Study on Bifunctionality of Mo/HZSM-5 Catalysts for Methane Dehydro-Aromatization under Non-oxidative Condition

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Abstract: The optimum Mo/[H+] ratio per unit cell of the active precursors in Mo/HZSM-5 catalysts for methane dehydro-aromatization, measured by 1H MAS NMR, was found to be about 1 when adjusting the acid sites by altering either the SiO2/Al2O3 ratios or the Mo loading. This implies that a concerted interaction between the Mo species and the Bronsted acid sites probably features the bifunctionality of the Mo/HZSM-5 catalyst. On the other hand, it was found that the driving force for Mo species to move into the HSZM-5 zeolite channels and the interaction between the Mo species and the Bronsted acid sites are closely and proportionally related with the amount of Bronsted acid sites per unit cell.

Key words: methane dehydro-aromatization, Mo/HZSM-5, SiO2/Al2O3 ratio, bifunctionality

1. Introduction

Zeolite materials modified with transition metal ions (TMI) have received great attention recently because they can offer us an innovative approach to discover new catalytic materials and new catalytic reactions. Following this direction, many researchers since 1993 have confirmed that HZSM-5 zeolites modified by Mo species are active and selective catalysts for methane dehydro-aromatization (MDA) [1-3]. It is well accepted that Mo/HZSM-5 is a bifunctional catalyst. The Mo species reduced by CH4 are probably in the form of Mo2C and/or MoOxCp, which are responsible for methane dehydrogenation and for the formation of C2 species, while the Brønsted acid sites in the zeolite channels are associated with the oligomerization of ethylene and the formation of benzene and other aromatics. The optimum Mo content is in the range between 2 and 6wt%, depending on the catalyst preparation procedure and the catalytic evaluation condition [4]. On the other hand, the optimum SiO2/Al2O3 mole ratio is in the range of 40-80 [5]. FT-IR measurements of pyridine adsorption revealed that Mo/HZSM-5 catalysts with an optimum SiO2/Al2O3 ratio around 40, showed maximum Brønsted acidity. There is a close correlation between the activity of benzene formation in MDA and the Brønsted acidity of Mo/HZSM-5, but not the Lewis acidity.

Concerning the bifunctional feature of TMI modified zeolite catalysts, Sachtler et al. [6] believed that during the reduction of the ion-exchanged metal cations, metal particles and acidic protons are coproduced, which will result in a bifunctional catalyst. The authors suggested that in the positively charged [MnH]+ adducts, the positive charge is distributed between metal and hydrogen atoms and the metal becomes “electron-deficient”. It is the electron-deficient state of the metal that leads to its high activity for some reactions. In this model of bifunctional catalysts, a metal active site and an acid site combine to

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form an integration. When the metal possesses a positive charge, the dehydrogenation and isomerization of hydrocarbons takes place on this $[\text{M}_x\text{H}]^{+}$ site. On the other hand, Iglesia et al. [7] pointed out that there are two bifunctional pathways, i.e., concerted bifunctional pathways and sequential bifunctional pathways. In general, concerted bifunctional pathways require sites to coexist within molecular distances, which is often the case in homogeneous and enzymatic catalysis. In heterogeneous catalysis, concerted interaction may be prevented by the fixed and inappropriate location of the sites in question, but rapid transfer of intermediates via surface or gas-phase diffusion leads to kinetic coupling between distant sites and thus to a sequential bifunctional pathway. However, no concrete description of the sequential bifunctional pathway of Mo/HZSM-5 for MDA exists. For example, Lin et al. [8], after their comparative FT-IR study on the interaction of CH$_4$ with silica, alumina and HZSM-5, suggested that CH$_4$ is activated by interacting with a proton to form an intermediate CH$_3^+$, which would be decomposed to CH$_3^+$, leading to a heterolytic cleavage of a C–H bond of CH$_4$. Therefore, the MDA reaction may require dehydrogenation and chain-growth steps that occur on Brønsted acid sites, and aided by hydrogen desorption sites provided by the MoC$_2$ species, as Iglesia et al. [7] have suggested for the aromatization of light hydrocarbons over Zn or Ga modified HZSM-5 catalysts.

