Multiple acidic sites in H-ZSM5 as revealed by solid state NMR spectroscopy-Insight from Framework Aluminum

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Abstract: Unambiguous characterization of the different acidic sites in zeolites is of fundamental importance in catalytic science. Here we provide a detail insight of the multiple acidic sites originated by the framework Al species in H-ZSM5 zeolite catalysts by our recently developed MAS NMR methods with quantitative trimethylphosphine oxide (TMPO) adsorptions. The existence of the framework aluminum Lewis acid sites have been demonstrated by sensitivity-enhanced two-dimensional (2D) ^{31}P-^{27}Al heternuclear correlation experiment, and the 2D ^{27}Al-^{27}Al homonuclear correlation experiment suggests close proximities between framework Brønsted and Lewis acid sites, which leads to the formation of super-acid sites in H-ZSM5 zeolite.

Keywords: H-ZSM-5, Solid state NMR, Acidic sites, Aluminum

1. Introduction

Heterogeneous catalysts with acid-base prosperities, such as zeolites have been widely used in petrochemical industry for cracking, hydrocracking, and isomerization reactions.[1-2] Brønsted and Lewis acid sites in aluminosilicates zeolites created by Al species play important role as active sites in heterogeneous catalysis. Therefore, understanding of the structures and properties of the acidic sites in zeolites is critical to explore the catalytic reaction mechanism and to optimize its catalytic performance.[3] It is well-known that the framework (FR) Al with tetrahedral coordination bridging hydroxyl (Si-OH-Al) in the viable H-forms of zeolites forms Brønsted acid sites. And the Lewis acids are generally recognized to extra-framework (ER) and even framework aluminum species, formed upon calcination or steaming of the zeolites. Solid-state NMR is a useful tool to study Brønsted and Lewis acid sites in catalytic materials, as it allows to provide unique insight into structural and dynamic properties of solids at atomic level. In this presentation, the nature of multiple acidic sites in dehydrated H-ZSM5 was carefully investigated by advanced solid-state NMR experiments coupled with TMPO probe molecules, and a detail insight of the multiple acidic sites arising from the framework Al species in H-ZSM5 zeolite catalysts was obtained.

2. Experimental

Untreated ZSM-5 with Si/Al=25 were purchased from Zeolyst International in the NH_4^+ form, and then, the sample was calcined at 773K under a dry air atmosphere for 10 h to remove the template and the H form of ZSM-5 was obtained, then the TMPO adsorbed sample was transferred into a ZrO_2 MAS rotor in the N2 glovebox prior to the solid-state NMR experiments. 2D sensitivity-enhanced ^{31}P {^{27}Al} PT-D-HMQC MAS NMR experiments[4] were performed on an 11.7 T Bruker AVANCE III spectrometer using commercial 7 mm outer diameter rotors with o-ring at the spinning frequency of 6 kHz. 2D ^{27}Al DQ correlation MAS NMR experiments were carried out on a 18.8 T Bruker AVANCE III spectrometer at a resonance frequency of 208.6 MHz with a 3.2 mm HXY triple-resonance MAS probe at a sample spinning rate of 20 kHz by using the $BR2_2^1$ pulse sequence. [5]

