Propane Aromatization over Mo/HZSM-5 Catalysts

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Abstract: Impregnation, mechanical mixing and hydrothermal treatment methods were used to introduce molybdenum species into the HZSM-5 zeolite. The structure and surface acidity of the catalysts were studied by means of XRD, FT-IR, NH$_3$-TPD, TPR and XPS. The effects of Mo content and reaction time on stream on the aromatization of propane were investigated. It was found that the performance of the Mo/HZSM-5 catalyst prepared by the hydrothermal treatment method was much better than that of the other two catalysts. For example, under the reaction conditions of 823 K and 600 h$^{-1}$, propane conversion and aromatics selectivity over the catalyst prepared by hydrothermal pretreatment could reach 89.17% and 78.56%, respectively. XRD and XPS results showed that the Mo species in the catalysts prepared by hydrothermal treatment were highly dispersed on the surface of the HZSM-5, and larger amounts of them could penetrate into the HZSM-5 channel, as compared with the other two kinds of catalysts. These factors may be responsible for their high activities for propane aromatization. IR and NH$_3$-TPD studies indicated that the number of Bronsted acid centers decreased and the Lewis acid centers increased after Mo was introduced into the HZSM-5 zeolite.

Key words: Mo/HZSM-5, propane, aromatization, preparation, hydrothermal treatment

1. Introduction

The conversion of lower hydrocarbons into more valuable aromatics (benzene, toluene, and xylenes) has received a great deal of attention since Csicsery [1–5] first described the process of alkanes to aromatics over bi-functional catalysts such as platinum on alumina in 1970. In the past two decades, reports on propane aromatization concentrated mostly on catalysts of Pt, Zn and Ga-modified HZSM-5 zeolite [6–10]. The reaction mechanism and the role of promoters have been discussed extensively. Some other transition metal oxides such as Ni and Cd were also studied as dehydrogenation promoters [11,12]. However, molybdenum oxides were seldom described [13,14]. Recently, methane aromatization in the absence of oxygen over Mo/HZSM-5 has attracted much interest and Mo/HZSM-5 is regarded as the most promising system [15–18]. Moreover, MoO$_3$ loaded on SiO$_2$ showed high catalytic activity in the dehydrogenation of propane [19]. So, we considered that the aromatization of propane should be promoted if Mo species were introduced into HZSM-5. In addition, it seems that the preparation and treatment methods play a crucial role in the processes of activation and aromatization. For example, the Mo/HZSM-5 catalyst obtained by a solid-state reaction demonstrated low selectivity towards aromatics, while the catalyst obtained by an impregnation method had high selectivity [13,14].

In this study, the catalysts were modified by molybdenum species introduced into the ZSM-5 zeolite by various methods, such as impregnation, mechanical mixing and hydrothermal treatment methods. Propane aromatization over the catalysts was then investigated. It was found that the catalysts prepared by the hydrothermal method had higher conversion of propane and higher selectivity for aromatics than the corresponding ones pre-
pared by the impregnation method. The effect of the methods for introducing the Mo species on the properties of the catalysts was studied by means of ammonia temperature-programmed desorption (NH$_3$-TPD), temperature-programmed reduction (TPR), X-ray diffraction (XRD), fourier transform infrared (FT-IR), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Catalyst preparation

HZSM-5 zeolite catalysts were prepared by calcining NH$_4$-ZSM-5 ($n$(Si)/$n$(Al)=46) in air at 823 K for 4 h. Molybdenum species were introduced into the HZSM-5 by impregnation, mechanical mixing and hydrothermal treatment methods, respectively. The Mo/HZSM-5 designated as M$_I$ was prepared by impregnating the NH$_4$-ZSM-5 powder with a solution of (NH$_4$)$_6$Mo$_7$O$_{24}$.6H$_2$O, and then drying at 383 K for 12 h. The catalyst M$_M$ was obtained by grinding NH$_4$-ZSM-5 with molybdenum oxide. M$_H$ was prepared by a hydrothermal treatment method which can be described as follows: a mixture of the NH$_4$-ZSM-5 powder and the (NH$_4$)$_6$Mo$_7$O$_{24}$.6H$_2$O solution was put into a sealed autoclave, then heated to a certain temperature and pressure, and retained at the temperature and pressure for 4 h, which would promote the Mo species to penetrate into the channels of the ZSM-5 [20]. The resulting Mo/HZSM-5 catalysts were subsequently calcined at 823 K for 4 h in air.

