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Surface *P* and Al Distribution in *P*-modified ZSM-5 Zeolites*

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Abstract. The surface composition of two commercial ZSM-5 zeolites with and without PO_4 modification was examined by X-ray photoelectron spectroscopy. Both zeolites were slightly enriched in aluminum on the surface. The surface silica/alumina ratio (SAR) was about half of that of the bulk. Calcination at 600°C decreased slightly this enrichment. After drying with H_3PO_4 followed by calcination, both zeolites showed surface enrichment of PO_4. The surface of the zeolite with large crystal was more enriched. Steaming resulted in enrichment of aluminum on the surface, in agreement with migration of extra-framework alumina. Increasing phosphate content decreased this enrichment.

Keywords: synthesis techniques, characterization of structure, properties, measurement methods

Introduction

The distribution of framework-aluminum in ZSM-5 has long been recognized to be important to determine its selectivity in catalytic reactions (Barthomeuf, 1980; Wei, 1982; Olson and Haag, 1984). This distribution was sensitive to the synthesis mechanism. Hence depending on the synthesis routes, particles with silicon rich, aluminum rich or homogenous surface can be obtained (Hughes, 1983). Moreover, during subsequent modification, this surface silica-alumina ratio could be altered. For example, by controlling the steaming conditions, different degrees of enrichment of non-framework aluminum on the surface were observed (Zhang et al., 1998). On the other hand, the introduction of phosphate to ZSM-5 is a common technique to modify their activity and selectivity (Butter and Kaeding; Kaeding, 1981a; Kaeding, 1981b; Kaeding, 1982). Vedrine et al. (1982) showed that the phosphorous species were concentrated at the pore mouths on the external surface of the crystals. On the other hand, other workers showed homogenous distribution into the crystal channels (Kaeding, 1980; Vinek, 1989). Hence, in general, a distribution of PO_4 species, depending on the zeolite and the preparation conditions is expected (Caro, 1980).

The presence of phosphate in ZSM-5 during steaming lead to stabilization of the zeolite towards dealumination and retained a larger number of active Brönsted acid sites (Degnan et al., 2000). The high temperature treatments generate non-framework alumina and various $AlPO_4$ phases, and may further cause a redistribution of phosphate species themselves. Hence, the surface composition of *P*-modified zeolite can give clues to zeolite quality as well as stabilization mechanism. In this work we examine two commercial zeolites with similar overall silica to alumina ratio, but different crystal sizes, with the objective to obtain information about how the PO_4 was distributed as a function of typical heat treatments and also as a function of the zeolite crystal sizes difference. Chemical information about $AlPO_4$ phase will also be inferred.

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Experimental

Samples

Two commercial zeolites, one with average particle size of 3 μm (TC3,0) and other with average particle size of 0,3 μm (TC0,3) were examined as received or subjected to treatments described further in the text. Phosphate was introduced onto the solid by mixing a suspension of zeolite with the desired amount H_3PO_4, dried overnight, and then followed by calcinations at 600°C for 1 h.

X-ray Photoelectron Spectroscopy

The XPS data were obtained with a VG Escalab MkII spectrometer with a non-monochromatic Al kα X-ray source (Al $k\alpha_{1,2} = 1486{,}6$ eV). Surface composition, alumina enrichment, NFA gradients and variations of binding energies (BE ± 0,2 eV) of the Si2s, P2p, Al2p, O1s and C1s peaks of samples were not subjected to any treatment prior to analysis. The zeolites were pressed into self-supported wafers with 10 mm diameter size and introduced in the pre-chamber of the spectrometer. The solids were out-gassed overnight at 1×10^{-7} mbar vacuum and room temperature. The residual pressure inside the analysis chamber was better than 1×10^{-9} mbar. The angle between the surface normal and the analyzer lens was 15°. The pass energy was set at 50 eV. In these conditions, the resolution determined by the full width at half-maximum (FWHM) of the Ag3$d_{5/2}$ peak of a standard silver sample was 1.7 eV.

