Catalytic Performances of Binder-free ZSM-5 Catalysts for Dehydration of Crude Methanol to Dimethyl Ether

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A series of binder-free ZSM-5 catalysts and a binder-containing catalyst were prepared and characterized with X-ray diffraction (XRD), X-ray fluorescence (XRF), ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR), N_2 sorption and ammonia temperature-programmed deposition (TPD) methods. The catalytic activity and selectivity in the dehydration of crude methanol to dimethyl ether (DME) were evaluated in a fixed-bed reactor for the catalysts. The outstanding structural characters such as high zeolite contents, sufficiently open channels and richness in mesopores have been proved on these binder-free catalysts. The influence of the solid-acidity, which is closely related to the framework silica alumina ratio (SAR) of the catalysts, on the catalytic properties has been discussed. A binder-free catalyst with a better potential in application has been selected for its high activity and selectivity, long life-time and non-sensitivity to water contents in the feed. The reason for its excellent performance of the catalyst was discussed.

Keywords　binder-free, ZSM-5, zeolite catalyst, crude methanol, dimethyl ether

Introduction

Dimethyl ether (DME), an alternative diesel fuel, has received much attention because of its low NO_x emission, near-zero smoke production and even lesser engine noise compared with traditional diesel fuels.[1-3] Moreover, DME is a building block for synthesizing many chemicals, such as methyl acetate, dimethyl sulfate, gasoline and aromatics.[4]

The industrial processes for methanol dehydration usually use zeolites, silica-alumina or γ-Al_2O_3 as the solid-acid catalyst,[5] among which ZSM-5 zeolite (MFI type) has been studied extensively for both academic and commercial purposes.[6-9] Due to its strong acidity and large amount of acidic sites, the zeolite was reported to be a good dehydration catalyst for DME synthesis from methanol. In practice for use, zeolite powder should be formed to get catalyst particles with certain shape, size, and mechanical strength using some inactive materials as binders. The corresponding decrease of the active zeolite component, and the build up of part channel windows in the formed catalysts caused by the addition of the binders, significantly result in depressing of the catalytic performance. Therefore, γ-Al_2O_3 has been commonly used as a binder because of its own catalytic activity.[10] The strong tendency for adsorbing water of the oxide reduces the activity of the catalyst in the dehydration of crude methanol containing 10%—20% of water.

In this study, we report the preparation and the characterizations of a series of binder-free and binder-containing ZSM-5 catalysts, and the evaluations of their catalytic properties for methanol dehydration to DME. An excellent binder-free catalyst with great potential in application has been selected, and the reason for its well performance in the catalytic reaction was discussed.

Experimental

Sample preparation

H-ZSM-5 powders of FXS-I, FXS-II, and FXS-III with SiO_2/Al_2O_3 ratios (SAR) of 30, 100 and 400 respectively are commercial products of Shanghai Fuxu Molecular Sieve Co., Ltd. The powders were mixed with an amorphous aluminosilicate binder gel with equal SAR, which was made with silica gel and aluminium sulfate based on a patent.[11] A binder-containing catalyst was then prepared by extrudating the mixture. Further the catalyst was placed in an autoclave filled with tetra-propylammonium hydroxide (TPAOH) solution and heated at 180 ℃ for 24 h for transforming the binder to ZSM-5 zeolite, and finally the binder-free catalyst was obtained. Both binder-containing and binder-free catalysts were ion-exchanged with 0.5 mol•L^{-1} HCl solutions at 95 ℃ for 4 h and washed,

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dried and calcined at 600 ℃ for 2 h to yield the ultimate catalysts.

Characterization

XRD patterns were collected on a Riguka D-MAX/II A X-ray diffractometer in a scanning range of 5°—35° (2θ) at the rate of 8 (°)/min with Cu Kα radiation, 30 kV/20 mA.

Chemical compositions were determined by X-ray fluorescence scattering spectroscopy (XRF, Bruker-AXS S4 EXPLORER) with rhodium target.

