

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIRECCIÓN DE NUEVAS CREACIONES**

202085
Bogotá, D.C.,

Abogado
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ASUNTO	Radicación	08-91695
	Trámite	002
	Evento	001
	Actuación	411
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	Folios	31

13044

Patente de Invención ☐ Patente de Modelo de Utilidad ☐

Via Nacional ☒

Via PCT (fase nacional) ☐ Cap. I ☐ Cap. II ☐

Fecha de Presentación: 2008-09-02

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Folios 3-16	2008-09-02
Reivindicaciones:	Folios 17-20	2008-09-02
Figuras	Folios 21-23	2008-09-02

2. Objeto de la invención

Título de la solicitud: Proceso de preparación de catalizadores útiles en la licuefacción directa de carbón y el catalizador así obtenido. Folio 1.

Objeto de la invención: El objeto de la presente solicitud de patente de invención se refiere a un procedimiento para la obtención de catalizadores de metales de transición soportados en un material carbonoso via impregnación con una solución de complejo de metal-tiourea y los catalizadores así obtenidos.

El problema técnico que se plantea en esta solicitud radica en la necesidad de diseñar un procedimiento económico y de bajo impacto ambiental para la obtención de un catalizador soportado, el cual no requiere la utilización de compuestos azufrados tales como CS₂ o H₂S. Para solucionar ese problema

técnico la solicitud plantea un procedimiento para la obtención de catalizadores de metales de transición soportados en un material carbonoso vía impregnación con una solución de complejo de metal-tiourea y los catalizadores así obtenidos.

El objeto de la presente solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): B01J 31/16; 27/049; 27/02; 37/02, C01G 1/00; 1/08.

3. De la solicitud de Patente

Reivindicaciones (artículo 30 D 486)

El capítulo reivindicatorio es demasiado amplio y no cumple con el requisito de concisión; asimismo se considera una generalización que no se encuentra enteramente soportada en la descripción.

Se llama la atención del solicitante frente a que las etapas y condiciones del proceso de interés son presentadas en un lenguaje muy general que no permite definir claramente el alcance de la invención. En este sentido sírvase definir específicamente el metal o metales de transición involucrados y el material carbonoso. Se le recomienda al solicitante que limite el alcance de su invención a aquella materia que se encuentre enteramente sustentada.

En consecuencia, el capítulo reivindicatorio no cumple con el requisito de concisión y sustento en la descripción de acuerdo al art. 30 de la Decisión 486.

Descripción (artículo 28)

La descripción resulta ser insuficiente para el amplio alcance que tiene el capítulo reivindicatorio. Se le recuerda al solicitante que la descripción debe ser una divulgación suficiente y adecuada para la materia que se está reclamando, pero el alcance de la misma va mucho más allá de aquella materia que se encuentra enteramente soportada en la descripción.

Se llama la atención del solicitante, frente a que los estudios presentados evalúan catalizadores soportados en coque térmico (y no en cualquier material carbonoso) y que utilizan como metal de transición el cobalto o el níquel (y no cualquier metal de transición ni mezclas de ellos). Dichas especificidades se alejan en gran medida de la generalidad reclamada. Esta Oficina no encuentra ninguna razón técnica para prever que un catalizador soportado sobre otro material carbonoso o que contenga otro metal de transición o incluso mezcla de ellos, tenga el mismo comportamiento. Una vez más, se le recomienda al solicitante que limite el alcance de la invención.

En consecuencia, la descripción no cumplió con el requisito de claridad y/o divulgación completa de acuerdo al art. 28 de la Decisión 486 y el art. 22 del Tratado PCT.

4. Determinación del Estado de la Técnica

Considerando la fecha de presentación de la solicitud 2008-09-02 se realizó la búsqueda en el estado de la técnica y se encontraron los documentos relacionados a continuación que pueden afectar la patentabilidad del objeto de la presente solicitud:

Nº	DOCUMENTO	TÍTULO	FECHA DE PUBLICACIÓN
D1	US5168088	Method for dispersing catalyst onto particulate material and product thereof	1992-12-01
D2	US5139990	Process for the preparation of a resulfided catalyst	1992-08-18

Los documentos son anexados al expediente

El documento D1 divulga un método para preparar un catalizador útil para la licuefacción directa de carbón u otro proceso de hidrogenación de carbón que comprende las etapas de depositar un precursor de catalizador hidratado tal como óxido de hierro hidratado (FeOOH) o sulfuros de hierro insolubles como la pirita, directamente sobre la superficie del carbón hasta formar una pasta húmeda. La pasta húmeda así obtenida puede incluir partículas de carbón u otro material carbonoso humedecido con una solución acuosa de iones férricos. El catalizador se activa mediante la conversión a la forma de sulfuro para la hidrogenación o licuefacción directa del carbón

El documento D2 divulga un procedimiento de pre-sulfuración *ex situ* de un catalizador para hidrotratamiento que comprende impregnar el catalizador con una solución acuosa de un compuesto orgánico sulfurado, posterior proceso de secado y activación.

5. Examen de patentabilidad (artículo 14 D486)

Nivel Inventivo (artículo 18 D486)

La reivindicación 1 reclama:

Un proceso para la obtención de un catalizador útil para la licuefacción directa de carbón caracterizado porque comprende las siguientes etapas:

- a) Preparación de los compuestos de coordinación metal-tiourea a partir de añadir una solución acuosa de una sal precursora de uno o varios metales de transición a una solución de tiourea, a temperatura ambiente que puede ser seleccionada del intervalo comprendido entre 290 y 307 K, en la que la adición de la sal precursora a la tiourea se realiza a un flujo de 0,5 a 1 mL/lmin;
- b) Impregnación del material carbonoso estabilizado térmicamente utilizado como soporte del catalizador bajo vacío y en presencia de agitación ultrasónica; y
- c) Activación del catalizador por tratamiento térmico y a presión atmosférica.

Características esenciales de la invención	Características esenciales del documento D1	Características esenciales del documento D2
Un proceso para la obtención de un catalizador útil para la licuefacción directa de carbón caracterizado porque comprende las siguientes etapas:	un método para preparar un catalizador útil para la licuefacción directa de carbón u otro proceso de hidrogenación de carbón que comprende las etapas	divulga un procedimiento de pre-sulfuración exsitu de un catalizador útil para procedimiento de hidrotratamiento catalítico.
a) Preparación de los compuestos de coordinación metal-tiourea a partir de añadir una solución acuosa de una sal precursora de uno o varios metales de transición a una solución de tiourea, a temperatura ambiente que puede ser seleccionada del intervalo comprendido entre 290 y 307 K, en la que la adición de la sal precursora a la tiourea se realiza a un flujo de 0.5 a 1 mL/lmin;	Depositar un precursor de catalizador hidratado tal como óxido de hierro hidratado (FeOOH) o sulfuros de hierro insolubles como la pirita, directamente sobre la superficie del carbón hasta formar una pasta húmeda.	preparar una solución de un compuesto azufrado orgánico por ejemplo tiourea
b) Impregnación del material carbonoso estabilizado térmicamente utilizado como soporte del catalizador bajo vacío y en presencia de agitación ultrasónica; y	Añadir amoníaco gaseoso o una solución de hidróxido de amoníaco para precipitar el óxido de hierro hidratado directamente sobre el material carbonoso en partículas. La pasta húmeda a continuación, es secada mezclada con disolvente para formar la alimentación al proceso de licuefacción.	Impregnar el medio acuoso que contiene el compuesto orgánico azufrado, con el catalizador soportado a temperatura ambiente.
c) Activación del catalizador por tratamiento térmico y a presión atmosférica	Posteriormente someter a calentamiento para que el precursor del catalizador, óxido de hierro hidratado, reaccione con un material azufrado tales como H ₂ S o CS ₂ o (NH ₄) ₂ S proporcionando las formas activas del hierro (Fe _{1-x} S) donde x es entre 0,01 y 0,2.	Posteriormente someter a un proceso de secado para eliminar el agua en exceso. Y luego activar el catalizador para obtener su forma activa como sulfuro de metal.

Los documentos D1 y D2 se consideran el estado de la técnica cercano a la invención definida en la reivindicación 1 porque:

El documento D1 divulga (columna 3 y ejemplos) un método para preparar un catalizador útil para la licuefacción directa de carbón u otro proceso de hidrogenación de carbón que comprende las etapas de depositar un precursor de catalizador hidratado tal como óxido de hierro hidratado (FeOOH) o sulfuros de hierro insolubles como la pirita, directamente sobre la superficie del carbón hasta formar una pasta húmeda. La pasta húmeda así obtenida puede incluir partículas de carbón u otro material carbonoso humedecido con una solución acuosa de iones férricos.

Específicamente, la preparación de la pasta húmeda consiste en una mezcla entre el carbón particulado de aproximadamente 10 a 250 micras de tamaño de partícula con una solución de sales de hierro solubles, tales como nitrato férrico o cloruro férrico. La cantidad de solución está limitada a no más que la cantidad en la que se produce la humedad incipiente.

Posteriormente se añade un agente que proporcione iones amonio tal como amoníaco gaseoso o una solución de hidróxido de amoníaco para precipitar el óxido de hierro hidratado directamente sobre el material carbonoso en partículas. La pasta húmeda es secada y mezclada con disolvente para formar la alimentación al proceso de licuefacción.

A las temperaturas elevadas requeridas para la licuefacción, el precursor del catalizador (óxido de hierro hidratado) reacciona con un material azufrado tal como H_2S o CS_2 o $(NH_4)_2S$ proporcionando las formas activas del hierro ($Fe_{1-x}S$) donde x es entre 0,01 y 0,2.

Obteniéndose así, sulfuro de hierro depositado directamente sobre las superficies de las partículas de carbón dentro de la mezcla de pasta húmeda.

La diferencia de D1 con la presente solicitud de patente radica en que D1 no divulga compuestos de coordinación metal-tiourea, como precursores del catalizador depositado.

El efecto que logra el utilizar un compuesto de coordinación para la obtención del precursor es que se obtiene un proceso ambientalmente más amigable, es decir que no se requiere de la utilización de H_2S o CS_2 u otro sulfuro de difícil manejo.

Por lo tanto, el Problema Técnico Objetivo que pretende resolver esta invención se puede formular así: "cómo modificar el procedimiento de D1 para lograr obtener un catalizador soportado cuya fase activa sea un sulfuro de metal de transición pero que no requiera la presencia de H_2S o CS_2 ?"

No obstante, el documento D2 enseña que se puede obtener la forma activa del metal (sulfuro del metal) depositado sobre un soporte inerte, por medio de la utilización de ligandos complejos orgánicos tales como la tiourea.

Específicamente el documento D2 divulga (reivindicaciones y ejemplos) un procedimiento de pre-sulfuración *exsitu* de un catalizador útil en procedimientos de hidrotratamiento catalítico.

Dichos catalizadores contienen comúnmente un material portador, tal como alúmina, sílice, sílice-alúmina o aluminosilicato cristalino, con uno o más metales o compuestos de metales, tales como óxidos, depositados sobre él, seleccionándose los metales de los grupos Ib, Vb, VIb, VIIb y VIII del Sistema Periódico. Ejemplos típicos de estos metales son hierro, cobalto, níquel, volframio, molibdeno, cromo, vanadio, cobre, paladio y platino, así como sus combinaciones. Se da preferencia al molibdeno, volframio, níquel, cobalto, platino y paladio y sus combinaciones. El contenido de metal de los catalizadores generalmente es de un 0,1-30 % en peso, calculado sobre el peso del catalizador total.

El compuesto orgánico azufrado utilizado debe ser soluble o miscible en agua, entre estos compuestos se incluye la tiourea. El documento D2 divulga que puede hacerse uso de métodos de impregnación convencionales para poner en contacto el catalizador con el medio acuoso que contiene el compuesto orgánico azufrado, por ejemplo inmersión, impregnación por pulverización e impregnación por vacío. En general, la impregnación se lleva a cabo a temperatura ambiente pero también puede tener lugar a temperaturas superiores.

Después de que el compuesto orgánico azufrado se ha incorporado al catalizador, se entra a una etapa de secado para eliminar el agua en exceso. Posteriormente, el catalizador presulfurado se activa para llevar al catalizador a la forma sulfurada. Tal activación se lleva a cabo haciendo pasar gas hidrógeno, en combinación o no con una alimentación que contiene hidrocarburos, sobre el catalizador

presulfurado a una temperatura en el intervalo de 100°C a 600°C, preferiblemente en el intervalo de 100°C a 400°C, y una presión de hidrógeno en el intervalo de 1 a 300 barías, preferiblemente de 5 a 100 barías. Esta etapa del proceso puede llevarse a cabo *ex situ*, es decir en un reactor separado, o *in situ*, es decir en el reactor en el que se usará el catalizador.

El catalizador así preparado es adecuado para ser usado en el hidrotratamiento catalítico de alimentaciones que contienen hidrocarburos. Los más significativos de estos procesos son hidrodesulfuración, hidrodesnitrogenación, hidrodesmetalización, hidrorreformaje, hidroisomerización e hidrocraqueo.

En otras palabras, la mejora del proceso, entendida como un proceso más amigable con ambiente debido al reemplazo de H₂S o CS₂ por compuestos coordinados de ligandos orgánicos, ya se había sido claramente sugerida desde el documento D2. En consecuencia, la persona del oficio normalmente versada en la materia, plantearía un procedimiento donde se incluyera una etapa de formación de un compuestos coordinados de con ligandos orgánicos para acomplejar el metal y la posterior activación del precursor, para llegar así al objeto de la reivindicación 1 de la solicitud. Por lo cual se considera obvia.

De forma equivalente el catalizador de la reivindicación 10 no es inventivo dado que su proceso de obtención (procedimiento de la reivindicación 1) tampoco lo es.

Se llama la atención del solicitante en cuanto a que existen múltiples referencias¹ que utilizan materiales carbonosos como soportes en catalizadores heterogéneos en diversos procesos. Así entonces, la utilización de carbón o coque como soporte se puede entender como una práctica común en campo de la tecnología de la catálisis heterogénea.

6. Conclusión

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

Nº	Documento Nº	Reivindicaciones afectadas	Requisito que afecta
D1	US5168088	1-17	Nivel Inventivo
D2	US5139990	1-17	Nivel Inventivo

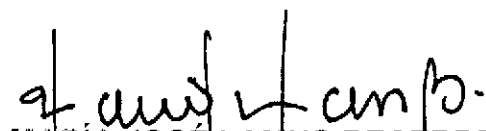
1 Limin Chen, Ding Ma,Barbara Pietruszka,Xinhe Bao
"Carbon-Supported Silver Catalysts for CO Selective Oxidation in Excess Hydrogen"
Journal of Natural Gas Chemistry, 15(2006)(3)181-190

M.J. Lázaro, A. Boyano, M.E. Gálvez, M.T. Izquierdo, E. García-Bordejé, C. Ruiz, R. Juan, R. Moliner. "Novel carbon based catalysts for the reduction of NO: Influence of support precursors and active phase loading". Catal. Today, 137, 215-221, 2008.

Yong Xiao, Qingya Liu, Zhenyu Liu, Zhanggen Huang, Yanxia Guo, Jianli Yang
"Roles of lattice oxygen in V₂O₅ and activated coke in SO₂ removal over coke-supported V₂O₅ catalysts". Applied Catalysis B: Environmental, 82(1-2): 114-119, 16 July 2008.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.


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El anterior requerimiento fue notificado por fijación en lista, de fecha

27 JUL 2012

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US005139990A

United States Patent [19]

de Jong et al.

[11] **Patent Number:** 5,139,990[45] **Date of Patent:** Aug. 18, 1992[54] **PROCESS FOR THE PREPARATION OF A
RESULFIDED CATALYST**

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[73] **Assignee:** Akzo NV, Arnhem, Netherlands

[21] **Appl. No.:** 672,253

[22] **Filed:** Mar. 20, 1991

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 387,466, Jul. 28, 1989,
abandoned.

[30] **Foreign Application Priority Data**

Jul. 29, 1988 [NL] Netherlands 8801907

[51] **Int. Cl.⁵** B01J 27/043

[52] **U.S. Cl.** 502/216; 502/219;
502/220; 502/221; 502/222; 502/223; 208/215

[58] **Field of Search** 502/216, 219, 220, 221,
502/222, 223; 208/215

[56] **References Cited****U.S. PATENT DOCUMENTS**

3,477,963	11/1969	Van Venrooy	502/216
3,959,179	5/1976	Mikovsky et al.	502/216
4,005,007	1/1977	O'Hara	208/111
4,020,012	4/1977	Miura et al.	502/216
4,320,030	3/1982	Happel et al.	578/714
4,581,125	4/1986	Stiefel et al.	208/134
4,622,128	11/1986	Young et al.	208/112
4,663,023	5/1987	McCandlish et al.	208/215
4,808,394	2/1989	Kolts et al.	423/437
4,814,315	3/1989	Kukes et al.	502/220
5,017,535	5/1991	Schoonhoven et al.	502/220
5,045,518	9/1991	Heinerman et al.	502/220

Primary Examiner—Anthony McFarlane

Attorney, Agent, or Firm—Louis A. Morris

[57] **ABSTRACT**

Ex situ presulfidation of hydrotreating catalysts comprising impregnating the catalysts with an aqueous solution of an organic sulfur compound, e.g. the diammonium salt of 2,5-dimercapto-1,3,4-thiadiazole and 2,2'-dithiodiethanol, followed by drying of the impregnated material. The dried material is activated by contacting it with hydrogen gas at elevated temperature.

2 Claims, No Drawings

lands. Very generally, the following reaction conditions apply here: temperatures in the range of 200° C. to 550° C., LHSV values in the range of 0.1 to 10 hours⁻¹, hydrogen partial pressures in the range of 10 to 300 bars, and hydrogen/hydrocarbon ratios in the range of 50 to 5000 Nm³/m³.

The invention will be further described in the following examples.

EXAMPLE 1

Presulfiding

In a rotating impregnator 1 kg of fresh catalyst KF-165® (ex Akzo Chemicals; catalyst composition: 15.4% by weight of MoO₃, 4.2% by weight of CoO, 15 alumina) PV (H₂O): 0.46 ml/g) was impregnated at room temperature with an aqueous solution prepared by dissolving 0.88 moles of diammonium salt of 2,5-dimercapto-1,3,4-thiadiazole in such an amount of water as to obtain a final volume of 460 ml, use being made of the pore volume saturation technique. Next, the resulting material was dried in an oven for 15 hours at 100° C. The sulfur content of the catalyst thus presulfided and the sulfur content of the catalyst in the sulfided state calculated therefrom are given in Table 1.

Activation and hydrotreatment

75 ml of the resulting catalyst were introduced into a reactor tube. The reactor tube had a diameter of 21 mm and in longitudinal direction it contained a thermocouple tube with a diameter of 6 mm. The length of the catalyst bed was 45 cm. Activation was as follows.

First the reactor was flushed with nitrogen to remove air. Next, hydrogen gas was passed upwardly over the catalyst at a pressure of 60 kg/cm² and at a rate of 65 l/hour, the temperature being increased from room temperature to 150° C. in a period of 1 hour. Subsequently, a light gas oil (LGO), the relevant data on which is provided in Table 2, was admixed in the hydrogen gas stream at a rate of 200 ml/hour and the temperature was incrementally raised to 368° C. over a period of 12 hours.

The catalyst thus activated was used in the same reactor for hydrotreating a vacuum gas oil (VGO), the relevant data on which is provided in Table 2. A first treatment was carried out at a temperature of 368° C., a hydrogen partial pressure of 50 bars, a hydrogen to oil ratio of 300 Nm³/m³, and an LHSV of 2.67 hours⁻¹. Subsequently, a treatment was carried out at an LHSV of 1.33 hours⁻¹, given otherwise identical conditions. The data obtained was used to determine the relative volume activity (RVA) of the catalyst for desulfurization, the catalyst according to EP-A 0,153,233 described in Example 6 below being used as standard. The value found for the RVA is given in Table 1.

EXAMPLE 2

The procedures described in Example 1 were repeated, except that presulfiding was carried out using 0.64 moles of diammonium salt of ethylene bis(dithiocarbamic acid). The results are given in Table 1.

EXAMPLE 3

The procedures described in Example 1 were repeated, except that presulfiding was carried out using 1.32 moles of 3,4-dithia adipic acid. The results are given in Table 1.

EXAMPLE 4

The procedures described in Example 1 were repeated, except that presulfiding was carried out using 1.27 moles of dimethylammonium salt of dimethyldithiocarbamic acid. The results are given in Table 1.

EXAMPLE 5

The procedures described in Example 1 were repeated, except that presulfiding was carried out using 1.32 moles of 2,2'-dithiodiethanol. The results are given in Table 1.

EXAMPLE 6 (comparative example)

A fresh KF-165® catalyst was presulfided using an aqueous solution of diammonium sulphide as described in EP-A 0,153,233, p. 19, 1. 12 through p. 20, 1. 20. After the second drying step in a nitrogen atmosphere the sulfur content of the presulfided comparative catalyst was 7.4% by weight. From it is calculated for the catalyst in the sulfided state a sulfur content of 8.0% by weight, which within the measuring error corresponds to the amount of 8.6 g of sulfur per 100 g of catalyst mentioned in the publication.

