aqueous solution higher than 2.0 is used for impregnation

In an embodiment, the sources of phosphorus are substantially metal free components, for example H3PO4, ammonium phosphates or organic P-compounds. "substantially metal free" means a metal proportion with has no adverse effect on the P introduction. By way of example this proportion can be below 1000 wppm.

The amount of phosphorus on the catalyst can be from 0.5 to 30 wt%, but preferably from 0.5 to 9 w%.

In an embodiment, the phosphatation step is performed before or simultaneously with introduction of metal oxides.

As regards step f), the introduction of metal oxides, advantageously said metals are selected among alkaline earth or rare earth metals. The alkaline earth or rare earth metal M is preferably selected from one or more of: Mg, Ca, Sr, Ba, La, Ce. More preferably, M is an alkaline earth metal. Most preferably, M is Ca. Particularly in the case of P-modification via steaming and leaching, M can be a rare earth metal such as La and Ce.

The M-containing component is preferably in the form of an organic compound, a salt, hydroxide or oxide. The compound is preferably in a solubilized form when bringing it into contact with the molecular sieve. Alternatively, the solution of the M-containing compound can be formed after bringing the molecular sieve in contact with said compound.

Possible M-containing compounds include compounds such as sulphate, formate, nitrate, acetate, halides, oxyhalides, borates, carbonate, hydroxide, oxide and mixtures thereof.

Those M-containing compounds, which are poorly water-soluble, can be dissolved to form a well-solubilized solution by heating and/or by modifying the pH of the solution by addition of phosphoric, acetic or nitric acid or corresponding ammonium salts of said acids.

As regards step g), a washing step can be envisaged. In accordance with the present invention, the catalyst is treated with water for a period of time from 0.1 to 48 hours, preferably for a period of time from about 0.5 to 36 hours and most preferably from about 1 to 24 hours. The water was at a temperature between about 20°C and 180°C, preferably between about 20°C and 100°C and most preferably between about 25°C and 60°C. By way of example the water can be at 30°C. Following the water treatment, the catalyst may be dried at about >60° C. Optionally, the water can contain at least one dissolved solid selected from the group consisting of ammonium chloride, ammonium phosphate, ammonium sulfate, ammonium acetate, ammonium carbonate, ammonium nitrate and mixtures thereof.

As regards step h), said calcination can be made in air or an inert gas, typically at a temperature of from 350 to 900°C for a period of from 1 to 48 hours. Optionally the air or an inert gas may contain steam in concentration from 10 to 90 vol%.

As regards step i), it is performed in the range 420 to 870°C, more preferably in the range 480 to 800°C. In an embodiment it is performed by steaming at temperature above 600, more preferably from 625 to 800°C and still more preferably from 700 to 800°C. In another embodiment it is performed in the

range 420 to 600°C. The water partial pressure may range from 13 to 100 kPa. The steam atmosphere preferably contains from 5 to 100 vol % steam with from 0 to 95 vol % of a gas, preferably nitrogen or air. The steam treatment is preferably carried out for a period of from 0,01 to 200 hours, preferably from 0,05 to 50 hours, more preferably for at least 0.1 hour and in a preferred way from 0,1 to 50 hours.

Hereunder are explained the steps of the second embodiment of the invention.

Step a) is the same as in the first embodiment.

As regards the Ion-exchange of step a), purpose is to get advantageously a zeolite before subjecting in a contact with a phosphatation agent having less than than 1000 wppm of alkali & alkali-earth metals, Na, K, Fe as well as less than 200 ppm of red-ox & noble elements such as Zn, Cr, Rh, Mn, Ni, V, Mo, Co, Cu, Cd, Pt, Pd, Ir, Ru, Re. This may be achieved by an optional back ion-exchange step known per se.

The ion exchange step is performed before the steaming of stepb) if any.

As regards the steaming of step b), it is similar to the one of step d) of the first embodiment.

As regards the introduction of P at step c), this is similar to the introduction of P already described at step e) in the first embodiment excepted that there is no binder and it is made by dry impregnation.

