

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
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TRA: 11 PCT-PATENTE DE INVENCION CAPITULOS I Y II	FOLIOS: 8
ACT: 476 TRASTITULARSOLI	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
MAURICIO JARAMILLO CAMPUZANO

Asunto: Radicación: 14-122746- -2
 Trámite: 11
 Evento: 378
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 Oficio: 5781
 Folios: 8

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional					
Vía PCT (Fase Nacional)	X	Capítulo I	X	Capítulo II	
No. Solicitud Internacional	PCT/US2011/062341				
Fecha de Presentación Internacional	29/11/2011				

1. Documentos estudiados

Descripción:	Rad 14-122746-00000-0000	06/junio/2014
Reivindicaciones:	Rad 14-122746-00000-0000	06/junio/2014
Prioridad:	Rad 14-122746-00000-0000	06/junio/2014
US 13/304052	23-11-2011	

2. Análisis de la Prioridad

Se acepta la reivindicación de prioridad porque ésta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del capítulo primero del Título 10 de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por el solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10) reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada. En este caso se encuentra el pago adicional de la tasa que cubre 18 reivindicaciones adicionales, de tal forma que se estudiará el capitulo reivindicatorio completo.

Título de la solicitud: Deshidrogenación de alcoholes para incrementar la producción de compuestos aromáticos. Folio 1.

Objeto de la invención: El objeto de la presente solicitud de patente de invención se refiere a un método para incrementar la producción de hidrocarburos aromáticos producidos durante la conversión de alcoholes en hidrocarburos.

El problema técnico planteado en la presente solicitud se refiere a la necesidad de disponer de un método para incrementar la producción de hidrocarburos aromáticos producidos durante la conversión de alcoholes en hidrocarburos. Para solucionar ese problema técnico la presente solicitud da a conocer un método para incrementar la producción de hidrocarburos aromáticos producidos durante la conversión de alcoholes en hidrocarburos.

El objeto de la presente solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): C07C 1/207, 15/04, 15/06, 15/08, 45/38.

4. De la solicitud de Patente

Descripción (artículo 28)

La descripción resulta ser completamente insuficiente para el muy amplio alcance que tiene el capítulo reivindicatorio. Se le recuerda al solicitante que la descripción debe ser una divulgación suficiente y adecuada de la materia que se está reclamando, pero definitivamente el alcance de la misma, va mucho más allá de aquella materia que se encuentra enteramente soportada en la descripción. En ese sentido, no se encuentra soporte técnico en la descripción para reclamar una extrapolación tan amplia a partir de estudios tan puntuales, los cuales se refieren específicamente a un método ejecutado bajo condiciones muy específicas.

La solicitante debe limitar el alcance del capítulo reivindicatorio y definir específicamente el método de interés, indicando de manera específica sus etapas de proceso y condiciones de ejecución.

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

Reivindicaciones (artículo 30 D 486)

En este mismo sentido, el capítulo reivindicatorio resulta ser muy amplio y no se encuentra enteramente sustentado en la descripción. Son tantas las posibilidades para el método reclamado, que la descripción no divulga de manera suficientemente clara y completa la materia divulgada en las reivindicaciones. No se encuentra ninguna razón técnica que sustente la extrapolación presentada. La solicitante debe definir específicamente la materia y el alcance de la invención a través de las características técnicas esenciales que se encuentran enteramente soportadas en la descripción, sírvase limitar el alcance de la invención.

Sírvase retirar y definir específicamente términos y expresiones tales como “*materia prima alcohólica, catalizador de la deshidrogenación, temperatura de deshidrogenación, presión de deshidrogenación, catalizador de la conversión de compuestos oxigenado, temperatura de conversión, presión de conversión, inferior a, más de, menos de, aproximadamente, por debajo de, compuesto oxigenado, ácido*”

carboxílico, un aldehído y un éster, hidrocarburos aromáticos, componente oxigenado adicional” los cuales son ambiguos y no permiten definir el alcance de la invención.

Ahora bien, el capítulo reivindicatorio no cumple con el requisito de concisión no sólo porque está escrito de una manera muy amplia, sino además porque comprende cinco reivindicaciones independientes para una misma categoría, es decir, cinco reivindicaciones de método. La solicitante debe limitar el alcance de su invención y definir una reivindicación independiente por categoría, las modalidades de la invención pueden ser presentadas en las reivindicaciones dependientes.

De otra parte, sírvase retirar la reivindicación 14, dado que no presenta ninguna característica técnica esencial del método de interés. La antigüedad de la materia prima no parece afectar el método reclamado.

De otra parte, en la reivindicación 1 se hace referencia a una miniemulsión y posteriormente se indica que es una emulsión, así: “una **miniemulsión** de aceite en agua; en donde dicha miniemulsión incluye al menos un ingrediente agrícolamente activo, donde la composición de la **emulsión** de aceite en agua...” Sírvase corregir dicha inconsistencia.

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

5. Determinación del Estado de la Técnica

Considerando que la fecha de la solicitud internacional es 23 de noviembre de 2011 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	US4789502	Carboxylic production	1988-12-06
D2	US 3907915	Conversion of carbonyl compounds to aromatics	1975-09-23

El documento D1 divulga un método para producir ácido carboxílico a partir de alcoholes que comprende poner en contacto un alcohol con un catalizador a temperatura y presiones efectivas para producir hidrógeno y un componente de compuesto oxigenado (resumen; Col 1, líneas 5-10; col 4, líneas 36-66).

El documento D2 hace referencia a un proceso de conversión de compuestos alifáticos que contiene carbonilo a hidrocarburos aromáticos, utilizando como catalizador una zeolita (resumen, ejemplos y reivindicaciones)

6. Examen de patentabilidad (artículo 14 D486)

Nivel Inventivo (Art 18 D486)

La reivindicación 1 consiste en un método para convertir alcanoles en hidrocarburos aromáticos, comprendiendo el método: exponer una materia prima alcanólica a un catalizador de la deshidrogenación a una temperatura de deshidrogenación y una presión de deshidrogenación para producir hidrógeno y un componente oxigenado; y exponer el componente oxigenado a un catalizador de la conversión de compuestos oxigenados a una temperatura de conversión de compuestos oxigenados y una presión de conversión de compuestos oxigenados para producir hidrocarburos aromáticos.

Radicado 14-211737-00000-0000.

Solicitud	D1	D2
Un método para convertir alcanoles en hidrocarburos aromáticos, que comprende	Un método para convertir un alcohol en un ácido carboxílico que comprende	Un método para convertir un compuesto oxigenado tipo carbonilo en hidrocarburos aromáticos, que comprende
Exponer una materia prima alcanólica a un catalizador de la deshidrogenación a una temperatura de deshidrogenación y una presión de deshidrogenación para producir hidrógeno y un componente oxigenado;	Poner en contacto un alcohol con un catalizador a temperatura y presiones efectivas para producir hidrógeno y un componente de compuesto oxigenado	No hace referencia
Y exponer el componente oxigenado a un catalizador de la conversión de compuestos oxigenados a una temperatura de conversión de compuestos oxigenados y una presión de conversión de compuestos oxigenados para producir hidrocarburos aromáticos	No hace referencia	

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 un método para producir ácido carboxílico a partir de alcoholes que comprende poner en contacto un alcohol con un catalizador a temperatura y presiones efectivas para producir hidrógeno y un componente de compuesto oxigenado (resumen; Col 1, líneas 5-10; col 4, líneas 36-66).

La diferencia entre la materia de D1 y la materia de la presente solicitud radica en que el documento D1 no hace referencia a la segunda etapa de proceso que consiste en convertir dichos compuestos oxigenados en hidrocarburos aromáticos.

El efecto que logra dicha diferencia es lograr obtener el producto deseado (hidrocarburos aromáticos) a partir de compuestos oxigenados.

De este modo, el Problema Técnico Objetivo que pretende resolver esta invención se puede formular así: ¿cómo obtener hidrocarburos aromáticos a partir de compuestos oxigenados?

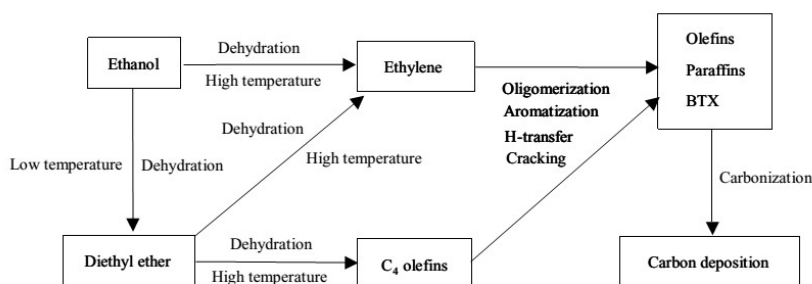
En contraste, el documento D2 divulga un método para convertir un compuesto oxigenado tipo carbonilo en hidrocarburos aromáticos, que comprende poner en contacto los compuestos alifáticos que contienen carbonilo con una zeolita como

catalizador a temperatura y presiones efectivas para producir hidrocarburos aromáticos (Resumen y ejemplos, reivindicaciones). Específicamente se indica que el compuesto oxigenado puede ser seleccionado de entre ésteres de ácidos carboxílicos, aldehídos y cetonas y que el catalizador utilizado es un tipo de zeolita ZSM-5. La tabla resumen revela un elevado porcentaje de conversión a hidrocarburos aromáticos.

De esta manera, una persona del oficio medianamente versada en la materia, tiene información suficiente a partir de la combinación de enseñanzas de los documentos D1 y D2, para plantear un único método para convertir alcanoles en hidrocarburos aromáticos, que comprenda una primera etapa de deshidrogenación del alcohol para obtener compuestos oxigenados como en D1 y posterior aromatización de dichos compuestos utilizando una zeolita como catalizador, como en D2, con la plena expectativa de éxito en cuanto a obtener una alto porcentaje de conversión. En consecuencia, esta Oficina considera que el método de interés se deriva de manera evidente del arte previo, no provoca ningún efecto técnico sorprendente o inesperado y carece de nivel inventivo. De forma análoga los métodos de las reivindicaciones 26, 27 y 28, tampoco son inventivos.

Ahora bien teniendo en cuenta la reivindicación 2 que presenta un método según la reivindicación 1, donde el componente oxigenado tiene una proporción efectiva de hidrógeno respecto a carbono inferior a 1.9. Este Despacho considera que los procesos de conversión de etanol o de alcanoles presentes en bio-materiales a hidrocarburos aromáticos, han sido ampliamente estudiados tal como lo demuestra la publicación citada en la descripción “*Catalytic conversion of biomass-derived feedstocks into olefins and aromatics with ZSM-5: the hydrogen to carbon effective ratio Huiyan Zhang, Yu-Ting Cheng, Tushar P. Vispute, Rui Xiaoa and George W. Huber Energy Environ. Sci., 2011, 4, 2297 (First published online 11 May 2011)*” y además la publicación “*ethanol conversion to aromatic hydrocarbons over several zeolite catalysts Megumu Inaba, Kazuhisa Murata, Masahiro Saito and Isao Takahara React.Kinet.Catal.Lett. Vol. 88, No. 1, 135–142 (2006)*” en donde se demuestra, no sólo que el uso de catalizadores basados en zeolitas son especialmente útiles para la obtención eficiente de hidrocarburos aromáticos a partir de compuestos oxigenados, sino además que la proporción efectiva de hidrógeno frente a carbono es un parámetro que afecta de forma directa el porcentaje de conversión al producto deseado, en este caso, a hidrocarburos aromáticos.

