

Methane Dehydrogenation and Aromatization over Mo/HZSM-5: *In Situ* FT-IR Characterization of Its Acidity and the Interaction between Mo Species and HZSM-5

Wei Liu and Yide Xu¹*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, P.O. Box 110, Dalian 116023, China*

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The acid sites of Mo/HZSM-5 and the interaction between Mo species and HZSM-5 have been characterized by *in situ* FT-IR spectroscopy using pyridine as the probe molecule. The results reveal that Mo species are mainly located on OH groups associated with silanol groups and bridged hydroxyl groups, Si(OH)Al. This is shown by the decrease in the intensities of their stretching modes at 3740 and 3618 cm⁻¹. On a 6 wt% Mo/HZSM-5 sample, the relative intensity of the band at 3618 cm⁻¹ decreases about 80%, and the band at 3740 cm⁻¹ decreases about 65%. Thus, the Mo species preferably locate on the Brønsted acid sites after calcination at 773 K. FT-IR characterization of adsorbed pyridine shows that both Brønsted and Lewis acid sites are present in all Mo/HZSM-5 samples. The relative integrated intensities of the bands of pyridine adsorbed on the Brønsted and Lewis acid sites, as well as the ratio of the Brønsted and Lewis acid sites concentration, [L]/[B], are estimated as a function of Mo loading. The strength distribution, investigated with stepwise evacuation under different desorption temperatures, is broader on Lewis acid sites than on Brønsted acid sites. An increase in the intensity of the band at 1549 cm⁻¹ is observed with the 15 wt% Mo/HZSM-5 sample, suggesting that new Lewis and Brønsted acid sites are generated. Combining the FT-IR study with previous catalytic evaluation, it is concluded that Mo/HZSM-5 is a bifunctional catalyst and that a certain amount (about 60%) of the original Brønsted acid sites on HZSM-5 kept free on the surface may be necessary for its good catalytic performance in methane dehydrogenation and aromatization. © 1999 Academic Press

Key Words: methane aromatization; Mo/HZSM-5; Brønsted acid site; Lewis acid site; pyridine adsorption.

INTRODUCTION

Recently Mo/HZSM-5 catalysts have received considerable interest due to their unique catalytic performance in methane dehydrogenation and aromatization (1–15). It is well established that the acidity and channel structure of HZSM-5, as well as the location and state of Mo species on/in HZSM-5, are crucial factors in its catalytic perfor-

mance (2). Various interactions may happen during its preparation and reaction since Mo/HZSM-5 is calcined at high temperatures and the reaction is carried out at 973 K. For example, the interaction between Mo species and acid sites, the interaction between Mo species and framework Al, and the reduction of Mo species by CH₄ and heavy carbonaceous deposit will all occur on Mo/HZSM-5 with serious effects on its catalytic behavior.

The interaction between Mo species and framework Al had already been studied in our previous paper by ²⁷Al and ²⁹Si MAS NMR (16). However, the interaction between Mo species and the acid sites of HZSM-5 is more interesting. After Mo species were introduced onto HZSM-5, an NH₃ desorption peak at the high temperature decreased, while a peak developed at a medium temperature (17). These changes implied that the number of strong acid sites decreased and a new kind of acid sites formed. Lately, Lunsford *et al.* (18) reported that, by using FT-IR technique, the intensities of three stretching bands at 3747, 3611, and 3670 cm⁻¹ were found to decrease after 2 wt% Mo species were introduced onto HZSM-5. The relative decreases were markedly different for various OH species. The weak band at 3670 cm⁻¹ almost completely disappeared. Meanwhile, the concentration of OH groups associated with terminal silanol species at 3747 cm⁻¹ decreased to a significantly greater extent than that of the Brønsted acid OH groups at 3611 cm⁻¹, which were located inside the zeolite channels. For their 2 wt% Mo/HZSM-5 sample, the intensity of the silanol OH band decreased to about 30%, while the Brønsted OH groups retained about 70% of the intensity observed for the unimpregnated HZSM-5. In the authors' opinion, this is evidence that the impregnated Mo species are located in the vicinity of hydroxyl groups and a suitable number of Brønsted OH groups left on the surface are necessary for methane aromatization.

