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Catalysis Today 30 (1996) 189–192

CATALYSIS TODAY

Lewis acid sites on dehydroxylated zeolite HZSM-5 studied by NMR and EPR

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Abstract

Zeolite HZSM-5 calcined at different temperatures were studied by ^{29}Si MAS NMR and EPR methods. It is proposed that over a certain temperature range, dealumination did not necessarily occur simultaneously with framework dehydroxylation and thus framework Lewis acid sites may emerge. A two-step mechanism of dehydroxylation may be present, and it dominates the dehydroxylation and dealumination processes at different temperatures.

Keywords: Lewis acid sites; Dehydroxylation; Dealumination; Zeolite HZSM-5; NMR; EPR

1. Introduction

The existence, strength and numerical quantities of Bronsted (B) and Lewis (L) acid sites are of great concern in the studies of modified zeolites. It has been generally accepted that the B-acid sites are due to bridging hydroxyl groups connected with framework aluminum in zeolites, the strength of which is weakened by other Al atoms appearing in its next nearest neighbors. The acidity of faujusite-type zeolites were studied experimentally by Barthomeuf et al. in the 1970s. Recently, the acidity of dealuminated faujusite was discussed in terms of a Monte Carlo simulation [1]. While for the form of L-acid, different opinions were held.

In the early work of Uytterhoeven et al. [2], tri-coordinated framework aluminum formed by dehydroxylation in calcined zeolite NH_4Y was regarded to act as strong L-acid sites. Nevertheless, the existence of tri-coordinated aluminum was excluded by a follow-up X-ray luminescence study by Kühl [3]. Jacobs and Beyer proposed that the Al-O species on extra-lattice positions were L-acid sites instead [4]. Freude et al. concluded further from detailed NMR studies that: (i) tri-coordinated lattice aluminum did not appear during the dehydroxylation process of zeolite HY and (ii) the dehydroxylation in the neighborhood of a lattice Al atoms was always accompanied by its release from the framework [5]. Non-framework Al has been proved to act as L-acid sites in USY and modified HM [6]. However, an investigation of X-ray photoelec-

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PII S0920-5861(96)00011-9

tron spectroscopy recently showed the presence of surface tri-coordinated Al species in dealuminated mordenites and indicated that the tri-coordinated Al species might reasonably be considered as belonging to the zeolite lattice [7].

EPR spectroscopy has been used to scale the strength of L-acid [8]. The electron-acceptor properties of zeolite has been demonstrated by the formation of organic cation radicals [9]. Chen et al. reported that the non-framework Al in zeolite HY and HM may be the electron-accepting sites by aniline and molecular oxygen adsorption [10], though the nature of the electron-accepting sites is still a subject of debate [11]. It is obvious that the existing form of L-acid has drawn a great deal of attention in the zeolite research field. In the present work, the dehydroxylation and dealumination in zeolite HZSM-5 samples calcined under different temperatures are studied by NMR and EPR observations. The study is aimed at examining whether the dehydroxylation process occurs simultaneously with the dealuminated process in high silicious zeolites such as ZSM-5. The experimentally obtained conclusions might touch upon the argument originated from the dehydroxylation of zeolite HY.

2. Experimental

Zeolite NaZSM-5 was synthesized without template and was exchanged to HZSM-5 by washing with 0.3 N HNO_3 solution at 90°C repeatedly. The Si/Al ratio by chemical analysis is 13.4. The HZSM-5 sample was calcined in a muffle furnace. The temperature was increased with a rate of 10°C/min up to the set temperature and kept for 2 h. The set temperatures were 550, 600, 650 or 700°C.NMR experiments were performed on Varian UNITY plus 400 spectrometer. For ^{29}Si MAS NMR, all the samples were hydrated in air for several days. The pulse width was 3.0 μs, the delay time was 5 s and the chemical shift was referenced to TMS. ^{27}Al MAS NMR was used to check the non-framework Al in parent HZSM-5 with a pulse width of 0.5 μs, a delay time of 0.5 s and the chemical shift was referenced to 0.1 M $Al(NO_3)_3$ solution. The spinning rate was 8 kHz.

Calcined HZSM-5 samples were loaded in EPR sample tubes, evacuated at 10^{-4} torr, 400°C for 6 h and cooled to room temperature. Then the adsorption of benzene was carried out at room temperature at the equilibrium vapor pressure for 12 h and then the tubes were sealed with a flame. After the pretreatment, the EPR observation of the samples was done with a JEOL FE-1XG spectrometer.

3. Results and discussion

3.1. Dealumination by calcination

The ^{29}Si MAS NMR spectra of HZSM-5 samples calcined at different temperatures are shown in Fig. 1. The peak at −112 ppm and a shoulder at −115 ppm are assigned to the signal of Si(0Al), and the shoulder at −107 ppm is the signal of Si(1Al). The framework Si/Al ratio and the extent of dealumination for

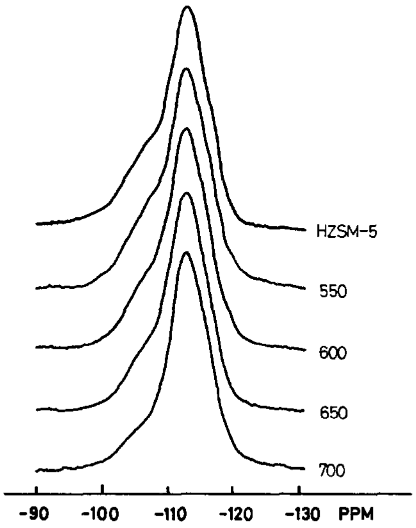


Fig. 1. ^{29}Si MAS NMR spectra of the samples, the figures are the calcination temperatures.

