A facile and effective method for the distribution of Mo/HZSM-5 catalyst active centers

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Post-steaming treatment of Mo/HZSM-5 catalysts results in more molybdenum species migrating into and residing in the HZSM-5 zeolite channels. This is confirmed by XRF and XPS measurements. ^{1}H MAS NMR and ^{29}Si MAS NMR also demonstrate that the number of free Brönsted acid sites decreases in the Mo/HZSM-5 catalysts that underwent post-steaming treatment, compared to untreated Mo/HZSM-5 catalysts. As a result, the deactivation rate constant (k_d) on the Mo/HZSM-5 catalyst after post-steaming treatment for 0.5 h is much smaller, and the catalyst therefore shows remarkable stability in the probe reaction of methane dehydro-aromatization. The results suggest that a more beneficial bi-functional balance between active Mo species for methane activation and acid sites for the following aromatization is developed over those Mo/HZSM-5 catalysts that have experienced post-steaming treatment for 0.5 h, in comparison with the untreated Mo/HZSM-5 catalysts.

KEY WORDS: methane dehydro-aromatization; Mo/HZSM-5; post-steaming treatment; Brönsted acid sites.

1. Introduction

It is now well recognized that Mo/HZSM-5 is a good catalyst for methane dehydro-aromatization in the absence of oxygen [1,2]. A report recently stated that selective silanation of the external acid sites on HZSM-5 using a large organosilane compound could decrease the acid site content as well as the number of MoO_x species retained on the external surface [3]. As a consequence, the formation rate of hydrocarbons increased by about 30% compared to the untreated Mo/HZSM-5 catalyst. A significant improvement could also be achieved on a Mo-based catalyst supported on pre-dealuminated HZSM-5 by steam treatment [4]. The solid-state MAS NMR measurement further confirmed that the number of Brönsted acid sites was remarkably diminished on the treated HZSM-5 zeolite and corresponding Mo/HZSM-5 catalyst, as compared to the parent HZSM-5 zeolite [5]. The results also demonstrated that only a small fraction of the Brönsted acid sites are required for the aromatization reaction. In addition, dealumination treatment of an HMCM-22 zeolite resulted in effective suppression of strong Brönsted acid sites and thus greatly benefited the catalytic performance of MDA over Mo-based dealuminated HMCM-22 catalysts [6]. All of these treatments are performed on zeolites prior to transitional metal oxide loading.

Recently, we discovered that the exchange of the Mo species with the Brönsted acid sites and the driving force for the migration of the Mo species into the zeolite channels strongly depend on the number of Brönsted acid sites [2]. Therefore, the effect of dealumination of HZSM-5 zeolites may inhibit the migration of Mo species into the channels and further exchange with Brönsted acid sites. In order to avoid this, we mainly focus on the investigation of the effects of post-steam treatment on the MoO_3/HZSM-5 catalyst in this experiment, i.e., steam-treating the Mo/HZSM-5 catalysts after the impregnation of Mo on the HZSM-5 zeolite and the calcination of the catalysts, on its catalytic stability in the MDA reaction and the corresponding differences in molybdenum location together with the number of Brönsted acid sites.

2. Experimental

2.1. Catalyst preparation

HZSM-5 zeolite with a Si/Al ratio of 25 was supplied by Nankai University (Tianjin, China). Two series of catalysts with different Mo loadings were prepared. The parent Mo/HZSM-5 catalysts with different Mo loadings were prepared by the conventional impregnation method as described in [7] and hereafter are denoted as x(wt%)Mo/HZSM-5, where "x" is the weight percentage of Mo. The x(wt%)Mo/HZSM-5(STAI-t) samples were obtained by further treating the x(wt%)Mo/HZSM-5 catalysts at 813 K in flowing steam with 0.3 atm partial pressure balanced with Ar.

