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Catalytic Ethylene Oligomerization over Ni/Al-HMS: A Key Step in Conversion of Bio-Ethanol to Higher Olefins

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Received: 12 October 2018; Accepted: 8 November 2018; Published: 12 November 2018

Abstract: Al-modified hexagonal mesoporous silica (HMS) materials were synthesized using dodecylamine as a template according to the methods reported in the literature. FT-IR spectra proved that Al^{3+} ions entered in the HMS framework in Al-HMS (prepared by sol-gel reaction) but Al^{3+} ions existed in the extra-framework in Al/HMS (prepared by post-modification). NH_3 -TPD indicated that either Al-HMS or Al/HMS had solid acid sites on the surface, and the acidic strength of Al/HMS was stronger than that of Al-HMS. For ethylene oligomerization at 200 °C under 1 MPa, Ni/Al-HMS showed an ethylene conversion of 96.3%, which was much higher than that over Ni/Al/HMS (45.6%). The selectivity for C_4H_8 , C_6H_{12} , C_8H_{16} , and C_{8+} was 37.7%, 24.5%, 24.0%, and 9.1% for ethylene oligomerization over Ni/Al-HMS, respectively. Ni/Al-MCM-41, which has been reported as an effective catalyst for ethylene oligomerization in the literature, showed a high ethylene conversion (95.2%) similar to that of Ni/Al-HMS in this study. However, the selectivity for C_8H_{16} over Ni/Al-MCM-41 (16.3%) was lower than that over Ni/Al-HMS (24.0%) in the ethylene oligomerization. For ethanol dehydration at 300 °C under 1 MPa, a commercial H-ZSM-5 catalyst showed a high ethylene yield (91.2%) after reaction for 24 h using a feed containing 90 wt.% ethanol and 10 wt.% water. In this study, a two-step process containing two fixed-bed reactors and one cold trap was designed to achieve the direct synthesis of higher olefins from bio-ethanol. The cold trap was used to collect the water formed from ethanol dehydration. By using H-ZSM-5 as a catalyst for ethanol dehydration in the first reactor and using Ni/Al-HMS as a catalyst for ethylene oligomerization in the second reactor, higher olefins were continuously formed by feeding a mixture containing 90 wt.% ethanol and 10 wt.% water. The yields of higher olefins did not decrease after reaction for 8 h in the two-step reaction system.

Keywords: bio-ethanol; dehydration; ethylene; oligomerization; higher olefins; Ni; Al-modified mesoporous silica

1. Introduction

The conversion of biomass to liquid fuels has become an important research field because biomass utilization has an effect in reducing greenhouse gas emission [1]. Bio-ethanol is produced in a large scale from sugary, starchy, and lignocellulosic biomasses by yeast fermentation [2]. Currently, bio-ethanol accounts for above 90% of worldwide biofuel production. Bio-ethanol is mainly used as fuel for automobiles by blending with gasoline. Although bio-ethanol is an attractive fuel; the needs of transportation fuel for automobiles will be reduced from now due to the popularization of electric vehicle and hydrogen-fueled car. Hence, bio-ethanol is expected to be in surplus in future years. It is necessary to develop new technologies to utilize the surplus bio-ethanol. Production of hydrogen by the steam reforming of bio-ethanol is an available technology [3]. However, hydrogen is expected

to be obtained from water electrolysis using the electric power from renewable energy. Recently, the technology for converting bio-ethanol to higher olefins has received extensive interests because the higher olefins can be used for producing jet fuel and fine chemicals [4,5].

Ethylene is a platform in conversion of bio-ethanol to higher olefins [6–8]. At first, ethylene is obtained through the hydration of bio-ethanol. Then, the formed ethylene is converted to higher olefins through the oligomerization of ethylene. Highly active catalyst for ethylene oligomerization is the key technology in conversion of bio-ethanol to higher olefins. Acid strength and pore size of the catalyst greatly influence the product distribution in ethylene oligomerization [9]. Acidic zeolites (H-ZSM-5 and H-Beta zeolite) usually form C_3 – C_4 olefins from ethylene oligomerization due to strong acidity and small micropores [10–12]. Also, the direct synthesis of C_3H_6 from bio-ethanol has been reported in the literature because direct synthesis has a high efficiency in industry [13].

Mesoporous silica materials (such as MCM-41, SBA-15, HMS, and so on) have high thermal stability (above 850 °C), large surface area (about 1000 m² g^{−1}), and uniform-sized pores [14–17]. Hexagonal mesoporous silica (HMS) can be easily synthesized using dodecylamine at room temperature [17]. Also, transition metal cations (such as Al³⁺, Ti⁴⁺, and so on) can be uniformly incorporated into the HMS framework with high content [18]. Al-HMS has physical and textural properties similar to those of Al-MCM-41 but has substantially higher Bronsted acidity [19]. Because HMS has these advantages among mesoporous silica materials, HMS-based materials have been used as catalysts or as supports in the catalysis field [16–29].

