MAS NMR, ESR and TPD studies of Mo/HZSM-5 catalysts: evidence for the migration of molybdenum species into the zeolitic channels

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NH_3-TPD, MAS NMR and ESR spectroscopies were employed to investigate Mo-modified HZSM-5 catalysts prepared by impregnation. It was found that the modification of Mo ions results in a pronounced decrease in the intensity of ^1H MAS NMR resonance originating from Brønsted acid sites in the zeolites and a distinct splitting of Mo^{5+} ESR signals, which is attributed to the interaction of Mo with the Al atom of the zeolite framework. This presents distinct evidence that Mo ions migrate from the external surface of the zeolite into the lattice channels during the impregnation and subsequent treatment. The remaining Brønsted acid sites associated with the migrated Mo ions form the bifunctional catalytic centers that may be responsible for the outstanding catalytic performance in methane aromatization.

Keywords: methane aromatization, bifunctional catalysis, molybdenum, magnetic resonance

1. Introduction

Zeolite-supported molybdenum catalysts, in particular Mo/HZSM-5 catalysts, are attracting widespread attention due to their unique catalytic performances in selective oxidation, HDS [2,3] and methane dehydro-aromatization under non-oxidative conditions [4–15]. Relevant aspects such as catalyst structures and the alteration of the chemical states of Mo species during catalyst preparation and subsequent treatment as well as in the course of catalytic reactions have been studied extensively. However, the influence of molybdenum species upon the acid properties of the parent zeolites is still not well understood. Regarding Mo location, some confused descriptions were reported frequently in the literature [2,3,16–18]. Based on IR and XRD data, some researchers found that the molybdates loaded with the conventional impregnation method on ZSM-5 interact preferentially with hydroxyl groups located on the outside of the zeolite, adsorbing and dispersing on the external surfaces. This is, however, contrary to the finding that the Brønsted acid sites, which are commonly known to be distributed predominantly in the lattice channels of ZSM-5, decrease pronouncedly with an increase in Mo loading. This discrepancy may be due to the difficulty of obtaining quantitative results on the amounts of acid sites and the distribution of OH groups between external and internal surfaces of zeolites using the conventional XRD and IR, due to possible differences in extinction coefficients for different hydroxyl species. MAS NMR is well known as a powerful method for characterizing the acid properties of zeolites [19–24]. With the application of an appropriate molecule as a probe, the acid properties between external and internal surfaces of zeolites can be efficiently distinguished by analyzing the relevant ^1H MAS NMR spectra. To determine the location of Mo ions in ZSM-5 and reveal the influence of Mo ions on the acid property of ZSM-5, a MAS NMR apparatus with an on-line device [25] for pretreatment of the samples has been used in the present study to follow the changes of the densities of the different types of hydroxyl groups with the loading of Mo ions. The interaction between Mo ions and the zeolite framework has also been studied by ESR measurements.

2. Experimental

A series of Mo/HZSM-5 catalysts were prepared as described in [5]. In brief, HZSM-5 powders were impregnated with aqueous solutions containing a given amount of ammonia heptamolybdate (AHM), then dried at RT and 373 K for 12 and 8 h, respectively. After calcination at 773 K for 5 h, the catalysts were crushed and sieved to 20–60 mesh granules.

NH_3-TPD was measured with a conventional TPD apparatus. Before adsorption, the sample (0.15 g) was dried in flowing He (99.99%, 30 ml/min) at 873 K for 0.5 h. Adsorption of pure NH_3 until saturation took place at 323 K, then the catalyst was flushed with He at the same temperature for 1 h. TPD measurements were done from 323 to 873 K with a heating rate of 15 K/min, with He as the carrier gas. The amount of desorbed ammonia was detected by a thermal conductive detector.