Spectra of ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) were recorded on a Bruker MSL 300 spectrometer operated at 78.205 MHz. The width of the spectrum was δ 200, and the rotor was spun at 3.0 kHz. The radio-frequency field was 51.0 kHz, the reversing angle was 18°, and the recycle time was 500 ms. $AlCl_3•6H_2O$ was used as a reference for the ^{27}Al chemical shift. The samples investigated with ^{27}Al MAS NMR were kept over a saturated solution of ammonium chloride at room temperature for at least 12 h.

The isotherms of N_2 adsorption and desorption were measured using a Micromeritric ASAP 2010 instrument at −196 ℃. The zeolite samples tested were dehydrated at 300 ℃ for 6 h before determination.

Temperature-programmed desorption of NH_3 (NH_3-TPD) was performed in a stainless steel U-type tube connected with a thermal conductivity detector (TCD) in GC equipment at atmospheric pressure. Prior to measurement, the samples were pre-hearted at 350 ℃ in He flow for 1 h. Pure gas of NH_3 was then injected into the tube till the samples reached adsorption saturation in the He flow at 120 ℃. The temperature was then raised up with a rate of 10 ℃/min from 120 to 600 ℃ for desorbing NH_3.

Catalysis reaction

Catalytic dehydration of methanol on the catalyst was carried out in a stainless steel fix-bed reactor at atmospheric pressure. In each run, 5.0 mL of catalyst was loaded, and the reactor was kept at a fixed reaction temperature in the range of (180—300)±1 ℃. The feed of crude methanol (90.3%, purchased from Shanghai Coking Co., Ltd.) was injected into the reactor by a micro-electron metering pump. The compositions of the reaction products were analyzed online by an Agilent 6820 GC equipped with an FID detector. The gas lines were kept at 200 ℃ for preventing the condensation of the reactants and the products.

Results and discussion

Catalyst characterization

Three binder-free catalysts with different framework SAR, MD1, MD2 and MD3 were studied in this work. Meanwhile, a binder-containing catalyst MD5, which is a precursor one of MD3 without treatment by binder transformation, was set as a contrast with the binder-free catalysts. Table 1 lists the data of the compositions of the catalysts. The framework SAR values, measured with XRF and calibrated by ^{27}Al MAS NMR, were 435, 92.4, 32.6 and 24.4, respectively for MD1, MD2, MD3 and MD5. Figure 1 presents the XRD patterns of the catalysts. No obvious differences exist in the patterns of the catalysts, except that the relative crystallinity of MD5 is about 80% in comparison with that of MD3 due to the amorphous binder in the bulk catalyst. As shown in Figure 2, evident hysteresis loops appear in the isotherms of these catalysts in $p/p_0=0.45—1.0$, indicating that pore size distributions in mesopore range exist in these catalysts. The obvious rising slope and the largest hysteresis loop are present in the lowest adsorption isotherm for MD5 (see Figure 2a). The fact proved that a significant adsorption in mesopore occurred at $p/p_0>0.4$, and implied a wide distribution of pore size in the binder-containing catalyst. Figure 3 shows the pore size distributions in these catalysts, in which the binder-free catalyst possesses the major average pore size at *ca.* 6.8 nm. In comparison, the binder-containing catalyst gives a wider pore size distribution consistent with the result of the adsorption isotherms (see Figure 3a). Based on the patent,[11] sesbania powder, one kind of forming assistant, was added into the mixture of a binder and the raw zeolite powder to prepare the column form particles of the catalyst with extrusion molding. After calcinations, the sesbania powder in the catalyst was burnt up, and some open space between zeolite crystallites appeared. This may result in the mesoporous structures. In catalyst MD5, some binder plugs the mesopores. For this reason the diameter of the mesopores decreases and the distribution of the pore size becomes wider.