Bifunctional catalysts containing Ni and solid acid are regarded as the most promising catalysts for the synthesis of C_{6+} higher olefins by ethylene oligomerization. The design of a large pore in a catalyst is an important task in the synthesis of higher olefins. The zeolites (H-ZSM-5 and H-Beta zeolite) with large cages and hierarchical-type porosity had been synthesized and they formed C_{6+} higher olefins from ethylene oligomerization [10]. However, coke was formed on the surface of acidic zeolite during the reaction due to the strong acidity of zeolite [10,12]. The coke blocked the pores of zeolite and caused the catalyst deactivation during the reaction. In order to overcome the catalyst deactivation, weak solid acids (such as amorphous silica-alumina, sulfated alumina, and so on) were used as supports for Ni in the ethylene oligomerization [30–32]. A relatively high reaction temperature was necessary to obtain a high ethylene conversion because using a weak solid acid increased the catalyst stability but decreased the reaction speed. Because mesoporous silica materials have uniformed large pores and weak solid acidity, catalysts containing Ni and mesoporous silica materials have been reported as effective catalysts in the synthesis of higher olefins by ethylene oligomerization [33–38]. Ni/Al-MCM-41 and Ni/Al-SBA-15 selectively formed C_4H_8 , C_6H_{12} , C_8H_{10} , and $C_{10}H_{20}$ from ethylene oligomerization (due to the large pores of MCM-41 and SBA-15), and they showed high catalytic stability because no coke was formed on the catalyst surface during the reaction (due to the weak acidity of Al-MCM-41 and Al-SBA-15) [37,38].

The catalytic ability of Al-modified HMS has not been investigated for the oligomerization of ethylene in the literature. Moreover, there is no report of the direct synthesis of C_4^+ higher olefins from bio-ethanol in the literature. In the present study, the catalysts containing Ni and Al-modified HMS have been used for ethylene oligomerization comparing with Ni/Al-MCM-41. Also, a continuous two-step process (combining ethanol dehydration and ethylene oligomerization) has been designed to achieve the direct production of higher olefins from bio-ethanol.

2. Results and Discussion

2.1. Characterization of Catalysts

Figure 1 shows the X-ray diffraction (XRD) patterns of mesoporous silica samples after calcining at 550 °C for 4 h. Al-MCM-41 showed a strong peak at about 2.5 degrees and two weak peaks at 4–6 degrees in the XRD pattern. The strong peak was corresponded to the (1 0 0) plane, and two weak peaks were corresponded to the (1 1 0) plane and the (2 0 0) plane [14]. This pattern implied

the existence of long-range linear mesoporous structure in Al-MCM-41 [15]. HMS exhibited a strong peak corresponding to the (100) plane at about 2.5 degrees and a broad band close to 5.3 degrees. This pattern implied the existence of wormhole mesoporous structure in HMS [16]. By calculating from the degree of (100) plane in the XRD pattern, HMS had a d_{100} spacing value of 35.3 Å. The value of d_{100} spacing in Al-HMS was lower than that of HMS because small Al^{3+} ions were incorporated in the HMS framework. On the other hand, the value of d_{100} spacing in Al/HMS was similar to that of HMS because Al^{3+} ions did not enter in the HMS framework.

Figure 1. X-ray diffraction (XRD) patterns of mesoporous silica samples after calcining at 550 °C for 4 h.

Figure 2 shows the FT-IR spectra of various HMS-based samples after calcining at 550 °C for 4 h. In the FT-IR spectrum of HMS, the peak at 1090 cm^{-1} was assigned to the asymmetric stretching of Si–O–Si and the peak at 810 cm^{-1} was assigned to the stretching of the tetrahedral SiO_4^{4-} structural units. HMS did not show a peak at 960 cm^{-1} in the FT-IR spectrum. Al-HMS showed a peak at 960 cm^{-1} in the FT-IR spectrum. Because the peak at 960 cm^{-1} was assigned to the stretching Si–O vibration with the neighborhood metal ions, this peak had been used to characterize the incorporation of metal ions in the silica framework [39]. The Al/HMS sample prepared by post-modification did not show a peak at 960 cm^{-1} in the FT-IR spectrum. Hence, Al^{3+} ions entered into the HMS framework in Al-HMS but existed at the outside of the HMS framework in Al/HMS.