2.2. Catalyst characterization

The actual Mo content (wt%) and the bulk Si/Al ratio of each catalyst were measured using a Philips MagiX X-ray fluorescence spectrometer. The Mo/Si ratios in

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the near-surface region of all catalysts were determined by XPS measurements carried out in a modified Leybold LHS 12 MCD system. The number of Brönsted acid sites per unit cell in the parent *x*Mo/HZSM-5 and *x*Mo/HZSM-5(STAI-0.5h) catalysts were estimated from the corresponding ^{1}H MAS NMR spectra by comparing their peak areas of Brönsted acid sites with the corresponding peak areas of the parent HZSM-5 zeolite. The number of Brönsted acid sites per unit cell in the parent HZSM-5 zeolite was estimated from the chemical formula of the HZSM-5 zeolite and the Si/Al ratio that was calculated from the ^{29}Si MAS NMR spectrum. All the MAS NMR spectra were recorded on a Bruker DSX-300 spectrometer. ^{29}Si MAS NMR spectra were recorded at 59.6 MHz using a 2.5-μs (π/4) pulse, a 10-s recycle delay and 300 scans. ^{1}H MAS NMR spectra were recorded at 300.1 MHz using a 2.11-μs (π/3) pulse, a 10-s recycle delay and 100 scans. The samples spun at 4 kHz for recording ^{29}Si MAS NMR spectra and 14 kHz for ^{1}H MAS NMR spectra.

2.3. Catalyst evaluation

Reaction tests were carried out at atmospheric pressure and 973 K in a quartz tubular fixed-bed reactor. The effluent gas was regularly and automatically sampled and analyzed by a Varian 3800 on-line gas chromatograph using the same analysis method described elsewhere [8].

3. Results and discussion

3.1. XRF and XPS

The results of elemental analysis from XRF measurements are listed in table 1. The Mo contents in the *x*Mo/HZSM-5 and *x*Mo/HZSM-5(STAI-0.5h) catalysts are almost the same, regardless of post-steam treatment. This suggests that the post-steam treatment under the given conditions did not result in the loss of Mo content in the bulk of all tested catalysts. Coincidentally, the bulk atomic Si/Al ratios obtained by XRF measurements remained the same for the samples with the same nominal Mo loading. Therefore, it is clear that there were no changes in the chemical compositions of all *x*Mo/HZSM-5 catalysts after post-steam treatment for 0.5 h under the given experimental conditions.

The near-surface Mo/Si ratio of both the *x*Mo/HZSM-5 and *x*Mo/HZSM-5(STAI-0.5h) catalysts were studied using the XPS technique, and the results are listed in table 1. The near-surface Mo/Si ratios of 2Mo/HZSM-5 and 2Mo/HZSM-5(STAI-0.5h) catalysts are almost the same, and it appears that no variation could be detected with the low Mo loading catalysts. On the other hand, the near-surface Mo/Si ratios did decrease in catalysts with higher Mo loading after the post-steam treatment. It decreased from 0.21 to 0.17 for the 4Mo/HZSM-5 catalyst and from 0.27 to 0.15 for the 6Mo/HZSM-5 catalyst. The bulk Mo concentrations of *x*Mo/HZSM-5 catalysts did not change after being exposed to steam for 0.5 h at 813 K, as reflected in XRF measurements. The XPS results seem to suggest that a portion of the Mo species migrate into the channels of the HZSM-5 and reside there during the post-steam treatment of the higher Mo loading catalysts. It is much easier for the Mo species to migrate into the HZSM-5 channels in the presence of water vapor, and one possible explanation for this is the formation of $MoO_2(OH)_2$ through the reaction of MoO_3 crystallites with water vapor [9,10]. The $MoO_2(OH)_2$ species thus formed will further interact and exchange with protons of Brönsted acid sites in the channels. The Mo species in the zeolite channels are more active for the MDA reaction as demonstrated by Iglesia and his co-workers [11,12].