As regards step d), and step e), as well as the proportions of zeolite and binder this is similar to step b) already described in the first embodiment, except that the zeolite has been P modified. In a related embodiment, the catalyst (zeolite+binder) has a volume of the pore between 30 Å and 1000 Å of at least 0.25 cc/g, advantageously between 0.25 and 1 cc/g preferably at least 0.26 cc/g, the most preferable between 0.27-0.92 cc/g.

As regards steps f) to i), they are the same as in the first embodiment.

As regards the dehydration process to convert an alcohol into an olefin, this process has been described in a lot of patent applications. One can cite WO/2009/098262, WO/2009/098267, WO/2009/098268 and WO 2009/098269, the content of which is incorporated in the present application. The alcohol is any alcohol provided it can be dehydrated to the corresponding olefin. Advantageously the alcohol has two or more carbon atoms. The corresponding olefin is an olefin having the same number of carbons as the alcohol. By way of example mention may be made of alcohols having from 2 to 10 carbon atoms. Advantageously the invention is of interest for ethanol, propanol, butanol and phenylethanol.

As regards the cracking of olefins, more precisely the present invention relates to a process for cracking an olefin-rich hydrocarbon feedstock which is selective towards light olefins in the effluent. In particular, olefinic feedstocks from refineries or petrochemical plants can be converted selectively so as to redistribute the olefin content of the feedstock in the resultant effluent. Said cracking of an olefin-rich feedstock is often referred in the following description and claims as OCP (Olefin Cracking Process). As regards the hydrocarbon feedstock containing one or more olefins sent to the OCP reactor, in accordance with the present invention, cracking of olefins is performed in the sense that olefins in a hydrocarbon stream are cracked into lighter olefins and selectively into propylene. The feedstock and effluent preferably have substantially the same olefin content by weight. Typically, the olefin content of the effluent is within ±15wt%, more preferably ±10wt%, of the olefin content of the feedstock. The feedstock may comprise any kind of olefin-containing hydrocarbon stream. The feedstock may typically comprise from 10 to 100wt% olefins and furthermore may be fed undiluted or diluted by a diluent, the diluent optionally including a non-olefinic hydrocarbon. In particular, the olefin-containing feedstock may be a hydrocarbon mixture containing normal and branched olefins in the carbon range C_4 to C_{10}, more preferably in the carbon range C_4 to C_6, optionally

in a mixture with normal and branched paraffins and/or aromatics in the carbon range C_4 to C_{10}. Typically, the olefin-containing stream has a boiling point of from around -15 to around 180°C. With regards to the OCP process, said process is known per se. It has been described in EP 1036133, EP 1035915, EP 1036134, EP 1036135, EP 1036136, EP 1036138, EP 1036137, EP 1036139, EP 1194502, EP 1190015, EP 1194500 and EP 1363983 the content of which are incorporated in the present invention.

As regards the MTO, said process produces light olefins such as ethylene and propylene as well as heavy hydrocarbons such as butenes. Said MTO process is the conversion of methanol or dimethylether by contact with a molecular sieve which can be a P modified zeolite.

As regards the alkylation of aromatic compounds with olefins and alcohols, said process produces, by way of example, para-xylene, ethylbenzenes and cumene. Alkylation of aromatic, for example, toluene methylation has been known to occur over acidic catalyst, particularly over zeolite or zeolite-type catalyst. In particular, ZSM-5-type zeolite, zeolite Beta and silicaaluminophosphate (SAPO) catalysts have been used for this process.

One skilled in the art will also appreciate that the olefins made by the dehydration process of the present invention can be, by way of example, polymerized. When the olefin is ethylene it can be, by way of example,

polymerized to form polyethylenes,

dimerized to butene and then isomerised to isobutene, said isobutene reacting with ethanol to produce ETBE,

dimerized to butane followed by reacting with ethylene via methatesis to produce propylene;

converted to propylene over metal, acid or bifunctional catalyst,used for alkylation of benzene to form ethyl -benzene,

dimerised to 1-butene, trimerised to 1-hexene or tetramerised to 1-octene, said alpha-olefins comonomers are further reacted with ethylene to produce polyethylene

dimerised to 1-butene, said 1-butene is isomerised to 2-butene and said 2-butene is further converted with ethylene by metathesis reaction into propylene and said propylene can be polymerised to polypropylene,

converted to ethylene oxide and glycol or

converted to vinyl chloride.

