甲醇脱水合成二甲醚的 Al_2O_3 -HZSM-5 组合固体酸催化剂

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摘要: 制备了可用于固定床反应器中甲醇脱水制备二甲醚的 Al_2O_3 -HZSM-5 组合固体酸催化剂系列, 并采用 X 射线衍射、扫描电镜、 N_2 物理吸附和氨气程序升温脱附等对其进行了表征。结果表明, 在浸渍法制备的组合 Al_2O_3 -HZSM-5 催化剂中, 细小的氧化铝颗粒高度分散在 HZSM-5 分子筛的周围; 在化学沉淀法制备的组合 Al_2O_3 -HZSM-5 催化剂中, 一层氧化铝膜覆盖在 HZSM-5 分子筛的颗粒外层。所制备的催化剂都具有较多的大孔和介孔比表面积, 在低温 (235 °C) 和高空速 (30 h^{-1}) 条件下具有较高的甲醇脱水反应活性和稳定性, 其中在化学沉淀法制备的组合 Al_2O_3 -HZSM-5 催化剂上, 二甲醚产率达到 13.5 g/(g·h)。

关键词: 组合固体酸; 氧化铝; HZSM-5; 甲醇; 二甲醚

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Synthesis of Dimethyl Ether via Methanol Dehydration over Combined Al_2O_3 -HZSM-5 Solid Acids

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Abstract: Combined Al_2O_3 -HZSM-5 solid acids were prepared and used for methanol dehydration to dimethyl ether (DME) in a fixed-bed reactor. The physicochemical properties of the combined solid acids were characterized by X-ray diffraction, field emission scanning electron microscopy, N_2 adsorption, and NH_3 temperature-programmed desorption. Al_2O_3 was highly dispersed in Al_2O_3 -HZSM-5 after impregnation (Al_2O_3 -HZSM-5-IM), while a layered Al_2O_3 -covered HZSM-5 structure solid acid was synthesized via chemical precipitation (Al_2O_3 -HZSM-5-CP). Both the combined Al_2O_3 -HZSM-5 solid acids prepared by impregnation and chemical precipitation have a higher surface area and more meso- and macropores. The combined Al_2O_3 -HZSM-5 solid acids exhibit higher methanol dehydration activity than pure Al_2O_3 and it possesses higher stability than pure HZSM-5 at a lower temperature (235 °C) and a higher LHSV (30 h^{-1}). The stable DME productivities for Al_2O_3 -HZSM-5-IM and Al_2O_3 -HZSM-5-CP at 235 °C reached 12.7 and 13.5 g/(g·h), respectively.

Key words: combined solid acid; alumina; HZSM-5; methanol; dimethyl ether

Dimethyl ether (DME) is an important alternative fuel for vehicle engines, especially to replace diesel. It is a fuel additive and can also be used for family cooking gas instead of liquefied petroleum gas [1]. DME and fluoro-dimethyl ether are also widely recommended as environmentally friendly aerosols and green refrigerants because they have zero ozone depletion potential and a lower global warming potential compared with traditional chlorofluorocarbons (CFCs, Freon) and R-134a (HFC-134a) [2–4]. DME is also an important intermediate for the manufacture of many

value-added chemicals such as lower olefins, methyl acetate, and dimethyl sulphate [5–7]. Therefore, the production and utilization of DME has attracted an ever increasing amount of attention because of the need for environmental protection and the increased price of crude oil.

One commercialized process of DME production is methanol dehydration as shown in Eq. (1):

Industrially this reaction is generally catalyzed by Al_2O_3 at higher than 300 °C because the acidity of Al_2O_3 is poorer

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than that of zeolites such as HZSM-5 and HY. However, higher reaction temperatures suffer from two major disadvantages: one is that it is thermodynamically unfavorable for methanol dehydration and the other is that deactivation occurs easily in the presence of water because of its hydrophilic nature. HZSM-5, HY, SAPOs, and a series of solid acids were also reported for methanol dehydration between 250 and 400 °C [7–18]. However, most zeolite catalysts produce undesirable side products such as hydrocarbons and even coke because of the presence of strong acid sites and the high dehydration temperature.

