Selective production of light olefins over MSE-type zeolite catalyst

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Abstract: Various preparation route to MSE-type zeolite catalysts, microporous aluminosilicates with a 12-10-10-ring micropore system, and their catalytic application for selective production of propylene from petroleum and non-petroleum resources was investigated. Variation of the synthetic route provided characteristic aluminosilicate MSE-type materials that exhibited improved catalytic performances for hexane cracking. Rare-earths or phosphate impregnation with further modification improved the catalytic performance for the dimethyl ether-to-olefin (DTO) reaction.

Keywords: MSE-type zeolite, Propylene, Post-synthetic modification.

1. Introduction

MCM-68 is a typical zeolite with the MSE framework ("type material" of MSE) first synthesized by Mobil researchers.[1] Organic structure-directing agents (OSDAs) are used in syntheses of MSEs, incorporating the rigid and bulky organic cation *N,N,N',N'*-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium ($TEBOP^{2+}$) for the syntheses of MCM-68. The MSE is an example of a new multi-dimensional framework with a 12-10-10-ring pore system, which contains a straight 12-ring channel that intersects with two independent tortuous 10-ring channels as well as an 18×12-ring supercage accessible only through the 10-ring channels.[1] In this presentation, we focus on the MSE-type zeolite catalysts prepared by various synthetic and post-synthetic techniques for the selective production of light olefins, especially propylene, from petroleum and non-petroleum resources.

2. Experimental

2.1. Synthesis

A typical gel composition is $1.0SiO_2 – 0.1TEBOP^{2+}(I^-)_2 – 0.375KOH – 0.1Al(OH)_3 – 30H_2O$ and the gel is kept statically at 160 ºC for 16 d to give the desired product. The aluminum-rich MSE-type zeolite successfully obtained in the presence of FAU-type zeolite and seed crystals has special physicochemical features, so is referred to as [Al]-YNU-3. The seed-assisted, OSDA-free synthesis of MSE-type zeolite (designated as MSE_{OSDAF})[2] was carried out by adding the calcined MCM-68 seeds (Si/Al = 11) to OSDA-free (Na, K)-aluminosilicate gels with the molar composition $1.0SiO_2 − 0.3[Na_2O+K_2O] − 0.01Al_2O_3 − 20H_2O$. Typical crystallization temperature and time were 140 ºC and 48 h, respectively.

2.2. Post-synthetic modification:

The zeolite samples were heated at 80–130 ºC in diluted or concentrated nitric acid for 2–24 h, resulting in the formation of MCM-68(11.0), YNU-3(7.4), MCM-68(64.5), YNU-3(69.4), and MSE_{OSDAF}(66.9), where the value in parentheses is Si/Al molar ratio. In the case of MSE_{OSDAF}, stabilization by steaming was necessary prior to the acid-treatment.[2] Alternatively, loading of various species including rare-earth oxide or phosphates was performed basically by impregnation followed by calcination.

2.3. Catalytic reaction

Hexane cracking and DTO (not shown) reactions were investigated as typical examples of the conversion of petroleum and non-petroleum resources, respectively. Prior to the reaction, pelletized, crushed, and sieved catalyst particles were placed in a fixed bed reactor. The temperature was raised to the pretreatment temperature under air flow. After pretreatment, the temperature was maintained at the reaction temperature. The substrate was introduced into the top of the down-flow reactor with helium. The reactants and products were analyzed by on-line GC-FID.

