Research Article

Production of C₃₊ Olefins and Propylene from Ethanol by Zr-Modified H-ZSM-5 Zeolite Catalysts

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Ethanol conversion to C₃₊ olefins, especially propylene, using Zr-modified H-ZSM-5 catalysts was investigated. Zr-modification to H-ZSM-5 zeolite could improve the initial yield of C₃₊ olefins and propylene and could reduce the initial yield of ethylene. In general, catalysts exhibiting the higher initial yield of propylene showed the steeper decrease in propylene yield as the reaction proceeded. However, Zr-modification to H-ZSM-5 could depress the decrease in propylene yield for aqueous ethanol. As cause of catalytic deactivation, carbon deposition on catalyst and framework collapse of zeolite support can be considered. The addition of water to Zr-modified H-ZSM-5 catalyst could depress carbon deposition in some degree, and, as a result, the decrease in propylene yield could be depressed.

1. Introduction

Major compounds used by the petrochemical industry, for example, ethylene, propylene, benzene, and toluene, are at present synthesized by cracking the naphtha fraction. However, petroleum resources are limited, both quantity-wise and geographically. Moreover, combustion of petroleum produces CO₂, a greenhouse gas. Recently, much attention has been paid to biomass as alternative resources for petroleum, since biomass is renewable and carbon-neutral resource that is readily available.

Ethanol is one of the main biomass products, which can be obtained by fermentation. Catalytic production of hydrocarbons from ethanol has been reported by many researchers [1–26]. In most cases, H-ZSM-5 zeolites have been used as catalysts [1–5] with aromatics being the main products. Saha et al. reported ethanol conversion using Zn- and Ga-doped ZSM-5 zeolite catalysts, which enhanced the formation of aromatics [6].

Recently, production of hydrocarbons from ethanol using modified ZSM-5 has also been reported. For example, Calsavara et al. have reported the effect of conditions for preparation of Fe-modified H-ZSM-5 catalysts on ethanol

conversion [7, 8]. Murata et al. have reported that W- and La-modification of H-ZSM-5 zeolite to be effective for enhancing the formation of lower olefins from ethanol [9]. Inoue et al. have reported the conversion of ethanol to propylene using La-modified H-ZSM-5 zeolite with Si/Al₂ ratio of 280, an especially high ratio for production of C₃₊ olefins from ethanol [10]. Fujitani et al. have reported that P- [11] or Zr-modified [12] H-ZSM-5 catalysts show improved catalytic activity and stability for conversion of ethanol to propylene in comparison with H-ZSM-5 without modification. Sano et al. have reported conversion of ethanol to propylene over HZSM-5 type zeolites containing alkaline earth metals [13]. Gayubo et al. had reported ethanol conversion to hydrocarbons over H-ZSM-5 without metals [3–5] and recently reported Ni- [14, 15] or alkali-modified [16, 17] H-ZSM-5 catalysts for ethanol conversion.

On the other hand, production of olefins from ethanol using catalysts other than H-ZSM-5 has also been reported. For example, Berrier et al. have reported the transformation of ethanol into higher hydrocarbons on Co/Al₂O₃ catalysts [18]. More recently, Baba et al. reported the highly selective conversion of ethylene to propylene over SAPO-34; they also found SAPO-34 to be effective for ethanol conversion to

FIGURE 1: Plots of the initial yield of propylene versus the change in propylene yield over H-ZSM-5 and (Fe or Zr)/H-ZSM-5 catalysts. Numbers in parenthesis denote calcination temperature ($^{\circ}\text{C}$).

propylene [19]. Iwamoto et al. reported that Ni ion-loaded mesoporous silica MCM-41 was effective for producing lower olefins from ethanol [20].