Pyridine adsorption monitoring with IR spectroscopy is a useful technique for identifying the acid sites of a solid (19–23). A band at 1450 cm⁻¹ is assigned to the vibration mode of pyridine adsorbed onto Lewis acid sites or to that of

¹ To whom correspondence should be addressed.

pyridine coordinately bonded to cations (i.e., Al-containing extra-framework species and/or the tricoordinated framework Al). This band provides information about Lewis acid sites. A band at 1540 cm^{-1} is due to pyridinium (PyH^+) ions formed at the expense of Brønsted acid sites. Finally, a band at 1490 cm^{-1} is attributed to both Lewis and Brønsted acid sites. Therefore, using the integrated intensities of the bands at 1540 and 1450 cm^{-1} as a measure of the amount of pyridine adsorbed on Brønsted and Lewis acid sites, valuable information can be obtained about the relative concentrations of these two kinds of acid sites and their ratio (22).

In this paper, Mo/HZSM-5 samples with different Mo loading were studied in more detail by *in situ* FT-IR. Pyridine was used as the probe molecule to study the acid sites of Mo/HZSM-5 samples. A detailed discussion will be given on the location of Mo species and on the interaction between Mo species and the acid sites of HZSM-5. The results are correlated with corresponding catalytic evaluation taken from Ref. (17).

EXPERIMENTAL

Mo/HZSM-5 samples with different Mo loading were prepared by impregnating HZSM-5 ($\text{Si}/\text{Al}=25$) with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ solution as described previously (17). The samples were then dried at 383 K overnight and calcined in air at 773 K for 6 h . The calcined samples were tableted, crushed, and sieved through $40\text{--}60$ mesh before use. Hereafter, Mo/HZSM-5 samples with different Mo loading are noted as $x\text{Mo}/\text{HZSM-5}$, where x is the nominal Mo content in weight percentage.

IR spectra of HZSM-5 and Mo/HZSM-5 catalysts were recorded by using self-supported sample wafers ($15\text{ mg}/\text{cm}^2$) introduced into a custom-made IR-cell with KBr windows, allowing *in situ* investigation at varying temperatures under vacuum or controlled atmosphere. All spectra were recorded on a BIO-RAD FTS-7 spectrometer at a resolution of 4 cm^{-1} from 4000 to 1000 cm^{-1} and are presented as difference spectra by subtracting the background spectra recorded at the corresponding temperatures. The wafer was heated *in situ* in a He stream from room temperature up to 773 K at a linear ramp rate of $10\text{ K}/\text{min}$, held at 773 K for 1 h , and then evacuated for 40 min under $7 \times 10^{-3}\text{ Pa}$. The cell was subsequently cooled down to room temperature under dynamic high vacuum in 40 min ; then the OH vibration spectrum was recorded at room temperature. Background spectrum was collected on the clean adsorbate-free sample to eliminate the overlap of IR absorption features that originate from the zeolite structural vibrations and/or other adsorbed surface species. The sample was then exposed to pyridine at room temperature for 30 min . After outgassing, the spectrum was recorded. To distinguish acid sites with different strengths, some of the pyridine-adsorbed samples were heated at different

temperatures and a corresponding spectrum was recorded. The relative adsorbed amount of pyridine bonded on Brønsted and Lewis acid sites was measured by using the relative integrated intensities of the pyridine bands at 1450 and 1540 cm^{-1} , taking a framework vibration band at 1850 cm^{-1} as reference.

RESULTS AND DISCUSSION

1. FT-IR Characterization of Hydroxyl Groups on Mo/HZSM-5 Samples

The initial examination of the decomposition of $\text{NH}_4\text{ZSM-5}$ revealed that the bands at 3618 and 3740 cm^{-1} (the band at 3672 cm^{-1} is not well resolved) characteristic of surface OH groups appeared at 573 K and developed more at higher temperatures, as we can see from Fig. 1.

For $1\text{Mo}/\text{HZSM-5}$ and $10\text{Mo}/\text{HZSM-5}$ samples, after evacuation at 573 K , the band at 3618 cm^{-1} was clearly developed (Figs. 2 and 3). However, with further increased outgassing temperature, i.e., at 673 K , the band at 3618 cm^{-1}