La grafica 6 de Zhang muestra que la proporción ideal para lograr el mayor porcentaje de conversión a hidrocarburos aromáticos está entre 1 y 2. Así que la proporción definida en la reivindicación 2 ya estaba divulgada en el mismo documento citado en la descripción.



Scheme 1. Supposed reaction pathway

Inaba 2006

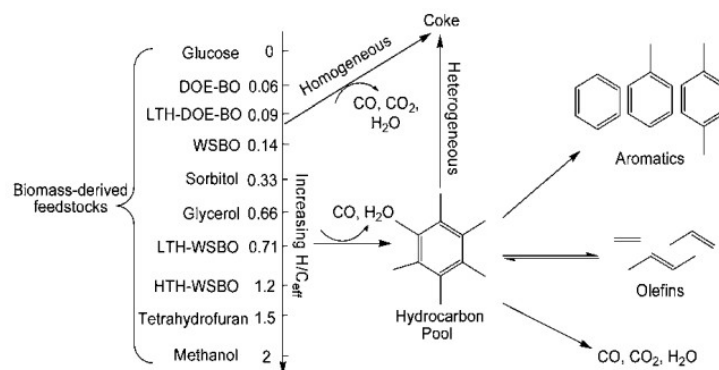


Fig. 1 Reaction schematic of biomass-derived feedstocks with ZSM-5 catalyst.

Zhang, 2011

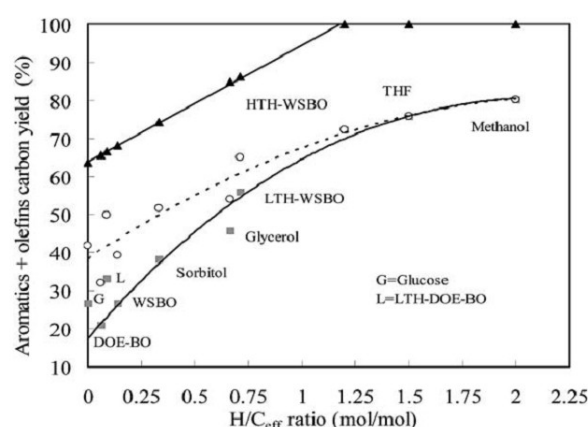


Fig. 6 The aromatic + olefin carbon yield for catalytic conversion of various biomass-derived feedstocks as a function of the hydrogen to carbon effective (H/C_{eff}) ratio. The H/C_{eff} ratios of the feedstocks: glucose, 0; DOE-BO, 0.06; LTH-DOE-BO, 0.09; WSBO, 0.14; sorbitol, 0.33; glycerol, 0.66; LTH-WSBO, 0.71; HTH-WSBO, 1.2; THF, 1.5 and methanol, 2. (▲ Theoretical carbon yield; ■ experimental carbon yield; ○ experimental/theoretical yield.)

Así las cosas, esta Oficina considera que la materia de interés no es inventiva, no solo porque las etapas generales son evidentes a partir del estado del arte citado, sino además porque no se observa ningún efecto técnico inesperado o sorprendente en el sentido en que la referencia de Zhang ya había indicado que la proporción efectiva de hidrógeno frente a carbono era un parámetro de optimización para lograr mejores porcentajes de conversión a hidrocarburos aromáticos. Este Despacho considera que la materia de esta solicitud corresponde a una optimización rutinaria de proceso, ya sugerida, que no provoca ningún salto cualitativo en la técnica y que no cumple con el requisito de nivel inventivo.

7. Conclusión

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

Nº	Documento Nº	Reivindicaciones afectadas	Requisito que afecta
D1	US4789502	1-28	Nivel inventivo
D2	US 3907915	1-28	Nivel inventivo

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 del día siguiente 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.

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante de sesenta (60) días para dar respuesta a este requerimiento y presentarla por escrito.

Finalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones, no pagará la tasa de modificación voluntaria pero sí la correspondiente al pago por reivindicación adicional.

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 No. 10 de 2001.


JESUS FERNEL GARCÍA GARCÍA
Director de Nuevas Creaciones (E)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2015-06-02

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PAPER

Catalytic conversion of biomass-derived feedstocks into olefins and aromatics with ZSM-5: the hydrogen to carbon effective ratio

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Catalytic conversion of ten biomass-derived feedstocks, *i.e.* glucose, sorbitol, glycerol, tetrahydrofuran, methanol and different hydrogenated bio-oil fractions, with different hydrogen to carbon effective (H/C_{eff}) ratios was conducted in a gas-phase flow fixed-bed reactor with a ZSM-5 catalyst. The aromatic + olefin yield increases and the coke yield decreases with increasing H/C_{eff} ratio of the feed. There is an inflection point at a H/C_{eff} ratio = 1.2, where the aromatic + olefin yield does not increase as rapidly as it does prior to this point. The ratio of olefins to aromatics also increases with increasing H/C_{eff} ratio. CO and CO₂ yields go through a maximum with increasing H/C_{eff} ratio. The deactivation rate of the catalyst decreases significantly with increasing H/C_{eff} ratio. Coke was formed from both homogeneous and heterogeneous reactions. Thermogravimetric analysis (TGA) for the ten feedstocks showed that the formation of coke from homogeneous reactions decreases with increasing H/C_{eff} ratio. Feedstocks with a H/C_{eff} ratio less than 0.15 produce large amounts of undesired coke (more than 12 wt %) from homogeneous decomposition reactions. This paper shows that the conversion of biomass-derived feedstocks into aromatics and olefins using zeolite catalysts can be explained by the H/C_{eff} ratio of the feed.

1. Introduction

Production of high-grade liquid fuels and chemicals from lignocellulosic biomass is one of the most promising ways to solve energy and environmental problems caused by our dependence on fossil oil.^{1,2} Zeolite catalysts are the workhorse of the petroleum industry efficiently converting petroleum-based feedstocks into targeted fuels and chemicals.^{3–6} Zeolite catalysts have also been shown to be promising for conversion of biomass-derived feedstocks into fuels and chemicals.^{7–14} The main

challenge for biomass and its derived feedstocks catalytic conversion is how to improve catalyst properties and process conditions to obtain high yields of hydrocarbons while minimizing coke formation on the zeolites.¹⁵ Over the last twenty years, there have been dozens of studies that focused on the catalytic conversion of biomass and its derived feedstocks with a range of zeolite catalysts including ZSM-5, Beta, Y, mordenite, FCC, Al-MCM-41, SBA-15, Al-MSU-F FER, MFI and MOR.^{16–44} Furthermore, the designs and applications of zeolite catalysts for biomass conversion have also been well reviewed.^{45–50} In these zeolite catalysts, ZSM-5 has shown the highest aromatic and olefin yields from lignocellulosic biomass.^{43,44} ZSM-5 has a 3-dimensional pore system with a pore size of 5.5–5.6 Å based on atomic radii.⁴⁴ The small pore size, internal structure and internal volume make it difficult for larger

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Broader context

Catalytic fast pyrolysis (CFP) is a promising technology to directly convert solid biomass into gasoline-range aromatics over zeolite catalysts. During CFP, biomass-derived feedstocks undergo a hydrocarbon pool mechanism occurring within the zeolite framework. The lifetime and product distribution of the hydrocarbon pool varies with different biomass-derived feedstocks. In this study we show that the product distribution from catalytic fast pyrolysis of biomass-derived feedstocks is a function of the hydrogen to carbon effective ratio (H/C_{eff}) of the feed. Upgraded bio-oils with higher H/C_{eff} ratios give more valuable products (olefins + aromatics) and less coke than those without upgrading. We suggest a H/C_{eff} value for upgrading biomass-derived feedstocks to optimize valuable products yield in the following CFP process. We also show how the catalyst activity changes with feedstocks that have different H/C_{eff} ratios.

aromatic coke precursors to form inside of the pores.^{9,44} Several reactions occur inside the zeolite including dehydration, decarboxylation, isomerization and decarbonylation thereby removing oxygen as water, carbon monoxide and carbon dioxide and converting the carbon and hydrogen into olefins and aromatics.³¹

The main problem for biomass conversion with zeolites is that the biomass-derived feedstocks typically produce large amount of coke, a wide variety of products are produced, and the zeolite catalyst is deactivated rapidly.^{11,51,52} Chen *et al.*⁵² introduced the hydrogen to carbon effective (H/C_{eff}) ratio, as shown in eqn (1), to describe whether a feed can be economically converted into hydrocarbons using zeolite catalyst according to the amount of oxygen, carbon, and hydrogen in the feed. The H, C and O in eqn (1) are the moles of hydrogen, carbon, and oxygen in the feed, respectively.

$$H/C_{\text{eff}} = \frac{H - 2O}{C} \quad (1)$$

Chen *et al.*⁵² stated that feedstocks with H/C_{eff} ratios less than 1 are difficult to upgrade to produce premium products over a ZSM-5 catalyst due to rapid aging and deactivation of the catalyst. The H/C_{eff} ratio of petroleum-derived feedstocks is between 1 and 2. The H/C_{eff} ratio of lignocellulosic biomass is between 0 and 0.3. Therefore, biomass is made of hydrogen-deficient molecules, and strategies for biomass and its derived feedstocks conversion must take their H/C_{eff} ratio into account.

Fig. 1 shows the reaction schematic of biomass-derived feedstocks over the ZSM-5 catalyst. Feedstocks with different H/C_{eff} ratios first undergo dehydration and decarbonylation reactions to make intermediate oxygenates as well as CO, CO₂, H₂O and homogeneous coke as by-products on the surface of the catalyst. Then these intermediate oxygenates diffuse into the zeolite catalyst pores and form aromatics and olefins as well as heterogeneous coke through a series of decarbonylation, decarboxylation, dehydration, and oligomerization reactions. The oxygen in the feedstocks is removed in the form of CO, CO₂ and H₂O. It has been reported that the aromatics formation reaction undergoes through a common intermediate or a “hydrocarbon pool” within the zeolite framework.^{53–59}

Recently, we outlined a new method for bio-oil upgrading where hydroprocessing of bio-oils with Ru/C and Pt/C catalysts followed by conversion with zeolite catalysts was able to produce aromatics and olefins in yields 2 to 3 times higher than zeolite conversion of the bio-oils without hydrogenation.⁶⁰ The purpose

of the hydroprocessing was to add hydrogen selectively to the biomass-derived feedstocks thereby increasing the H/C_{eff} ratio of the feed. We also tested the zeolite conversion of other feedstocks and showed that the aromatic + olefin yield increased with an increasing H/C_{eff} ratio of the feed. The purpose of this paper is to explain more in depth how the product selectivity and catalyst activity change for ten different biomass-derived feedstocks over a ZSM-5 catalyst. Thermogravimetric analysis (TGA) was used to obtain the homogeneous coke yield of all the feedstocks. The deactivation rates of the ZSM-5 catalyst were calculated. Furthermore, the formations of homogeneous and heterogeneous coke were discussed as well as how the product selectivity changes with different feedstocks.