The present invention relates also to said polyethylenes, polypropylene, propylene, butene, hexane, octene, isobutene, ETBE, vinyl chloride, ethylene oxide and glycol.

When the olefin is propylene it can be, by way of example,

polymerized to form polypropylene,

used for alkylation of aromatics etc.....

[Examples]

EXAMPLE 1

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (contained 250 ppm of Na & synthesized without template) was blended with a silica binder in a ratio 80:20 followed by addition of extrusion additives and shaping. A final Na content in the catalyst was 320 ppm.

The extruded sample was dried for 2h at 140°C, calcined for 2h at 600°C followed by steaming at 550°C for 6h in 100% steam.

Steamed solid was incipient wetness impregnated with an aqueous solution of phosphoric acid to introduce about 3wt% of phosphorus to the catalyst. The impregnated solid was dried for 16h at 110°C.

Then, the phosphated sample was incipient wetness impregnated with a solution of calcium nitrate obtained by dissolution of calcium carbonate to introduce about1wt% of calcium to the solid. The impregnated solid was dried for 16h at 110oC.

Resulted catalyst containing 2.8wt% of phosphorus and 0.8 % of calcium was steamed at 600°C for 2h in 100% of steam. The sample is hereinafter identified as **sample A.**

Resulted catalyst containing about 2.8wt% of phosphorus and 0.8 % of calcium was steamed at 750°C for 1h in 100% of steam. The sample is hereinafter identified as **sample B.**

Catalyst tests were performed on 1 ml of catalyst grains (35-45 meshes) loaded in a tubular reactor with internal diameter 11mm. A mixture 25wt%EthOH/75wt% H_2O was subjected to a contact with catalyst described in the example I in a fixed bed reactor at 380°C, WHSV = $7h^{-1}$ P=2 bara. The results are given in table 1 hereunder. The values are the weight percents on carbon basis.

Example 2

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (containing 250 ppm of Na & synthesized without template) was blended with a silica binder in a ratio 80:20 followed by addition of extrusion additives and shaping. A final Na content in the catalyst was 320 ppm.

The extruded sample was dried for 16h at 110°C, calcined for 10h at 600°C followed by steaming at 550°C for 6h in 100% steam.

Steamed shaped zeolite was then contacted with an aqueous solution of H_3PO_4 (85%wt) for 2h under reflux condition (4ml/1g zeolite). Then 1 g of $CaCO_3$ was introduced. After stirring during 30min, the system is cooled down at room temperature and the excess of solution is removed by filtration without washing. The recovered solid is dried at 110°C for 16h followed by steaming at 600°C for 2h in 100% of steam.

Resulted catalyst contained about 1.7wt% of phosphorus and 0.4wt% of calcium. The sample is hereinafter identified as **sample C**

The performances of the catalyst were then evaluated under the same operating conditions as described above, using 1 ml of catalyst (35-45 mesh) loaded in a tubular reactor with internal diameter 11mm. A mixture of 25wt%EtOH/75wt% H_2O has been processed on catalyst C, in a fixed bed reactor at 380°C, WHSV = $7h^{-1}$ P=2 bara. The results are given in table 1. The values are the weight percents on carbon basis.

EXAMPLE 3

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (containing 250 ppm of Na & synthesized without template) was blended with a silica binder in a ratio 80:20 followed by addition of extrusion additives and shaping. A final Na content in the catalyst was 320 ppm.

The extruded sample was dried for 16h at 110°C, calcined for 10h at 600°C followed by steaming at 550°C for 6h in 100% steam.

12g of steamed solid was incipient wetness impregnated with an aqueous solution containing 1.54g of NH4H2PO4. The impregnated solid was dried for 16h at 110°C.

Then, the phosphated sample was incipient wetness impregnated with a solution of calcium nitrate obtained by dissolution of 0.3g calcium carbonate in nitric acid. The impregnated solid was dried for 16h at 110°C.