We investigated the production of hydrocarbons from ethanol using modified H-ZSM-5 catalysts and found that Fe-addition to H-ZSM-5 zeolite could improve the selectivity of C_{3+} olefins [21, 22]. Fe is nontoxic and cheap metal. Moreover, olefins, especially propylene, are useful as not only fuels but also chemicals. Polymerized olefins can be used as plastics and can fix CO_2 from the atmosphere when in use. We examined the effect of Fe-loading and reaction temperature to improve selectivity for C_{3+} olefins and propylene and found that lower loading of Fe (1 wt%) and higher reaction temperature (450°C) results in higher selectivity of propylene and catalytic stability [23]. Moreover, to improve catalytic performance, P-addition to Fe/H-ZSM-5 was tried, since it has been reported that phosphorous modification of H-ZSM-5 zeolite can lead to better hydrothermal stability and resistance to coke deposition [11, 24]. We found that P- and Fe-modification to H-ZSM-5 leads to the improved propylene selectivity and stability for water in ethanol in comparison with H-ZSM-5 without modification and Fe-modified H-ZSM-5 catalysts [25].

In this paper, to improve the catalytic activity and stability, the effect of Zr-modification was investigated.

2. Experimental

2.1. Catalyst Preparation. As zeolite support, H-ZSM-5 ($\text{Si}/\text{Al}_2 = 30$, Zeolyst) was used. The zeolite was calcined at

FIGURE 2: Plots of TG weight loss versus the change in propylene yield over H-ZSM-5 and (Fe or Zr)/H-ZSM-5 catalysts.

500°C in a muffle furnace for 6 h, prior to use as support. H-ZSM-5 was used as not only support but also catalyst: when used as catalyst, additional calcination at 700°C in a muffle furnace for 3 h was carried out after 500°C -calcination. Two kinds of H-ZSM-5 zeolite were used as catalysts: (1) H-ZSM-5 calcined at 500°C (denoted H-ZSM-5 (500)) and (2) H-ZSM-5 calcined at 700°C after 500°C -calcination (H-ZSM-5 (700)). Zr-modified H-ZSM-5 catalysts were prepared by impregnation method. $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Wako Pure Chemicals) was used as Zr source, and loading of Zr was varied from 1 to 10 wt%. To make a comparison, Fe-modified H-ZSM-5 catalyst was also prepared. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Iwai Chemical) was used as Fe source, and loading of Fe was 1 wt%, referring to our previous work [25]. After impregnation, the wet Fe- or Zr-loaded catalysts were dried at 120°C , followed by calcination at 700°C in air-flow for 3 h.

2.2. Catalytic Activity. The catalytic activity was measured in a fixed-bed reactor with atmospheric pressure. The weight of catalyst was 0.15 g. Reaction gas was obtained by mixing N_2 and vaporized EtOH, with the flow rate of N_2 set at $60 \text{ cm}^3 \text{ min}^{-1}$, resulting in the concentration of N_2 and ethanol being 61.4 and 38.6 vol.%, respectively: WHSV was 28.7 h^{-1} . To distinguish the difference in catalytic activity (i.e., ethanol conversion), WHSV was set higher than our previous work [21–23, 25]: WHSV was 7.45 h^{-1} , and ethanol conversion was always ca. 100%. As ethanol, neat ethanol and bioethanol were used, bioethanol was obtained by mixing of neat ethanol and commercial vodka (alcohol = 50%) in ratio of 1 : 3, giving a concentration of ethanol of approximately 87.5%. Reaction temperature was 450°C , and the change

FIGURE 3: Plots of the ratio of XRD peak intensity at 23.1° (after reaction/before reaction) versus the change in product yield over H-ZSM-5 and (Fe or Zr)/H-ZSM-5 catalysts. (a) Propylene yield and (b) aromatics yield.

FIGURE 4: NH₃-TPD profiles of H-ZSM-5 and (Fe or Zr)/H-ZSM-5 catalysts.

in catalytic performance with time-on-stream was observed. Analysis of vodka by gas chromatography (GC) confirmed the chief organic compound in vodka to be ethanol, with only traces of other organic compounds present.

The effluent gas was analyzed by gas chromatography (GC) equipped with Molecular Sieve 5A and Porapak Q columns (Shinwa Chemical Industries). Two detectors were used: thermal conductivity detector (TCD) was used to detect light products (hydrogen, carbon monoxide, and carbon dioxide) and flame ionization detector (FID) to detect hydrocarbons, alcohols, aldehydes, and ethers.

The selectivity for each product was defined as (number of C atoms in the product)/(total number of C atoms in all gaseous products) $\times$ 100 (%).

