

## Selective Conversion of Dimethyl Ether to Propylene and Light Olefins over Modified H-ZSM-5

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Light olefins especially propylene was formed selectively with a propylene/ethylene ratio of 10, from direct conversion of dimethyl ether over ZrO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>-modified H-ZSM-5 catalyst at atmospheric pressure. The improved propylene selectivity was due to adjusted acid property and shape-selective microspores of the modified H-ZSM-5.

Dimethyl ether (DME) can be directly synthesized from syngas with the thermodynamic advantage over methanol and several new DME industrial processes are under development. DME can be used as LPG (liquefied petroleum gas) alternative, clean diesel engine fuel without soot. Besides these energy-related utilizations, chemical conversion is expected. On the other hand, propylene need increases dramatically, resulting in very high price over ethylene. Based on these facts, it is very significant to develop a catalyst to selectively convert DME to propylene.

It is known that there exists fast conversion equilibrium among methanol, DME and water. Although methanol-to-hydrocarbons has been extensively studied,<sup>1</sup> for example, by changing acid strength and topology of catalysts,<sup>2</sup> or using various shape-selective catalysts or two-stage reactor,<sup>3</sup> controlling of the product distribution remains different. Methanol to olefin (MTO) process usually produces mixed C<sub>2</sub>–C<sub>4</sub> lighter olefins<sup>4–8</sup> while high selectivity to ethylene can be obtained over modified SAPO catalyst.<sup>9</sup> ZSM-5 exhibits high selectivity to aromatics and paraffins in methanol conversion.<sup>10</sup> Improved selectivity to light olefins can be achieved using modified ZSM-5 and suitable process conditions.<sup>4–6</sup> But the selectivity to propylene over ZSM-5-related catalysts is extremely low until now.

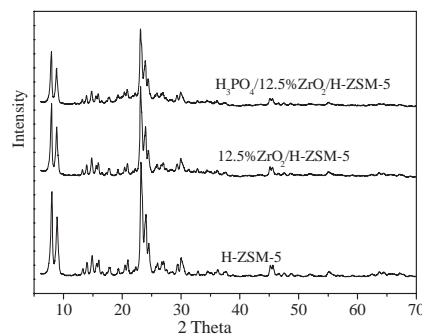
Recently using ZrO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>-modified H-ZSM-5 catalyst, we found that propylene was selectively formed from direct conversion of DME. This was attributable to the adjusted acid property and shape-selective microspores of H-ZSM-5.

Table 1 shows the results of DME conversion over ZrO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>-modified H-ZSM-5.<sup>11</sup> For comparison, the result of DME conversion over pure H-ZSM-5 is listed. It is clear that DME converted completely over H<sub>3</sub>PO<sub>4</sub>/12.5%-ZrO<sub>2</sub>/H-ZSM-5 at 723 K (Run 1). The products terminated at C<sub>9</sub> hydrocarbons and centered at propylene with selectivity of 45.4%. The ratio of propylene/ethylene was near 10 and the C<sub>2</sub>–C<sub>4</sub> olefins selectivity was 64.6%. The formation of lighter olefins was significantly improved, compared with that using H-ZSM-5, where the ratio of propylene/ethylene was 1.5 and the selectivity to C<sub>2</sub>–C<sub>4</sub> olefins was 40.1% (Run 4). Moreover, DME showed very low conversion at 523 K while the selectivity of C<sub>2</sub>–C<sub>4</sub> olefins was 75.2% and the ratio of propylene/ethylene was 1.9 (Run 2). Thirty hours of continuous activity test of H<sub>3</sub>PO<sub>4</sub>/12.5%-ZrO<sub>2</sub>/H-ZSM-5 at the same conditions as shown in Run 3