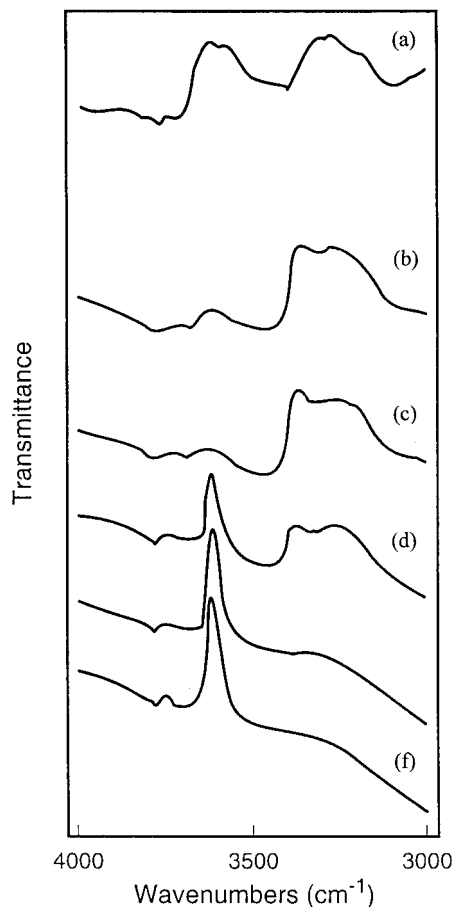


FIG. 1. FT-IR spectra in the range $3000\text{--}4000\text{ cm}^{-1}$ for $\text{NH}_4\text{ZSM-5}$ decomposition recorded at (a) room temperature, (b) 423 K , (c) 473 K , (d) 573 K , (e) 673 K , and (f) 773 K .

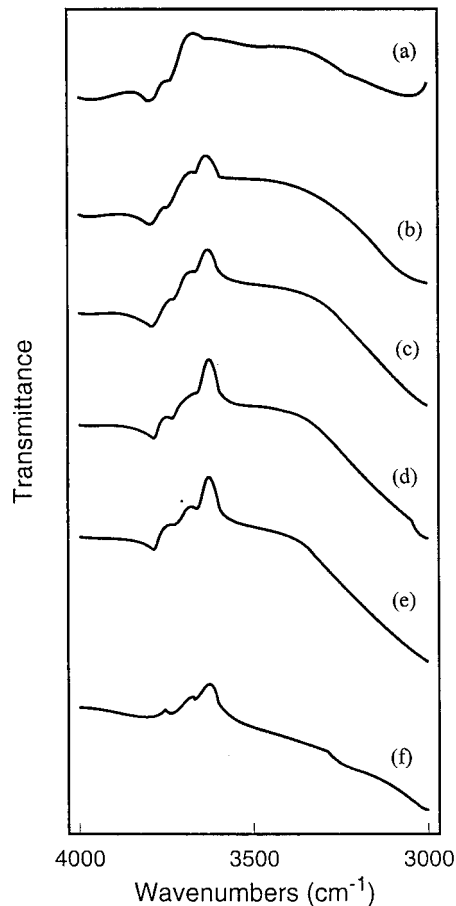


FIG. 2. *In situ* FT-IR spectra in the range 3000–4000 cm^{-1} for 1Mo/HZSM-5 decomposed at (a) room temperature, (b) 423 K, (c) 473 K, (d) 573 K, (e) 673 K, and (f) 773 K.

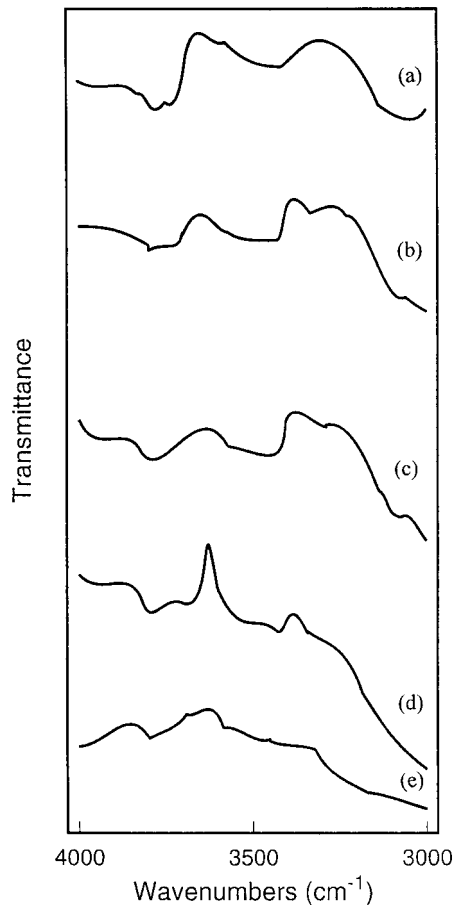


FIG. 3. *In situ* FT-IR spectra in the range 3000–4000 cm^{-1} for 10Mo/HZSM-5 decomposed at (a) room temperature, (b) 423 K, (c) 473 K, (d) 573 K, and (e) 673 K.