2. Experimental section

2.1. Materials

2.1.1. Biomass-derived feedstocks. Ten biomass-derived feedstocks with different H/C_{eff} ratio were converted, including pure compound solutions and bio-oil derived feedstocks. Pure compound solutions, including glucose, sorbitol, glycerol, tetrahydrofuran (THF) and methanol, were dissolved and/or mixed in water with a mass percentage of 12.5 wt%. The bio-oil derived feeds were made from DOE bio-oil (DOE-BO) and pine wood bio-oil (PWBO), including DOE-BO, low-temperature hydrogenated DOE bio-oil (LTH-DOE-BO), water-soluble bio-oil of pine wood (WSBO), low temperature hydrogenated water-soluble bio-oil (LTH-WSBO) and high temperature hydrogenated water-soluble bio-oil (HTH-WSBO). DOE-BO was supplied by the US Department of Energy (DOE) and was manufactured by the National Renewable Energy Laboratory (NREL) from white oak pellets using the Thermochemical Process Development Unit (TCPDU). PWBO was obtained from the Mississippi State University and was produced by pyrolysis of dry pine wood in an auger reactor. LTH-DOE-BO was obtained by low temperature hydrogenation of DOE-BO with 5 wt% Ru/C catalyst at a temperature of 125 °C, pressure of 100 bar and WHSV of 1.6 h⁻¹. The WSBO was prepared by mixing 7 g PWBO with 28 g water and decanting the top layer. Detailed information about how the hydrogenated bio-oils were produced can be found in our previous work.⁶⁰ In brief summary, LTH-WSBO was produced by hydrogenation of WSBO with 5 wt% Ru/C catalyst at a temperature of 125 °C, pressure of 52 bar and WHSV of 3 h⁻¹. HTH-WSBO was produced from two-stage hydrogenation of WSBO. The first stage was operated with 5 wt% Ru/C catalyst at a temperature of 125 °C, pressure of 100 bar and WHSV of 3 h⁻¹. The second stage was operated with 5 wt% Pt/C catalyst at a temperature of 250 °C, pressure of 100 bar and WHSV of 3 h⁻¹. The distributions of the products identified in the bio-oil fractions are listed in Table 1. In the WSBO fraction over 55% of the carbon was identified. The remaining carbon was probably present as carbohydrate oligomers that were not detected by our methods. Only about one-third of the products can be identified in DOE-BO and LTH-DOE-BO. The pure bio-oil fractions contained large amounts of polymeric lignin oligomers which had a M_w from 300 to 7000 daltons (Da). Compared to DOE-BO, the LTH-DOE-BO has a higher concentration of oligomers with a molecular weight greater than 400 Da.

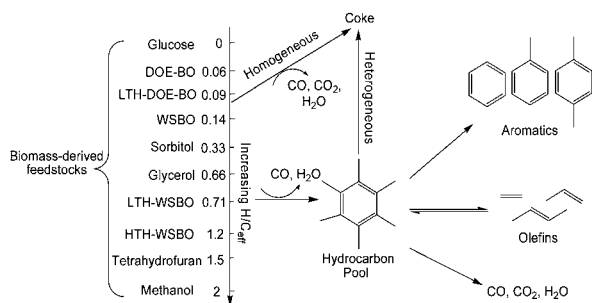


Fig. 1 Reaction schematic of biomass-derived feedstocks with ZSM-5 catalyst.

Table 1 Carbon product selectivity (%) of the bio-oil feedstocks (for DOE-BO and LTH-DOE-BO, based on elemental analysis; for WSBO, LTH-WSBO and HTH-WSBO, based on the total carbon measured by TOC)

Compound	DOE-BO	LTH-DOE-BO	WSBO	LTH-WSBO	HTH-WSBO
Acetic acid	8.42	10.01	6.29	5.66	3.08
Methyl acetate	0.13	0.25			
Hydroxyacetone	1.63	2.17	5.14		
2-Furanone	0.50	0.40	0.97		
3-Methyl-1,2-cyclopentadione	0.44		1.18		
1-Hydroxy-2-butanone	0.52		0.52		
2-Cyclopenten-1-one	0.31		0.56		
Hydroxyacetaldehyde	8.96		11.02		
Furfural	0.63	0.44	0.54		
5-Hydroxymethylfurfural	0.64		1.65		
Phenol	0.11	0.35	0.06		
γ -Butyrolactone	0.22			2.87	3.25
γ -Valerolactone				0.27	0.37
4-Hydroxymethyl- γ -butyrolactone				1.95	1.38
Tetrahydrofuran					0.18
2-Methyltetrahydrofuran					0.63
2,5-Dimethyltetrahydrofuran					0.58
Methanol	0.27	0.27	0.63	1.37	1.67
Ethanol				0.55	1.41
1-Propanol				0.27	1.25
1-Butanol				0.12	0.34
2-Butanol					0.44
1-Pentanol					0.25
2-Pentanol					0.13
Ethylene glycol				13.87	13.66
Cyclopentanol				0.26	0.68
2-Hexanol					0.23
Propylene glycol				5.11	9.32
2,3-Butanediol					1.02
Cyclohexanol				3.47	1.51
1,2-Butanediol				0.89	4.03
Tetrahydrofurfuryl alcohol				0.03	2.13
1,4-Butanediol				1.51	2.01
Glycerol					1.43
1,2-Cyclohexanediol				2.98	3.16
Sorbitol		0.17		10.78	0.64
Guaiacol			0.27		
Catechol			6.44		
4-Methyl catechol			1.22		
3-Methylcyclopentanol					1.00
1,2,3-Butanetriol					0.86
1,4-Pentanediol					0.68
3-Methylcyclohexanol					1.01
4-Methylcyclohexanol					0.60
1,2-Hexanediol					0.81
1,2,6-Hexanetriol					0.42
Levogluconan	8.73	7.48	16.82	9.52	
Sugars	1.75	1.36	3.21	1.20	0.19
Total carbon identified	33.26	22.9	56.52	62.68	60.35
Unidentified carbon	66.74	77.1	43.48	37.32	39.65

2.1.2. Catalyst. A ZSM-5 catalyst (CBV 3024E, SiO₂/Al₂O₃ = 30) obtained from Zeolyst was used for all of these studies. The catalyst was sieved to a particle size of 425–800 μ m before being placed into the reactor (described below). The catalyst was calcined in the reactor at a temperature of 600 °C with 60 mL min⁻¹ air (Airgas, regular-high purity, dehumidified by a drierite tube) for 6 hours prior to reactions.

2.2. Experimental setup

2.2.1. Gas-phase flow fixed-bed reactor. A gas-phase flow fixed-bed reactor system was built for catalytic conversion of biomass-derived feedstocks into olefins and aromatics as shown

in Fig. 2. This reactor consists of a gas feed system, a liquid feeding unit, the reactor, the heater for the reactor, a condensor and a gas sample collecting unit. A quartz tube of 12.5 mm OD was used as the reactor. Sieved ZSM-5 powders were held in the reactor by quartz beads (250–425 μ m) and quartz wool. The reaction temperature was measured *via* a K-type thermocouple inserted into an inner tube at the top of the catalyst bed. Prior to reactions, the catalyst was calcined as described in Section 2.1.2. Helium was used as a carrier gas (Airgas, 99.999%). The liquid feedstock was introduced into the reactor through a PTFE tube by a syringe pump (Fisher, KDS100). A condenser in an ice-water bath was used to trap heavy products. After reactions, the reactor was flushed by helium with a flow rate of 100 mL min⁻¹

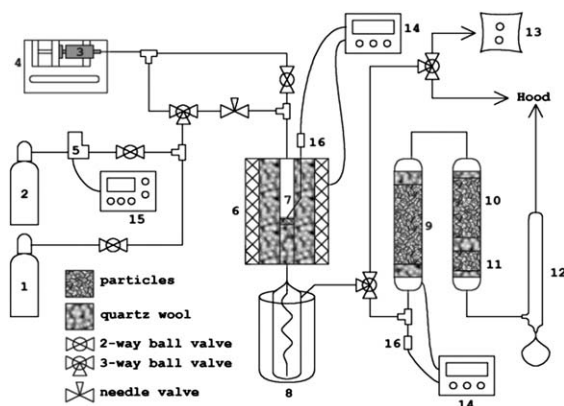


Fig. 2 Schematic diagram of catalytic conversion of biomass-derived feedstocks into olefins and aromatics system. (1) Air cylinder; (2) He cylinder; (3) syringes; (4) syringe pump; (5) mass flow controller; (6) furnace; (7) quartz tubular reactor; (8) ice-water condenser; (9) copper converter; (10) moisture trap (drierite); (11) CO₂ trap (ascarite); (12) bubble flow meter; (13) gas sampling bag; (14) temperature controller; (15) mass flow controlling box; and (16) K-type thermocouple.

for 30 min at the reaction temperature. The condensed products were extracted by adding 10 mL of ethanol into the condenser to obtain liquid products. Gas phase products were collected by an air bag for analysis.

After reaction the carrier gas was switched to air at 60 mL min⁻¹ to regenerate the used catalyst. During the regeneration, the produced CO was further converted into CO₂ by using a copper converter catalyst (13 wt% CuO on alumina, Sigma-Aldrich) which was heated to 250 °C. The CO₂ was trapped by a CO₂ trap (Ascarite, Sigma-Aldrich). The coke yield was obtained by measuring the mass change of the CO₂ trap.

Unless otherwise mentioned, the typical reaction conditions for catalytic conversion of biomass-derived feedstocks used in this study were: temperature of 600 °C, a carrier gas flow rate of 204 mL min⁻¹, a weight hourly space velocity (WHSV) of 11.7 h⁻¹ and a ZSM-5 mass of 26 mg.

2.2.2. Thermogravimetric analysis (TGA) experiments. Thermogravimetric analysis (TGA) of the ten feedstocks was carried out in a TGA instrument (TA Instrument, SDT Q600). Before the experiment, an alumina pan filled with 15 mg sample was put into the TGA chamber that was continuously purged by helium at 100 mL min⁻¹. The chamber was programmed with the following temperature regime: hold at room temperature for 0.5 min, ramp to 700 °C at 1.5 °C min⁻¹ and hold at 700 °C for 30 min.

2.3. Product analysis and data evaluation

2.3.1. Gas product analysis. The gaseous product was analyzed using a Shimadzu 2014 GC system. A Restek Rtx-VMS capillary column (Catalog No. 19915) (with FID detector) was used to quantify aromatic hydrocarbons, while a HAYSEP D packed column from Supelco was used to analyze CO and CO₂ (with TCD detector). Both FID and TCD detectors were maintained at 240 °C. Ultra high purity helium was used as carrier gas. The following temperature ramp was used in this study: hold at 35 °C for 5 min, ramp to 140 °C at 5 °C min⁻¹, ramp to 230 °C at 50 °C min⁻¹ and hold at 230 °C for 8.2 min.

