Unrevealing the synergic site in metal modified ZSM-5 zeolite by solid state NMR spectroscopy

Jun Xu, * **Guodong Qi, Qiang Wang, Pan Gao, Feng Deng***
National Centre for Magnetic Resonance in Wuhan, State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan, 430071, China
**Corresponding author: +86-27-87199291, E-mail: xujun@wipm.ac.cn; dengf@wipm.ac.cn*

Abstract: The outstanding catalytic performance of metal-supported catalysts is frequently ascribed to the synergic effect. We reported the direct detection of surface Zn species and $^{1}H/^{67}Zn$ internuclear interaction between Zn^{2+} ions and Brønsted acid sites on Zn-modified ZSM-5 zeolites by high-field solid-state NMR spectroscopy. The concentration of synergic active sites was determined by ^{1}H–^{67}Zn double-resonance solid-state NMR spectroscopy. The Lewis/Brønsted acid synergy in methanol-to-aromatics conversion on Ga-modified ZSM‑5 zeolites was explored as well.

Keywords: active sites; solid-state NMR spectroscopy; zeolites

1. Introduction

Synergetic catalysis causes catalytic enhancements in terms of both activity and selectivity in a broad range of catalytic reactions[1]. The introduction of metal species, such as Zn and Ga on acidic zeolite supports often leads to bifunctionality of modified zeolites on which the synergic effect was found as well. The synergic effect is supposed to originate from the interfacial interactions, but the structures of synergic active sites have remained elusive[2,3,4]. Moreover, the quantification of synergic active sites that is a prerequisite for comparison of the intrinsic activity between different catalysts in terms of turn-over frequencies still remains challenging. We recently investigated the synergic effect between Brønsted acid sites and zinc species on Zn- and Ga-modified ZSM-5 zeolites[5,6]. We provided solid-state NMR experimental evidence on the spatial proximity/interaction between the metal species and the Brønsted acid sites of zeolite. Quantification of the synergic active sites was achieved by double resonance solid-state NMR spectroscopy.

2. Experimental

Zn- and Ga- modified ZSM-5 samples were prepared by incipient wetness impregnation. Isotope enriched ^{67}Zn metal (89.6 %) was used as the zinc precursor. ^{67}Zn HS (hyperbolic secant)-QCPMG (Quadrupolar Carr–Purcell–Meiboom–Gill) and ^{1}H-{^{67}Zn} S-RESPDOR solid-state NMR experiments were carried out at 18.8 T on a Bruker Avance III 800 spectrometer, using a 4 mm HX low gamma probe at a spinning rate of 10 kHz. All the ^{71}Ga related NMR experiments were performed at 11.7 T on a Bruker Avance III 500 spectrometer.

3. Results and discussion

As shown in Figure 1, in addition to the ZnO clusters (238 ppm), Zn^{2+} ions were observed on ZSM-5(I2) and ZSM-5(I6) with different Zn loadings. The ^{1}H NMR shows that most of the Brønsted acidic protons of ZSM-5 have been replaced by the introduced Zn^{2+} ions. In the difference spectra of the ^{1}H-{^{67}Zn} SRESPDOR solid-state NMR experiments (Figure 2), the ^{1}H signals from SiOHAl (at 4.3 ppm), SiOH (at 2.3 ppm), and ZnOH (at 1.2 ppm) are all observable, due to direct dipolar interactions between the protons and Zn species. The ^{1}H-{^{67}Zn} S-RESPDOR signals build up curves indicate that the three hydroxy groups experience different degrees of dipolar interactions with Zn atoms. The proximate Zn^{2+} and acidic protons shows synergic effect in promoting the activation C-H bond of methane by reducing the activation energy.

We further quantified the synergic site by the double resonance NMR method, which is calculated to be 3.8–4.4 and 3.9–4.5 μmolg^{-1} for ZSM-5(I2) and ZSM-5(I6) respectively. The Brønsted/Lewis acid synergy in methanol-to-aromatics conversion on Ga-Modified ZSM-5 zeolites was explored by the ^{1}H–^{71}Ga double-resonance NMR and ^{1}H-^{1}H single- quantum-double-quantum magic angle spinning (SQ-DQMAS) NMR spectra. The synergic effect generated by the spatial interaction/proximity between acidic proton and GaO$^+$ species brings about an enhanced Brønsted acidity.

