Zeolite SUZ-4 as Selective Dehydration Catalyst for Methanol Conversion to Dimethyl Ether

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Zeolite SUZ-4 is found to be a very selective and stable catalyst for producing dimethyl ether in methanol dehydration because the formed dimethyl ether is hardly converted to hydrocarbons, different from ZSM-5 zeolite.

Dimethyl ether (DME), a natural gas derived product, has been received much attention recently as an alternative clean fuel for diesel engines because of its low NO_x emission, near-zero smoke, and less engine noise compared with traditional diesel fuels.[1] DME is commercially produced in small quantities by the catalytic dehydration of methanol over solid acid catalysts;[2] however, water[2] or coke[3] blocks active sites for methanol dehydration. The formation of DME from syngas using both the dehydration catalyst and the traditional methanol synthesis catalyst has been proposed as an economic way of DME production,[4] but development of a stable solid acid catalyst for methanol dehydration is still necessary for establishing the process.

SUZ-4 zeolite is reported in 1992 and the potassium form ($Si/Al = 6.21$) is usually obtained.[5] Some exchangeable potassium ions in K-SUZ-4 are preferably located in small cages.[6] The structure of SUZ-4 is considered to be a three-dimensional channel system including main straight ten-membered ring channels intersected by two arrays of eight-membered ring channels and small cages linked through double six-membered rings.[7] The minimum and maximum dimensions of the ten-membered ring are 4.6 and 5.2 Å, respectively. Recently, it has been reported that zeolite SUZ-4 is a promising support for lean-NO_x catalysts for high temperature applications.[8] It has been proposed that SUZ-4 zeolite has potential as a catalyst and may display unusual shape-selective properties in comparison with other zeolites.[9] However, despite its potential applications in catalysis, SUZ-4 has been scarcely studied.[7–9] In this communication, we add another new catalytic property of SUZ-4 on very selective formation of DME in methanol dehydration.

Zeolite SUZ-4 was prepared by a hydrothermal crystallization. In a typical synthesis, an aluminum foil (0.4 g, Alfa Aesar) was dissolved into preformed aqueous KOH solution (KOH 3.29 g, H_2O 50.63 g). To the clear solution, 7.93 g of TEAOH (Aldrich, 20–25 wt %) and 18.23 g of Ludox-As-40 (Aldrich, SiO_2 40 wt %) were added successively while stirring (500 rpm) at 333–353 K. The final mixture with the molar composition of 16.21 SiO_2:Al_2O_3:7.92 K_2O:1.83 TEAOH:506.39 H_2O was transferred to a 100-mL Teflon autoclave and crystallized for 48 h at 438 K under stirring (500 rpm). The solid product was washed with water, dried at 393 K for 12 h, and calcined in air at 823 K for 18 h. The XRD patterns showed that as-synthesized material was pure K-SUZ-4. Calcined K-SUZ-4 was ion exchanged with aqueous 1 N NH_4NO_3 solution under reflux, washed three times with deionized water, dried at 393 K for 2 h and then calcined in flowing air at 823 K for 10 h. Through three times of this exchange procedure, the resulting proton-exchanged zeolite with ion-exchange degree of 75% was obtained, and the sample denotes as H-SUZ-4(75). The XRD pattern of the ion-exchanged product showed the crystallinity remained constant after the exchange/calcination cycles.

NH_3-TPD and pyridine-IR results indicate the presence of strong acid sites on the surface of H-SUZ-4(75) comparable with those of H-ZSM-5,[10] which is in good agreement with previous report.[9] Moreover, most of the strong acid sites of H-SUZ-4(75) are identified as Brönsted-type ones.

Methanol dehydration was carried out with a fixed-bed reaction system at atmospheric pressure described elsewhere.[3] The

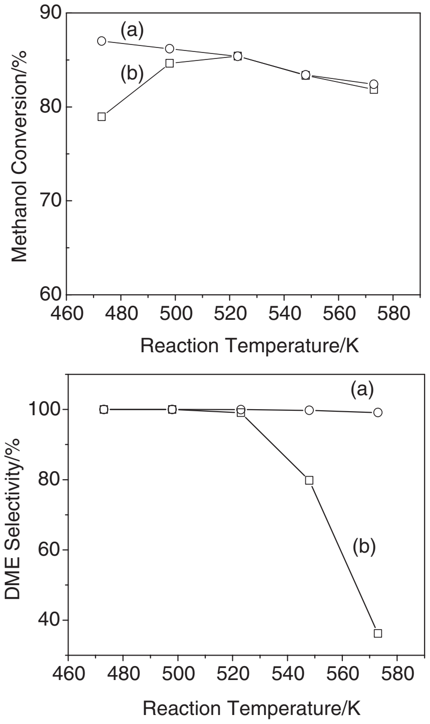

Figure 1. Dehydration of methanol over (a) H-SUZ-4(75) and (b) H-ZSM-5 catalysts. Reaction conditions: catalyst loading = 0.1 g, 20–40 mesh; N_2 flow rate = 360 mL/h; WHSV = 4 h^{-1}; $p_{CH_3OH} = 0.06$ MPa; time on stream = 2 h.

