Methane dehydrogenation and aromatization in the absence of oxygen on Mo/HZSM-5: A study on the interaction between Mo species and HZSM-5 by using ^{27}Al and ^{29}Si MAS NMR

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Abstract

By using a high-resolution solid state nuclear magnetic resonance spectrometer with ^{27}Al and ^{29}Si probes, the interaction between Mo species and HZSM-5 of Mo/HZSM-5 catalysts has been studied. The results show that there is a strong interaction between Mo species and HZSM-5 zeolite. The framework aluminum in the zeolite can be easily extracted by the introduction of Mo species. The extractability of framework aluminum by Mo species increases with increasing Mo loading and the calcination temperature. The extraction process leads to the formation of non-framework Al at first and then a new crystalline phase of $Al_2(MoO_4)_3$. The dealumination of the catalyst having a Mo loading of 15% and had been calcined at 973 K is so severe that all the aluminum in the framework are extracted and no framework Al could be detected by ^{27}Al MAS NMR. The catalyst, therefore, lost its catalytic activity for methane dehydrogenation and aromatization in the absence of oxygen. The Si/Al ratio measured from ^{29}Si MAS NMR further confirms the dealumination process observed by ^{27}Al MAS NMR. The MAS NMR results give us an evidence that $Al_2(MoO_4)_3$ crystallites are much less active for the reaction.

Keywords: ^{27}Al and ^{29}Si MAS NMR; Dealumination; Mo/HZSM-5; $Al_2(MoO_4)_3$; Methane activation

1. Introduction

Recently Mo/HZSM-5 catalysts have been reported to be active for methane conversion without adding O_2 for the formation of aromatics [1–4]. The outstanding catalytic property of the catalyst has been attributed to its acidity and channel structure and the location and state of Mo species on/in HZSM-5 zeolite [2,5]. Our previous studies have shown that, after impregnation of HZSM-5 with ammonium heptamolybdate (AHM) solution and calcination, some kinds of interaction may happen between Mo species and HZSM-5 which lead to an obvious decrease in BET surface area and strong acidity of HZSM-5 [6,7]. At the same time, the location and coordination of Mo species and their reducibilities change a lot. Moreover, in-situ XPS examination revealed obviously that the valence state of Mo species also changes because CH_4 is a quite strong reducing agent,

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particularly at a reaction temperature as high as 973 K [8]. XRD and FT-IR observations also show that MoO_3 and $Al_2(MoO_4)_3$ crystallites have been formed depending on Mo loading and calcination temperature [6,7]. It seems that the interaction between Mo species and HZSM-5 is complicated. The situation can be even more complicated, since as far as the interaction between Mo species and HZSM-5 is concerned, the other important aspect is that the extraction of framework Al will be more severe by introduction of Mo species on/in the zeolite such as HY [9]. Therefore, the knowledge of the coordination and quantification of the different Al species is also essential in understanding the reactivity of Mo/HZSM-5 catalyst for methane dehydrogenation and aromatization in the absence of oxygen.

It is well known that zeolites are crystalline aluminosilicates composed of silicon–oxygen and aluminum–oxygen tetrahedra. The aluminum atom has a nuclear spin of 5/2 and therefore a nuclear quadrupole moment which can interact with the electric field gradient at the site of the nucleus caused by surrounding ions. For a perfect tetrahedral surrounding of aluminum by four oxygens, the electric field gradient is zero. Any distortion of this tetrahedron, however, should cause a field gradient at the aluminum site and consequently, a quadrupole interaction of the aluminum nuclear spin. So ^{27}Al MAS-NMR is a powerful technique to provide direct information pertaining to the local environment of these Al nuclei in zeolite structures [10–13]. Meanwhile, ^{29}Si MAS-NMR is a very important method that offers us a direct measurement of the various ways which aluminum atoms are coordinated to Si atoms in the framework of zeolites [14–16]. In principle, from ^{29}Si MAS-NMR spectra, the ratio of silicon to aluminum in the framework (Si/Al) can be determined.