Table 2 summarizes the surface and porous properties of the catalysts calculated from the adsorption and desorption isotherms above. The adsorption properties of the catalysts MD1, MD2 and MD3 are similar with each other. Whereas, the surface area and the pore volume of MD5 are much smaller than thoes of the binder-free catalysts. The reason is that the existing

Table 1 Chemical compositions of catalysts

Sample	SAR measured by XRF	^{27}Al MAS NMR		Framework SAR	Na_2O/wt%
		Framework	Extra-framework		
MD5	23.0	94.2%	5.8%	24.4	0.06
MD1	435	100%		435	—
MD2	92.4	100%		92.4	—
MD3	31.0	95.1%	4.9%	32.6	0.02

Table 2 Adsorption properties of catalysts

Sample	BET surface area/ $(m^2 \cdot g^{-1})$	Langmuir surface area/ $(m^2 \cdot g^{-1})$	Total pore volume/ $(cm^3 \cdot g^{-1})$	Micropore volume/ $(cm^3 \cdot g^{-1})$	Cumulative pore volume/ $(cm^3 \cdot g^{-1})$
MD1	380.6	479.3	0.21	0.13	0.27
MD2	370.4	470.4	0.20	0.11	0.29
MD3	374.3	476.7	0.21	0.12	0.31
MD5	212.4	268.5	0.17	0.06	0.17
FXS-I	386.8	476.8	0.21	0.16	0.07
FXS-II	374.1	469.4	0.22	0.17	0.05
FXS-III	376.3	472.5	0.21	0.18	0.04

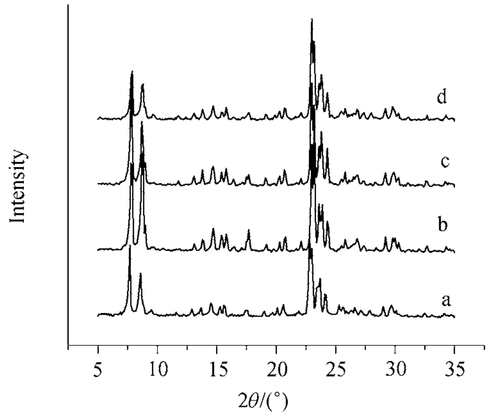

Figure 1 XRD patterns of the catalysts: (a) MD5, (b) MD1, (c) MD2 and (d) MD3.

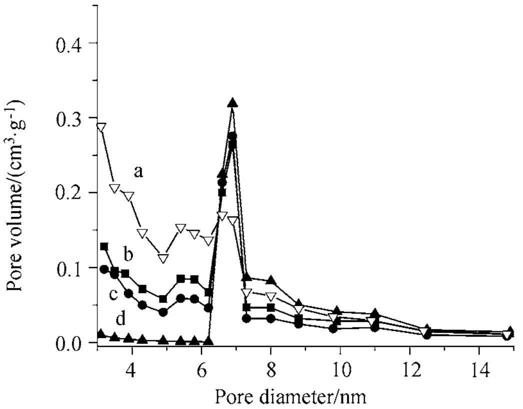

Figure 3 Pore size distribution for the catalysts: (a) MD5, (b) MD1, (c) MD2 and (d) MD3.

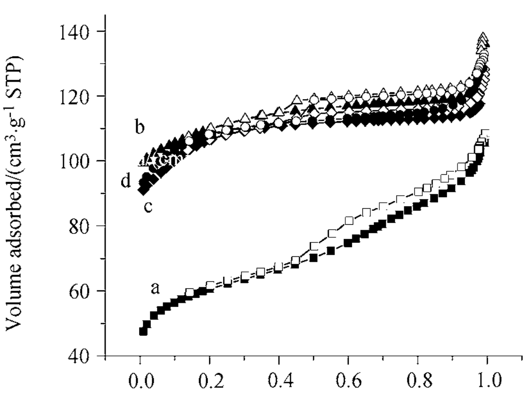

Figure 2 Adsorption isotherms of N_2 on the catalysts: (a) MD5, (b) MD1, (c) MD2 and (d) MD3.

amorphous binder plugs the channel windows of the zeolite powder in the catalyst, resulting in significant decrease of the adsorption properties. Evidently, a principal promoting of the pore properties for these catalysts occurs in the process of binder transformation. 212 m^2/g of BET surface area, 0.06 cm^2/g of micropore volume and 0.17 cm^3/g of cumulative pore volume for MD5 were elevated to 374 m^2/g, 0.12 cm^3/g and 0.31 cm^3/g, respectively for MD3. In fact, the BET surface area and micropore volume for these binder-free catalysts are much close to thoes of pure ZSM-5 zeolite powder. Open channels, high surface area, more mesopores and large pore volumes caused by the binder-transformation must benefit the molecule diffusion of the reactants and the products, resulting in the better performance of these catalysts than that of the binder-containing one.