Figure 2. FT-IR spectra of various HMS-based samples after calcining at 550 °C for 4 h. (A): HMS; (B): Al/HMS; (C): Al-HMS.

Figure 3 shows the NH_3 -TPD profiles of various samples after calcining at 550 °C for 4 h. The NH_3 -TPD measurement was used to evaluate the acidic strength of solid acids. The absorbed NH_3 molecules desorbed from weak solid acids at low temperatures and desorbed from strong solid acids at high temperatures. As shown in Figure 3, no peak could be observed in the NH_3 -TPD profile of HMS, indicating that HMS did not have any acid sites on the surface. Al-HMS had solid acid sites on the surface because a peak at 220 °C was observed in the NH_3 -TPD profile. The maximum temperature of NH_3 desorption of Al/HMS was higher than that of Al-HMS in the NH_3 -TPD profiles, implying that the acid sites in Al/HMS were stronger than those in Al-HMS. Because Al^{3+} ions were introduced in Al-HMS at the preparation step, Al^{3+} located uniformly in the HMS framework in Al-HMS. On the other hand, because Al^{3+} ions were introduced in Al/HMS by post-modification, the Al^{3+} ions existed at the extra-framework in Al/HMS. It has been reported that the extra-framework Al^{3+} ions had stronger acidity compared with the intra-framework Al^{3+} ions in Al-containing MCM-41 catalysts [40]. H-ZSM-5 exhibited two peaks at 220 and 450 °C in the NH_3 -TPD profile. Hence, H-ZSM-5 had both weak solid acid and strong solid acid on the surface. The peak at the highest temperature in the NH_3 -TPD profile corresponds to the strongest acid sites on the solid surface. H-ZSM-5 is a strong solid acid because the strongest acid sites determine the ability of a solid acid catalyst. According to the peak position at the maximum temperature in the NH_3 -TPD profiles, the acidic strength of various samples was in the order of H-ZSM-5 $\gg$ Al/HMS > Al-HMS > HMS (no acidity).

Figure 3. NH_3 -TPD profiles of various samples after calcining at 550 °C for 4 h.

2.2. Development of Catalyst for Ethylene Oligomerization

Table 1 shows the reaction results of ethylene oligomerization over various catalysts containing Ni and solid acid. Ni/H-ZSM-5 showed a high ethylene conversion of 90.7% at a low reaction temperature of 150 °C due to strong solid acidity of H-ZSM-5. Ni/H-ZSM-5 formed C_4H_8 as the major product and did not form any olefins larger than C_6H_{12} . Also, Ni/H-ZSM-5 formed a relatively large amount of C_3H_6 from the cracking of C_6H_{12} formed in the reaction. Hence, Ni/H-ZSM-5 is not a suitable catalyst for producing higher olefins from ethylene oligomerization. Three catalysts containing Ni and mesoporous silica used in this study produced higher olefins larger than C_6H_{12} from the ethylene oligomerization at 200 °C. Ni/Al-HMS showed an ethylene conversion of 96.3%, which was much higher than that over Ni/Al/HMS (45.6%) for the reaction. In Al-HMS, Al^{3+} ions entered in the positions of Si^{4+} ions in the framework and existed in the neighborhood of Si^{4+} ion. In Al/HMS, Al^{3+} ions did not enter in the positions of Si^{4+} ions and existed far from Si^{4+} ion. Hence, the existence of Al^{3+} ions in the neighborhood of Si^{4+} ions is important for improving the catalytic activity of

Ni-based catalyst in the ethylene oligomerization. Ni/Al-MCM-41 has been reported as an effective catalyst for the synthesis of higher olefins from ethylene oligomerization [34,38]. As shown in Table 1, Ni/Al-MCM-41 showed an ethylene conversion of 95.2% at 200 °C. Ni/Al-MCM-41 showed a C₈C₁₆ selectivity of 16.3%, which was lower than that over Ni/Al-HMS (24.0%) for the reaction.

Table 1. Reaction results of ethylene oligomerization over various catalysts containing Ni and solid acid ^a.

Catalyst ^b	Conversion (%)	Selectivity (%)				
		C ₄ H ₈	C ₆ H ₁₂	C ₈ C ₁₆	C ₈₊	Others ^c
Ni/Al-HMS	96.3	37.7	24.5	24.0	9.1	2.9
Ni/Al/HMS	45.6	30.3	19.4	33.7	11.8	3.8
Ni/Al-MCM-41	95.2	45.6	28.5	16.3	6.2	2.6
Ni/H-ZSM-5 ^d	90.7	77.6	1.1	0	0	19.2

^a Reaction conditions: catalyst amount: 2 g; feed gas flow rate: 60 mL min^{−1}; feed gas composition: 90% C₂H₄ + 10% Ar; reaction temperature: 200 °C; reaction pressure: 1 MPa. ^b Ni content: 2 wt.%. ^c Others: C₃H₆, C₂H₆, and so on. ^d Reaction at 150 °C.