2.2. Catalyst test

Propane aromatization was carried out in a fixed-bed continuous flow micro-reactor with an inner diameter of 6 mm. The stainless steel reactor was loaded with 1 ml catalyst (compressed, crushed, with a sieve fraction of 20–40 mesh). The catalyst was reduced for 1 h at 823 K under a H$_2$ atmosphere, and then purged by N$_2$. Finally, the catalyst was exposed to pure propane at a gas hourly space velocity (GHSV) of 600 h$^{-1}$. The products were analyzed using an on-line gas chromatograph GC-7A, equipped with a squalane column and an FID detector. The conversion of propane and the aromatics selectivity were calculated according to a carbon balance method and expressed as weight percents.

2.3. X-ray diffraction

X-ray diffraction determinations of the pretreated samples were conducted by using a Rigaku D/MAX-rA X-ray diffractometer with a Cu K$_\alpha$ radiation source operated at 40 kV and 40 mA. Powder diffractions of the samples were recorded over a range of 2 $\theta$ values from 5$^\circ$ to 60$^\circ$. All XRD patterns were stored and processed by a computer system.

2.4. X-ray photoelectron spectroscopy

XPS measurements were performed on a VG Scientific ZSCALAB-2201-XL spectrometer with an aluminum anode (h$\nu$=1.486.6 eV) as the X-ray source. The base pressure of the spectrometer was less than $1.25 \times 10^{-7}$ Pa during the experiments. Charging effects were corrected by adjusting the adventitious carbon peak C$_1$s to the position at 284.6 eV. The accuracy of the binding energy with respect to this standard value was within 0.2 eV.

2.5. FT-IR spectra

FT-IR spectra were recorded on a Bio-Rad FTS-15/90 spectrometer at 353 K. The samples pretreated at 773 K for 4 h in air were pressed into self-supporting wafers and placed in a quartz in-situ IR cell. Then it was evacuated to $1 \times 10^{-3}$ Pa at 773 K for 3 h, cooled to room-temperature and exposed to saturated pyridine vapor. After adsorption for 1 h, the excess and weakly adsorbed pyridine was removed by evacuation at 423 K for 0.5 h to a pressure below $1 \times 10^{-2}$ Pa, thus leaving only chemisorbed pyridine on the sample.

2.6. Temperature-programmed desorption

The experiments were carried out in a conventional flow system with a thermal conductivity detector (TCD). The loaded catalyst was 0.1 g (particle size 60–80 mesh). It was first flushed with Ar (40 ml/min) at 773 K for 0.5 h, then cooled to 393 K and saturated with NH$_3$ until equilibrium. The sample was then flushed with Ar again until the base line of the integrator was stable. NH$_3$-TPD was then promptly started at a heating rate of 10 K/min from 393 K to 823 K.

2.7. Temperature-programmed reduction

TPR was performed on a conventional flow apparatus. A sample of 0.1 g was loaded in a quartz reactor and was heat-treated under a N$_2$ gas flow to 773 K.
After being maintained at 773 K for 0.5 h, the sample was cooled to room temperature under the same gas flow. Then a H₂ (5 Vol%) / N₂ stream at a flow rate of 20 ml/min was introduced to the reactor and a heating program was started to raise the temperature from room temperature to 973 K at 10 K/min.

3. Results and discussion

3.1. Effect of preparation methods on catalytic activity of Mo/HZSM-5

Mo/HZSM-5 catalysts with 4 wt% Mo loading were prepared by means of impregnation, mechanical mixing and hydrothermal treatment methods, respectively, and the results of aromatization of propane are shown in Table 1.