Recently, Kim et al. [11] found that a mechanical mixture of Na₄₀-H-ZSM-5 (30%) and Al₂O₃ exhibited a wide operative temperature range and an improved stability for the dehydration of methanol to DME. However, the reported catalysts must be operated at temperatures as high as 270 °C and a space velocity (liquid hourly space velocity, abbreviated as LHSV) as low as 10 h⁻¹ because its activity is lower than that of NaHZSM-5 due to its fewer active sites.

Theoretically, methanol dehydration is favored at lower temperatures because it is an exothermic reaction [15] and the formation of byproducts such as ethylene, carbon monoxide, hydrogen, and/or coke is significant at higher temperatures. In this paper, we report a series of combined Al₂O₃-HZSM-5 solid acid catalysts that were efficient in methanol dehydration for DME production. We found that the catalyst exhibits higher activity and stability at a reaction temperature as low as 235 °C and a LHSV as high as 30 h⁻¹.

1 Experimental

1.1 Catalyst preparation

Combined Al₂O₃-HZSM-5 solid acids were prepared separately by chemical precipitation (CP) and impregnation (IM) as follows.

For the preparation of Al₂O₃-HZSM-5-CP, 8 g of HZSM-5 powder (H type with Si/Al = 50, Nankai University, China) was poured into 170 ml of an aqueous Al(NO₃)₃ solution (with an Al³⁺ concentration of 0.25 mol/L) at room temperature under vigorously stirring. An aqueous solution of ammonia (27%–28%) was added dropwise to the above-mentioned slurry until the pH reached 7.0. The precursor was further stirred for 2 h, filtered and washed with deionized water, and then dried at 120 °C overnight and finally calcined at 550 °C for 4 h. The final solid catalyst weighed 9.8 g and is denoted Al₂O₃-HZSM-5-CP. Inductively coupled plasma (ICP, Plasma-Spec-II spectrometer) analysis showed that the Si/Al ratio in the prepared Al₂O₃-HZSM-5-CP was 6.20, which indicates that the weight ratio of Al₂O₃/HZSM-5 was 2/8.

For the preparation of Al₂O₃-HZSM-5-IM, a specific amount of boehmite powder (Jiangyin, China) was dissolved in a 0.1% acetic acid solution at room temperature to form an aqueous colloidal solution. HZSM-5 powder (H type with Si/Al = 50, Nankai University, China) was put into a three-necked glass bottle, heated to 150 °C in an oil bath and degassed under vacuum for 2 h. A specific amount of aqueous colloidal solution was then added dropwise to the HZSM-5 powder under vacuum at room temperature. The precursor was dried at 120 °C overnight and then calcined at 550 °C for 4 h. The catalysts were designated Al₂O₃-HZSM-5-IM, where the amount of added Al₂O₃ was the same as that of Al₂O₃-HZSM-5-CP.

Commercial spherical γ -Al₂O₃ sized between 0.25 and 0.42 mm (40–60 mesh) was purchased from Huahua Catalysis Co. (Wenzhou, China) and tested as a reference catalyst. Before the methanol dehydration experiment and characterization, γ -Al₂O₃ was calcined at 550 °C for 4 h.

1.2 Characterization

The physicochemical properties of these combined solid acids were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), N₂ adsorption, and NH₃ temperature-programmed desorption (NH₃-TPD).

XRD analysis was performed on an automated power X-ray diffractometer system (Cu K α radiation, 40 kV, 40 mA) (Rigaku, RINT 2500). FESEM images were obtained using a Philips XL-30 at an accelerating voltage of 15 kV. Energy dispersion X-ray (EDX) analysis was carried out using a Thermo NORAN VANTAGE ESI X-ray with a take off angle of 30° and a live time of 100 s.

N₂ adsorption was carried out at –196 °C using an auto-adsorption analyzer (OMNISORP, 100CX). The sample was first degassed under high vacuum at 250 °C for 2 h while the surface area and pore size distribution were calculated using the adsorption isotherm. In addition, the surface area of the meso- and macropores ($A_{t\text{-plot}}$) was calculated by the t -plot method with an adsorbed film-thickness between 0.35 and 0.50 nm.

NH₃-TPD was performed using an autocatalytic adsorption system (AMI-200, Zeton Altamira, Pittsburgh, USA), which included an on-line thermal conductivity detector (TCD). Sample (100 mg) was placed in a quartz tubular reactor and pretreated at 500 °C with an Ar flow of 30 ml/min for 1 h and then cooled to 50 °C. Ammonia (20% NH₃-80% Ar) was introduced at a flow rate of 30 ml/min for 0.5 h at 50 °C and then an Ar stream was blown in until a constant TCD level was obtained. The reactor temperature was programmed at a ramp rate of 10 °C/min and the effluent was dried by powdered KOH to remove moisture and

then ammonia was measured using the TCD and recorded as function of temperature.