2.3.2. Liquid product analysis. Liquid products were identified by GC-MS (Shimadzu-2010) and quantified by GC-FID (Agilent 7890A). Restek Rtx-VMS capillary column (Catalog No. 19915) was used in the GC-MS system. It was operated at a constant flow rate of 1.9 mL min⁻¹ with ultra high purity helium as the carrier gas. The injector and detector were both held at 240 °C. The GC oven was programmed with the following temperature regime: hold at 30 °C for 5 min, ramp to 140 °C at 7.5 °C min⁻¹, ramp to 240 °C at 40 °C min⁻¹ and hold at 240 °C for 15 min. The GC-FID system also used ultra high purity helium as the carrier gas. The FID detector was maintained at 250 °C. The product separation was carried out in an Agilent capillary column (Catalog No. 19091J-413). The following column temperature regime was used: hold at 40 °C for 5 min, ramp to 250 °C at 20 °C min⁻¹, and hold at 250 °C for 20 min. However, some compounds such as sugars, sugar alcohols and levoglucosan in bio-oil derived feedstocks cannot be detected by GC-MS and GC-FID. In this study, a high-performance liquid chromatography (HPLC, Shimadzu) system was used to analyze these compounds. An RI detector (held at 30 °C) was used in the system to quantify sugars, sugar alcohol and levoglucosan. Bio-Rad's Aminex HPX-87H column (Catalog No. 125-0140) was used with 0.005 M H₂SO₄ as the mobile phase with the flow rate of 1 mL min⁻¹. The column oven temperature was held at 30 °C. The carbon content in WSBO, LTH-WSBO and HTH-WSBO were determined by Total Organic Carbon (TOC) analysis. The carbon contents in DOE-BO and LTH-DOE-BO were determined by elemental analysis.

2.3.3. Data evaluation. The following calculations were used in this paper:

$$\text{WHSV} = \frac{\text{Mass flow rate of feed (g/h)}}{\text{Mass of catalyst (g)}} \quad (2)$$

$$\text{Carbon yield} = \frac{\text{Moles of carbon in a product}}{\text{Moles of carbon fed in}} \times 100\% \quad (3)$$

$$\text{Carbon selectivity} = \frac{\text{Moles of carbon in a product}}{\text{Moles of carbon in identified products}} \times 100\% \quad (4)$$

$$\text{Coke yield in TGA} = \frac{\text{Mass of residue}}{\text{Mass of feed}} \times 100\% \quad (5)$$

$$\text{Deactive rate} = \frac{y_{c,\max} - y_{c,19.5}}{y_{c,\max} \times (t_{\max} - 19.5)} \times 100\% \quad (6)$$

where $y_{c,19.5}$ is the aromatic + olefin carbon yield at 19.5 min, while $y_{c,\max}$ and $t_{\max}$ are the maximum aromatic + olefin carbon yield and corresponding time, respectively.

3. Results

3.1. Thermal stability of biomass-derived feedstocks

Biomass-derived feedstocks typically have a low thermal stability meaning that they decompose forming coke, H₂O, CO and CO₂ when heated above a certain temperature in the absence of

Table 2 Homogeneous coke yields obtained using a TGA instrument with the temperature programmed from room temperature to 700 °C at 1.5 °C min⁻¹, followed by an isotherm period of 30 min at 700 °C in an ultra high helium atmosphere. (Glucose, sorbitol, glycerol, THF and methanol are water solutions with a concentration of 12.5 wt%; WSBO contains 12.5 wt% oil fraction.)

Feedstock	Glucose	DOE-BO	LTH-DOE-BO	WSBO	Sorbitol	Glycerol	LTH-WSBO	HTH-WSBO	THF	Methanol
H/C_{eff} ratio	0	0.06	0.09	0.14	0.33	0.66	0.71	1.2	1.5	2
Coke yield (wt%)	23.1	19	13.64	12.8	6.14	0.4	2.82	0.24	0	0

oxygen. TGA was used to study the thermal stability of the feedstocks as stated in Section 2.2.2. Table 2 lists the homogeneous coke yields of the different feedstocks. The coke yield decreases with an increasing H/C_{eff} ratio, indicating that the feedstock with lower H/C_{eff} ratio has lower thermal stability. The feeds with a H/C_{eff} of less than 0.2 had high coke yields from 13 to 23 wt%. Only trace amounts of homogeneous coke was formed for feeds with a H/C_{eff} ratio of greater than 0.6.

3.2. Gas-phase product yields for catalytic conversion of various biomass-derived feedstocks

The product yields for the different feedstocks as a function of time on stream are shown in Fig. 3. The products include aromatics, olefins, CO, CO₂ and coke. The product yields first increase with time on stream to a maximum value and then gradually decrease. After the experiment, products continue to desorb from the catalyst surface (see 20 to 25 minutes time on stream in Fig. 3). This may be due to the decomposition of the real catalytic active center, the hydrocarbon pool, inside the zeolite catalyst. In the first step of the reactions, the feedstocks are consumed to form a hydrocarbon pool inside the zeolite. This hydrocarbon pool needs to take some time to build up. The active centers of the hydrocarbon pool then convert the feed into olefins, aromatics, CO and CO₂. Coke also builds up inside the zeolite which causes deactivation of the active centers and the decrease of aromatic and olefin yields. After reactions, the products that are trapped inside the zeolite take some time to diffuse out after reaction. The aromatic and olefin yields with respect to time on stream for tetrahydrofuran (THF) and methanol are different from the other feedstocks. When THF is the feedstock the olefin yield increases and aromatic yield decreases with time on stream. Catalytic conversion of methanol shows completely opposite trends. This indicates that different hydrocarbon pools were involved in the THF and methanol catalytic conversion. This phenomenon has also been shown in other papers for conversion of methanol with zeolite catalysts.^{61,62} This suggests that with methanol the formation of aromatics undergoes several steps which take some time to reach steady state. Methanol first forms dimethyl ether (C₂) and then C₃, C₄, C₅ to C₆. Only C₆ compounds can form aromatic compounds.⁵⁸ This means the rate of the hydrocarbon pool formation of methanol for producing aromatics is much slower than the other feedstocks, which are at least C₄ compounds. During the methanol conversion process, the olefins are built up in the hydrocarbon pools and finally converted into aromatics.

Table 3 shows the detailed product carbon yields for catalytic conversion of the ten feedstocks. The identified carbon in gas products is between 83% and 100% for all feedstocks. The missing carbon is some oxygenated compounds (for bio-oil

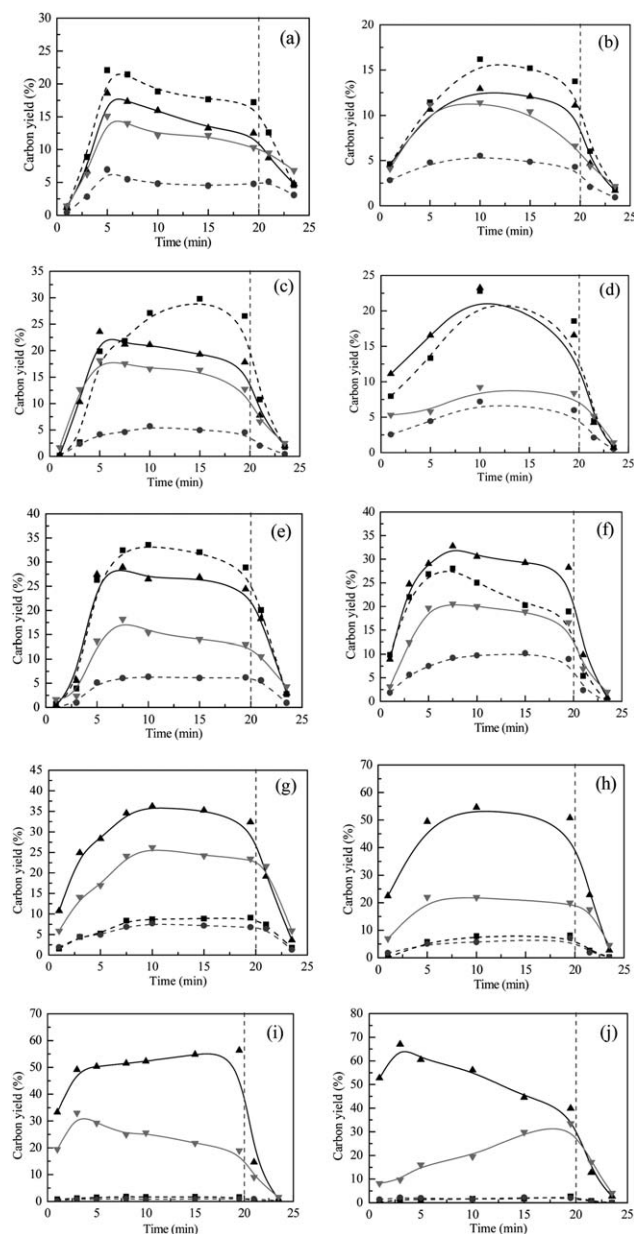


Fig. 3 Product carbon yields as a function of time for catalytic conversion of various biomass-derived feedstocks. (a) 12.5 wt% glucose–water solution; (b) DOE bio-oil; (c) LTH-DOE bio-oil; (d) 12.5 wt% WSBO; (e) 12.5 wt% sorbitol–water solution; (f) 12.5 wt% glycerol–water solution; (g) low temperature hydrogenated WSBO; (h) high temperature hydrogenated WSBO; (i) 12.5 wt% tetrahydrofuran–water solution and (j) 12.5 wt% methanol–water solution. (▲ Olefins; ▼ aromatics; ■ CO; ● CO₂. Yields are based on carbon molar selectivity.)

Table 3 Product carbon yields for catalytic conversion of various biomass-derived feedstocks. (Glucose, sorbitol, glycerol, THF and methanol are water solutions with a concentration of 12.5 wt%; WSBO contains 12.5 wt% oil fraction.)