Table 1
Content of non-framework Al after calcination

Sample	HZSM-5	550	600	650	700
Si/Al_{NMR}	13.5	13.8	14.1	14.4	17.9
NFA[a] (%)	< 1	3.6	4.4	6.3	24.6

[a] Non-framework Al.

each sample can easily be determined. Since the parent HZSM-5 contained merely trifling non-framework Al, the non-framework Al in a calcined sample can then be quantified by its dealumination extent. The total Al content in the parent sample gives the measure of the non-framework Al (in percentage), which is calcination temperature dependent. The calculated measures of non-framework Al of calcined samples are listed in Table 1 and illustrated in Fig. 3 for their temperature dependence. It can be seen that the quantity of non-framework Al increases dramatically only after 650°C and up to 25% of the total Al content.

3.2. Generation of L-acid

The EPR signal of the calcined HZSM-5 samples after pretreatment exhibits hyperfine structure due to benzene monomeric and dimeric radicals [10,12] (see Fig. 2, for example). The relative quantity of L-acid sites in a calcined sample can be described by the relative intensity of its EPR signal, which is scaled by a Mn standard with a normalized mass of 50 mg samples. The parent sample shows weak EPR signal as well, which might be due to the fact that when the parent sample was evacuated at 400°C, some dehydroxylation or dealumination may have taken place. During calcination, the sample is dehydroxylated, which transforms some of B-acids into L-acids (whether on framework of zeolite or not) in some way. Therefore, it is expected that the EPR signal increases with the calcination temperature.

Fig. 2. EPR signal of calcined HZSM-5 after benzene adsorption.

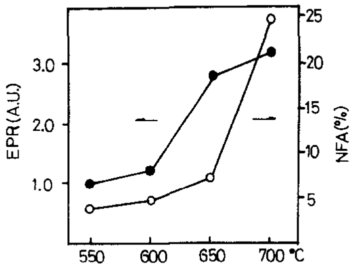


Fig. 3. Correspondence of EPR signals and non-framework Al formed by calcination.

3.3. L-acid sites and non-framework Al

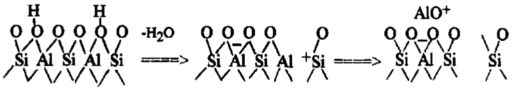
The measure of L-acid sites (monitored by EPR signal intensity) and that of non-framework Al (determined from ^{29}Si MAS NMR) increase with calcination temperature are shown in Fig. 3. Though both the temperature dependences show increasing trends, it is interesting to note their departure.

It was found that only after 650°C, a steep increase of non-framework Al takes place so there are no corresponding increase in non-framework Al to explain the significant generation of L-acid sites in the calcination temperature range of 600–650°C. Whereas in the temperature range 650–700°C, the fact that a large amount of Al atoms are released from the framework does not cause a sharp increase of L-acid sites.

It should be noticed that whether the change of the EPR signal intensities is due to different benzene accessibility to the samples caused by some structure change after dealumination. The Si/Al ratio of the parent HZSM-5 is 13.5, that is to say Al atoms occupy ca. 7% of the total tetrahedral atoms (Si and Al) of the sample.

Concerning the extent of dealumination (4.4% at 600°C, 6.3% at 650°C), the non-framework Al occupy only 0.31% or 0.44% of all the Si and Al atoms, and this may cause neither great change of the channels and openings of the sample nor obvious difference of the structure of channels and openings between the samples calcined at 600°C and 650°C. Thus it may be concluded that destruction by dealumination is not a main factor for the change of EPR signal intensities.

3.4. *Two-step model of dehydroxylation and formation of L-acid in HZSM-5*



(I)

A two-step model (I) for the dehydroxylation of bridging OH groups was discussed by Kühl in 1977 [3]. In the first step of the model, tri-coordinated atoms of Al and(or) positively-charged Si are formed. Recently, the tri-coordinated sites (Si) of the zeolite framework was discussed by Hunger [13] and Freude [14] again, and they concluded that there were tri-coordinated positively-charged Si in calcined HY, though the content might be very small. According to the model, dehydroxylation takes place in the first step and dealumination takes place afterwards. In the present study, we assume that:

(i) After the first step, the system ends up in a metastable state.

(ii) The mestable state tends to be transferred to a more stable state through the second step, which needs the condition: the tri-coordinated Al can be released from the framework easily due to the existence of next nearest neighbor Al atoms which makes the Al atoms less stable. In highly silicious zeolite, such as ZSM-5 (here the Si/Al ratio of the parent sample is 13.4), because of its low Al content (here the Si/Al ratio is higher than 13), nearly all the B-acid sites are isolated. Therefore, in ZSM-5, a much worse condition (in comparing with zeolite HY for instance) for the second step is expected. In the mestable state of zeolite HZSM-5, the tri-coordinated Al is generated by dehydroxylation and possesses the condition to be able to remain in the framework, so the existence of tri-coordinated framework Al might be one of the reason for the presence of L-acid.

4. Conclusion

Based on the results mentioned above, the dehydroxylation and dealumination processes in zeolite HZSM-5 might be explained by a two-step model. The first step is dominated by the dehydroxylation process taking place between 600–650°C. In this step tri-coordinated Al forms which are L-acid sites and accounts for the sudden increase in the EPR signal while the non-framework Al content increases only a little. The dealumination process occurs mainly in the second step, at around 650°C or higher.

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