2.3. Characterization. As cause of catalytic deactivation, carbon deposition can be considered, since in the case of sole H-ZSM-5 zeolite used as catalyst, carbon deposition causes catalytic deactivation [4, 5]. Therefore, to estimate carbon deposition on catalysts, thermogravimetric (TG) analyses of catalysts after 7 h reaction were carried out (Mac Science, TG-DTA2000) in flowing air with temperature varied from room temperature to 800°C at 10°C min⁻¹.

Framework collapse of zeolite support, due to dealumination of zeolite framework during reaction, may be considered as another cause of catalytic deactivation [5, 10–17, 22, 23, 25], since solid acidity of zeolite, essential for this reaction, is generated by Al atoms incorporated into zeolite framework. Therefore, X-ray diffraction (XRD) measurements were carried out (Mac Science, M18XHF22-SRA), and intensity of XRD peak of zeolite framework before and after reaction was compared to investigate the framework collapse of zeolite during reaction. Here, intensity of XRD peak at 23.1° was used as index of crystallinity. Fe species were not detected for Fe/H-ZSM-5. Zr species were

TABLE 1: Catalytic activity of H-ZSM-5 and (Fe or Zr)/H-ZSM-5 zeolite catalysts.

Metal	EtOH	EtOH conv./%	Ethylene	C ₃₊ olefins	C-selectivity/% (Propylene)	Paraffins	Aromatics
No (500)	Neat EtOH	86.4	19.1	21.3	8.6	25.3	33.8
	Vodka + EtOH	99.2	17.8	21.8	11.4	14.5	45.6
No (700)	Neat EtOH	84.3	48.9	22.6	8.3	13.7	12.0
	Vodka + EtOH	61.5	45.0	18.9	7.3	11.6	18.6
Fe	Neat EtOH	72.0	48.3	22.9	9.2	13.7	13.1
	Vodka + EtOH	86.3	49.7	21.2	8.2	12.2	15.5
Zr (1 wt%)	Neat EtOH	86.4	26.7	28.8	14.2	19.0	24.6
	Vodka + EtOH	99.2	22.0	29.8	14.2	18.3	29.6
Zr (2 wt%)	Neat EtOH	93.7	29.0	27.3	13.8	18.2	24.5
	Vodka + EtOH	94.8	24.1	26.5	12.8	17.3	31.4
Zr (5 wt%)	Neat EtOH	77.5	31.0	26.2	12.5	17.4	23.4
	Vodka + EtOH	96.7	22.4	30.7	14.3	18.8	26.2
Zr (10 wt%)	Neat EtOH	91.9	25.3	34.8	15.2	21.8	16.7
	Vodka + EtOH	69.0	45.6	20.2	9.0	13.7	18.5

Numbers of 500 and 700 mean calcination temperature (°C).

not detected for Zr/H-ZSM-5 (Zr = 1–5 wt%) but detected for Zr/H-ZSM-5 (Zr = 10 wt%) at about 30°.

NH₃-temperature-programmed-desorption (TPD) experiments of H-ZSM-5 and (Zr or Fe)/H-ZSM-5 catalysts were carried out (Nihon Bell, BEL-CAT) to measure the solid acidity. After pretreatment in flowing He at 500°C for 60 min, followed by adsorption of NH₃ at 100°C for 90 min and desorption of weak adsorbed NH₃ in He flow at 100°C for 30 min, TPD profiles were obtained under conditions of He flow with the temperature varying from 100 to 800°C at 10°C min⁻¹.

