

A high-resolution MAS NMR study on the potential catalysts Mo/HBeta for olefin metathesis: The interaction of Mo species with HBeta zeolite

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Abstract

The interfacial interaction of Mo species with the HBeta zeolite was studied by multinuclear MAS NMR, XRD and N₂ adsorption. As proved by the quantitative ²⁷Al MAS NMR, this interaction is so strong as to dealuminate the framework of HBeta, and leads to a new peak appearing at −14 ppm, which indicates the formation of crystalline Al₂(MoO₄)₃. This can also be detected by XRD measurements when the Mo loading is as high as 9.0 wt.%. The corresponding quantitative ²⁹Si and ¹H MAS NMR spectra show that the amount of silanols and Brønsted acidic sites decrease obviously with increasing Mo loading. This also reveals an interaction between Mo species and HBeta support through an oxygen bridge resulting from condensation with the hydroxyls on the support. At higher Mo loadings, the interaction is so strong that it results in an extraction of aluminum from the zeolite framework, and subsequently appearance of Al₂(MoO₄)₃ and loss of Brønsted acidic sites. These can be correlated to the low catalytic activity of Mo/HBeta in metathesis of ethylene and 2-butylene to propylene.

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Keywords: MAS NMR; Mo/HBeta catalyst; HBeta zeolite; Interaction; Olefin metathesis reaction; Ethylene; 2-Butylene; Propylene

1. Introduction

Zeolite Beta has a three-dimensional network of 12-membered rings and is considered as a large pore zeolite between faujasite-Y and Linde type L zeolites [1]. Since its discovery in 1967, great interest has been paid because of its potential applications in petroleum chemistry such as cracking [2], isomerization [3], alkylation and disproportionation of hydrocarbon compounds [4]. Recently our laboratory reported that supported Mo/HBeta-Al₂O₃ exhibits good activity in the metathesis reaction of ethylene and 2-butylene to propylene [5]. This is an alternative way to produce propylene due to its rapid demand in the world-wide market [6]. Supported Mo/HBeta catalysts also show some activities for the olefin metathesis, but the catalytic performance increases remarkably after addition of Al₂O₃ [5]. So the clarification of the inter-

action between Mo species and HBeta is very important for shedding light on the function of Al₂O₃ in the support, and it is also helpful to make clear the role of acidity in the metathesis reaction.

It is well known that multinuclear solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) is a powerful tool for studying the structure of zeolite and other heterogeneous catalysts [7]. ²⁷Al MAS NMR spectra can discriminate framework and non-framework aluminum species. The cross-polarization (CP) technique may be used for signal enhancement and the detection of protons closely connected to Al or Si atoms [8]. In our study, HBeta zeolite was used as the support and different Mo loading catalysts were prepared by the impregnation method. A multinuclear solid-state NMR study including ²⁷Al, ²⁹Si CP/MAS NMR and ¹H MAS NMR was performed to evaluate the interaction between Mo species and HBeta zeolite. This kind of interaction may influence the distribution of Mo species and is related to the performance of Mo/HBeta catalysts in the metathesis reaction of ethylene and 2-butene to propylene.

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2. Experimental

2.1. Sample preparation

Fully exchanged HBeta zeolite was obtained by ion exchange of NaBeta (Si/Al = 15, provided by Fushun Petroleum Company, China) with a 0.8 M aqueous solution of ammonium nitrate at 80 °C for three times, followed by drying at 120 °C and calcination at 520 °C. Supported Mo/HBeta catalysts were prepared by impregnating HBeta with an appropriate amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ for 0.5 h, then dried at 120 °C and finally calcined at 680 °C for 2 h. The samples were designated as *n*Mo/HBeta, where *n* stands for the weight percent of molybdenum. In order to investigate the influence of Mo incorporation on the HBeta zeolite, a blank HBeta sample was also calcined at 680 °C for 2 h.

