Short Communication

Catalytic dehydration of methanol to dimethyl ether over aluminophosphate and silico-aluminophosphate molecular sieves

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ARTICLE INFO	**ABSTRACT**

A series of aluminophosphate and silico-aluminophosphate molecular sieves, i.e., AlPO-5, AlPO-11, AlPO-41, SAPO-5, SAPO-11, and SAPO-41, were synthesized and studied as possible catalysts for methanol dehydration. Extremely high DME yield of 84.1% with 100% selectivity could be achieved over silico-aluminophosphate SAPO-11 at low reaction temperature of 250 °C. The aluminophosphate and silico-aluminophosphate molecular sieves employed in this study were characterized by XRD, SEM, NH₃-TPD, and TG-DTA techniques. Based on the catalytic and characterization results, the effects of reaction temperature and acid sites on the catalytic behavior of different molecular sieves in methanol dehydration were discussed.

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1. Introduction

Air pollution is one of the most serious environmental problems, and a major source of air pollution comes from automobile exhaust in particular from diesel engines. Dimethyl ether (DME), due to its cleanness, non-toxicity, and environmentally benign behavior, has drawn great attention as a substitute of diesel oil and liquefied petroleum gas in recent years [1–4].

Generally, DME can be synthesized by dehydration of methanol over a solid acid catalyst (Eq. (1)) or synthesized directly from syngas (a mixture of H_2 and CO) over a hybrid catalyst consisting of metal oxide and a solid acid (Eq. (2)) [5].

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \tag{1}$$

$$3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2 \tag{2}$$

It is generally accepted that the methanol dehydration is the initial stage of methanol to olefin (MTO) or methanol to gasoline (MTG) process. The main reason for catalyst deactivation in methanol dehydration is associated with the production of hydrocarbons (HC) as byproducts and subsequent coke formation, due to the strong acidity of catalysts or high reaction temperature. Accordingly, catalysts with moderate or weak acid sites are desirable for methanol dehydration at relatively low temperature.

In the research of catalysts for methanol dehydration, extensive studies have been carried out on adjusting the acidity of solid acid materials.

Modified microporous aluminosilicates, e.g., ZSM-5 [6,7], clinoptilolite [8,9], and mordenite [1,2], have been proved to be good catalysts for methanol dehydration. Aluminophosphate and silico-aluminophosphate molecular sieves generally possess much weaker acid sites compared to aluminosilicate. It can be expected that these types of materials may exhibit good activity for methanol dehydration. Moreover, non-porous aluminum phosphate salts have been reported to exhibit high methanol dehydration activity [10–12]. In contrast, aluminophosphate and silico-aluminophosphate molecular sieves receive much less attention as possible catalysts for methanol dehydration [13]. In the present study, several types of aluminophosphates and silico-aluminophosphates with similar one-dimensional channels are studied as promising catalysts for methanol dehydration. The research focus is laid on the effects of acid sites and reaction temperatures on the catalytic performances.

2. Experimental Section

2.1. Catalysts Preparation

All the aluminophosphate and silico-aluminophosphate molecular sieves were synthesized by hydrothermal method. The as-prepared molecular sieves were calcined in static air at 550 °C for 6 h to remove the occluded organic structure-directing agents. The chemical compositions of the synthetic mixtures and the synthesis conditions of molecular sieves are summarized in Table 1.

2.2. Catalysts Characterization

X-ray diffraction (XRD) patterns of samples were recorded on a Bruker D8 diffractometer with Cu Kα radiation (λ = 1.5418 Å).

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Table 1
Synthesis parameters for molecular sieves employed in this study.

Sample	Batch composition [a]	Temperature (°C)	Time (h)	References
AlPO-5	$1Al_2O_3{:}1P_2O_5{:}1TEA{:}50H_2O$	200	72	Flanigen et al. [14]
AlPO-11	$1Al_2O_3{:}1P_2O_5{:}1DPA{:}50H_2O$	200	72	Flanigen et al. [14]
AlPO-41	$1Al_2O_3{:}1P_2O_5{:}4DPA{:}50H_2O$	200	72	Ma et al. [15]
SAPO-5	$1Al_2O_3{:}1P_2O_5{:}0.4SiO_2{:}2Pr_3N{:}50H_2O$	200	48	Murthy et al. [16]
SAPO-11	$1Al_2O_3{:}1P_2O_5{:}0.4SiO_2{:}2Pr_2NH{:}50H_2O$	200	48	Murthy et al. [16]
SAPO-41	$1Al_2O_3{:}1P_2O_5{:}0.2SiO_2{:}4DPA{:}50H_2O$	200	96	Ma et al. [17]