1.3 Catalytic reaction

Methanol dehydration was carried out in a high pressure microreactor system (MRC8004, Huayang, China) using the following procedure. The catalyst (0.2 g sized between 0.25 and 0.42 mm) was placed in a stainless-steel fixed-bed reactor, pretreated at 300 °C in N_2 for 3 h, cooled to 190 °C and purged to 0.5 MPa. The feed was then changed to 70% CH_3OH -30% N_2 . The methanol feed was controlled by a micro-stoichiometric pump (Syltech P501, USA), gasified at 200 °C and mixed with N_2 carrier gas. The products in the effluent were analyzed using an on-line gas chromatograph (HP5890, Series II, Hewlett-Packard) with a TCD detector. The reaction temperature was varied from 190 to 300 °C and the LHSV of methanol was maintained at 30 h^{-1} . The stability of the combined Al_2O_3 -HZSM-5 solid acid catalysts was investigated at 235 °C and at a LHSV of 30 h^{-1} .

The conversion of methanol and the selectivity for DME were calculated using the following equations:

$$X(\text{CH}_3\text{OH}) = ([\text{CH}_3\text{OH}]_{\text{mol-in-feed}} - [\text{CH}_3\text{OH}]_{\text{mol-in-effluent}}) / [\text{CH}_3\text{OH}]_{\text{mol-in-feed}} \quad (2)$$

$$S(\text{DME}) = 2 \times [\text{DME}]_{\text{mol-in-effluent}} / ([\text{CH}_3\text{OH}]_{\text{mol-in-feed}} - [\text{CH}_3\text{OH}]_{\text{mol-in-effluent}}) \quad (3)$$

2 Results and discussion

2.1 Physicochemical properties of the combined solid acids

Figure 1 shows the XRD patterns of the combined Al_2O_3 -HZSM-5 solid acids prepared by chemical precipita-

Fig. 1. XRD patterns of HZSM-5, $\gamma\text{-Al}_2\text{O}_3$, and Al_2O_3 -HZSM-5.

tion and impregnation. HZSM-5 ($2\theta = 8.1^\circ, 9.1^\circ, 15.6^\circ, 23.4^\circ, 24.6^\circ$, and 45.8°) was detected in both the combined solid acids and its crystalline structure remained intact. The Al_2O_3 diffraction peak is quite weak in the combined Al_2O_3 -HZSM-5, which indicates that Al_2O_3 formed during either impregnation or chemical precipitation and that it is highly dispersed on the surface of HZSM-5. The inserted fine spectrum of Al_2O_3 -HZSM-5-IM and Al_2O_3 -HZSM-5-CP from 60° – 75° shows that separate Al_2O_3 particles are present at 67° in Al_2O_3 -HZSM-5-IM. These results indicate that smaller Al_2O_3 particles exist in the sample prepared by impregnation but no separate Al_2O_3 particles were detected for Al_2O_3 -HZSM-5-CP.

Figure 2 shows the SEM images of HZSM-5, $\gamma\text{-Al}_2\text{O}_3$, and the combined Al_2O_3 -HZSM-5 solid acids prepared using different methods with the same Al_2O_3 content (20%). Pure $\gamma\text{-Al}_2\text{O}_3$ shows clear seed-like particles of 0.05–0.2 μm in size and these seeds aggregate easily to form large agglomerated particles (see the bottom of Fig. 2(a)) because of the higher surface energy and higher capillary force of the Al-OH groups [19]. Highly dispersed HZSM-5 particles of 0.8–2.2 μm in size were also detected and are shown in Fig. 2(b).

Layered Al_2O_3 -covered HZSM-5 particles are clearly present in the Al_2O_3 -HZSM-5-CP image and the amount of separated Al_2O_3 particles is low. There is no clear boundary between Al_2O_3 and HZSM-5 (Fig. 2(c)). EDX analysis indicated that the surface Si/Al ratio of Al_2O_3 -HZSM-5-CP is 31.24/8.58. This amount of surface Al content is higher than that of the bulk composition (Si/Al = 6.20, see Table 1) suggesting that the Al_2O_3 layers mainly cover the outer surface of the HZSM-5 particle. Additionally, core-shell structured solid acids (with a layer of Al_2O_3 covering the crystal core of HZSM-5) were formed in Al_2O_3 -HZSM-5-CP. This was confirmed by the FESEM analysis obtained using a much higher magnification (Fig. 2(d)).