**Table 1.** DME conversion over modified H-ZSM-5<sup>a</sup>

Run	1	2	3	4
Temp. (K)	723	523	723	723
DME conv. (%)	100	8.60	100 <sup>b</sup>	100 <sup>c</sup>
Product distribution (C-mol %)				
C <sub>1</sub>	0.77	2.91	0.26	0.42
C <sub>2</sub> <sup>=</sup>	4.57	25.0	2.74	13.4
C <sub>2</sub>	0.06	0	0.03	0.16
C <sub>3</sub> <sup>=</sup>	45.4	47.3	44.5	19.6
C <sub>3</sub>	0.04	0	0	10.1
<i>i</i> -C <sub>4</sub>	0	0	0	11.2
C <sub>4</sub> <sup>=</sup>	14.6	2.94	15.9	7.13
<i>n</i> -C <sub>4</sub>	10.8	9.05	11.2	7.88
C <sub>2</sub> <sup>=</sup> –C <sub>4</sub> <sup>=</sup> (C-mol %)	64.6	75.2	63.1	40.1
C <sub>5</sub> <sup>d</sup>	15.0	6.70	15.5	10.8
C <sub>6</sub> <sup>d</sup>	5.23	4.15	5.96	5.30
C <sub>7</sub> <sup>d</sup>	2.81	1.95	2.02	4.51
C <sub>8</sub> <sup>d</sup>	0.72	0	1.15	7.32
C <sub>9</sub> <sup>d</sup>	0	0	0.74	2.18

<sup>a</sup>Catalyst, H<sub>3</sub>PO<sub>4</sub>/ZrO<sub>2</sub> (12.5%, wt.)/H-ZSM-5, DME/N<sub>2</sub> (mol), 1:5; W/F (DME), 10 g·h·mol<sup>-1</sup>; 0.1 MPa; 2 h; <sup>b</sup>Time-on-stream, 30 h; <sup>c</sup>H-ZSM-5 catalyst; <sup>d</sup>C<sub>5</sub>–C<sub>9</sub>, including all forms of hydrocarbons.



**Figure 1.** XRD patterns of modified H-ZSM-5.

demonstrated that DME conversion was stable. The ratio of propylene/ethylene was even 16.

XRD results (Figure 1)<sup>12</sup> indicated that after ZrO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> modification, both 12.5%-ZrO<sub>2</sub>/H-ZSM-5 and H<sub>3</sub>PO<sub>4</sub>/12.5%-ZrO<sub>2</sub>/H-ZSM-5 showed similar diffraction peaks as H-ZSM-5, except slight weakness in intensity. The crystallite particle sizes of H-ZSM-5 by SEM at the amplifying times of 5000 were about 120–300 nm. The particles changed in appearance and morphology, tending to cohere after the modification. Pore size distribution of the modified H-ZSM-5 is shown in Figure 2.<sup>13</sup> Compared with H-ZSM-5, the pore size of the

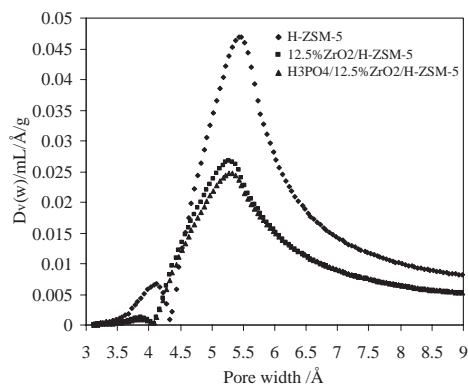


Figure 2. Pore size distributions of modified H-ZSM-5.

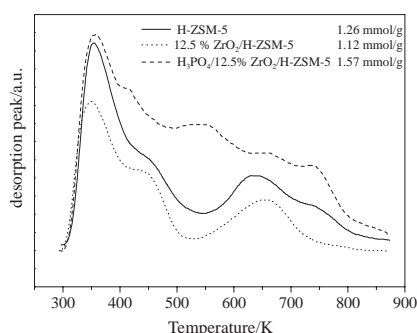


Figure 3.  $\text{NH}_3$ -TPD profiles of modified H-ZSM-5.

