

Surface acidity and the dehydration of methanol to dimethyl ether

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Abstract

Microcalorimetry and infrared spectroscopy for ammonia adsorption have been used to study the nature, strength and number of surface acid sites of H-ZSM-5, steam de-aluminated H-Y zeolite (SDY), γ -Al₂O₃ and Ti(SO₄)₂/ γ -Al₂O₃ catalysts for the dehydration of methanol to dimethyl ether (DME). The conversion of isopropanol was also performed as a probe reaction to characterize the acid strength. The H-ZSM-5 and SDY possessed strong Brønsted acidity and exhibited high activity for the conversion of methanol to DME at relatively low temperatures, but they did not seem to be suitable as the dehydration component of the hybrid catalyst for the direct synthesis of DME from syngas since the two zeolite catalysts produced hydrocarbons and coke from methanol at temperatures higher than 513 K. The coke was serious over the two zeolite catalysts at 553 K. The dehydration of methanol to DME on γ -Al₂O₃ was found to be low at the temperatures below 573 K though the DME selectivity is high. The modification of the γ -Al₂O₃ by Ti(SO₄)₂ greatly enhanced the surface Brønsted acidity and also the reaction activity for the dehydration of methanol to DME. In addition, no detectable hydrocarbon by-products and coke were formed on the Ti(SO₄)₂/ γ -Al₂O₃ catalyst in the temperature range of 513–593 K. Thus, the Brønsted acid sites with suitable strength may be responsible for the effective conversion of methanol to DME with high stability.

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1. Introduction

Dimethyl ether (DME) may become a fundamental chemical feedstock in the near future. It can be produced in large quantity through natural gas or coal. It is easily liquefied and can be used as a transportation fuel.

DME can be synthesized by dehydration of methanol over an acidic catalyst [1–3]. It can also be synthesized directly from syngas via a so-called STD (syngas to DME) process by employing a hybrid catalyst comprising a methanol synthesis component and a solid acid [4,5], which is more attractive in consideration of the equilibrium limitation. Typically, the Cu/ZnO/Al₂O₃ catalyst is used as a methanol synthesis component in the hybrid catalyst [5,6], and the solid acids

used for the dehydration of methanol are H-ZSM-5, H-Y zeolite, γ -Al₂O₃, silica-alumina and so on [3,5,7,8]. Since the acidic component and the Cu/ZnO/Al₂O₃ component are totally different, the lateral interactions between the two components must be considered for the direct synthesis of DME. The currently used industrial Cu/ZnO/Al₂O₃ catalysts are usually operated at 493–553 K. The reaction at lower temperature leads to the low reaction activity, while higher temperature results in the sintering of the catalysts. Thus, an ideal dehydration component must be operated at the temperature range for the Cu/ZnO/Al₂O₃ catalyst if it is used with Cu/ZnO/Al₂O₃ for the direct synthesis of DME. It must be highly active and stable in the temperature range from 493 to 553 K.

Among the solid acids used for methanol dehydration, H-ZSM-5 and γ -Al₂O₃ are the two catalysts that have been studied intensively both for academic and commercial purposes [1,6,9–11]. They can be used for the direct dehydration

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of methanol to DME [1,2] or as the dehydration components in the STD process [6,12]. H-ZSM-5 was reported to be a good dehydration catalyst by several groups. For example, Ge et al. [12] prepared some bi-functional STD catalysts using H-ZSM-5 as a dehydration component. Kim et al. [3] reported that both Na-ZSM and H-ZSM-5 zeolites could be used as effective dehydration components in STD process. They pointed out that the optimized ZSM-5 composition in the admixed catalysts was determined by the acid strength of the acid component [3]. On the other hand, some researchers reported that hydrocarbons were formed at 543 K or at higher temperatures with H-ZSM-5 zeolite as a dehydration component [2,5,10], and the CO_x conversion decreased rapidly with time on-stream in the STD process [6]. This is due to the strong acidity of the H-ZSM-5 that catalyzes the conversion of methanol to hydrocarbons and even coke [5,10]. Selective poisoning of the strong acid sites by Na⁺ or NH₃ on the H-ZSM-5 inhibited the hydrocarbon formation and enhanced the catalyst stability [6,10].

Although the DME selectivity is high for methanol dehydration on γ -Al₂O₃ [2,10], the γ -Al₂O₃ exhibits much lower activity than that of H-ZSM-5 [2,5,10]. Some researches ascribed the low activity to its Lewis acidity [2,5,10].