Feedstock	Glucose	DOE-BO	LTH-DOE-BO	WSBO	Sorbitol	Glycerol	LTH-WSBO	HTH-WSBO	THF	Methanol
H/C_{eff} ratio	0	0.06	0.09	0.14	0.33	0.66	0.71	1.20	1.5	2
Product carbon yields (%)										
CO	18.10	13.49	22.58	17.88	28.30	21.99	8.14	6.82	1.48	1.79
CO ₂	5.18	4.80	4.42	5.81	5.75	8.35	6.87	5.71	0.91	2.00
Coke	32.60	49.48	35.29	32.33	14.21	9.35	18.86	14.83	5.71	2.26
Olefins										
Ethylene	5.74	5.79	9.74	7.68	11.01	15.58	10.38	16.27	6.28	23.43
Propylene	6.48	4.06	6.63	8.48	10.51	9.66	18.08	27.27	39.22	23.16
Butylenes	2.08	1.33	2.09	2.31	2.93	2.76	4.24	7.23	5.94	8.93
Sum	14.30	11.18	18.46	18.47	24.45	28.00	32.70	50.77	51.44	55.52
Aromatics										
Benzene	2.85	1.74	2.49	2.17	3.58	3.25	4.08	5.79	8.25	1.37
Toluene	5.14	3.97	5.49	3.80	6.16	8.80	10.56	10.64	11.02	5.23
Xylene	2.78	2.28	5.70	1.70	2.80	4.46	7.34	4.09	4.05	16.53
Ethyl benzene	0.44	0.20	0.50	0.13	0.37	0.38	0.64	0.48	0.42	0.52
Styrene	0.54	0.42	0.37	0.22	0.29	0.38	0.43	0.27	0.28	0.46
Indene	0.34	0.79	0	0.11	0.49	0.51	0.31	0.10	0.37	0.42
Naphthalene	0.23	0.41	0.19	0.06	0.20	0	0	0.10	0.08	0.15
Sum	12.32	9.81	14.74	8.19	13.89	17.78	23.36	21.47	24.47	24.68
Furan	0.63	0.74	1.12	0.63	1.39	0.05	0.81	0.21	0	0
Total carbon yield	83.13	89.5	96.61	83.31	87.99	85.52	90.74	99.81	84.01	86.25

Table 4 Liquid product compositions produced from catalytic conversion of bio-oil derived feedstocks

Compound	Carbon yield (%)				
	WSBO	LTH-WSBO	HTH-WSBO	DOE-BO	LTH-DOE-BO
Phenol	1.26	0.46	0.37	0.02	0.03
3-Methyl-phenol	0.49	0.28	0.18	0	0
2-Methyl-phenol	0.98	0.49	0.31	0.01	0.02
2,6-Dimethyl-phenol	0.28	0.18	0.08	0	0
2,3-Dimethyl-phenol	0.14	0.09	0.03	0	0
4-(2-Furanyl)-3-buten-2-one	0	0.29	0.21	0.09	0.16
2,4-Dimethyl-phenol	0.11	0.07	0.06	0	0
2,3-Dihydro-benzofuran	0.63	0	0	0	0
1-Methyl-naphthalene	0.49	1.15	0	0	0
1-Naphthalenol	0.53	0	0	0	0
2-Naphthalenol	1.26	0.29	0.21	0.08	0.11
Fluorene	0.77	0.42	0.31	0.22	0.48
7-Methyl-1-naphthol	0.95	0	0	0	0
Total yield	7.89	3.72	1.76	0.42	0.8

derived feeds) and C₅ hydrocarbons (for methanol) in liquid products (see Table 4 and ref. 63).

3.3. The carbon selectivities of olefin and aromatic products

The olefins produced include: ethylene, propylene and butylenes. The main aromatics detected include: benzene, toluene and xylene. Their selectivities in the products as a function of time on stream can further monitor the change of the hydrocarbon pools with time. Fig. 4 and 5 show the olefin and aromatic selectivities for the ten feedstocks as a function of time on stream, respectively. After the formation of the hydrocarbon pools (>5 min), the selectivities of ethylene and propylene are much higher than those of butylenes for all feeds. For DOE-BO and LTH-DOE-BO, the selectivities of ethylene and butylenes increase with time on stream, whereas for WSBO and glycerol, those of propylene and butylenes increase with time on stream.

For LTH-WSBO and HTH-WSBO, the selectivity of propylene is higher than that of ethylene and is almost the same during the first 20 min.

As shown in Fig. 5, toluene has the highest aromatic selectivity for conversion of all feeds except for methanol. Catalytic conversion of methanol produced xylene in a 70% aromatic selectivity. For catalytic conversion of glucose, DOE-BO, LTH-DOE-BO, WSBO, sorbitol and glycerol (all of them are low H/C_{eff} ratio feedstocks), the aromatic products selectivity shows a significant change with time on stream during the hydrocarbon pool formation phase (the first 5 min of time on stream). After the 5 minutes time on stream formation of the pool, the xylene selectivity decreases and the benzene and toluene selectivities increase for sorbitol, glycerol, LTH-WSBO and HTH-WSBO. The benzene selectivity increases and the toluene selectivity decreases for THF. The aromatic selectivity for methanol has no change after the first 5 min.

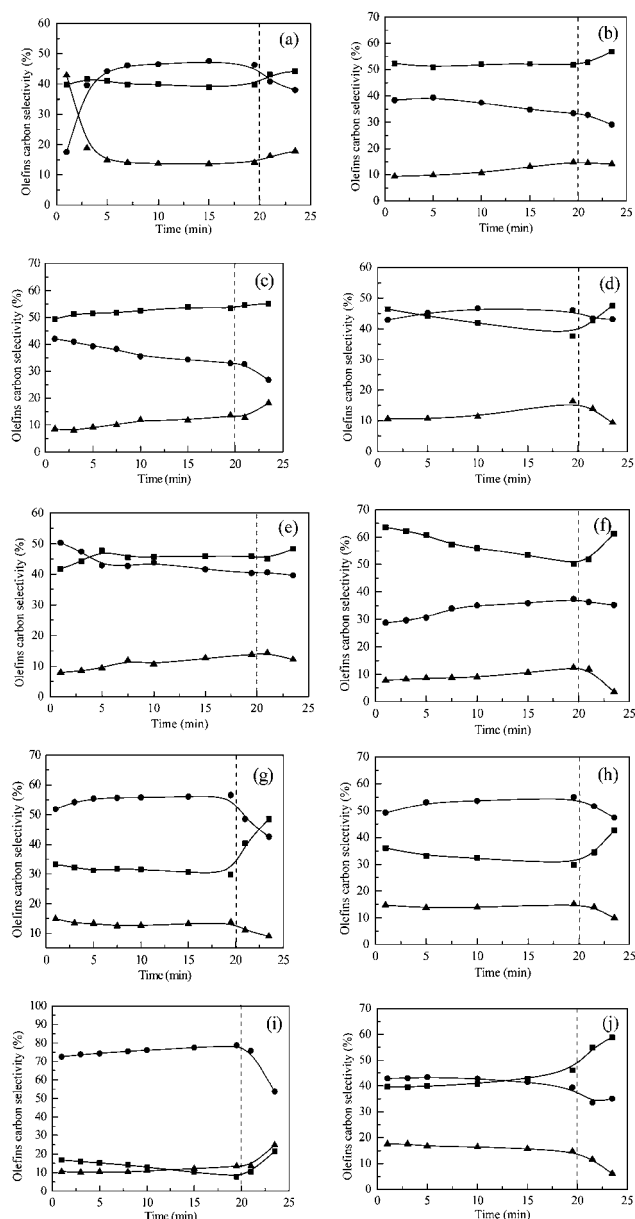


Fig. 4 Olefin product selectivity as a function of time on stream for conversion of: (a) 12.5 wt% glucose–water solution; (b) DOE-BO; (c) LTH-DOE-BO; (d) WSBO; (e) 12.5 wt% sorbitol–water solution; (f) 12.5 wt% glycerol–water solution; (g) LTH-WSBO; (h) HTH-WSBO; (i) 12.5 wt% THF–water solution and (j) 12.5 wt% methanol–water solution. (■ Ethylene; ● propylene; ▲ butylenes. Yields are based on carbon molar selectivity.)

3.4. Liquid-phase product yields for catalytic conversion of various bio-oil derived feedstocks

Small amounts of liquid products were also produced for the bio-oil feedstocks. These liquid products contained primarily single-ring phenols, naphthalenols and fluorene as shown in Table 4. The yield of the phenolics decreases in the following order: WSBO > LTH-WSBO > HTH-WSBO > LTH-DOE-BO > DOE-BO. The single-ring phenols in the liquids include phenol, 3-methyl-phenol, 2-methyl-phenol, 2,6-dimethyl-phenol, 2,3-dimethyl-phenol and 2,4-dimethyl-phenol. For WSBO, LTH-

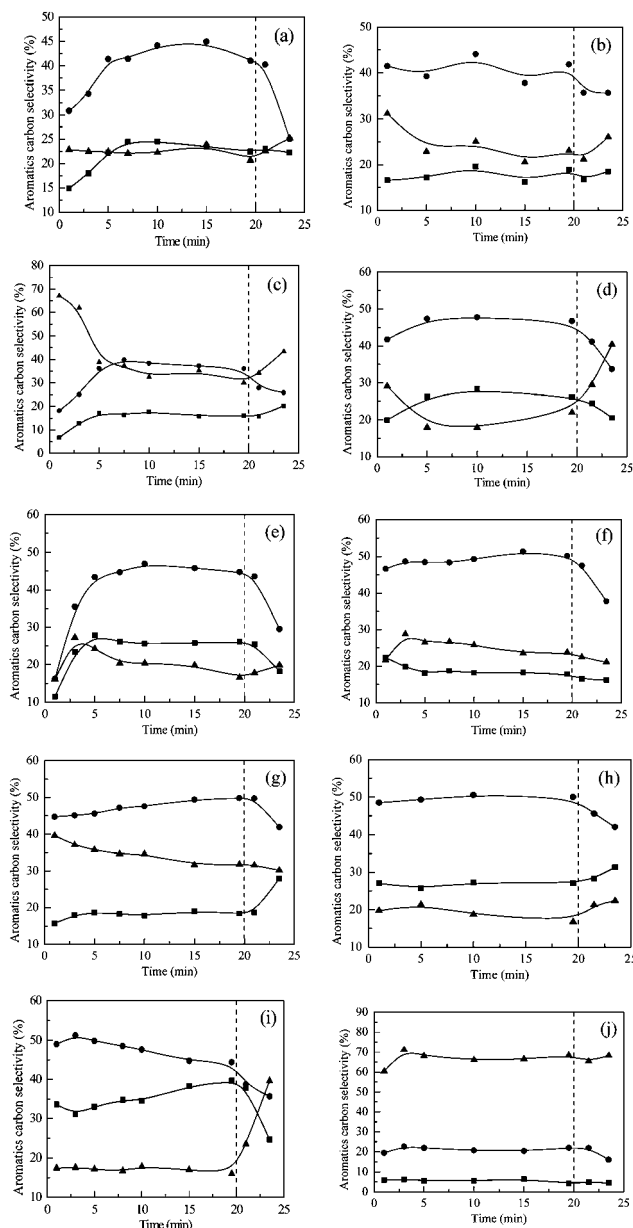


Fig. 5 Aromatic product selectivity as a function of time on stream for conversion of: (a) 12.5 wt% glucose–water solution; (b) DOE-BO; (c) LTH-DOE-BO; (d) WSBO; (e) 12.5 wt% sorbitol–water solution; (f) 12.5 wt% glycerol–water solution; (g) LTH-WSBO; (h) HTH-WSBO; (i) 12.5 wt% THF–water solution and (j) 12.5 wt% methanol–water solution. (■ Benzene; ● toluene; ▲ xylene. Yields are based on carbon molar selectivity.)

WSBO and HTH-WSBO, the yields of these single-ring phenols are 3.26%, 1.57% and 1.04%, respectively.