modified H-ZSM-5 slightly changed from 5.5 Å to 5.3 Å. The pore volume changed from 0.047 mL/Å/g to 0.026 mL/Å/g for 12.5%-ZrO<sub>2</sub>/H-ZSM-5 and to 0.025 mL/Å/g for H<sub>3</sub>PO<sub>4</sub>/12.5%-ZrO<sub>2</sub>/H-ZSM-5, respectively. This suggested that ZrO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> were well dispersed on the outer and inner surface of H-ZSM-5, and demonstrated that the slight shrink of pores of H-ZSM-5 happened after the modification. Figure 3 shows the  $\text{NH}_3$ -TPD profiles and the corresponding total acid amount of the catalysts.<sup>14</sup> Compared with H-ZSM-5, H<sub>3</sub>PO<sub>4</sub>/ZrO<sub>2</sub>/H-ZSM-5 showed a higher desorption amount of  $\text{NH}_3$  (1.57 mmol/g) while ZrO<sub>2</sub>/H-ZSM-5 a lower amount (1.12 mmol/g). The stronger acidity distribution of H<sub>3</sub>PO<sub>4</sub>/ZrO<sub>2</sub>/H-ZSM-5 was different from that of H-ZSM-5. It should mainly originate from Lewis acid sites (related to ZrO<sub>2</sub>) and Brønsted acid sites (related to H<sub>3</sub>PO<sub>4</sub>) as reported.<sup>15</sup>

For MTO process it is generally accepted that methanol is firstly dehydrated to DME, and then to light olefins. The light olefins react to form paraffins, aromatics, naphthenes, and higher olefins by hydrogen transfer, alkylation and polycondensation. In order to decrease the selectivity of aliphatics and aromatics on ZSM-5, reducing the acidity of ZSM-5 is needed.<sup>16</sup>

From the test and characterization results, the modified H-ZSM-5, on one hand, possessed adjusted acid property, that is, weakened acidic strength but increased acidic sites density com-

pared with H-ZSM-5, which reduced hydrogen transfer reaction. In addition, the Brønsted basic sites by ZrO<sub>2</sub> benefited to deprotonation of surface-bound methoxy species, and improved olefin formation. On the other hand, the modified H-ZSM-5 possessed shape-selective micropores slightly shrunk after the modification, which constrained larger hydrocarbon formation. These two factors resulted in high selectivity to propylene from direct conversion of DME.

## References and Notes

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- 11 Modified H-ZSM-5 catalysts were prepared as follows. A suspension of H-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 83.7$ , Süd Chem.) and  $\text{Zr}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  was stirred at 353 K for 2 h. Then it was adjusted to pH 9 using ammonia and continuously stirred for 2 h. After filtration and washing, the cake was dried at 393 K overnight to obtain  $\text{Zr}(\text{OH})_4/\text{H-ZSM-5}$ , and then calcined at 773 K in air for 3 h. A mixture of  $\text{Zr}(\text{OH})_4/\text{H-ZSM-5}$  and 1 M  $\text{H}_3\text{PO}_4$  (1 g/10 mL) was stirred for 0.5 h at room temperature. After filtration, the cake was dried at 393 K overnight and calcined at 773 K in air for 3 h to obtain  $\text{H}_3\text{PO}_4/\text{ZrO}_2/\text{H-ZSM-5}$ . Catalysts (20–40 mesh) tests were conducted in a flow-type fixed-bed quartz reactor. All products were analyzed via on-line gas chromatographs: One with a thermal conductivity detector (TCD) and a Porapak N column for  $\text{N}_2$ , DME analysis. Another with a flame ionization detector (FID), a methanator and a Porapak Q column for carbon oxides, hydrocarbons, and oxygenates analysis.
- 12 XRD (X-ray diffraction) measurement was performed on a Rigaku XRD instrument with  $\text{Cu K}\alpha$  radiation.
- 13 Pore size distribution was measured on a Quantachrome Autosorb-1 gas sorption system with  $\text{N}_2$  as adsorbent by H-K model.
- 14 After  $\text{NH}_3$  saturation,  $\text{NH}_3$  desorbed from the catalyst as temperature linearly increased from 293 to 873 K.
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