The presulfided catalyst was then activated and used to hydrotreat VGO in the manner described in Example 1. The activity of this catalyst was arbitrarily rated 100. See Table 1.

The results listed in Table 1 clearly show that the catalysts which were presulfided by the process according to the invention display a desulfurizing activity superior to that of the catalyst according to EP-A 0,153,233.

TABLE 1

Example	Sulfur Content (wt. %)		RVA
	Presulfided	Sulfided	
1	7.3	7.8	155
2	7.1	7.6	152
3	6.8	7.8	138
4	6.7	7.5	141
5	7.1	7.8	152
6*	7.4	8.0	100

*Comparative Example

TABLE 2

Feed	N (wt. ppm)	S (wt. %)	Density 50° C. (g/ml)	Boiling point fract. (°C.)				
				10%	30%	50%	70%	90%
LGO	92	1.17	0.8145	224	262	288	313	349
VGO	970	2.93	0.9018	391	421	451	486	527

EXAMPLE 7

Sulfur retention test

This test provides a simple yet effective method of determining the suitability for use as (pre)sulfiding reagent of sulfur compounds.

The test is carried out as follows.

Use is made of an impregnated KF-165® catalyst subsequently dried at 100° C.; see for instance the presulfided catalyst prepared in Example 1. It is heated for 16 hours in an atmosphere of static air, in an oven, at 160° C. Care should be taken that the catalyst material is spread evenly and has a maximum bed height of 1 cm.

Next the composition of the starting material and the product material is determined by chemical analysis,

5,139,990
catalyst
solid
pore volume
activation
hydrogen
gas
oil
LGO
VGO
RVA
Sulfur Content
Boiling point fract.

PROCESS FOR THE PREPARATION OF A RESULFIDED CATALYST

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my prior copending application Ser. No. 07/387,466, filed Jul. 28, 1989, now abandoned, incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The field of art to which this invention pertains is the preparation of catalyst for the hydrotreatment of hydrocarbon-containing feeds. The invention relates to a process for the preparation of a presulfided catalyst, a process for the preparation of a sulfided catalyst, and the use of said sulfided catalyst in the catalytic hydrotreatment of hydrocarbon-containing feeds.

2. Prior Art

In the oil industry many processes are known in which hydrocarbon-containing feeds are catalytically treated with hydrogen, such as hydrodesulfurization, hydrodenitrogenation, and hydrocracking. In such processes use is made of catalysts built up from a carrier material, such as alumina, on which there are deposited one or more catalytically active metals or compounds thereof; examples of such metals are molybdenum, nickel, cobalt and tungsten.

It is common knowledge that optimum results are obtained in using such catalysts when the catalytically active metals are in their sulfided form. See for instance H. Hallie's article in *Oil & Gas Journal*, Dec. 20, 1982, Technology, pp. 69-74, which also describes several techniques for preparing sulfided catalysts. These techniques comprise treating a fresh catalyst in a reactor at elevated temperature with a combination of hydrogen sulfide and hydrogen, a naturally sulfurous feed (non-spiked feed), or a feed to which a sulfur compound, such as carbon disulfide or dimethyldisulfide, has been added (spiked feed).

Although these techniques are practiced on a large scale, they nevertheless display several drawbacks. For instance, they require accurate control to achieve the desired result and are time-consuming, and the sulfur compounds used cause odor nuisance. Moreover, protracted interruption of the actual hydrotreatment of the hydrocarbons is needed if, as is often the case in actual practice, the reactor in which these processes are carried out is used for sulfiding catalysts.

To meet these drawbacks it is proposed in European patent application No. 0,153,233 that the fresh catalyst or a regenerated one should be contacted *ex situ*, i.e. outside the reactor in which the actual hydrotreatment of hydrocarbon-containing feeds is carried out, with an aqueous solution of diammonium sulfide, and the resulting material be dried to obtain a presulfided catalyst, whereupon the resulting presulfided catalyst is activated in situ or not in the presence of hydrogen, i.e. is brought into the sulfided state. This proposal also has its drawbacks, however. Firstly, aqueous diammonium sulfide is a reagent which produces an extremely objectionable odor. Secondly, if the total amount of the catalytically active metal is to be brought into the sulfided form, then, according to the teachings of the patent specification, the presulfiding should comprise at least two impregnating steps with the aqueous diammonium

sulfide; in this process each impregnating step should be followed by a drying step, and the final drying step should preferably be carried out in an inert atmosphere, such as nitrogen. A disadvantage to such a preparative process is its laboriousness when used in actual industrial practice. Thirdly, it has been found that the drying during the preparation of catalysts according to said patent specification is attended with the release of hydrogen sulfide, causing environmental problems. Finally, it has been found that these catalysts display an objectionably poor activity.

U.S. Pat. No. 3,477,963 (Van Venrooy) describes the sulfiding of hydrotreating catalyst. Van Venrooy requires first transforming an organic sulfur compound into a mixture of gases (by passing it over a presulfided catalyst) comprising H_2S , CH_4 , CH_3-SH and CH_3-S-CH_3 . It is this mixture of gases that is contacted with the unsulfided catalyst in a second step or stage.

U.S. Pat. No. 4,814,315 (Kukes et al.); 4,020,012 (Miura et al.) and 3,959,179 (Mikovski et al.) are typical of prior art references which require calcining of presulfided catalysts in air prior to any contact of the catalyst with a reducing atmosphere. This results in the finished catalyst containing little if any of the catalytically active metals being in their sulfided form. As mentioned above, optimum results for use of such catalysts will be realized only when the catalysts are in their sulfided form.

U.S. Pat. No. 4,320,030 (Happel et al.) describes making particles of active metal salts obtained from a solution of such salts in molten ammonium thiocyanate or thiourea (no carrier material is employed). Water is removed from the solution and the mixture heated to decompose the organic sulfur compounds and the mixture heated to decompose the organic sulfur compounds and evolve gases including sulfur dioxide and yield a black solid mass. Eventually, particles of this mass are heated in a reducing atmosphere. This reference teaches that the organic sulfur compound is a precursor for hydrogen sulfide.

U.S. Pat. No. 4,845,068 (Takahashi et al.) describes the use of organic thiol-group-containing organic acids to presulfide hydrotreating catalysts which are then activated with hydrogen gas at elevated temperature.

SUMMARY OF THE INVENTION

The present invention has for its primary object to meet the drawbacks to the teachings of the above prior art.

Accordingly, the invention is a process for the preparation of a catalyst useful in the catalytic hydrotreatment of hydrocarbon-containing feeds comprising:

- obtaining a catalyst comprising a carrier material having deposited thereon one or more metals or metal compounds catalytically active for the hydrotreatment of hydrocarbon-containing feeds;
- contacting the catalyst of step a) with an aqueous medium containing an organic sulfur compound to incorporate an effective amount of the organic sulfur compound into the catalyst; the organic sulfur compound being selected from the group consisting of salts of ethylene bis(dithiocarbamic acid), salts of 2,5-dimercapto-1,3,4-thiadiazole, salts of dimethyldithiocarbamic acid, thiourea, ammonium thiocyanate, dimethyl sulfoxide, 3,4-dithia adipic acid, salts of 3,4-dithia adipic acid, and 2,2'-dithiodiethanol;

c) drying the sulfur-containing catalyst of step b); and
 d) activating the dried sulfur-containing catalyst of
 step c) by contacting said catalyst with hydrogen
 gas at a temperature of from 100° C. to 600° C.
 It is essential that calcining not be effected between 5
 steps b) and d).

DETAILED DESCRIPTION

The present invention enables catalysts having a rela-
 tively high sulfur content to be prepared in a simpler
 manner than is described in EP-A 0,153,233, and, more-
 over, they do not cause odor nuisance during their
 preparation and display a greater activity during the
 hydrotreatment of hydrocarbon-containing feeds than do
 those according to the teachings of said patent speci-
 fication.

As compared to the above prior art which teaches
 calcination (heating in air at a temperature and condi-
 tions sufficient to cause a loss of sulfur which is signifi-
 cant with respect to a loss of catalytic desulfurizing
 activity) of the catalyst between the impregnation with
 the organic sulfur step and the activation step the pro-
 cess of the present invention yields a catalyst having a
 very high sulfur retention. This sulfur, when present in
 the hydrotreating reactor, will enable good activity.

With regard to Takahashi et al., it has been found that
 the thiol-group-containing organic acids disclosed by
 that reference for effecting presulfiding cause corrosion
 in the hydrotreating reactor. The organic sulfur com-
 pounds employed in the process of the present inven-
 tion do not exhibit that undesirable property.

The fresh or regenerated catalysts to be presulfided
 according to the process of the invention are those
 which are known in the prior art as suited for use in
 sulfided form in the catalytic hydrotreatment of hydro-
 carbon-containing feeds, for instance in hydrodesulfuri-
 zation, hydrodenitrogenation, hydrodemetallization,
 hydroreforming (which process, in the present context,
 is also considered a hydrotreatment), hydroisomeriza-
 tion, hydrocracking, hydroalkylation, and hydrodeal-
 kylation. Such catalysts commonly contain a carrier
 material, such as alumina, silica, silica-alumina, or crys-
 talline aluminosilicate, with deposited thereon one or
 more metals or compounds of metals, such as oxides, the
 metals being selected from the groups Ib, Vb, VIb, 35
 VIIb, and VIII of the Periodic System. Typical exam-
 ples of these metals are iron, cobalt, nickel, tungsten,
 molybdenum, chromium, vanadium, copper, palladium,
 and platinum as well as combinations thereof. Prefer-
 ence is given to molybdenum, tungsten, nickel, cobalt,
 platinum and palladium and combinations thereof. The
 metal content of the catalysts generally is 0.1-30% by
 weight, calculated on the weight of the total catalyst.

In addition, the catalysts may still contain other com-
 ponents, such as phosphorus, halogen, barium, zeolites
 and clays—including pillared clays.

The shape of the catalysts is dependent on the process
 in which they are used. Most frequently used are ex-
 truded particles (cylindrical, polylobes) and also fluidiz-
 able particles.

The sulfur compound to be used is organic, i.e. hav-
 ing at least one carbon atom in the molecule. The com-
 pound is either water-soluble or water-miscible. These
 compounds permit the preparation of aqueous mediums
 which at 25° C. and per 100 ml contain at least 1, prefer-
 ably at least 2, and more particularly as least 3 g of
 homogeneously distributed sulfur, i.e. the compound is
 fully dissolved or mixed.

The compounds to be used are
 salts of ethylene bis(dithiocarbamic acid),
 salts of 2,5-dimercapto-1,3,4-thiadiazole,
 salts of dimethyldithiocarbamic acid,
 thiourea,
 ammonium thiocyanate,
 dimethyl sulfoxide,
 3,4-dithia adipic acid and salts thereof, or
 2,2'-dithiodiethanol.

Also, use may be made of combinations of the above
 compounds.

Preference is given to sulfur compounds with at least
 two sulfur atoms in the molecule.

It should be noted that when a salt of a sulfur com-
 pound is used in the presulfiding process according to
 the invention, it must not be an alkali metal salt or an
 earth alkali metal salt. It is common knowledge that
 alkali metal ions and earth alkali metal ions in catalysts
 have a negative effect on the catalytic action. Salts that
 are preferred, also for reasons of economy, are ammo-
 nium salts and mono-, di-, tri-, and tetra alkyl ammo-
 nium salts. The methyl group is the most suited alkyl
 group.

Use may be made of conventional impregnation
 methods for contacting the fresh or regenerated catalyst
 with the aqueous medium containing the organic sulfur
 compound, for instance immersion, impregnation by
 spraying, impregnation by vacuum and soaking.

The length of this treatment may range from several
 minutes to several hours.

In general the impregnation will be carried out at
 room temperature. Optionally, however, the operation
 may also take place at higher temperatures.

The amount of sulfur compound to be used is depen-
 dent on the degree of sulfiding desired for the ready-for-
 use catalyst. Conventional degrees of sulfiding are in
 the range of 0.5 × stoichiometric to 1.5 × stoichiomet-
 ric, on which basis it is easy for the skilled man to deter-
 mine the amount of sulfur compound to be used in the
 presulfiding process.

After the organic sulfur compound has been incorpo-
 rated into the catalyst, the resulting material need be
 dried to remove excess water. To this end use may be
 made of conventional equipment, such as ovens and belt
 driers.

Next, the resulting presulfided catalyst should be
 activated in order to bring the catalyst into the sulfided
 form. Such activation is carried out by passing hydro-
 gen gas, in combination or not with a hydrocarbon-con-
 taining feed, over the presulfided catalyst at a tempera-
 ture in the range of 100° C. to 600° C., preferably in the
 range of 100° C. to 400° C., and a hydrogen pressure in
 the range of 1 to 300 bars, preferably 5 to 100 bars. This
 process step may be carried out either ex situ, i.e. in a
 separate reactor, or in situ, i.e. in the reactor in which
 the catalyst will be used.

The catalyst thus prepared is suitable to be used in the
 catalytic hydrotreatment of hydrocarbon-containing
 feeds. The most significant of these processes are hydro-
 desulfurization, hydrodenitrogenation, hydrodemetalli-
 zation, hydroreforming, hydroisomerization, and hy-
 drocracking. The process equipment to be used and the
 conditions under which the reactions are carried out
 vary with the process used and have been described in
 detail in the prior art. See for instance M. De Wind et
 al., Proceedings of symposium on catalyst performance
 testing, Mar. 28/29, 1988, pp. 29-42; published by Uni-
 lever Research Laboratories, Vlaardingen, The Nether-

and the sulfur content is calculated on the basis of the total weight excluding i) water that may be present and ii) the constituents other than sulfur originating from the original sulfur compound. From the resulting sulfur contents of the starting material (Ss) and the product material (Sp) can be calculated the sulfur retention (Sr) by the formula

$$Sr = \frac{Sp}{Ss} \times 100\%$$

Table 3 lists the Sr values for the compounds used in the preceding Examples.

TABLE 3

Example	Sr (%)
1	92
2	91
3	98
4	80
5	75
6*	51

*Comparative Example

As a rule, those sulfur compounds are suited to be used in the presulfiding process according to the invention which in the sulfur retention test have an Sr value of at least 55%, preferably of at least 65%, and more particularly of at least 80%.

EXAMPLE 8

Presulfiding

In a rotating impregnator 1 kg of a fresh commercial mild-hydrocracking catalyst (catalyst composition: 10.0 wt.% of MoO₃, 2.7 wt.% of CoO, silica-alumina support; PV (H₂O): 0.60 ml/g) was impregnated at room temperature with an aqueous solution prepared by dissolving 0.86 moles of 2,2'-dithiodiethanol in such an amount of water as to obtain a final volume of 600 ml, use being made of the pore volume saturation technique. Next, the resulting material was dried in an oven for 15 hours at 100° C. The sulfur content of the catalyst thus presulfided was 4.8 wt.% and that of the catalyst in the sulfided state calculated therefrom 5.2 wt.%.

Activation and hydrotreatment

100 ml of the resulting catalyst were introduced into the reactor tube, the details of which are described in Example 1. Activation was carried out according to the procedure also described in Example 1.

The catalyst thus activated was used in the same reactor for hydrotreating a vacuum gas oil, the relevant data on which is given in Table 2.

For a first hydrodesulfurization and hydrodenitrogenation treatment the conditions (i) included a temperature of 370° C., a hydrogen partial pressure of 50 bars, a hydrogen to oil ratio of 600 Nm³/m³ and an LHSV of 1.50 hours⁻¹. After a subsequent change for a mild-hydrocracking treatment the conditions (ii) included a temperature of 407° C., a hydrogen partial pressure of 50 bars, a hydrogen to oil ratio of 320 Nm³/m³ and an LHSV of 0.5 hours⁻¹.

The data obtained was used to determine the RVA of the catalyst for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and mild-hydrocracking (MHC), the catalyst according to EP-A 0,153,233 described in Example 9 below being used as standard. The RVA values are given in Table 4.

EXAMPLE 9 (comparative example)

A fresh commercial mild-hydrocracking catalyst (the same type as used in Example 8) was presulfided using an aqueous solution of diammonium sulfide as described

in EP-A 0,153,233, p. 19, l. 12 through p. 20, l. 20. After the second drying step in a nitrogen atmosphere the sulfur content of the presulfided comparative catalyst was 5.0 wt.%. From it is calculated for the catalyst in the sulfided state a sulfur content of 5.3 wt.%.

The presulfided catalyst was then activated and used to hydrotreat VGO in the manner described in Example 8. The RVA values of this catalyst were arbitrarily rated 100. See Table 4.

The results in Table 4 show that the catalyst which was presulfided by the process according to the invention displays activities superior to those of the catalyst according to EP-A 0,153,233.

TABLE 4

Example	RVA				
	Condition I		Condition II		
	HDS	HDN	HDS	HDN	MHC
8	>200	163	>200	120	125
9*	100	100	100	100	100

*Comparative Example

EXAMPLE 10

A catalyst was prepared generally in accordance with the method set forth in Example 1 except that presulfiding was carried out using dimethylsulfoxide. The sulfur content of the dried catalyst was 5% by weight.

A sulfur retention test was carried out according to Example 7, the S_r value found was 61%.

COMPARATIVE EXAMPLE 11

A catalyst was prepared essentially in accordance with the process described in Miura et al. by impregnating KF-165 ® with an aqueous solution of dimethylsulfoxide, drying it at 110° C. and calcining at 537° C. The sulfur content of the obtained catalyst was 0.7% by weight, indicative of a loss of sulfur highly significant with respect to the desulfurizing activity of the catalyst. We claim:

1. A process for the preparation of a catalyst useful in the catalytic hydrotreatment of hydrocarbon-containing feeds comprising:

a) obtaining a catalyst comprising a carrier material having deposited thereon one or more metals or metal compounds catalytically active for the hydrotreatment of hydrocarbon-containing feeds;

b) contacting the catalyst of step a) with an aqueous medium containing an organic sulfur compound to incorporate an effective amount of the organic sulfur compound into the catalyst; the organic sulfur compound being selected from the group consisting of

salts of ethylene bis(dithiocarbamic acid),
salts of 2,5-dimercapto-1,3,4-thiadiazole,
salts of dimethyldithiocarbamic acid,
thiourea,

ammonium thiocyanate,
dimethyl sulfoxide,

3,4-dithia adipic acid,
salts of 3,4-dithia adipic acid, and
2,2'-dithiodiethanol;

c) drying the sulfur-containing catalyst of step b); and
d) activating the dried sulfur-containing catalyst of step c) by contacting said catalyst with hydrogen gas at a temperature of from 100° C. to 600° C., calcining not being effected between steps b) and d).

2. The process of claim 1 wherein the organic sulfur compound has at least two sulfur atoms in the molecule.

* * * * *



US005168088A

United States Patent [19]

Utz et al.

[11] **Patent Number:** **5,168,088**[45] **Date of Patent:** **Dec. 1, 1992**[54] **METHOD FOR DISPERSING CATALYST
ONTO PARTICULATE MATERIAL AND
PRODUCT THEREOF**[75] **Inventors:** Bruce R. Utz; Anthony V. Cugini,
both of Pittsburgh, Pa.[73] **Assignee:** The United States of America as
represented by the United States
Department of Energy, Washington,
D.C.[21] **Appl. No.:** 743,968[22] **Filed:** Aug. 12, 1991**Related U.S. Application Data**[62] **Division of Ser. No. 531,722, Jun. 1, 1990, Pat. No.**
5,096,570.[51] **Int. Cl.**⁵ B01J 23/74; B01J 21/18;
B01J 27/043; B01J 27/20; B01J 37/02; B01J
37/20[52] **U.S. Cl.** 502/185; 502/222;
502/338[58] **Field of Search** 502/185, 314, 315, 316,
502/222, 180, 336, 332, 335, 338[56] **References Cited****U.S. PATENT DOCUMENTS**

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Primary Examiner—W. J. Shine*Assistant Examiner*—Douglas J. McGinty*Attorney, Agent, or Firm*—Hugh W. Glenn; Robert J.
Fisher; William R. Moser[57] **ABSTRACT**

A method for dispersing finely divided catalyst precursors onto the surface of coal or other particulate material includes the steps of forming a wet paste mixture of the particulate material and a liquid solution containing a dissolved transition metal salt, for instance a solution of ferric nitrate. The wet paste mixture is in a state of incipient wetness with all of this solution adsorbed onto the surfaces of the particulate material without the presence of free moisture. On adding a precipitating agent such as ammonia, a catalyst precursor such as hydrated iron oxide is deposited on the surfaces of the coal. The catalyst is activated by converting it to the sulfide form for the hydrogenation or direct liquefaction of the coal.