Figure 4 exhibits the curves of NH_3-TPD for the investigated catalysts. Two obvious broad peaks are present in the curves, among which the peaks in the temperature range of 130—250 ℃ and of 400—550 ℃ are usually considered belonging to weak acid sites (WAS) and strong acid sites (SAS), respectively. The MD1 catalyst, with the highest SAR of 435, possesses the lowest acidity and very small amount of WAS as shown in the NH_3-TPD curve (see Figure 4b). Whereas, the strong acid sites usually play a dominative role in most acidic catalysis reactions. No obvious change for the strength of the strong acidity in MD2 can be observed compared to that of MD1, but the decrease of the amount of SAS is evident according to the smaller peak surface area in the NH_3-TPD curve for MD2 in the temperature range of 400—550 ℃ (see Figure 4b and 4c). However, the acid strength of WAS in the TPD curves is much stronger, and the related acid amount on MD2 is significantly more than that on MD1 based on the higher temperature for desorbing NH_3 and the larger peak surface area. In the situation of MD3, the weak acidity further gets stronger and the amount of the re-

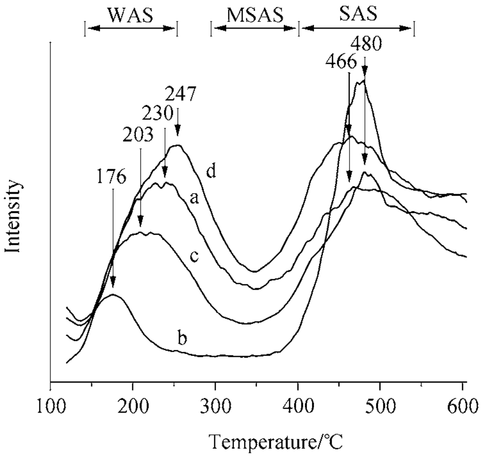

Figure 4 NH_3-TPD curves for the catalyst of (a) MD5, (b) MD1, (c) MD2 and (d) MD3.

lated acid sites is larger than that of all the catalysts investigated herein (see Figure 4d). Due to the existence of inactive binder, the acidity of MD5 is slightly weaker than that of MD3 even both catalysts exhibit very similar TPD curves. Moreover, the peak widths for both of WAS and SAS significantly increase with decreasing the SAR of the catalysts. Both peaks in the TPD curves even overlap with each other (see Figure 4a and 4d). The phenomenon is possibly attributed to the appearance of medium strength acid sites (MSAS) around 300—400 ℃ in the curve contributed by the extra framework aluminum in the low SAR catalysts MD3 and MD5.

Catalytic performance

Figure 5 presents the curves for the yield of MDE on the catalysts of MD1, MD2, MD3 and MD5 vs. the dehydration reaction temperatures at liquid hourly space velocity (LHSV) of 2 h^{-1}. The dehydration of methanol occurred on these catalysts at the temperature as low as 150 ℃. The yields of DME were obviously enhanced to above 85% as increasing the reaction temperature from 150 to 200 ℃ on MD2, MD3 and MD5 (see Figure 5a, 5c and 5d), and from 150 to 260 ℃ on MD1 (see Figure 5b). In progressing of the dehydration on the zeolite catalysts with high activity, coke deposition and deactivation usually easily take place as a result of forming hydrocarbons.[10] Therefore, the dehydration reaction on these high active catalysts should run with enough but not too high conversion for preventing the production of hydrocarbons. The yields of DME on the catalysts significantly increase in the order of MD3 (SAR=32.6)> MD5 (SAR=24.4)>MD2 (SAR=92.4)>MD1 (SAR=435) at the reaction temperature below 250 ℃ (see Figure 5). The fact reveals that the acidity corresponding to the SAR of the catalyst is a key factor for the activity of ZSM-5 catalysts in dehydration of methanol to DME.