Reaction mechanisms have been suggested for methanol dehydration over solid-acid catalysts. Knözinger and co-workers [11] proposed that the DME was formed via a surface reaction between an adsorbed methanol on an acidic site and an adsorbed methoxy anion on a basic site. Bandiera and Naccache [13] proposed that Brønsted acid–Lewis base pair sites might be responsible for DME formation in methanol dehydration over an H-mordenite.

The objective of this work is to examine the effect of surface acidity on the dehydration of methanol to DME. Microcalorimetric adsorption of ammonia and the isopropanol decomposition reaction have been used to probe the number and strength of surface acidity of H-ZSM-5, steam dealuminated H-Y, γ -Al₂O₃ and Ti(SO₄)₂ modified γ -Al₂O₃. Infrared spectroscopy of adsorbed ammonia has been used to probe the change of nature of surface acidity of γ -Al₂O₃ upon the addition of Ti(SO₄)₂.

2. Experimental

2.1. Catalysts

An H-ZSM-5 zeolite was prepared by calcining at 823 K for 3 h a commercial NH₄-ZSM-5 zeolite (Huahua Co., China) with a bulk SiO₂/Al₂O₃ ratio of 25. The dealuminated H-Y (SiO₂/Al₂O₃ = 7.8) was prepared from commercial NaY zeolite (Huahua Co., China) by ammonium exchange followed by steam treatment at 873 K for 5 h. The sample thus obtained was termed as SDY. Porous γ -Al₂O₃ was supplied by Fushun Catalyst Co., China. The Ti(SO₄)₂ modified γ -Al₂O₃ was obtained by impregnating the porous γ -Al₂O₃ with an aqueous solution of Ti(SO₄)₂. The sam-

ple was then dried at 383 K overnight and calcined at 723 K for 1.5 h. The Ti(SO₄)₂/ γ -Al₂O₃ contained 5% Ti(SO₄)₂ by mass. The surface areas of the catalysts are given in Table 1.

2.2. Test reaction

The dehydration of methanol was carried out in a fix-bed micro-reactor made of stainless steel with an inner diameter of 6 mm. The methanol was introduced to the reaction zone by bubbling N₂ (99.999%) through a glass saturator filled with methanol (AR) maintained at 303 K. In each test, 0.2 g catalyst was loaded, and the gas hourly space velocity (GHSV) was 3400 ml g_{cat}⁻¹ h⁻¹. The feed composition was maintained at methanol:N₂ = 21:79. The tail gas out of the reactor was analyzed by an on-line GC equipped with an FID detector. The column used was PEG20M for the separation of methanol, DME and other organic compounds. The gas lines were kept at 383 K to prevent condensation of the reactant and products. The reaction was carried out at atmospheric pressure.

2.3. Microcalorimetric adsorption

The measurements of surface acidity of the catalysts were performed at 423 K using an adsorptive microcalorimeter equipped with a C-80 calorimeter (Setaram, France). The calorimeter was connected to a volumetric system equipped with a Baratron capacitance manometer for the pressure measurement and gas handling. Usually, 0.1–0.2 g sample was loaded and activated at 673 K under 500 Torr O₂ and then evacuated at the same temperature for 1 h.

2.4. Isopropanol probe reaction

Isopropanol probe reaction was used to characterize the surface acidity and basicity. The probe reaction was carried out in a fixed-bed glass tube reactor in this work. About 100 mg sample was loaded for the isopropanol probe reaction. Isopropanol was introduced to the reaction zone by bubbling N₂ (99.999%) through a glass saturator filled with isopropanol maintained at 295 K. Isopropanol and reaction products were analyzed by an online gas chromatograph, using a PEG 20M packed column connected to an FID. Each catalyst was pre-treated by heating in N₂ at 673 K for 1 h and then cooled in N₂ flow to the reaction temperature.

Table 1
BET surface areas

Catalyst sample	Surface area (m ² g ⁻¹)
H-ZSM-5 (SiO ₂ /Al ₂ O ₃ = 25)	450
SDY (SiO ₂ /Al ₂ O ₃ = 7.8)	581
γ -Al ₂ O ₃	290
Ti(SO ₄) ₂ / γ -Al ₂ O ₃	291

2.5. FT-IR spectra

FT-IR spectra were collected with a Vector 22 FT-IR system. Each spectrum was recorded at 4 cm^{-1} resolution with 40 scans. For each catalyst, 10–15 mg of the sample was pressed into a self-supported pellet with a diameter of 1 cm. The pellet was loaded into a quartz cell equipped with a CaF_2 window, followed by the same treatments as for the microcalorimetric adsorption studies. About 40 Torr of ammonia was introduced into the cell at room temperature. The sample was evacuated at room temperature before the FT-IR measurement.

