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Catalytic dehydration of methanol to dimethyl ether (DME) over Al-HMS catalysts

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ABSTRACT

A series of Al-HMS with different Si/Al ratio was used as a solid acid catalyst for methanol dehydration to dimethyl ether (DME). The effect of temperature, feed composition, space velocity, and the catalyst Si/Al ratio on the catalytic dehydration of methanol was investigated. By decreasing Si/Al, the temperature required to reach equilibrium conversion of methanol decreased due to the increased number of acidic sites. Compared to commercial γ-Al_2O_3, Al-HMS-5 and Al-HMS-10, catalysts exhibited a high yield of DME. Among all Al-HMS catalysts, Al-HMS-10 exhibited an optimum yield of 89% with 100% selectivity and excellent stability for methanol dehydration to DME.

1. Introduction

Dimethyl ether (DME) has received considerable attention due to its potential uses as an alternative to diesel oil and LPG because of similarity of its thermal efficiency to that of traditional fuels, low NO_x emission, negligible smoke amounts, and less engine noise [1–4]. It has already been used as an ozone-friendly aerosol propellant to replace ozone destructive CFCs [5]. In addition, it is an important intermediate for producing highly valuable chemicals such as lower olefins, dimethyl sulfate and methyl acetate [6,7].

DME can be produced directly from syngas over bifunctional Cu-based catalysts or synthesized by methanol dehydration over solid acid catalysts at 200–450 °C in a pressure of up to 18 atm [8–12]. Among different kinds of solid acids used for methanol dehydration, H-ZSM-5 and γ-Al_2O_3 have been investigated intensively both in laboratory and commercial scales. H-ZSM-5 has been reported to be more active than γ-Al_2O_3, but rapid deactivation occurs on its strong acidic sites due to the generation of undesirable hydrocarbons [13,14]. On the other hand, γ-Al_2O_3 is more selective to DME, but it has some disadvantages including low activity and rapid deactivation in the presence of water.

Water is both produced in significant amounts through direct synthesis of DME from synthesis gas, and it is also present in large quantities (20–30%) in the crude methanol. It is reported that replacing pure methanol with crude methanol would bring about great industrial benefits. Therefore, researchers are trying to develop effective catalysts to optimize the DME production from crud methanol and improve the catalyst stability [14,15].

Recently, ordered mesoporous materials have been the subject of a large number of studies because of their high surface areas, regular frameworks, and large pore size with narrow distribution [16]. Pure mesoporous silica does not have enough acidity, but acidity can be improved through the insertion of foreign metal ions into its structure during the synthesis [17–19]. Among such materials, Al-incorporated mesoporous molecular sieves which possess the acidic sites and good hydrothermal stability are more favorable. HMS is a hexagonal mesoporous silica with a particular wormlike pore structure. It has a simple preparation method using cheap primary alkyl amines which can be extracted without pollution [20]. Surprisingly, despite its wide uses for catalytic reactions, to the best of our knowledge, aluminated hexagonal mesoporous material (Al-HMS) has not been employed as an acidic catalyst to the dehydration of methanol up to now.

In continuation of previous studies on the application of Al-HMS mesoporous material as a solid acid catalyst for various reactions [21,22], here we report catalytic behavior of this material in the reaction of methanol dehydration to DME. The main objective of this study is to investigate the effects of the incorporation of Al into the HMS framework on the activity, selectivity, and durability in the methanol dehydration. Also, the effects of temperature, and feed composition on catalytic performance were studied. BET, XRD, XRF, NH_3-TPD, FT-IR pyridine, and TG/DTA techniques were employed for the material characterization.

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2. Experimental

2.1. Materials and methods

Al-HMS mesoporous materials with four different Si/Al ratios of 5, 10, 20, and 35 were synthesized via neutral templating pathway similar to the procedure reported in previous studies [23] using tetraethylorthosilicate (TEOS) as the silica source, aluminum isopropoxide ($Al(OPr^i)_3$) as the aluminum source and dodecylamine (DDA) as the surfactant. The molar composition of final gel was 1.0 SiO2:x $Al(OPr^i)_3$:0.25 DDA:10 isopropyl alcohol:100 H_2O, where the value of x is dependent on various Si/Al ratios. Each solid product was separated by filtration and dried at 110 °C overnight and calcined at 540 °C for 6 h in the flowing air. The prepared samples were named Al-HMS(x), where x is the Si/Al ratio.

2.2. Characterization of catalysts

An X-ray diffraction (XRD) analysis of the calcined samples was performed in the 2θ range of 1–10°, by using an X-PERT diffractometer employing Ni-filtered Cu Kα radiation at 45 kV and 50 mA.

The specific surface area and pore volume of the samples were measured in an ASAP-2010 Micromeritics (USA) using low temperature N_2 physisorption isotherms. Before the analysis, the sample was evacuated at 350 °C under vacuum conditions.