In this paper, we report the results obtained from ^{27}Al and ^{29}Si MAS-NMR measurements of Mo/HZSM-5 catalysts with different Mo loading and calcining at different temperatures. The effects on the structure of HZSM-5 zeolite after introducing Mo species were evaluated in order to shed more light on the nature of the interaction between Mo species and HZSM-5 zeolite.

2. Experimental

2.1. Catalyst preparation

HZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 50 was supplied by the NanKai University and was used without further treatment. Catalysts with Mo loading of 3% and 15% were prepared by impregnating HZSM-5 with aqueous solutions of ammonium heptamolybdate (AHM). The samples were then dried at 383 K overnight and calcined in air at the desired temperatures for 6 h. They were coded as xMo/HZ-y hereafter, where x is the nominal content of Mo in the sample, and y is the calcination temperature of the sample.

2.2. NMR measurements

The NMR measurements were performed using a Bruker 400-MSL spectrometer with a magnetic field of 9.4 T. ^{27}Al and ^{29}Si MAS-NMR were performed at 104.2 and 79.46 MHz, respectively. Magic angle spinning speeds of 4 kHz were used for both. The recycle time was 0.5 s for [27]Al and 10 s for [29]Si. The sweep width was 41.67 kHz for [27]Al and 31.25 kHz for [29]Si, and chemical shifts are referred to TMS and dilute $Al(NO_3)_3$ solution. Short $\pi/9$ radio frequency (rf) pulses were employed for [27]Al spectra and $\pi/3$ rf pulses were used for [29]Si spectra. The different profiles in the [29]Si spectra were deconvoluted using Jandel Scientific Peakfit program. The best fits of the [29]Si spectra were obtained with Gaussian and Lorentzian line forms.

2.3. XRD measurement

X-ray powder diffraction patterns were obtained on a Rigaku diffractometer using Cu K α

radiation at room temperature. Powder diffrac-
tograms of samples were recorded over a range
of 2θ values from 5–50° under the conditions
of 40 kV and 100 mA at a scanning rate of 8
deg/min. All the XRD patterns recorded can be
processed with a computer system attached to
the instrument.

2.4. Methane dehydrogenation and aromatization

A catalytic test was performed with a fixed
bed continuous flow quartz reactor as men-
tioned in a previous paper [2]. Briefly, the cata-
lyst charge was 0.2 g with particle size ranging
from 40 to 60 mesh. The tail gas was sampled
after 40 min running and analyzed by Shimadzu
GC-9AM chromatography. The conversion of
methane and selectivity of products were calcu-
lated on the basis of carbon number balance.

3. Results and discussion

3.1. The thermal stability of Mo / HZSM-5 cata-lysts revealed from ^{27}Al MAS NMR spectra

^{27}Al MAS-NMR offers a strong and effective
instrument for characterizing the structure of
zeolites. It can discriminate between framework
aluminum atoms in tetrahedral coordination and
non-framework aluminum atoms in octahedral
coordination or penta-coordination [10–13]. The
samples must be hydrated enough in order to
reduce the ^{27}Al NMR line width which is mainly
caused by the quadrupolar interaction of the
aluminum nuclear spin.

^{27}Al MAS-NMR spectra of 3Mo and
15Mo/HZSM-5 catalysts together with HZSM-
5 zeolite calcined at different temperatures are
shown in Figs. 1 and 2, respectively. There are
two main peaks as expected. One at 53 ppm,
which is typical for tetrahedrally coordinated
framework aluminum in ZSM-5 zeolite, and the
other at 0 ppm, which can be attributed to
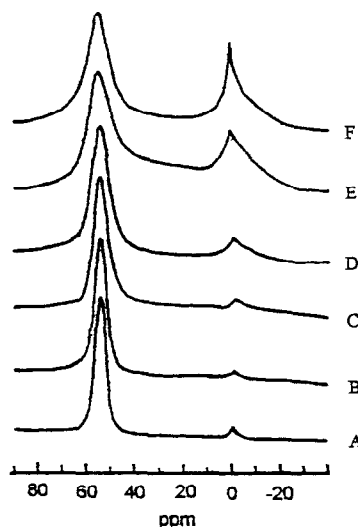octahedral non-framework aluminum.

