

An Effective Catalyst for Syngas-to-Dimethyl Ether Process with Steamed Zeolite HMC-49 as Dehydration Component

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The HMC-49 zeolites before and after steam treatment were commingled with methanol synthesis catalyst to perform the single-step syngas-to-dimethyl ether process. The high temperature steam treatment meliorated the acidity of HMC-49 zeolite, and consequently enhanced the selectivity to dimethyl ether significantly by reducing the formation of by-products like carbon dioxide and hydrocarbons.

Zeolite MCM-49, first synthesized by Bennett et al.¹ in 1993, has the same framework topology as calcined MCM-22, which contains two nonintersecting pore systems. One of them is constituted of two-dimensional sinusoidal, 10-membered ring channels and the other consists of 12-membered ring supercages that are accessible through 10-membered rings. As an aluminum-rich zeolite, MCM-49 is supposed to be a potential catalyst in many acid-catalyzed reactions because of its abundant acidic sites and unique structure.^{2,3}

Dimethyl ether (DME) was disclosed to have better combustion performance than diesel fuel, e.g., lower NO_x emission, less smoke and engine noise.⁴ Recently, a process called single-step syngas to DME (STD) has attracted increasing attention for its high conversion of carbon monoxide and simplified procedures.^{5–8} Although no agreement has been reached concerning the carbon source of methanol synthesis at present, the reactions involved in the STD process are generally supposed to be methanol synthesis (1), methanol dehydration (2), and water gas shift (WGS) reaction (3),^{5,7,8}



The combination of reactions (1)–(3) results in a synergistic effect which relieves the unfavorable thermodynamics for methanol synthesis (1): methanol, the product of reaction (1), is consumed for the formation of DME and water in reaction (2). The water generated from reaction (2) is shifted by the WGS reaction (3). The hydrogen produced in reaction (3) is, in return, the reactant for methanol synthesis in reaction (1). Thus, one of the products of each step is a reactant for another. This creates a strong driving force for the overall reaction, allowing very high CO conversion and selectivity to DME in one pass.

The catalysts applied in STD process are composed of two essential components: a copper-based catalyst for methanol synthesis and a solid acid catalyst for methanol dehydration. Compared with that of methanol synthesis, the research on the component for methanol dehydration has received less attention. To date, a few solid acids such as Al₂O₃,⁵ silica–alumina,⁷ and

HZSM-5 zeolite^{6,8} have been used for DME synthesis. However, the reaction temperature of the former two does not match that of methanol synthesis while strong acidity of the latter often deteriorates the selectivity to DME because of the water reforming reaction of methanol/dimethyl ether producing carbon dioxide⁹ and the subsequent reaction of the produced dimethyl ether producing hydrocarbons.^{7,10}

Here, we adopted H-form MCM-49 (HMC-49) as the solid acid component in STD catalyst, which exhibited an excellent performance after deliberately adjusting the acidity of this solid acid by high-temperature steam treatment. To the best of our knowledge, the use of MCM-49 zeolite in this reaction has not been reported so far.

The zeolite HMC-49 applied in our study was prepared as described by Xu et al.¹¹ The steam treatments of HMC-49 were carried out in a quartz tube heated by electric furnace. The samples were heated to 400–600 °C at 10 °C min⁻¹ and maintained at these temperatures for 4 h in a flow of steam–air mixture which was composed of 12 mL min⁻¹ g⁻¹ of water and 100 mL min⁻¹ g⁻¹ of air. Samples that were untreated and treated at 400, 500, and 600 °C were named as S0, S1, S2, and S3, respectively. Then the zeolites of S0–3 were mechanically mixed with an industrial methanol synthesis catalyst (Cu:Zn:Al = 60:30:10 atomic ratio) at the weight ratio of 1:2, followed by reducing in a dilute hydrogen flow (5% in N₂) at 240 °C for 6 h. After that the activity tests were carried out in a fixed-bed reactor at 260 °C under 4 MPa, which ensured the good performances on conversion of syngas.^{7,11} The space velocity of synthesis gas (H₂/CO = 2, CO₂ = 2.2%) was 1500 mL g⁻¹ h⁻¹. The effluent products were heated electrically to avoid the condensation, and analyzed by an on-line gas chromatograph equipped with a TCD for CO₂ and CO, and a FID for methanol, DME and hydrocarbons (HCs).

Table 1 lists the CO conversions and the selectivities of various products on the prepared composite catalysts containing HMC-49 zeolites as the dehydration components. It was found that besides methanol and DME, a large amount of by-products

Table 1. Catalytic performance of the HMC-49-containing composite catalysts for STD reaction^a

Solid Acid	CO Conversion /%	Selectivity/%			
		HCs	Methanol	DME	CO ₂
S0	87.81	9.44	2.96	34.60	53.01
S1	92.19	5.43	3.22	56.55	35.13
S2	93.99	0.88	3.06	62.03	34.04
S3	93.85	0.78	3.12	62.34	33.76

^a260 °C, 4 MPa, H₂/CO = 2, CO₂ = 2.2%, 1500 mL h⁻¹ g⁻¹, and the data were taken at the stable period of ca. 4 h time on stream. Selectivity = mole of C in certain product/total converted C mole.

like hydrocarbons and CO_2 was found on the unmodified HMCM-49 zeolite. After steam treatment, especially at the temperatures $\geq 500^\circ\text{C}$, the formation of CO_2 and hydrocarbons decreased remarkably, so the selectivity to DME increased significantly from 34.60% for the parent HMCM-49 to $>62\%$. Furthermore, higher CO conversions were also achieved on the modified zeolites for the increase of the “driving force” for the overall reaction (4). The highest DME yield (58.5%) was achieved with HMCM-49 zeolite treated at 600°C . This value was close to the equilibrium yield of DME in our experimental conditions (ca. 65%).