Figure 4 shows the dependence of Ni content in Ni/Al-HMS for the oligomerization of ethylene. Al-MHS (without Ni) showed a very low ethylene conversion of 2.2%, indicating that the weak acidity of Al-HMS just had a very low catalytic activity for ethylene oligomerization at 200 °C. The ethylene conversion greatly increased by introducing Ni in Al-HMS, suggesting that the Ni sites in Ni/Al-HMS were the main active sites in the ethylene oligomerization. The ethylene conversion increased with increasing Ni content from 0 to 2 wt.%, and then slightly decreased at above 2 wt.% in Ni/Al-HMS. It has been reported that the Ni species exchanged into the pores of mesoporous silica are catalytically active species and the Ni species loaded on the mesoporous silica are inactive for the ethylene oligomerization on Ni/Al-MCM-41 [41]. Hence, about 2 wt.% Ni could be exchanged into the pores of Al-HMS and the excessive Ni was loaded on the Al-HMS surface when the Ni content was larger than 2 wt.% in Ni/Al-HMS. The selectivity for C₄H₈ decreased with increasing Ni content from 0 to 1.5 wt.% and almost did not change at above 1.5 wt.% in Ni/Al-HMS. On the contrary, the selectivity for C₆H₁₂ and the selectivity for C₈H₁₆ increased with increasing Ni content from 0 to 1.5 wt.% and almost did not change at above 1.5 wt.% in Ni/Al-HMS. Hence, C₄H₈ was the primary product and it converted to C₆₊ higher olefins during the reaction.

Figure 4. Dependence of Ni content in Ni/Al-HMS for the oligomerization of ethylene. Reaction conditions: same as those listed in Table 1.

Figure 5 shows the reaction pathway of C_8H_{16} formation in the oligomerization of ethylene on Ni/Al-HMS. As discussed above, Ni sites are the main active sites for the ethylene oligomerization over Ni/Al-HMS. The oligomerization of ethylene on Ni is a Schulz–Flory type oligomerization. Any intermediate products formed during the reaction undergo further oligomerization (with ethylene) on Ni or desorption from Ni at the same time. Therefore, the products should obey a Schulz–Flory distribution with decreasing in the order of $C_4 > C_6 > C_8 > C_{10}$. However, the selectivity for C_8H_{16} was similar to the selectivity for C_6H_{12} at each Ni content in Ni/Al-HMS (as shown in Figure 4). Hence, some other active species (except Ni) improved the amount of C_8H_{16} from the ethylene oligomerization over Ni/Al-HMS. As discussed above, although Al-HMS had acid sites on the surface (by introduction of Al^{3+} ions), the acidity of Al-HMS was weak and thus Al-HMS showed a very low activity for the ethylene oligomerization. Also, C_4H_8 formed from the ethylene dimerization was the primary product in the ethylene oligomerization over Ni/Al-HMS. Because C_4H_8 had a higher reactivity than ethylene, it can be assumed that the primary product C_4H_8 dimerized to C_8H_{16} on the acid site of Al-HMS. On Ni/Al-HMS, C_8H_{16} was formed not only from the reaction of C_6H_{12} with C_2H_4 on Ni sites but also from the dimerization of C_4H_8 on acid sites of Al-HMS. The acid sites in Al-HMS improved the amount of C_8H_{16} and caused a non-Schulz–Flory type distribution of the products in the oligomerization of ethylene over Ni/Al-HMS.

Figure 5. Reaction pathway of C_8H_{16} formation in the oligomerization of ethylene on Ni/Al-HMS.

Figure 6 shows the illustration of Bronsted acid sites in Ni/Al-HMS. The Bronsted acid sites are formed on the O^{2-} ions which simultaneously bond with Si^{4+} ions and Al^{3+} ions in Ni/Al-HMS. This model has been suggested in the literature for the oligomerization of ethylene over Ni/Al-MCM-41 and Ni/Al-SBA-15 [35,37]. This is the reason that the introduction of Al^{3+} ions brought solid acid sites in Al-HMS. The Bronsted acid sites have been assumed as the active sites for the olefin dimerization. Proton-type ion-exchange resin, a type of solid catalyst containing only Bronsted acid (without Lewis acid), has been known as an effective catalyst for the olefin dimerization [42]. Also, the Bronsted acid sites in Ni/Al-MCM-41 have been reported as the active sites for the dimerization of C_4H_8 [35]. Furthermore, it has been reported that Al-HMS has physical and textural properties similar to those of MCM-41 but with substantially higher Bronsted acidity [19]. Hence, Al-HMS is expected to have a stronger ability for C_4H_8 dimerization compared with that of Al-MCM-41. This is the reason that the selectivity for C_8H_{16} over Ni/Al-HMS was larger than that over Ni/Al-MCM-41 in the oligomerization of ethylene (as shown in Table 1).