[a] Molar ratio.
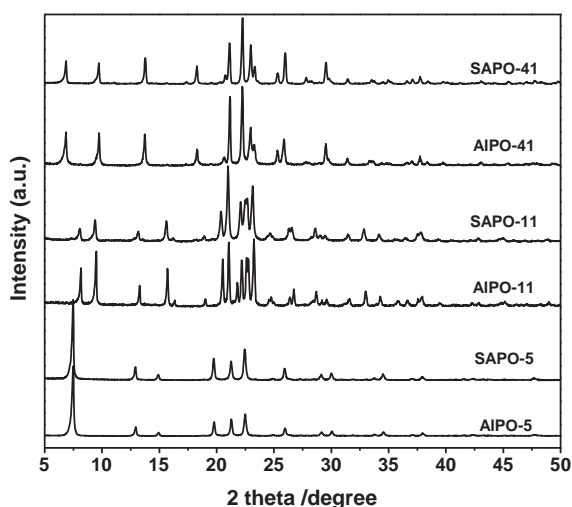
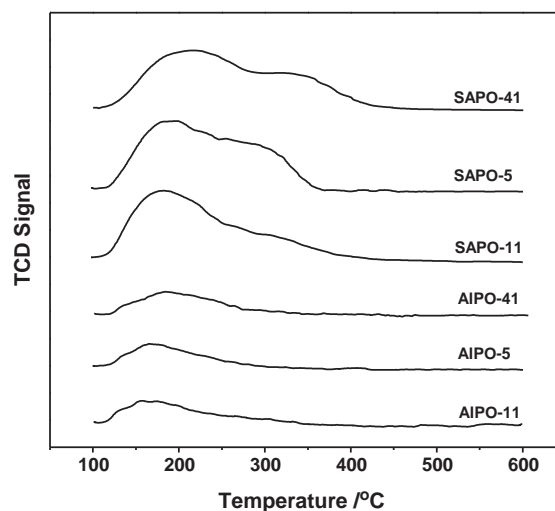**Fig. 1.** XRD patterns of aluminophosphate and silico-aluminophosphate molecular sieves.

A HITACHI S-4700 scanning electron microscope (SEM) was used to investigate the morphology of samples. SEM images were recorded on the samples covered with a thin layer of gold deposited by sputtering.

Temperature-programmed desorption of ammonia (NH_3-TPD) was used to investigate the acid properties of samples, and the experiments were performed on a chemisorption analyzer (Quantachrome ChemBet 300). In a typical process, sample of 0.1 g was pretreated at 450 °C for 1 h in He flow, cooled to 100 °C, and then saturated with 5% NH_3/Ar. After purging with He at 100 °C to eliminate the physical absorbed ammonia, NH_3-TPD was performed in the temperature range of 100–600 °C at a heating rate of 10 °C/min.

After methanol dehydration reaction, catalyst samples were grinded into powders and directly analyzed by TG-DTA on a Rigaku standard type thermogrametric analyzer. In a typical process, sample of 0.1 g was heated in an Al_2O_3 crucible from room temperature to 800 °C at a heating rate of 10 °C/min, with air purging at 30 ml/min.

Fig. 2. NH_3-TPD profiles for calcined molecular sieves.

2.3. Catalytic Test

The catalytic dehydration of methanol was performed in a fixed-bed flow microreactor at atmospheric pressure. Typically, sample of 0.4 g (sieve fraction, 0.25–0.5 mm) was placed in a stainless steel reactor and pretreated in N_2 at 450 °C for 1 h. Methanol was then pumped in at 0.5 ml/h, corresponding to a WHSV of 1/h. The products were analyzed on-line by gas chromatography equipped with a flame ionization detector and a packed-column Porapak Q to separate methanol, DME, and C_1–C_8 hydrocarbons. The activity and selectivity for various catalysts were calculated according to following equations, where n^i and n^0 represent the number of moles of the component at the inlet and outlet streams, respectively.

$$X_{MeOH} = \frac{n^i_{CH_3OH} - n^0_{CH_3OH}}{n^i_{CH_3OH}} \times 100\%, \quad DME\ selectivity = \frac{2n^i_{DME}}{n^i_{CH_3OH} - n^0_{CH_3OH}} \times 100\%$$

3. Results and Discussion

3.1. Physico-chemical Properties of Aluminophosphates and Silico-aluminophosphates

In the powder XRD patterns in Fig. 1, typical diffraction lines corresponding to AlPO-5, AlPO-11, AlPO-41, SAPO-5, SAPO-11, and SAPO-41 [18] are observed, indicating that pure phase of these topologies are obtained for as-synthesized molecular sieves. The BET surface areas of aluminophosphates and silico-aluminophosphates after calcination are in the range of 200–250 m^2/g, as shown in Table 2.

