A Combined Spectroscopic Characterization of P-modified ZSM-5 catalyst

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Abstract: P-modification to ZSM-5 catalysts increases the hydrothermal stability which is important in catalytic naphtha cracking process. Despite extensive studies, the exact nature of the interaction between P and ZSM-5 has not been fully understood. Here we present a combined spectroscopy results by solid-state NMR and UV Raman spectroscopy, and synchrotron small angle X-ray scattering.

Keywords: P-ZSM-5, NMR, UV Raman, SAXS.

1. Introduction

ZSM-5 has been widely used in the petroleum industry as a heterogeneous catalyst. P-modified ZSM-5 shows higher activity and selectivity than ZSM-5 in many catalytic reactions. Phosphorous acts as a promoter in the methanol-to-hydrocarbon reaction. P-modification also improves the hydrothermal stability of ZSM-5, which is significant in naphtha cracking process to produce light olefins such as propylene. Many structural models of ZSM-5 interacting with P have long been proposed. However, the exact nature of the interaction has not yet been known.[1] A combined spectroscopy provides more comprehensive information than a single spectroscopy does. Here we present an example of a combined scattering and spectroscopic investigation, including small angle X-ray scattering, solid-state NMR and UV Raman spectroscopy, which provides complementary information at the nano, atomic, and molecular scales.

2. Experimental

P-modified ZSM-5 (P-ZSM5) catalysts were prepared by incipient wetness impregnation using HZSM-5 and H_3PO_4 solution. H_3PO_4-added HZSM-5 were dried at 100°C overnight and calcined at 550°C for 6 hours. The naphtha cracking activity of the P-modified ZSM-5 was evaluated in a fixed-bed reactor before and after steaming at 800°C for 24 h in 100 % steam.[2]

Solid-state MAS NMR experiments were performed on a Bruker Avance III HD spectrometer with a MAS 2.5-3.2 mm probe, operating at 10-20 kHz spinning speeds. ^{27}Al, ^{29}Si, ^{31}P MAS NMR spectra were referenced to 1M $Al(NO_3)_3$, TMS, 1M H_3PO_4, respectively at 0 ppm. UV excitation wavelengths for UV Raman measurements were provided by third- or fourth-harmonic generation output of a 4 kHz repetition rate, nanosecond pulsed, wavelength-tunable Ti:Sapphire laser. The scattered light from the sample was refocused by using a home-made 90° off-axis ellipsoidal reflector with the backscattering geometry to a triple-grating spectrometer where Rayleigh light is filtered out and stray light is significantly suppressed.[3] UV Raman light was collected by a liquid N_2-cooled UV-enhanced CCD detector. Small Angle X-ray Scattering (SAXS) measurements[4] were performed at the 12-ID-B high-flux undulator beamline at the Advanced Photon Source in Argonne national laboratory. The incident X-ray beam energy was tuned to be 14.0 keV (0.8856 Å) and focused onto the sample. The scattering angle 2θ was converted into the magnitude of the scattering vector, $q= 2\pi/d =4\pi \sin\theta/\lambda$ where d is Bragg spacing, λ is wavelength, and 2θ is scattering angle.

3. Results and discussion

Fig. 1 compares ^{27}Al-NMR spectra for ZSM-5 (‘Z’), steam-treated Z (‘ZS’), P-ZSM5 (‘ZP’), steam-treated P-ZSM5 (‘ZPS’) catalysts. The peaks at 53 ppm and -1.1 ppm appear in ‘’Z’ spectrum and are due to tetrahedrally coordinated framework Al and octahedrally coordinated framework Al species with three Si-O (i.e., Al-O-Si) bonds and three Al-(OH_2) bonds, respectively.[5] In contrast, the spectrum of ‘ZS’ does not show any notable ^{27}Al peak, suggesting the formation of 3-coordinate Al, which is ^{27}Al-NMR silent due to strong quadrupolar interactions of the low-symmetry site. A ^{29}Si-NMR and UV Raman spectroscopic comparison of ‘Z’ and ‘ZS’ indicates a slight elongation of Si-Si distance (in Si-O-Si bonds) and almost complete removal of Al atoms from the zeolite framework (i.e., dealumination) after the steam treatment. A SAXS comparison suggests a significant increase in external surface area of ZSM-5 particles and the formation of small nanoparticles, consistent with the results of N_2 adsorption measurements and TEM images.

The effect of P modification is also shown in Fig. 1 (^{27}Al-NMR only). Intensity-normalized ^{29}Si-, ^{27}Al-, ^{31}P-NMR spectroscopic comparison of ‘Z’ and ‘ZP’ shows a slight elongation of Si-Si distance, a decrease of Brønsted acidity, and the formation of O_h-coordinated short-chain phosphates, highly likely at the zeolite external surface rather than in the pores of zeolites. However, P-induced elongation of Si-Si distance in Si-O-Si bonds and the decrease of Brønsted acidity suggests the presence of P in the zeolite pores, too. UV Raman spectra suggest a specific structure of phosphate, which coordinates to the external surface and the pores of ZSM-5. And, solid-state NMR, UV Raman, and SAXS comparison of ZS and ZPS will also be discussed in the presentation.

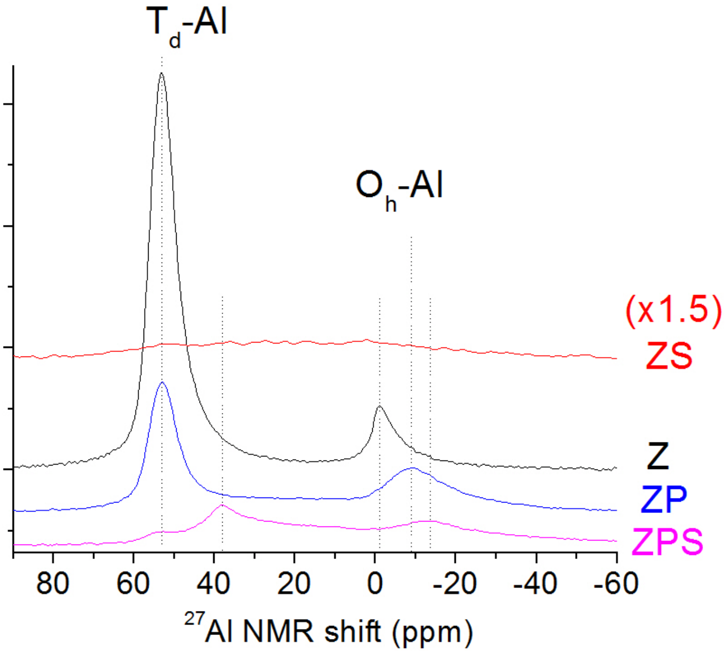

Figure 1. ^{27}Al-NMR spectra for ZSM-5 (‘Z’), steam-treated Z (‘ZS’), P-ZSM5 (‘ZP’), steam-treated P-ZSM5 (‘ZPS’) catalysts

4. Conclusions

Solid-state NMR, small angle X-ray scattering, and UV Raman spectroscopic investigation of P-ZSM5 provides useful, complementary information at the nano, atomic, and molecular scales. This work also shows the first UV Raman spectroscopic and SAXS measurements for P-ZSM5.

References

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