It is well recognized that Mo species will diffuse into the zeolite channel and will replace the Si–OH–Al hydroxyl during the preparation and calcination of Mo/HZSM-5 catalysts. It is the strong interaction between the Mo species and the Brønsted acid sites that promotes the dispersion of the Mo species on the surface of the zeolite and enhances its thermal stability. Iglesia et al. [9] demonstrated that for their Mo/HZSM-5 catalysts, prepared via a solid-state reaction between MoO$_3$ and HZSM-5 zeolite, Mo species would migrate inside the zeolite channels and exchange with Brønsted acid sites, resulting in the formation of H$_2$O. They also suggested that a di-tetrahedral structure of (Mo$_2$O$_5$)$_{2+}$ can interact with two cationic exchangeable sites [10]. However, in the early stage of the reaction, i.e., during the induction period, the (Mo$_2$O$_5$)$_{2+}$ species are reduced by CH$_4$, and the Brønsted acid sites are regenerated. In this way, two kinds of sites are required for the conversion of CH$_4$ to aromatics: MoC$_x$ for C–H bond activation and initial C–C bond formation, and the acid sites for oligomerization and cyclization of C$_2$ hydrocarbons to form stable aromatics. The interaction and replacement by the Mo species of the Brønsted acid sites were reconfirmed recently by using $^1$H MAS NMR technique [11]. NH$_3$-TPD, and $^1$H spin-echo MAS NMR spectra of Mo/HZSM-5 catalysts with various Mo loadings prepared by impregnation showed that the Mo species migrated into the zeolite channels, interacted with and replaced the Brønsted acid sites, as both the peak area of the high temperature peak in NH$_3$-TPD profiles and the intensities of the chemical shift at $\delta=3.9$, which is attributed to the Brønsted acid sites, decreased with the increase of the Mo loadings. Zhou et al. [12] recently studied the migration of the Mo species in the channels of HZSM-5 by a density functional theory (DFT) calculation. The authors found that Mo species did interact with the Brønsted acid sites and suggested that one Mo species will connect with framework Al through two oxygen bridges and form the precursors of the Mo-containing active species. However, in situ $^1$H spin-echo MAS NMR spectra of the Mo/HZSM-5 under MDA condition did not observe the regeneration of the Brønsted acid sites even in the very early stage of the reaction [13].

The diversified points of view mentioned above stimulated us to work further on the topic of the interaction between the Mo species and the Brønsted acid sites. In this work, the $^1$H MAS NMR technique was used to characterize the Brønsted acid sites for two series of Mo/HZSM-5 catalysts. One series is the 6Mo/HZSM-5 catalysts in which Mo loading was fixed to 6%, while the acid sites were changed by using HZSM-5 zeolites with different SiO$_2$/Al$_2$O$_3$ ratios (from 24 to 250). The other series was Mo/HZSM-5(55) with different Mo loadings. The results are combined with the catalytic performances in order to shed some light on the bifunctional features of the Mo/HZSM-5 catalysts for the MDA.

2. Experimental

2.1. Catalysts preparation

HZSM-5 zeolites with different SiO$_2$/Al$_2$O$_3$ mole ratios (indicated in the bracket) were provided by Huaheng Chemical Co., China. Mo/HZSM-5 catalysts were prepared by the impregnation method reported previously [14]. HZSM-5 powders were impregnated with aqueous solutions containing a given amount of ammonium heptamolybdate (AHM). The
samples were dried at room temperature for 12 h and then at 373 K for 5 h. Then, they were calcined at 773 K for 4 h. The samples were paledized, crushed and sieved to 20–60 mesh for further use. The actual Mo content in weight percentage of each catalyst was analyzed by the XRF technique. XRF experiment was carried out on a Philips Magix X-ray fluorescence spectrometer.

2.2. Characterization

2.2.1. $^1$H MAS NMR

$^1$H MAS NMR experiments were carried out at 400.1 MHz on a Bruker DRX-400 spectrometer with BBI MAS probe and using 4 mm ZrO$_2$ rotors. Prior to the experiment, the samples were first dehydrated at 673 K for 24 h in a homemade apparatus for removing the water adsorbed on the samples. Then the treated samples were put into the NMR rotors for measurement, without exposure to air. Each sample was spun at 8 kHz and 200 scans were accumulated for each spectrum. The chemical shifts were referenced to a saturated aqueous solution of 4,4-dimethyl-4-silapentane sulfonate sodium (DSS). The $^1$H MAS NMR spectra were deconvoluted by software obtained from the Bruker Co. The number of Brønsted acid sites per unit cell in the parent zeolite was calculated from the corresponding unit cell composition. The number of Brønsted acid sites per unit cell of the Mo/HZSM-5 catalysts was estimated by comparing the peak areas of the $^1$H MAS NMR spectra with their corresponding parent zeolites.