3. Results and Discussion

3.1. Catalytic Performance. Initial conversion of ethanol and initial selectivity of each product among gaseous products are shown in Table 1: main gaseous products were ethylene, C₃₊ olefins (C₃–C₇ olefins were detected), paraffins, and aromatics (benzene, toluene, xylenes, mesitylene, and pseudocumene). Zr-addition to H-ZSM-5 improved ethanol conversion in comparison with H-ZSM-5 (700), but effect of Fe-addition on ethanol conversion was not clear. Presence of water enhanced ethanol conversion for H-ZSM-5 (500), Fe/H-ZSM-5, and Zr/H-ZSM-5 (Zr = 1–5 wt%) but reduced conversion for H-ZSM-5 (700) and Zr/H-ZSM-5 (Zr = 10 wt%), suggesting that adequate amount of Zr enhances ethanol conversion but excess amount of Zr reduces ethanol conversion by presence of water. In comparison with H-ZSM-5 (700) and Fe/H-ZSM-5, Zr-modification improved selectivity of C₃₊ olefins, propylene, paraffins, and aromatics but reduced ethylene selectivity. In general, catalysts exhibiting high ethylene selectivity showed low selectivity of C₃₊ olefins and propylene, and catalysts exhibiting high selectivity of paraffins and aromatics showed high selectivity of C₃₊ olefins and propylene. In most cases, presence of water contained in ethanol enhanced the aromatics selectivity and reduced the selectivity of ethylene, C₃₊ olefins, propylene, and paraffins.

Ethanol conversion, selectivity, and yield of each product changed with time-on-stream and propylene yield decreased. Yield (%) was defined as (ethanol conversion (%)) × (selectivity of each product (%))/100. Figure 1 shows the plot of the initial yield of propylene versus change in propylene yield during 7 h reaction. In general, catalysts showing the higher initial yield of propylene showed the larger decrease in propylene yield. For neat ethanol, Zr-addition led to the higher initial yield of propylene but led to the larger decrease in propylene yield, while, for aqueous ethanol, 1–5 wt% of Zr-addition improved the initial yield of propylene with inhibiting the decrease in propylene yield, but 10 wt% reduced the initial yield of propylene and the decrease in yield. On the other hand, Fe-addition was not so effective for the increase in propylene yield and the suppression of decrease in propylene yield.

3.2. Carbon Deposition. Figure 2 shows plots of weight loss during TG analyses due to combustion of deposited carbon versus change in propylene yield during 7 h reaction. In general, catalysts exhibiting the larger amount of deposited carbon showed the steeper decrease in yield, suggesting that carbon deposition during reaction may be a cause of catalytic deactivation. Moreover, for neat ethanol, Zr-modification to H-ZSM-5 enhanced carbon deposition in comparison with H-ZSM-5 (700), while, for aqueous ethanol, Zr-modification did not affect the amount of deposited carbon so significantly. These results suggest that water contained in ethanol can reduce the amount of deposited carbon, and, as a result, the decrease in propylene yield can be inhibited in some degree. On the other hand, Fe-addition did not lead to increase in carbon deposition, and the effect to change in propylene yield was not clear.

It has been reported that addition of P [11] or alkali earth metal [13] can inhibit carbon deposition. However, in the case of Zr-modification, different results from these cases were obtained.

FIGURE 5: Catalytic performance as a function of time. (a) H-ZSM-5 (700) using neat EtOH, (b) Zr/H-ZSM-5 (Zr = 5 wt%) using neat EtOH, and (c) Zr/H-ZSM-5 (Zr = 5 wt%) using mixture of vodka and EtOH.

3.3. Framework Collapse of Zeolite. Figure 3 shows plots of the ratio of XRD peak intensity (after reaction/before reaction) versus change in product yield during 7 h reaction: (a) propylene yield and (b) aromatics yield. As shown in Figure 3(a), except for Zr/H-ZSM-5 (Zr = 10 wt%), water in ethanol enhanced framework collapse. In most cases, Zr-modified catalysts showed higher ratio of peak intensity (after reaction/before reaction) than sole H-ZSM-5, suggesting that Zr-modification can inhibit framework

collapse of zeolite support during reaction. These results are consistent with Fujitani's report [12]. There seems to be a weak inverse correlation between the ratio of intensity (after reaction/before reaction) and change in propylene yield: catalysts showing significant framework collapse could inhibit the decrease in propylene yield.

Figure 3(b) shows no clear correlation between the ratio of XRD peak intensity and change in aromatics yield. However, for each catalyst, the decrease in aromatics was

larger for aqueous ethanol than for neat ethanol. These results suggest that the decrease in acidic site by framework collapse of zeolite reduces aromatics formation and leads to decrease in propylene yield. Catalysts showing large decrease in aromatics yields could inhibit the decrease in propylene yield relatively.