4. Discussion

4.1. Product yields as a function of hydrogen to carbon effective (H/C_{eff}) ratio

In zeolite upgrading of an oxygenated hydrocarbon, C6–C8 aromatic hydrocarbons, C2–C4 olefins, CO, and H₂O are the

major products. Oxygen is removed from the feed in the form of CO or H₂O. In this study, the theoretical yield was calculated assuming toluene as the targeted product and CO and H₂O as the byproducts. The overall stoichiometry is shown in eqn (7):



where

$$a = (x + 0.5y - z)/11 \quad (8)$$

$$b = (4x - 3.5y + 7z)/11 \quad (9)$$

$$c = (4z + 3.5y - 4x)/11 \quad (10)$$

When $b < 0$, we assumed H₂ as one of the byproducts instead of CO. Fig. 6 shows the experimental and theoretical aromatic + olefin yield as a function of the H/C_{eff} ratio. The experimental aromatic + olefin yield increases from 27% to 80% with the increase of the H/C_{eff} ratio from 0 (glucose) to 2 (methanol). There is an inflection point at a H/C_{eff} ratio = 1.2, where the aromatic + olefin yield does not increase as rapidly as it does before. This is also the same point where the theoretical yield is 100%. At this point all of the carbon in the feedstock is converted into carbon in the aromatics. This suggests that, if cheap hydrogen is available, the amount of hydrogen that is added to the biomass feedstock should be enough to bring it to a H/C_{eff} ratio of 1.2. Adding more hydrogen to the biomass feedstock would be a waste of hydrogen resources and increase the cost of the process. This also suggests that future biorefineries should target an enrichment of the biomass feedstock to a H/C_{eff} ratio of 1.2.

The experimental/theoretical yield or percentage of the theoretical yield increases with increasing H/C_{eff} ratio as shown in Fig. 6. The theoretical yield of glucose is only 42%, whereas that of methanol is about 80%. This suggests that methanol is a more efficient feedstock for producing hydrocarbons than glucose with the current catalyst at these reaction conditions.

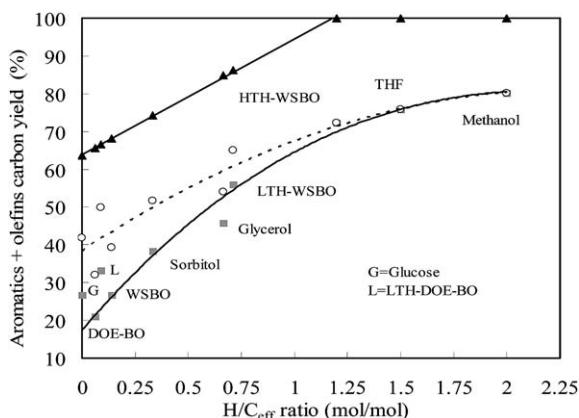


Fig. 6 The aromatic + olefin carbon yield for catalytic conversion of various biomass-derived feedstocks as a function of the hydrogen to carbon effective (H/C_{eff}) ratio. The H/C_{eff} ratios of the feedstocks: glucose, 0; DOE-BO, 0.06; LTH-DOE-BO, 0.09; WSBO, 0.14; sorbitol, 0.33; glycerol, 0.66; LTH-WSBO, 0.71; HTH-WSBO, 1.2; THF, 1.5 and methanol, 2. (▲ Theoretical carbon yield; ■ experimental carbon yield; ○ experimental/theoretical yield.)

Compared with DOE-BO, the aromatic + olefin yield of LTH-BO increases from 21% to 33%. The low temperature hydrogenation process resulted in an increase of the H/C_{eff} ratio of the bio-oil from 0.06 to 0.09. This process only used a small amount of hydrogen but resulted in a large increase in the yield of usable petrochemicals. This is probably because the hydrogenation step was able to stabilize the most unstable compounds in the bio-oil, which tends to form homogeneous coke when heated as shown in Table 2. The most unstable compounds formed coke on the catalyst surface during the hydrogenation step and thus the LTH-DOE-BO contains less thermally unstable molecules than DOE-BO (14% vs. 19%). These unstable molecules that tend to form homogeneous coke include aldehydes, ketones and furan derived oxygenates which contain unsaturated bonds.

In a separate reaction, we have previously converted furan (H/C_{eff} ratio = 0.5) under similar reaction conditions but short time on stream (5 min).⁴² The catalyst deactivated rapidly within 5 min time on stream with a coke yield of 33% carbon. Tetrahydrofuran (THF) is the saturated form of furan. However, catalytic conversion of THF only produced 6% coke (see Fig. 8). This indicates that catalytic conversion of unsaturated compounds like furan produces large amounts of coke which rapidly deactivates the zeolite.

Low temperature hydrogenation of WSBO increased the H/C_{eff} ratio from 0.14 (WSBO) to 0.71 (LTH-WSBO). The aromatic + olefin yield improved from 27% to 56%. However, the LTH-WSBO still contains some hydrogen deficient compounds such as acetic acid (H/C_{eff} ratio = 0), levoglucosan (H/C_{eff} ratio = 0) and sorbitol (H/C_{eff} ratio = 0.33) (Table 1). These molecules need to be upgraded into hydrogen-rich molecules to further increase the petrochemicals yield. Hence we subjected LTH-WSBO to high temperature hydrogenation and converted it into high temperature hydrogenated WSBO (HTH-WSBO). With the H/C_{eff} ratio of HTH-WSBO increasing to 1.2, the aromatic + olefin yield increases to 72%. These results disclose that we can enhance the hydrocarbon yield by increasing the H/C_{eff} ratio of the feed. This is consistent with the results obtained by Gayubo *et al.*⁶⁴ who increased the hydrocarbon yield dramatically by co-conversion of bio-oil with methanol.

The product yields as a function of the H/C_{eff} ratio are shown in Fig. 7 and 8. As shown in Fig. 7(a), the aromatic and olefin yields increase from 12% and 15% to 24% and 56% with increasing H/C_{eff} ratio, respectively. For all feedstocks, the olefin yield is higher than the aromatic yield, and the gap increases with an increase of the H/C_{eff} ratio. If liquid hydrocarbons are the desired product then these olefins must be recycled or oligomerized.⁴² The reaction temperature is high (600 °C) which favors the production of olefins.

The CO and CO₂ yields go through a maximum with respect to the H/C_{eff} ratio (Fig. 7(b)). CO was most likely produced by decarbonylation. Feedstocks with low H/C_{eff} ratio should make more CO because they are hydrogen-deficient compounds, which limits oxygen transferring into water and favors CO production. As shown in Fig. 7(b), sorbitol (H/C_{eff} ratio = 0.33) gave 28% CO yield which is more than that of glycerol (H/C_{eff} ratio = 0.66) which gave 22% CO yield. However, glucose, DOE-BO, LTH-DOE-BO and WSBO which have lower H/C_{eff} ratio than sorbitol produced less CO. This can be explained by homogeneous coke formation reactions where a large part of these feedstocks was

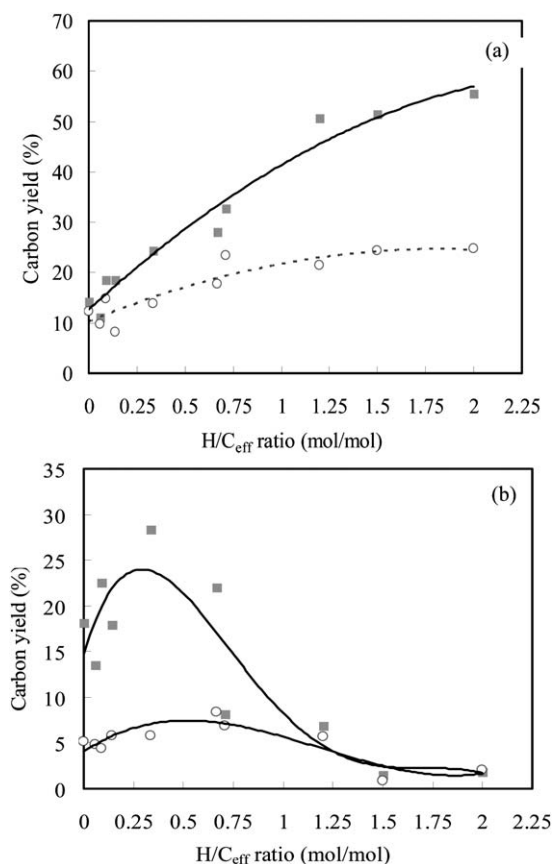


Fig. 7 Product carbon yields of catalytic conversion of various biomass-derived feedstocks as a function of the hydrogen to carbon effective (H/C_{eff}) ratio. (a) Olefin and aromatic yields (■ olefins; ○ aromatics); (b) CO and CO₂ carbon yields (■ CO; ○ CO₂). The H/C_{eff} ratios of the feedstocks: glucose, 0; DOE-BO, 0.06; LTH-DOE-BO, 0.09; WSBO, 0.14; sorbitol, 0.33; glycerol, 0.66; LTH-WSBO, 0.71; HTH-WSBO, 1.2; THF, 1.5 and methanol, 2.

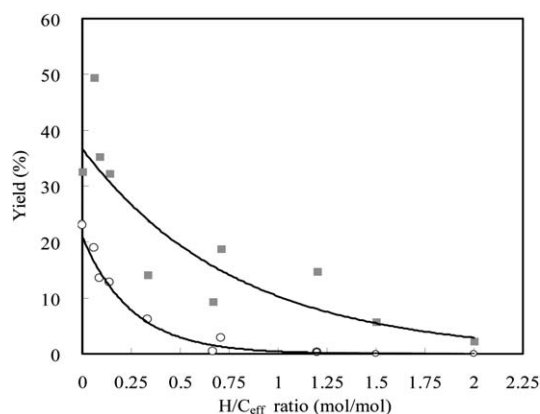


Fig. 8 Coke carbon yield (based on the total carbon of the feed) of catalytic conversion obtained from flow reactor and coke yield (based on the mass of the feed) of that obtained from TGA as a function of the hydrogen to carbon effective (H/C_{eff}) ratio of the feed. The H/C_{eff} ratios of the feedstocks: glucose, 0; DOE-BO, 0.06; LTH-DOE-BO, 0.09; WSBO, 0.14; sorbitol, 0.33; glycerol, 0.67; LTH-WSBO, 0.71; HTH-WSBO, 1.2; THF, 1.5 and methanol, 2. (■ Catalytic coke carbon yield; ○ homogeneous coke yield.)

converted into homogeneous coke before catalytic cracking with the catalyst. We conducted some blank experiments for homogeneous coke formation in the reactor. The experiments were operated at typical conditions as catalytic conversion run but without a catalyst. 45% carbon in the feed was converted into coke for WSBO, whereas only 5% carbon was converted into CO. However, catalytic conversion of WSBO gave about 18% carbon yield of CO. This indicates that CO is mainly produced in the catalytic process. Since CO₂ is mainly produced by water-gas shift reaction,⁹ its yield as a function of the H/C_{eff} ratio has the same trend with that of CO. For bio-oil derived feedstocks, CO₂ can also be produced by decarboxylation reaction of acetic acid.