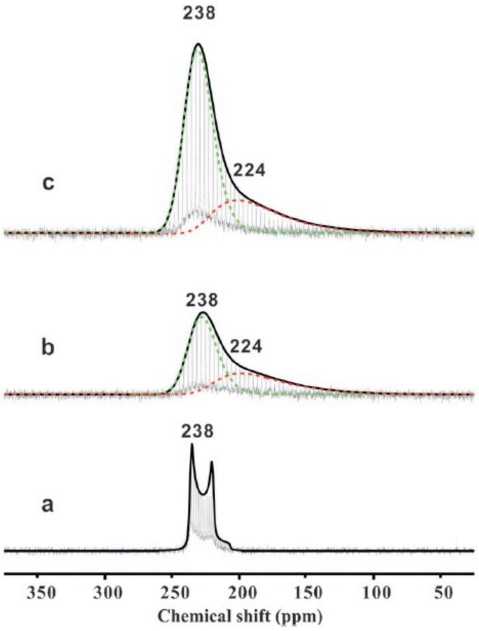

Figure 1. ^{67}Zn HS-QCPMG NMR spectra recorded at 18.8 T of a) ZSM-5(G2), b) ZSM-5(I2), and c) ZSM-5(I6). The isotropic chemical shifts are indicated on the top of the peaks.

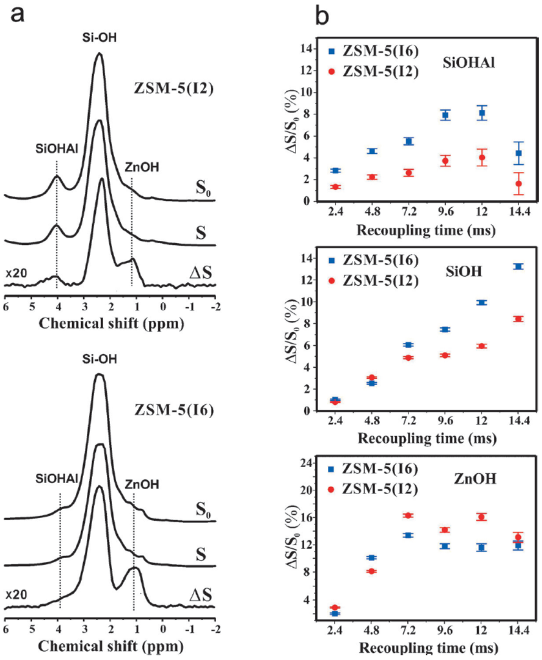

Figure 2. ^{1}H-{^{67}Zn} S-RESPDOR NMR spectra recorded at 18.8 T of ZSM-5(I2) and ZSM-5(I6) with a recoupling time of 9.6 ms (a) and $\Delta S/S_0$ signal fraction versus the total recoupling time (b).

4. Conclusions

We have presented the spectroscopic evidence on the spatial proximity/interaction between the metal ions (i.e., Zn^{2+} and GaO$^+$) and Brønsted acid sites on metal-modified ZSM-5 zeolites, which generates synergic effect for methane activation and methanol conversion. The double-resonance NMR technique offers a reliable strategy to detect and quantify the synergic active sites on zeolites and enable structural determination of the spatially interacting active sites.

References

(1) Ono, Y. *Catal. Rev.: Sci. Eng*. 1992, 34, 179–226. 2014.

(2) E. Iglesia, D. G. Barton, J. A. Biscardi, M. J. L. Gines, S. L. Soled, *Catal. Today* 1997, 38, 339–360;

(3) P. Meriaudeau, C. Naccache, *Catal. Rev.* 1997, 39, 5–48.

(4) G. Buckles, G. J. Hutchings, C. D. Williams, *Catal. Lett.* 1991, 11, 89–93.

(5) G. Qi, Q. Wang, J. Xu, J. Trébosc, O. Lafon, C. Wang, J.-P. Amoureux, F. Deng, *Angew. Chem. Int. Ed*., 2016, 55, 15826-15830.

(6) P. Gao, Q. Wang, J. Xu, G. Qi, C. Wang, X. Zhou, X. Zhao, N. Feng, X. Liu, F. Deng, *Acs Catal*. 2018, 8, 69−74