3.2. Multinuclear MAS NMR

Figure 1 shows the ^{1}H MAS NMR spectra of the *x*Mo/HZSM-5 and *x*Mo/HZSM-5(STAI-0.5h) samples. Several types of hydroxyl groups can be identified on each ^{1}H MAS NMR spectrum after the deconvolution of the corresponding spectrum according to Gaussian and Lorentzian line shapes. As far as the Brönsted acid sites are concerned, two types are distinguished. One consists of the free Brönsted acid sites (denoted as B1) in the channels at a peak of 3.9 ppm, and the other is the

Table 1
Properties of *x*Mo/HZSM-5 and *x*Mo/HZSM-5(STAI-0.5h) samples from XRF and XPS measurements

Sample	Mo loading (%)[a]	Mo/Si[b]	Si/Al ratio in bulk[a]
2Mo/HZSM-5	1.78	0.21	22.0
2Mo/HZSM-5(STAI-0.5h)	1.81	0.21	21.8
4Mo/HZSM-5	3.37	0.21	22.6
4Mo/HZSM-5(STAI-0.5h)	3.29	0.17	22.7
6Mo/HZSM-5	5.33	0.27	23.1
6Mo/HZSM-5(STAI-0.5h)	5.28	0.15	23.4

[a]Data determined by XRF measurement.[b]Data obtained from XPS measurement.

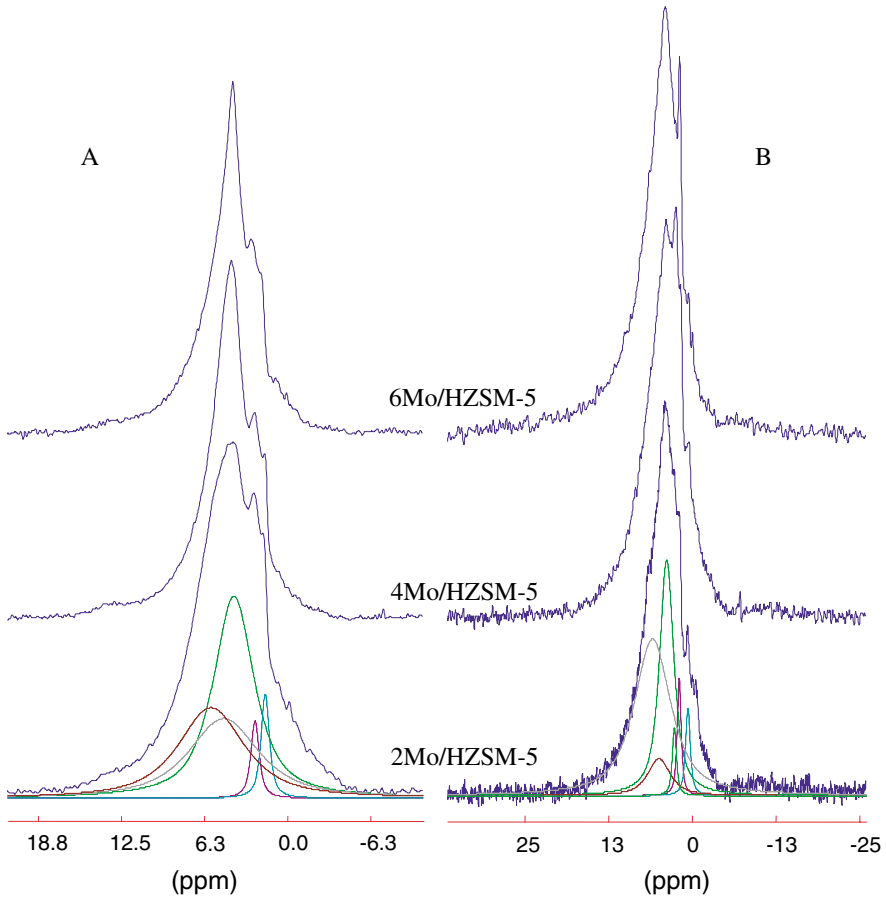

Figure 1. ^{1}H MAS NMR spectra of (a) *x*Mo/HZSM-5 and (b) *x*Mo/HZSM-5(STAI-0.5h) catalysts.