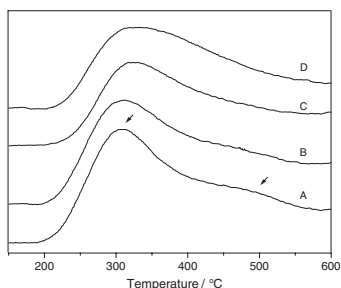


Figure 1. TPD curves for ammonia of the parent HMCM-49 zeolite (A) and steam treated at 400°C (B), 500°C (C), and 600°C (D).

Figure 1 presents the NH_3 -TPD profiles of the HMCM-49 zeolites. Although there are some debates on assigning the peaks in the NH_3 -TPD profile, it is widely accepted that the peak at higher temperature is referred to the strong acidic sites while the peak at lower temperature is corresponding to weak acidic sites. Accordingly, two types of acidic sites exist on the surface of the parent HMCM-49 zeolite, which are represented by the peaks of ammonia desorbed at about 300°C and 500°C , respectively (pointed out by arrows in Figure 1). After steam treatment, the peak at high temperature was weakened and almost disappeared when the treating temperature was $\geq 500^\circ\text{C}$, implying that the steam treatment can remove the strong acidic sites on HMCM-49. Strong acidic sites have been believed to catalytically produce hydrocarbons and water.^{7,10} Furthermore, the produced water promoted the water reforming reaction of methanol/dimethyl ether, resulting in the formation of larger amount of CO_2 .⁹ The elimination of strong acid sites of HMCM-49 through steam treatment would minimize the side-reactions, increasing the selectivity of dehydration reaction. Meanwhile, the equilibrium conversion of reaction (4) would shift toward the right-hand side owing to the decrease in the formation of CO_2 . Therefore, the CO conversion also increased evidently by steam modification. On the other hand, although the acidity of zeolite was decreased apparently by steam treatment, the selectivity to methanol of all catalysts were very low, indicating that acidity of each catalyst was strong enough to dehydrate the methanol. This result is in contrast to that by Kim et al.,⁸ who reported recently that the strong acid sites of HZSM-5 zeolites are responsible for the formation of DME, while the acid sites appearing below 450°C in the NH_3 -TPD spectra are inactive for dehydration of methanol to DME.

Figure 2 shows the ^{27}Al MAS NMR spectra of HMCM-49 zeolites. All of the samples showed two NMR signals. The peak situated at 55 ppm is assigned to the tetrahedral (T_d) Al species, i.e., the framework Al (FAL), while the peak at 0 ppm is as-

signed to the octahedral (O_h) Al species, i.e., the extraframework Al (EFAL). The two NMR signals remained almost unchanged when the samples were steamed at $\leq 400^\circ\text{C}$, but peak at 55 ppm became lower and peak at 0 ppm was broadened when the treating temperatures were $\geq 500^\circ\text{C}$. The weakened signal at 55 ppm showed that part of T_d Al was removed from framework of HMCM-49 and changed to EFAL (O_h Al). Hence, it is the removal of FAL that leads to the decrease of acidic sites on HMCM-49. The broadened peak at 0 ppm indicated the aggregation of EFAL.¹² The cooperation of T_d and O_h Al species was believed to have strong ability to produce hydrocarbons in the methanol conversion process.¹³ So, besides the decrease of strong acidic sites, the aggregation of EFAL of the steamed HMCM-49 should be another important reason for the decrease of hydrocarbons.

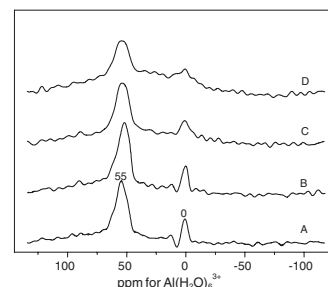


Figure 2. ^{27}Al MAS NMR spectra of the parent HMCM-49 zeolite (A) and steam treated at 400°C (B), 500°C (C), and 600°C (D).

In conclusion, zeolite HMCM-49 can be used as the methanol dehydration component in STD catalyst. Steam treatment was a good method to ameliorate the acidity of zeolite by removing FAL from the framework of HMCM-49. After high temperature steam treatment, the conversion of CO increased about 6%, while the selectivity of DME was enhanced almost two times. The modified HMCM-49 zeolite was a potential replacer of the methanol dehydration component in STD catalyst.

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