2.2.2. TPR and TPO

TPR was carried out in a setup equipped with a thermal conductivity detector(TCD). The sample charge was 0.15 g. It was first flushed with Ar at room temperature and then heated to 873 K at a heating rate of 10 K/min and maintained for 30 min. Then, it was cooled to room temperature before being switched to a H$_2$/Ar mixture (5% H$_2$, 20 ml/min). The TPR was run from 323 to 1193 K at a heating rate of 10 K/min.

TPO experiments were performed in a quartz tubular fixed-bed reactor equipped with an online quadruple mass spectrometer (Balzers, QMS 200). The catalyst charge was 0.15 g. It was first reacted with CH$_4$ at 973 K for 3 h, then cooled to room temperature and flushed with a 10% O$_2$/He mixture (20 ml/min) for 1 h. The temperature was raised from 303 to 1023 K at a heating rate of 8 K/min during which the m/e intensities for 44 (CO$_2$), 28 (CO) and 18 (H$_2$O) were recorded.

2.3. Catalyst evaluation

The reaction was carried out in a quartz tubular fixed-bed reactor. The catalytic test was carried out at atmospheric pressure and 973 K. The catalyst was first heated under He stream to 973 K and maintained at this temperature for 30 min. After the pretreatment the reactant gas was introduced into the reactor at a space velocity of 1500 ml/(g·h). The products were analyzed by an online gas chromatograph (Shimadzu GC-9A) equipped with a flame ionization detector (FID) for the analysis of CH$_4$, C$_2$H$_6$, C$_7$H$_8$, C$_{10}$H$_{12}$ and a thermal conductivity detector (TCD) for the analysis of H$_2$, N$_2$, CH$_4$, CO, C$_3$H$_4$, C$_2$H$_4$. 10.68% N$_2$ in the feed was used as an internal standard for the analysis of all products involving coke deposition, as described by Shu et al. [15].

3. Results and discussion

3.1. $^1$H MAS NMR spectra of 6Mo/HZSM-5 with different SiO$_2$/Al$_2$O$_3$ ratios

The $^1$H MAS NMR spectra of HZSM-5 parent zeolites with different SiO$_2$/Al$_2$O$_3$ ratios, as well as their corresponding 6Mo/HZSM-5 catalysts and their respective deconvolution profiles are shown in Figure 1. $^1$H MAS NMR spectra of HZSM-5 zeolites were quite common and could be deconvoluted into four signals as reported in ref. [8, 16]. The $\delta=1.7$ signal is ascribed to the hydroxyl Si–OH–Si; the $\delta=2.4$ signal is attributed to the hydroxyl associated with extra-framework Al–OH; the $\delta=3.7$ signal is due to the bridging OH groups of Al–OH–Si, i.e., the free Brønsted acid sites; and the last one at about $\delta=6.0$ is also associated with the Brønsted acid sites that interact with oxygen atoms of the framework. With an increase in SiO$_2$/Al$_2$O$_3$ ratios, the signal intensity at $\delta=3.7$ noticeably decreased on the HZSM-5 samples. Based on the compositions of their unit cells, it is easy to calculate the number of Brønsted acid sites per unit cell for each HZSM-5 sample, and the results are listed in Table 1. With the introduction of Mo species the signals at $\delta=3.9$ recorded from 6Mo/HZSM-5 catalysts markedly decreased except for the sample with a SiO$_2$/Al$_2$O$_3$ ratio of 250. This is evidence that,
with the introduction of the Mo species, part of the Mo species migrated into the zeolite channels during the calcinations, replaced the Brönsted acid sites and thus led to a decrease in the amount of Brönsted acid sites.

The dependence of the number of Brönsted acid sites per unit cell on the SiO$_2$/Al$_2$O$_3$ ratios of the parent HZSM-5 zeolites and their corresponding 6Mo/HZSM-5 catalysts is shown in Figure 2. As expected, the number of Brönsted acid sites per unit cell of the parent HZSM-5 zeolites decreased with the increase of their SiO$_2$/Al$_2$O$_3$ ratios. The number of Brönsted acid sites per unit cell steeply decreased in the range of the SiO$_2$/Al$_2$O$_3$ ratio between 20 and 120, and then smoothly decreased in the range of the SiO$_2$/Al$_2$O$_3$ ratio between 120 and 250. The higher the SiO$_2$/Al$_2$O$_3$ ratio of the parent HZSM-5 zeolite, the smaller the decrease in the number of Brönsted acid sites.