restricted Brönsted acid sites (denoted as B2) with a chemical shift of 5.9 ppm, which is influenced by an additional electrostatic interaction from the zeolite framework [13]. The quantitative results of the change in the number of Brönsted acid sites per unit cell are listed in table 2. Despite the fact that the framework Si/Al ratios did not significantly change, the number of B1 and B2 sites per unit cell in *x*Mo/HZSM-5 catalysts gradually decreased with increasing Mo loading, which further confirms that Mo species interacted with the Brönsted acid sites. However, they further decreased after the *x*Mo/HZSM-5 samples were treated with steam for half an hour under the given experimental conditions. At the same time, the Si/Al ratios in the framework calculated from the ^{29}Si MAS NMR spectra also revealed that a portion of the Al species in the framework were extracted after the steam treatment of the *x*Mo/HZSM-5 catalysts.

On combining the corresponding XRF and XPS measurements with the suppression of free Brönsted acid sites per unit cell on *x*Mo/HZSM-5(STAI-0.5h) and the increase in the framework Si/Al ratios (table 2), two changes are lucid compared to those of the untreated *x*Mo/HZSM-5 catalysts. One change involves more Mo species migrating into and residing in the channels and the other is the increase in the Si/Al ratio in the framework resulting from the extraction of the framework Al during the post-steam treatment.

3.3. Catalyst evaluation

The catalytic performance of the MDA reaction over *x*Mo/HZSM-5 and *x*Mo/HZSM-5(STAI-0.5h) catalysts versus time on stream was tested. Figure 2 shows the effect of the post-steaming treatment on the BTX yield over *x*Mo/HZSM-5 and *x*Mo/HZSM-5(STAI-0.5h) catalysts in the MDA reaction. Remarkable performance is apparent over the *x*Mo/HZSM-5(STAI-0.5h) catalyst, and the catalytic performance was greatly improved after the post-steaming treatment, as we can see from figure 2. The BTX yield increased by 68% after a 10-h reaction on the 2Mo/HZSM-5(STAI-0.5h) catalyst and by 28% on the 4Mo/HZSM-5(STAI-0.5h) catalyst relative to that of the corresponding untreated catalysts. Moreover, the BTX yield on the 6Mo/HZSM-5(STAI-0.5h) catalyst was twice as high as that on the 6Mo/HZSM-5 catalyst. These demonstrate that the post-steaming treatment of the *x*Mo/HZSM-5 catalyst for half an hour is very effective for improving its reaction activity for the MDA reaction over Mo/HZSM-5 catalysts.

Table 2
The number of different Brönsted acid sites per unit cell in each sample and the corresponding framework Si/Al ratios

Sample	Numbers of Brönsted acid sites per unit cell		Si/Al ratio[a]
	B1 (3.9 ppm)	B2 (5.9 ppm)	
HZSM-5	2.4	1.0	27.5
2Mo/HZSM-5	1.86	1.34	27.7
4Mo/HZSM-5	1.64	1.15	27.8
6Mo/HZSM-5	0.95	0.57	30.4
2Mo/HZSM-5(STAI-0.5h)	0.59	0.97	38
4Mo/HZSM-5(STAI-0.5h)	0.56	0.94	40.2
6Mo/HZSM-5(STAI-0.5h)	0.76	0.74	43.8

[a]The data are obtained by ^{29}Si MAS NMR measurements.