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^{1}H MAS NMR spectra were recorded at 400.1 MHz on a Bruker DRX-400 spectrometer with BBI MAS probe using 4 mm ZrO_2 rotors. Prior to the measurements, the samples were dehydrated at 673 K for about 20 h in a home-made apparatus, by which the treated sample can be filled *in situ* into a NMR rotor, sealed and transferred to the spectrometer without exposure to air [25]. A [$\pi/2$–τ–π–τ–acquire] spin-echo pulse ($\pi/2 = 4.5$ μs) was used to acquire ^{1}H spectra and τ was set to one rotor period. 200 scans were accumulated for each spectrum. Samples were spun at 5 kHz, and chemical shifts were referenced to a saturated aqueous solution of DSS. ^{1}H{^{27}Al} spin-echo double resonance MAS NMR experiments were performed according to the method of Beck et al. [20]. In the experiments, a [$\pi/2$–τ–π–τ–acquire] spin-echo pulse was applied to the ^{1}H channel and aluminum was irradiated simultaneously during the first τ period. The deconvolution of the spectra was conducted using the Bruker software.

A home-made ESR reactor was employed to study the step-wise reduction of Mo/HZSM-5 catalysts by methane. Generally, the catalysts were treated in CH_4 flow (1500 ml/g h) at RT, 373, 573 and 773 K for 1 h, respectively. After each reduction, X-band ESR spectra were recorded on a Jeol ES-EO3X spectrometer at room temperature in a methane atmosphere. A microwave frequency ν of 9.42 GHz with a power of 1 mW was used.

3. Results and discussion

The NH_3-TPD profiles of the HZSM-5 and Mo/HZSM-5 samples with different Mo loadings are shown in figure 1. The spectra of HZSM-5 exhibited the typical double-peak characteristics of zeolites with the MFI-structure [26,27]. The two fairly well resolved peaks, named as the l and h peak and centered respectively at about 540 and 740 K, could be observed distinctly. Normally, the area of a specific peak corresponds to the amount of ammonia desorbed from the sample, and could be taken as a standard to quantify the acidity of the sample [28]. As shown in figure 1(b), the amount of desorbed ammonia decreased compared with the parent zeolite when loaded with 2% molybdenum, and it further decreases with the increase of the molybdenum concentration (figure 1 (c) and (d)). Of these two peaks, the decrease of the h peak was more pronounced, and the peak position shifted to lower temperatures. For the 10% Mo/HZSM-5, the peak temperature shifted from 738 to 693 K, and the amount of desorbed ammonia decreased to 23.8% of that of HZSM-5. A relatively linear dependence of the area of the h peak on the concentration of molybdenum can be found. (The TPD profiles were deconvoluted by the Gauss curve fitting method, as demonstrated in figure 1(d). The numerical data of the fitting are listed in table 1.) At the same time, between these two peaks, a moderate temperature peak at about 620 K appeared. It increased with the increase of the Mo loading. The appearance of a moderate temperature peak in the NH_3-TPD profiles after the loading of molybdenum is quite interesting. Segawa et al. [29] have reported that after the loading of molybdenum on Al_2O_3, the acid sites of the catalyst experienced a decrease at first, then they were restored. The regeneration of the acid sites was suggested to be associated with the supported Mo component (see also [30]). Probably, the appearance of the moderate temperature peak in our present NH_3-TPD experiments has some connection with this phenomenon, and the understanding of the appearance of this peak needs further investigation.