A large number of highly dispersed small Al_2O_3 particles (sized between 0.05–0.1 μm) were detected around HZSM-5 (sized between 0.8–2.2 μm) in Al_2O_3 -HZSM-5-IM (Fig. 2(e)). EDX analysis (circled area in Fig. 2(e)) showed that the surface Si/Al ratio of Al_2O_3 -HZSM-5-IM is 3.49 (see Table 1). These results indicate that impregnating HZSM-5 powder with an aqueous colloidal solution of Al_2O_3 can improve the dispersion of Al_2O_3 . Layered Al_2O_3 -covered HZSM-5 particles can be synthesized by the chemical precipitation of $\text{Al}(\text{OH})_3$ on the HZSM-5.

Table 1 summarizes the surface elemental content of the combined Al_2O_3 -HZSM-5 solid acids as detected by EDX and the bulk Si/Al ratio determined by ICP. The detected surface Si/Al ratios of Al_2O_3 -HZSM-5-CP and Al_2O_3 -HZSM-5-IM are 3.64 and 3.49, respectively, and these values are far lower than those of the bulk composition (Si/Al

Fig. 2. FESEM images of HZSM-5, γ - Al_2O_3 , and the combined Al_2O_3 -HZSM-5. (a) γ - Al_2O_3 ; (b) HZSM-5; (c) Al_2O_3 -HZSM-5-CP; (d) Al_2O_3 -HZSM-5-CP; (e) Al_2O_3 -HZSM-5-IM.

Table 1 The elemental content of the Al_2O_3 -HZSM-5 catalysts determined by EDX analysis

Sample	Elemental content (mol%)			Surface	Bulk
	Si	Al	O	Si/Al ratio	Si/Al ratio*
HZSM-5	—	—	—	50.0	50.0
Al_2O_3 -HZSM-5-IM	30.75	8.81	60.44	3.49	6.20
Al_2O_3 -HZSM-5-CP	31.24	8.58	60.18	3.64	6.20

*Calculated from the ICP analysis.

= 6.20). This indicates that Al_2O_3 is highly dispersed on the external surface of the HZSM-5 particles in these combined solid acids.

The porous structure of the combined Al_2O_3 -HZSM-5 solid acids was characterized by N_2 adsorption and is summarized in Table 2. The measured surface areas of pure HZSM-5, Al_2O_3 -HZSM-5-IM, Al_2O_3 -HZSM-5-CP, and pure γ - Al_2O_3 are 331.1, 306.9, 367.5, and 184.3 m^2/g , respectively. However, the surface area of the meso- and macropores ($A_{t\text{-plot}}$) and the pore volume of Al_2O_3 -HZSM-5-IM increased from 133.1 m^2/g and 0.216 ml/g (pure HZSM-5) to 153.1 m^2/g and 0.263 ml/g (Al_2O_3 -HZSM-5-IM), respectively. The values for these properties further increased to 205.3 m^2/g and 0.348 ml/g for Al_2O_3 -HZSM-5-CP. The micropore volume of Al_2O_3 -HZSM-5-CP is 0.04 ml/g and this value is quite low compared with that of pure HZSM-5 and Al_2O_3 -HZSM-5-IM. This decrease can be attributed to the portion of Al^{3+} that enters the pore channel of HZSM-5 before precipitation, which forms Al_2O_3 and blocks the partial micropore. Previous work has revealed that longer hydrocarbons and coke form easily on strong acid sites in micropores, resulting in deactivation [5]. A decrease in the mi-

crore pore volume can improve the stability of the catalysts.