The nominal amount of Mo loading for all Mo/HZSM-5 catalysts with different SiO$_2$/Al$_2$O$_3$ ratios used in this work was set on 6 wt%. The corresponding analytical amounts of these samples by the XRF technique are quite close to each other, as shown in Table 1. For all of the 6Mo/HZSM-5 catalysts the number of Brönsted acid sites per unit cell decreased

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**Figure 1.** $^1$H MAS NMR spectra of HZSM-5 and 6Mo/HZSM-5 with different SiO$_2$/Al$_2$O$_3$ ratios. SiO$_2$/Al$_2$O$_3$ mole ratio: (1) 24, (2) 55, (3) 120, (4) 250.

**Figure 2.** Variation of the Brönsted acid sites per unit cell of HZSM-5 zeolite and 6Mo/HZSM-5 catalyst with the increase of SiO$_2$/Al$_2$O$_3$ ratios.
with the increase in their SiO$_2$/Al$_2$O$_3$ ratios. By comparing the signals of $^1$H MAS NMR of the parent HZSM-5 zeolites with those recorded from the corresponding 6Mo/HZSM-5 catalysts, we found that there are quite different trends for the 6Mo/HZSM-5 samples with high SiO$_2$/Al$_2$O$_3$ ratios than for those 6Mo/HZSM-5 samples with low SiO$_2$/Al$_2$O$_3$ ratios. With the introduction of the Mo species, the peak area at $\delta=1.7$ associated with Si–OH obviously decreased for the HZSM-5 sample with the SiO$_2$/Al$_2$O$_3$ ratio of 250. However, the peak intensity at $\delta=3.9$ associated with the bridging hydroxyl Si–OH–Al or associated with the free Brønsted acid sites remained almost constant. There is not any exchange at all between the Mo species and the Brønsted acid sites when the parent HZSM-5 has a SiO$_2$/Al$_2$O$_3$ ratio of 250, and all the introduced Mo species resided on the external surface of the zeolite. On the other hand, for the samples with a SiO$_2$/Al$_2$O$_3$ ratio of 55 or 24 after the introduction of the Mo species, the decrease in peak intensity at $\delta=3.9$ was quite obvious. Moreover, the number of Brønsted acid sites per unit cell decreased from 4.09 to 1.92 for the sample with a SiO$_2$/Al$_2$O$_3$ ratio of 55, as shown in Table 1 and Figure 2. In other words, the driving force behind the migration of Mo species into the channels of the zeolite strongly depends on its acidic properties. All this data implies that there are two parts of Mo species, one resided on the external surface of the zeolite that would locate on Si–OH groups preferentially, while the other part diffused into the channels, and would interact with and replace the Brønsted acid sites, thus leading to a decrease in the Brønsted acid sites. For the Mo/HZSM-5 sample with a low SiO$_2$/Al$_2$O$_3$ ratio, the Mo species will diffuse more easily into the channels of the zeolite, and there will be more Mo species to interact with and replace the Brønsted acid sites, as compared with the Mo/HZSM-5 samples with a high SiO$_2$/Al$_2$O$_3$ ratio.

The dependence of the interaction between the Mo species and the Brønsted acid sites on the SiO$_2$/Al$_2$O$_3$ ratio was also demonstrated by the TPR experiments. Figure 3 shows the TPR profiles for the 6Mo/HZSM-5 catalysts with different SiO$_2$/Al$_2$O$_3$ ratios and the corresponding peak temperatures. The TPR profiles of the 6Mo/HZSM-5 samples with low SiO$_2$/Al$_2$O$_3$ ratios were quite different from those with high SiO$_2$/Al$_2$O$_3$ ratios. The TPR profile of the 6Mo/HZSM-5(55) sample was very unique. It has the highest peak temperature for Peak I and the lowest peak temperature for Peak II.