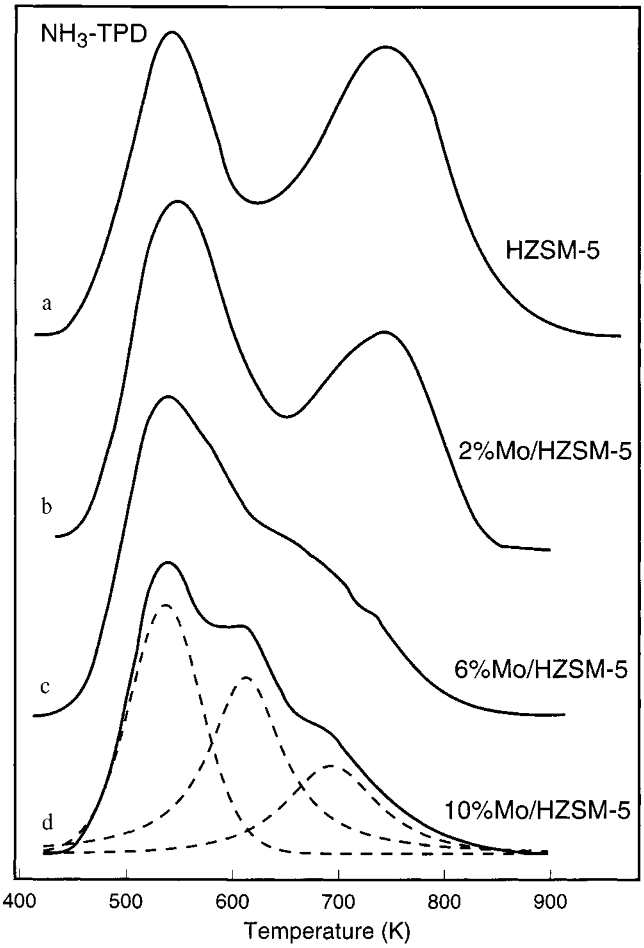

Figure 1. NH_3-TPD profiles of HZSM-5 and a series of Mo/HZSM-5 catalysts with different molybdenum loadings. The deconvoluted curves of 10% Mo/HZSM-5 catalysts are presented as an example.

NH_3-TPD of HZSM-5 and other kinds of zeolites have been extensively studied by various researchers [26–28,31–33], and the relationships of NH_3-TPD with IR, microcalorimetry and benzene adsorption have received great attention. Hidalgo et al. [26] found that the peak desorbed at high temperature (h peak) was always associated with the ammonia adsorbed on the acidic hydroxide group ≡Si–OH–Al≡. The result has also been verified by Post et al. [27] and Meshram et al. [28] by ammonia desorption on HZSM-5 zeolites of different Si/Al ratios. On the other hand, the ascription of the low-temperature peak is uncertain, e.g., from physisorbed ammonia [32], from ammonia adsorbed on Si–OH or from non-zeolitic impu-

Table 1

Numerical results of NH_3-TPD profiles by the Gauss and Lorentz curve fitting method and catalytic performance of the catalysts.

Catalyst	Peak position (K)			Peak area (arb. unit)			SA	Depleting rate of CH_4[a]	Formation rate of C_6H_6[a]
	T_1	T_2	T_3	A_1	A_2	A_3	(m^2/g)	(nmol/g s)	(nmol/g s)
HZSM5	544		738	516		720	360.3	109.3	–
2% Mo/HZSM5	547	620	735	505	112	453	337.5	1626.3	731.9
6% Mo/HZSM5	537	622	699	477	259	226	270.4	1776.2	983.4
10% Mo/HZSM5	537	613	693	350	316	172	243.2	1798.5	821.3

[a] Catalytic data are taken after 90 min reaction (973 K, 1 atm) and formation rate of benzene are based on the methane consumed.