The atomic concentrations were calculated using peak areas that were normalized on acquisition parameters and sensitivity factors as the mean free path varies according to the $KE^{1/2}$ and the transmission function varyies according to the $KE^{-1/2}$. Because the mean free path of the photoelectrons is in order of 0.5–1.5 nm, under the experimental conditions used, the results obtained corresponded to the uppermost atomic layers of the surface ranging in order of 2–6 nm. The surface excess of aluminum is estimated with the hypothesis that the Si did not present any concentration gradient. Yet we consider that the samples as received already contain non-framework alumina, as shown by Al MAS-NMR. Hence:

$$\mathrm{Al\,s_{excess}} = \mathrm{Al\,s_{XPS}} - \mathrm{Al\,b} = (\mathrm{Al_F} + \mathrm{Al_{NFA}})\mathrm{s} - (\mathrm{Al_F} + \mathrm{Al_{NFA}})\mathrm{b} \qquad (1)$$

Assuming there is no gradient in the framework aluminum:

$$\mathrm{Al\,s_{excess}} = \mathrm{Al_{NFA}s} - \mathrm{Al_{NFA}b} \qquad (2)$$

Where s and b denote the surface and the bulk; F denotes the framework aluminum and $_{\mathrm{NFA}}$ the rest of aluminum species, including especially all $AlPO_4$ phases. This surface excess gives information of the migration of non-framework species. For chemical analysis of the surface composition the C1s peak of the residual carbon contamination (C—C, C—H) was used as internal reference by adjusting its binding energy to 284.5 eV.

TPD n-Propylamine

A method based on *n*-propilamine decomposition has been developed for measuring the Brönsted-acid site densities using a tubular reactor with an on-line gas chromatograph (GC) (Kresnawahjuesa et al., 2002). After exposing a sample to *n*-propylamine vapor and flushing it in flowing He at 473 K, the sample was ramped in flowing He to 773 K while trapping the products in the GC sample loop using liquid nitrogen. Site densities were determined from the quantity of propene formed by the decomposition of the *n*-propylammonium ions via the Hofmann-elimination reaction.

Results and Discussion

Samples as Received or After Calcination

The results of the analysis of the samples as received or calcined were shown in Table 1, and Table 2.

For samples without phosphate modification, one could observe that both samples as received had a

Table 1. Results on samples as received or only after calcinations.

			Surface concentration			
Code	P_2O_5 (%)	Treatments (Temp °C, time h)	SAR_S	% P_2O_{5S}	Al s_{excess}	Al b
TC0,3	0	As received	18.1	–	1.2	2.2
TC0,3C0	0	Cal (600,1)	20.2	–	1.0	2.1
TC0,3C2	2	Cal (600,1)	22.5	4.2	0.7	2.1
TC3,0	0	As received	14.0	–	2.3	2.3
TC3,0C0	0	Cal (600,1)	20.0	–	0.7	2.4
TC3,0C2	2	Cal (600,1)	17.0	6.7	1.3	2.4

Table 2. Binding energies of elements studied.

Code	P_2O_5 (%)	Treatments (Temp C, time h)	Binding Energies of elements			
			O1s	Si2s	Al2p	P2p
TC0,3	0	As received	531,7	153,5	73,7	
TC0,3C0	0	Cal (600, 1)	531,9	153,8	74,4	
TC0,3C2	2	Cal (600,1)	532,0	153,9	74,6	134,6
TC3,0	0	As recieved	531,7	153,6	73,8	
TC3,0C0	0	Cal (600, 1)	532,0	153,8	74,4	
TC3,0C2	2	Cal (600,1)	532,2	154,0	74,8	134,6

surface already enriched in aluminum. However, both showed similar surface enrichments and, upon calcination, the surface is slightly less enriched as if some aluminum enters the bulk of the crystal.

The similarity in surface composition between the two commercial samples may be a co-incidence since they were manufactured by two different technologies. The enrichments were understandable as these samples had probably been subjected to ammonium exchange followed by calcinations to remove ammonia. The calcination could result in dealumination and consequently generation of non-framework alumina, which migrated towards the external surface of the crystals. As mentioned before, 27 Al MAS-NMR indicated the presence of non-framework alumina in both samples. For the sample modified by phosphate, we observed that phosphorous species were enriched on the surface as expected. The larger crystals sample was more enriched than the other one. The phosphate modification did not affect the aluminum distribution significantly. The phosphorous surface enrichment was expected from numerous literature reports and indirect experimental evidence (Kaeding, 1981).