Thus, it appears that for a zeolite sample with a low SiO$_2$/Al$_2$O$_3$ ratio, there will be many more Brønsted acid sites that can accommodate Mo species. When the Mo species diffuse into the channels and interact with the Brønsted acid sites, this interaction will lead to a decrease in the number of Brønsted acid sites per unit cell. Suppose that one Mo-containing

<table>
<thead>
<tr>
<th>SiO$_2$/Al$_2$O$_3$ mole ratio</th>
<th>Brønsted acid site (u.c.) in HZSM-5</th>
<th>Brønsted acid site (u.c.) in 6Mo/HZSM-5</th>
<th>Mo content$^a$ (wt%) per unit cell</th>
<th>Mo/[H$^+$] ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>7.39</td>
<td>2.90</td>
<td>5.64</td>
<td>1.54</td>
</tr>
<tr>
<td>55</td>
<td>4.09</td>
<td>1.92</td>
<td>5.52</td>
<td>1.13</td>
</tr>
<tr>
<td>120</td>
<td>1.57</td>
<td>1.20</td>
<td>5.94</td>
<td>0.31</td>
</tr>
<tr>
<td>250</td>
<td>0.76</td>
<td>0.78</td>
<td>5.28</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$: Mo content analyzed by XRF.

![Figure 3. H$_2$-TPR profiles for 6Mo/HZSM-5 with different SiO$_2$/Al$_2$O$_3$ ratios.](image-url)
species will replace one Brønsted acid site, we can estimate the value of the Mo/[H\(^+\)] per unit cell of the 6Mo/HZSM-5 catalysts with different SiO\(_2\)/Al\(_2\)O\(_3\) ratios, where the Mo refers to those diffused into the channels. The results are listed in Table 1. The value of the Mo/[H\(^+\)] ratio per unit cell decreased monotonously with the increase of the SiO\(_2\)/Al\(_2\)O\(_3\) ratio. It was 1.13 for the 6Mo/HZSM-5(55) catalyst and was zero for the 6Mo/HZSM-5(250) catalyst. This indicates that with the change in the acidity caused by the change in the SiO\(_2\)/Al\(_2\)O\(_3\) ratio of the parent zeolite, the dispersion state of the Mo species on the surface as well as the interaction between the Mo species and the Brønsted acid sites are quite different.

### 3.2. \(^1\)H MAS NMR spectra of Mo/HZSM-5(55) with different Mo loadings

Besides altering the SiO\(_2\)/Al\(_2\)O\(_3\) ratio at a fixed Mo loading, there is another way to change the Brønsted acid sites, i.e., by altering the Mo loading of a given HZSM-5 zeolite with a definite SiO\(_2\)/Al\(_2\)O\(_3\) ratio. We used a HZSM-5 zeolite with a SiO\(_2\)/Al\(_2\)O\(_3\) ratio of 55 to prepare Mo/HZSM-5(55) catalysts with different Mo loadings. Figure 4 shows the relation of the actual Mo loading analyzed by XRF with different nominal Mo loadings. It is interesting to note that the higher the Mo loading, the larger the difference between the actual Mo loading and the nominal Mo loading.

The spectra of \(^1\)H MAS NMR recorded from the Mo/HZSM-5(55) catalysts with different Mo loadings are shown in Figure 5, and the deconvolution results of these spectra are listed in Table 2. As expected, the number of Brønsted acid sites per unit cell monotonously decreased with increasing Mo loading. This means that with the increase in Mo loading, there are more Mo species diffusing into the channels and replacing the bridging hydroxyl, so that fewer Brønsted acid sites remain unchanged. The value of the ratio of Mo(in channels) to [H\(^+\)] per unit cell becomes larger and larger with the increase of the Mo loading. It is interesting to notice that for the 6%Mo/HZSM-5(55) catalyst, the value of the Mo/[H\(^+\)] ratio per unit cell is about 1.1.