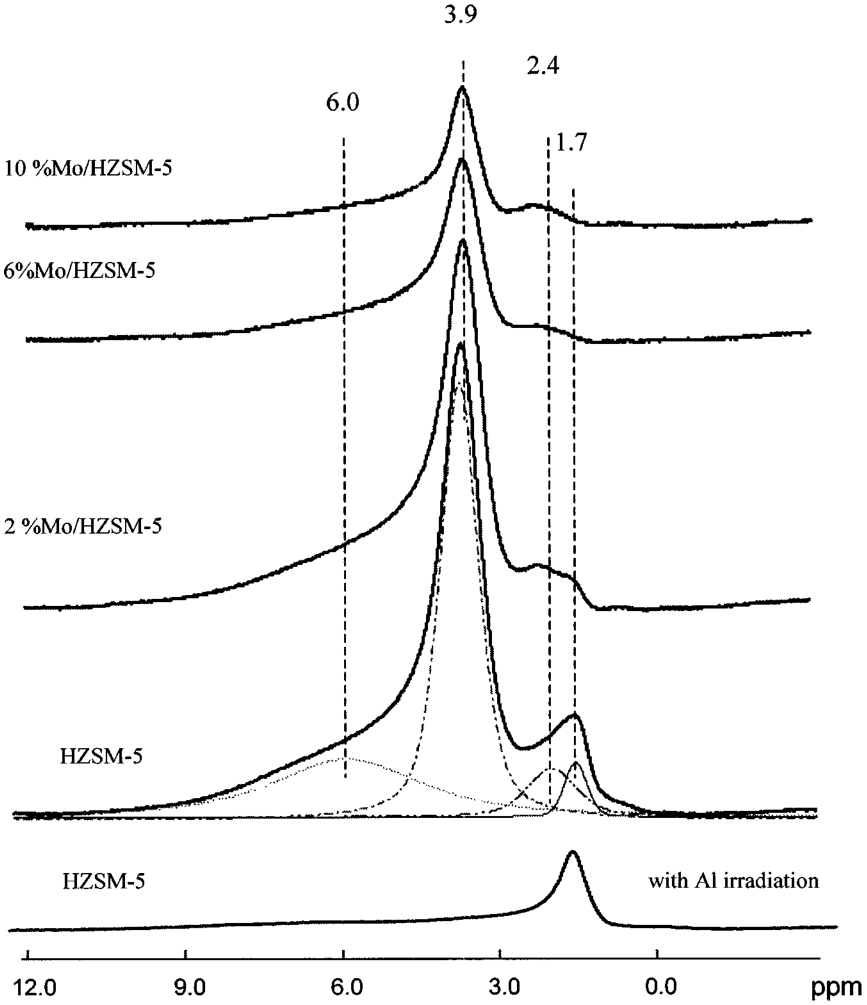

Figure 2. ^{1}H spin-echo MAS NMR spectra of HZSM-5 and Mo/HZSM-5 catalysts with various molybdenum loadings as well as $^1H\{^{27}Al\}$ spin-echo double resonance MAS NMR of HZSM-5. All the spectra were recorded at a resonance frequency of 400.1 MHz with a sample spinning rate of 5 kHz and 200 scans.

rity [33], as well as from both Si–OH and ≡Si–OH–Al≡ groups [26].

We propose that the decrease of the high-temperature peak with increase of the concentration of molybdenum be due to the lowering of the amount of Brønsted sites, which results from modification/interaction of Mo ions, whereas the l peak is due to the physisorbed ammonia since linear dependence of its intensity on the corresponding surface areas can be found. To get deeper insight into the relationship between the Brønsted acidity and the molybdenum content, ^{1}H MAS NMR was performed. The representative ^{1}H MAS NMR spectra of HZSM-5 with various Mo loadings are illustrated in figure 2.