As well known, SAS on the catalyst surface could facilitate the formation of hydrocarbons, and thereby accelerate coking process. As a result, the lifetime of the catalyst with time-on-steam will be eventually shortened.[7] Yaripour *et al.*[12] suggested that DME formation from methanol should be directly related to WAS and MSAS. This is the reason that MD3 and MD5 catalysts with low SAR present better catalytic performance due to their large amounts of WAS and MSAS than those of the catalysts with higher SAR.

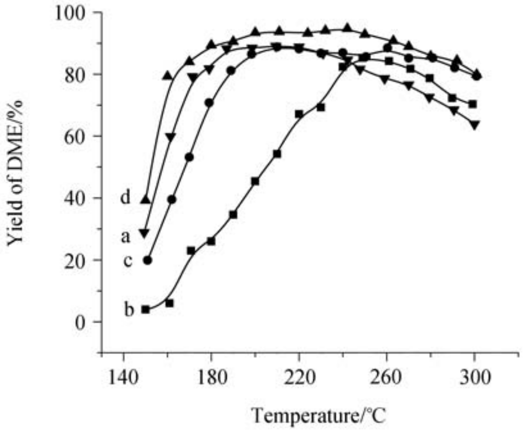

Figure 5 Effect of temperature on the dehydration of methanol to DME at LHSV=2 h^{-1} over the catalysts: (a) MD5, (b) MD1, (c) MD2 and (d) MD3.

Hydrocarbons began to form when the reaction temperature rose to above 250 ℃. As a result, the yield of DME decreases with increasing the temperature. The phenomenon obviously occurred on MD5, the binder-containing catalyst. In the low temperature range of 150—250 ℃, DME yield on MD5 is much higher than thoes on both binder-free catalysts MD1 and MD2. However, compared to that of the binder-free catalyst, DME yield on MD5 decreases quickly in higher temperature range because of the formation of a large amount of hydrocarbons as by-products. The possible reason is that the amorphous binder plugs the windows of the zeolite channels, reduces the effective pore sizes, and lowers the surface areas of the catalysts. As a result, the diffusion of DME molecules from the zeolite channels of the catalysts is significantly restricted, which finally induces the deep reaction of DME to form hydrocarbons.

The effect of water in the crude methanol upon the yield of DME was investigated on MD3. The yield of DME on the catalyst was kept at a level of higher than 90% (see Figure 6) with 100% DME selectivity in the dehydration reaction with the feeds containing 30% of water. Even the water content was elevated to 40% and 50% in the feed, the catalyst still reached about 86% and 79% of DME yield, respectively. The results reveal that the MD3 catalyst possesses excellent catalytic activity and selectivity for methanol dehydration to DME in a wide range of water content in the feed. Around 10% fluctuation of water content in the feed made even no negative effect to the dehydration of methanol, which implies that the prospect in industrial application of the catalyst is better than that of γ-Al_2O_3 catalyst and the zeolite catalyst with aluminum matrix binder.

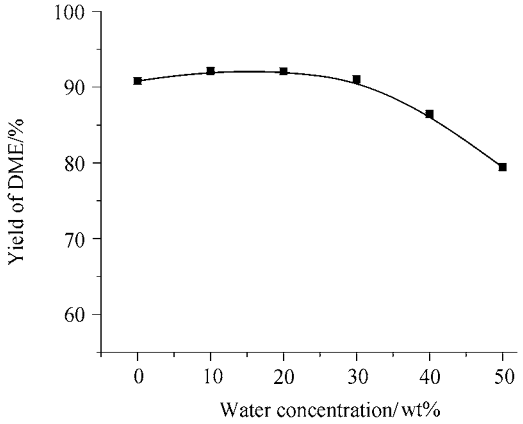

Figure 6 Effect of water concentration in feeds on the dehydration of methanol to DME over the catalyst of MD3 at 230 ℃ and LHSV＝2 h^{-1}.