The acidic properties of different molecular sieves are evaluated by NH_3-TPD, and the ammonia desorption profiles are shown in Fig. 2. For

Table 2
Surface areas and acidic properties of molecular sieves employed in this study.

Samples	BET Surface area (m^2/g)	Distribution of acid sites ($mmol_{NH3}$/g) Weak acid 100–250 °C	Moderate acid 250–400 °C	Strong acid 400–600 °C	Total amount ($mmol_{NH3}$/g)
SAPO-5	237	0.47	0.32	–	0.79
SAPO-11	207	0.41	0.09	–	0.50
SAPO-41	235	0.53	0.29	–	0.82
AlPO-5	218	0.09	–	–	0.09
AlPO-11	219	0.08	–	–	0.08
AlPO-41	216	0.09	–	–	0.09

Table 3
Catalytic dehydration of methanol to DME over different molecular sieves.[a]

Sample	Temperature (°C)	Methanol Conversion (%)	Selectivity (%)		DME yield (%)
			DME	HC	
SAPO-5	250	85	68.1	31.9	57.9
	300	98.6	12.1	87.9	11.9
	350	100	1.8	98.2	1.8
	400	100	0	100	0
SAPO-11	200	43.7	100	0	43.7
	250	84.1	100	0	**84.1**
	300	80.1	83.2	16.8	66.6
	350	84.2	41.7	58.3	35.1
	400	95	10.5	89.5	10.0
SAPO-41	250	81.3	82.1	17.9	66.7
	300	92.1	51.4	48.6	47.3
	350	100	3.7	96.3	3.7
	400	100	0	100	0
AlPO-5	250	34.6	100	0	34.6
	300	79.6	99.9	0.1	79.5
	350	81.0	99.6	0.4	**80.7**
	400	79.2	91.7	8.3	72.6
AlPO-11	250	43.8	100	0	43.8
	300	79.3	99.9	0.1	79.2
	350	81.4	99.9	0.1	**81.3**
	400	76.1	98.8	1.2	75.2
AlPO-41	250	47.1	100	0.0	47.1
	300	80.3	99.9	0.1	80.2
	350	82.4	99.9	0.1	**82.3**
	400	75.9	98.8	1.2	75.0

[a] WHSV = 1/h, time on stream = 5 min.

aluminophosphates, similar small desorption peaks at around 170 °C are observed, corresponding to ammonia interacting with Lewis acid sites inside the cavities [19]. For silico-aluminophosphates, two types of ammonia desorption peaks can be observed: the low-temperature peaks at around 170 °C corresponding to weak acid sites and medium-temperature peaks at around 300 °C corresponding to moderate acid sites. The introduction of silicon atoms into the framework of aluminophosphates not only results in the appearance of moderate

acid sites but also leads to the increase in the amount of weak acid sites. The amounts of weak acid sites in silico-aluminophosphates are quite similar, while the amounts of moderate acid sites are observed as SAPO-5 > SAPO-41 > SAPO-11. The quantitative information on the acidic properties obtained from NH$_3$-TPD analysis is summarized in Table 2.

3.2. Catalytic Performance of Aluminophosphates and Silico-aluminophosphates

Table 3 shows the methanol conversion and product selectivity over different molecular sieves in the initial 5 min. At 250 °C, high methanol conversion with DME as the major product is obtained over silico-aluminophosphates SAPO-5, SAPO-11, and SAPO-41. With increasing reaction temperature from 250 to 400 °C, the methanol conversion increases while the DME selectivity decreases. Especially, high DME yield of ca. 84% is achieved on SAPO-11 at low reaction temperature of 250 °C. For aluminophosphates AlPO-5, AlPO-11, and AlPO-41, DME is the major product in the whole temperature range of 250 to 400 °C and the maximal DME yield of >80% can be obtained at 350 °C. Based on the results, AlPO-5, AlPO-11, AlPO-41, and SAPO-11 appear to be promising catalysts for methanol dehydration. The main advantage of these molecular sieves over other solid-acid catalysts is the extremely high DME selectivity, which is essential for industrial application. Although high methanol conversion can be obtained on non-porous aluminophospates, e.g., 83% on aluminum phosphate [11] and 82% on amorphous AlPO$_4$ [12], the DME selectivity is relatively lower, e.g., 89.8% [11] and 99% [12], respectively.