3. Results and discussion

Comparison of catalytic performance of MSE-type zeolites prepared by various techniques is shown in Fig. 1. Both hexane conversion and product yield change with time during the cracking of n-hexane at 650 ºC over various MSE-type zeolite catalysts.[2] Non-dealuminated MCM-68(11.0) and YNU-3(7.4) were deactivated very rapidly caused by heavy coking, showing conversions and product distributions similar to those of thermal cracking (a–c). MCM-68(64.5), one of the dealuminated versions of MCM-68, exhibited adequate catalytic activity for the hexane cracking process, but was gradually deactivated until the hexane conversion at 305 min was below 50% (d). This deactivation was again likely caused by the large amount of coke (33.4 mg-coke (g-catalyst)$^{-1}$ after 305 min of reaction) formed on the catalyst. In contrast, YNU-3(69.4), one of the dealuminated versions of YNU-3 maintained its initial catalytic activity after 305 min and showed a minimal coke formation (1.8 mg-coke (g-catalyst)$^{-1}$ at 305 min) (e). Surprisingly, MSE$_{\mathrm{OSDAF}}$(66.9), the stabilized, dealuminated version of MSE$_{\mathrm{OSDAF}}$, showed much improved catalytic activity and comparatively less coke formation (3.3 mg-coke (g-catalyst)$^{-1}$ at 305 min). Hexane conversion with this catalyst was always much higher than that over YNU-3(69.4). Looking at the product selectivity at the point of 70% hexane conversion at 650 ºC, MSE$_{\mathrm{OSDAF}}$(66.9) exhibited higher selectivity to propylene (ca. 44%; the same level as the less active YNU-3(69.4)) and lower BTX selectivity (1%) compared to MCM-68(64.5) (ca. 41% and 3%, respectively) (f). Propylene yield over MSE$_{\mathrm{OSDAF}}$(66.9) was much higher than over other MSE-type catalysts at any point in the reaction, indicating that optimally modified MSE$_{\mathrm{OSDAF}}$ may be a viable candidate for application as a long-lived paraffin-cracking catalyst for the selective production of propylene.[2]

Reaction conditions: catalyst weight, 100 mg; W/F = 19.6 g-cat. h mol^{-1}; partial pressure of hexane = 5 kPa; He gas flow rate, 40.0 cm^3(N.T.P.) min^{-1}. BTX is the mixture of benzene, toluene and xylenes.

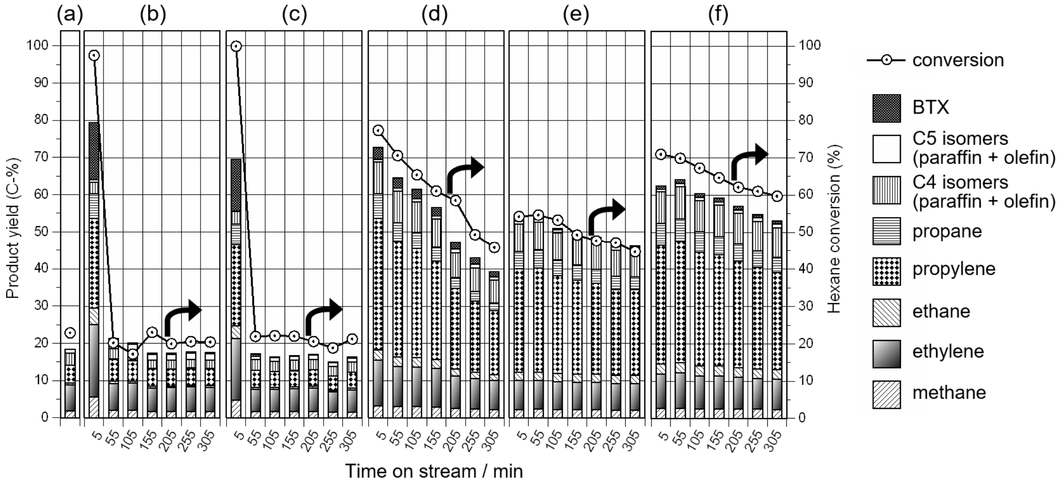

Figure 1. Hexane conversion and product yield (C-%) for hexane cracking over zeolite catalysts at 650ºC. The reactions were carried out (a) without catalyst or catalyzed by (b) MCM-68(11.0), (c) YNU-3(7.4), (d) MCM-68(64.5), (e) YNU-3(69.4), and (f) MSE$_{\mathrm{OSDAF}}$(66.9). Values in parentheses following the zeolitic material name are Si/Al ratios determined by ICP-AES analysis.

4. Conclusions

The dealuminated version of various Al-rich MSE-type zeolites showed high levels of coking resistance in addition to a significant yield of propylene in the hexane-cracking reaction, and the order of catalytic performance after post-synthetic modification was as follows: conventional MCM-68 < MSE synthesized by hydrothermal conversion of an FAU-type zeolite (YNU-3) < MSE synthesized under OSDA-free conditions (MSE$_{\mathrm{OSDAF}}$). The Al-rich MSE products obtained in this study, especially YNU-3 and MSE$_{\mathrm{OSDAF}}$, are promising parent materials for industrial applications as highly selective and long-lived catalysts. MCM-68 was also effective for DTO reaction especially when modified with rare-earths or phosphates.

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References

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