Figure 7 exhibits the effect of LHSV on the methanol dehydration process, where the yield of DME decreases with increasing the LHSV. Due to the low operating temperature, 1.5—2.0 h^{-1} of LHSV was preferred for that the reactants should have enough time to stay and contact with the catalyst for getting complete reaction. Because of the open pore system in the binder-free catalyst with more mesopores, the reactants and the products easily transfer in the catalysts.

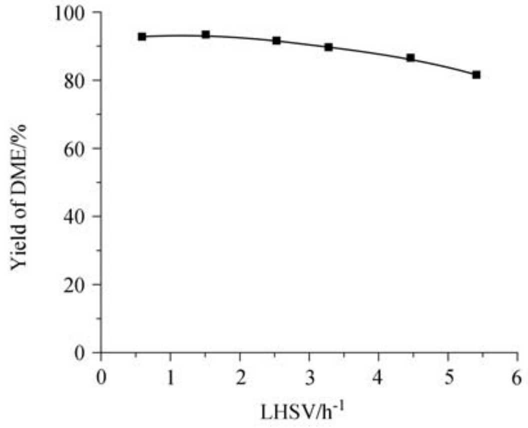

Figure 7 Effect of LHSV on the dehydration of methanol to DME over the catalyst of MD3 at 230 ℃.

The binder-free catalyst MD3 possesses very high stability on methanol dehydration in a wide temperature range for operating. As shown in Figure 8, the catalytic activity of MD3 decreases slowly in 800 h of the reaction period at 230 ℃, and DME yield remains above 80% with the selectivity of 100%. Whereas the catalytic activity of MD5 significantly decreased with the reaction, even less than 70% of DME yield remained after 200 h of time on stream (TOS). The catalytic activity of deactivated MD3 catalyst was easily recovered by calcination in hot air flow, indicating that the deactivation of the catalyst is mostly caused by coke deposition in the zeolite.

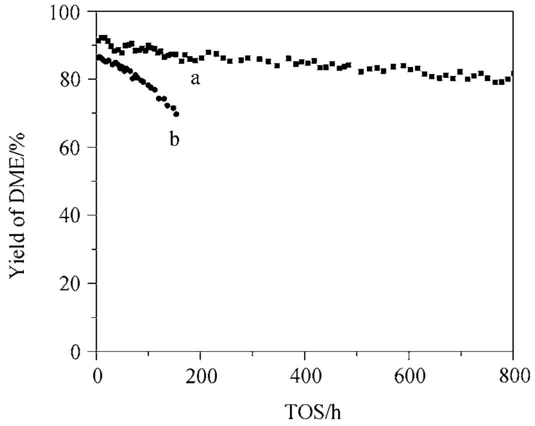

Figure 8 DME yield with time on stream in the methanol dehydration over catalysts: (a) MD3, (b) MD5 at 230 ℃ and LHSV ＝2 h^{-1}.

In H-ZSM-5, SAS prefers to induce the formation of hydrocarbons in the dehydration of methanol. The catalyst with low concentration of SAS and rich mesopores possesses an advantage of mass transfer in the zeolite. Therefore, the binder-free catalyst exhibits outstanding performance on the catalytic reaction of methanol dehydration to DME.

Conclusion

A series of binder-free ZSM-5 zeolite catalysts with various SAR were prepared and evaluated in methanol dehydration to DME process. Compared with a binder-containing catalyst, these catalysts exhibit the common excellent adsorption characteristics related to their high zeolite contents, sufficiently open channels and richness in mesopores. The MD3 catalyst with the lowest SAR, presents the best catalytic performance because of its large amount of weak acid sites and medium strength acid sites, which are considered to be the active acid sites for forming DME. The catalyst contains rich mesopores, which are beneficial to mass transfer, and shows non-sensitivity to water in the crude methanol. These advantages significantly enhance the lifetime of the catalysts in methanol dehydration process.

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