almost disappeared for 10Mo/HZSM-5. The intensity of the band at 3618 cm^{-1} measured at 773 K for 1Mo/HZSM-5 was less than that measured at 673 K. It appears that Mo species tend to disperse and migrate into the channel and preferentially locate on the hydroxyl groups associated with framework Al. Moreover, with increasing Mo loading the three bands in the range 3400–3800 cm^{-1} changed in different ways. Unfortunately, due to the overlap of these three bands and the difference in their extinction coefficients, it is difficult to make a quantitative determination of the individual absorption intensity of the bands. However, a relative comparison may be available. We choose the band at 2000 cm^{-1} , which is attributed to the vibration mode caused by the skeleton and is stable and not sensitive to the environment, as an internal standard to examine the change of the relative numbers of surface hydroxyl groups of the zeolite in more detail. Figure 4 shows that there is a decrease in the relative intensities of different hydroxyl groups with increasing Mo loading. The relative intensity of the band at 3672 cm^{-1} decreased a little with increasing Mo loading at first and then increased. This implies that Mo species could

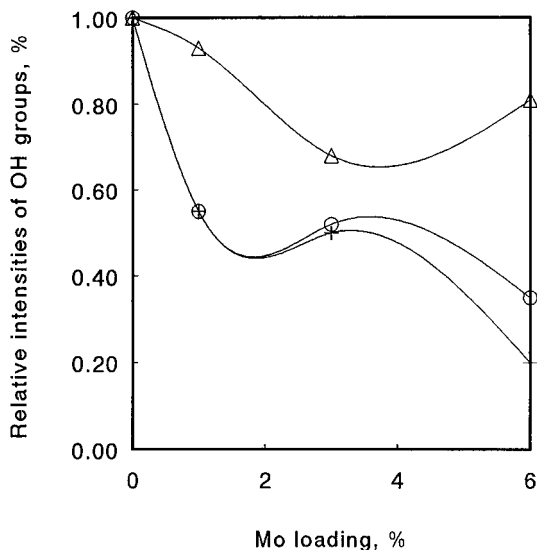


FIG. 4. Effect of Mo loading on the relative intensities of the band at 3618 cm^{-1} (+), the band at 3672 cm^{-1} (O), and the band at 3740 cm^{-1} (Δ).

extract framework Al to some extent, resulting in an increase in extra-framework Al. The relative intensities of the bands at 3618 and 3740 cm^{-1} decreased in the same way in Mo/HZSM-5 with a Mo loading lower than 3%, showing that Mo species will equally locate either on the external surface or in an internal channel after calcination at 773 K. This is different from the results reported by Lunsford *et al.* (18). This may be caused by the differences in HZSM-5 chemical composition and pretreatment procedure for the samples used in the two cases. With further increases in Mo loading, more Mo species tend to migrate into the channel, so the relative intensity of the band at 3618 cm^{-1} decreases more quickly than the intensity of the band at 3740 cm^{-1} . For our 6Mo/HZSM-5 sample, the relative intensity of the band at 3618 cm^{-1} decreases about 80%, and it decreases about 65% for the band at 3740 cm^{-1} . This is evidence that for high Mo loading samples (Mo loading equal to and/or higher than 6%), Mo species preferably locate on Brønsted acid sites after calcination at 773 K.

2. FT-IR Characterization of Adsorbed Pyridine on Mo/HZSM-5 Samples

Spectra obtained from pyridine adsorption on HZSM-5 are shown in Fig. 5. According to (23, 24), all the physically adsorbed and hydrogen-bonded pyridine molecules were removed if the wafer was evacuated at room temperature and then at 423 K for 0.5 h. Therefore, the IR spectrum in Fig. 5c reveals pyridine chemisorbed on Brønsted and Lewis acid sites of HZSM-5.