16 Claims, 2 Drawing Sheets

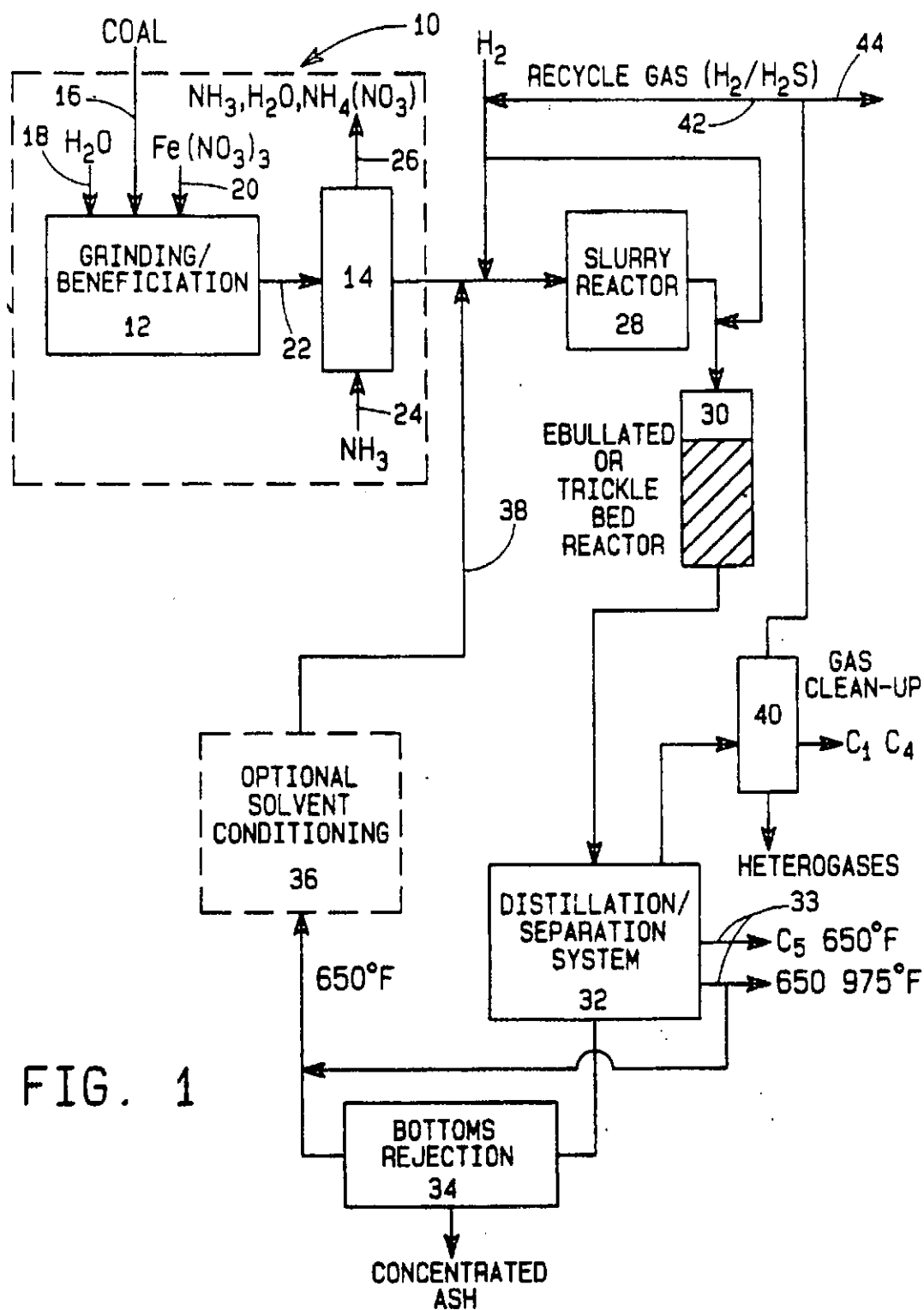


FIG. 1

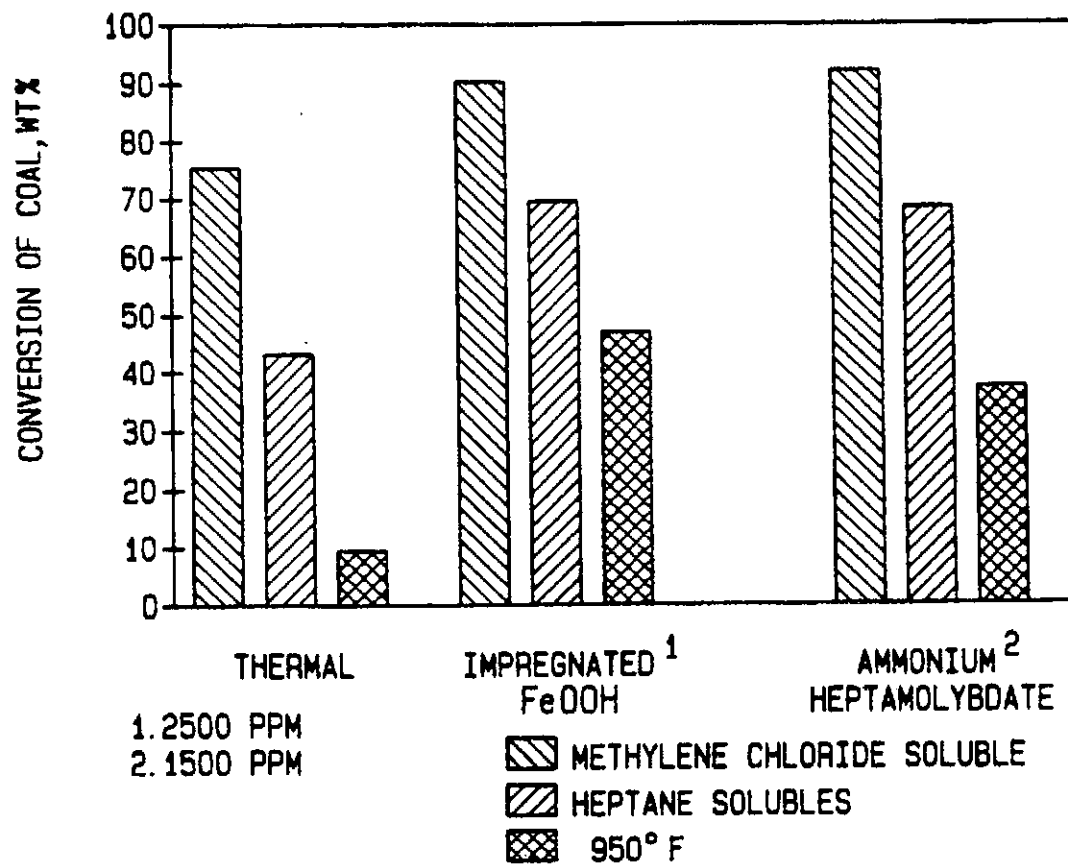


FIG. 2

METHOD FOR DISPERSING CATALYST ONTO PARTICULATE MATERIAL AND PRODUCT THEREOF

CONTRACTUAL ORIGIN OF THE INVENTION

The U.S. Government has rights in this invention pursuant to the employee/employer relationship of the inventor to the U.S. Department of Energy at the Pittsburgh Energy Technology Center.

This is a division of application Ser. No. 531,722 filed Jun. 1, 1990, now U.S. Pat. No. 5,096,570.

BACKGROUND OF THE INVENTION

The present invention relates to a method for dispersing finely divided catalysts onto the surface of a particulate material. More particularly, it relates to an improved method for dispersing hydrated iron oxide onto the surface of carbonaceous material such as coal in a manner to permit effective catalytic activity at relatively low concentrations of iron.

Iron and other transition metals have been used as dispersed-phase catalysts in processes for the hydrogenation and the direct liquefaction of coal. One major advantage of dispersed-phase catalysts is the potential for once through use with high initial activity. Representative processes of this type are described in U.S. Pat. No. 3,775,286 to Mukherjee et al. and in various technical publications such as Mitra et al., "A Comparative Study on Deposited and Mixed Iron Oxide Catalysts for Hydrogenation of Coal", FUEL PROCESSING TECHNOLOGY, 8(1924) 283-291. In this prior work, hydrated iron oxide was precipitated from solution by the addition of ammonium hydroxide onto particulate coal in suspension. Loadings typically of about 1.9 weight percent iron (19,000 ppm) were employed to obtain acceptable catalytic activity. The intimate mixture of iron and coal could then be drained of excess moisture, dried and subjected to hydrogenation or direct liquefaction of the coal. Prior workers also found the sulfide form of iron to be a more active hydrogenation catalyst.

Other prior workers have employed techniques in which water-soluble iron salts are impregnated into coal through contact with a solution of the salts. On subsequent drying with the gradual removal of water from the coal surfaces, the water-soluble, iron salt migrates into ever smaller water droplets resulting in the crystallization or precipitation of large particles of iron oxide. The inability to retard particle growth resulted in the requirement for high concentrations of iron when impregnated iron precursors were used as coal liquefaction catalysts.

SUMMARY OF THE INVENTION

Therefore in view of the above, it is an object of the present invention to provide a method for dispersing finely divided catalysts onto the surface of particulate support material.

It is also an object of the invention to provide an improved catalytic method for hydrogenating solid carbonaceous material.

It is a further object of the invention to provide a method for preparing a highly dispersed iron catalyst adsorbed onto the surface of a support material.

It is likewise an object of the invention to provide a method for distributing highly dispersed transition

metal catalysts onto the surface of a carbonaceous material for hydrogenation.

It is also an object to provide a method for impregnating catalyst precursor into carbonaceous material to provide increased activity at lower catalyst loadings.

In accordance with the present invention, a method for dispersing finely divided catalysts onto the surface of particulate support material involves forming a wet paste mixture of incipient wetness of the particulate material and a solution containing a soluble salt of the catalyst. The wet paste mixture is contacted with an agent capable of reacting with the soluble salt to disperse a catalyst precursor in finely divided form directly onto the support material.

In more specific aspects of the invention, the soluble catalytic salt is selected from iron, cobalt or nickel and the particulate support material can include carbonaceous material such as particulate carbon or carbonaceous fuels such as coal. Other support materials such as alumina are also contemplated. The support material with finely divided, adsorbed catalyst precursor can be uniformly mixed into additional particulate carbonaceous material in preparation for a hydrogenation reaction such as the direct liquefaction of coal.

In other aspects of the invention, a catalytic method of hydrogenating solid carbonaceous material is provided in which a wet paste mixture of particulate carbonaceous material is formed from a liquid solution of soluble transition metal salt with the amount of solution limited to no more than an amount at which incipient wetness occurs. The wet paste mixture is contacted with an agent such as an ammonia affording material to form an insoluble compound such as an oxide of the transition metal onto the surface of the particulate carbonaceous material. The wet paste mixture is then subjected to a catalytic hydrogenation process under hydrogenation conditions such as in the direct liquefaction of coal.

In other aspects of the invention a sulfur affording material is reacted with the catalyst precursor to form a transition metal sulfide which is catalytically active. For instance, pyrrhotite, $Fe_{1-x}S$ can be formed.

In more specific aspects of the invention, the condition of incipient wetness in the wet paste mixture will include sufficient liquid solution to uniformly wet the carbonaceous material but without forming drops of free liquid and the transition metal catalyst concentration is limited to no more than 5000 ppm adsorbed on the carbonaceous material.

DETAILED DESCRIPTION OF THE DRAWING

The present invention is illustrated in the accompanying drawings wherein:

FIG. 1 is a diagrammatic representation of a process for the direct liquefaction of coal including catalyst preparation.

FIG. 2 is a bar graph comparing the conversion of coal by the process of the present invention with that of prior processes.

DETAILED DESCRIPTION OF THE INVENTION

In one manner of carrying out the method of the present invention, a finely divided iron catalyst or catalyst precursor is adsorbed onto the surfaces of particulate coal in the initial steps of a coal liquefaction or other coal hydrogenation process. The method involves precipitating or depositing a catalyst precursor, typi-

cally hydrated iron oxide (FeOOH), directly onto the coal surface from a wet paste mixture. In addition to FeOOH , insoluble iron sulfides such as iron pyrite are contemplated as precursors to the active form of the catalyst.

The wet paste mixture can include particulate coal or other carbonaceous material wetted with an aqueous solution of ferric ions limited in volume to no more than that required for incipient wetness. A wet paste of incipient wetness will include that amount of liquid mixed and adsorbed onto a solid material just before drops of free moisture or liquid begin to form. In the case of a wet paste mixture of bituminous particulate coal, incipient wetness typically will occur at about 30% to 50% by weight moisture adsorbed on the coal particles. However, with other solids such as highly porous carbon up to about 75 weight percent moisture may be contained in a mixture of incipient wetness before drops of free liquid appear. In all cases a wet paste of incipient wetness is distinguishable from a suspension of solids in liquid in that all of the liquid is adsorbed on (or absorbed in) the solid without the presence of free liquid.

Inasmuch as all of the solution containing the iron catalyst precursor is adsorbed on the surface of the particulate carbonaceous material, a highly dispersed, iron precipitate can be deposited and maintained in a high dispersion even after drying and conversion to a more active catalytic form. The inventors have found that the precipitated iron compounds, adsorbed on the carbonaceous material in a highly dispersed state are not nearly so subject to nucleation or flocculation as those merely precipitated in mixture with a suspension of carbonaceous material. Thus, extremely small particles of catalytic iron of high activity can be provided on the support material by the process of this invention. The inventors have found that the iron catalyst precursor particles will be no more than about 1000 angstroms in size.

In preparing the wet paste mixture, particulate coal of about 10 to 250 microns particle size is mixed with a solution of soluble iron salts such as ferric nitrate or ferric chloride. The amount of solution is limited to no more than the amount at which incipient wetness occurs. An ammonia affording agent such as ammonia gas or a solution of ammonia hydroxide is brought into contact with the wet paste mixture to precipitate hydrated iron oxide directly onto the particulate carbonaceous material. The wet paste mixture can then be dried and mixed with hydrogenated coal solvent to form the feed to a coal hydrogenation or liquefaction process. At the elevated temperatures required for liquefaction, the catalyst precursor, hydrated iron oxide, reacts with a sulfur affording material such as H_2S or CS_2 to convert the iron to its active form generally considered to be a form of pyrrhotite, Fe_{1-x}S where x is between 0.01 and 0.2. Although some sulfur affording agents are expected to be in the coal, it may be required to add the above sulfur affording materials into the liquefaction reactor to fully activate the iron catalyst.

Alternatively, the inventors contemplate precipitating an iron sulfide such as pyrite directly onto the coal particle surfaces within the wet paste mixture. To accomplish this a sulfur affording agent such as H_2S , CS_2 or $(\text{NH}_4)_2\text{S}$ will be passed into contact with the wet paste mixture to react with the soluble iron salt.

The following examples are presented merely by way of illustration and are not intended to limit the present

invention beyond that defined in the accompanying claims.

EXAMPLE I

About one gram of ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is per Amend. dissolved into 40 grams of distilled water. The solution was added to 50 grams of particulate Illinois #6 coal having a particle size of about 10-15 microns to form a wet paste mixture of incipient wetness. The wet paste was rapidly added to a solution of 20 grams of ammonia hydroxide (29% NH_3) and 200 grams of distilled water. The resulting suspension was filtered and the coal solids with adsorbed FeOOH were dried. The dried solids were mixed with tetralin as solvent in a ratio of 2:1 solvent to coal and subjected to direct liquefaction in a microautoclave at a temperature of 425° C., cold pressure of 1000 psig hydrogen (2000 psig at temperature) for a residence time of one hour.

EXAMPLE II

The procedure of Example I was followed except 0.1 gram of CS_2 was added to the coal/solvent mixture to convert the iron to the sulfide form.

EXAMPLE III

(Comparative Example)

One gram of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved into 40 grams of distilled water. Twenty grams of ammonia hydroxide (29% in NH_3) were added to the solution resulting in precipitation of hydrated iron oxide. The solids were separated by filtration, dried and added to a liquefaction test reactor as FeOOH .

EXAMPLE IV

(Comparative Example)

In a procedure similar to that described in U.S. Pat. No. 3,775,286 to Mukherjee et al., FeOOH was precipitated into mixture with a suspension of Illinois #6 coal in ferric nitrate solution. Sufficient FeOOH was included with the coal to provide a catalyst loading of 2500 ppm iron for comparison with the results obtained with the catalyst of Example II. The solids were filtered from solution, dried and processed in a microautoclave as in Example II.

Other comparative microautoclave screening tests were conducted with no catalysts, powdered ferric oxide, powdered pyrite and ammonium molybdate. The results of these tests, along with those of Examples I-IV are presented in Table I.

TABLE I

Microautoclave Studies		
Temperature - 425° C., Pressure - 2000 psig H_2		
Residence Time - 1 hour, 2:1 Tetralin to Illinois #6 Coal		
	Coal Conversion to:	
	Methylene Chloride Solubles	Heptane Solubles
Thermal	39.1	27.1
Thermal + H_2S	39.2	32.5
Fe_2O_3^1	39.2	32.1
FeOOH^1	62.3	35.4
(Example III)		
$\text{FeOOH}^1 + \text{H}_2\text{S}$	71.7	42.5
Mukherjee et al. + H_2S^2	74.2	42.9
(Example IV)		
Impregnated FeOOH^2	70.4	40.8
(Example I)		
Impregnated $\text{FeOOH}^2 + \text{H}_2\text{S}$	85.4	62.5
(Example II)		

TABLE 1-continued

Microautoclave Studies		
Temperature - 425° C., Pressure - 2000 psig H ₂		
Residence Time - 1 hour, 2:1 Tetralin to Illinois #6 Coal		
	Coal Conversion to:	
	Methylene Chloride Solubles	Heptane Solubles
Ammonium Molybdate ³ + H ₂ S	88.3	63.3
¹ Catalyst Concentration - 5000 ppm (based on coal)		
² Catalyst Concentration - 2500 ppm (based on coal)		
³ Catalyst Concentration - 1500 ppm (based on coal)		

In addition to the above, experiments were conducted on a batch one-liter autoclave to confirm the results observed in the microautoclaves. The experiments were conducted under the same conditions as the microautoclave tests, however, a coal-derived distillate solvent (V-1074) obtained from run 257 at the Wilsonville Advanced Coal Liquefaction Test Facility was used as the solvent instead of tetralin and a pressure of 2500 psig (3% H₂S) was imposed. Experiments using impregnated hydrated iron oxide catalyst were compared to those conducted thermally and with ammonium heptamolybdate. Hydrogen sulfide was added in all of the experiments. The results from these tests are illustrated in FIG. 2 showing the yield structure obtained using the highly dispersed catalyst of this invention to be comparable to the distillate structure using ammonium molybdate.

The catalyst prepared in accordance with Mukherjee et al. was also tested in a one-liter autoclave test, similar to the tests illustrated in FIG. 2. The conversion to -950° F. boiling material (useful in the preparation of transportation fuels) using the Mukherjee preparation procedure was only 37% (not shown in FIG. 2) compared to 48% obtained with the Impregnated FeOOH procedure of this invention.

It is therefore seen that catalysts obtained from the impregnated FeOOH precursor are substantially as effective for coal liquefaction as ammonium molybdate. Through use of the incipient wetness impregnation technique, a high dispersion of the hydrated iron oxide on the coal is formed which acts as a catalyst precursor in coal liquefaction. The coal conversion with iron concentrations as low as 2500 ppm compare favorably with those observed with molybdenum catalyst at 1500 ppm.

It will also be clear that this method of incipient wetness impregnation is applicable to any group VIII metal. For instance, with nickel or cobalt as well as iron. In addition, it is expected that the dispersion of catalytic iron sulfides can be precipitated from an incipient wetness mixture including impregnated ferrous chloride solution by the addition of ammonium sulfide.

In other variations of the invention, iron or other group VIII metal can be precipitated only into a selected fraction of the coal to be hydrogenated. This selected fraction, as wet paste mixture, can then be uniformly mixed with at least an equal weight of particulate carbonaceous material. For instance, 10%-50% of the coal can be spiked with the catalyst precursor and subsequently thoroughly mixed in with the full volume of coal or other carbonaceous material to be liquefied or hydrogenated.

The method is not limited to the dispersion of catalysts onto the carbonaceous material itself but is also applicable to incipient wetness precipitation onto another support material such as highly porous carbon or

alumina. The supported catalysts then can be blended with the carbonaceous material in preparation for the hydrogenated process.

One example of the present invention applied to coal liquefaction is illustrated schematically in FIG. 1. The catalyst precursor is conveniently impregnated into the coal in the coal beneficiation step 10. Typically, grinding and aqueous beneficiation 12 are used to pretreat the coal 16 with added water 18. A solution of ferric nitrate 20 can be added to form a wet paste of incipient wetness 22 which is contacted and reacted with ammonia gas 24 during the drying step 14. Conventional packed bed, fluidized bed or other industrial dryers can be selected for use in drying step 14. As described above the ammonia reacts with the wet paste as a part of or prior to drying to deposit a highly dispersed, catalyst precursor, FeOOH, onto the coal surfaces. Unreacted gases and reaction products 26 are withdrawn or conditioned for recycling. The remainder of the FIG. 1 process is a conventional two stage coal liquefaction process with a slurry reactor 28 and ebullated bed reactor 30. Product distillation 32 provides liquefied product 33 and conditioning steps 34 and 36 provide solvent recycle 38. Gas clean-up and separation processes 40 provide recycle H₂S for activation of the catalyst precursor. Excess H₂S can be withdrawn at 44 for further separation and processing.