It should be noted that the coke obtained from catalytic conversion in the flow reactor is a total coke which includes homogeneous coke (defined as coke deposited on the reactor) and heterogeneous cokes (defined as coke deposited on the catalyst). In order to distinguish these two types of coke, the TGA experiments were conducted without catalyst to only obtain homogeneous coke. Fig. 8 shows the catalytic coke yield (based on the total carbon of the feed) and the non-catalytic coke yield (based on the mass of feedstock) as a function of the H/C_{eff} ratio. Both catalytic coke and non-catalytic coke yields decrease with increasing H/C_{eff} ratio. This decrease is greatest at H/C_{eff} ratios less than 0.25. The coke yield reaches a stable value at higher H/C_{eff} ratios. Compared with their H/C_{eff} ratio, catalytic cracking of the bio-oil derived feedstocks (including DOE-BO, LTH-DOE-BO, WSBO, LTH-WSBO and HTH-WSBO) produced more total coke due to a lot of homogeneous coke formation.

4.2. Deactivation rate of the catalyst as a function of hydrogen to carbon effective (H/C_{eff}) ratio

The rate of catalyst deactivation as defined in eqn (6) is introduced to describe the deactivation of the catalyst during the catalytic conversion process of biomass-derived feedstocks. The catalyst deactivation rates for catalytic conversion of different

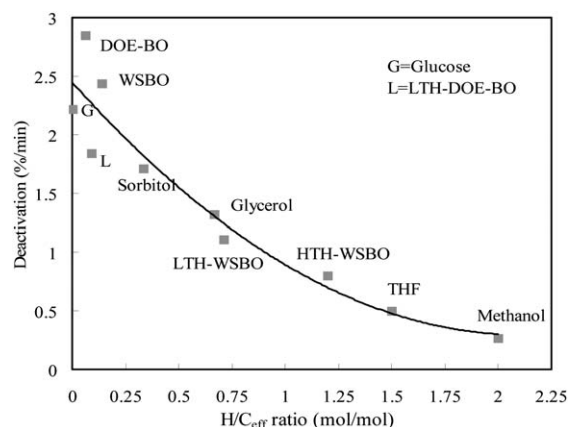


Fig. 9 The catalyst deactivation rates for catalytic conversion of different biomass-derived feedstocks as a function of hydrogen to carbon effective (H/C_{eff}) ratio. The H/C_{eff} ratios of the feedstocks: glucose, 0; DOE-BO, 0.06; LTH-DOE-BO, 0.09; WSBO, 0.14; sorbitol, 0.33; glycerol, 0.66; LTH-WSBO, 0.71; HTH-WSBO, 1.2; THF, 1.5 and methanol, 2.

biomass-derived feedstocks as a function of the H/C_{eff} ratio are shown in Fig. 9. As shown in the figure, the deactivation rate decreases with increasing H/C_{eff} ratio. Similar to coke carbon yield, the deactivation rate curve also decreases rapidly at low H/C_{eff} ratio and becomes stable at high H/C_{eff} ratio. This result indicates that the increase of the H/C_{eff} ratio of feedstocks can increase the stability of the catalyst due to low coke accumulation on the catalyst.

5. Conclusions

The general conclusion of this study is that the hydrogen to carbon effective (H/C_{eff}) ratio of biomass-derived feedstock can be used to estimate the overall olefin and aromatic yield, the coke yield, and the catalyst deactivation rate for the catalytic conversion of a range of biomass feedstocks using zeolite based catalysts. The aromatic + olefin carbon yield increases with increasing H/C_{eff} ratio. Lower H/C_{eff} ratio feedstocks produced more coke which rapidly deactivates the zeolite catalyst. Coke was produced from both homogeneous and heterogeneous reactions. TGA was done to determine the homogeneous coke yield. The result shows the formation of coke from homogeneous reactions decreases with increasing H/C_{eff} ratio. This can be used to guide the catalytic conversion of biomass and its derivatives into high yields of olefins and aromatics. Hydrogen deficient biomass feedstocks can be hydrogenated to increase their H/C_{eff} ratio before reaction with zeolite catalysts. The optimal amount of hydrogen to add to the biomass-derived feedstock for aromatic and olefin production is around a H/C_{eff} ratio of 1.2.

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RKCL4850

ETHANOL CONVERSION TO AROMATIC HYDROCARBONS OVER SEVERAL ZEOLITE CATALYSTS

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Abstract

H-ZSM-5 (Si/Al₂ = 29) zeolite showed especially high activity in the conversion of ethanol to BTX (benzene, toluene, xylenes), while other zeolites exclusively formed ethylene. Noble metal catalysts supported on H-ZSM-5 (29) zeolite have high activity for the formation of BTX. Of these, Au/H-ZSM-5 catalyst can partially inhibit carbon deposition during the reaction, thus maintaining constant catalytic activity for BTX formation.

Keywords: Ethanol conversion, BTX production, metal catalysts supported on zeolites

INTRODUCTION

Currently, the main chemical compounds in industry are synthesized from petroleum. However, petroleum resources are limited and the combustion of petroleum produces CO₂, the chief greenhouse gas. Much attention has been paid to biomass as alternative resource to petroleum, since biomass is a renewable resource and its combustion does not lead to increased CO₂ in the

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atmosphere. Ethanol is one of the main biomass-derived products. In this study, we experimented with several zeolite catalysts and several metal catalysts supported on zeolite for the conversion of ethanol to hydrocarbons, and found that the low Si/Al₂ ratio version of H-ZSM-5 has high activity for the production of higher hydrocarbons, as reported elsewhere [1-7]; moreover, we found that loading of Ga and noble metals on H-ZSM-5 support enhances the formation of aromatic hydrocarbons.

EXPERIMENTAL

As zeolite supports, H-Beta (27), H-ZSM-5 (29, 190), USY (6.3) and H-mordenite (18.3) were used (numbers in parentheses denote the Si/Al₂ ratio). These zeolites were obtained from Tosoh. Before use, the zeolites were calcined at 500°C in a muffle furnace for 6 h. Several metals were impregnated in the zeolite supports. Mg, Cr, Fe, Co, Ni, Cu, Ga, Ru, Rh, Pd, Ag, Re, Ir, Pt and Au were used as pure metals. Metal nitrate hydrates were used as sources of Mg, Cr, Fe, Co, Ni, Cu, Ga and Rh. Ru(NO₃)₃(NO), AgNO₃, [Pt(NH₃)₄](NO₃)₂ and HAuCl₄·4H₂O were used as sources of Ru, Ag, Pt and Au, respectively. Aqueous solutions of these metal sources were used for impregnation. (NH₃)₂Pd(NO₂)₂, NH₄ReO₄ and (NH₄)₂IrCl₆ were used as sources of Pd, Re and Ir, respectively, where aqueous solutions containing dissolved ammonia were used. As a rule, the metal loading was 10 wt.%, except in the cases of Ru, Rh, Pd, Ir, Pt and Au, where the loading was 2 wt.%. After impregnation, the wet catalysts were dried at 120°C in an oven, followed by calcination at 700°C in air for 3 h.

Catalytic activity was measured using a fixed-bed reactor. The weight of catalyst was 0.2 and 0.4 g. Reaction gas was obtained by mixing N₂ and vaporized ethanol, with the flow rate of N₂ set at 60 cm³ min⁻¹, resulting in the concentrations of N₂ and ethanol being 82.14 and 17.86 vol.%, respectively. WHSV was 0.1589 and 0.0795 EtOH-mol/g-cat/h for 0.2 and 0.4 g of catalysts, respectively. Reaction temperature was changed from 200 to 600°C in 100-K steps. Reactions at a constant 400°C were also carried out to investigate the effect of reaction time on change in catalytic performance. The effluent gas was analyzed using a gas chromatograph (GC) equipped with Molecular Sieve 5A and Porapak Q columns.

NH₃-temperature-programmed desorption (TPD) analyses (Nihon Bell, TPD-1-AT-SP) of zeolite supports were carried out to measure the solid acidity of the supports. X-ray diffraction (XRD) (Mac Science, M18XHF²²-SRA) measurements of metal/zeolite catalysts were carried out to investigate the state of the loaded metals. The size of metal crystallites was calculated by Sherrer's formula. Thermogravimetry (TG) analyses (Mac Science, TG-DTA2000) of

catalysts after reaction were carried out to evaluate the amount of carbon deposited on the catalysts during reaction.

RESULTS AND DISCUSSION

First, the catalytic activity of zeolite catalysts with no metal loaded (0.2 g) was investigated. In most zeolites, at below 400°C, the low reaction temperature favored the exclusive formation of diethyl ether by intermolecular dehydration between two ethanol molecules, although the conversion of ethanol was low. The conversion of ethanol and the selectivity of ethylene increased with increasing reaction temperature, while the selectivity of diethyl ether decreased. Ethylene was formed by intramolecular dehydration. Above 400°C, higher hydrocarbons were predominantly formed and the selectivity of ethylene was decreased over H-ZSM-5 (29) zeolite, while other zeolites produced ethylene at high selectivity, even above 400°C. For example, at 400°C, H-ZSM-5 (29) yielded xylenes at selectivity of 30.91%, while H-ZSM-5 (190) formed ethylene at high selectivity (Table 1), suggesting that solid acidity of the catalyst is essential to this reaction. H-ZSM-5 (29) zeolite showed 585 $\mu\text{mol g}^{-1}$ of NH_3 adsorption by NH_3 -TPD measurement; this value is smaller than those of H-Beta (27) and H-mordenite (18.3) (1215 and 2453 $\mu\text{mol g}^{-1}$, respectively), although the Si/ Al_2 ratios were not very different among these zeolites. H-ZSM-5 (190) and USY (6.3) showed 269 and 1431 $\mu\text{mol g}^{-1}$ of NH_3 adsorption, respectively. These results suggest that the presence of a large number of acidic sites does not always lead to high BTX selectivity.

These results for zeolites alone suggest that H-ZSM-5 zeolite with a low Si/ Al_2 ratio is ideal for the production of higher hydrocarbons from ethanol. Chaudhuri *et al.* reported that strong Brönsted acid sites and more than one proton per unit cell of H-ZSM-5 are important for catalytic activity [4]. Therefore, modest acidity of the zeolite could be important for the formation of higher hydrocarbons, but not of ethylene.

To improve the catalytic activity, we tried several metal/H-ZSM-5 (29) catalysts. XRD measurement showed that Mg, Cr, Fe, Co, Ni, Cu, Ru, Ag, Ir, Pt and Au exist as MgO (17.1 nm), Cr_2O_3 (32.1 nm), Fe_2O_3 (24.8 nm), Co_3O_4 (27.7 nm), NiO (23.9 nm), CuO (20.4 nm), RuO_2 (22.6 nm), Ag (24.0 nm), IrO_2 (17.4 nm), Pt (22.6 nm) and Au (31.0 nm), respectively; the numbers in parentheses indicate the size of the crystallite. On the other hand, Ga, Rh, Pd and Re showed no XRD peaks, suggesting that these metals are present at high dispersion.