Also noteworthy was that the aluminum distribution seemed to be little affected by P-modification. As we observed by NMR, about 30% of Al was present in the form of $AlPO_4$ species. This small variation in Al distribution indicated the phosphate species did not remain only on the external surface of the crystal but found the aluminum species throughout the crystal and formed the $AlPO_4$ species. After *P*-modification we observed that there was no preferential population $AlPO_4$ species on the surface of the samples.

Effect of Steaming

Data for the samples after steaming were shown in Table 3. One could observe that steaming caused surface enrichment in aluminum as compared to a SAR_S on the order of 20 for the calcined samples and a surface excess of Al less than 2. This enrichment decreased when the amount of phosphate species increased. In fact, 2% P_2O_5 addition did not caused much observable effect.

The amount of surface P_2O_5 increased as the total P content of the sample was increased. The surface enrichment of P in terms of the difference between the surface and that of the bulk % $P_2O_{5(S-B)}$ was almost constant, in the range of 5%, as if after the surface accumulate certain amount of phosphate species, the additional amount was forced to go into the interior of the crystal. Hence, the concentration of *P* on the surface relative to the total amount, as shown by the last column P_s/P_{total}, showed a decrease instead of an increase as a function of % P_2O_5.

The decrease in enrichment of Al as a function of *P* loading gave further support for the role of the POx species during steaming. Either these species is retarding the process of dealumination itself or it is retarding the migration of the extra-framework aluminum formed during dealumination.

Figure 1 shows the variation of the surface excess of aluminum and that of the number of acid sites determined by the measurement of amount of ammonia from TPD of *n*-propyl-amine as a function of phosphorus content in the same set of zeolites.

Table 3. Surface composition for samples after 5 h steaming at 800°C.

Code	% P_2O_5	SAR_S	Al s_{excess}	% $P_2O_{5\,S}$	% $P_2O_{5\,(S-B)}$	P_s/P_{total}
TC0,3S0	0	7.5	5.9	–	–	–
TC0,3S2	2	7.1	5.8	7.6	5.6	3.7
TC0,3S5	5	9.5	4.1	10.2	5.2	2.0
TC0,3S8	8	13.9	2.2	13.0	5.0	1.6
TC3,0S0	0	7.9	5.3	–	–	–
TC3,0S2	2	7.5	5.3	7.6	5.6	3.4

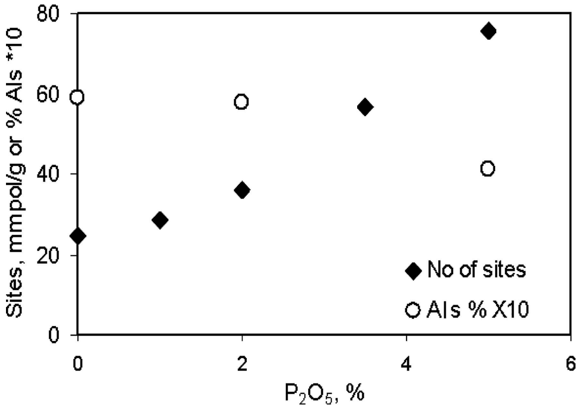

Figure 1. Variation of active sites and surface excess of Al as a function of *P* loading.

One could observe that the number of active sites increased, yet the surface excess decreased. If we used the acid sites as a measure of the degree of dealumination, then the increased amount of acid sites after steaming showed the effect of retarding dealumination in general.

Conclusions

The enrichment of PO_x and Al species as a function of calcination and steaming observed by XPS indicate two important aspects to be included in the model of phosphate stabilization of ZSM-5: The introduction of phosphate did not lead to change of distribution of Al, indicating that the phosphate species penetrate the crystal and find the aluminum species for association. The reduction of surface enrichment of aluminum suggests the inhibition of de-alumination by the phosphate, as reported in the literature. Further, the phosphate retard the migration of the extra-framework species generated. Other experiments are being carried out to separate the importance of the two effects.

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