3.3. TG-DTA Analysis of Catalysts After Reaction

Generally, the formation of coke is the key reason for the deactivation of catalysts in the process of methanol dehydration. TG-DTA analysis results of the catalysts after reaction at 350 °C for 6 h are shown in Fig. 3. The weight losses at <200 °C, corresponding to endothermic peaks in DTA curves, are ascribed to desorption of weakly adsorbed water and/or organic molecule. The weight losses at >400 °C, corresponding to exothermic peaks in DTA curves, are
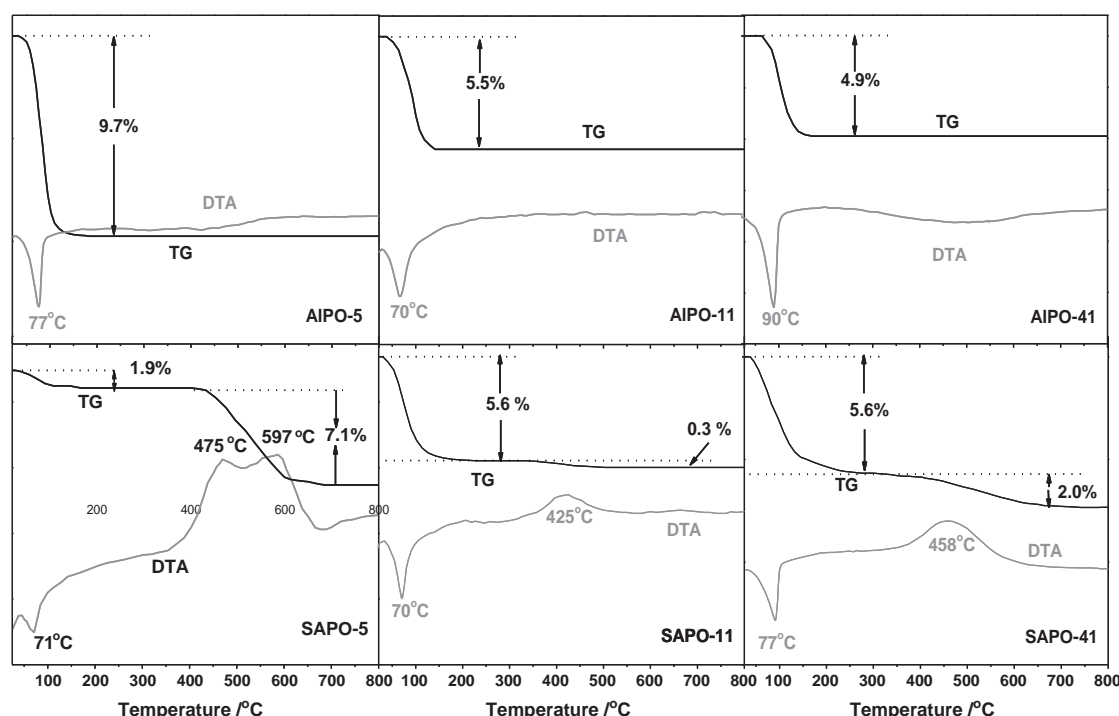

Fig. 3. TG-DTA curves of molecular sieves after DME reaction at 350 °C for 6 h.

ascribed to the combustion of occluded organic materials in molecular sieves. For aluminophosphates AlPO-5, AlPO-11, and AlPO-41, only weakly adsorbed species are detected after reaction and these species are not cumulative during reaction at high temperature of 350 °C. That is to say, aluminophosphates AlPO-5, AlPO-11, and AlPO-41 should not be deactivated by coke formation during reaction. While for silico-aluminophosphates SAPO-5, SAPO-11, and SAPO-41, occluded organic materials are detected in samples after reaction. These species should be the so-called coke, the formation of which is originated from the presence of moderate acid sites in silico-aluminophosphates. The amount of coke in silico-aluminophosphates after reaction correlates well the amount of moderate acid sites in molecular sieves.