products were analyzed with an on-lined gas chromatography equipped with a GS-Q capillary column and flame ionization detector. The catalytic performances of these two zeolites are compared at various reaction temperatures as shown in Figure 1. The two zeolites exhibit very similar conversions in the reaction temperature range of 498–573 K (Figure 1a). However, the DME selectivity over H-SUZ-4(75) is much higher than that over H-ZSM-5 at high temperature (Figure 1b) even though H-SUZ-4(75) possesses strong acid sites. High DME selectivity on H-SUZ-4(75) is ascribed to its low activity for conversion of DME, which is an intermediate in methanol dehydration to hydrocarbons.[11] It is noted that H-SUZ-4(75) is unusually very inactive for DME conversion reaction even at 723 K, indicating that the subsequent reactions of DME to hydrocarbons over H-SUZ-4(75) are almost prohibited. In contrast, H-ZSM-5 exhibits high DME conversion, 93% at 673 K, as illustrated in Figure 2. It is assumed that the active sites over H-SUZ-4(75) for methanol dehydration may be different from those for DME conversion. Moreover, the H-SUZ-4(75) catalyst is very stable without coke formation for more than 40 h of the reaction, while H-ZSM-5 is deactivated in the reaction after 8 h owing to the coke formation.

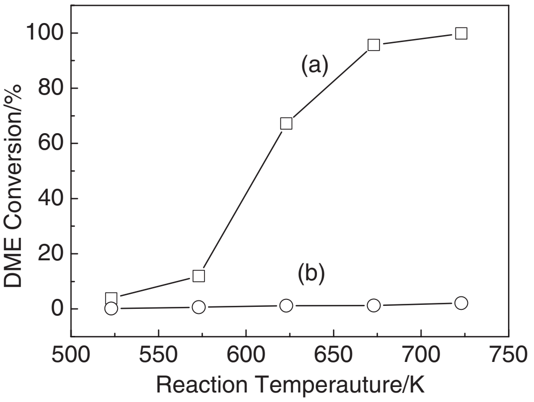

Figure 2. Conversion of DME to hydrocarbons over (a) H-ZSM-5 and (b) H-SUZ-4(75). Reaction conditions: catalyst loading = 0.1 g; GHSV = 3000 mL-DME·g-catalyst^{-1}·h^{-1}.

The FTIR spectra of zeolites after methanol adsorption at 373 K and further evacuation at 523 K are presented in Figure 3. It is obvious that upon methanol adsorption H-SUZ-4(75) zeolite contains skeletal methoxyl groups at 2969 cm^{-1} and adsorbed methanol species at 2854 cm^{-1}, which are known to produce DME and water on condensation.[11] In the case of H-ZSM-5 not only skeletal methoxyl groups but also $AlOCH_3$ species at 2955 cm^{-1} are present together with a trace of adsorbed methanol species. Kubelkova et al. reported the formation of similar species on HY and H-ZSM-5 with chemisorption of methanol.[12] The surface $AlOCH_3$ species on H-ZSM-5 are assigned to methoxy groups formed on nonskeletal Al species, which can be considered to enhance the C–C bond formation.[13] The concentration of $AlOCH_3$ species on surface of H-SUZ-4(75) is very low compared with the case of H-ZSM-5 so that this might lead to the less formation of hydrocarbons over HK-SUZ-4 compared with H-ZSM-5.

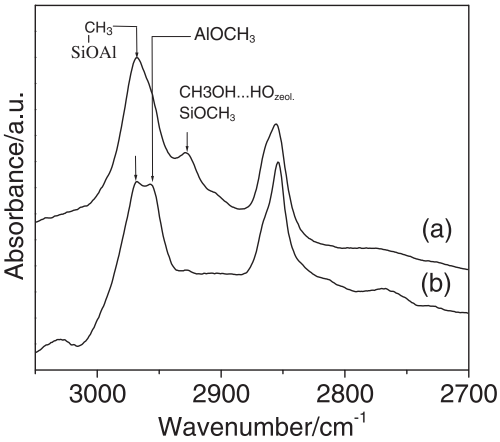

Figure 3. FTIR spectra of (a) H-SUZ-4(75) and (b) H-ZSM-5 after the adsorption of methanol (100 Torr) at 373 K and subsequent evacuation at 523 K for 30 min.

In summary, this work demonstrates that H-SUZ-4(75) zeolite exhibits unique catalytic properties in methanol dehydration to exhibit high DME selectivity and catalyst stability, indicating that it has potential as a catalyst for dehydration of alcohols.

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