![Graph showing variation of actual Mo loading](image)

**Figure 4.** Variation of the actual Mo loading on Mo/HZSM-5(55) analyzed by XRF for different nominal Mo loadings.

![Graph showing 1H MAS NMR spectra](image)

**Figure 5.** \(^1\)H MAS NMR spectra of Mo/HZSM-5(55) with different Mo loadings.

### Table 2. Brønsted acid sites per unit cell of Mo/HZSM-5(55) with different Mo loadings estimated from the deconvolution results of the corresponding \(^1\)H MAS NMR spectra

<table>
<thead>
<tr>
<th>Nominal Mo loading (wt%)</th>
<th>Mo content *&lt;sup&gt;a&lt;/sup&gt; (wt%)</th>
<th>Brønsted acid site (u.c.)</th>
<th>Mo/[H(^+)] ratio per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0</td>
<td>4.09</td>
<td>0</td>
</tr>
<tr>
<td>2%</td>
<td>1.61</td>
<td>3.02</td>
<td>0.35</td>
</tr>
<tr>
<td>4%</td>
<td>3.60</td>
<td>2.10</td>
<td>0.95</td>
</tr>
<tr>
<td>6%</td>
<td>5.13</td>
<td>1.93</td>
<td>1.12</td>
</tr>
<tr>
<td>8%</td>
<td>5.71</td>
<td>1.81</td>
<td>1.26</td>
</tr>
</tbody>
</table>

*a: Mo content analyzed by XRF.*
3.3. Change of Brönsted acid sites of Mo/HZSM-5 in the early stage of MDA

It is well accepted that the Mo species of Mo/HZSM-5 catalysts will be reduced and carburized to form Mo carbide active species in the early stage of the MDA reaction. In their study on the reduction of MoO_x/HZSM-5 catalysts, prepared by solid state reaction, by CH_4 in the early stage of the MDA reaction, Iglesia et al. [10] demonstrated, by monitoring the formation of H_2O and the isotopic exchange of D_2 with OH groups in HZSM-5 before and after the reaction with CH_4 at different intervals of time, that regeneration of the Brönsted acid sites, which interacted with and were replaced by (MoO_2)_2^{2+} species during the calcinations, will happen during the reduction and carbonization of the (MoO_2)_2^{2+}. In this way, the catalytically inactive Mo oxo species are activated during their contact with CH_4, and then two sites required for the conversion of CH_4 to aromatics are formed: namely, the MoC_x site for C-H bond activation and initial C-C bond formation, and the acid sites for oligomerization and cyclization of C_2 hydrocarbons to form stable aromatics. Figures 6 and 7 show the spectra of in situ ^1H MAS NMR of 6Mo/HZSM-5(55) and 6Mo/HZSM-5(250) catalysts in the early stage of the reaction.

![Figure 6: In situ ^1H MAS NMR spectra of 6Mo/HZSM-5(55) reacted with CH_4 at 973 K for different time on stream.](image)

![Figure 7: In situ ^1H MAS NMR spectra of 6Mo/HZSM-5(250) reacted with CH_4 at 973 K for different time on stream.](image)

In the case of the 6Mo/HZSM-5(55), the intensity of the peak corresponding to the Brönsted acid sites at \( \delta = 4.0 \) obviously decreased after running the reaction at 973 K with CH_4 for 5 min, and then smoothly increased. However, even after running the reaction for 120 min, the intensity of the peak at \( \delta = 4.0 \) for the 6Mo/HZSM-5(55) catalyst was still smaller than the original one. Meanwhile, in the case of 6Mo/HZSM-5(250), the intensity of the peak corresponding to Brönsted acid sites did recover a bit after running the reaction for about 30 min. Therefore, more definite experimental results are needed to show the change during the early stage of the reaction.

3.4. MDA reaction over Mo/HZSM-5 catalysts

Table 3 listed the reaction results of the 6Mo/HZSM-5 catalysts with different SiO_2/Al_2O_3 ratios, and Figure 8 shows the change of their catalytic performances for 6 h on stream. Again, these four catalysts can be divided into two sorts according to their catalytic performances. The 6Mo/HZSM-5 catalysts with low SiO_2/Al_2O_3 ratios showed good catalytic activity and higher selectivity towards aromatics, while the 6Mo/HZSM-5 catalysts with high SiO_2/Al_2O_3 ratios showed lower activity and selectivity to aromatics and most of the methane was transformed into car-
bonaceous deposits in the reaction. Among the tested catalysts, the 6Mo/HZSM-5 with a SiO$_2$/Al$_2$O$_3$ ratio of 55 is the best. The highest yield of aromatics was 8.6% after running the reaction for 90 min at a methane conversion of 13.6%.