Although the present invention is described in terms of specific materials and process steps, it will be clear to one skilled in the art that various changes and modifications may be made in accordance with the invention described in the accompanying claims.

The embodiment of the invention in which an exclusive property or privilege is claimed is defined as follows:

1. A method for dispersing finely divided, iron-containing catalyst onto the surface of particulate support material comprising:

forming a wet paste mixture of incipient wetness including the particulate material and a solution containing a soluble iron salt of the catalyst precursor;

contacting the wet paste mixture with an agent capable of reacting with the soluble iron salt to disperse finely divided particles of the catalyst precursor, containing iron, directly on the support material.

2. The method of claim 1 wherein a sulfur-affording material is reacted with the catalyst precursor to form a catalytically active, iron sulfide.

3. The method of claim 1 wherein the particulate support material containing finely divided, dispersed catalyst is uniformly mixed into additional particulate carbonaceous material in preparation for hydrogenation.

4. An iron-containing, catalyst precursor mixture suitable to afford a catalyst, said mixture comprising particulate material having dispersed particles of an iron compound adsorbed as precipitated from a wet paste of incipient wetness onto the surfaces of the particulate material.

5. The catalyst precursor mixture of claim 4 wherein the iron compound is suitable for reaction with a sulfur-containing material to form a catalytically active, iron sulfide.

6. The catalyst precursor mixture of claim 5 wherein the iron sulfide is pyrrhotite, Fe_{1-x}S, where x is between 0.01 and 0.2.

7. The catalyst precursor mixture of claim 4 in further mixture with at least an equal weight portion of particulate carbonaceous material in preparation for the hydrogenation of the particulate carbonaceous material.

8. The catalyst precursor mixture of claim 4 wherein the iron compound is hydrated iron oxide capable of reacting with a sulfur-containing material selected from the group consisting of H_2S and CS_2 to form a catalytically active iron sulfide.

9. The catalyst precursor mixture of claim 4 wherein the particulate material is particulate carbonaceous material with a compound of iron dispersed as finely divided particles of no more than 1000 angstroms size and limited to no more than 5000 ppm based on the carbonaceous material.

10. The method of claim 1 wherein the wet paste mixture is formed by blending an aqueous solution of ferric nitrate or ferric chloride with particulate material and an ammonia-containing material is added to disperse finely divided particles of hydrated iron oxide onto the particulate material.

11. The method of claim 10 wherein the ammonia-containing material is ammonia gas passed into contact with the wet paste mixture following comminution of the particulate material in the presence of ferric nitrate solution.

12. The method of claim 10 wherein a sulfur-containing material selected from the group consisting of H_2S and CS_2 is reacted with the hydrated iron oxide to form a catalytically active iron sulfide.

13. The method of claim 1 wherein sufficient catalyst precursor solution is present in the wet paste mixture to uniformly wet the particulate material but without exceeding the liquid required for incipient wetness.

14. The method of claim 13 wherein the catalyst precursor is a compound of iron dispersed as finely divided particles of no more than 1000 angstroms size on the support material.

15. The method of claim 14 wherein the wet paste mixture is uniformly mixed with at least an equal weight of particulate carbonaceous material prior to subjecting the mixture to catalytic reaction.

16. An iron-containing, catalyst precursor mixture suitable to afford a catalyst, said mixture comprising particulate carbonaceous material having dispersed particles of hydrated iron oxide adsorbed as precipitated from a wet paste mixture of incipient wetness onto the surfaces of the particulate material, the wet paste mixture including particulate carbonaceous material and aqueous ferric nitrate solution suitable for reacting with ammonia to disperse finely divided particles of hydrated iron oxide onto the carbonaceous material.

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Article

Carbon-Supported Silver Catalysts for CO Selective Oxidation in Excess Hydrogen

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[Manuscript received May 18, 2006; revised July 4, 2006]

Abstract: Carbon materials were used as supports for Ag catalysts that are prepared using the conventional wet impregnation method, and their catalytic properties for CO selective oxidation in excess hydrogen at temperatures below 483 K were tested. A variety of techniques, e.g. N_2 adsorption, XPS, TPD, UV-Vis DRS, TEM and SEM, were used to determine the influence of physical and chemical properties of the carbon on the properties of Ag catalyst. It was found that defects on the carbon surface served as nucleation sites for silver ions, while functional groups on carbon surface induced their reduction to the metallic form. The formation of silver particles on carbon was governed by homogeneous and/or heterogeneous nucleation during the impregnation and subsequent activation processes. The best catalytic performance was obtained with a Ag/carbon black catalyst with a uniform size distribution of silver nanoparticles (about 12 nm), moderate BET surface area (with a mesoporous structure), and a limited amount of carbon-oxygen groups. The research indicates that carbon materials are potentially good supports for silver catalysts for preferential oxidation of CO in excess hydrogen.

Key words: carbon support; catalytic property; defect; functional group

1. Introduction

Research on the catalytic oxidation of carbon monoxide has surged due to the possible applications in air cleaning, orbiting, closed-cycle CO_2 lasers, and other remote sensing techniques [1–3]. Recently, the preferential oxidation (PROX) of CO in excess hydrogen has been studied intensively for applications in polymer electrolyte membrane fuel cells (PEMFCs), aiming at reducing CO concentration down to 1.0×10^{-3} %, and thus preventing the fuel cell electrodes from being poisoned [4,5]. An important issue in this regard is to integrate the catalyst directly into fuel cells and to enhance its catalytic performance at low operating temperature (about 353 K) [6]. Noble metals such as Pt, Pd, Ru and Au supported over carbon materials have been reported to be efficient cata-

lysts for PROX of CO or CO oxidation reaction [7–13]. Recently, it was reported by us that silica-supported silver catalysts are, however, active at temperature as low as 333 K in the reaction mixture containing 1 vol% CO, 0.5 vol% O_2 , and 98.5 vol% H_2 [14,15]. This finding indicates that relatively cheap silver catalysts may be able to replace noble metal catalysts for PROX of CO in excess hydrogen at low temperatures. However, to integrate the catalyst directly into fuel cells, the electron-conductive support is essential. As carbon materials show good electron conductivity; therefore, it can be used as supports for PROX of CO in the present study.

In addition, compared with oxide supports, carbon materials have considerable advantages, such as (1) a high specific surface area up to $3000 \text{ m}^2/\text{g}$, (2) high stability in acidic and basic media [16], (3)

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Project was supported by the Chinese Ministry of Science and Technology (2003CB6 15806) and the Natural Science Foundation of China (National Key Project: 90206036).

easy modification of textural properties and functional groups, and (4) easy recovery of supported metals by burning off the catalyst. Moreover, the varieties of available forms (e.g., graphite, carbon black (CB), activated carbon (AC), activated carbon fibers (ACF), carbon nanotubes (CNTs), and carbon molecular sieves (CMS)) make carbon materials very attractive as catalysts or supports for metal catalysts [17,18].

As reported by Rodríguez-Reinoso [19–21], when using carbon materials as a catalyst support, both the physical and chemical properties of the carbon materials should be considered. The physical properties (surface area; micro-, meso-, or macroporous structures) are of the choices we can make, and the surface chemical properties (such as the types and the population of the heteroatom containing surface functional groups) can, at certain levels, be controlled and/or modified, both of which make carbon materials potentially good catalyst supports for PROX of CO.

In this article, carbon materials were used as the support for silver catalysts. The research study focused on the influences of the properties of carbon materials (surface area, porosity, and surface functional groups) on the formation and distribution of silver species during the catalyst impregnation and subsequent calcination processes and on the extent to which this could manipulate the catalytic properties in the PROX of CO in excess H_2 .

2. Experimental

2.1. Catalyst preparation

Three different kinds of carbon materials were used as supports for silver catalysts. Carbon black (CB) was purchased from Acros, and coal-based carbon material (Coal) and activated carbon fibers (ACF) were obtained from Beijing Guanghai Woods Plant (Beijing, China). All catalysts, containing 12 wt% Ag, were prepared by the conventional wet impregnation method using silver nitrate ($AgNO_3$, 99.9%, Shanghai Chemical Reagent Company, China). Samples were dried at 333 K in air overnight and activated in the flow of He (30 ml/min) at 773 K for 2 h before the catalytic evaluation was carried out.

2.2. Support and catalyst characterization

The textural properties of carbon supports were

determined by N_2 adsorption-desorption isotherms at 77 K using an AS-1-MP adsorption instrument. Samples were outgassed at 383 K overnight before the measurements were carried out [20].

The oxygen-containing functional groups on carbon surface (before and after silver nitrate impregnation) were characterized using temperature-programmed desorption (TPD) in combination with X-ray photoelectron spectroscopy (XPS). After the impregnation, some of the silver species were already anchored onto the supports, and the existence of additional silver nitrate on the carbon surface will affect the detection of O 1s signal in XPS and also the signals of carbon oxides in TPD experiments (carbon will be oxidized during nitrate decomposition). Taking this into consideration, additional silver nitrate was removed by washing at room temperature before XPS and TPD measurements were made.

XPS measurements were performed on an Amicus XPS spectrometer using nonmonochromatic Mg $K\alpha$ radiation (1253.6 eV). The deconvolution of C 1s peaks was conducted according to the previous study [22,23]. The C 1s binding energy (BE) of the graphitic carbon (284.6 eV) was used as reference. The atomic ratios of total oxygen to total carbon (O_t/C_t) were calculated from XPS spectra after correcting the peak areas by sensitivity factors.

The TPD experiments were carried out in a quartz U-type microreactor, connected with an online quadrupole mass spectrometer (Balzers, QMS 200). The samples (0.1 g) were first flushed with He (30 ml/min) at room temperature for 2 h. Subsequently, the temperature was increased to 1173 K at a rate of 5 K/min and then kept at 1173 K for 40 min. MS intensities for 2 (H_2), 4 (He), 15 (CH_4), 18 (H_2O), 28 (CO), 32 (O_2), 44 (CO_2), and 46 (NO_2) were measured as a function of temperature.

UV-Vis diffuse reflectance spectra (UV-Vis DRS) were recorded on a JASCO V-550 UV-Vis spectrophotometer, in the wavelength range of 190–800 nm with a scanning speed of 100 nm/min.

Scanning electron microscopy (JSM-6360 JEOL/EO) and transmission electron microscopy (JEOL JEM-2000EX) were used to observe the surface microscopic structures and distributions of silver particles.

2.3. Catalytic reaction

The selective oxidation of CO was carried out in a fixed-bed flow reactor. A gas mixture contain-

ing 1% CO and 0.5% O₂ (volume ratio) in H₂ was fed at the flow rate of 50 ml/min. The composition of the effluent gas was monitored with an on-line gas chromatograph (Agilent Technologies GC-6890N) equipped with PN and TDX-01 columns. Besides the feed gases, only two products, CO₂ and H₂O, were detected. CO and O₂ conversions were calculated from the difference between their inlet and outlet concentrations, while the oxygen selectivity to CO₂ (S) is defined as follows:

$$S = \{0.5 \times ([CO]_{in} - [CO]_{out}) / ([O_2]_{in} - [O_2]_{out})\} \times 100\%,$$

where [O₂]_{in} and [CO]_{in} are inlet, and [O₂]_{out} and [CO]_{out} are outlet concentrations of O₂ and CO, respectively.

3. Results and discussion

3.1. Catalytic activity

Figure 1 shows O₂ and CO conversions (a and b, respectively) and the oxygen selectivity to CO₂ (c) over various carbon materials supported silver catalysts. For all the catalysts investigated, the conversion of O₂ increased with temperature, eventually reaching 100%. The temperature for 100% O₂ conversion over Ag/CB catalysts is about 360 K, whereas on Ag/Coal and Ag/ACF catalysts the full oxygen conversion was obtained at 450–480 K. Similarly, conversion of CO increased along with the increase of temperature, reaching the maximum at 360–380 K and decreased gradually with the further increase of temperature. Apparently, Ag/CB catalyst showed the best activity, with the full oxygen conversion and maximum CO conversion (about 12%) at 362 K. On the contrary, for ACF and Coal-supported catalysts, the best CO conversion is 3%–5% (373 K). Upon further increase of reaction temperature, the activity of these catalysts was enhanced but oxidation of hydrogen was promoted as well, thus lowering selectivity toward CO₂.

As shown in Figure 1(c), the selectivity toward CO₂ is to a certain extent similar to those of Ag/SiO₂ catalysts reported previously [14,15]. The Ag/CB and Ag/Coal catalysts show the highest selectivity toward CO₂ at low temperature, where the conversions of CO and O₂ are limited. However, with increase of temperature, the selectivity toward CO₂ decreased over all the catalysts investigated.

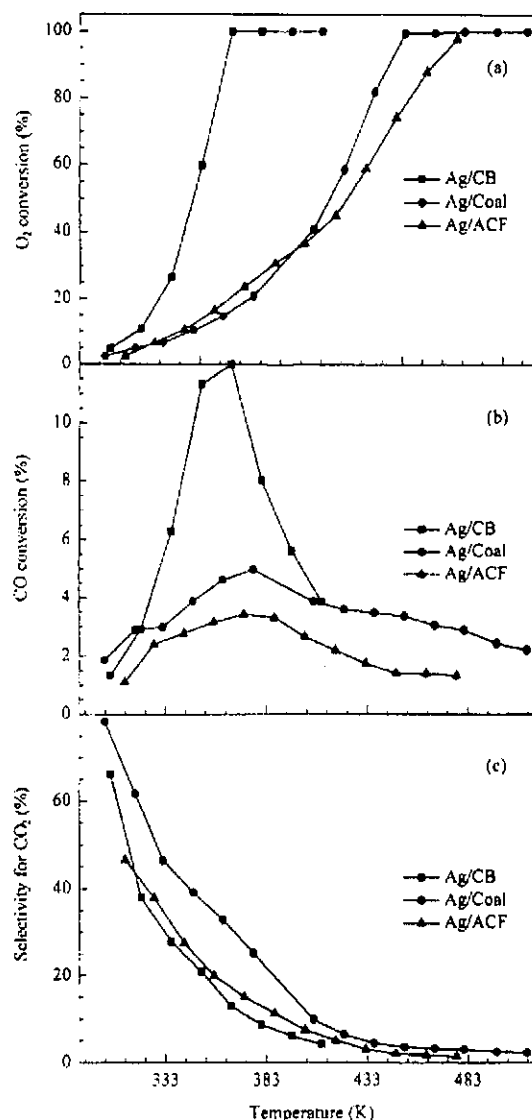


Figure 1. O₂ conversion (a), CO conversion (b), and the oxygen selectivity to CO₂ (c) over carbon-supported silver catalysts after pre-treatment in H₂ (30 ml/min) at 773 K for 2 h

Reaction conditions: 0.12 g catalyst, feed gas 1 vol% CO, 0.5 vol% O₂ and 98.5 vol% H₂; flow rate 50 ml/min

3.2. Physical properties of carbon supports: porosity and surface area

Figure 2 shows the adsorption-desorption isotherm (N₂, 77 K) of ACF and CB (that of Coal is not shown), and corresponding textural properties are listed in Table 1. For CB, type IV isotherm is present, indicating its mesoporous structure. Coal and ACF show the type I isotherm, thus micropores

are dominant on those two materials. The corresponding BET surface areas changed significantly, from relatively small change of 75.8 m²/g for CB, to 756.9 and 1247.0 m²/g for Coal and ACF, respectively. The mean pore sizes are 6.5, 0.4, and 0.5 nm, respectively (Table 1).

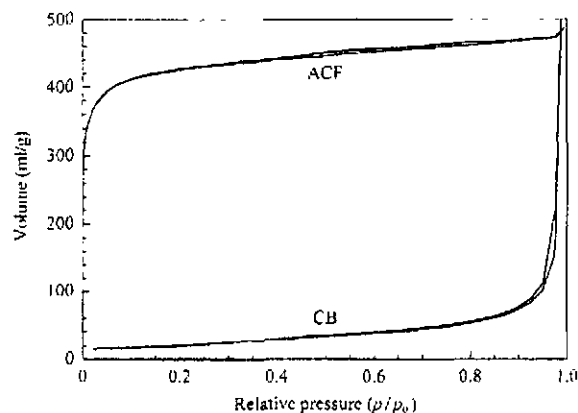


Figure 2. N₂ adsorption-desorption isotherm profiles of ACF and CB supports (measured at 77 K)

Table 1. Textural properties of carbon supports obtained by N₂ adsorption

Carbon support	BET surface area (m ² /g)	Mean pore size (nm)	Pore volume (ml/g)
CB	75.8	6.5	0.98
Coal	756.9	0.4	0.45
ACF	1247.0	0.5	0.75

By looking for a correlation between the catalytic performance and the properties of carbon materials (surface area and mean pore size), it can be concluded that carbon materials with mesoporous structure and relatively low surface area (e.g., CB) are the most suitable supports for silver catalysts in the selective oxidation of CO.

3.3. Chemistry of the carbon surface

Although carbon is considered to be an inert material in comparison with other oxide supports (Al₂O₃, SiO₂, zeolites, etc.), its surface has a significant proportion of active sites, constituted by unsaturated valences at the edges and defects of the graphitic layers. The higher the surface area, the larger the populations of these active sites. At the same time, the presence of heteroatoms (mainly oxygen, hydrogen, and nitrogen atoms) also introduces functional groups into the carbon materials, and consequently the carbon surface is not as inert as ex-

pected [19]. These defects play an important role in the preparation process of the catalysts, providing nucleation sites for reduced metal species, while the functional groups are able to act as the reducing agents, i.e. the anchored ions can be reduced by a wide range of the functional groups and/or by adsorbed hydrogen present on the surface [21,24–26]. From this point of view, it is of great interest to study the role of surface chemistry of carbon materials in the catalyst preparation.

3.3.1. XPS results

XPS measurements were carried out to investigate the changes of carbon-oxygen groups of carbon materials during the silver nitrate impregnation. To save space, only the XPS spectra of the C 1s region of ACF support and the corresponding silver catalyst are shown in Figure 3. Those of Coal and CB are not shown here, but the numerical results are summarized in Table 2.

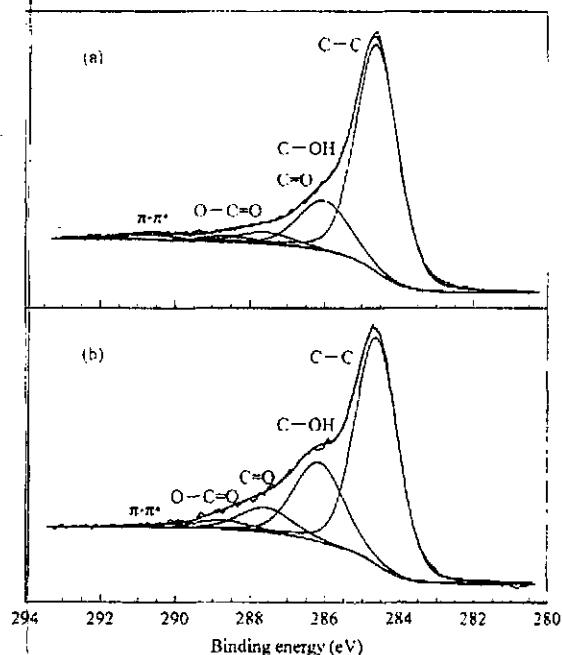


Figure 3. XPS spectra of C 1s region of the ACF support (a) and the Ag/ACF catalyst (b)

Before measurements, the catalyst was washed to remove the additional silver nitrate

As presented in Figure 3, the XPS spectra show that the C 1s signal has an asymmetric tailing toward higher BE values, arising partly from the intrinsic asymmetry of the graphitic peak and partly from carbon-oxygen functional groups [22]. Decon-

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olution of the C 1s signal yields six peaks representing different carbon species: (a) BE=284.6 eV: C—C bonds (aromatics and/or aliphatic), (b) BE=286.1 eV: C—O— (phenol, alcohol or ether), (c) BE=287.4 eV: C=O (carbonyl and quinone), (d) BE=288.6 eV: C—OO— (carboxyl or ester), (e) BE=290.2 eV: adsorbed CO₂, and (f) BE=291.5 eV: surface plasmon peak ($\pi \rightarrow \pi^*$ transition peak) [22,23]. For the CB support and the corresponding Ag/CB catalyst, changes in the C 1s signal are very small (not shown). For the other supports, the intensity of high BE value peaks increased significantly after silver impregnation, indicating the increase of the concentration of carbon-oxygen groups, mainly C—OH and C=O groups (Figure 3).