Fig. 1. ^{27}Al MAS-NMR spectra of HZSM-5 zeolite calcined at 773
K (A) and 973 K (B) and 3Mo/HZSM-5 catalysts calcined at 773
K (C); 873 K (D); 923 K (E) and 973 K (F).

The ^{27}Al MAS-NMR spectra of HZSM-5 cal-
cined at 773 K and 973 K are similar and this
shows the high thermal stability of HZSM-5
framework. The thermal stability of the HZSM-5
framework seems to change with Mo loading
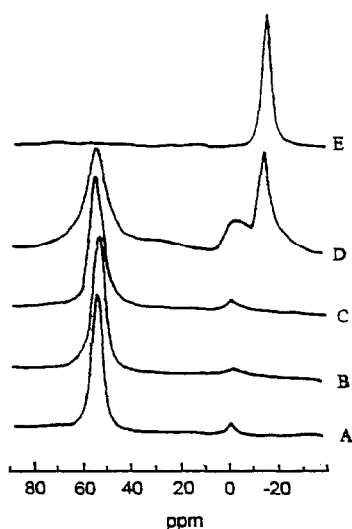and calcination temperature. For the

Fig. 2. ^{27}Al MAS-NMR spectra of HZSM-5 zeolite calcined at 773
K (A) and 973 K (B) and 15Mo/HZSM-5 catalysts calcined at
773 K (C); 873 K (D) and 973 K (E).

3Mo/HZSM-5 sample, only little change could be detected on the NMR spectra if the sample was calcined at 773 K. This means that the original framework of HZSM-5 zeolite is remained if Mo loading is as low as 3% and calcined at 773 K. However, with increasing calcination temperature, the amount of non-framework aluminum increases. At the same time, the corresponding peak width also increases as shown in Fig. 1.

The increase in the amount of non-framework aluminum for 3Mo/HZSM-5 samples with calcination temperatures shows that Mo species interact with framework aluminum. The interaction is so strong with increasing calcination temperature that aluminum is extracted by Mo species from the framework of zeolite.

The increase in the line width of ^{27}Al MAS NMR spectra implies an increase in the quadrupolar interaction between the octahedral coordinated aluminum and water molecules, since the magic angle spinning cannot eliminate the quadrupolar interaction. On the one hand, there may be an overlapping resonance with chemical shift at 30 ppm which may be assigned to penta-coordinated non-framework aluminum [12,13]. Because of the relative low spinning frequency in our experiments (about 4 kHz), the spectrum is not well resolved. Although the intensity of the peak at 0 ppm increased obviously when 3Mo/HZSM-5 was calcined at 973 K, a large portion of the framework aluminum of HZSM-5 remained.