3.4. Factors Controlling the Activity and Selectivity of Catalysts

Many factors, e.g., the reaction temperature, the acidity, and pore structure of molecular sieves, may influence the catalytic performance in methanol conversion. In this study, we select aluminophosphates and silico-aluminophosphates with similar one-dimensional pore structure for methanol to DME (MTD) reaction, aiming to minimize the influence from pore structure. Besides, the one-dimensional pore structure allows an easy diffusion of small molecules during reaction and the acid sites in molecular sieves are easily accessible. Hereafter, we will focus on the effects of reaction temperature and acid sites in molecular sieves on the catalytic performances in MTD process.

The reaction of methanol dehydration is an exothermic reaction, and lower reaction temperatures favor the process of reaction from thermodynamics consideration. Meanwhile, higher reaction temperatures lead to a high reaction rate from kinetics consideration. As an integrated result, maximal DME yield is achieved at a proper reaction temperature of 350 °C over aluminophosphates when the side reaction of MTO can be neglected. For MTD reaction over silico-aluminophosphates, the circumstances are much more complicated due to the existence of moderate acid sites. On one side, moderate acid sites in silico-aluminophosphates promote the MTD reaction at low temperature. As we can see from catalytic results in Table 3, much higher DME yield is obtained at 250 °C (when MTD is the major reaction) on silico-aluminophosphate than that on aluminophosphate with the same topological structure. On the other side, moderate acid sites in silico-aluminophosphates boost the side reaction of MTO and thus lead to the decrease in DME yield at high temperatures of 300–400 °C. The strength of moderate acid sites in SAPO-5, SAPO-11, and SAPO-41 is quite similar, while the amount of moderate acid sites

differs greatly (Fig. 2 and Table 2). For SAPO-11, the existence of moderate acid sites greatly promotes MTD reaction and the very low concentration of moderate acid sites is not enough to initiate the MTO reaction at low temperatures. Therefore, very high DME yield of 84.1% with perfect DME selectivity can be achieved at 250 °C.

3.5. Stability in MTD Reaction

SAPO-11 appears to be most promising catalyst for methanol dehydration and its primary durability in reaction is thus tested. As shown in Fig. 4, methanol conversion of >85% with DME selectivity of >99.9% can be preserved for as long as 200 h at 250 °C. After reaction at 250 °C, no occluded organic materials in SAPO-11 catalyst can be detected by TG-DTA analysis (different to the case at 350 °C in Fig. 2). Besides SAPO-11, aluminophosphates AlPO-5, AlPO-11, and AlPO-41 also exhibit good durability for methanol catalytic dehydration at higher reaction temperature of 350 °C, as shown in Fig. S2.

4. Conclusions

Several aluminophosphates and silico-aluminophosphates with similar one-dimensional pore structure were synthesized and studied as catalysts for methanol dehydration. The reaction temperature and acid sites of molecular sieves showed great effects on the catalytic performances. Silico-aluminophosphate SAPO-11 with weak acid sites and very low concentration of moderate acid sites exhibited high MTD activity at low temperature of 250 °C. Methanol conversion of >85% with DME selectivity of >99.9% could be obtained and be preserved for as long as 200 h. The high DME yield and perfect DME selectivity, together with good durability, demonstrated the great potential of SAPO-11 for future application.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2010.11.019.

Fig. 4. Time-on-stream behavior of SAPO-11 in methanol catalytic dehydration to DME at 250 °C.

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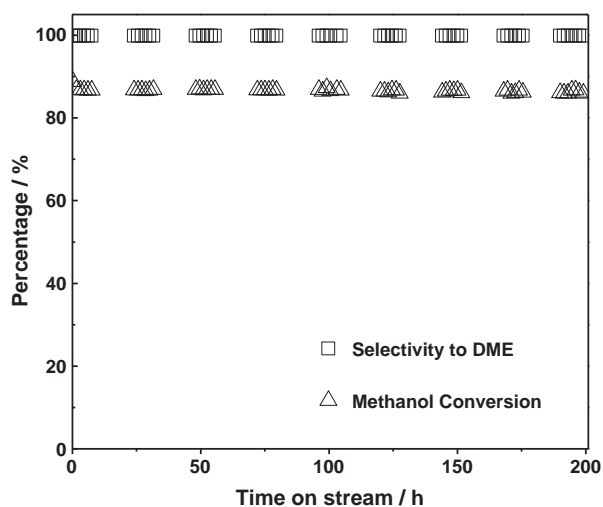[19] G.V.A. Martins, G. Berlier, C. Bisio, S. Coluccia, H.O. Pastore, L. Marchese, J. Phys. Chem. C 112 (2008) 7193.