The product distribution shows that the selectivity for CH₄ and C₂= over HZSM-5 is higher than that over Mo/HZSM-5 catalysts. This indicates that the activation of propane via C—C cracking is serious, resulting in a low selectivity towards aromatics. When Mo was introduced, however, the selectivities for CH₄, C₂=, C₃=, C₄ and C₅ decreased, while the selectivity towards aromatics increased. This implies that the cracking of propane is depressed and the dehydrogenation of propane is enhanced. Subsequently, the cracking of intermediates such as C₄—C₅ linear olefins would also be depressed. Consequently, the cyclization and dehydroaromatization would be promoted, and the selectivity for aromatics increased.

It was also found that the propane conversion and the selectivity for aromatics increased markedly when Mo species were introduced into HZSM-5. However, the effect of the introduction methods on the aromatization performance of the catalysts is different, and the catalytic activities of the catalysts follow the order: M₇ > M₅ > M₄. This can be explained because the migration of the Mo species would be very difficult for the impregnated and the mixed catalysts due to the diameter of MoO₃ limiting its dispersion into the channels of ZSM-5. However, the penetration of Mo into the HZSM-5 channels could be promoted by the water vapor in the air during calcination [15]. Guo et al. [20] have also demonstrated that the hydrothermal treatment method could promote more Mo species to enter the channels of HZSM-5 and modify the acidic properties of HZSM-5.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Propane Aromatics Aromatics Product distribution (%)</th>
<th>CH₄</th>
<th>C₂=</th>
<th>C₃=</th>
<th>C₄+C₅</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Xylene</th>
<th>EB+C₉+</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>60.08 33.99 20.42</td>
<td>14.76</td>
<td>14.18</td>
<td>11.38</td>
<td>10.42</td>
<td>14.80</td>
<td>9.27</td>
<td>15.88</td>
<td>8.04</td>
</tr>
<tr>
<td>M₇</td>
<td>77.20 69.95 54.00</td>
<td>8.19</td>
<td>6.39</td>
<td>5.58</td>
<td>3.11</td>
<td>6.76</td>
<td>20.74</td>
<td>33.15</td>
<td>16.05</td>
</tr>
<tr>
<td>M₅</td>
<td>67.07 61.56 41.29</td>
<td>9.45</td>
<td>9.12</td>
<td>7.53</td>
<td>6.19</td>
<td>6.14</td>
<td>20.77</td>
<td>28.03</td>
<td>11.65</td>
</tr>
<tr>
<td>M₄</td>
<td>69.35 50.55 35.02</td>
<td>14.38</td>
<td>10.64</td>
<td>10.25</td>
<td>6.56</td>
<td>7.61</td>
<td>16.94</td>
<td>22.26</td>
<td>9.76</td>
</tr>
</tbody>
</table>

Reaction conditions: T=823 K, GHSV=600 h⁻¹.
M₇: catalyst prepared by the hydrothermal treatment method; M₅: catalyst prepared by the impregnation method; M₄: catalyst prepared by the mechanical mixing method; EB: ethylbenzene.

3.2. Effect of Mo content on catalytic activity of Mo/HZSM-5

The effect of Mo content on the catalytic activity of propane aromatization was investigated for the Mo/HZSM-5 catalyst (M₇ and M₅). The results obtained after running for 2 h at 823 K and 600 h⁻¹ are shown in Figure 1.

Although Mo species could promote the aromatization of propane, the catalyst activity is different for different Mo contents in the Mo/HZSM-5 system. For the impregnated catalyst M₅, the aromatization performance was found to be maximal at 2 wt% Mo loading. The conversion of propane and the selectivity for aromatics reached 67.0% and 61.58%, respectively. The highest yield of aromatics could be obtained at 6 wt% Mo loading for the catalyst M₇. The propane conversion of 89.17% and aromatics selectivity of 78.61% could be achieved, respectively. Over
the Mo loading range investigated, the performance of $M_H$ was better than that of the corresponding $M_I$. This indicates that the enhancement in activity and selectivity of the $M_H$ catalysts might be related to the fact that more Mo species migrated into the channels of the HZSM-5, thus promoting not only the activation of propane, but also the dehydrogenation of the intermediates.

