

Strongly and Weakly Attached Phosphorous Species to PZSM-5 Zeolites Characterized by Solid-State ^{31}P and ^{27}Al NMR

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Abstract: While the role of stabilization of active centers of ZSM-5 by phosphorous compounds has been quite established from catalytic measurements, the interaction of P with zeolites is not explained by the characteristics of the species formed. Probably, this is due to high dispersion and multiple P-Al phases on the zeolite. This work presents a detailed characterization of the phosphorous and aluminum species of a 5% P_2O_5 ZSM-5, after typical treatments using ^{31}P and ^{27}Al solid-state NMR. ^{27}Al 3QMAS experiments were used to assign the aluminum species. In order to make the species chemically interacting with the zeolite, a washing step was introduced to remove the excess P species not strongly held on the sample. ^{31}P spectra show that Q^0 (0ppm) and Q^1 (-6ppm) phosphorous species are removed from the calcined zeolite when washed with hot water. Similar spectra were then assigned to steamed samples for which strongly held species were expected. ^{27}Al spectra show that a distorted tetrahedral aluminum species ($\text{Al}_{\text{tet-dis}}$) (30-50ppm) has an important contribution in the calcined, steamed and even washed samples. Thus, Q^0 and Q^1 phosphorous species have little relevance to this $\text{Al}_{\text{tet-dis}}$ species. On further calcination of the washed samples, the phosphorous species absorbing from -17 to -20ppm in the ^{31}P spectra slightly decreased, whereas the $\text{Al}_{\text{tet-dis}}$ species further increased. This P species appears to have a major role in the stabilization of the zeolite, forming $\text{Al}_{\text{tet-dis}}$ species rather than condensed extra-framework alumina, upon severe steam treatment.

While the role of stabilization of acid sites or active centers of ZSM-5 by P compounds has been quite established from numerous catalytic measurements, the interaction of P with zeolites leading to this phenomena remains obscure¹. One of the obstacles for the modeling of this interaction is the lack of structural information of P-Al species on the zeolite.

To improve the understanding of P and Al species formed on the surface of a 5% P_2O_5 activated ZSM-5 zeolite, a sample was

submitted to different treatments (Figure 1), followed by ^{31}P and ^{27}Al MAS NMR and ^{27}Al 3QMAS experiments.

All samples showed to have high crystallinity and were calcined after being washed to guarantee the same hydration condition of their precursors. ^{31}P and ^{27}Al MAS and ^{27}Al 3QMAS spectra were obtained at ambient temperature on a Varian/Chemagnetics Infinity-400 NMR 9.4T spectrometer operating at 161.9 MHz for ^{31}P and 104.2 MHz for ^{27}Al . For ^{31}P MAS experiments, a single pulse

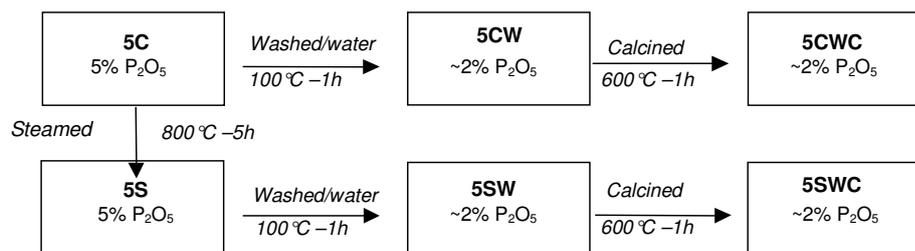


Figure 1. Treatment scheme of the 5% P₂O₅ activated ZSM-5 sample
C = calcined; S = steamed; W = washed

excitation (1.0 μ s) with ¹H decoupling, a 30s pulse interval, and 1000-2000 transients were accumulated. ²⁷Al MAS used $\pi/20$ pulses, 1s recycled delay and 6000 transients. ²⁷Al 3QMAS spectra were acquired using a Z-filtered-FAM-I pulse sequence, with pulse lengths of 2.0, 0.7 and 7.0 μ s, RF field amplitudes of 170kHz (hard pulses) and 12kHz (soft pulses) and 24000 transients.