For the high Mo loaded sample, 15Mo/HZSM-5, the effect of calcination temperature on dealumination is even more severe. Only a small difference between 15Mo/HZSM-5 and HZSM-5 could be detected, if they were both calcined at 773 K for 6 h. The interaction between Mo species and HZSM-5 is not strong
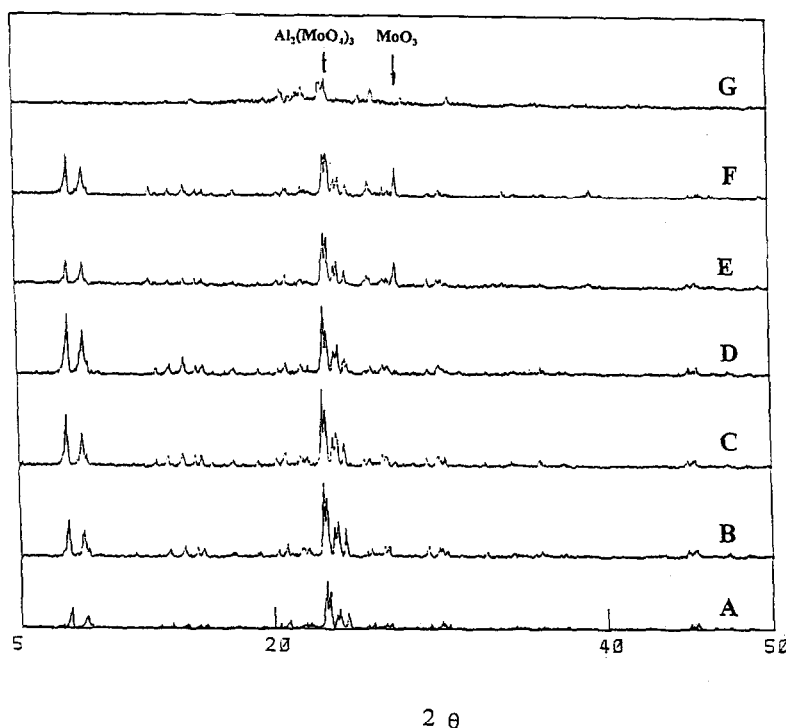

Fig. 3. XRD patterns for different samples. HZ-773 (A); 3Mo/HZ-773 (B); 3Mo/HZ-873 (C); 3Mo/HZ-973 (D) 15Mo/HZ-773 (E); 15Mo/HZ-873 (F) 15Mo/HZ-973 (G).

enough to dealuminate the framework aluminum. With increasing calcination temperatures, the interaction becomes severe as shown in Fig. 2d. A new peak with a chemical shift at − 15 ppm appeared. The peak is attributed to octahedral aluminum ion in crystalline $Al_2(MoO_4)_3$ [17]. If 15Mo/HZSM-5 was calcined at 973 K for 6 h, the ^{27}Al MAS-NMR spectrum has only one peak at − 15 ppm. The peaks at 53 ppm and 0 ppm reflecting the existence of framework and non-framework aluminum, respectively, cannot be detected. The formation of new $Al_2(MoO_4)_3$ crystalline phase has also been confirmed by XRD (Fig. 3).

The above results show that Mo species interact with the framework aluminum of HZSM-5 zeolite, and the interaction increases with increasing Mo loading and calcination temperature. The strong interaction finally leads to the extraction of framework aluminum and the formation of new $Al_2(MoO_4)_3$ crystalline phase.

3.2. The changes in the ratios of Si / Al of Mo / HZSM-5 catalysts revealed from ^{29}Si MAS-NMR spectra

The framework Si/Al ratio can be determined according to the equation given by Klinowski [18]:

$$Si/Al = \left[\sum_{n=0}^{4} I_{Si(nAl)} \right] \bigg/ \left[\sum_{n=0}^{4} \tfrac{1}{4} n I_{Si(nAl)} \right]$$

where $I_{Si(nAl)}$ is the intensity of the individual Si(nAl) peaks (% area) obtained from the deconvoluted spectra.