Table 2. XPS numerical results from C 1s region

Entry	Concentration ^a (%)			Δ^c	O_t/C_t
	286.1 ^b C—OH	287.4 ^b C=O	288.6 ^b C—OOH		
CB	8.2	4.2	—	—	0.02
Ag/CB ^d	8.9	4.0	—	—	0.04
Coal	21.0	4.3	2.3	13.3	0.15
Ag/Coal ^d	25.4	7.5	3.6	13.3	0.30
ACF	18.9	4.8	2.5	17.6	0.12
Ag/ACF ^d	25.5	8.9	2.8	17.6	0.35

^aConcentration of different carbon-oxygen groups is expressed by atom%;

^bBinding energy of carbon-oxygen bonds, eV;

^c $\Delta = 2 \times \Delta C-OH + \Delta C=O + \Delta C-OOH$; it represents relative amount of the electrons transferred during the reduction of silver ions;

^dBefore the measurements, the catalysts were washed to remove the additional silver nitrate

In Table 2, the concentrations of different carbon-oxygen groups and the atomic ratio of total oxygen to total carbon (O_t/C_t) are presented. Obviously, after the silver nitrate impregnation, the total concentration of carbon-oxygen groups (C—OH, C=O, and C—OOH) increased, so did the atomic ratio of O_t/C_t .

The CB has very few carbon-oxygen groups, and the O_t/C_t value is only 0.02, changing to just 0.04 even after the introduction of silver (Ag/CB). The amount of carbon-oxygen groups remained almost unchanged after the introduction of Ag, approximately equaling to 12.4% of the total amount of detected carbon. Over the other carbon samples (Coal and ACF), the amounts of carbon-oxygen groups are much higher, above 26%, and after the silver deposition they increased significantly. The O_t/C_t value, after the introduction of Ag, was about two times for Coal and almost three times for ACF as compared with that

of their parent supports. The increases of different carbon-oxygen groups are different, but generally the contributions of C—OH and C=O groups were the most significant. Over the Coal, the increases of both groups (C—OH and C=O) were 3%–4%, whereas over the ACF, the C—OH content increased significantly from 18.9% to 25.5%. The observed changes of the carbon-oxygen groups (C—OH, C=O, and C—OOH) were due to the reduction-oxidation processes during the introduction of silver ions. Silver ions were reported to be responsible for the oxidation of C—H, C—OH, and C=O to form C—OH, C=O, and COOH groups, respectively [21,24–26]. Two mole electrons were transferred in the oxidation of a mole C—H to C—OH while one mole electron was needed in the oxidation of a mole of other two groups, respectively [24]. Thus, by using the changes of the relative amount of groups (difference of the amounts of carbon-oxygen groups before and after silver impregnation), the amount of electrons transferred in the reduction of Ag ions can be estimated (Table 2, the third column: $\Delta = 2 \times \Delta C-OH + \Delta C=O + \Delta C-OOH$). As seen, between CB and Ag/CB, the changes were barely noticeable, whereas over the other samples, the increases of carbon-oxygen groups were significant, i.e. 17.6% for the ACF, 13.3% increase for coal. It represents the ability of carbon supports to reduce silver ions: CB does not show the reducing capability, whereas the other supports are much more active. This seems to be in opposite correlation with the catalytic activities. The more the silver ions that were reduced during the impregnation process, the lower the catalytic activity for CO selective oxidation.

3.3.2. TPD results

The XPS analysis provides information about surface composition, whereas the temperature-programmed desorption (TPD) measurements, using inert gas (He, Ar, N₂), were one of the widely used methods in the determination of carbon-oxygen groups on carbon materials [27–30]. Different carbon-oxygen groups decompose and release CO and/or CO₂ at different temperatures [27–30]. Carboxylic acid and lactol (also lactone) groups release CO₂ at about 540 K and 650–940 K, respectively, whereas carboxylic anhydride groups decompose with simultaneous formation of CO and CO₂ at 700–840 K. Phenol and carbonyl/quinone groups are more stable on the carbon surface and decompose to CO at about 900 and 1080 K, respectively.

Figure 4 shows the profiles of CO (Figure 4(a)) and CO₂ (Figure 4(b)) release from the carbon supports and corresponding catalysts during the TPD measurements. For the CB support, no emission of CO₂ or CO was detected (not shown), while after the introduction of silver only CO₂ release (Figure 4(b)) was observed. The CO₂ profile contained a peak centered at about 620 K with a shoulder at 720 K; both peaks originating from the decomposition of carboxylic anhydride and/or lactones groups. The lack of CO₂ peak at temperature below 540 K indicates the absence of carboxylic groups over the CB catalyst, which is in good agreement with the XPS results (Table 2). The CO and CO₂ profiles of other carbon materials (ACF and Coal) and corresponding catalysts (Ag/ACF, Ag/Coal) differ significantly in terms of the intensities and shapes of peak (CO and CO₂). Generally, after the impregnation, the intensities of both CO₂ and CO peaks increased, indicating the increases of carbon-oxygen groups due to the surface oxidation.

The CO profiles of both supports and corresponding catalysts show large peaks at the high temperature (about 1080 K), which contain complex information about decomposition of carboxylic anhydride, phenol, and/or carbonyl/quinone groups (Figure 4(a)). A CO peak centered at 450 K was observed for Ag/Coal and Ag/ACF catalysts. It mainly corresponds to the fragments of CO₂. After the introduction of silver, the intensity of main CO peaks (at around 1080 K) increased for all catalysts, and their positions slightly shifted to lower temperature. Over the Coal support, two CO peaks at about 950 K and 1130 K, which can be assigned to phenol and carbonylic/etheric groups, respectively, can be distinguished. Over the Ag/Coal catalyst, the intensities of all the groups increased (compared with Coal); however, the increase of peak corresponding to phenol groups is more obvious (Figure 4(a)). For ACF, a small CO peak was detected at 620 K, corresponding to the decomposition of carboxylic anhydride group. At the same temperature, a CO₂ peak was also observed (Figure 4(b)). The CO profiles of the ACF and Ag/ACF show two peaks over 1000 K, probably from phenolic/carbonylic/etheric groups. For ACF, the intensity of low-temperature peak is lower than that of high-temperature peak, whereas in the case of Ag/ACF catalyst, the intensity of low-temperature peak is higher. This indicates that the amount of phenol groups increased significantly after the impregnation of silver species, which is also evident by XPS measurements (see Table 2).

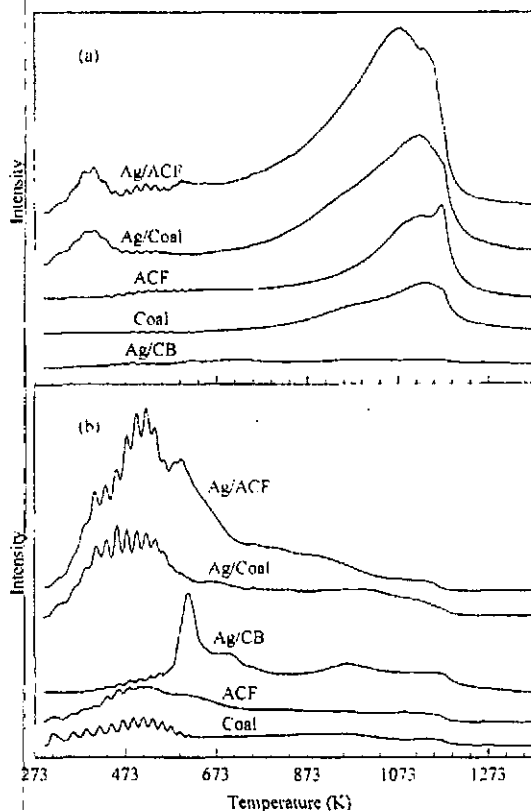


Figure 4. TPD curves of the CO (a) and CO₂ (b) release from carbon supports and corresponding catalysts

(The samples (0.1 g) were first flushed with He (30 ml/min) at room temperature for 2 h. Subsequently, the temperature increased at a heating rate of 5 K/min till 1173 K and then was maintained at the same temperature for 40 min. All the catalysts were washed to remove additional silver nitrate before TPD experiment was carried out.)

The CO and CO₂ profiles were integrated to obtain more information about the changes between supports and corresponding catalysts (Table 3). In brief, the increase of CO and CO₂ release was due to the formation of C—OH, C=O, and COOH groups during the silver impregnation. It was the reduction of Ag ions that resulted in the oxidation of carbon to form these groups. Then, it can be estimated that the relative amount of silver ions reduced during the impregnation, as can be seen from the ($\Delta\text{CO}_2 + 2 \times \Delta\text{CO}$) column in Table 3. (However, the formation of C=O, which results from the oxidation of C—OH, will not lead to the increase of CO emission. Thus, the amount of silver ions reduced is underestimated.) The amount of Ag ions reduced by carbon supports follows the order: CB << Coal < ACF. This observation is in agreement with XPS results.

Table 3. Numerical results of TPD profiles of CO and CO₂ release from supports and catalysts

Entry	Peak area ($\times 10^{-5}$)		ΔCO_2 ($\times 10^{-8}$)	Δ^a ($\times 10^{-8}$)
	CO ₂	CO		
CB	0.25	0.43	7.30	12.28
Ag/CB ^b	7.55	2.92		
Coal	3.24	9.47	8.29	42.49
Ag/Coal ^b	11.53	26.57		
ACF	5.06	17.53	13.75	70.00
Ag/ACF ^b	18.81	45.65		

^a $\Delta = (\Delta\text{CO}_2 + 2 \times \Delta\text{CO})$; 2 mole electrons transfer during a mole C-H oxidation to form C—OH.

^b Before the measurements, the catalysts were washed to remove the additional silver nitrate

3.3.3. UV-Vis DRS results

The UV-Vis diffuse reflectance spectra of as-prepared silver catalysts are shown in Figure 5. Three overlapped bands centered at about 230, 270, and 340 nm can be distinguished in all the three samples. According to literature [31], the band at 220–230 nm can be attributed to isolated Ag ions. The absorption bands at around 270 and 330 nm correspond to the absorption of Ag₄⁺ and Ag₅ clusters, respectively, as reported by Henglein *et al.* [32]. In addition, as suggested by Sato *et al.* [33], the bands in the range of 238–272 and 275–326 nm correspond to the adsorption of Ag_n^{δ+} and Ag_m clusters, respectively. In other words, the absorption bands detected over the catalysts described in this study at about 270 and 330 nm can be attributed to small silver cationic clusters and silver clusters, respectively [34]. The UV-Vis DRS measurements indicate that isolated Ag⁺, small silver clusters (Ag_n^{δ+} and Ag_m) are present in all the catalysts. No surface plasmon adsorption band [35,36] was observed, indicating absence of silver metal nanoparticles in the samples after impregnation.

The Ag/CB catalyst spectrum shows relatively the highest adsorption band at 230 nm, with two shoulders at 270 and 340 nm, representing relatively the highest amount of isolated Ag ions, a small amount of silver clusters and silver cationic clusters. The Ag/ACF catalyst spectrum presents three well-resolved peaks centered at the same wavelength but intensity variation indicates lower concentration of Ag⁺ and relatively much more reduced silver clusters. The observation of relatively large amount of Ag ions on Ag/CB catalyst is in good agreement with the XPS and TPD results. As CB has less defects or functional groups on its surface, very small amount

of Ag ions can be reduced during silver nitrate impregnation and subsequent drying at 333 K. Consequently, most of silver species will remain as Ag ions on the surface of CB. In the case of Ag/Coal, similar to Ag/ACF catalyst, substantial amount of Ag ions has been reduced, leading to the formation of silver clusters.

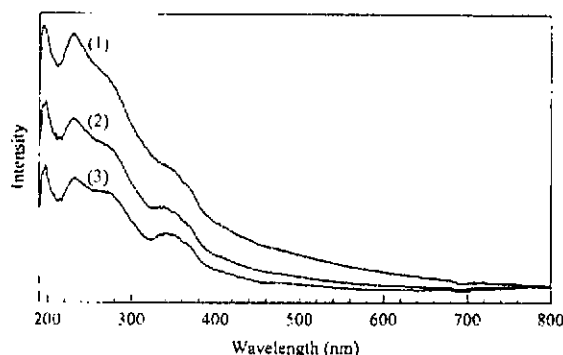


Figure 5. UV-Vis diffuse reflectance spectra of as-prepared carbon-supported silver catalysts (12 wt% Ag)

(1) Ag/CB, (2) Ag/Coal, (3) Ag/ACF

3.4. Discussion

3.4.1. Catalytic properties

In comparison with the catalysts investigated in the present case, the CB-supported silver catalyst showed the highest activity, with the full oxygen conversion and maximum CO conversion (about 12%) at 362 K. Later experiments indicate that even 4 wt% Ag was supported over CB after pretreatment with H₂ at 773 K for 2 h before reaction; CO conversion can be further increased to about 20%, the specific reaction results of which are presented in Figure 6. On the other hand, over ACF and Coal-supported catalysts, the CO conversion was only 3%–5% at 373 K, whereas higher reaction temperatures (at the same time, higher oxygen conversions) promoted the oxidation of H₂, thus resulting in a lower selectivity to CO₂.

Ag/CB catalyst after activation in H₂ at 773 K for 2 h exhibited much higher CO conversion at 353 K than the previously reported Ag/C or Ag-Co/C catalysts for PROX of CO in excess H₂ [37] and CO oxidation in air [38] below 373 K. At the same time, Ag/CB catalyst after activation in H₂ exhibited comparable CO conversion (353 K) to those of Ag-Co and Ag-Mn composite oxides catalysts at higher reaction temperature (383 K) [39].

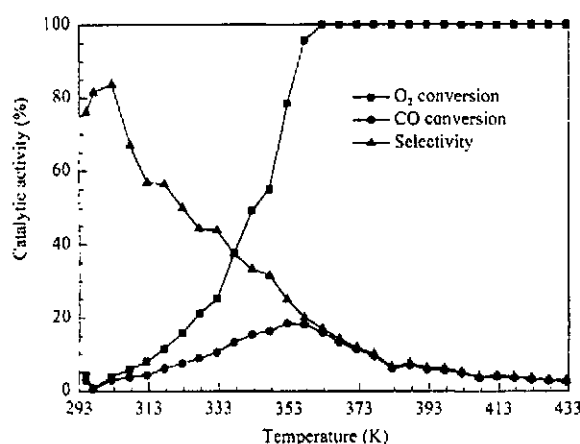


Figure 6. Catalytic activity of 4 wt% Ag/CB catalyst after activation in H₂ at 773 K for 2 h
Reaction conditions: 0.12 g of catalyst; feed gas 1 vol% CO, 0.5 vol% O₂, and 98.5 vol% H₂; flow rate 50 ml/min

For silver catalysts that were reported previously, usually Ag₂O was considered to be the active phase for the oxidation of CO [39,40]. It is known that Ag₂O, if consumed during the reaction with CO, is difficult to regenerate. Only the addition of a second active compound (Co or Mn) or employing the reactive support can increase the stability of the silver catalyst by the oxygen spillover from the second compound or by the reactive support to silver species [39,40]. However, in the present case, the Ag/CB catalyst shows good CO oxidation activity, which can be attributed to the role of metallic silver phase (in contrast to the Ag₂O phase ever considered). Obviously, the carbon-supported Ag or Ag-Co catalysts that were reported previously have much lower CO oxidation activity when compared with that reported in this study, which may originate from different carbon supports and/or chemical states of silver [37,38].

In summary, CB can also be used as a suitable support for Ag catalyst for PROX of CO in excess H₂, and Ag/CB catalyst after activation under H₂ resulted in above 20% CO conversion at 353 K. Optimizing activation methods, modifying textural structure and/or functional groups of carbon materials, adding a second metal, or increasing the O₂ concentration in the feed may further increase CO conversion, and this is still under investigation.

3.4.2. Relationship between properties of carbon supports and silver particle size

By combining XPS data with TPD results, both of which show the changes of the carbon-oxygen

groups after silver deposition, the image of reduction of Ag ions by carbon supports can be analyzed. The results showed that the amount of Ag ions reduced following the order of the reducing ability of the supports, CB << Coal < ACF.

Relative amounts of silver ions and reduced silver species of the as-prepared catalysts can be directly obtained from UV-Vis DRS measurements. After impregnation and subsequent drying (at 333 K) processes, the Ag/CB catalyst has relatively the largest amount of Ag ions and small amount of reduced silver species. At the same time, the Ag/ACF catalyst has relatively the lowest amount of Ag ions, with large amount of metallic silver clusters. The distribution of silver species on Ag/Coal catalyst is intermediate between these two catalysts.

As mentioned above, the surface of carbon has a portion of active sites and, moreover, the population of these active sites will increase along with the increase in surface area and porosity. As reported by Zubimendi *et al.* [41], the electroless deposition of Pt on highly oriented pyrolytic graphite (HOPG) involved nucleation of Pt particles and their 3D growth at surface defects, particularly at steps and edges of the substrate, as observed by Scanning Tunneling Microscopy (STM). Zoval *et al.* reported the same phenomena [24].

For the carbon supports that are studied in the present case, when silver is introduced on carbon surfaces, there are different paths for the growth of metallic silver particles. On the one hand, if there are sufficient reducing groups (in this case, surface functional groups) and nucleation sites (defects; the amount of which is governed by the surface area and texture of carbon support) on the carbon support, reduction of Ag ions and the nucleation will occur during the impregnation and drying processes, leading to the formation of silver clusters (composed of several silver atoms). In the subsequent activation process, the silver clusters will serve as the nucleation center for 3D growth of silver particles (the metallic silver is derived from silver nitrate decomposition). This process can be defined as the heterogeneous nucleation. Normally, it will lead to the formation of large metal particles. On the other hand, Ag ions that were not reduced during the impregnation and subsequent drying processes remained as ions. Subsequently, they undergo a homogeneous nucleation in the activation process, which leads to the appearance of narrowly distributed considerably small silver particles. Over the Ag/ACF catalyst, large amounts of metallic sil-

ver clusters were formed during impregnation. After activation, a bimodal silver particle size distribution was found, as shown in Figure 7 (a) and (b).

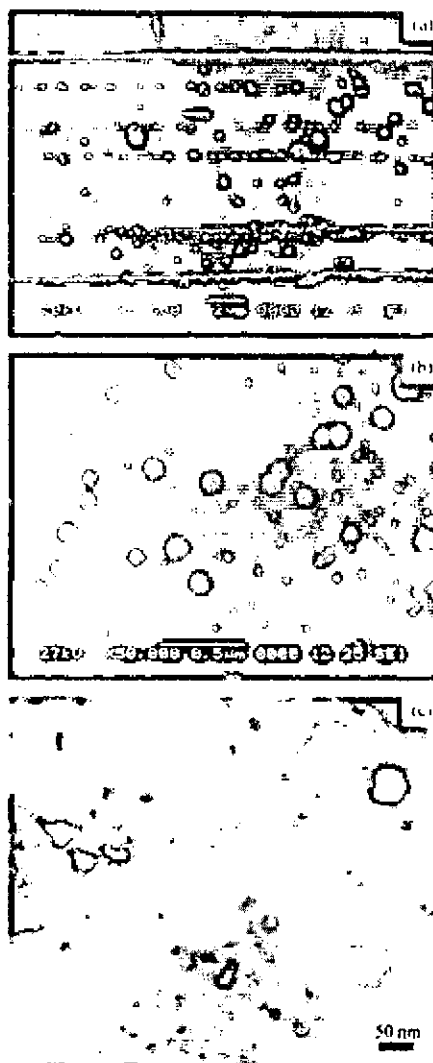


Figure 7. SEM images of 12 wt% Ag/ACF (a and b) and TEM image of 12 wt% Ag/CB (c) Catalysts after activation in He at 773 K for 2 h

The bigger particles are around 200 nm, whereas the smaller ones are about 25 nm, which are the contribution of heterogeneous and homogeneous nucleation, respectively. On the contrary, in the case of Ag/CB catalyst, as there are very limited amount of reducing groups, most of the silver species remain as Ag ions after impregnation, which mainly underwent the homogeneous nucleation during activation. Thus, nearly uniformly distributed small silver nanoparticles (about 12 nm) were obtained (Figure 7(c)). For Ag/Coal catalyst, after impregnation, the situation is generally intermediate between these two, but similar

to Ag/ACF catalyst; it has the bimodal silver particle size distribution.

Among the three catalysts that were investigated, Ag/CB catalyst demonstrated the best catalytic properties in the selective oxidation of CO in excess hydrogen. Coupling various characterization techniques, it is concluded that the mesoporous structure, together with moderate surface area, and a limited amount of surface functional groups are pivotal for the formation of narrowly distributed small silver particles (around 12 nm), thus conferring superior catalytic properties in the selective oxidation of CO.