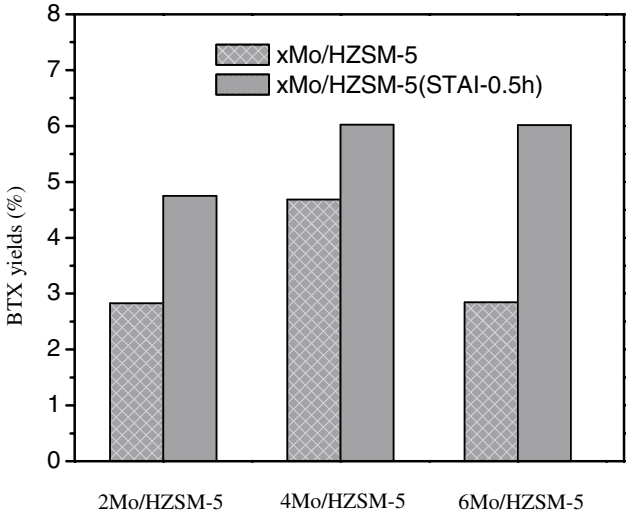

Figure 2. BTX yields of *x*Mo/HZSM-5 and *x*Mo/HZSM-5(STAI-0.5h) catalysts after 600 min on stream of the methane aromatization reaction. (BTX is the abbreviation of benzene, toluene and xylene).

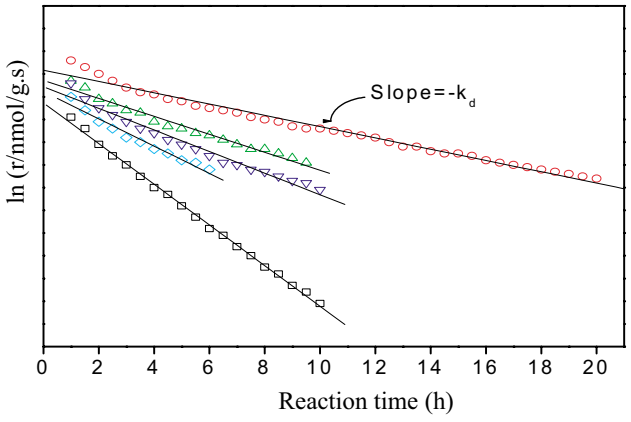

Figure 3. Profile of catalytic stability for (○ 6Mo/HZSM-5(STAI-0.5h), (△) 6Mo/HZSM-5(STAI-1h), (▽) 6Mo/HZSM-5(STAI-2h), (◇) 6Mo/HZSM-5(STAI-3h) and (□) 6Mo/HZSM-5 catalysts.

The effect of the post-steaming treatment time on the catalytic stability of the 6Mo/HZSM-5(STAI-*t*) catalyst was also investigated. Figure 3 shows the deactivation curve by plotting the natural logarithm of the formation rate of benzene versus the reaction time for 6Mo/HZSM-5 and 6Mo/HZSM-5(STAI-*t*) according to the approach of Levenspiel [14]. Here, we assume that the deactivation rate is independent of the reactant concentration. It is clear that the deactivation rate constants on the untreated 6Mo/HZSM-5 catalyst are much larger than those on the 6Mo/HZSM-5(STAI-*t*) samples. Moreover, the post-steaming time is also a crucial factor (the longer the post-steaming time, the larger the deactivation rate constant). This indicates that mild post-steam treatment can effectively improve the catalytic stability of 6Mo/HZSM-5, whereas severe post-steam treatment will not produce satisfactory catalytic performance. The excellent catalytic MDA reaction performance over the 6Mo/HZSM-5(STAI-0.5h) catalyst might be the result of the formation of a better bifunctional catalyst.

4. Conclusions

Post-steam treatment of *x*Mo/HZSM-5 catalysts did not cause a decline in the bulk of Mo contents or Al and Si contents in the HZSM-5 zeolite under the given experimental conditions. On the contrary, more Mo species migrate into the channels of the HZSM-5 zeolite after the post-steam treatment, particularly in the case of higher Mo loading, and this results in a decrease in the number of free Brönsted acid sites per unit cell. Excellent catalytic performance and a longer lifetime in the methane dehydro-aromatization reaction can be obtained with a remarkable enhancement in BTX yields after post-steaming treatment of *x*Mo/HZSM-5 catalysts. However, severe steam treatment, with longer steaming time, of the *x*Mo/HZSM-5 catalyst will diminish its catalytic stability compared to that of Mo/HZSM-5(STAI-0.5h).

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