2.2. NMR measurements

All the NMR measurements were performed on a Varian Infinityplus-400 spectrometer equipped with a 4 mm MAS probe. ^{27}Al MAS NMR spectra were recorded at a resonance frequency of 104.2 MHz with a spinning rate of 10 kHz. Chemical shifts were referenced to $(\text{NH}_4)\text{Al}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$ at -0.4 ppm as a secondary reference. The spectra were accumulated for 200 scans with $\pi/12$ flip angle and 2 s pulse delay. For a quantitative comparison, all samples were weighted and the spectra were calibrated by measuring a known amount of $(\text{NH}_4)\text{Al}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$ under the same conditions [9]. ^{29}Si MAS NMR spectra with high-power proton decoupling were recorded at 79.4 MHz. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane sulfonate sodium (DSS). A 2200 scans were accumulated with a $\pi/4$ pulse width of 1 μs and a 4 s recycle delay. $^1\text{H} \rightarrow ^{29}\text{Si}$ CP/MAS NMR experiments were performed with a 4 s recycle delay, 4000–6000 scans, and a contact time of 2.5 ms. Before the ^1H MAS NMR measurements, samples were dehydrated at 400 °C and at a pressure below 10^{-2} Pa for 20 h. ^1H MAS NMR spectra were collected at 399.9 MHz using single-pulse sequence with $\pi/4$ pulse, 4 s recycle delay. $^1\text{H}\{^{27}\text{Al}\}$ spin-echo double resonance experiments were performed with a spin-echo pulse applied to the ^1H channel and aluminum was irradiated simultaneously during the first τ period. The excitation pulse length was 2.6 μs ($\pi/2$), and τ was set to one rotor period. The ^{27}Al irradiation field was about 60 kHz. All the single-pulse ^1H spectra were accumulated for 200 scans and spun at 8 kHz. Chemical shifts were referenced to a saturated aqueous solution of DSS. The deconvolution of the spectra was conducted using Winfit software.

2.3. XRD, BET and XRF measurements

X-ray diffraction patterns were obtained at room temperature on a Rigaku D/Max-RB diffractometer using Cu K α radiation. Powder diffractograms of samples were recorded over a range of 2θ values from 5° to 50° under the conditions of 40 kV and 100 mA at a scanning rate of 8° min $^{-1}$. The nitrogen sorption experiments were performed at 77 K on an ASAP 2000 system

in the static measurement mode. The samples were outgassed at 350 °C for 10 h before the measurement. The overall aluminum contents of all the samples were analyzed using a SRS 3400 X-ray fluorescence spectrometer (XRF).

2.4. Catalytic evaluation

The catalysts were tested in a fixed-bed flow microreactor. Briefly the catalyst charge was ca. 2 g with an average particle size from 16 to 32 mesh. The catalyst was activated for 1 h at 550 °C under nitrogen and then cooled in nitrogen to the reaction temperature. Catalytic tests were carried out at 120 °C under 1 MPa. The reaction products were analyzed by a GC-8A gas chromatograph with an FID detector. The conversion of ethylene and 2-butylene was calculated on the basis of carbon number.

3. Results and discussion

3.1. ^{27}Al MAS NMR

^{27}Al MAS NMR offers a strong and effective tool for characterizing the structure of zeolite. Species with different structures or different environments will have a different chemical shift in the ^{27}Al MAS NMR spectra. Fig. 1 shows the ^{27}Al MAS NMR spectra of HBeta zeolite with different Mo loadings. There are two main peaks as expected: one at 54 ppm is typically associated with four-coordinated framework aluminum in HBeta zeolite and the other at 0 ppm is commonly attributed to six-coordinated non-framework aluminum [10–14]. With increasing Mo loading, the peak intensity of the framework Al decreases while its half-height line width broadens. At the same time the amount of non-framework Al at 0 ppm increases. When the Mo loading reaches 4% a new peak at about -14 ppm appears which can be attributed to the octahedral aluminum in crystalline $\text{Al}_2(\text{MoO}_4)_3$ [10,11]. From Fig. 1 we can see the incorporation of Mo species first leads to the formation of more non-framework aluminum. With increasing Mo loading the interaction becomes