The ^{29}Si MAS-NMR spectra are shown in Figs. 4 and 5, for 3Mo/HZSM-5 and 15Mo/HZSM-5 calcined at different temperatures, respectively. The corresponding deconvoluted spectra showing the separate peaks are shown in Figs. 6 and 7, respectively. The chemical shifts and the peak areas of Si(nAl) resonance calculated by curve fitting with Gaussian and Lorentzian line shapes are shown in Table 1. According to Loewenstein's rule, Al–O–Al
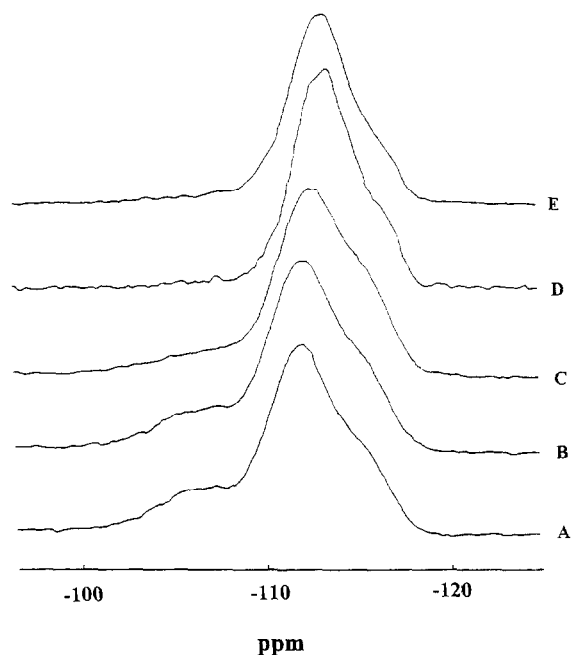

Fig. 4. ^{29}Si MAS-NMR spectra for HZSM-5 calcined at 773 K (A) and 3Mo/HZSM-5 calcined at 773 K (B); 873 K (C); 923 K (D); 973 K (E).

linkage cannot exist in zeolite: one Al atom must be coordinated to four Si atoms, whereas one Si atom can be coordinated by 0, 1, 2, 3 and
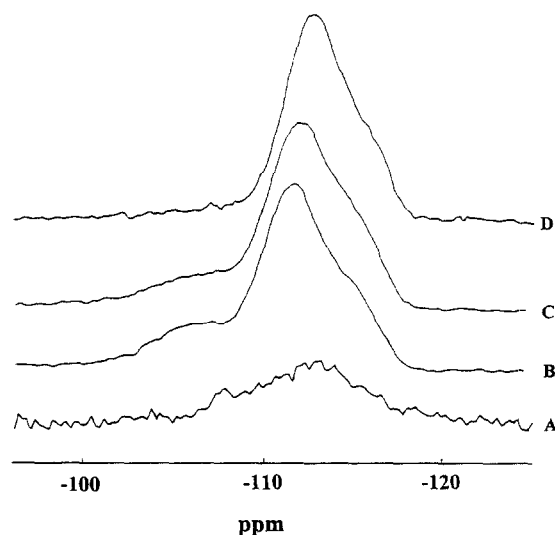

Fig. 5. ^{29}Si MAS-NMR spectra for HZSM-5 calcined at 773 K (B) and 15Mo/HZSM-5 catalysts calcined at 773 K (C); 873 K (D); and 973 K (A).

4 Al atoms which are represented with Si(0Al), Si(1Al), Si(2Al), Si(3Al), and Si(4Al), respectively. For ZSM-5 zeolite, only Si(0Al) and Si(1Al) configurations exist because its SiO_2/Al_2O_3 ratio is larger than 12 [19,20].

From Figs. 6 and 7, we can see that there are three peaks in ^{29}Si MAS-NMR spectra with chemical shifts at -106 ppm, -112 ppm, and -115 ppm. The first one can be attributed to Si(1Al), and the other two can be attributed to Si(0Al) [21]. Table 1 list the results in more detail. For the samples of HZ-773 zeolite, 3Mo/HZ-773 and 15Mo/HZ-773, the Si/Al ratios calculated from the spectra are 22.51, 22.73, and 22.96, respectively. These data clearly show that the dealumination is negligible at this stage, no matter with or without Mo species. With increasing calcination temperature, the ratios of Si/Al in the framework are increasing sharply. For example, the Si/Al ratio

of 3Mo/HZ-873 and 15Mo/HZ-873 is 52.02 and 132.0, respectively. The intensity of Si(1Al) in this 15Mo/HZ-873 sample decreases seriously. As we can see from Table 1, the Si/Al ratio for 15Mo/HZ-973 is nearly infinite. Only a weak peak is seen with chemical shift at -110 ppm, as shown by amorphous Si, which indicates the framework structure of ZSM-5 zeolite is no longer existed. The result is in agreement with that obtained from ^{27}Al MAS-NMR.