Figure 1. Effect of Mo content on the aromatization activity of Mo/HZSM-5 catalysts.

![Figure 1](image1)

Reaction conditions: $T=823$ K, GHSV=600 h$^{-1}$.
(a) Selectivity: (1) aromatics ($M_H$), (2) aromatics ($M_I$).
(b) Conversion: (1) propane ($M_H$), (2) propane ($M_I$).

3.3. Effect of time on stream on catalytic activity of Mo/HZSM-5

Figure 2 shows the effect of time on stream of the reaction on the aromatization activity of the $M_H$ with 6 wt% Mo loading and the $M_I$ with 2 wt% Mo loading. It illustrates that the conversion of propane reached a stable state after the fresh $M_H$ catalyst was subjected to the feed gas for 5 h. The propane conversion and aromatics selectivity did not noticeably decrease up to 18 h on stream. Even after running for 24 h, the conversion and selectivity still remained at 70.9% and 64.7%, respectively. However, the conversion and selectivity over the $M_I$ catalyst declined to 48.5% and 46.7% after running for 24 h. But the conversion of propane over $M_H$ decreased faster than that over $M_I$ after running the reaction for 18 h. This might be due to the high activity of the $M_H$ catalyst which is favorable for the cracking of the reacting species such as C$_4$–C$_9$ linear olefins intermediates and the resulting alkyl-aromatics, so that the formation of coke over the $M_H$ catalyst would be faster than that over the $M_I$ catalyst. Accordingly, the deactivation rate of $M_H$ was faster than that of $M_I$ after running the reaction for 18 h.

Figure 2. Effect of time on stream on the aromatization activity of Mo/HZSM-5 catalysts.

![Figure 2](image2)

Reaction conditions: $T=823$ K, GHSV=600 h$^{-1}$.
(a) Selectivity: (1) aromatics ($M_H$), (2) aromatics ($M_I$).
(b) Conversion: (1) propane ($M_H$), (2) propane ($M_I$).
3.4. Effect of preparation methods on the structure of Mo/HZSM-5

A study by Chen et al. [16] demonstrated that the Mo species introduced into ZSM-5 by the impregnation or the mechanical mixing method would not affect the structure of HZSM-5 when the Mo content is lower than 4 wt%. In order to study the influence of the preparation methods on the structure of HZSM-5, 10 wt% Mo was introduced into HZSM-5 by the hydrothermal treatment and the impregnation methods, respectively, and the XRD results are shown in Figure 3.

![Figure 3. XRD patterns of the catalysts.](image)

(1) HZSM-5, (2) M₁, (3) M₂.

The intensity of the diffraction peaks of ZSM-5 for the M₁ catalyst was much weaker than that of HZSM-5. The relative intensity of the peaks at 8° and 8.9° also decreased, as compared with that of the peaks at 23.1° and 23.8°. A similar phenomenon was reported in the aromatization of methane by Wang et al. [17]. They suggested that the structure of ZSM-5 was partly destroyed by the introduction of the Mo species. From Figure 3 we can also see that the MoO₃ phase can be observed at 13°, 25.8° and 27.3° over the catalyst M₁. This indicates that for the M₁ catalyst, although part of the Mo species could disperse on the surface of ZSM-5 and enter the channels, a large amount of them still remained on the outer surface of the ZSM-5. However, MoO₃ peaks could not be found in the pattern of the M₂ catalyst, which demonstrated that MoO₃ was highly dispersed in HZSM-5 so that more Mo species would enter the channels of HZSM-5. Guo et al. [20] also reported that the diffraction peaks of MoO₃ could not be observed even when the Mo loading was above 20 wt%. Therefore, we can infer that the hydrothermal treatment method has wielded little effect on the structure of HZSM-5.

3.5. Effect of preparation methods on the surface acidity of Mo/HZSM-5

FT-IR and NH₃-TPD techniques were used to study the surface acidity of the Mo/HZSM-5 catalysts, and the results are shown in Figure 4 and Figure 5, respectively.