4. Conclusions

Various carbon-supported silver catalysts were prepared by the conventional wet impregnation method, and their catalytic properties for PROX of CO in excess hydrogen were studied. Employing a variety of techniques, *i.e.* N_2 adsorption, XPS, TPD, UV-Vis DRS, SEM and TEM, the effects of the porosity, surface area, and surface chemistry of the carbon supports on the preparation of the catalysts and the catalytic properties have been studied. It was concluded that:

1. The defects on the carbon surface serve as nucleation sites of metallic silver particles, whereas the surface functional groups contribute to the reduction of Ag ions in the impregnation and subsequent drying processes.
2. During the catalyst activation process, additional silver species decompose to metallic silver, undergoing homogeneous and/or heterogeneous nucleation. The latter resulted in a bimodal distribution of silver particle size.
3. Carbon materials have a mesoporous structure with moderate surface area and a limited amount of surface functional groups that are suitable supports for Ag catalysts, which result in uniform size of silver particle, thus conferring better catalytic properties for the Ag/CB catalyst.
4. Carbon materials-supported silver catalysts are potentially good catalysts for PROX of CO in excess H_2 in fuel cells. To satisfy the requirements of the PEMFCs applications, further research to improve the CO conversion and selectivity to CO_2 is ongoing, including the addition of second active component and optimizing oxygen concentration in the feed.

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Novel carbon based catalysts for the reduction of NO: Influence of support precursors and active phase loading

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Available online 27 December 2007

Abstract

Carbon-supported catalysts in the form of powder, briquettes and monoliths have been prepared. Powder and briquette samples have been obtained using a Spanish low-rank coal as raw material for carbon support through a pyrolysis process whereas monoliths were prepared by coating cordierite monoliths with a blend of two polymers. Vanadium was chosen as active element and impregnated by equilibrium adsorption from 1 to 8 wt% on the surface of as-prepared supports. All samples were tested in the selective catalytic reduction of NO with NH₃ as reducing agent at low temperature (150 °C), demonstrating a considerable efficiency which was enhanced mainly by oxidation treatments and an increase of vanadium loading up to vanadium agglomerates formation. The nature of carbon precursor determines the porosity development and surface chemistry of supports, what results in a different dispersion and fixation of active phase. An enhancement of NO efficiency is achieved by increasing microporosity and the amount of surface oxygen groups in pyrolysed coal whereas in polymer blend, mesoporosity and just a certain amount of surface oxygen groups should be promoted. An excess in vanadium loading decreases NO reduction efficiency because of a pore blockage and the formation of vanadium agglomeration what makes to expose a lower vanadium surface to the reactants.

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Keywords: Carbon based catalysts; Vanadium loading; SCR-NH₃

1. Introduction

The removal of nitrogen oxides from outgases is one of the most challenging problems of 21st century. Until now, the most efficient method of NO_x removal from stationary sources used on industrial scale is selective catalytic reduction (SCR) with ammonia. The most frequently used catalyst is V₂O₅/WO₃/TiO₂ prepared in the form of a monolith [1]. The catalyst performance is, however, far from an ideal one since: a higher activity at either low (<250 °C) or high (>400 °C) temperature range, broader temperature window, higher resistance to water and SO₂, and last, but not least, reducing production and operational costs are required. These properties are highly dependent on the support material and consequently a large number of materials have been tested. Among them coal is one of the most promising due to its abundance a potentially lower

cost, possibility of obtaining samples with proper geometry, good mechanical resistance [2]. Apart from these characteristics, one of the main advantages is the possibility to tailor their properties, both textural and chemical (acidity, redox properties, etc.) by means of the preparation procedure that consists of several steps, such as: pyrolysis, activation, acidic pre-treatment and impregnation [3].

According to the carbon precursor election, there are many types of materials which can be used as carbon based supports, but nowadays the most important ones are those coming from coals and polymeric blends. Each precursor presents a series of advantages and drawbacks. On one hand, coals are known to be easily available and depending on their rank they could be a really low-cost raw material. Low-rank coals have a high amount of ashes what can be considered as an additional advantage since previous investigations indicated that could have a catalytic effect on NO reduction [4–7]. Catalytic effect for the NO reduction of coal-supported catalyst is mainly attributed to alkaline and alkaline earth metals [8–12] and some first-series transition metals (Fe, Cu, Cr, Co, Ni) [13–17].

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However, other authors argue that the incorporation of an additional active phase on the coal surface is required to enhance their NO removal activity [18,19].

Polymer blends are usually considered a good option because they do not involve using mineral matter and consequently can get a higher selectivity towards nitrogen, since no side-reactions are catalyzed. Polymer characteristic promotes the application of carbon blends as catalyst washcoats when they are supported on structures such as monoliths since the development of meso and microporosity ensures a good contact between reactants and the active phase [20].

As commented before, each preparation step has an influence on carbon support. Pyrolysis provides a possibility of tailoring porous structure, through the opening of constrictions in the char porosity and the development of new interconnecting pores [21]. Activation results depending on the activation agent, temperature and residence time, in the formation of either micro or mesoporosity. Moreover, activation causes a change on the chemistry surface of carbon materials. All literature studies unanimously show that the catalytic activity of activated carbons for NO conversion increases with the oxygen concentration on the carbon surface [4–9]. However, there are still several unanswered questions concerning the effect of anchoring active phase and if the presence of determined oxygen groups could influence the formation of the aggregates on the surface.

Active phase impregnation may be introduced as the last step of the preparation. The influence of the nature of precursors, loading and impregnation method was also studied [4–5,15]. Marbán et al. [15] found that NO reduction increases with higher active phase loading up to a maximum where dispersion of this component starts to drop off. Vanadium is without any doubt the most common active element for SCR reactions [22]. When it is used supported on carbon based catalysts they can enhance NO reduction at low temperatures being this fact considered as one of the most outstanding properties of vanadium loaded carbon-supported catalysts.

In this work, the results of catalytic tests for carbon samples in the form of powder, briquettes and monoliths are presented. Samples were prepared with two different carbon precursors modified by means of various activation and oxidation procedures and containing different amounts of active phase precursors. These catalysts have been characterized by means of a series of physical–chemical methods like N_2 adsorption, TPD, SEM and AFM techniques showing that the preparation steps as well as active phase precursors have a great influence on their whole performance.

2. Experimental

2.1. Catalyst preparation

Three kinds of carbon based catalysts under different forms and compositions have been prepared. Firstly, powder catalysts with a particle size between 0.2 and 0.5 mm was obtained from a low-rank coal from SAMCA coal mining company in Teruel

(Spain). This coal was pyrolysed in N_2 at 800 °C, activated with 20% steam in N_2 and finally oxidized with HNO_3 as described in detail elsewhere [19]. Secondly, briquette carbon support was obtained from the above mentioned pyrolysed coal and commercial pitch. Briefly, the preparation process consists in coal pyrolysis, blending with the ground commercial tar pitch, briquetting process by pressure performed in a device specially designed to this purpose, curing in an electric furnace with air, pyrolysis of briquettes under N_2 , activation either with 20% of water vapour in N_2 or CO_2 at different temperatures and oxidation with HNO_3 (1N). The activation as well as the pyrolysis, were conducted in a fixed-bed reactor as described in more detail elsewhere [23]. Finally, carbon coated cordierite monolith supports were prepared. In this case cordierite monoliths were coated with a carbon layer by means of the dipcoating method as described in details elsewhere [20]. Briefly, it consists in dipping the cordierite monolith (400 cpsi, 1 cm diameter and 5 cm length) into a liquid polymer that is subsequently cross-linked and carbonized. To coat the monoliths two carbon precursors were used polyethylene-glycol (PEG) 6000 mol wt (Sigma–Aldrich) and Furan resin (Huttenes-Albertus). After dipcoating, the sample was cured, carbonized in Ar, activated with CO_2 and treated with 2N and 4N HNO_3 at room temperature to create superficial oxygen groups [25].

In all cases, after carbon support preparation, catalysts were loaded with 1, 3, 5, 6 or 8% (w/w) V by equilibrium adsorption using commercial vanadium compounds provided by Aldrich (either V_2O_5 or NH_4VO_3) as active phase precursor. A solution/suspension of each of these compounds in deionized water was stirred and the sample was introduced inside for 3 h. In the case of NH_4VO_3 solution in distilled water was improved by adding around 10 mg of oxalic acid. After stirring samples were rinsed and dried overnight. Just in order to clarify the used abbreviation, it is worth including in this section a short description of all of them. Samples structured as powder were named as follows: SCA750/PV/1%/AD/E where SCA accounts for the carbon support prepared from the low-rank coal, as stated before, 750 is the temperature of activation used, when AC appears instead of SCA this indicates that in that case the catalyst was prepared using a commercial activated carbon as support, PV is commercial vanadium model, PCA is ashes of a petroleum coke, 1, 3 or 5% is the vanadium loading, AD is adsorption equilibrium and finally E means that the excess of dispersant was removed by means of evaporation. In the case of briquettes samples, they were named as follows: Br/AC/750/2h/ H_2O + PCA where Br means briquette, AC is activated carbon and P pyrolyzed, 750 is the activation temperature in °C, 2 h is the activation time and H_2O or CO_2 are the activation agent, PCA is the active phase precursor used that always provides a loading of 3 wt%. Finally monolith samples were named as 1% V_2O_5 /AC where 1% is the loading and V_2O_5 the active phase precursor used. 30PEG or 50PEG mean the quantity of PEG used, respectively, and ACN for carbon activated and subsequently oxidized with HNO_3 (2N).

2.2. Catalyst characterization

Carbon support and catalysts were physically and chemically characterized by means of two different methods and techniques: Adsorption of N_2 at 77 K and temperature programmed desorption (TPD). Specific surface area was calculated from the N_2 adsorption isotherms applying BET equation in an ASAP-2000 apparatus. On the other hand, TPD tests were performed heating 600 mg of sample at a constant rate (10 °C/min) from 150 to 1050 °C in a flow of 30 ml He/min. Samples were collected in gas samples bags and CO and CO_2 were measured in a chromatograph equipped with a thermoconductivity detector.

Two techniques (SEM and AFM) have been used for the optical characterization of the active phase. SEM pictures were obtained in a SEM EDX Hitachi S-3400 N using backscattered electrons detection. The AFM apparatus was operated in a dynamic mode, where the cantilever is oscillated at its eigenfrequency (72 kHz). Topographic image and height data were collected simultaneously.

2.3. Activity tests

The NO reduction efficiency of the catalysts was determined at 150 °C by passing a gas mixture containing 1000 ppmv of NO, 1500 ppmv of NH_3 and 3.5% (v/v) of O_2 in Ar through a fixed bed containing 0.4 g of sample in the case of powder and briquette samples or just a single monolith for cordierite support. The low rate of powder and briquette catalysts was 22 ml/min while monoliths permit a flow rate of 100 ml/min. The composition of the gas exiting the reactor was continuously measured in a quadrupole mass spectrometer (Balzers 422) connected on-line. The conversion of NO was calculated as follows:

$$\%NO \text{ reduction} = \frac{(C_{NO}^i - C_{NO})}{C_{NO}^i} \cdot 100 \quad (1)$$

where C_{NO}^i is the initial concentration of NO and C_{NO} corresponds to its concentration once steady state is reached.

3. Results and discussion

3.1. Influence of support nature and thermal preparation steps on the NO reduction efficiency

Carbon support characteristics have shown to be a key factor in the NO reduction efficiency of the catalysts prepared. At the sight of the results presented in Tables 1a and 1b, both mineral and polymer blend carbon catalysts show efficiencies in the NO reduction in the range of 28 and 88%. The large difference between these values could be due to either the nature of the supports as well as the conditions used in the preparation steps that can modify the chemistry and porosity of catalysts and consequently their NO reduction efficiency.

Regarding to the activation step, all supports achieved a porosity development by an increase in temperature and

residence times of activation. Especially in coal supports (powder and briquette samples) the activation process results in an increase of porosity due to the opening of constrictions in the char porosity and the development of new interconnecting pores [21]. The activation step was carried out under several conditions, steam or CO_2 activation agent and several temperatures showing that the use of CO_2 as activation agent provides a larger microporosity. This fact agrees with other authors [26–28]. In those works, authors studied the different effect of the activating agent (CO_2 or steam) in the development of porosity of a char obtained from the pyrolysis of an organic carbon. After the studies, they concluded that the CO_2 produces an opening, followed later by widening of narrow microporosity whereas steam widens the microporosity from the early stages of the activation process and consequently microporosity is favoured by CO_2 activation while meso and macroporosity are both favoured by steam activation.

Generally speaking, coal supports have mainly a microporous structure whereas monoliths are mainly mesoporous. Monoliths prepared with a polymer blend were activated under CO_2 at different temperatures. In these cases, activation process causes an increase in the microporous structure although the microporous volume adsorption did not reach the mesoporosity, being considered on the whole such as mesoporous materials. Porous structure of samples seems to have a great influence on the NO reduction activity reached. In the case of coal catalysts an increase in the porous structure causes an increase in the NO reduction activity although it does not seem to be a mathematical relationship between them but a threshold around 100 m²/g that should be overcome to avoid pore blockage. On the other hand, polymer blend based catalysts show a higher dependence to the structural development. A well-developed mesoporosity is essential to favour a high amount of oxygenated surface groups that can be responsible for dispersion and fixation of active phase whereas narrow microporosity developed by CO_2 activation does not seem to play a significant role in the improvement of the catalyst prepared [27].

On the other hand, activation procedures and especially oxidation ones have a great effect on the surface chemistry. Surface chemistry plays an important role on the NO reduction. Oxidized coal supports have an average increase of 25% in the surface oxygen groups evolved such as CO or CO_2 in the TPD runs in comparison to non-oxidized samples. This enhancement is expected to be a consequence of HNO_3 treatment where new oxygen groups are created (Table 1b). The activity increases notably when subjecting the briquette to the HNO_3 oxidizing treatment prior to its impregnation. This fact could be indicating that the surface oxygen functionalities created upon HNO_3 treatment can probably favour both the fixation of the active phase and the adsorption of some reactant, likely NH_3 , during the reaction, thus resulting in an increased catalytic activity. However, and although it is not shown, oxidation process of coal supports causes an important decrease in porosity what is likely due to a demineralization and redistribution of the mineral matter in coal. That matter could be displaced to the outer or inner walls of microporous what

Table 1a

Reduction of NO at 150 °C. textural and surface chemistry parameters of catalysts prepared without oxidation step

Sample	NO red (%)	S_{BET} (m ² /g)	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)	CO (cm ³ /g)	CO ₂ (cm ³ /g)
Powder samples						
SCA600/PV/3%/AD/E	33	8	0.04	0.010	31	13
SCA600/VA/3%/AD/E	32	6	0.04	0.011	38	11
SCA600/PCA/3%/AD/E	28	8	0.05	0.016	43	10
SCA750/PV/3%/AD/E	56	385	0.26	0.24	44	19
SCA750/VA/3%/AD/E	46	377	0.23	0.18	51	17
SCA750/PCA/3%/AD/E	46	344	0.23	0.20	53	17
Briquette samples						
Br/AC/600/2 h/H ₂ O + PCA	34	3	0.10	–	25	49
Br/AC/750/2 h/H ₂ O + PCA	52	278	0.12	–	9	32
Br/AC/750/2 h/H ₂ O + V ₂ O ₅	47	285	0.21	–	9	32
Br/AC/750/2 h/CO ₂ + PCA	42	106	0.05	–	16	49
Br/AC/800/1 h/CO ₂ + PCA	50	182	0.08	–	13	41
Br/AC/800/2 h/CO ₂ + V ₂ O ₅	54	197	0.08	–	13	41
Monolith samples						
30PEG-AC	–	406	0.13	0.64	–	–
50PEG-AC	–	473	0.11	0.96	–	–
50PEG-ACN	72	–	–	–	–	–
AC	10	836	0.22	1.57	3.5	0.4

blocks or reduces their capacity [29]. Despite this fact, it could be observed that the loss of textural properties due to demineralization does not affect in the catalytic activity or at least, it is not as important as the influence of the surface oxygen groups formed by the oxidation process.

In the case of monolith catalysts two oxidation process where carried out by using 2N and 4N HNO₃, respectively. Comparing both samples, it is observed that increasing the severity of HNO₃ treatment entails some decrease of micro-mesopore surface area while the variation of pore volume has little significance. It could be explained by the collapse of pore walls and the ensuing widening of the pores [30]. As a consequence of this decrease in surface area, the more severe oxidized sample seems to adsorb a lower amount of vanadium and therefore reaches a lower catalytic activity.

Support nature and thermal treatments also influence in the catalysts stability. Carbon supports are known to suffer from gasification when temperature rises. In order to determine the maximum temperature at which carbon supports were stable TGA runs were performed. According to the results shown in more detail in [35,36] coal supports reach a maximum temperature around 350 °C while polymer blend supports permit a higher temperature around 400 °C. In both cases, the impregnation with vanadium results in a slightly decrease of stability that mainly depends on the active phase precursor and oxidation treatment. Time-on-stream conversion was also examined in [35] showing that catalysts resist more than 24 h without any sign of deactivation.

Finally, carbon based catalysts, both coal and polymer blend-supported catalysts have been tested in a large range of

Table 1b

Reduction of NO at 150 °C. textural and surface chemistry parameters of catalysts prepared with oxidation step

Sample	NO red (%)	S_{BET} (m ² /g)	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)	CO (cm ³ /g)	CO ₂ (cm ³ /g)
Powder samples						
SCA750/PV/3%/AD/E (HNO ₃ 65% w/w, Troom)	86	290	0.12	0.23	41.6	51.7
SCA750/PV/3%/AD/E (HNO ₃ 1N, Troom)	87	300	0.15	0.22	41.6	51.7
SCA750/PCA/3%/AD/E (HNO ₃ 65% (w/w), Troom)	88	267	0.13	0.19	21.3	24.8
SCA750/PCA/3%/AD/E (HNO ₃ 1N, Troom)	72	275	0.12	0.22	21.3	24.8
Briquette samples						
Br/AC/600/2 h/H ₂ O + PCA (HNO ₃ 1N, Troom)	28	1	–	–	34	44
Br/AC/750/2 h/H ₂ O + PCA (HNO ₃ 1N, Troom)	42	189	0.08	–	27	27
Br/AC/750/2 h/H ₂ O + V ₂ O ₅ (HNO ₃ 1N, Troom)	48	181	0.06	–	27	27
Br/AC/750/2 h/CO ₂ + PCA (HNO ₃ 1N, Troom)	71	70	0.03	–	31	31
Br/AC/800/1 h/CO ₂ + PCA (HNO ₃ 1N, Troom)	67	183	0.07	–	31	31
Br/AC/800/2 h/CO ₂ + V ₂ O ₅ (HNO ₃ 1N, Troom)	79	113	0.05	–	28	31
Monoliths samples						
V ₂ O ₅ /AC + HNO ₃ 2N	43	825	0.18	0.78	65.0	49.0
V ₂ O ₅ /AC + HNO ₃ 4N	40	775	0.20	1.48	60.5	29.1
V ₂ O ₅ /AC + conc HNO ₃	37	363	0.18	0.27	66	51

Table 2
Influence of vanadium loading on activity and textural properties

Sample	NO red (%)	S_{BET} (m ² /g)	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)
Powder samples				
SCA750/0%PCAorPV	28	–	–	–
SCA750/PV/1%/AD/E	52	347	0.18	0.25
SCA750/PV/3%/AD/E	55	384	0.26	0.22
SCA750/PV/5%/AD/E	42	302	0.15	0.22
SCA750/PCA/1%/AD/E	45	373	0.18	0.26
SCA750/PCA/3%/AD/E	46	344	0.23	0.20
SCA750/PCA/5%/AD/E	50	324	0.15	0.22
Monolith samples				
0% V ₂ O ₅ /AC + HNO ₃ (2N)	12	617	0.18	0.78
3% V ₂ O ₅ /AC + HNO ₃ (2N)	43	620	0.23	0.61
4% V ₂ O ₅ /AC + HNO ₃ (2N)	56	629	0.23	0.63
6% V ₂ O ₅ /AC + HNO ₃ (2N)	68	607	0.20	0.70
8% V ₂ O ₅ /AC + HNO ₃ (2N)	67	529	0.16	0.61

temperature (75–350 °C) and their activity has been compared to other commercial catalysts activity found in the literature [36,37]. As shown in these studies, carbon based catalysts present a higher activity at lower temperatures than commercial catalyst what can avoid the need of gas reheating in an industrial facility.

3.2. Influence of vanadium loading on the NO reduction efficiency

As described previously, all samples were loaded with vanadium by means of equilibrium adsorption method. It is known that in the preparation of supported catalysts by impregnation, the sorption of metal ions in solution is influenced

by the physical–chemical properties of the support, pH of impregnation, and nature of the solvent. When the pH of impregnation solution is higher than the point zero charge (PZC), the surface of the support will become negatively charged, and the adsorption of cations is favoured [31]. The main goal of the oxidation with HNO₃ is to obtain a more hydrophilic surface with a relatively large number of surface oxygen groups, hence decreasing the PZC. However, if carbon based supports have been prepared under the same preparation procedure, both the nature of precursor and the loading of vanadium have a great influence on the catalytic behaviour of the samples.