Figure 6. Illustration of Bronsted acid sites in Ni/Al-HMS.

2.3. Catalytic Ethanol Dehydration over H-ZSM-5

Bio-ethanol produced by the fermentation of biomass is a mixture of ethanol and water. Because ethanol and water form a binary azeotrope system containing 95.6 wt.% ethanol and 4.4 wt.% water, the conventional distillation cannot produce high-purity ethanol above 95.6 wt.%. The direct use of hydrous ethanol to produce ethylene is an environmentally friendly method by avoiding a strenuous separation process. The development of catalyst for the dehydration of ethanol to ethylene has been researched for many years [43]. The recent researches focus on improvement of catalyst stability in diluted bio-ethanol and improvement of catalyst activity at low reaction temperatures [6,7].

The dehydration of ethanol to ethylene is an acid-catalytic reaction which needs the existence of acid sites on the catalyst surface. Acidic zeolites, transition metal oxides, acidic clays, and heteropolyacids have been used in the dehydration of ethanol to ethylene [43]. Among various catalysts, acidic zeolite H-ZSM-5 is known as a highly active catalyst for the dehydration of ethanol [44]. Hence, we investigated a commercial H-ZSM-5 for the dehydration of ethanol in this study.

Table 2 shows the effect of reaction temperature in the dehydration of ethanol over H-ZSM-5. The data were obtained after reaction for 1 h at various reaction temperatures. The C₂H₅OH conversion was 64.8% and the selectivity for C₂H₄ was 75.6% for the reaction at a low temperature of 250 °C. The selectivity for the by-product C₂H₅OC₂H₅ was high (23.8%) at 250 °C but it greatly decreased with increasing reaction temperature from 250 to 325 °C. Both the C₂H₅OH conversion and the selectivity for C₂H₄ increased with increasing reaction temperature from 250 to 300 °C. When the reaction was carried at a high temperature of 325 °C, the C₂H₅OH conversion continuously increased to 98.7% but the selectivity for C₂H₄ began to decrease due to CH₃CHO formation. In the dehydration of ethanol at 300 °C, the C₂H₅OH conversion was 95.4% and the selectivity for C₂H₄ was 96.9%, which gave a C₂H₄ yield of 92.4% for the dehydration of ethanol over H-ZSM-5.

Table 2. Effect of reaction temperature in the dehydration of ethanol over H-ZSM-5 ^a.

Temperature (°C)	C ₂ H ₅ OH Conversion (%)	Yield (%)			
		C ₂ H ₄	C ₂ H ₅ OC ₂ H ₅	CH ₃ CHO	Others ^b
250	64.8	75.6	23.8	0	0.6
275	82.5	90.3	8.3	0.2	1.2
300	95.4	96.9	1.4	0.4	1.3
325	98.7	93.5	0.5	4.4	1.6

^a Reaction conditions: catalyst: 2 g; liquid feed rate: 0.13 g min^{−1}; liquid feed composition: 90 wt.% C₂H₅OH + 10 wt.% H₂O; Ar flow rate: 10 mL min^{−1}; reaction pressure 1 MPa. ^b Others: CH₄, C₂H₆, and so on.

Equations (1)–(4) list the main reactions that occurred in the dehydration of ethanol on the solid acid catalysts. C₂H₄ was formed through the dehydration from one C₂H₅OH molecule (Equation (1)). C₂H₅OC₂H₅ was formed through the dehydration between two C₂H₅OH molecules (Equation (2)) [39]. At high reaction temperatures, the by-product C₂H₅OC₂H₅ decomposed to C₂H₅OH and C₂H₄ (Equation (3)) [8]. CH₃CHO was formed at high temperatures through the dehydrogenation of ethanol (Equation (4)) [8].

Figure 7 shows the influence of water amount in feed for the dehydration of ethanol over H-ZSM-5. When a pure ethanol (without water) was fed for the reaction, the C₂H₄ yield almost did not decrease after reaction at 300 °C for 24 h. Using a feed containing 90 wt.% ethanol and 10 wt.% water, the C₂H₄ yield was 92.4% after reaction for 1 h and the C₂H₄ yield decreased to 91.2% after reaction for

24 h. By increasing water amount in feed from 10 wt.% to 50 wt.%, the C_2H_4 yield after reaction for 1 h slightly decreased, and the C_2H_4 yield after reaction for 24 h obviously decreased during the reaction. A large amount of water in feed caused the catalyst deactivation in the dehydration of ethanol over H-ZSM-5.