As demonstrated in figure 2, after dehydration, HZSM-5 (Si/Al = 25) shows at least four kinds of characteristic resonance lines in the ^{1}H MAS NMR spectra [19,20,23,24]. The high-field peak at $\delta = 1.7$ ppm can be ascribed to external Si–OH groups, while the signal with $\delta = 2.2$–2.4 ppm belongs to the extraframework Al–OH. The low-field peak at about 3.8 ppm is due to the ≡Si–OH–Al≡ groups, which are the Brønsted acid sites of zeolites. The broad resonance at about 5.9 ppm can be ascribed to another kind of Brønsted acid sites, which is influenced by additional electrostatic interaction of the zeolite framework or the residual ammonium ions [24]. To support the assignment, ^{1}H{^{27}Al} spin-echo double resonance MAS NMR experiments [20] were performed (figure 2). After Al irradiation, only the peak at 1.7 ppm (Si–OH) retained, and it suggests that other resonances are aluminum concerned. The ^{1}H MAS NMR spectra of HZSM-5 and Mo/HZSM-5 with different Mo loadings are shown in figure 2. It is apparent from these spectra that the total ^{1}H signal intensity decreased with molybdenum loading, and the resonance at 1.7 ppm is preferentially reduced compared with those at 2.2, 3.9 and 5.8 ppm. By deconvolution, for the 2% molybdenum, the amount of Brønsted sites decreased to 71% of that of HZSM-5, and the decrease of the amount of external silanols is more pronounced (47%). They decreased further with an increase in Mo loading. In the case of 10% Mo/HZSM-5, only 23% of Brønsted sites, 2% of Si–OH groups and 13% of Al–OH groups remained, as compared with those of the parent HZSM-5 zeolites. A more direct result can be seen in figure 3, in which the numbers of OH groups per unit cell of the zeolites with different Mo loadings are presented as estimated from the integrated areas of the relevant ^{1}H MAS NMR spectra. For HZSM-5 of normal particle size (larger than 1 μm), most of (>90%) the Brønsted sites are on the internal surface of the HZSM-5 [34]. Our recent study [35] using perfluorotributyl amine (which has a diameter of 0.94 nm and cannot enter the channels of HZSM-5) as a probe to determine the concentration of internal and external Brønsted sites on HZSM-5 zeolites with different particle sizes shows that for HZSM-5 with diameter about 1000 nm, the concentration of external surface Brønsted sites is about 3% of the total B sites. In the present HZSM-5 zeolite, the amount of the external Brønsted sites is about 4%, and the ^{1}H MAS NMR spectrum after loading perfluorotributyl amine is not shown here. These results demonstrate that a decrease of the amount of internal Brønsted acid sites must have happened. The observed reduction of the amount of Brønsted acid sites may be due to two different reasons: (1) during the preparation and calcination processes, molybdenum may diffuse into the lattice channels of the HZSM-5 and substitute the Brønsted protons; and (2) the introduction of the Mo species on the HZSM-5 zeolite may accelerate the dehydration process of closed Brønsted acid sites within HZSM-5 channels comparing with the parent zeolite. (This is conceptually similar to the "remote control" effect that was developed by Delmon [36,37] in the spillover phenomenon. However, they suggested that, in their catalysis system, the role of the spillover species is to protect some Brønsted acidity of the acceptor.) Borry III had reported that, during the calcination of the Mo/HZSM catalysts, H_2O was released from the catalysts [38]. They ascribed it to the condensation of the Brønsted protons with the migrated Mo species. However, since process (2) also can give out H_2O molecules, we cannot simply rule it out.

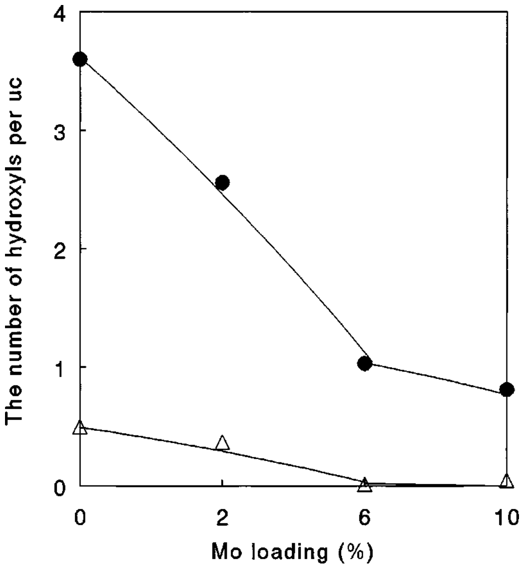

Figure 3. Variation of the number of hydroxyls per unit cell with the increase of Mo loading on ZSM-5 (calculated from the deconvolution of the relevant ^{1}H MAS NMR spectra). (●) Brønsted acid sites and (△) other hydroxyl species.

Some catalytic results are also summarized in table 1. For the tested catalyst, 6% Mo/HZSM-5 shows the proper methane reaction rate and the largest benzene formation rate. It has been suggested that, in this system, Mo species are responsible for the methane activation while the following aromatization process is conducted on the acid centers of the zeolite. It seems that a moderate acid density as well as the proper Mo content may be beneficial to the formation of benzene (6% Mo/HZSM-5), otherwise, a worse catalytic performance could be imaging. (Notice the reaction rate of methane, the benzene formation rate and the difference between them.)