The framework of HZSM-5 is stable in Mo/HZSM-5 with low Mo loading and calcination temperature. The Si/Al ratio of the framework in the samples is hardly changed. With increasing Mo loading and calcination temperature, the interaction between Mo species and HZSM-5 zeolite intensifies which at last leads to severe dealumination of the framework of HZSM-5. The framework collapses completely
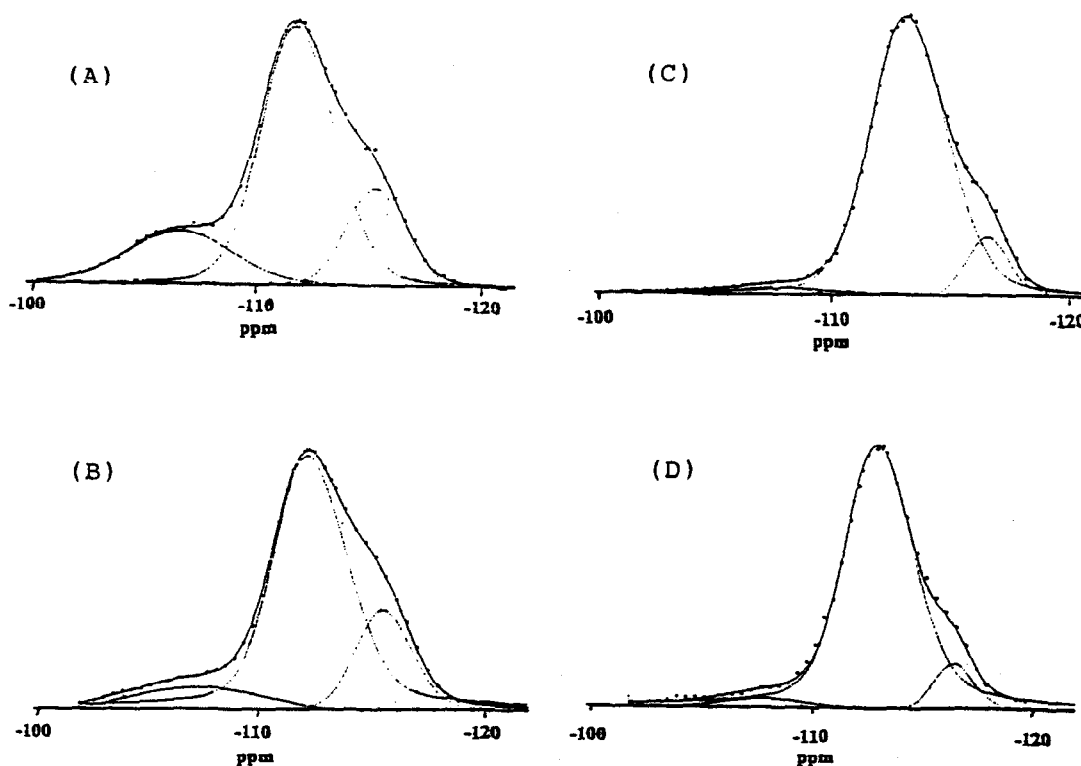

Fig. 6. Spectra corresponding to separate peaks for 3Mo/HZSM-5 catalysts calcined at different temperatures. (A) 773 K; (B) 873 K; (C) 973 K and (D) 973 K.

at extreme conditions, i.e. Mo loading as high as 15% and calcined at 973 K. The extraction of aluminum from the framework of HY zeolite by Mo species has been reported by Ezzamarty [9]. Mo species prefer to attack the Si sites with more Al atoms attached to it and extract aluminum from the framework. Although the number of Al atom coordinated Si atom in HZSM-5 is not as high as that in HY zeolite in one unit cell, the interaction leading to dealumination of the framework is still very strong in 15Mo/HZ-973 sample.