Resulted catalyst contained about 2.54wt% of phosphorus and 0.82wt% of calcium. The sample is hereinafter identified as **sample D.**

The performances of the catalyst were then evaluated under the same operating conditions as described above, using 1 ml of catalyst (35-45 mesh) loaded in a tubular reactor with internal diameter 11mm. A mixture of 25wt%EtOH/75wt% H_2O has been processed on catalyst D, in a fixed bed reactor at 380°C, WHSV = $7h^{-1}$ P=2 bara. The results are given in table 1. The values are the weight percents on carbon basis.

Table 1

Sample	A	B	C	D
P (bara)	2	2	2	2
T (°C)	380	380	380	380
WHSV (H-1)	7	7	7	7
EtOH conversion (% wt CH2)	99.9	99.8	99.9	99.9
DEE	0.0	0.0	0.0	0.0
Acetaldyde	0.31	0.17	0.17	0.13
EtOH	0.10	0.20	0.05	0.05
Yield on C-basis (%wt CH2)				
CH4	0.00	0.00	0.00	0.00
C2	0.13	0.06	0.11	0.12
C2=	97.9	99.0	97.3	97.4
C3=	0.56	0.07	0.7	0.8
C4+ olef	0.86	0.48	1.6	1.4
Unknown	0.10	0.06	0.07	0.08
Selectivity on C-basis (%wt CH2)				
C2=	98.0	99.20	97.4	97.4
C2's cut purity (%)	99.87	99.94	99.88	99.87

EXAMPLE 4

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (contained 250 ppm of Na & synthesized without template) was blended with a binder containing silica and kaolin in a ratio 70:10:20 followed by addition of extrusion additives and shaping.

The extruded sample was dried for 2h at 140°C, calcined for 10h at 600°C followed by steaming at 550°C for 6h in 100% steam.

Steamed solid was incipient wetness impregnated with an aqueous solution of phosphoric acid to introduce about 3wt% of phosphorus to the catalyst. The impregnated solid was dried for 16h at 110°C.

Then, the phosphated sample was incipient wetness impregnated with a solution of calcium nitrate obtained by dissolution of calcium carbonate to introduce about 1wt% of calcium to the solid. The impregnated solid was dried for 16h at 110oC.

Resulted catalyst containing 2.94wt% of phosphorus and 0.8 % of calcium was steamed at 750°C for 2h in 100% of steam. The sample is hereinafter identified as **sample E.**

EXAMPLE 5

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (synthesized without template) was calcined for 10h at 600°C followed by steaming at 550°C for 6h in 100% steam.

100g of steamed solid was incipient wetness impregnated (dry impregnated) with an aqueous solution containing 9.86g of phosphoric acid. The impregnated solid was dried for 16h at 110°C.

Then, 16g of the phosphated sample was extruded with 4g of silica binder and 0.4g of $CaCO_3$.

The resulted catalyst was calcined at 600°C for 10h followed by steaming at 600oC for 2h in 100% of steam. The sample is hereinafter identified as **sample F.**

EXAMPLE 6 (OCP test)

Catalyst tests were performed on 0.8g of catalyst grains (35-45 meshes) loaded in the tubular reactor. The feedstock which contains substantially non cyclic olefins C4 (~60%) was subjected to catalytic cracking in the presence of catalyst in a fixed bed reactor at T_{in}-550°C, WHSV= $16h^{-1}$, P=1.5 bara. The results are in table

2. The values in the table 2 are the average catalyst performance for 1-10 hours-on-stream given in weight percents on carbon basis.

The data given below illustrate good cracking activity and high selectivity of the P-zeolite in C4 olefins conversion to propylene and ethylene.

Table 2

Sample	E	F
P (bara)	1.5	1.5
T_{in} (°C)	550	550
WHSV (h^{-1})	16	16
C4 olefins conversion, %	65.4	65.2
Purity C3's, %	94.9	96.0
Yield on C-basis, %		
Methane	0.07	0.14
Aromatics	1.2	1.4
Propane	1.0	0.8
Ethylene	3.5	3.4
Propylene	19.5	19.1

CLAIMS

1 Method to make a phosphorus modified zeolite comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c)

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus,

f) optionally introducing metal oxides, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step.

2 Method according to claim 1 wherein the shaped zeolite (or molecular sieve) of step b) contains less that 1000 wppm of sodium.