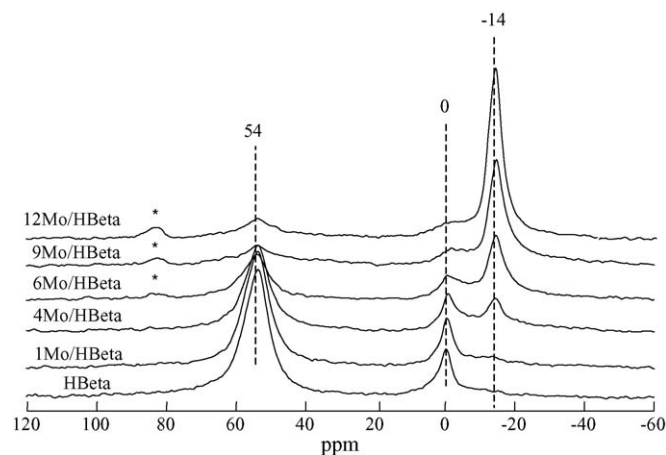


Fig. 1. ^{27}Al MAS NMR spectra of HBeta zeolite with different Mo loadings recorded at a resonance frequency of 104.2 MHz with a sample spinning rate of 10 kHz and 800 scans (prior to measurements, samples were exposed to air. Asterisk denotes the spinning side bands).

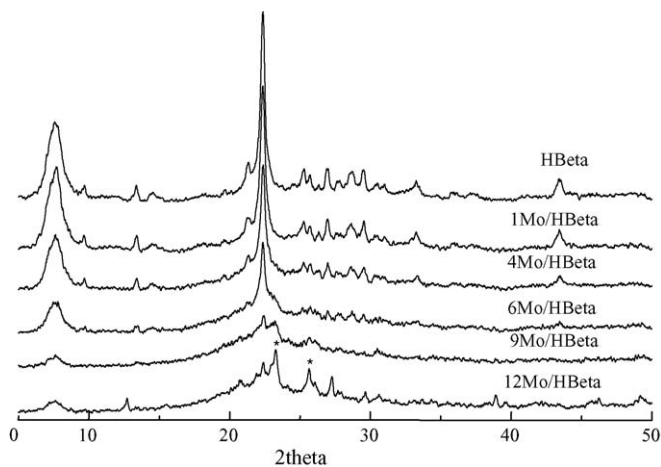


Fig. 2. Power XRD patterns of HBeta zeolite with different Mo loadings (asterisk denotes the $\text{Al}_2(\text{MoO}_4)_3$ crystallites).

stronger; for 12Mo/HBeta sample, the signal of framework aluminum at 54 ppm decreases greatly while only a strong peak ascribed to $\text{Al}_2(\text{MoO}_4)_3$ appears. So, the interaction between Mo species and HBeta zeolite is so strong that aluminum is extracted by Mo species from the zeolitic framework, and finally leads to the formation of crystalline $\text{Al}_2(\text{MoO}_4)_3$. This new crystalline phase was also detected by XRD on the Mo-loaded HBeta zeolite as shown in Fig. 2. The diffraction peak intensity characteristic of HBeta decreases with increasing Mo loading. But no diffraction peaks characteristic of MoO_3 are presented in the patterns. As listed in Table 1, the BET surface areas of the corresponding samples decrease obviously with increasing Mo loading. This also indicates that interactions may occur between the Mo species and the HBeta support. When the Mo loading is as high as 12.0 wt.%, the BET surface area reduces greatly to $67 \text{ m}^2/\text{g}$. This means the framework of HBeta support may be destroyed.

When the sample was fully hydrated by the saturated NH_4NO_3 solution for a week, a broad new peak closely connected to the signal at around 0 ppm appears, as shown in Fig. 3. This suggests that the initially invisible octahedral alu-

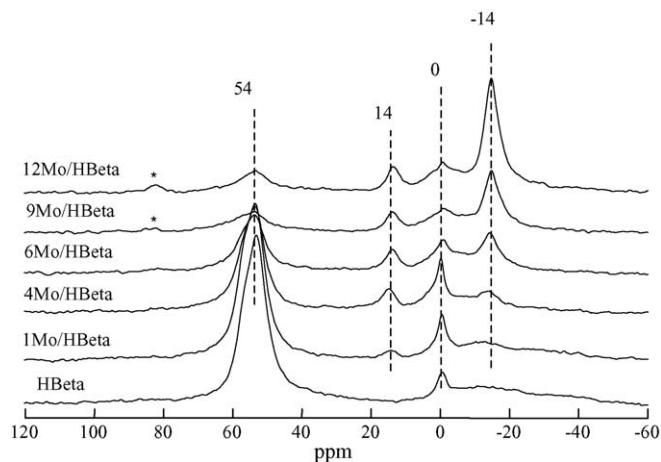


Fig. 3. ^{27}Al MAS NMR spectra of HBeta zeolite with different Mo loadings (prior to measurements, samples were completely hydrated in a desiccator with saturated NH_4NO_3 solution. Asterisk denotes the spinning side bands).