Figure 7. Influence of water amount in feed for the dehydration of ethanol over H-ZSM-5. Reaction conditions: catalyst: 2 g; liquid feed rate: 0.13 mL min^{-1} ; Ar flow rate: 10 mL min^{-1} ; reaction pressure 1 MPa; reaction temperature: 300°C .

The purpose of this study is designing a continuous process for the direct synthesis of higher olefins from bio-ethanol by combining ethanol dehydration and ethylene oligomerization, but is not developing a highly active catalyst for the dehydration of ethanol. Because an ethylene yield of 91.2% could be obtained after reaction for 24 h using a feed containing 90 wt.% ethanol and 10 wt.% water (as shown in Figure 7), commercial H-ZSM-5 had a high catalytic performance for the dehydration of hydrous ethanol at 300°C . Hence, we used the commercial H-ZSM-5 as a catalyst for the dehydration of hydrous ethanol in the following part.

2.4. Production of Higher Olefins from Hydrous Ethanol by Two-Step Process

A two-step reaction system was designed in this study to achieve the direct synthesis of higher olefins from bio-ethanol by combining ethanol dehydration and ethylene oligomerization. H-ZSM-5 was used as a catalyst for the first step of ethanol dehydration, and Ni/Al-HMS was used as a catalyst for the second step of ethylene oligomerization.

Because the binary azeotrope system of ethanol and water contains 4.4 wt.% of water, a mixture of ethanol and water is usually used as a feed in the ethanol dehydration. Moreover, a large amount of water (steam) is formed from the first step of ethanol dehydration (as shown in Equations (1) and (2)). The water certainly causes the catalyst deactivation in the following step of ethylene oligomerization over Ni/Al-HMS. It is necessary to remove the steam from the mixed gas before introducing the gas into the second reactor of ethylene oligomerization. A cold trap has been used for separating steam from other gas products in some reaction systems, such as in Fischer–Tropsch synthesis and in methanol dehydrogenation [45,46].

Figure 8 shows an illustration of the reaction process for the production of higher olefins from hydrous ethanol. The system contained two fixed-bed reactors and one cold trap. The two fixed-bed reactors were used to achieve ethanol dehydration and ethylene oligomerization, respectively. The cold trap was used to eliminate the steam from the mixed gas before the second step of ethylene oligomerization. The reaction pressure in the system was controlled at 1 MPa by a back-pressure regulator.

Figure 8. Illustration of reaction process for the production of higher olefins from hydrous ethanol. (1) Ethanol-water tank, (2) Ar cylinder, (3) fixed-bed reactor A (for ethanol dehydration), (4) cold trap, (5) ice-water tank, (6) fixed-bed reactor B (for ethylene oligomerization), (7) back-pressure regulator, (8) on-line GC system.

During the reaction, a mixture of ethanol and water (containing 90 wt.% ethanol and 10 wt.% water) was fed from a tank by a high-pressured micro-pump to reactor A (packed with H-ZSM-5 catalyst) to achieve the dehydration of ethanol to ethylene at 300 °C. At the same time, Ar was also introduced in reactor A from a cylinder as a carry gas and an inner standard material for calculation. Then, the gas which flowed out from the outlet of reactor A was introduced into a cold trap (cooled by ice-water) to collect the formed water, unreacted ethanol, by-products diethyl ether and acetaldehyde from the first step of ethanol dehydration. Finally, the gas which flowed out from the cold trap was introduced into reactor B (packed with Ni/Al-HMS catalyst) to achieve the oligomerization of ethylene at 200 °C.

Figure 9 shows the time course of olefin yield obtained from the system containing two fixed-bed reactors and one cold trap. A mixture of 90 wt.% C_2H_5OH and 10 wt.% H_2O was fed in the reactor A with a rate of 0.13 g min^{-1} . By assuming the yield of C_2H_4 was 92% over H-ZSM-5 (Table 2) in the reactor A and water was collected in the cold trap, the gas which introduced in the reactor B contained 52.4 mL min^{-1} of C_2H_4 and 10 mL min^{-1} of Ar. After reaction for 1 h in the two-step process, the yields of C_2H_4 , C_4H_8 , C_6H_{12} , C_8H_{16} , and C_{8+} were 1.8%, 35.7%, 22.5%, 22.1%, and 7.6%, respectively. Moreover, the yield of each olefin formed from the two-step process almost did not change after reaction for 8 h under a reaction pressure of 1 MPa.