3. Results and discussion

Fig. 1 shows the results for the dehydration of methanol to DME over the different catalysts. Briefly, the activities follow the order of $\text{H-ZSM-5} > \text{SDY} > \text{Ti}(\text{SO}_4)_2/\gamma\text{-Al}_2\text{O}_3 > \gamma\text{-Al}_2\text{O}_3$. It is seen that the H-ZSM-5 exhibited high activity even at the temperature as low as 423 K. At 443 K, the activity reached maximum and then decreased with the further increase of temperature. This is due to the equilibrium limitation since the reaction is exothermic. At the temperatures above 513 K, organic by-products were detected on H-ZSM-5. This is consistent with the result of Takeguchi et al. [5]. At 553 K, large amount of by-products were observed, and the methanol conversion decreased with the prolonged time on stream. It was observed that the catalyst was seriously coked after the reaction at 553 K for 1 h. This result indicated that the strong surface acidity of H-ZSM-5 catalyzed the conversion of methanol to hydrocarbons and caused serious coking. Thus, the surface acidity of H-ZSM-5 must be modified properly before it can be used with $\text{Cu/ZnO/Al}_2\text{O}_3$ for the direct synthesis of DME from syngas. Selective poisoning of the strong acid sites on H-ZSM-5 with NH_3 or amine could eliminate the formation of hydrocarbons and coke and increase the catalyst stability [6]. Partial substitution of Na^+ in H-ZSM-5 resulted in the similar effect [10].

The surface acidity of H-Y was enhanced due to the de-alumination. In addition, steam de-alumination produced

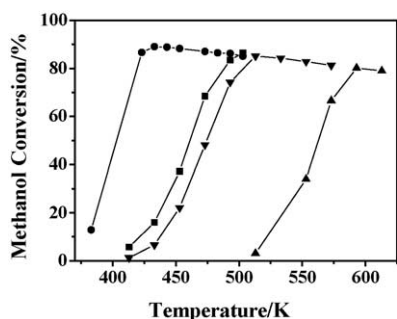


Fig. 1. Dehydration of methanol over H-ZSM-5 (●), SDY (■), $\gamma\text{-Al}_2\text{O}_3$ (▲) and $\text{Ti}(\text{SO}_4)_2$ modified $\gamma\text{-Al}_2\text{O}_3$ (▼). $\text{GHSV} = 3400\text{ ml g}_{\text{cat}}^{-1}\text{ h}^{-1}$, $\text{methanol:N}_2 = 21:79$.

Lewis acidity due to the production of extra-framework aluminum cations. Accordingly, the activity of SDY for the dehydration of methanol was significantly higher than that of $\gamma\text{-Al}_2\text{O}_3$, as can be seen in Fig. 1. Fig. 1 also shows that the SDY was not as active as the H-ZSM-5 for the dehydration of methanol. However, the SDY was still active enough to produce hydrocarbon by-products at the temperatures higher than 513 K. Coke formation was observed over the SDY after 1 h reaction at 553 K.

Thus, the H-ZSM-5 and SDY exhibited high activity for the dehydration of methanol to DME at relatively low temperatures. However, the two catalysts produced organic by-products and coke in the temperature range for the methanol synthesis on $\text{Cu/ZnO/Al}_2\text{O}_3$. The coking led to the decreased activity and selectivity to DME and therefore, the catalysts without proper modification do not seem to be suitable as the dehydration components for the direct synthesis of DME from syngas.

The formation of surface polymeric hydrocarbons may possess the autocatalytic feature that accelerates the formation of hydrocarbon by-products. Coke formation was further confirmed by the regeneration. A de-activated SDY catalyst was regenerated by flowing air through the catalyst bed at 773 K for 2 h in order to burn off the deposited surface carbon species. Table 2 shows that the regeneration recovered the activity completely, clearly indicating that the de-activation was indeed due to the coking.

Fig. 1 shows that the $\gamma\text{-Al}_2\text{O}_3$ used showed the low activity for the dehydration of methanol to DME. At 513 K, the methanol conversion was only 3%. The conversion increased to 66% at 573 K and to 80% at 593 K. It is interesting to mention that coking was not found over the catalyst at the reaction temperatures used, but its low activity at the temperature range (493–553 K) did not meet the requirement as an acidic component for the synthesis of DME. A modification is needed to increase the surface acidity and thereby to increase the activity of dehydration.