Table 1
Surface areas, Si/Al ratios and Al contents of the HBeta zeolites with different Mo loadings

Catalyst	BET surface area (m^2/g of HBeta)	Si/Al ratio (from ^{29}Si MAS NMR)	Al(V) (10^{-4} mol/g of HBeta) ^a	Al(OH) _n (H ₂ O) _{6-n} · <i>ln</i> (MoO ₄) (10^{-4} mol/g of HBeta) ^a	Al(VI) (10^{-4} mol/g of HBeta) ^a	Al ₂ (MoO ₄) ₃ (10^{-4} mol/g of HBeta) ^a	Al content from NMR (10^{-4} mol/g of HBeta) ^a	Al content from XRF (10^{-4} mol/g of HBeta)	NMR invisible Al (%)
HBeta	585	24	5.79	—	1.87	—	7.66	9.78	21
1Mo-HBeta	530	26	5.23	0.06	1.09	0.87	7.25	9.35	22
4Mo-HBeta	321	33	4.08	0.54	1.28	0.74	6.64	9.38	29
6Mo-HBeta	210	40	2.83	0.48	1.17	1.72	6.2	9.21	32
9Mo-HBeta	78	—	1.37	0.35	1.03	2.03	4.78	9.66	50
12Mo-HBeta	67	—	1.03	0.44	1.07	3.34	5.88	9.76	40

^a Al contents determined from ^{27}Al MAS NMR measurements using $(\text{NH}_4)_2\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ as the external standard.

minimum becomes visible after coordination with water molecules [12]. Moreover, another new peak at ca. 14 ppm can be clearly resolved in the ^{27}Al MAS NMR spectra of Mo/HBeta catalysts, and the intensity of this peak enhances with the increase in Mo loading. This peak can be attributed to the hydrated form of an $\text{Al}_2(\text{MoO}_4)_3$ phase with a tentative formula of $[\text{Al}(\text{OH})_n(\text{H}_2\text{O})_{6-n}]_n(\text{MoO}_4)$ ($n = 1$ or 2), which has been monitored in the Mo/HZSM-5 and Mo/MCM-22 catalytic systems [10,14]. The quantitative analysis of the aluminum contents from ^{27}Al MAS NMR and XRF is listed in Table 1. It is found that the tetrahedral framework Al of the support decreases gradually with increasing Mo loading. Meanwhile more and more extra-framework Al(VI) and aluminum molybdates appear with increasing introduced Mo species, which leads to the decrease of the BET surface areas of the samples. Quantitative ^{27}Al MAS NMR and XRF measurements suggest that the fraction of NMR invisible Al in the Mo/HBeta catalysts increases with increasing Mo loading. This can be due to the extraction of framework aluminum leading to asymmetric surroundings around Al atoms, which may cause the NMR invisible Al [13]. This may also indicate the strong interfacial interaction between Mo species and HBeta support. Compared with HZSM-5 and MCM-22 supports [10,14], Mo species are easier to interact with the framework Al in HBeta support. The above results show that Mo species interact with the framework aluminum of HBeta zeolite, and the interaction becomes stronger with Mo loading. The strong interaction finally leads to the extraction of framework aluminum and the formation of the $\text{Al}_2(\text{MoO}_4)_3$ crystalline phase.