The samples were packed in a 3.2mm zirconia rotor with spinning speed at MAS of 20kHz. The spectra were referenced to an 85% H₃PO₄ sample (0ppm) for ³¹P and to a solution of 1M aluminum nitrate (0ppm) for the ²⁷Al MAS and 3QMAS spectra.

³¹P NMR spectra (Figure 2) show that the Q⁰ (PO₄³⁻ at 0ppm) and Q¹(polyphosphate terminal groups at -6ppm) phosphorous species are absent from the calcined zeolite (5C) when washed with hot water (5CWC). Similar spectra of steamed samples were observed, for which strongly attached species (AlPO_x at -25 to -45 ppm) were expected (5CW x 5S). ²⁷Al spectra (Figure 3) show that a distorted tetrahedral aluminum species (Al_{tet-dis}) (broad peak at 30-50ppm) has an important influence on the calcined, steamed and even washed samples. Therefore, the Q⁰ and Q¹ phosphorous species have little relevance to this Al_{tet-dis} species.

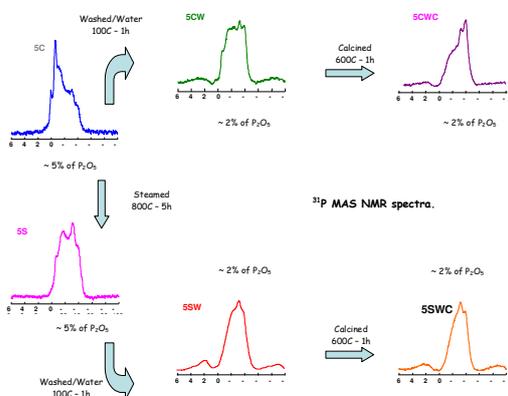


Figure 2. ³¹P MAS NMR spectra of treated samples

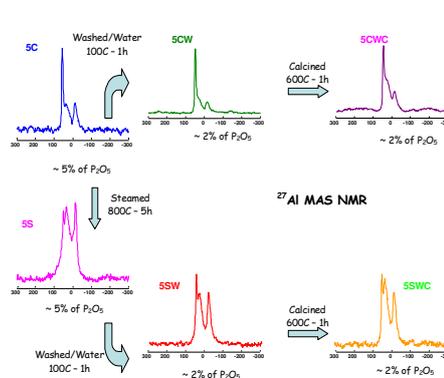


Figure 3. ²⁷Al MAS NMR spectra of treated samples

Peak	δ_{iso}	Cq	η	Relative Intensities
Al _{tet-F} (1)	55.2± 2	3.4± 2	0.0	16± 5
Al _{tet-dis} (2)	49.2± 2	7.8± 2	0.5	48± 10
AlPO _x (3)	-5.9± 1	4.6± 1	0.0	36± 5

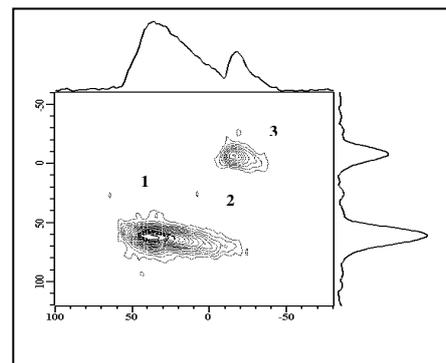


Figure 4. ²⁷Al 3QMAS spectrum and data of sample 5S

The assignment of ²⁷Al spectra was possible with the of 3QMAS experiment shown here only for the 5S sample (Figure 4). On further calcination of the washed samples, the phosphorous species absorbing from -17 to -20 ppm in the ³¹P spectra slightly decreased whereas the Al_{tet-dis} species further increased (5C x 5CWC and 5S x 5SWC).

This P species appears to play another role in the stabilization of the zeolite, forming Al_{tet-dis}

species rather than condensed extra-framework alumina (at ~0ppm), upon severe steam treatment.

Reference

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