Figure 9. Time course of olefin yield obtained from the system containing two fixed-bed reactors and one cold trap. Reaction pressure: 1 MPa; liquid feed rate: 0.13 g min^{−1}; liquid feed composition: 90 wt.% C₂H₅OH + 10 wt.% H₂O; Ar flow rate: 10 mL min^{−1}. First reactor: H-ZSM-5: 2 g; reaction temperature: 300 °C. Second reactor: 2 wt.% Ni/Al-HMS: 2 g; reaction temperature: 200 °C.

3. Experimental Section

3.1. Catalyst Syntheses

HMS was prepared using dodecylamine as a template according to the method in the literature [16]. A clear solution of Si(OC₂H₅)₄ (1.00 mol) in ethanol (6.54 mol) was added to a stirring solution of dodecylamine (0.27 mol) and HCl (0.02 mol) in water (36.3 mol). Then, the resulting gel was aged for 18 h at room temperature to form a crystalline templated product. The solid sample obtained by filtration was dried at 110 °C for 24 h. Finally, the sample was calcined in air at 550 °C for 4 h to remove the template.

Al-HMS which incorporated Al³⁺ ions in the HMS framework was prepared according to the method in the literature [19]. A clear solution containing 0.02 mol of Al(iso-OC₃H₇)₃ in 35 mL isopropyl alcohol and 0.2 mol of Si(OC₂H₅)₄ in 80 mL ethanol (Al:Si = 1/10 (molar ratio)) was heated at 70 °C for 4 h with vigorous stirring. Then, the solution was added to a solution containing 0.05 mol dodecylamine in 80 mL of water and 120 mL of ethanol. The solid sample obtained by filtration was dried at 110 °C for 24 h. Finally, the sample was calcined in air at 550 °C for 4 h to remove the template.

Al/HMS was prepared by grafting Al³⁺ ions on HMS external surface according to the method in the literature [18,29]. The HMS sample which calcined at 550 °C for 4 h was impregnated with Al(iso-OC₃H₇)₃ in isopropyl alcohol (Al:Si = 1/10 (molar ratio)), following by adding 25 mL H₂O to precipitate aluminum oxide. After stirring at room temperature for 3 h, the solid product was filtrated, dried at 110 °C for 24 h, and calcined in air at 550 °C for 4 h.

Al-MCM-41 was prepared using cetyltrimethylammonium bromide (CTMABr) (25% in water) as a template according to the method in the literature [14,15]. Tetramethylammonium silicate solution (with a molar ratio of OH[−] to Si of 0.26) was used as a silica source. The gel with a molar composition of 4 Si:0.4 Al:CTMABr:250 H₂O was heated at 100 °C for 4 days. As-synthesized Al-MCM-41 was obtained by filtration. The as-synthesized Al-MCM-41 was dried at 110 °C for 24 h, and then calcined in air at 550 °C for 4 h to remove the structurally incorporated template.

Ni/Al-HMS, Ni/Al/HMS, and Ni/Al/MCM-41 were prepared by cationic exchange with NH₄NO₃ solution according to the method in the literature [34]. Al-HMS, Al/HMS, or Al/MCM-41 was treated with an aqueous solution of NH₄NO₃ to form NH₄-type sample. Then, the NH₄-type

sample was added an aqueous solution of $\text{Ni}(\text{NO}_3)_2$ and was stirred at 50 °C for 3 h for exchange of NH_4^+ with Ni^{2+} . The exchange sample was dried at 110 °C for 24 h and calcined in air at 550 °C for 4 h.

Acidic zeolite H-ZSM-5 was prepared from Na-ZSM-5 (Tosho Co., Tokyo, Japan, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23.2$, surface area: $322 \text{ m}^2 \text{ g}^{-1}$) by ion-exchange. Na-ZSM-5 was treated with an aqueous solution of NH_4NO_3 to form NH_4 -ZSM-5. The obtained NH_4 -ZSM-5 was dried at 110 °C for 24 h and calcined in air at 550 °C for 4 h to form H-ZSM-5.

Ni/H-ZSM-5 was prepared by an wetness impregnation of H-ZSM-5 in $\text{Ni}(\text{NO}_3)_2$ aqueous solution. The water solvent was removed by evaporating at 95 °C. After impregnation, the obtained solid sample was dried at 110 °C for 24 h and calcined in air at 550 °C for 4 h.