With further increased evacuation temperatures, the bands of pyridine adsorption changed in different ways. If the sample was evacuated at 473 K the integrated intensity of the band at 1452 cm^{-1} decreased about 30%. It decreased to about 50% if evacuated at 673 K. At the same time, the band shifted to a higher wavenumber, from 1452 cm^{-1} at 423 K to 1456 cm^{-1} at 673 K. This indicates that the strength distribution of Lewis acid sites is energetically heterogeneous in HZSM-5 and that pyridine molecules adsorbed on weak Lewis acid sites can be readily removed at relatively low temperatures. In contrast, the band at 1551 cm^{-1} , which is attributed to pyridine adsorption on Brønsted acid sites, did not change significantly with increasing evacuation temperature up to 673 K. It appears that the pyridine molecules adsorption on Brønsted acid sites is much stronger than those adsorbed on Lewis acid sites and the molecules cannot be easily removed.

Spectra obtained from pyridine adsorption on Mo/HZSM-5 catalysts with different Mo loading are presented in Fig. 6. The intensities of the bands at about 1456 and 1549 cm^{-1} showed some decrease with increasing Mo loading. If a sample had Mo loading higher than 10%, the intensity of the band at 1456 cm^{-1} even increased a bit. Meanwhile an increase in the intensity of the band at 1549 cm^{-1} could be clearly observed in the 15Mo/HZSM-5 sample.

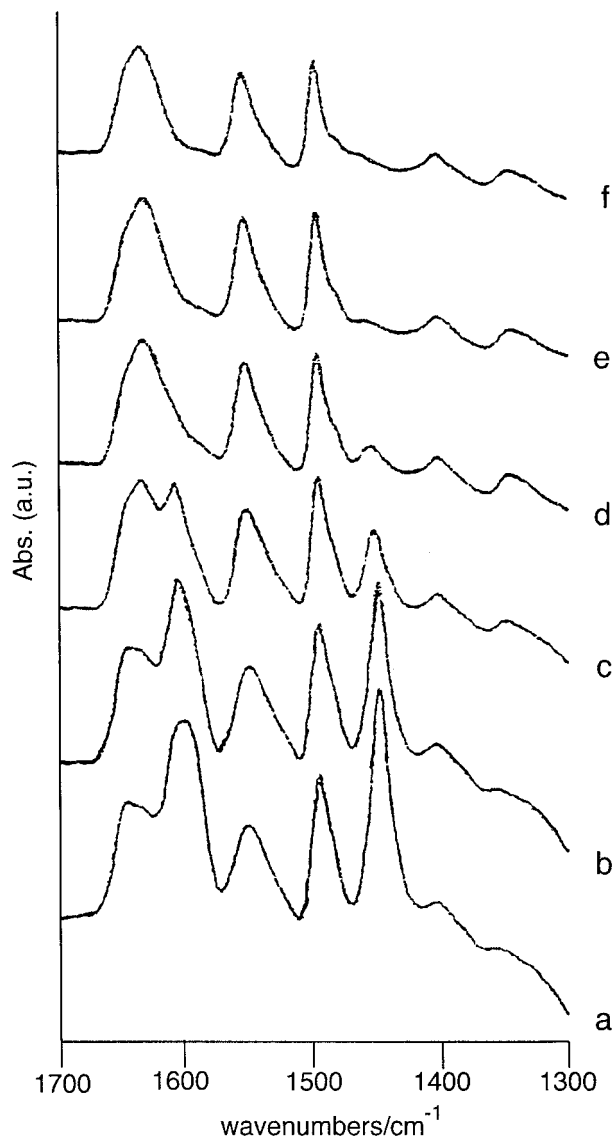


FIG. 5. FT-IR spectra in the range 1300–1700 cm^{-1} for pyridine adsorption on HZSM-5 pretreated at 773 K: (a) after pyridine adsorption, and after desorption at (b) room temperature, (c) 423 K, (d) 473 K, (e) 573 K, and (f) 673 K.

This implies that new Lewis and Brønsted acid sites are generated on high Mo loading samples. Therefore, the study of pyridine adsorption on Mo/HZSM-5 with different Mo loading reveals that the interaction between Mo species and acid sites seems to be more complicated than expected.

