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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.

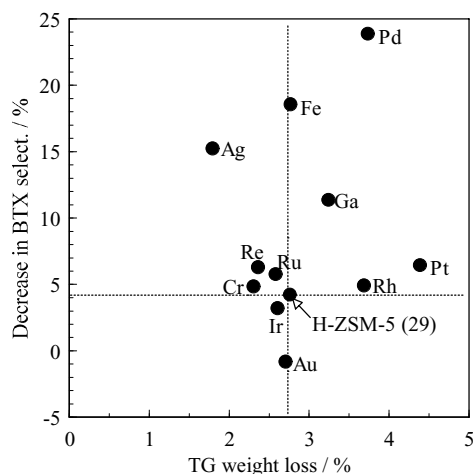
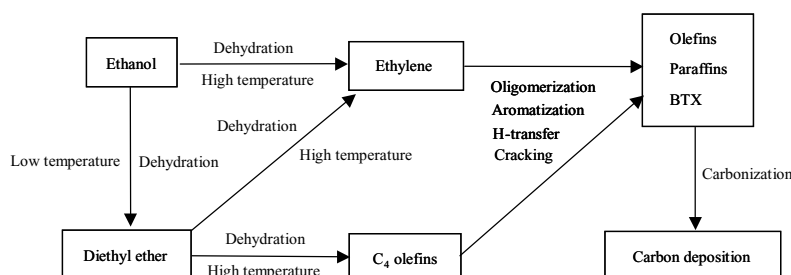


Fig. 1. Plots of the weight loss of catalyst after reaction by TG vs. the decrease in BTX selectivity at 400 °C over 0.2 g of catalyst.

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.

REFERENCES

1. E.G. Derouane, J.B. Nagy, P. Dejaifve, J.H.C. van Hooff, B.P. Spekman, J.C. Védrine, C. Naccache: *J. Catal.*, **53**, 40 (1978).
2. J.C. Oudejans, P.F. van den Oosterkamp, H. van Bekkum: *Appl. Catal.*, **3**, 109 (1982).
3. V.R. Choudhary, S. D. Sansare: *Appl. Catal.*, **10**, 147 (1984).
4. S.N. Chaudhuri, C. Halik, J.A. Lercher: *J. Mol. Catal.*, **62**, 289 (1990).
5. S.K. Saha, S. Sivasanker: *Catal. Lett.*, **15**, 413 (1992).
6. A.G. Gayubo, A.M. Tarrío, A.T. Aguayo, M. Olazar, J. Bilbao: *Ind. Eng. Chem. Res.*, **40**, 3467 (2001).
7. A.T. Aguayo, A.G. Gayubo, A. Atutxa, M. Olazar, J. Bilbao: *Ind. Eng. Chem. Res.*, **41**, 4216 (2002).