3.3. Catalytic performance on Mo / HZSM-5 zeolite catalysts

The results of dehydrogenation and aromatization of methane without using oxygen over HZSM-5 and Mo/HZSM-5 catalysts are listed in Table 2. The conversion of methane over HZSM-5 is 0.1%. It is very low compared with the methane conversion on Mo/HZSM-5 catalysts. The best activity for methane dehydrogenation and aromatization is obtained on 3Mo/HZSM-5 catalysts calcined at 773 K and 873 K where the methane conversion reaches 6.3% and the selectivity to aromatics is about 90%. For 15Mo/HZ-773, although the conversion is lower, the selectivity to aromatics is still higher than 90%. With increasing calcination temperature, for 15Mo/HZ-973, the conversion of methane and the selectivity to aromatics decrease dramatically. Methane is hardly activated on this catalyst. After running for 2 h, the methane conversion is 0.2% and the selectivity to aromatics is 43.4%. By combining the cat-
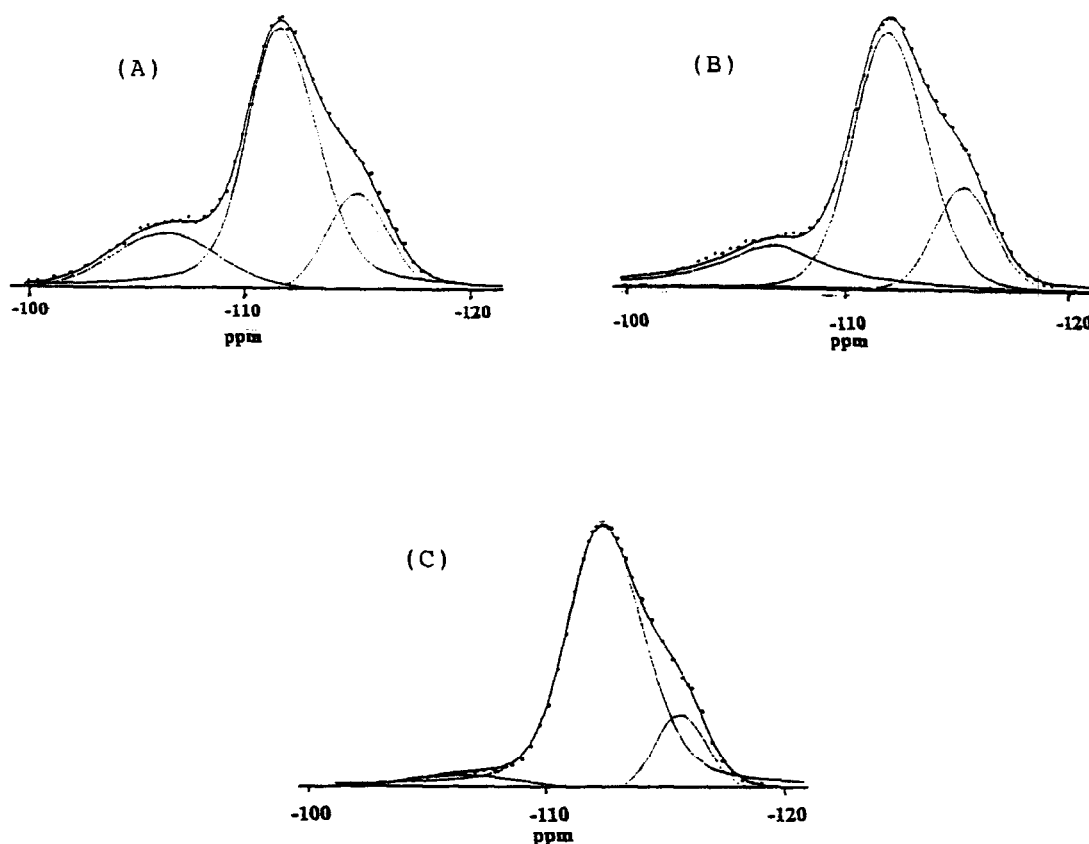

Fig. 7. Spectra corresponding to separate peaks for HZSM-5 calcined at 773 K (A) and 15Mo/HZSM-5 catalysts calcined at 773 K (B) and 873 K (C).