Anderson and Klinowski (25) suggested that the ratio of the concentration of Lewis and Brønsted acid sites in a sample, $[L]/[B]$, can be calculated with the formula

$$\frac{[L]}{[B]} = \frac{(E_{1490}^B/E_{1490}^L)(E_{1490}^L/E_{1450})A_{1450}}{A_{1490} - (E_{1490}^L/E_{1450})A_{1450}}$$

where A is an absorbance and E is an extinction coefficient. The extinction coefficient ratio, E_{1490}^L/E_{1450} , is calculated

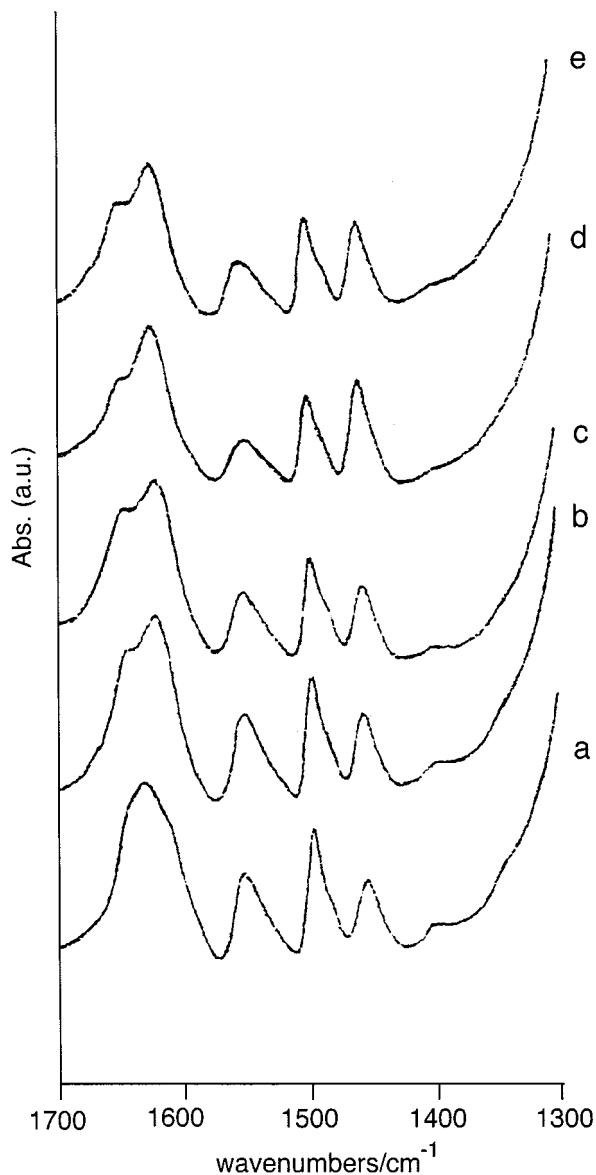


FIG. 6. FT-IR spectra in the range 1300–1700 cm^{-1} for pyridine adsorption on Mo/HZSM-5 catalysts pretreated at 773 K and recorded after evacuation at 423 K: (a) 1Mo/HZSM-5, (b) 3Mo/HZSM-5, (c) 6Mo/HZSM-5, (d) 10Mo/HZSM-5, (e) 15Mo/HZSM-5.

by taking the least-squares fit in a set of 22 different spectra and is equal to 0.56. According to the result by Basila and Kantner (26), $E_{1490}^B/E_{1490}^L = 6$. Therefore, the ratio of [L]/[B] can be estimated in Mo/HZSM-5 samples by using the values of A at 1450 and 1490 cm^{-1} from the spectra in Fig. 6 recorded after evacuation at 423 K. The relative integrated intensities of the bands of pyridine adsorbed on the Brønsted and Lewis acid sites, referring with the framework band at 1850 cm^{-1} , as a function of Mo loading are plotted in Fig. 7. The ratios of [L]/[B], calculated according to Anderson's equation, are also plotted in Fig. 7. Both the relative intensities of pyridine adsorption on Brønsted and

Lewis acid sites decreased with Mo loading in the range of 0–6%. However, the relative intensity of pyridine adsorption on Lewis acid sites increased with Mo loading between 6 and 10% and then kept nearly constant, whereas the relative intensities of pyridine adsorption on Brønsted acid sites decreased. The ratio [L]/[B] remained nearly constant in the Mo loading range of 0–6% and then increased with increasing Mo loading, suggesting that more Lewis acid sites may be created by introducing more Mo species onto HZSM-5. So, on the basis either of the relative integrated intensity of the bands concerned or of Anderson's equation, both methods lead to the same conclusion.