Direct evidence of the interaction of molybdenum with lattice Al^{3+} ions comes from the ESR measurement (figure 4). Besides the external octahedral coordinated MoO_3 oct crystallites (signal A, $g_{\perp_a} = 1.943$, $g_{\|_a} = 1.882$) and MoO_xsqu phase with a square pyramidal coordination (signal B, $g_{\perp_b} = 1.954$, $g_{\|_b} = 1.882$) (figure 4(b)) [39–41], when the 2% Mo/HZSM-5 catalyst was reduced at 773 K for 1 h, a split signal with perhaps 10–12 components can be observed. The signal, superimposed with the signals of MoO_3oct and MoO_xsqu species, constructs a rather broad signal, as shown in figure 4(d). The symmetrical signal at $g = 2.003$ is attributed to organic impurities such as the incompletely decomposed templates introduced during the synthesis of the zeolites. If the catalysts underwent 1 h treatment by flowing O_2 at 813 K before CH_4 reduction, the impurities are burned off and such signals did not appear. The presence of the splitting signal is most interesting. Normally, the formation of hfs comes from the interaction between unpaired electrons of Mo^{5+} and nuclei with non-zero spin quantum number. In the current case, the possible $I \neq 1$ nuclei consist of odd isotopes of molybdenum (^{95}Mo and ^{97}Mo with nuclear spin

Figure 4. ESR spectra of 2% Mo/HZSM-5 reduced by methane at RT (a), 373 K (b), 573 K (c) and 773 K (d) for 1 h each (GV = 1500 ml/g h).

$3/2$, natural abundance 15.7 and 3.5%, respectively), adsorbed ^{13}C species or the Al atoms with $I = 3/2$. In the ESR spectra, the hyperfine structures caused by ^{95}Mo and ^{97}Mo can be found at the low-field part of the spectra (with g value $> g_e = 2.0023$), and it coincided with those of Mo/SiO$_2$ catalysts [41]. It is of little possibility that the hfs can be attributed to adsorbed ^{13}C species since the methane used is not ^{13}C enriched. Thus the splitting in the present case may be induced by the presence of the ^{27}Al atom ($I = 5/2$) near the Mo(V) cations. Similar superhyperfine structures were reported by Kucherov et al. on Cr(V)/HZSM-5 [3] and V(IV)/HZSM-5 [42] catalyst systems. They pointed out that since the lattice Al atoms mainly stay in the zeolite channels, the migration and coordination of the metal ions in the cationic positions of the zeolites must be concluded. Therefore, in the present case, we suggest that the splitting in figure 4(d) comes from the interaction between the unpaired electron of Mo(V) and the adjacent ^{27}Al atom as a result of the substitution of Brønsted H atoms by Mo(V) ions that migrated into the zeolite channels during the impregnation and calcination processes. This is in good agreement with the decrease of the Brønsted sites in figures 1 and 2 when HZSM-5 zeolites were loaded with molybdenum. Moreover, the presence of about 10–12 components of the hfs indicates that two discrete sites for the location of Mo^{5+} ions exist in the channels of the HZSM-5 zeolite. The identification and assignment of these species need further investigation.

4. Conclusions

The present results demonstrated that, for impregnation-prepared Mo/HZSM-5 catalysts, the molybdenum ions can migrate into the lattice channels of HZSM-5 zeolites. The acid sites in the zeolites act as powerful traps for the migrating molybdenum ions. By substituting of the Brønsted H atoms, molybdenum can interact with the adjacent lattice ^{27}Al atom. Both the decrease of the Brønsted sites in NH$_3$-TPD/^{1}H MAS NMR and the splitting signals in ESR spectra confirmed the above conclusions. The proper conjugation of the Brønsted sites and the migrated molybdenum leads to high activities of the catalysts in the methane dehydro-aromatization reaction

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