Table 1
The results of ^{29}Si MAS NMR of Mo/HZSM-5 catalysts

Sample	Si(nAl)	δ (ppm)	FWHM (Hz)	I (%area)	Si/Al
HZ-500	Si(1Al)	−106.3	439.2	17.77	
	Si(0Al)	−111.7	299.2	82.23	22.51
		−115.1	254.5		
3Mo/HZ-500	Si(1Al)	−106.6	436.0	17.60	
	Si(0Al)	−112.0	305.4	82.40	22.73
		−115.4	237.0		
3Mo/HZ-600	Si(1Al)	−107.2	527.1	7.69	
	Si(0Al)	−112.5	309.7	92.31	52.02
		−115.7	232.7		
3Mo/HZ-650	Si(1Al)	−107.6	245.8	2.81	
	Si(0Al)	−113.3	298.6	97.19	142.3
		−116.6	161.1		
3Mo/HZ-700	Si(1Al)	−107.7	291.6	2.67	
	Si(0Al)	−113.3	296.0	97.73	149.8
		−116.5	160.5		
15Mo/HZ-500	Si(1Al)	−106.7	455.6	17.42	
	Si(0Al)	−112.1	306.2	82.58	22.96
		−115.5	246.2		
15Mo/HZ-600	Si(1Al)	−106.2	407.3	3.03	
	Si(0Al)	−112.6	299.5	96.97	132.0
		−115.6	197.1		
15Mo/HZ-700					infinite

alytic performance with the results of ^{27}Al and ^{29}Si MAS NMR, it seems clear that the Mo species in $Al_2(MoO_4)_3$ crystallites is much less active for methane dehydrogenation and aromatization. This is in agreement with our previous study [7].

Table 2
Methane conversion over Mo/HZSM-5 catalysts calcined at different temperatures

Catalyst	C_{CH_4} (%)	$Y_{C_2H_4}$ (%)	Y_{Ar} (%)	S_{Ar} (%)
HZSM-5	0.1	0.0	0.0	16.8
3Mo/HZ-773	6.3	0.2	6.0	94.8
3Mo/HZ-873	6.3	0.2	6.0	94.5
3Mo/HZ-973	3.1	0.3	2.7	85.8
15Mo/HZ-773	3.9	0.1	3.6	94.2
15Mo/HZ-973 [a]	0.0	0.0	0.0	0.0
15Mo/HZ-973 [b]	0.2	0.1	0.1	43.4

[a] Sampling after running 40 min.
[b] Sampling after running 2 h.

4. Conclusion

Mo/HZSM-5 catalysts for methane dehydrogenation and aromatization have been studied by using ^{27}Al and ^{29}Si MAS-NMR. It was found that there is a strong interaction between Mo species and the framework aluminum in HZSM-5. With increasing Mo loading and calcination temperatures, the interaction develops so strong that all the aluminum in the framework can be extracted by Mo species, and at last forms a new $Al_2(MoO_4)_3$ crystalline phase. The framework of ZSM-5 zeolite collapses at the end, and the catalytic activity for methane dehydrogenation and aromatization drops dramatically. On the basis of these results, it is confirmed that the formation of $Al_2(MoO_4)_3$ crystallite is a main detrimental factor for methane dehydrogenation and aromatization on Mo/HZSM-5 catalysts in the absence of oxygen.

Acknowledgements

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