It is well known that the HZSM-5 crystalline framework consists of two types of intersecting channel systems made up of ten membered ring openings. The pore volume of HZSM-5 is limited (0.216 ml/g) and its average pore diameter is small (0.56 nm) [20,21]. The surface areas of the meso- and macropores of the samples are summarized in Table 2 and were calculated considering an adsorbed film-thickness range from 0.35 to 0.50 nm. For HZSM-5 these properties are due to the pores formed by the piling up of zeolite particles (see the FESEM images of HZSM-5 in Fig. 2(b)). The surface areas of the meso- and macropores and the pore volume obviously increased for the combined Al_2O_3 -HZSM-5 catalysts and this can be attributed to the strong interaction between Al_2O_3 (in the form of fine particles or a layer) and the HZSM-5 particles (Fig. 2(c)). We have previously reported that the deep dehydration of methanol and DME in the micropores of zeolites brings about carbon deposition, which leads to the quick deactivation of pure zeolite catalysts [5,22]. In this case, the en-

Table 2 Porous structure of the combined Al_2O_3 -HZSM-5 catalysts

Sample	$A_{\text{BET}}/(\text{m}^2/\text{g})$	Pore volume (ml/g)	Micropore volume (ml/g)	$A_{t\text{-plot}}^*/(\text{m}^2/\text{g})$
HZSM-5	331.1	0.216	0.15	133.1
Al_2O_3 -HZSM-5-IM	306.9	0.263	0.12	153.1
Al_2O_3 -HZSM-5-CP	367.5	0.348	0.04	205.3
γ - Al_2O_3	184.3	0.553	0.00	—

*Calculated by the t -plot method with an adsorbed film-thickness range from 0.35 to 0.50 nm.

hanced pore volume and surface area of the meso- and macropores improved the accessibility of reactants to the active sites, resulting in high reactivity and increased catalyst stability.

2.2 Surface acidity of the combined solid acids

NH_3 -TPD profiles of these combined solid acids are shown in Fig. 3. The pure HZSM-5 consists of two kinds of acid sites because NH_3 desorption peaks are present at peak temperatures of 250 and 490 °C, respectively. On the surface of $\gamma\text{-Al}_2\text{O}_3$, two NH_3 desorbed peaks were detected at 185 and 360 °C and the total amount of released NH_3 is several times smaller than that of HZSM-5 and the combined solid acids. It is quite interesting to note that the detected NH_3 desorption profiles can be deconvoluted into three peaks for the combined Al_2O_3 -HZSM-5 solid acids. The first one, at around 190 °C, is related to weakly adsorbed ammonia or ammonia adsorbed on separated Al_2O_3 . The second peak at 280 °C corresponds to NH_3 adsorbed on extra-framework aluminum species on the zeolite. Finally, ammonia that is strongly adsorbed on the Brönsted acid sites located inside the channels of the zeolite desorbs at much higher temperatures between 400 and 600 °C [5,8, 21–25]. Therefore, three kinds of acid sites from separated Al_2O_3 and HZSM-5 were identified on the combined Al_2O_3 -HZSM-5 solid acids. The number of acid sites in these samples was calculated and is summarized in Table 3.

Fig. 3. NH_3 -TPD profiles of the Al_2O_3 -HZSM-5 catalysts. (1) $\gamma\text{-Al}_2\text{O}_3$; (2) Al_2O_3 -HZSM-5-IM; (3) Al_2O_3 -HZSM-5-CP; (4) HZSM-5.

2.3 Evaluation of catalytic performance

The catalytic performance of methanol dehydration over HZSM-5, the combined Al_2O_3 -HZSM-5 solid acids, and $\gamma\text{-Al}_2\text{O}_3$ at different reaction temperatures are shown in Fig. 4. Under the selected reaction conditions (catalyst 0.2 g, methanol 0.1 ml/min, 0.5 MPa, from 190 to 290 °C), the calculated selectivity for DME is close to 100% so only the conversion of methanol is described and discussed here.

Table 3 The number of acid sites in the Al_2O_3 -HZSM-5 catalysts

Sample	Number of acid sites (mmol/g)			
	Weak	Medium	Strong	Total
HZSM-5	—	0.204	0.123	0.327
Al_2O_3 -HZSM-5-IM	0.013	0.111	0.100	0.224
Al_2O_3 -HZSM-5-CP	0.021	0.118	0.118	0.257
$\gamma\text{-Al}_2\text{O}_3$	0.019	0.069	—	0.088

Fig. 4. Methanol dehydration to DME. (1) $\gamma\text{-Al}_2\text{O}_3$; (2) Al_2O_3 -HZSM-5-IM; (3) Al_2O_3 -HZSM-5-CP; (4) HZSM-5. Reaction conditions: catalyst 0.2 g, methanol 0.1 ml/min, 0.5 MPa.