3.2. ^{29}Si MAS NMR

The ^{29}Si MAS NMR spectra of samples and their corresponding $^1\text{H} \rightarrow ^{29}\text{Si}$ CP/MAS NMR spectra are shown in Fig. 4. The ^{29}Si MAS NMR spectrum of HBeta exhibits three main peaks at around -117 , -113 and -107 ppm. The first two lines are

attributed to the inequivalent framework T sites of the HBeta zeolite which correspond to Si(OAl) groupings [10,15,16]. The line at -107 ppm is supposed to come from the contribution of Si(1Al) groupings [15,16]. After cross-polarization, the intensity of the peak at ca. -103 ppm shows a great increase, which indicates that this signal should be related to the species coupling strongly with the hydroxyl protons, and it can be assigned to the silanols with the structure of Si(3Si)OH [10,15,16]. According to the Loewenstein's rule [17], the framework Si/Al ratio can be calculated by deconvolution of the ^{29}Si MAS NMR spectrum and the results are listed in Table 1. It can be seen that the framework Si/Al ratio increases with increasing Mo loading. This is consistent with the above results from ^{27}Al MAS NMR measurements that the amount of framework Al decreases with increasing Mo loading. This fact further reveals that the introduction of Mo species causes the dealumination of the HBeta framework, which is in accordance with the above results from ^{27}Al MAS NMR. When the Mo loading is up to 9 wt.%, the line width of the whole spectrum broadens and the total peak intensity drops down sharply. This may be due to the destruction of microporous structure, which leads to a longer relaxation time of silicon atoms. So, Mo species have strong interaction with zeolite Beta and such an interaction destroys or changes the zeolite lattice. From the XRD patterns (Fig. 2) we can see that the framework of HBeta zeolite has almost collapsed when the Mo loading is 12.0 wt.%.

3.3. ^1H MAS NMR

High-resolution ^1H MAS NMR is a useful and direct method for characterizing the acidic sites in zeolites. Compared with IR, it can provide quantitative information on the interaction between the metal ions and the hydroxyl species on the support without the difficulties of extinction coefficients. The ^1H MAS NMR spectrum of HBeta zeolite is shown in Fig. 5. The signal

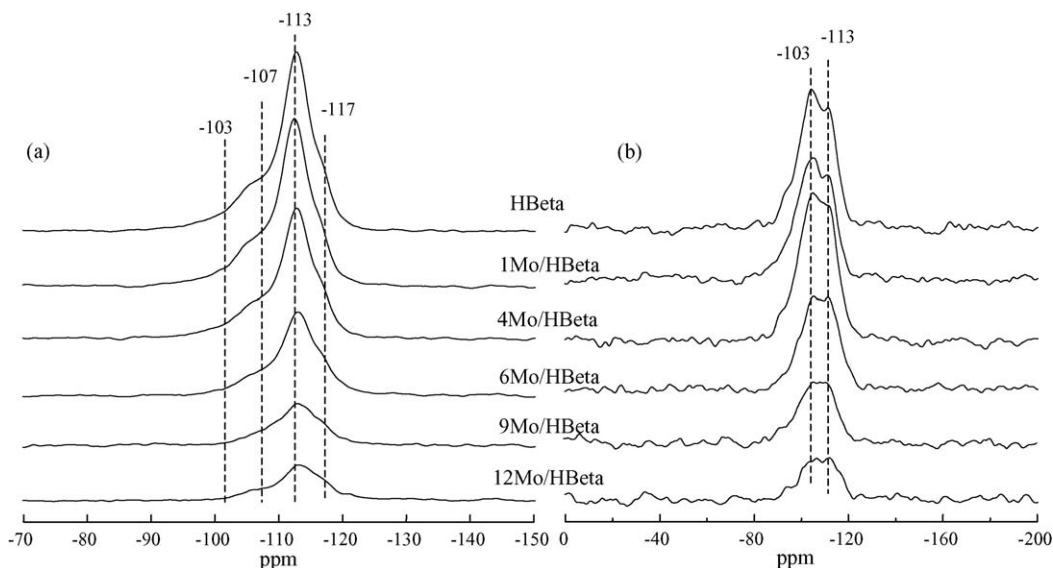


Fig. 4. ^{29}Si MAS (a) and $^1\text{H} \rightarrow ^{29}\text{Si}$ CP/MAS NMR (b) spectra of HBeta zeolite with different Mo loadings. The contact time for the CP/MAS NMR spectra was 2.5 ms, and a 4 s recycle delay was used for all spectra.