3 Method according to claim 2 wherein the shaped zeolite (or molecular sieve) of step b) contains less that 1000 wppm of sodium, less that 1000 wppm of potassium and less that 1000 wppm of iron.

4 Method according to any one of the preceding claims wherein at step d) the treatment is performed in the range 420 to 870°C.

5 Method according to any one of the preceding claims wherein at step i) the treatment is performed in the range 420 to 600°C.

6 Method according to any one of claims 1 to 4 wherein at step i) the treatment is performed in the range 625 to 800°C.

7 Method to make a phosphorus modified zeolite comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally making an ion-exchange,

b) optionally steaming said zeolite,

c) introducing phosphorus on the zeolite to introduce at least 0.1 wt% of phosphorus and said introduction is made by dry impregnation,

d) mixing said zeolite of step c) with at least a component selected among one or more binders and shaping additives,

e) shaping said mixture,

f) optionally introducing metal oxides, optionally simultaneously with step d),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step.

8 Method according to claim 7 wherein the zeolite (or molecular sieve) prior to step c) contains less that 1000 wppm of sodium.

9 Method according to claim 8 wherein the shaped zeolite (or molecular sieve) prior to step c) contains less that 1000 wppm of sodium, less that 1000 wppm of potassium and less that 1000 wppm of iron.

10 Method according to any one of claims 7 to 9 wherein at step i) the treatment is performed in the range 420 to 600°C.

11 Method according to any one of claims 7 to 9 wherein at step i) the treatment is performed in the range 625 to 800°C.

12 Method according to any one of the preceding claims wherein the zeolite is selected from the MFI, MTT, FER, MEL, TON, MWW, EUO, MFS.

13 Method according to claim 12 wherein the zeolite is ZSM-5 with Si/Al atomic ratio ranging from 11 to 30, which has been made without direct addition of organic template.

14 Method according to claim 12 wherein the zeolite is MFI with Si/Al atomic ratio ranging from 30 to 200.

15 Method according to any one of the preceding claims wherein the amount of phosphorus on the catalyst is from 0.5 to 30 wt%.

16 Method according to claim 11 wherein the amount of phosphorus on the catalyst is from 0.5 to 9 w%.

17 Method according to any one of the preceding claims wherein the metal in the metal oxides is an alkaline earth or rare earth metal M preferably selected from one or more of: Mg, Ca, Sr, Ba, La, Ce.

18 Method according to any one of the preceding claims wherein the catalyst (zeolite+binder) has a volume of the pores between 30 Å and 1000 Å of at least 0.25 cc/g.

19 Method according to any one of the claims 1 to 6 wherein the phosphorus introduction is made by incipient wetness (IW) or incipient wetness impregnation (IWI).

20 Use of the catalyst made according to any one of the preceding claims in processes wherein said catalyst is operated in the presence of steam at temperature above 300°C and up to 800°C.

21 Process to dehydrate an alcohol to convert at least said alcohol into the corresponding olefin wherein said dehydration is made in the presence of a catalyst made according to any one of claims 1 to19.

22 Process to make cracking of olefins to make lighter olefins wherein said cracking is made in the presence of a catalyst made according to any one of claims 1 to19.

23 Process to make cracking of methanol or dimethylether to produce light olefins such as ethylene and propylene wherein said cracking is made in the presence of a catalyst made according to any one of claims 1 to19.

24 Process to make alkylation of aromatics by alcohols or olefins wherein said alkylation is made in the presence of a catalyst made according to any one of claims 1 to19.

ABSTRACT

The present invention relates, in a first embodiment, to a method to make a phosphorus modified zeolite comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c),

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus,

f) optionally introducing metal oxides, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step.

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less that 1000 wppm of sodium.

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less that 1000 wppm of sodium, less that 1000 wppm of potassium and less that 1000 wppm of iron.

In a second embodiment the phosphorus is introduced in the zeolite prior to the mixing with the binder.