Methanol dehydration began at about 210 °C on pure $\gamma\text{-Al}_2\text{O}_3$, while the initiation temperature decreased to 190 °C or even lower over the combined Al_2O_3 -HZSM-5 solid acids. At the same time, the highest reaction temperature at which methanol reached its equilibrium conversion decreased from 296 °C (on pure $\gamma\text{-Al}_2\text{O}_3$) to 242 °C (on Al_2O_3 -HZSM-5-IM). Because these experiments were performed at a higher LHSV (30 h^{-1}) and at higher pressure (0.5 MPa), the temperature for maximum methanol conversion for Al_2O_3 -HZSM-5-IM is lower than that for phosphorus, Fe-, or Mg-treated ZSM-5 [8,15,17], $\gamma\text{-Al}_2\text{O}_3$ mixed with Na-modified HZSM-5 [11] and rare earth modified HY [5,22]. The activity of these catalysts relates well to their total acidity (see Fig. 3 and Table 3).

Figure 5 shows the stability of $\gamma\text{-Al}_2\text{O}_3$, HZSM-5, and the combined Al_2O_3 -HZSM-5 solid acids at a reaction temperature of 235 °C. $\gamma\text{-Al}_2\text{O}_3$ showed the best stability during the 80 h on stream but its activity was quite low (methanol conversion of 33.2 % and DME productivity of 5.72 g/(g·h)). The lowest activity of pure $\gamma\text{-Al}_2\text{O}_3$ is attributed to its acidity, as it was the lowest among the tested samples (see Fig. 3). $\gamma\text{-Al}_2\text{O}_3$ had the highest stability and this is attributed to the lack of strongly acidic Brönsted acid sites. Pure HZSM-5 has the highest initial activity and the highest deactivation rate, which is consistent with its acidity and the higher proportion of strongly acidic Brönsted acid sites. The combined Al_2O_3 -HZSM-5 solid acids exhibit higher activity and better stability at 235 °C and a LHSV of 30 h^{-1} . DME

Fig. 5 Activity and stability of the Al_2O_3 -HZSM-5 catalysts at 235 °C (1) γ - Al_2O_3 ; (2) Al_2O_3 -HZSM-5-IM; (3) Al_2O_3 -HZSM-5-CP; (4) HZSM-5; (5) Al_2O_3 -HZSM-5-IM. LHSV = 20 h^{-1} .

productivities on Al_2O_3 -HZSM-5-IM and Al_2O_3 -HZSM-5-CP are 12.7 and 13.5 $\text{g}/(\text{g}\cdot\text{h})$, respectively. At a lower LHSV (20 h^{-1}), the measured methanol conversion decreased slightly from 82.2% to 79.6% during 100 h on stream over the Al_2O_3 -HZSM-5-IM catalyst. The activity and stability of the combined Al_2O_3 -HZSM-5 solid acids are higher than that of zeolite HY and modified HY, as we reported previously [5,22]. However, the stability of these catalysts decreased with an increasing amount of strong acid sites. These results indicate that the strong acid sites in the solid acids bring about deactivation, even at lower temperatures (235 °C).

3 Conclusions

Combined Al_2O_3 -HZSM-5 solid acids that preserve the acidity and structure of the parent HZSM-5 and Al_2O_3 were prepared via impregnation and chemical precipitation. Layered Al_2O_3 -covered HZSM-5 particles were successfully synthesized by chemical precipitation. The surface areas of meso- and macropores and the pore volume of the combined Al_2O_3 -HZSM-5 solid acids are higher than that of pure HZSM-5 and Al_2O_3 . The enhanced pore volume and surface area of the meso- and macropores improved the accessibility of reactants to the active sites. The combined Al_2O_3 -HZSM-5 solid acids exhibit higher methanol dehydration activity than pure γ - Al_2O_3 and they possess higher stability than that of pure HZSM-5 at lower temperature (235 °C) and a higher LHSV (30 h^{-1}). The best DME productivity was 13.5 $\text{g}/(\text{g}\cdot\text{h})$ and was found for Al_2O_3 -HZSM-5-CP at 235 °C. However, the stability of the combined Al_2O_3 -HZSM-5 solid acid catalyst decreased with an increase in the number of strong acid sites.

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