3.2. Catalyst Characterization

The crystalline structure was characterized by an X-ray diffractometer (MAC Science MXP-18, MAC Science Co. Japan, Tokyo, Japan) operated at 40 kV and 50 mA using Cu $K\alpha$ radiation. Fourier transform infrared spectra (FT-IR) measurement were recorded using a JASCO FT/IR spectrometer (JASCO Co., Osaka, Japan) under atmospheric conditions. A KBr pellets technology was used in the FT-IR measurement and the mass ratio of sample to KBr was 1:100. Temperature-programmed desorption of ammonia (NH_3 -TPD) measurement was carried out using a BELCAT-B automatic system (Bell Co. Japan, Tokyo, Japan). A thermal conductivity detector (TCD) (Shimadzu Co., Kyoto, Japan) and an Omnistar Q-mass (Shimadzu Co., Kyoto, Japan) were used for detecting ammonia. In a typical NH_3 -TPD measurement, 0.05 g sample was pretreated in a He flow (50 mL min^{-1}) at 400 °C for 1 h. After the furnace was cooled to 100 °C, ammonia was adsorbed onto the sample's surface. The sample was evacuated at 100 °C for 1 h to eliminate the weakly physical adsorbed ammonia, and then NH_3 -TPD was recorded from 100 to 600 °C by heating the furnace with a rate of $8 \text{ }^\circ\text{C min}^{-1}$.

3.3. Reactions and Instruments

The oligomerization of ethylene was performed in a fixed-bed catalytic reaction system. The catalyst (24–60 meshes) was packed in a stainless-steel reactor (*i.d.*: 1 cm; length: 40 cm), and was pretreated in a N_2 flow at 500 °C for 2 h. After the reactor was cooled down to reaction temperature, a mixed gas containing 90% C_2H_4 and 10% Ar was introduced in the reactor from a cylinder. The reaction pressure was 1 MPa and the main reaction temperature was 200 °C.

The dehydration of ethanol was performed in a fixed-bed catalytic reaction system. The catalyst (24–60 meshes) was packed in a stainless-steel reactor (*i.d.*: 1 cm; length: 40 cm), and was pretreated in a N_2 flow at 500 °C for 2 h. After the reactor was cooled down to the reaction temperature, a mixture of ethanol and water was fed in the reactor from a tank by a high-pressured micro-pump (Shimadzu LC-10, Shimadzu Co., Kyoto, Japan). At the same time, Ar was introduced in the reactor from a cylinder as a carrier gas and an inner standard material for calculation.

During the reaction, the products were continuously analyzed using an on-line GC analysis system. Inorganic gases were analyzed using a Shimadzu 14B TCD-GC (Shimadzu Co., Kyoto, Japan) equipped with a packed column filled by SHINCARBON. C_1 – C_4 gas hydrocarbons were analyzed using a Shimadzu GC-2014 FID-GC (Shimadzu Co., Kyoto, Japan) equipped with a RT-QPLOT capillary column (Agilent Technologies Inc., Santa Clara, CA, USA). Liquid organic compounds were analyzed using a Shimadzu GC-2014 FID-GC equipped a Stabilwax capillary column (Restek Co., Bellefont, PA, USA). A standard mixed gas (from a cylinder) with known concentration for each component was used to calculate the factors of gas samples. A standard mixed solution with known concentration for each component was prepared to calculate the factors of liquid organic compounds.

The carbon mass balance (before and after reaction) had an error less than $\pm 5\%$ for the reactions carried out in this study.

4. Conclusions

Ni/Al-HMS was an effective catalyst for the oligomerization of ethylene to higher olefins. The selectivity for C_8H_{16} over Ni/Al-HMS was larger than that over the reported Ni/Al-MCM-41 catalyst. The existence of Al^{3+} ion in the neighborhood of Si^{4+} ion was important to improve the catalytic activity of Ni/Al-HMS in the oligomerization of ethylene. Ni sites were the main active sites in the ethylene oligomerization over Ni/Al-HMS. The primary product was C_4H_8 and the formed C_4H_8 was converted to larger olefins in the oligomerization of ethylene. The weak acid sites in Al-HMS had activity for the dimerization of the primary product C_4H_8 (formed on Ni sites) to C_8H_{16} , but they almost had no activity for the dimerization of C_2H_4 to C_4H_8 . H-ZSM-5 was an effective catalyst for the dehydration of ethanol to ethylene, but a large amount of water in the feed caused the catalyst deactivation during the reaction. Using a reaction system containing two fixed-bed reactors (to achieve ethanol dehydration on H-ZSM-5 and ethylene oligomerization on Ni/Al-HMS) and one cold trap (to eliminate water), higher olefins were continuously produced by feeding a mixture containing 90 wt.% ethanol and 10 wt.% water.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflicts of interest.

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