![Figure 4. FT-IR spectra of the catalysts.](image)

(1) HZSM-5, (2) M₁ with 2 wt%Mo, (3) M₂ with 2 wt%Mo, (4) M₁ with 6 wt%Mo.

![Figure 5. NH₃-TPD curves of the catalysts.](image)

(1) HZSM-5, (2) M₁ with 2 wt%Mo, (3) M₂ with 2 wt%Mo, (4) M₁ with 6 wt%Mo, (5) M₂ with 6 wt%Mo.
In the pyridine-adsorbed IR spectra, the bands at 1,545 cm\(^{-1}\) and 1,447 cm\(^{-1}\) can be attributed to Brønsted acid centers and Lewis acid centers of the catalysts, respectively. When Mo was introduced into HZSM-5, the intensity of the Brønsted acid peak decreased, while the Lewis acid peak increased. There are two factors that explain this result. First, the Brønsted acid centers of HZSM-5 were covered partly by MoO\(_3\), which caused a reduction of the Brønsted acid peaks. Second, part of the Mo species had exchanged with those Brønsted acid centers that were capable of transforming into Lewis acid centers. Thus, the peak of the Lewis acid increased.

Liu et al. [21] proposed that the Mo species are located on the \(-\text{OH}\) groups of HZSM-5, so that the solid ion-exchange reaction between Mo and Brønsted acid caused an increase in Lewis acid centers. In addition, the peak intensities of the B-acid and L-acid centers of Mo/HZSM-5 did not change as remarkably as those of the Zn-modified HZSM-5 zeolite catalysts [22]. This demonstrated that only part of the Mo species could enter the channels and exchange with the Brønsted acid, while a large number of them still stayed on the outer surface of HZSM-5. For the M\(_1\) catalyst, the Mo species gathered around the entrance of the HZSM-5 channels and were incorporated with unsaturated O\(^{2-}\). The gathered Mo species increased with the increase in Mo content. Thus, crystallized MoO\(_3\) was formed and part of the channels of the HZSM-5 were blocked by them. This caused the quick deactivation of the catalyst. However, for the M\(_2\) catalyst, a larger number of Mo species could enter the channels of HZSM-5 and cause an increase in Lewis acid centers due to the unsaturated coordination of Mo. Moreover, the alteration process of the Brønsted acid centers of the catalyst prepared by the hydrothermal treatment method was different from that of the impregnation ones. It is very probable that during the hydrothermal treatment at high pressure, some Lewis acid centers of HZSM-5 could convert into Brønsted acid by oxidation-reduction and hydrolysis of \((\text{NH}_4)\_6\cdot\text{Mo}_7\text{O}_{24}\cdot6\text{H}_2\text{O}\). This would partly compensate for the loss of Brønsted acid during calcination [23].

Two desorption peaks, which characterize respectively strong and weak acids in the HZSM-5 zeolite, are observed in Figure 5 at about 673 K and 473 K, respectively. There was a deep valley between the higher temperature peak and the lower temperature one. For the M\(_1\) catalyst, the desorption peak of weak acids drifts to a higher temperature, while the strong acid peak shifts to a lower temperature with a markedly reduced peak area. Moreover, with an increase in the Mo content, the area of the strong acid peak declined and the valley slightly rose. For the M\(_2\) catalyst, however, the valley obviously rose, which indicates that more moderately-strong acid centers were produced.

From the results of FT-IR and \(\text{NH}_3\)-TPD, we can propose that for the catalyst prepared by the hydrothermal treatment method the strongest Brønsted acid centers having high cracking activity decreased in number, while the number of the moderately-strong acid centers that are attributed to dehydrogenation activity increased, as compared with those of HZSM-5. These properties, however, were not observed in the impregnated catalyst. The reason for the high activity and selectivity of the M\(_2\) catalyst with higher Mo contents can be explained as follows: (a) more Mo species entered the channels of HZSM-5 and enhanced the dehydrogenation activity of the catalyst; (b) the interaction between the Mo species and the Brønsted acid centers caused a decrease in the number of the strongest acid centers, and depressed the cracking activity of the catalyst.