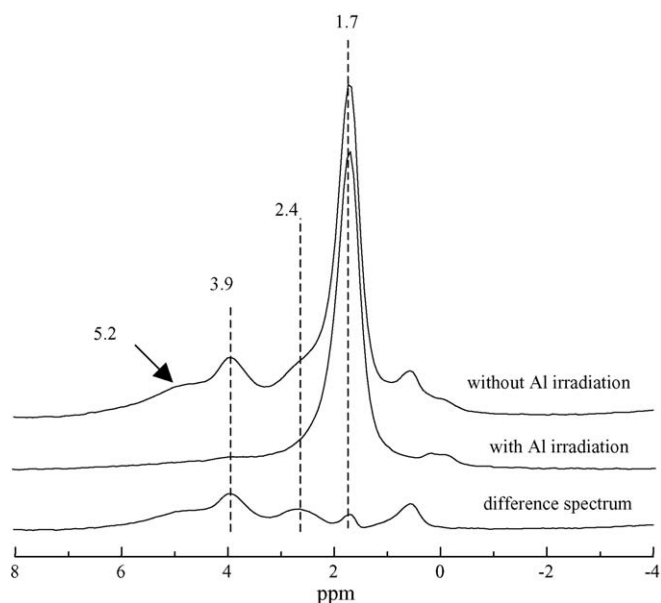


Fig. 5. $^1\text{H}\{^{27}\text{Al}\}$ spin-echo double resonance MAS NMR spectra of HBeta zeolite. The upper spectrum was recorded without Al irradiation, while the middle one was with Al irradiation, and the difference spectrum is shown at the bottom. The spinning speed was set to 4 kHz, and τ period was equal to one rotor period in the experiment.

between 0 and 1.0 ppm is attributed to the non-acidic unperturbed extra-framework aluminum hydroxyls [18]. The presence of hydrogen bonds between Al-OH and neighboring oxygen atoms shifts the signal to the low field at ca. 2.4 ppm [18]. The silanol groups appear at 1.7 ppm. The peak at 3.9 ppm should be assigned to the bridging hydroxyl groups, i.e. Brønsted acidic sites [18]. Moreover, another broad peak centered at about 5.2 ppm is observed clearly. It may be attributed to adsorbed water molecules or another kind of Brønsted acidic sites. To clarify this, $^1\text{H}\{^{27}\text{Al}\}$ spin-echo double resonance experiments were carried out, which is analogous to the dipolar dephasing experiment described by Fyfe et al. [19]. Under strong aluminium irradiation during the spin-echo pulse sequence applied to the proton, the signal of the proton groups that are strongly coupled to aluminium will be significantly suppressed, while the other protons will be unchanged. Therefore, it offers the possibility to differentiate between the OH signals of species close to an aluminum atom and those of species that are further away. As shown in the spectra of the HBeta support (Fig. 5), the intensities of the peaks at 5.2, 3.9, 2.4 and ca. 0.6 ppm decrease with Al irradiation, while the peak at 1.7 ppm remains unchanged. Thus, we deduced that the peak at 5.2 ppm is due to the hydroxyl protons associated with aluminium species. It can be attributed to a second Brønsted acidic site in HBeta zeolite, which interacts electrostatically with the zeolite framework [18,20]. Fig. 6 shows that the total ^1H signal intensity decreases upon Mo loading, and the peaks at 1.7 and 2.4 ppm are preferentially reduced compared to those at 3.9 and 5.2 ppm. This indicates that during the preparation of catalysts Mo species first react with the non-acidic silanols and non-framework AlOH groups on the surface of the zeolites. A similar phenomenon was observed in the preparation of Mo/HZSM-5 catalysts [10].

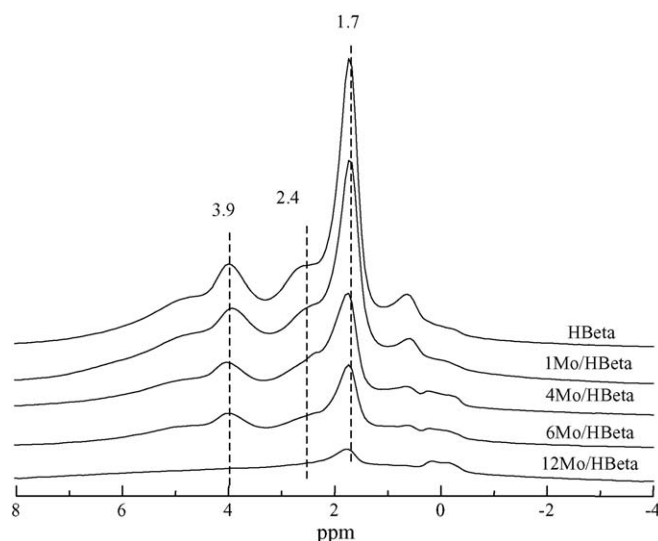


Fig. 6. ^1H MAS NMR spectra of HBeta zeolite with different Mo loadings. The spinning rate was 8 kHz, and 200 single-pulse scans were accumulated.