An increase of vanadium loading leads in all cases to an enhancement of the activity until a certain extend where a drop off in catalytic activity starts. As shown in Table 2 an increase in loading leads to an important increase in the catalytic activity. When polymer blend are tested the activity increases up to a 6% of vanadium whereas coal based catalysts show a higher activity but only up to a 5% in vanadium. This fact could be attributed to a possible pore blockage together with agglomeration leading to poor dispersion of the active phase, when an excess of vanadium precursor is used. According to literature the amount of active phase that can find place on the catalysts surface depend on the structural and surface chemistry of supports [15]. Comparing both supports, coal based catalysts present a lower surface area what can restrict the dispersion of active phase on the catalyst surface inducing the formation of vanadium aggregates and consequently a decrease in the catalytic activity. This fact was characterized by means of N₂ adsorption and SEM pictures show in Table 2 and Fig. 1, respectively. At the sight of results, from a 5% of vanadium loading on there is a decrease in the total volume adsorbed an especially in those related to the micropore and mesopore

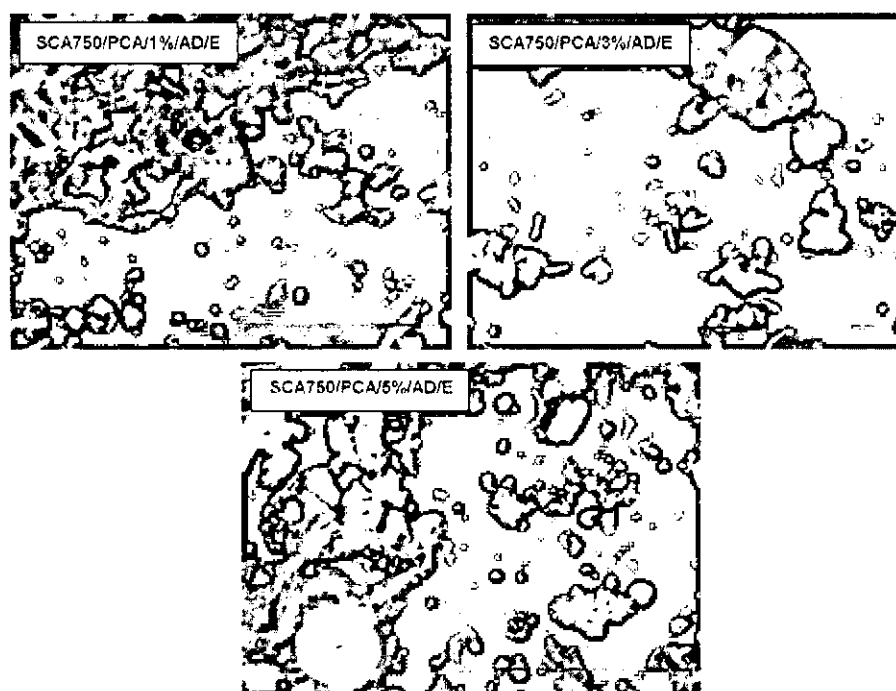


Fig. 1. SEM picture of the vanadium agglomeration on powder samples.

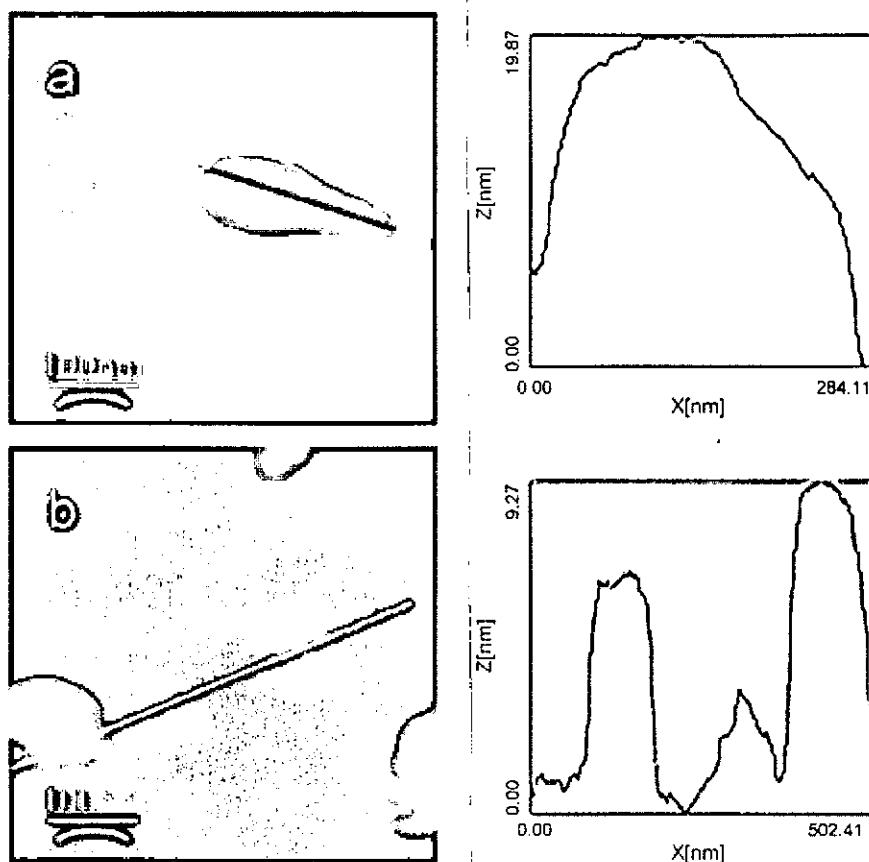


Fig. 2. AFM picture of vanadium agglomeration on monolith samples. Samples with 8% vanadium. Left AFM top view, right profile along the line in the top view [27].

volume what can point out a pore blockage due to the higher amount of active phase incorporated. Moreover, SEM pictures of 5% vanadium loaded catalyst show evidence of agglomeration of metals (left lower corner) that cannot be observed on the 1 and 3% of vanadium pictures.

Polymer blend carbon catalysts equally show a vanadium loading limit from which the catalytic activity no longer increases. However, this limit seems to be slightly higher. The characterization of vanadium dispersion was carried out by means of two microscopy techniques such as SEM and AFM. AFM pictures are shown in Fig. 2. The different contrast between the features and the support in the phase-shift image enables us to state that the features in the picture have a different chemical composition than the carbon support; i.e. these crystallites can be unambiguously ascribed to vanadium compound. According to Fig. 2 (at the left there is a top view image and at the right there is the profile in nanometers along the line drawn in the top view) the higher the vanadium loading the higher the agglomeration of the active phase on the surface and consequently the worse the dispersion of vanadium causing a decrease in the NO reduction efficiency. Moreover, it should be taken into account that with this technique there is impossible to characterize vanadia aggregates smaller than 4 nm since they cannot be discerned from the roughness of the support [24].

From the catalytic experiments a relationship between the morphology of vanadium compound and the catalytic behaviour

arises. The catalytic activity is increasing up to the monolayer coverage but drops in samples where crystallites are formed because of the amount of inactive vanadium and the reduction of vanadium surface which is exposed to the gas phase. Furthermore, the decrease in BET surface area of these samples suggests that some vanadium can be buried in the micropores.

From all the above, the dispersion of vanadium is crucial for both the efficiency and the selectivity of the catalysts. This is consistent with most of the results in the literature for the SCR of NO at higher temperatures in which vanadium is supported on metal oxide [32–34]. All these authors emphasize the necessity of well-dispersed vanadium overlayers, regardless the reaction mechanism that they suggest.

4. Conclusions

In this work, carbon based catalyst in powder, briquette and monolith samples have shown to be considerably active for the NO reduction with the addition of ammonia at low temperature (150 °C). The nature of carbon support as well as the preparation procedure influence greatly on the catalytic activity. On one hand, powder and briquette catalysts have been prepared from a low-rank coal. These catalysts have demonstrated that the porous structure, as determined from N₂ adsorption isotherms at 77 K, plays an important role in high catalytic activities. It could be said that the total volume increases with the severity of the activation and reduces with

oxidation treatment, thus a proper development of the porous structure is fundamental in order to avoid pore blockage, but the presence of surface oxygen functionalities is even more important since it provides an adequate distribution and fixation of the active phase. The presence of these groups may contribute also to the adsorption of the reactants during the NO reduction reaction.

On the other hand, polymer blend based catalysts show a higher dependence to the structural development. A well-developed mesoporosity is essential to favour a high amount of oxygenated surface groups that can be responsible for dispersion and fixation of active phase whereas narrow microporosity developed by CO₂ activation does not seem to play a significant role in the improvement of the catalyst activity. In this way, an increase in the severity of HNO₃ treatment entails some decrease of micro-mesopore surface area allowing a lower amount of vanadium adsorbed on the surface and consequently a lower catalytic activity.

An increase of vanadium loading leads in all cases to an enhancement of activity, until a certain extend where vanadium agglomeration starts and activity drops off. This fact could be attributed to either a possible pore blockage or the formation of crystallites on the surface, decreasing the total active vanadium as well as the global vanadium area exposed.

Acknowledgements

This research was financed by the projects PPQ2002-02698 and MMA 437/2003/3-13.1. The authors are indebted to the Spanish MCyT, "Aragon Government" and Spanish MCyT y MMA for this financial support. A. Boyano acknowledges the CSIC for her I3P-Predocctoral Grant.

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Roles of lattice oxygen in V_2O_5 and activated coke in SO_2 removal over coke-supported V_2O_5 catalysts

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Received 27 June 2007; received in revised form 23 November 2007; accepted 8 January 2008

Available online 15 January 2008

Abstract

This paper systematically investigates the roles of lattice oxygen in V_2O_5 and activated coke over coke-supported V_2O_5 catalysts in SO_2 removal process at 200 °C. The results show that one SO_2 molecule reacts with one O atom in a surface V_2O_5 molecule to form an intermediate (a $VOSO_4$ -like structure), which then reacts with gaseous O_2 to form sulfur species (SO_3 or H_2SO_4 in the presence of H_2O) and V_2O_5 . The SO_3/H_2SO_4 migrates over the coke surface and stores in the pores in the vicinity of V_2O_5 sites. Mineral matters, oxygen and nitrogen species in the activated coke are unfavorable to migration of SO_3/H_2SO_4 . The pores effective for storage of SO_3/H_2SO_4 are those less than 1 nm in size.

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Keywords: V_2O_5 ; Pore size distribution; Lattice oxygen; SO_2 removal

1. Introduction

SO_2 and NO in flue gas are major air pollutants and must be removed before emission. Among various emission control technologies [1–3], activated coke (AC) and activated carbon fiber (ACF) were found to have good SO_2 removal activities at temperatures below 100 °C [3–8]. However, flue gases are usually maintained at temperatures around 150 °C or higher for self-ventilation. This makes the use of AC/ACF-based technologies difficult because flue gases must be cooled down for SO_2 removal and then be heated up for ventilation.

Our recent work [9,10] found that supporting V_2O_5 onto an AC (V_2O_5/AC) results in high activities in SO_2 removal as well as in selective catalytic reduction (SCR) of NO_x by NH_3 at temperatures around 200 °C. This V_2O_5/AC -based technology not only allows flue gas self-ventilation, but also solves NO pollution simultaneously. Studies regarding SCR reaction over

V_2O_5/AC have been reported in our earlier works [11,12]; SO_2 removal over V_2O_5/AC is studied in detail in this paper.

The SO_2 removal process over porous carbon materials was found involving a number of steps: adsorption of SO_2 , oxidation of SO_2 to SO_3 , reaction of SO_3 with H_2O to form H_2SO_4 , and storage of H_2SO_4 in pores [4,13,14]. Surface oxygen groups were found to be important for absorption and oxidation of SO_2 [13,15], and surface area and pore volume were important for absorption of SO_2 and storage of H_2SO_4 [4,16,17]. Since storage of H_2SO_4 or SO_3 in the pores decreases SO_2 removal activity, the SO_2 -captured catalyst/sorbent has to be regenerated at a certain conversion level by water washing or reductive decomposition to recover its activity.

SO_2 removal over V_2O_5/AC consists of two steps: removal and regeneration. The mechanism proposed for SO_2 removal was [9]:

- (1) adsorption of SO_2 on V_2O_5 sites or on AC sites adjacent to V_2O_5 sites;
- (2) activation of SO_2 by V_2O_5 to form a $VOSO_4$ -like intermediate;
- (3) reaction of the $VOSO_4$ -like intermediate with O_2 to form SO_3 and V_2O_5 ;

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- (4) migration of SO_3 over the surface, reaction of SO_3 with H_2O to form H_2SO_4 , and storage of H_2SO_4 in the pores of AC.

Apparently, SO_2 removal mechanism of $\text{V}_2\text{O}_5/\text{AC}$ is different from that of AC/ACF in catalytic oxidation of SO_2 . In the absence of V_2O_5 , oxygen functional groups on AC/ACF are responsible for SO_2 oxidation, which is effective at temperatures below 100°C . However, in the presence of V_2O_5 , V_2O_5 is responsible for SO_2 oxidation, especially at temperatures around 200°C . In addition to the role of V_2O_5 , the higher SO_2 removal activities of $\text{V}_2\text{O}_5/\text{AC}$ should also be related to the properties of AC since poor SO_2 removal activity was found for V_2O_5 supported on other materials. In this regard, it is interesting to quantify the effects of V_2O_5 and AC on SO_2 removal at around 200°C . This information is of importance for validating catalytic mechanism of $\text{V}_2\text{O}_5/\text{AC}$.

2. Experimental

2.1. Preparation of catalysts

A coal-derived coke (a commercial product of Xinhua Chemical Company, Taiyuan, China) is used as the raw material. The coke is activated in steam at 850°C for 40, 60, 80, 120 and 160 min to yield a variety of ACs with different surface textures. These ACs are named AC40, AC60, AC80, AC120 and AC160 according to the activation time. To eliminate possible influence of minerals (ash), all the AC samples are subjected to acid wash at 60°C for 12 h using an aqueous solution containing 2 mol/l HCl and 2 mol/l HF. The demineralized AC samples (with ash contents $<0.6\%$) are marked with a prefix DM-. To introduce oxygen functional groups to AC's surface, DM-AC80 is treated with an aqueous HNO_3 solution (2 mol/l) at 60°C for 12 h and then washed with distilled water to neutral and dried at 110°C for 5 h. The resulting sample is named NDM-AC80.

The $\text{V}_2\text{O}_5/\text{AC}$ catalysts are prepared by pore volume impregnation of the AC supports with an aqueous solution containing ammonium metavanadate and oxalic acid. The catalysts are then dried at 50°C for 5 h and at 110°C overnight and subsequently calcined in N_2 at 500°C for 5 h and then exposed in air at 250°C for 5 h. The catalysts are named according to their components. V2/(DM-AC80) refers to DM-AC80 supported with 2 wt.% V_2O_5 , for example.

2.2. Activity measurement

A fixed bed reactor is used for SO_2 removal experiment. The feed contains 1600 ppm SO_2 , 500 ppm NO , 4.5% O_2 , 2.5% H_2O , balance N_2 and 500 ppm NH_3 . It should be pointed out that 500 ppm NO is introduced into the feed to simulate flue gas and 500 ppm NH_3 is to reduce NO . Our previous work [9] found that NO and NH_3 in the feed do not influence SO_2 removal over $\text{V}_2\text{O}_5/\text{AC}$. Therefore, SO_2 removal behavior is investigated in the presence of NO and NH_3 .

To identify the different roles of O_2 and the lattice oxygen of V_2O_5 in SO_2 removal, O_2 -response experiments were

Table 1
BET surface area and pore volume of the catalysts

Catalyst	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Pore volume ($<1\text{ nm}$) (cm^3/g)
V2/(DM-AC40)	306	0.13	0.09
V2/(DM-AC60)	405	0.19	0.12
V2/(DM-AC80)	621	0.26	0.16
V2/(DM-AC120)	700	0.27	0.15
V2/(DM-AC160)	496	0.26	0.12
V2/AC80	609	0.28	0.17
V2/(NDM-AC80)	631	0.28	0.16

performed in the fix bed reactor. The feed contains 500 ppm SO_2 , 4.5% O_2 (when used), 2.5% H_2O and balance N_2 . All the experiments are made at 200°C with 3 g catalysts and a total flow of 400 ml/min, corresponding to a space velocity of 8000 l/kg h. SO_2 , NO and O_2 concentrations of the feed and the effluent are measured on line by a flue gas analyzer (Dräger, Germany).

2.3. Characterizations of physical and chemical properties

BET surface area and pore volume of the $\text{V}_2\text{O}_5/\text{AC}$ samples are determined by N_2 adsorption at 77 K using a surface analyzer (ASAP2000, Micromeritics). Pore size distribution is calculated based on Density Functional Theory (DFT). BET surface area and pore volume of the catalysts are shown in Table 1.

X-ray diffraction (XRD) pattern of the $\text{V}_2\text{O}_5/\text{AC}$ samples are obtained on a Rigaku computer-controlled D/max 2500X using $\text{Cu K}\alpha$ as the radiation source. The applied current and voltage are 30 mA and 40 kV, respectively.

C, H, O, N and S contents in ACs are measured on an element analyzer (Vario EL, Germany). It should be pointed out that O content in ACs is the amount of surface oxygen and the amount of lattice oxygen can be estimated according to V_2O_5 loading (5 lattice oxygen in 1 V_2O_5 molecule). Results show that the former is higher than 2.3 wt.% and the latter is no more than 0.9 wt.%.

Mineral matter characterization was carried out according to GB/T 1574-1995 method designated for analysis of ash composition of coals.

3. Results and discussion

3.1. The role of lattice oxygen in V_2O_5 in SO_2 removal

Fig. 1 shows SO_2 removal behavior of DM-AC80 supported with different amounts of V_2O_5 . SO_2 removal activity of the support DM-AC80 is very low, but the activity increases greatly with an increase in V_2O_5 loading. This indicates the importance of V_2O_5 in SO_2 removal, although the amount of lattice oxygen in V_2O_5 , no more than 0.9 wt.% (V2/(DM-AC80)), is much lower than that of surface oxygen, 2.75 wt.%.

In our previous work [9], it was found that an adsorption peak of VOSO_4 was observable on the used $\text{V}_2\text{O}_5/\text{AC}$ through Fourier transformed infrared spectroscopy (FTIR) and dis-

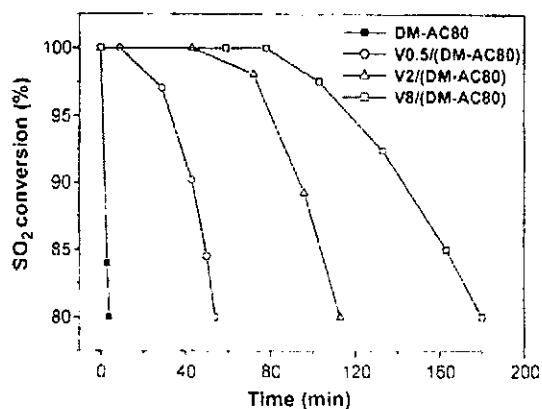


Fig. 1. SO_2 conversions of DM-AC80-supported V_2O_5 catalysts. Reaction conditions: 1600 ppm SO_2 ; 500 ppm NO ; 500 ppm NH_3 ; 4.5% O_2 ; 2.5% H_2O ; 200 °C.

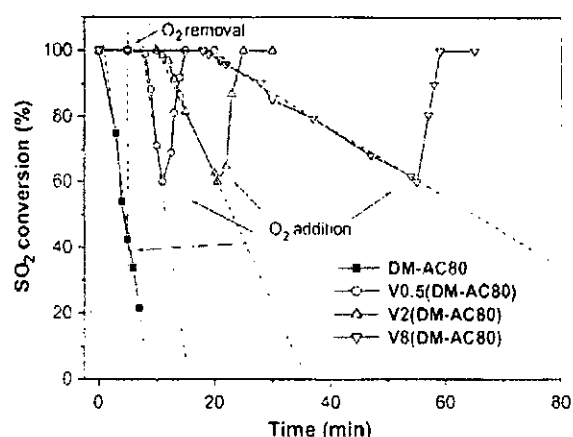


Fig. 2. O_2 -response experiments during SO_2 removal over DM-AC80-supported V_2O_5 catalysts. Reaction conditions: 500 ppm SO_2 ; 2.5% H_2O ; 4.5% O_2 (when used); 200 °C.

appeared after exposition to an $\text{O}_2 + \text{H}_2\text{O}$ environment at 200 °C. These suggest that V_2O_5 chemically absorbs SO_2 to form a VOSO_4 -like intermediate firstly, and then the intermediate reacts with O_2 to form SO_3 [9]. To differentiate the effect of these two steps on SO_2 removal activity, O_2 -response experiments are carried out in this work, where O_2 is removed from the feed at a time on stream of 5 min and then resumed at a SO_2 conversion of 60%. The removal of O_2 aims to terminate reactions between the VOSO_4 -like intermediate and O_2 , and to evaluate the amount of intermediate formed. The results in Fig. 2 show that SO_2 conversion of DM-AC80 drops quickly before the O_2 interruption while SO_2 conversions of all the V_2O_5 -loaded DM-AC80 catalysts maintain at 100% for some time after the O_2 interruption (this time is defined as breakthrough time). Additionally, a higher V_2O_5 loading results in a longer breakthrough time and a slower decrease in SO_2 conversion after the SO_2 breakthrough. When O_2 is resumed to the feed, SO_2 conversions of all V_2O_5 -loaded samples rise to 100% at the same rate, regardless of the differences in V_2O_5 loading or the amounts of VOSO_4 -like intermediate formed. These data indicate that the reaction between the VOSO_4 -like intermediate and gaseous O_2 is very fast and does not limit the overall SO_2 removal process under the conditions used. In other words, the formation rate of VOSO_4 -like intermediate is the limiting step, which is influenced by V_2O_5 loading.