The results at 400°C over 0.2 g of catalyst are shown in Table 1. Except for the case of Mg, ethanol conversion was above 90 %, suggesting that the presence of alkali earth metals suppresses the conversion of ethanol. The BTX selectivity was as follows: Ga >> Pd > Ir > Au > Ru > Rh > blank, where blank

Table 1
Catalytic activity at 400°C over 0.2 g of zeolite catalysts without metal loaded and several metal catalysts supported on H-ZSM-5 (Si/Al₂ = 29) zeolite

Catalyst	Ethanol conv. / %	C-selectivity / %							TG weight loss / %	
		Diethyl ether	Ethylene	C ₃ + olefins	Paraffins	Benzene	Toluene	Xylenes		
A	94.77	1.66	86.50	3.18	3.14	0.93	1.02	2.00	3.95	34.34
B	92.24	5.79	10.48	15.62	13.22	3.07	18.90	30.91	52.88	3.31
C	96.41	0.33	97.58	1.72	0.03	0.00	0.00	0.00	0.00	0.64
D	93.70	0.42	96.21	0.42	1.23	0.00	0.00	0.00	0.00	21.35
E	79.83	0.00	95.77	1.04	2.57	0.00	0.00	0.00	79.83	14.37
Mg	36.90	6.76	92.49	0.04	0.03	0.00	0.00	0.00	0.00	0.65
Cr	93.85	5.70	23.81	17.52	9.02	1.15	10.52	29.92	41.59	3.01
Fe	96.96	2.31	11.15	29.76	5.63	0.92	12.81	37.42	51.15	2.44
Co	94.82	0.98	76.16	8.90	2.76	0.00	2.06	8.14	10.20	11.97
Ni	95.56	2.59	30.05	21.05	6.21	0.71	10.69	27.35	38.75	82.41
Cu	90.06	0.20	91.89	0.61	0.11	0.06	1.03	3.44	4.53	0.94
Ga	93.39	3.86	4.78	10.79	6.98	2.52	24.49	46.57	73.58	5.46
Ru	91.48	4.82	12.20	17.28	10.09	3.99	20.77	30.59	55.35	3.81
Rh	94.04	4.27	13.04	17.08	9.87	3.20	19.15	32.81	55.16	6.54
Pd	92.89	4.66	10.38	15.09	8.82	3.37	20.88	36.58	60.83	9.69
Ag	97.09	3.76	38.66	14.55	9.31	0.64	8.86	23.18	32.68	2.71
Re	98.58	3.48	56.04	7.09	5.13	0.91	5.43	16.96	23.30	3.76
Ir	91.50	4.09	11.49	17.67	9.34	3.97	22.56	30.83	57.36	4.32
Pt	98.45	1.30	33.60	6.75	6.93	3.36	14.73	32.65	50.74	10.43
Au	92.88	5.02	6.59	19.12	12.43	4.33	21.96	30.55	56.84	2.55

A: H-Beta (27), B: H-ZSM-5 (29), C: H-ZSM-5 (190), D: USY (6.3), E: H-Mordenite (18.3),
Number in parenthesis stands for Si/Al₂ ratio.

means H-ZSM-5 (29) zeolite alone. The selectivity of benzene was as follows: Au > Ru > Ir > Pd > Pt > Rh > blank. The selectivity of toluene was as follows: Ga > Ir > Au > Pd > Ru > Rh > blank, and that of xylenes was as follows: Ga > Fe > Pd > Rh > Pt > blank. Rh and Pd catalysts showed higher selectivity of all of BTX than H-ZSM-5 zeolite alone. Saha *et al.* reported that Ga-doped H-ZSM-5 has higher activity for the conversion of ethanol to aromatic compounds than H-ZSM-5 alone [5]. On the other hand, other types of metals suppressed the production of aromatic compounds.

Next, the effect of catalyst weight was investigated, since the reaction may proceed while ethanol or intermediates of this reaction pass through the catalyst layer: catalyst weight was increased to 0.4 g. In the case of zeolites alone, the ethanol conversion was slightly higher than for 0.2 g of zeolite catalyst. With the use of 0.4 g of H-ZSM-5 (29), successive reactions of lower olefins (such as ethylene) and paraffins occurred and the selectivities of benzene (8.08%) and toluene (34.40%) were drastically improved in comparison with the case of 0.2 g, but selectivity of xylenes (31.37%) was only slightly improved. On the other hand, over other zeolites, ethylene appears to be the final product, regardless of the catalyst amount used, since the selectivity of higher hydrocarbons was not drastically improved by the increased catalyst weight.

The effect of the weight of metal catalysts was also investigated. In this case, also, catalyst weight was 0.4 g. In all cases, ethanol conversion was above 90%. Ga catalyst showed BTX selectivity of 75.38%, higher than that of H-ZSM-5 (29) catalyst without metal loaded (73.82%). However, all the other catalysts showed lower BTX selectivity than H-ZSM-5 (29). Moreover, no catalyst showed higher benzene selectivity than H-ZSM-5 (29) (8.05%). The selectivity of toluene was as follows: Ga (35.66%) > Au (35.56%) > blank (34.40%), and that of xylenes was as follows: Pt (40.57%) > Pd (39.44%) > Ni (37.06%) > Rh (34.68%) > Ag (34.30%) > Ga (33.67%) > Cr (33.43%) > Fe (31.81%) > blank (31.37%). Other metals suppressed the production of aromatic compounds. In all cases, the selectivity of toluene was improved by the increase in the weight of the catalyst; however, over H-ZSM-5 (29) catalyst, the increase in catalyst weight resulted in increased toluene selectivity. Therefore, only Ga and Au catalysts are effective for improving the formation of toluene, since these catalysts showed higher toluene selectivity than H-ZSM-5 (29) catalyst, irrespective of catalyst weight, whereas these catalysts showed decreased selectivity of xylenes with increased catalyst weight. On the other hand, for most metal catalysts, the selectivity of xylenes was improved by increasing the catalyst weight. Among these catalysts, Rh, Pd and Pt catalysts were especially effective for the formation of xylenes, since they showed higher xylene selectivity than H-ZSM-5 (29) at both 0.2 and 0.4 g of catalyst weight.

In general, noble metals are effective for the formation of aromatic compounds from ethanol; Au is especially efficient for the formation of toluene,

while Rh, Pd and Pt are effective for xylenes. Moreover, Ga, not a noble metal, can enhance the formation of toluene. On the other hand, other metals, such as Cr, Fe and Ni appear to be effective for the formation of C_{3+} olefins and paraffins, which may be precursors of aromatics. Mg is effective for ethylene formation.

Carbon deposition on the catalyst, which may lead to catalytic deactivation, occurred during the reaction. The weight loss of catalysts after reaction (200–600°C) by TG is also shown in Table 1. In general, catalysts yielding BTX at high selectivity deposit large amounts of carbon. This result is consistent with a previous report [4]. However, among the zeolites alone, H-Beta (27), USY (6.3) and H-mordenite (18.3) formed no or little BTX, but were prone to heavy deposits of carbon, while H-ZSM-5 (29), which gave high yields of BTX, was subject to a moderate quantity of carbon deposits, suggesting that the larger micropore structure of zeolite may encourage carbon deposition. H-ZSM-5 (190), yielding no BTX, was subject to minor carbon deposits. On the other hand, in the case of metal/H-ZSM-5 (29) catalysts, there is a correlation between the yield of BTX and the amount of deposited carbon, except for Co and Ni catalysts, which show a large amount of carbon deposition for the selectivity of BTX. Only the Au catalyst showed a slightly higher BTX selectivity and a slightly lower amount of carbon deposition than H-ZSM-5 (29) alone.

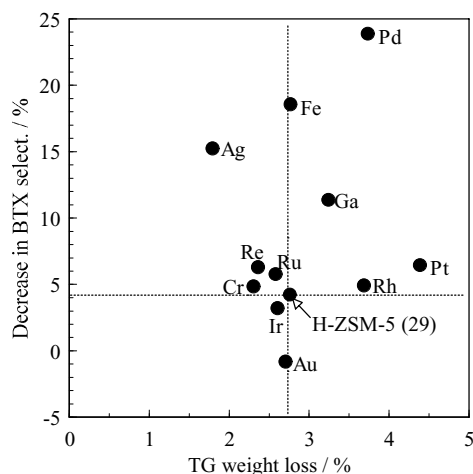
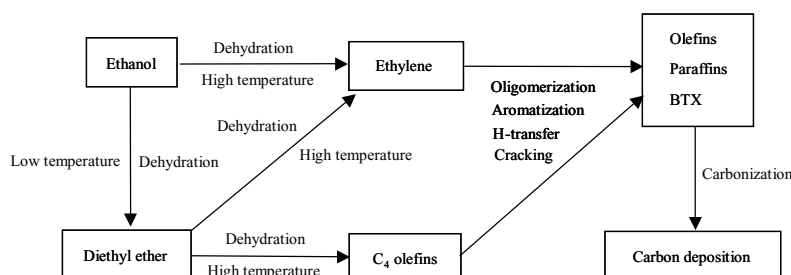


Fig. 1. Plots of the weight loss of catalyst after reaction by TG vs. the decrease in BTX selectivity at 400 °C over 0.2 g of catalyst.

The number in parenthesis denotes Si/Al₂ ratio.

The catalytic performance of H-ZSM-5 and metal/H-ZSM-5 catalysts as a function of time was investigated, at a catalyst weight of 0.2 g, and with reaction temperature held at 400°C. A decrease in BTX selectivity was observed over most catalysts, while ethanol conversion was almost constant, and the selectivity of ethylene increased with time. The difference in BTX selectivity between 50 and 450 min after starting the reaction was calculated and adopted as the decrease in the BTX selectivity. The weight loss of catalyst after reacting at 400°C for 450 min was obtained by TG analysis. Figure 1 is a plot of the decrease in BTX selectivity vs. TG weight loss. Although carbon deposition proceeded less at 400°C than at above 400 °C, but with no clear correlation found, some metals showed characteristic results: for example, Rh and Pt showed a great deal of deposited carbon, while the decrease in selectivity was small, suggesting that these metals give some immunity to carbon deposition. Ag showed small amounts of carbon but showed a large decrease in selectivity. Ir and Au showed less deposited carbon and less decrease in selectivity than H-ZSM-5 (29); Au in particular showed no decrease in selectivity.



Scheme 1. Supposed reaction pathway

Scheme 1 shows the assumed reaction pathway. At low temperatures, the exclusive formation of diethylether by intermolecular dehydration between two ethanol molecules occurs. However, a higher reaction temperature favors the formation of ethylene by intramolecular dehydration of ethanol or diethylether. It appears that diethylether can be converted to C₄ olefins as well as to ethylene by dehydration, since has been reported that dimethylether (DME) can be dehydrated to ethylene [1]. Ethylene and C₄ olefins, formed by dehydration, could undergo further reactions such as oligomerization, aromatization, H-transfer or cracking, to give higher hydrocarbons (olefins, paraffins and BTX). These reactions are enhanced by solid acidity and, probably, the micropores in the catalysts; and some metals supported on zeolites can enhance the formation of BTX, while other metals suppress their formation. Some hydrocarbons may

be transformed to deposited carbon by excess reaction. Solid acidity enhances the excess reaction; however, the addition of some metals, such as Au, can lead to inhibition of the reaction, while other metals enhance the carbonization reaction.

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