The above discussion clearly demonstrates that the condensation reaction between the Mo species and the hydroxyl species of HBeta occurs in the impregnation and calcination processes of the catalysts. Both the ^{27}Al and ^1H MAS NMR spectra show that Mo species and Brønsted acidic sites (i.e., framework Al) also interact. The acidic sites in the zeolites may act as powerful traps for the impregnated Mo species. If the Mo species strongly interact with the framework Al through an oxygen bridge after exchange with protons of the Brønsted sites, an extraction of aluminum from the zeolite framework could occur, as has also been proven by the above ^{27}Al and ^{29}Si MAS NMR spectra.

3.4. Catalytic performance on the Mo/HBeta catalysts

Fig. 7 shows the catalytic performance of Mo/HBeta in the metathesis of ethylene and 2-butene to propylene. The highest activity for this reaction is obtained after 2 h reaction on the 1.0 wt.% Mo/HBeta catalyst where the 2-butene conversion reaches 16% and the selectivity of propylene is about 27%. With

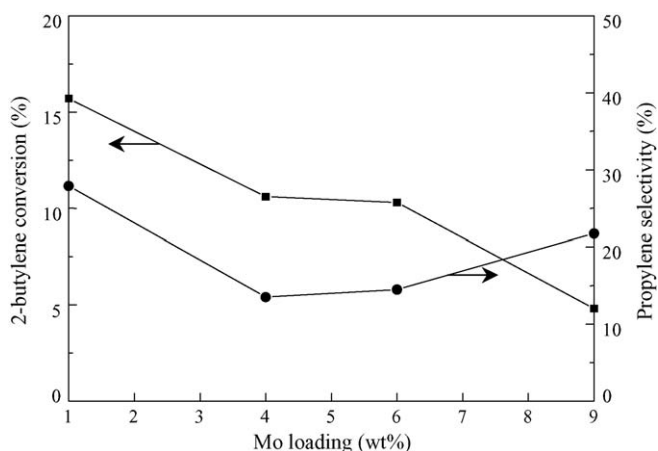


Fig. 7. Catalytic performance of HBeta zeolite with different Mo loadings after reaction of 2 h.

increasing Mo loading the conversion of 2-butene decreases dramatically. By combining the catalytic performance with the results of ^{27}Al , ^{29}Si and ^1H MAS NMR, it seems that the formation of crystalline $\text{Al}_2(\text{MoO}_4)_3$ in the course of catalyst preparation causes the Mo/HBeta to be less active for the olefin metathesis. Higher Mo loadings will lead to the destruction of HBeta framework and formation of more $\text{Al}_2(\text{MoO}_4)_3$. This will cause the decrease in the activity of Mo/HBeta in the olefin metathesis reaction. Therefore, a moderate acidity and interaction of Mo species with HBeta is crucial for the olefin metathesis.

4. Conclusions

Mo/HBeta catalyst for metathesis reaction of ethylene and 2-butylene to propylene has been studied by multinuclear MAS NMR techniques. It was found that there is strong interaction between Mo species and HBeta support. With increasing Mo loading the interaction becomes so strong that most of the aluminum in the framework can be extracted with the Mo species and forms the crystalline $\text{Al}_2(\text{MoO}_4)_3$. It seems that the formation of the $\text{Al}_2(\text{MoO}_4)_3$ causes the catalysts to become less active for the olefin metathesis. As proved by the ^1H MAS NMR experiments, Mo species also react with the hydroxyls on the surface of HBeta during impregnation and calcination processes. A proper acidity and interaction between Mo species and HBeta support in the Mo/HBeta catalyst is crucial for the olefin metathesis.

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