It is reasonable to believe that lattice oxygen in V_2O_5 is responsible for the formation of VOSO_4 -like intermediate. The amount of lattice oxygen involved in the intermediate formation at each V_2O_5 loading can be estimated from the amount of SO_2 adsorbed during the O_2 -interruption, which is determined by extrapolation of the decreasing SO_2 conversion after the breakthrough to the horizontal axis (the dash lines in Fig. 2) and integration of the area under the SO_2 conversion curve. Since the amount of residual O_2 in the system after the O_2 -interruption is small (at a space velocity of 8000 l/kg h) and the support DM-AC80 absorbs little SO_2 after the O_2 -interruption, the amount of SO_2 determined from the integration (in mole, termed δSO_2) corresponds to the amount of lattice oxygen used for the formation of VOSO_4 -like

intermediate. This type of lattice oxygen is termed "effective lattice oxygen" (ELO in short) to distinguish them from all the oxygen in V_2O_5 . If one SO_2 molecule combines one ELO atom in the intermediate formation, the amount of ELO equals δSO_2 (in mole). Fig. 3 shows the amount of ELO determined for the three V_2O_5 -loaded catalysts (solid squares). If one V_2O_5 molecule provides one ELO atom, a straight line can also be obtained (the dash line in Fig. 3). Apparently, the amount of ELO increases with an increase in V_2O_5 loading. In addition, the amount of ELO at a low V_2O_5 loading of 2.8×10^{-5} mol/g (0.5 wt.%) is very close to the dash line while those at higher V_2O_5 loadings are far from the dash line. These may indicate that the highest usage of O atom in a V_2O_5 molecule is about one, but the O usability decreases with increasing V_2O_5 loading. This is understandable because a lower V_2O_5 loading may result in finer dispersion of V_2O_5 on AC while a higher V_2O_5 loading usually results in more agglomerated V_2O_5 particles and relatively less surface V_2O_5 . To show the difference in particle size of V_2O_5 , XRD analyses were performed. However, there are no diffraction peaks of V_2O_5 for all the samples and no valuable information can be obtained.

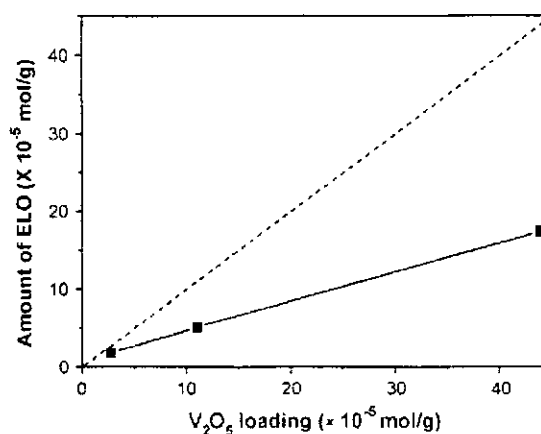


Fig. 3. Amount of effective lattice oxygen (ELO) vs. V_2O_5 loading over DM-AC80.

The information obtained so far indicates that one surface V_2O_5 molecule provides one ELO atom, which adsorbs and oxidizes one SO_2 molecule to form one $VOSO_4$ -like intermediate. In this process, the valence of V changes from V^{5+} to V^{4+} , which is consistent with the XPS analysis reported by Ma et al. for the same type of catalyst [10].

3.2. Usability of ACs' pores and its relation with V_2O_5

Since the role of V_2O_5 on SO_2 removal is to provide lattice O to oxidize SO_2 to a $VOSO_4$ -like intermediate, the differences in V_2O_5 loading affect only the rate of SO_2 oxidation. However, the data in Fig. 1 show that the rate of SO_2 oxidation is high enough for all the V_2O_5 -loaded catalysts because their initial SO_2 conversions are all 100%. This suggests that the different SO_2 removal behavior of the V_2O_5 -loaded catalysts results from other factors. According to the proposed SO_2 removal mechanism reported by Ma et al. [10], the SO_3/H_2SO_4 storage capacity of AC is a possible factor.

It is logical to believe that not all the pores in the AC is usable for storage of SO_3/H_2SO_4 , and only the pores in the vicinity of V_2O_5 sites are able to accept and store SO_3/H_2SO_4 migrated from V_2O_5 sites. A lower V_2O_5 loading yields fewer and smaller V_2O_5 sites and thus fewer pores for storage of SO_3/H_2SO_4 and therefore a lower SO_2 removal activity. A higher V_2O_5 loading yields more and possibly larger V_2O_5 sites, and thus more pores to be accessible for storage of SO_3/H_2SO_4 . It is worth to note that at higher V_2O_5 loadings, some of the pores in the vicinity of one V_2O_5 site may be close to other V_2O_5 sites. This hypothesis is shown in Fig. 4.

To estimate the pore usability of AC in SO_2 removal process, the volumes of H_2SO_4 stored, termed "effective pore volume" or EPV in short, are calculated by subtracting the amounts of SO_2 combined with ELO from corresponding SO_2 capacities. The SO_2 capacities, termed ΔSO_2 , are determined from Fig. 1 as the areas between SO_2 conversion curves of V_2O_5 -loaded catalysts and that of the support (DM-AC80). Fig. 5 shows that EPV increases with an increase in V_2O_5 loading but the values are small, even much smaller than the volume of pores with diameters less than 1 nm. This phenomenon agrees with the hypothesis in Fig. 4.

The discussions presented so far show that the role of V_2O_5 in V_2O_5/AC in SO_2 removal is to provide lattice O for SO_2 oxidation, and to serve as a center for distribution of SO_3/H_2SO_4 to the AC's pores in its vicinity. To show these roles more clearly, the catalyst-mass-based parameters ELO, EPV and ΔSO_2 presented above are divided by the loading of V_2O_5 (in mole)

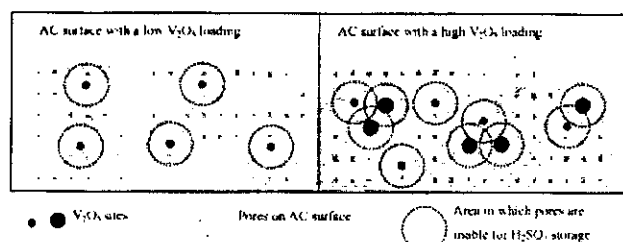


Fig. 4. Hypothetic mapping of V_2O_5/AC catalyst surface.

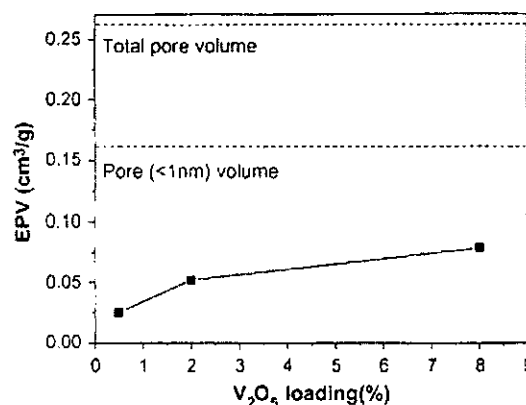


Fig. 5. Effective pore volume (EPV) of the catalysts vs. V_2O_5 loading.

in the catalysts, and the results are shown in Fig. 6. The values of ELO/V_2O_5 , EPV/V_2O_5 and $\Delta SO_2/V_2O_5$ all decrease with an increase in V_2O_5 loading, but the decreases in EPV/V_2O_5 and $\Delta SO_2/V_2O_5$ are relatively faster than that in ELO/V_2O_5 . This indicates that V_2O_5 sites preferentially locate at certain parts of AC surface, resulting in less increase in EPV in comparison to an increase in ELO when V_2O_5 loading is increased. This is also demonstrated by the ratios of EPV/ELO , which are 1330, 990 and 530 cm^3/mol for $V0.5/(DM-AC80)$, $V2/(DM-AC80)$ and $V8/(DM-AC80)$, respectively. All these information indicate that the decrease in SO_2 conversion in the later stage of SO_2 removal as shown in Fig. 1 is influenced mainly by the EPV, which is affected by the distribution of V_2O_5 on the AC surface.

3.3. Effects of ACs' physical and chemical properties on EPV

It is important to note that EPV is still a superficial parameter of AC. It may depend not only on volume of pores available for H_2SO_4 storage but also on surface properties which possibly influences migration of SO_3/H_2SO_4 from V_2O_5 sites to nearby pores.

3.3.1. Effects of ACs' physical properties on EPV

Fig. 7 shows SO_2 removal behavior of various V_2O_5/AC catalysts with 2 wt.% V_2O_5 but different AC supports. As

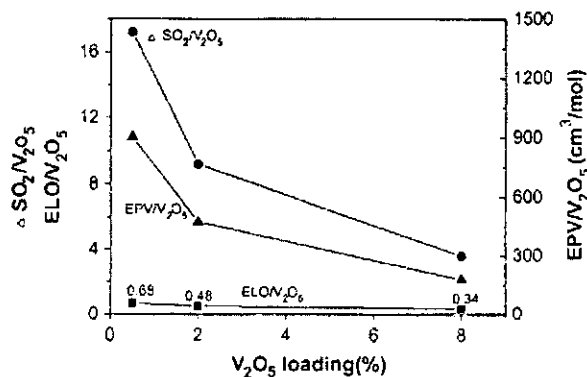


Fig. 6. Mole ratio of ELO/V_2O_5 , $\Delta SO_2/V_2O_5$ and EPV/V_2O_5 vs. V_2O_5 loading on DM-AC80.

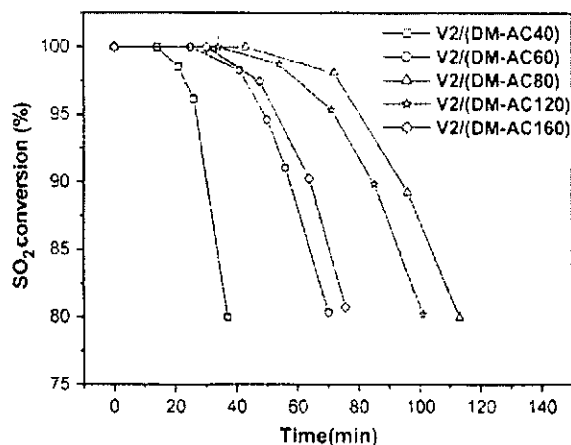


Fig. 7. SO_2 conversions of the catalysts with 2 wt.% V_2O_5 but different ACs. Reaction conditions: 1600 ppm SO_2 ; 500 ppm NO ; 500 ppm NH_3 ; 4.5% O_2 ; 2.5% H_2O ; 200 °C.

stated in the experimental section, these AC supports were made from the same coke but subjected to steam activation at 850 °C for different periods of time, which ensures that the differences of ACs are mainly in pore texture. The results in Fig. 7 apparently indicate that the SO_2 removal capacity increases with an increase in steam activation time from 40 to 80 min, but then decreases with a further increase in steam activation time to 160 min. To see whether the amount of ELO changes with the steam activation time, O_2 -response experiments are performed on V2/(DM-AC60), V2/(DM-AC80) and V2/(DM-AC120) and the results are shown in Fig. 8. As expected, the three catalysts show the same behavior, indicating the same amount of ELO. This indicates that the steam activation time of AC has little effect on distribution of V_2O_5 and the different SO_2 behaviors in Fig. 7 can be attributed mainly to the difference in EPV.

Fig. 9a shows the relations of EPV determined from Fig. 7 and physical properties of the catalysts with activation time. Among the four curves, the changes in EPV seem correlating well only with the changes in volume of pores smaller than 1 nm. This is understandable because H_2SO_4 is mainly stored in

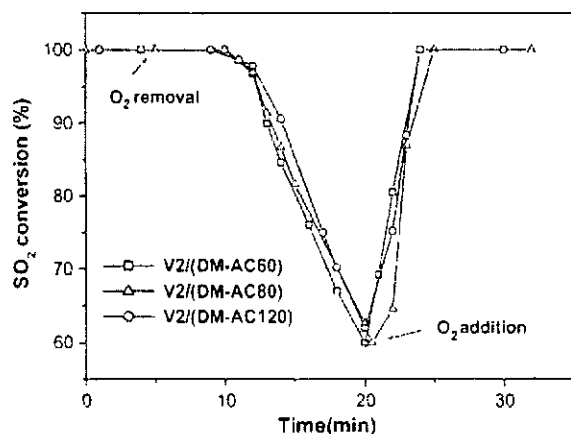


Fig. 8. O_2 -response experiments during SO_2 removal over V2/(DM-AC60), V2/(DM-AC80) and V2/(DM-AC120). Reaction conditions: 500 ppm SO_2 ; 2.5% H_2O ; 4.5% O_2 (when used); 200 °C.

the micro-pores as reported in the literature [4,18]. Fig. 9b correlates EPV with volume of pores smaller than 1 nm for all the catalysts with 2 wt.% V_2O_5 . It is clear that the data of the catalysts with DM-AC as supports form a straight line, indicating a strong relation between EPV and pores smaller than 1 nm.

The significant deviations for V2/AC80 (not subjected to the de-mineralization treatment) and V2/(NDM-AC80) (subjected to a HNO_3 treatment after the de-mineralization treatment) from the straight line indicate that chemical properties also affect the value of EPV.

3.3.2. ACs' chemical properties and its relation with EPV

Fig. 10a shows SO_2 conversion behaviors of V2/AC80, V2/(DM-AC80) and V2/(NDM-AC80) as well as that of the supports. The supports themselves (filled symbols) show little SO_2 removal capacity, but they do make significant differences in SO_2 removal behavior when 2 wt.% V_2O_5 is loaded onto them (open symbols). Compared to V2/AC80, the de-mineralized support increases the SO_2 removal capacity (see V2/(DM-AC80)) but a further HNO_3 treatment decreases the SO_2 removal capacity (see V2/(NDM-AC80)). To see whether the differences in AC supports affect ELO, O_2 -response experiments are performed on these V_2O_5 -loaded catalysts. The results in Fig. 10b shows similar amounts of ELO for the three catalysts, which indicates again that the differences in SO_2 removal behaviors of the catalysts result

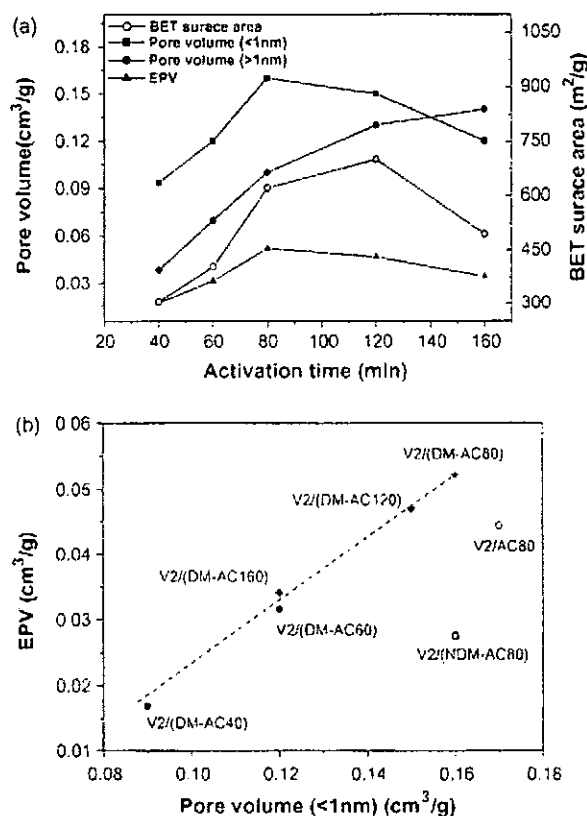


Fig. 9. (a) BET surface area, pore volume and EPV vs. activation time; (b) EPV vs. pore volume (<1 nm).

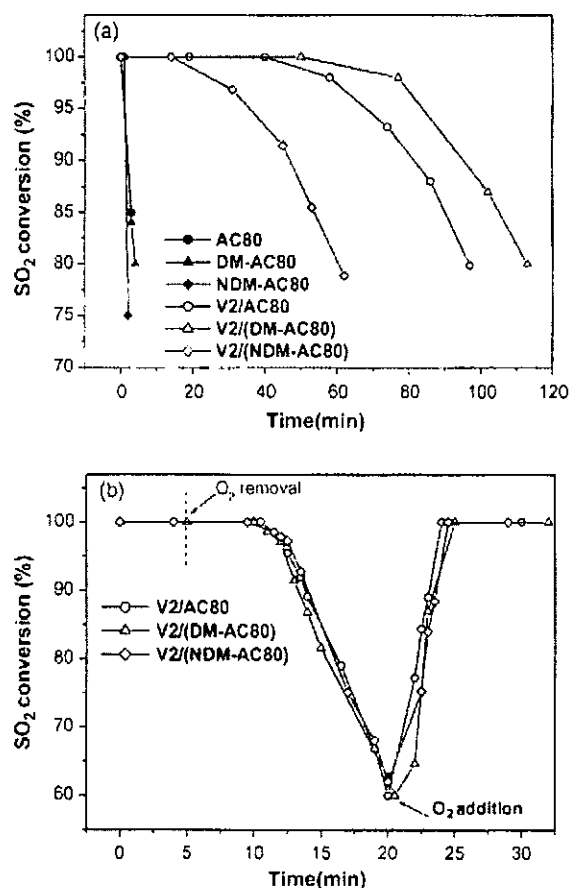


Fig. 10. Effect of AC treatments on SO₂ removal. (a) SO₂ conversions at 200 °C; reaction conditions: 1600 ppm SO₂; 500 ppm NO; 500 ppm NH₃; 4.5% O₂; 2.5% H₂O and (b) O₂-response experiment; reaction conditions: 500 ppm SO₂; 2.5% H₂O, 4.5% O₂ (when used); 200 °C.

from the differences in EPV of the AC supports. Since these AC supports show similar physical properties (see Table 1), their differences should mainly be attributed to differences in chemical properties. Table 2 shows that the demineralization of AC80 results in a significant reduction in ash content, from 8.2% to 0.25%, but not in the contents of other elements (see AC80 and DM-AC80). Treatment of DM-AC80 with HNO₃ results in significant increases in O and N contents, from 2.75% to 5.85% and from 0.79% to 1.50%, respectively, but little changes in contents of other compo-

Table 2
Elemental and ash analyses of the different activated cokes (wt.%)^a

Sample	C	H	O ^b	N	S	Ash
DM-AC40	94.87	0.71	2.64	0.64	0.56	0.58
DM-AC60	95.58	0.61	2.31	0.60	0.57	0.33
DM-AC80	94.99	0.68	2.75	0.79	0.54	0.25
DM-AC120	94.34	0.79	3.01	0.86	0.54	0.46
DM-AC160	95.26	0.52	2.54	0.68	0.61	0.39
AC80	87.36	0.59	2.56	0.74	0.55	8.20
NDM-AC80	91.20	0.69	5.85	1.50	0.54	0.22

^a Moisture-free basis.

^b By difference.

nents. These data suggest that the minerals, O-containing and N-containing functional groups in AC prevent migration of SO₃/H₂SO₄. This finding indicates that oxygen functional groups play different roles in SO₂ removal at different temperatures.

4. Conclusions

Compared to activated cokes (AC), V₂O₅/AC are more active for SO₂ removal from flue gases at temperatures around 200 °C. The role of V₂O₅ is to provide lattice oxygen to absorb and oxidize SO₂ into a VOSO₄-like intermediate. The intermediate then reacts with gaseous O₂ to form SO₃ and V₂O₅. The amount of lattice oxygen in V₂O₅ used for the intermediate formation (this type of lattice oxygen is termed ELO) is dependent on the V₂O₅ loading and independent of the properties of AC support under the conditions used. The maximum amount of ELO is one atom per V₂O₅ molecule at low V₂O₅ loadings.

The role of AC is to store the SO₃/H₂SO₄ from V₂O₅ sites. Only the pores in the vicinity of V₂O₅ sites are available for storage of SO₃/H₂SO₄. The volume of these pores, termed EPV, is influenced by the physical properties of AC support, which is proportional to but significantly smaller than the volume of pores smaller than 1 nm. The EPV is also influenced by the chemical properties of AC support. Minerals, O-containing and N-containing functional groups in AC may inhibit migration of SO₃/H₂SO₄.

Acknowledgement

The authors gratefully acknowledge the financial support from the Natural Science Foundation of China (20736001 and 20503038).

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