The addition of $\text{Ti}(\text{SO}_4)_2$ (5 mass%) greatly enhanced the activity of methanol dehydration reaction on $\gamma\text{-Al}_2\text{O}_3$. The conversion reached equilibrium at 513 K (about 85% methanol converted). At higher temperatures, the conversion decreased because of the equilibrium limitation. Even at 593 K, no hydrocarbon by-products and coking were observed over this catalyst for the dehydration reaction. The formation of Brønsted acid sites due to the incorporation of SO_4^{2-} might be responsible for the enhanced reaction activity. One can assume that this surface acidity is not very strong

Table 2
Regeneration of coked SDY catalyst

Catalyst	Conversion of methanol/%
Fresh catalyst	86.5
After coking	46.2
After regeneration	87.5

The catalyst was regenerated in air at 773 K for 2 h and the reaction of methanol conversion was performed at 503 K.

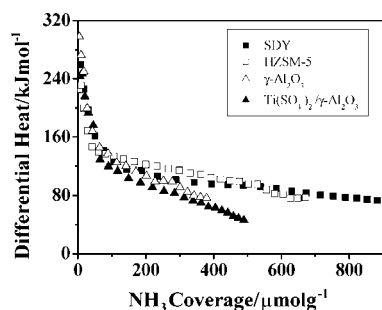


Fig. 2. Differential heat vs. coverage for ammonia adsorption at 423 K over SDY (■), H-ZSM-5 (□), γ -Al₂O₃ (△) and Ti(SO₄)₂ modified γ -Al₂O₃ (▲).

since the side-reactions and coking were negligible over the catalyst at the reaction temperatures up to 593 K.

In Fig. 2 is shown the results of microcalorimetric adsorption of ammonia for the catalysts used for the dehydration of methanol. All the catalysts exhibited high initial heats of ammonia adsorption, in which the γ -Al₂O₃ and SDY showed the higher initial heats than the other two samples. However, the H-ZSM-5 exhibited the highest activity for the dehydration reaction at relatively low temperatures at which the γ -Al₂O₃ displayed the low dehydration activity. It is known that γ -Al₂O₃ possessed mainly the Lewis acidity [5,14]. The SDY had substantial amount of Lewis acidity owing to the presence of extra-framework Al³⁺ formed by de-alumination treatment [15]. These results suggest that the Brønsted acidity might exhibit higher activity than Lewis acidity for the dehydration of methanol. It has been shown that the strength of Lewis acid sites on γ -Al₂O₃ was decreased upon the adsorption of water [16], and since water is a product of methanol dehydration, the presence of water decreased the strength of Lewis acidity under reaction conditions. Xu et al. [2] observed that the partial pressure of water had a strong negative effect on the activity of γ -Al₂O₃ for the dehydration of methanol to DME, while this effect was not apparent for the H-ZSM-5. The authors believed that water reduced the number of Lewis acid sites while had little effect on Brønsted acid sites [9,10]. Hindin and Weller [17] also observed that the dried Al₂O₃ was very sensitive to poisoning by water when they studied the hydrogenation of ethylene on Al₂O₃. And about 0.15% water was sufficient for complete poisoning, which corresponded to the coverage of about 2% of the total alumina surface [17].

Takeguchi et al. [5] have studied the co-adsorption of NH₃ and H₂O on silica-alumina catalysts using the TPD method,

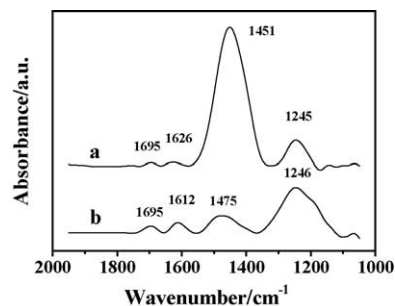


Fig. 3. FT-IR spectra for NH₃ adsorption at room temperature on Ti(SO₄)₂ modified γ -Al₂O₃ (a) and γ -Al₂O₃ (b).

and they confirmed that water and NH₃ were competitively adsorbed on Lewis acid sites, whereas the adsorption of NH₃ on Brønsted acid sites was not much affected by the presence of water.

The FT-IR spectra for Ti(SO₄)₂/ γ -Al₂O₃ and γ -Al₂O₃ after ammonia adsorption are compared in Fig. 3. The bands at 1612 and 1245 cm⁻¹ originate from NH₃ molecules coordinated to aluminum cations, revealing Lewis acid sites on γ -Al₂O₃ [14]. The bands at 1475 and 1695 cm⁻¹ are due to NH₄⁺ formed by the interaction of NH₃ with Brønsted acid sites on γ -Al₂O₃ [14].