The acidity of Al-HMS was measured by TPD of ammonia in a TPD/TPR analyzer (2900 Micromeritics) with a thermal conductivity detector. To determine and analyze the type of acidic sites, pyridine adsorption on the samples was performed on a Fourier-transform infrared spectrometer (170-SX). The Si/Al ratio of Al-HMS was determined by XRF (XRF-8410 Rh 60 kV). The content of coke laid down on the surface of used catalysts was measured by thermogravimetric analyzer using a STA503M TG/DTA instrument.

2.3. Catalytic evaluation

Vapor phase dehydration of methanol was carried out at the temperature range of 250–400 °C and atmospheric pressure in a continuous fixed-bed micro-reactor packed with 0.5 g of the catalyst. Prior to each experiment, the catalyst was pretreated for 1 h at 300 °C in an N_2 flow. Nitrogen saturated by pure methanol (11% MeOH in N_2) was used as feed with the space velocity (WHSV) 1.0 h^{-1}. Moreover, methanol–water mixture (methanol 80 mol% + water 20 mol%) was introduced to the reactor under aforementioned conditions to investigate the capability of Al-HMS as a dehydration catalyst for the crude methanol dehydration. The performance of the catalysts was measured after 0.5 h time on stream (TOS) at noted temperatures for each experiment. The analysis of the reaction products was carried out by on-line gas chromatography using a gas chromatograph (Shimadzu-8A) equipped with a thermal detector.

3. Results and discussion

3.1. Characterization

Fig. 1 shows that the XRD patterns of the Al-HMS materials are similar to those reported in literature [20,24]. There is a single broad reflection that can be assigned to a lattice with the short-range hexagonal symmetry. The increase of Al content in the samples results in the broadening of the peak, indicating that the incorporation of Al is associated with increasing the lattice disorder.

The chemical compositions, BET surface area, and pore volume of calcined Al-HMS materials are given in Table 1. It can be seen that the actual Si/Al ratios are very similar to added metal amounts in the gel compositions, suggesting that most of the added aluminum heteroatoms are embedded into the HMS bulk. It can be inferred from Table 1 that the surface area and pore volume decrease with the increase of Al amounts. This may be attributed to decrease in the structural order of the samples as a result of Al incorporation as proved by XRD.

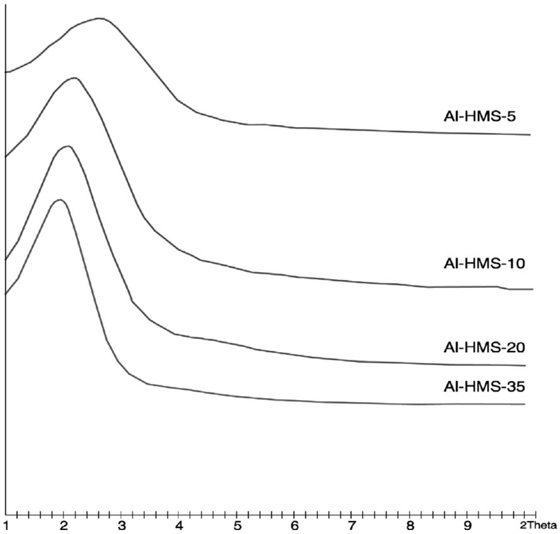

Fig. 1. XRD patterns of Al-HMS catalysts with different Si/Al ratio.

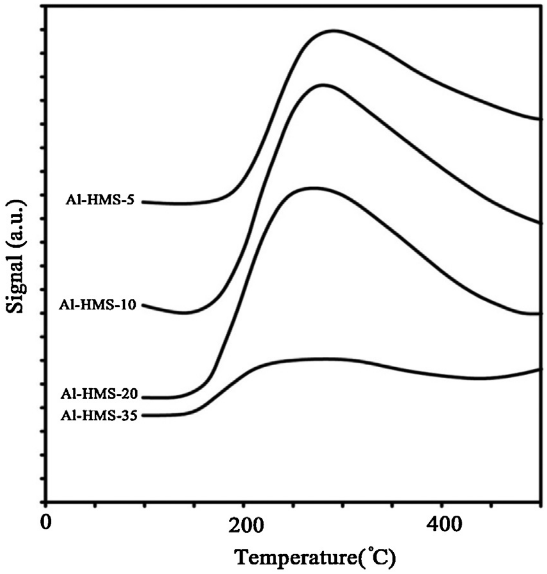

Fig. 2. NH_3-TPD on Al-HMS catalysts with different Si/Al ratio.

Fig. 2 shows NH_3-TPD profiles of all Al-HMS materials with different Si/Al ratios. The asymmetric shapes of the desorption profiles indicate the presence of different surface acid sites in the range of 150–500 °C, corresponding to the distribution of acid sites from weak to strong. The maximum of desorption peak is in the range of 250–300 °C corresponding to the medium acid sites responsible for the selective formation of DME [25,26]. The TPD profile of pure HMS shows no evident peak due to the absence of acidic sites on the HMS (not shown here). Table 1 shows that the concentration of acidic sites of Al-HMS increases with the decrease of Si/Al ratios. It can be seen that the maximum of the TPD diagram shifts to the high temperatures with the decreasing Si/Al ratios. It is