3. Results and discussion

Fig.1 displays the 2D ^{31}P {^{27}Al} D-PT-HMQC MAS NMR spectrum of dehydrated H-ZSM with a low quantitative adsorption of TMPO. The different ^{31}P signals corresponding distinct acidic sites/strengths caused by the framework ^{27}Al signals was clearly mapped. Two main types of correlations can be observed, one is the ^{31}P signal at 76 ppm interacting with the symmetric tetrahedrally coordinated aluminum (Al_a) from Brønsted acid sites at 55 ppm, and the others are the ^{31}P signals at 65 ppm and 68 ppm correlated with more distorted tetrahedrally coordinated aluminums, Al_b and Al_c, with ca. 7 MHz of quadrupolar coupling constance (QCCs), which can be resolved in 2D ^{27}Al 3QMAS spectrum (not shown). The latter correlations were assigned to TMPO adsorbed on Lewis acid sites, in which the distorted tetrahedrally coordinated aluminum sites formed through tri-coordinated framework Al species (QCCs > 20 MHz) [6] of dehydrated sample incorporated with the O atom of TMPO. Due to its low content, there was no correlation observed with respect to the ^{31}P signal at 88 ppm. Interestingly, this distinctive low-field ^{31}P signal at 88 ppm, usually defined as the fingerprint of super-acid sites, could disappear with the increase of adsorption quantity of TMPO or exposure of the sample to humidity. Fig. 2 shows the ^{27}Al DQ homonuclear correlation spectrum of TMPO adsorbed sample. It exhibits two auto-correlation peaks (along diagonal); the blue part indicates that tetra-coordinate FAL species (Al_a) are in close proximity to another one, and the orange part is auto-correlation peak from Al_b-Al_b with low intensity. The cross-correlation (in red) between Al_a and Al_b illustrates the close spatial proximity between Brønsted and Lewis acid sites, suggesting the possibility of Brønsted/Lewis acid synergic site in structure of H-ZSM5 zeolites.

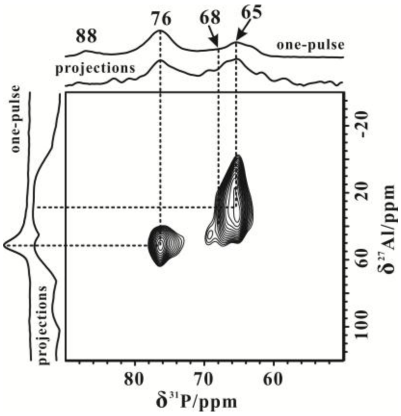


Figure 1. 2D ^{31}P {^{27}Al} D-HMQC MAS NMR spectra of ZSM-5 zeolite (Si/Al=25) recorded at 11.4 T with a low quantitative TMPO adsorbed.

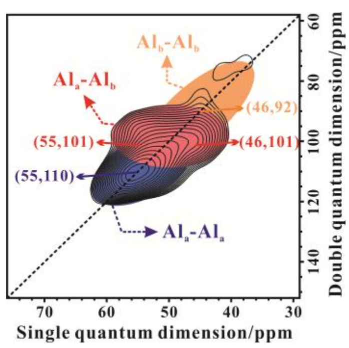
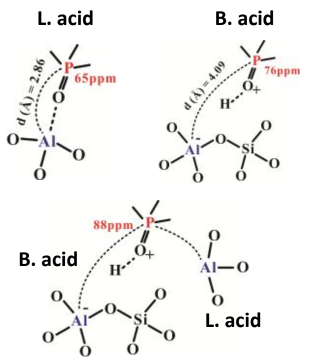


Figure 2. ^{27}Al DQ-SQ MAS NMR spectra of dehydrated and TMPO adsorbed sample



Scheme 1. Proposed three adsorption structure models of TMPO adsorbed H-ZSM-5 zeolites.

4. Conclusions

Our recently developed sensitivity-enhanced heteronuclear correlation MAS NMR methods allow us to obtain the first 2D map between the ^{31}P of adsorbed TMPO and ^{27}Al of the framework aluminum species in H-ZSM5 zeolites, which could unambiguously elucidate the type, strength, and concentration of different acidic sites originated by the framework Al species. In particular, the Lewis acids generated by the framework Al, i.e. tri-coordination aluminum, were revealed in this study. Moreover, the 2D ^{27}Al-^{27}Al double quantum (DQ) correlation experiments on TMPO-adsorbed H-ZSM-5 confirmed the spatial proximities between the Brønsted and Lewis acid sites, and thus the relative Brønsted acidic strengths was affected by the nearby Lewis acid sites, suggesting the existence of Brønsted/Lewis acid synergy in H-ZSM5 zeolites.

References

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