The intensity of the band at 1475 cm⁻¹ for Brønsted acid sites on γ -Al₂O₃ increased drastically upon the addition of Ti(SO₄)₂, while the relative intensity of the bands at 1612 and 1245 cm⁻¹ for Lewis acid sites decreased. Furthermore, the band of surface NH₄⁺ shifted to lower wave number around 1450 cm⁻¹, indicating the strong interaction between the Brønsted acid sites and the absorbed NH₃ [18]. Apparently, the greatly increased surface Brønsted acidity on the modified γ -Al₂O₃ is responsible for the greatly increased methanol dehydration activity.

Table 3 presents the results of isopropanol probe reaction over the catalysts. The activity for the isopropanol conversion followed the same order as methanol dehydration: H-ZSM-5 > SDY > Ti(SO₄)₂/ γ -Al₂O₃ > γ -Al₂O₃. The H-ZSM-5 was very active. The rate of isopropanol conversion was 64 mmol g⁻¹ h⁻¹ for the H-ZSM-5 at 423 K, which was about 50 times higher than that for the γ -Al₂O₃ at 453 K. SDY zeolite was less active than H-ZSM-5, but it was much more active than the two γ -Al₂O₃ samples. The modification of γ -Al₂O₃ with Ti(SO₄)₂ resulted in a significant increase of the reaction rate (about 2.5 times more active than the unmodified γ -Al₂O₃). The H-ZSM-5 exhibited high selectivity

Table 3
Rate and selectivity of isopropanol conversion over the catalysts

Catalyst	Reaction temperature (K)	Reaction rate		Product selectivity (%)		
		mmol g ⁻¹ h ⁻¹	μmol m ⁻² h ⁻¹	Propylene	Acetone	DIPE
HZSM-5	423	64.0	142	99.1	0.9	0.0
SDY	423	17.8	30.6	52.5	0.0	47.5
γ -Al ₂ O ₃	453	1.3	4.5	70.2	0.0	29.8
Ti(SO ₄) ₂ / γ -Al ₂ O ₃	453	3.4	11.7	76.3	1.1	22.6

to propylene (99%), while the other three samples showed also the selectivity to DIPE. It is generally true that the rate of propylene formation increases with the increase of the surface acidity, while the rate of acetone formation relates to the synergetic effect of acidic and basic sites on a surface [19,20]. Diisopropyl ether (DIPE) is usually produced on weak acid sites [21].

The conversion of isopropanol to DIPE indicated that substantial amount of weak surface sites were present over the SDY, γ -Al₂O₃ and Ti(SO₄)₂/ γ -Al₂O₃ catalysts. These weak acid sites might be Lewis sites, which were responsible for the formation of DIPE. On the other hand, strong Brønsted acid sites seemed to catalyze the conversion of isopropanol to propylene.

Although the Ti(SO₄)₂/ γ -Al₂O₃ exhibited excellent performance for the dehydration of methanol to DME in terms of activity and stability, its suitability for use as an acidic component for the direct synthesis of DME from syngas is doubtful. Since the Cu/ZnO/Al₂O₃ catalyst for methanol synthesis is usually sensitive to sulfur poisoning, the presence of sulfur in the Ti(SO₄)₂/ γ -Al₂O₃ may prevent its use as an acidic component with the Cu/ZnO/Al₂O₃ for the direct synthesis of DME from syngas. However, Ti(SO₄)₂/ γ -Al₂O₃ may be useful for the indirect synthesis of DME, i.e., through two stage synthesis from syngas to methanol and then from methanol to DME. A recent study showed that the indirect route might be economically competitive considering the low investment cost by using widely available methanol synthesis facilities [22].

4. Conclusions

In conclusion, the H-ZSM-5 and SDY catalysts possessed strong Brønsted surface acidity and exhibited high activity for the dehydration of methanol to DME at relatively low temperatures. However, these catalysts also catalyzed the conversion of methanol to hydrocarbons and coke. On the other hand, γ -Al₂O₃ possessed strong Lewis acidity, but exhibited low activity for the dehydration of methanol, probably because H₂O was preferentially absorbed on the Lewis acid sites and poisoned the strong Lewis acidity under the reaction conditions where the water was an inevitable product. The modification of γ -Al₂O₃ by Ti(SO₄)₂ enhanced the number and strength of surface Brønsted acidity and thereby the dehydration activity. More importantly, no carbon deposition was observed over this catalyst and therefore it did not seem to

de-activate during the reaction of dehydration of methanol to DME. Thus, a proper modification of γ -Al₂O₃ may result in a solid acid catalyst that possesses intermediate strength of Brønsted acidity that catalyzes the stable conversion of methanol to DME. This catalyst may become a candidate for the direct dehydration of methanol to DME in the two-stage synthesis of DME from syngas.

Acknowledgements

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