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Date of mailing *(day/month/year)* 14 September 2012 (14.09.2012)	
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RECIBO DE CAJA

No. 14 - 0022690

Bogotá D.C., Febrero 27 de 2014 - 14:32:34

RECIBIDO DE : POSSE HERRERA & RUIZ S.A. NI 830.022.196 RE

*** Soporte del Pago ***

TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	VR PAGO
RECIBO DE CA	999999999	17322	13/02/2014		1.000.00
CONSIGNACION	BANCO DE BOGOTA	062754387	529733525	27/02/2014	8.409.000.00
CONSIGNACION	BANCO DE BOGOTA	062754387	650524206	27/02/2014	3.390.000.00

*** Conceptos Pagados ***

CANT.	RENTISTICO	CONCEPTO	Vr.UNDITARIO	Vr.CONCEPTO
1	50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE INVENCION	515.000.00	515.000.00
				$515.000.00

SON: **QUINIENTOSQUINCE MIL PESOS MONEDA CORRIENTE***

Responsable: _____
-*********-

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
No. 14-042046- -00000-0000
Fecha: 2014-02-27 15:19:28 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve. 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 125

129

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
NIT : 800.176.089-2
- / -

Industria y Comercio
SUPERINTENDENCIA

RECIBO DE CAJA

No. 14 - 0022694

Bogotá D.C., Febrero 27 de 2014 - 14:32:34

RECIBIDO DE : POSSE HERRERA & RUIZ S.A. NI 830.022.196 RE

*** Soporte del Pago ***

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RECIBO DE CA	999999999	17322	13/02/2014		1.000.00
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CONSIGNACION	BANCO DE BOGOTA	062754387	650524206	27/02/2014	3.390.000.00

*** Conceptos Pagados ***

CANT.	RENTISTICO	CONCEPTO	Vr.UNDITARIO	Vr.CONCEPTO
19	50005-01-01 SOLICITUDES	1607 REIVINDICACION PATENTE UNITARIA ADICIONAL A LAS 10 INIC	31.000.00	589.000.00
				$589.000.00

SON: **QUINIENTOS OCHENTA Y NUEVE MIL PESOS MONEDA CORRIENTE***

Responsable: _____
-***-

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
No. 14-042046- -00000-0000
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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

No. 14-042046- -00000-0000

Fecha: 2014-02-27 15:19:28 Dep: 2020 DIR.NUEVASCR ES
Tra: 11 PATENTEIYII Eve: 378 FASENACIONALI
Act: 411 PRESENTACION Folios: 125

125

PATENTE DE INVENCIÓN ☐ **MODELO DE UTILIDAD** ☐ **Art 33 Decision 486/00**

- ☐ Indicación que se solicita una patente.
- ☐ Datos de identificación del solicitante o de la persona que presenta la solicitud
- ☐ Descripción de la invención
- ☐ Dibujos de ser estos pertinentes
- ☐ Comprobante de pago de las tasas establecidas (De ser el caso formato de descuento)

Completa ☐ Incompleta ☐

PATENTE DE INVENCIÓN PCT ☐ **MODELO DE UTILIDAD PCT** ☐ **Art.33 Decisión 486/00, Circular Única**

- ☐ Indicación que se solicita una PCT
- ☐ Copia de la solicitud en español, tal como fue presentada inicialmente (capítulo descriptivo, reivindicatorio, resumen)
- ☐ Dibujos de ser estos pertinentes
- ☐ Comprobante de pago de las tasas establecidas (de ser el caso formato de descuento)

Completa ☐ Incompleta ☐

DISEÑO INDUSTRIAL ☐ **(Art. 119 Decisión 486/00)**

- ☐ Indicación que se solicita Diseño industrial
- ☐ Datos de identificación del solicitante o de la persona que presenta la solicitud
- ☐ Representación gráfica y fotográfica del Diseño industrial o muestra del material que incorpora el diseño
- ☐ Comprobante de pago de las tasas establecidas

Completa ☐ Incompleta ☐

ESQUEMA DE TRAZADO ☐ **(Art. 92 Decisión 486/00)**

- ☐ Indicación que se solicita un esquema de trazado
- ☐ Datos de identificación del solicitante o de la persona que presenta la solicitud
- ☐ Representación gráfica de un esquema de trazado
- ☐ Comprobante de pago de las tasas establecidas

Completa ☐ Incompleta ☐