The strength distribution of the Brønsted and Lewis acid sites has also been investigated by *in situ* FT-IR spectroscopy with stepwise evacuation under various temperatures. The results are presented in Fig. 8. The relative integrated intensity of pyridinium ions adsorbed on Brønsted acid sites of HZSM-5 first increased and then decreased slightly. Meanwhile the relative integrated intensity of pyridine adsorbed on Lewis acid sites decreased noticeably as the evacuation temperature increased from 423 to 473 K. It then remained nearly constant with further increase in temperature. The results suggest that the weak acid sites of HZSM-5 are mainly Lewis acid sites, while most of the Brønsted and half of the Lewis acid sites are the strong ones. Although the relative integrated intensity of pyridine adsorbed on the Brønsted acid sites decreased remarkably with Mo loading, with increasing evacuation temperature its change on 3Mo/HZSM-5 and 15Mo/HZSM-5 samples

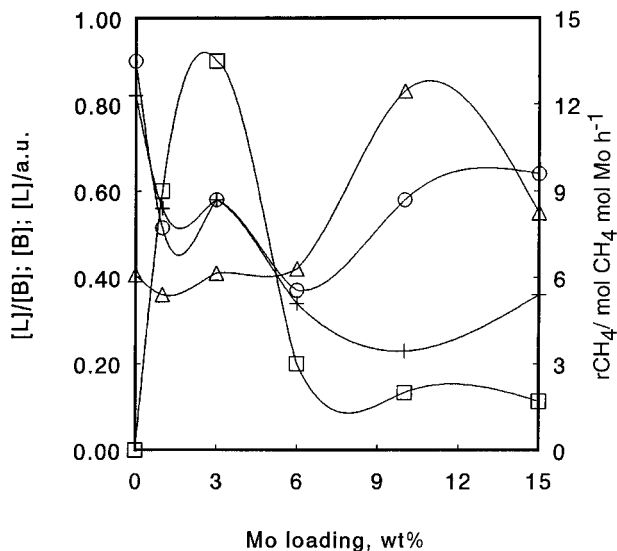


FIG. 7. Effect of Mo loading on the relative integrated intensities of Brønsted and Lewis acid sites calculated from Fig. 5 and on the depletion rate of methane, r_{CH_4} , at 973 K: (+) Relative integrated intensity of the Brønsted acid sites, (O) relative integrated intensity of the Lewis acid sites, (Δ) ratio [L]/[B], and (\square) depletion rate of methane in $\text{mol CH}_4/\text{mol Mo h}^{-1}$.

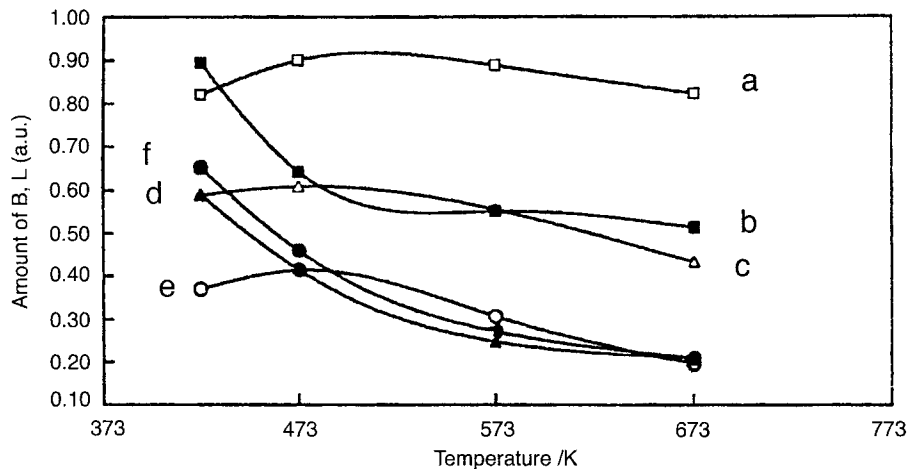


FIG. 8. Effect of evacuation temperature on the relative integrated intensities of the Brønsted (with unfilled symbols) and Lewis (with filled symbols) acid sites on HZSM-5 (a and b), 3Mo/HZSM-5 (c and d), and 15Mo/HZSM-5 (e and f) samples pretreated at 773 K.

followed the same trend as it did on HZSM-5. This implies that, having a narrow strength distribution on the Brønsted acid sites, Mo species will affect and/or occupy the Brønsted acid sites at random. It is obvious that, as we can see from Fig. 8, the relative integrated intensities of the Lewis acid sites on 15Mo/HZSM-5 and 3Mo/HZSM-5 are close to each other, but obviously less than the intensity on HZSM-5. This means that Mo species preferably locate on Lewis acid sites to a certain extent and then locate on Brønsted acid sites. The higher the Mo loading, the more Brønsted acid sites will be affected and/or occupied by Mo species and the fewer Brønsted acid sites will remain free on the surface.