### Table 3. Catalytic performance of 6Mo/HZSM-5 catalysts with different SiO$_2$/Al$_2$O$_3$ ratios for MDA

<table>
<thead>
<tr>
<th>SiO$_2$/Al$_2$O$_3$ mole ratio</th>
<th>CH$_4$ Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield of aromatics$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>13.5</td>
<td>C$_6$H$_6$: 37.7</td>
<td>38.8</td>
</tr>
<tr>
<td>55</td>
<td>13.6</td>
<td>C$_{10}$H$_8$: 11.8</td>
<td>20.5</td>
</tr>
<tr>
<td>120</td>
<td>6.5</td>
<td>C$_2$: 2.3</td>
<td>5.8</td>
</tr>
<tr>
<td>250</td>
<td>5.7</td>
<td>CO: 9.3</td>
<td>71.6</td>
</tr>
</tbody>
</table>

$^a$: Yields of aromatics include C$_6$H$_6$, and C$_{10}$H$_8$.

Reaction conditions: WHSV=1500 ml/(g·h), T=973 K, reaction time=90 min.

A series of Mo/HZSM-5(55) catalysts with different Mo loadings were prepared and the corresponding reaction results are given in Table 4 and Figure 9. With the increase in Mo loading, methane conversion and selectivity to aromatics increased, and the values were the highest with the 6Mo/HZSM-5(55) catalyst. On the other hand, the selectivity to coke decreased with the Mo loading and attained the lowest value of 27.4% with the 6Mo/HZSM-5(55) catalyst.

### Figure 8. Catalytic performances of 6Mo/HZSM-5 catalysts with different SiO$_2$/Al$_2$O$_3$ ratios.

Reaction conditions: WHSV=1500 ml/(g·h), T=973 K.

### Figure 9. Catalytic performances of Mo/HZSM-5(55) catalysts with different Mo loadings.

Reaction conditions: WHSV=1500 ml/(g·h), T=973 K.
Table 4. Catalytic performance of Mo/HZSM-5 catalysts with different Mo loadings for MDA

<table>
<thead>
<tr>
<th>Mo loading (%)</th>
<th>CH(_4) Conversion (%)</th>
<th>C(_6)H(_6)</th>
<th>C(_{10})H(_8)</th>
<th>C(_2)</th>
<th>CO (%)</th>
<th>Coke (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td>9.3</td>
<td>21.5</td>
<td>6.5</td>
<td>3.2</td>
<td>10.6</td>
<td>58.1</td>
</tr>
<tr>
<td>4%</td>
<td>12.7</td>
<td>42.5</td>
<td>11.3</td>
<td>3.1</td>
<td>7.1</td>
<td>36.1</td>
</tr>
<tr>
<td>6%</td>
<td>13.6</td>
<td>43.0</td>
<td>20.5</td>
<td>2.5</td>
<td>5.8</td>
<td>27.4</td>
</tr>
<tr>
<td>8%</td>
<td>13.8</td>
<td>39.6</td>
<td>14.1</td>
<td>2.9</td>
<td>7.2</td>
<td>36.4</td>
</tr>
</tbody>
</table>

a: Yields of aromatics include C\(_6\)H\(_6\), and C\(_{10}\)H\(_8\).

Reaction conditions: WHSV=1500 ml/(g h), T=973 K, reaction time=90 min.

TPO results on 6Mo/HZSM-5 catalysts with different SiO\(_2\)/Al\(_2\)O\(_3\) ratios after running the reaction for 3 h are shown in Figure 10, and the corresponding peak temperatures and peak areas are listed in Table 5. On the 6Mo/HZSM-5 catalysts with low SiO\(_2\)/Al\(_2\)O\(_3\) ratios, there are three peak temperatures at ca. 700, 770 and 890 K, respectively. However, only two peak temperatures could be detected for the 6Mo/HZSM-5 catalysts with high SiO\(_2\)/Al\(_2\)O\(_3\) ratios. Therefore, it is reasonable that the peak with the highest temperature is associated with the coke formed on free Brønsted acid sites.