XRD peak of deposited carbon was not observed. Similar results were obtained by Ouyang's research: bioethanol was converted to ethylene over La-modified H-ZSM-5 catalysts [26]. In the case of addition of P [11] or alkali earth metal [13], also, the framework collapse due to dealumination could be suppressed.

3.4. Results of NH_3 -TPD Measurements. Figure 4 shows the NH_3 -TPD profiles of H-ZSM-5 and (Fe or Zr)/H-ZSM-5 catalysts. H-ZSM-5 (500) showed NH_3 -desorption peak at ca. 400°C. The acidic site showing this desorption peak is essential for the aromatics formation. For 1–5 wt% of Zr-loading, strong desorption peak appeared, while, for 10 wt%, desorption peak was slightly weakened. H-ZSM-5 (700) showed weak desorption peak, while, in the Fe/H-ZSM-5, NH_3 -desorption peak was not clear. These results suggest that calcination at 700°C after 500°C-calcination to H-ZSM-5 reduces the amount of acidic site of zeolite by framework collapse due to dealumination, and Fe-addition enhances the framework collapse. However, adequate degree of Zr-modification could inhibit the framework collapse.

3.5. Catalytic Performance as a Function of Time. Catalytic performance as a function of time was investigated. Figure 5 shows the catalytic performance: (a) H-ZSM-5 (700) using neat ethanol, (b) Zr/H-ZSM-5 (Zr = 5 wt%) using neat ethanol, and (c) Zr/H-ZSM-5 (Zr = 5 wt%) using aqueous ethanol.

In the case of H-ZSM-5 (700) using neat ethanol (Figure 5(a)), ethanol conversion decreased from 84.3 to 32.8%. Selectivity of C_{3+} olefins and propylene decreased (22.6 → 16.3% and 8.3 → 5.5%, resp.). Aromatics selectivity decreased from 12.0 to 8.0%, while ethylene selectivity increased from 48.9 to 60.9%.

In the case of Zr/H-ZSM-5 using neat ethanol (Figure 5(b)), ethanol conversion decreased from 77.5 to 43.7%. Selectivity of C_{3+} olefins and propylene decreased (26.2 → 19.5% and 12.5 → 7.8%, resp.). Degree of decrease in ethanol conversion was smaller than H-ZSM-5 (700), while initial conversion of ethanol was slightly lower than H-ZSM-5 (700). Zr-addition enhanced selectivity of C_{3+} olefins and propylene. On the other hand, aromatics selectivity decreased from 23.4 to 10.0%, while ethylene selectivity increased from 31.0 to 54.5%. By Zr-addition, initial selectivity of aromatics increased and that of ethylene decreased. However, change in selectivity with time-on-stream was larger than the case of H-ZSM-5 (700).

In the case of Zr/H-ZSM-5 using aqueous ethanol (Figure 5(c)), ethanol conversion did not change at near 100% (96.7 → 97.8%). Selectivity of C_{3+} olefins and propylene was higher than for neat ethanol, and the selectivity did not decrease so significantly (30.7 → 26.7% and 14.3 → 10.7%, resp.). On the other hand, change in selectivity of

aromatics and ethylene (26.2 → 8.7% and 22.4 → 49.1%, resp.) was larger than for neat ethanol.

These results suggest that Zr-addition is effective for ethanol conversion to C_{3+} olefins and propylene, and the effect is more significant for aqueous ethanol than for neat ethanol.

4. Conclusions

In catalytic production of C_{3+} olefins and propylene from ethanol using modified H-ZSM-5 zeolite catalysts, Zr-modification could improve the initial yield of C_{3+} olefins and propylene. In general, catalysts exhibiting the higher initial yield of propylene showed the steeper decrease in propylene yield. However, Zr-addition could depress the decrease in propylene yield for aqueous ethanol. As cause of catalytic deactivation, carbon deposition and framework collapse of zeolite support can be considered. The addition of water to Zr-modified H-ZSM-5 catalyst could depress carbon deposition in some degree, and, as a result, the decrease in propylene yield could be depressed. Though effect of Zr-addition on catalytic activity was reported by Fujitani et al. [12], the effect of presence of water in ethanol was not reported. Therefore, the results in this study show that Zr-modified H-ZSM-5 catalysts are promising candidate for conversion of aqueous ethanol to propylene.

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