3. Correlation of the Catalytic Activity with the Relative Concentrations of Brønsted and Lewis Acid Sites on Mo/HZSM-5 Catalysts

The depletion rate of CH_4 , expressed in $\text{mol CH}_4/\text{mol Mo} \cdot \text{h}$, based on our previous measurement (17) on the same sample series, is also shown in Fig. 7. The figure seems to be complicated. We observe an obvious decrease in the relative integrated intensities of Brønsted and Lewis acid sites with increasing Mo loading from 0 to 3%, but the depletion rate of CH_4 increases quickly. The depletion rate of CH_4 reaches its maximum at 3% Mo loading, whereas at this loading the relative integrated intensities of pyridine adsorption on Brønsted and Lewis acid sites decrease to 50–60% of that observed for unimpregnated HZSM-5. In the Mo loading range from 3 to 6%, the depletion rate of CH_4 decreases sharply with increasing Mo loading; at the same time the relative integrated intensities of Brønsted and Lewis acid sites decrease to about 40%. In addition, our FT-IR characterization also revealed that some new Lewis and Brønsted acid sites might be formed due to the introduction of high amounts of Mo species, particularly with Mo loading higher than 6% on HZSM-5. But these

newly created acid sites, most of which are Lewis acid sites, probably have no effect on methane aromatization, since the activities remain almost at the same level on the catalysts with Mo loading higher than 6%, as we can see from Fig. 7. Therefore, Lewis acid sites may not be directly involved in the reaction. On the other hand, HZSM-5 zeolite has the largest number of Brønsted and Lewis acid sites, and its catalytic performance in methane aromatization is much poorer than that on Mo/HZSM-5. These results suggest that Mo species, possibly in Mo_2C form (4–6, 18, 27) or in $\text{MoO}_{(3-x)}$ form (7), and the Brønsted acid sites on the surface play a key role in methane dehydrogenation and aromatization. Therefore, our present FT-IR results strongly support the idea that Mo/HZSM-5 is a bifunctional catalyst. The fact that the best activity is obtained on 3Mo/HZSM-5 also suggests that a certain number, probably about 60%, of the original Brønsted acid sites on HZSM-5 should be kept free on the surface for good catalytic performance in methane dehydrogenation and aromatization. One point that should be mentioned is that the catalytic reaction is carried out at 973 K, whereas the FT-IR characterization is performed with samples only pretreated at 773 K. Therefore, further characterization of the Mo/HZSM-5 catalysts under real reaction conditions is necessary to get a more precise picture of the relationship between the catalytic activity and the concentration of the Brønsted acid sites.

CONCLUSIONS

1. Mo species are mainly located on OH groups associated with silanol groups and bridged hydroxyl groups, $\text{Si}(\text{OH})\text{Al}$, as shown by the decrease in the intensities of their stretching modes at 3740 and 3618 cm^{-1} . It is estimated that for the 6Mo/HZSM-5 sample, the relative intensity of the band at 3618 cm^{-1} decreases about 80%, and the band

at 3740 cm^{-1} decreases about 65%. Therefore, Mo species preferentially locate on Brønsted acid sites after calcination at 773 K.

2. A decrease in the relative integrated intensities of the bands of pyridine adsorption on Brønsted and Lewis acid sites is observed with Mo loading in the range 0–6%. However, the relative integrated intensity of the band of pyridine adsorbed on Lewis acid sites increases with Mo loading between 6 and 10% and then stays constant, whereas the relative integrated intensity of pyridine adsorbed on Brønsted acid sites decreases. The strength distribution on the Lewis acid sites is broader than that on the Brønsted acid sites. The number of Brønsted acid sites decreases with Mo loading. An increase in the intensity of the band at 1549 cm^{-1} is observed with 15Mo/HZSM-5 catalyst, suggesting that new Lewis and Brønsted acid sites are generated.

3. Mo/HZSM-5 is a bifunctional catalyst and a certain number (about 60%) of the original Brønsted acid sites on HZSM-5 may need to be kept free on the surface for its good catalytic performance in methane dehydrogenation and aromatization.

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