Table 5. Deconvolution results of TPO profiles of 6Mo/HZSM-5 samples with different SiO\(_2\)/Al\(_2\)O\(_3\) ratios after running the reaction for 3 h

<table>
<thead>
<tr>
<th>SiO(_2)/Al(_2)O(_3) mole ratio</th>
<th>Peak I</th>
<th></th>
<th></th>
<th>Peak II</th>
<th></th>
<th></th>
<th>Peak III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Area</td>
<td>Temp. (K)</td>
<td>Area</td>
<td>Temp. (K)</td>
<td>Area</td>
<td>Temp. (K)</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>0.97E-9</td>
<td>697</td>
<td></td>
<td>3.09E-9</td>
<td>735</td>
<td></td>
<td>0.33E-9</td>
</tr>
<tr>
<td>55</td>
<td>0.70E-9</td>
<td>698</td>
<td></td>
<td>2.66E-9</td>
<td>748</td>
<td></td>
<td>0.25E-9</td>
</tr>
<tr>
<td>120</td>
<td>1.49E-9</td>
<td>696</td>
<td></td>
<td>2.17E-9</td>
<td>783</td>
<td></td>
<td>—</td>
</tr>
<tr>
<td>250</td>
<td>8.22E-9</td>
<td>695</td>
<td></td>
<td>2.68E-9</td>
<td>740</td>
<td></td>
<td>—</td>
</tr>
</tbody>
</table>

Figure 10. TPO profiles for the 6Mo/HZSM-5 catalysts with different SiO\(_2\)/Al\(_2\)O\(_3\) ratios after running the reaction for 3 h. SiO\(_2\)/Al\(_2\)O\(_3\) mole ratio: (1) 24, (2) 55, (3) 120, (4) 250.

3.5. Bifunctionality of Mo/HZSM-5 catalysts for MDA

By supposing that one Mo atom replaces one Brønsted acid site, the value of Mo/[H\(^+\)] ratio per unit cell of the 6Mo/HZSM-5 catalysts with different SiO\(_2\)/Al\(_2\)O\(_3\) ratios as well as the Mo/HZSM-5(55) catalysts with different Mo loadings can be calculated (see Tables 1 and 2). It was discovered with the \(^1\)H MAS NMR technique that there was no regeneration of the Brønsted acid sites on the 6Mo/HZSM-5(55) catalyst when it was brought into contact with CH\(_4\). This suggests that the Mo species are still keeping contact with the framework Al through two oxygen bridges. It appears that only two oxo bonds of the Mo species will be reduced and transformed into an oxy-carbide form. The catalytic performances of these two series of catalysts were evaluated in a fixed bed reactor system. Methane conversion and the yield of benzene were plotted with the change in the Mo/[H\(^+\)] ratio per unit cell, which are shown in Figure 11. No matter how the change in the Mo/[H\(^+\)] ratio per unit cell of Mo/HZSM-5 catalysts was caused (in the present case, it is in two different ways, i.e., the 6Mo/HZSM-5 catalysts with different SiO\(_2\)/Al\(_2\)O\(_3\) ratios and the Mo/HZSM-5(55) catalysts with different Mo loadings), both the conversion of CH\(_4\) and the yield of C\(_6\)H\(_6\) fit in a similar trend. For the 6Mo/HZSM-5(55) catalyst during the preparation about half of the Brønsted acid sites per unit cell will be replaced by Mo species. Only with this Mo/[H\(^+\)] ratio can the
Mo species cooperate with the remaining Brønsted acid sites harmoniously to function on the work of activating methane and then transforming the intermediates into aromatics.

![Figure 11](image)

Figure 11. Dependences of methane conversion and aromatics yield on the Mo/[H\(^+\)] ratios per unit cell of the 6Mo/HZSM-5 catalysts with different SiO\(_2\)/Al\(_2\)O\(_3\) ratios and Mo/HZSM-5 catalysts with different Mo loadings.

4. Conclusions

The present results demonstrated that the Brønsted acid sites are important for methane dehydro-aromatization over Mo/HZSM-5 catalysts under non-oxygen conditions. Firstly, the Brønsted acid sites are necessary for driving Mo species into the zeolite channels. Secondly, the Brønsted acid sites are needed to anchor Mo species into the zeolite channels. This kind of anchoring is quite stable and the anchoring Mo species can only be reduced partially with CH\(_4\) even at 973 K and may form MoO\(_x\)C\(_y\) species. The MoO\(_x\)C\(_y\) species combine with the residual Brønsted acid sites to make the Mo/HZSM-5 catalysts possessing bifunctionality. There is an optimum value of the Mo(in channels)/[H\(^+\)] ratio which is equal to about 1.0 for HZSM-5 zeolites impregnated with Mo. This means that about half of the free Brønsted acid sites will be taken up by Mo species diffusing into the channel. Only the catalyst possessing this optimum value of Mo/[H\(^+\)] can catalyze the reaction effectively and smoothly.

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References