3.6. Effect of preparation methods on the surface structure of Mo/HZSM-5

XPS was used to study the dispersion and the states of the Mo species in the Mo/HZSM-5 catalysts. A comparison of the results between M\(_1\) and M\(_2\) is shown in Table 2.

Table 2 illustrates that all of the Mo species existed as Mo\(^{6+}\) after calcination in air and MoO\(_3\) was the most probable form. Mo\(^{6+}\) was partly reduced to Mo\(^{4+}\) after treatment in hydrogen at 823 K for 1 h, so that Mo\(^{6+}\) and Mo\(^{4+}\) co-existed in the reduced samples. In the oxidized state, the binding energy of MoO\(_3\) is 0.55 eV lower than that of the standard sample. The chemical shift indicates that there was a strong interaction between Mo and HZSM-5, which could stabilize the active Mo species. Because Si is more stable than other elements in HZSM-5, we compared the surface concentration of Mo before and after reduction with that of Si. For the reduced M\(_1\) and M\(_2\) catalysts, the surface concentrations of Mo declined 1.03% and 1.75% respectively, as compared with their oxidized states. This demonstrates that H\(_2\) reduction is beneficial for the migration of the Mo species into the channels of HZSM-5. Table 2 also shows that the surface Mo species of the M\(_2\) catalyst were less...
in quantity than those of the corresponding M1 catalyst, regardless if they existed in a reduced state or an oxidized state. This implies that the hydrothermal treatment method could promote more Mo species to enter the channels of HZSM-5.

3.7. TPR study of Mo/ZHSM-5 catalysts

Mo/ZHSM-5 catalysts with different Mo contents prepared by the impregnation method were studied by TPR in order to understand the reduction properties of the Mo species in Mo/ZHSM-5. The results are shown in Figure 6.

The main reduction peak of the Mo/ZHSM-5 catalysts shifted to a higher temperature as the Mo content increased, accompanied by a shoulder peak growing gradually at about 700 K. The position of this peak drifted slightly and could not be observed in the pure MoO3 sample. Recalling the fact that only a limited number of the Mo species could enter the HZSM-5 channels and were in a highly dispersed state, we can infer that most of the Mo species would stay on the outer surface and exist in a crystallized state. This crystallized MoO3 was difficult to be reduced, so the reduction peak shifted to high temperatures [25] and appeared at about 950 K. On the other hand, the Mo species that were highly dispersed in the channels of HZSM-5 could be reduced easily because these Mo species had a small particle diameter and the Mo=O bonds were weakened by interacting with the strong Brønsted acid. Therefore, we suggest that the shoulder peak should be ascribed to the reduction of the Mo species in the channels, and the main peak can be ascribed to the Mo species on the outer surface of HZSM-5. Moreover, the aromatization of propane occurs most likely at active sites located in the channels of HZSM-5. During the course of propane aromatization, the reduction of Mo6+ to Mo4+ leads to the formation of MoO2, which has a smaller diameter than MoO3 and favors the Mo species to enter the channels of ZSM-5. Therefore, we infer that the high catalytic activity of Mo/ZHSM-5 should be attributed to the increase in the number of the Mo4+ species in the channels of HZSM-5.

4. Conclusion

The performance of the aromatization of propane over HZSM-5 catalysts could be promoted by introducing molybdenum oxide into the HZSM-5. Preparation methods of the Mo/ZHSM-5 catalysts have various effects on their catalytic properties. Especially, the catalyst prepared by the hydrothermal treatment method has a high aromatization activity and selectivity, over which the propane conversion and aromat-
ics selectivity could reach 89.17\% and 78.61\% respectively, under the conditions of 823 K and 600 h\(^{-1}\).

The hydrothermal treatment method favors the dispersion of the Mo species on HZSM-5, which promotes the penetration of Mo into the channels of HZSM-5, especially during the reduction procedure. These lead to a decrease in the number of the Brönsted acid centers and an increase in the number of the Lewis acid centers of HZSM-5.

References