Synergic Effect of Active Sites in Zinc-Modified ZSM-5 Zeolites as Revealed by High-Field Solid-State NMR Spectroscopy

Guodong Qi, Qiang Wang, Jun Xu, Julien Trébosc, Olivier Lafon, Chao Wang, Jean-Paul Amoureux, and Feng Deng

Abstract: Understanding the nature of active sites in metal-supported catalysts is of great importance towards establishing their structure–property relationships. The outstanding catalytic performance of metal-supported catalysts is frequently ascribed to the synergic effect of different active sites, which is however not well spectroscopically characterized. Herein, we report the direct detection of surface Zn species and \( ^1\)H–\( ^{67}\)Zn intermolecular interaction between Zn\(^{2+}\) ions and Brønsted acid sites on Zn-modified ZSM-5 zeolites by high-field solid-state NMR spectroscopy. The observed promotion of C–H bond activation of methane is rationalized by the enhanced Brønsted acidity generated by synergic effects arising from the spatial proximity/interaction between Zn\(^{2+}\) ions and Brønsted acidic protons. The concentration of synergic active sites is determined by \( ^1\)H–\( ^{67}\)Zn double-resonance solid-state NMR spectroscopy.

Synergetic catalysis causes catalytic enhancements in terms of both activity and selectivity in a broad range of catalytic reactions. The synergic effect between different active sites frequently occurs on heterometallic nanoparticles, supported graphenes, and porous supported catalysts, such as mesoporous TiO\(_2\) and metal–organic frameworks (MOFs). The introduction of metal species, such as Zn and Ga on acidic zeolites, often leads to bifunctionality of the active sites, on which the synergic effect was also found. For example, the enhanced conversion of propane on Ga-modified zeolites, such as H-ZSM-5 was attributed to the synergic action of Ga species and Brønsted acidic protons.

More recently, a synergic effect was claimed on Pt-modified BEA zeolite in the conversion of methycyclopentane. The synergic effect is supposed to originate from the interfacial interactions, but the structures of synergic active sites have remained elusive. Even if solid-state NMR spectroscopy has been used to probe \( ^1\)H–\( ^{27}\)Al or \( ^{27}\)Al spatial interactions between Brønsted and Lewis acid sites in dealuminated zeolites, there is a lack of experimental evidence on the hetero-nuclear interaction between the transition metal-atoms and acidic protons of metal-modified zeolites. 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.

Herein, we investigate the synergic effect between Brønsted acid sites and zinc species on Zn-modified ZSM-5 zeolites. The high catalytic activity of the zeolites has provoked intensive studies on the activation of lower alkanes, particularly methane. Herein we provide first solid-state NMR experimental evidence on the spatial proximity/interaction between the zinc species and the Brønsted acid sites of zeolite. The active-site synergy arising from the spatial interaction is demonstrated by both the enhanced acid strength of Zn-modified zeolites and the promoted C–H bond activation in methane H/D exchange. Quantification of the synergic active sites is achieved by \( ^1\)H–\( ^{67}\)Zn double-resonance solid-state NMR spectroscopy.

Zn-modified ZSM-5 (Si/Al = 21) samples containing 2 wt.% and 6 wt.% Zn, respectively, were prepared by incipient wetness impregnation and denoted as ZSM-5(12) and ZSM-5(16) (see Supporting Information for details). For comparison, a Zn-modified sample with 2 wt.% Zn was prepared by mechanically mixing zinc oxide with H-ZSM-5 (denoted as ZSM-5(G2)). X-ray diffraction analysis and \( ^{27}\)Al MAS NMR spectroscopy show that the introduction of Zn species did not cause any detectable structural change of the zeolite on all the Zn-modified samples (Figures S1 and S2 in the Supporting Information).

Solid-state \( ^{67}\)Zn NMR spectroscopy on Zn-modified zeolites is challenging owing to the unfavorable NMR characteristics of Zn (\( I = 5/2\)) nucleus, very low gyromagnetic ratio (\( \gamma = 1.678 \times 10^7 \) \( \text{rad T}^{-1}\text{s}^{-1}\)), and low natural abundance of the NMR active isotope (4.1%, \( ^{67}\)Zn). Moreover, the difficulty in observing Zn NMR signals is exacerbated by the low concentration of zinc species present on the zeolite support. Herein, the sensitivity enhanced HS-QCPMG (hyperfine (quantum) Carr-Purcell-Meiboom-Gill) NMR technique was employed at high magnetic field (18.8 T) to characterize the Zn-modified ZSM-5.

[*] Dr. G. D. Qi, Dr. Q. Wang, Prof. J. Xu, Dr. C. Wang, Prof. F. Deng
National Centre for Magnetic Resonance in Wuhan, State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, CAS Key Laboratory of Magnetic Resonance in Biological Systems, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences
Wuhan 430071 (China)
E-mail: xujun@wipm.ac.cn
dengf@wipm.ac.cn
Homepage: http://denggroup.org/

Dr. J. Trébosc, Prof. O. Lafon, Prof. J.-P. Amoureux
Univ. Lille, CNRS, ENSCL, UMR 8181, Unité de Catalyse et de Chimie du Solide
59000 Lille (France)
Prof. J.-P. Amoureux
East China Normal University
Shanghai 200062 (China)

[†] These authors contributed equally to this work.
Supporting information for this article can be found under:
http://dx.doi.org/10.1002/anie.201608322.
5 samples. We firstly optimized the HS-QCPMG experiment on a natural abundance pure ZnO powder sample, and could achieve a 16-fold signal enhancement (Figure S4). To further improve the NMR sensitivity, $^{67}$Zn ($^{67}$Zn, 89.6%) enriched precursors were used in preparation of the Zn-modified zeolite samples. The $^{67}$Zn HS-QCPMG NMR spectrum of ZSM-5(G2) exhibits a typical second-order quadrupolar line shape with an isotropic chemical shift of 238 ppm (Figure 1a), due to ZnO particles.\(^{[14]}\) Interestingly, two $^{67}$Zn signals with isotropic chemical shifts of 238 ppm and 224 ppm are observable, respectively, for ZSM-5(I2) and ZSM-5(I6) (Figure 1b,c), which can be well fitted by taking the chemical shift distributions into account (Table S1). The signal at 238 ppm can be assigned to ZnO species.\(^{[14]}\) The lack of quadrupolar line shape stems from the Czjzek quadrupolar distribution,\(^{[15]}\) indicating that highly dispersed ZnO particles on ZSM-5. Note that the signal at 224 ppm has a much broader linewidth. We assign it to Zn\(^{2+}\) ions located on the cation exchange sites of ZSM-5 zeolite. The local structural asymmetry induced by the zeolite framework may lead to an increase of quadrupolar interaction, which results in the line broadening. Additional shielding effect imposed by zeolite framework oxygen atoms on Zn ions would cause an upper-field chemical shift. Quantitative analysis of the zinc species on ZSM-5(I2) and ZSM-5(I6) by $^{67}$Zn NMR spectra (Figure 1b,c) shows that increasing the Zn loading leads to a much increase of the ZnO signal (238 ppm) as compared to that of the Zn\(^{2+}\) ions signal (224 ppm; Table S1). This can be explained by the fact that the Zn\(^{2+}\) ions require two Brønstad base sites (SiO\(^-\)Al) of zeolite as the cation exchange sites which are limited on ZSM-5.

The acid sites on these Zn-modified samples were probed by \(^1\)H MAS NMR. Two major signals are observed at 4.3 and 2.3 ppm in the \(^1\)H MAS NMR spectra acquired with single-pulse excitation (Figure 2a), which can be assigned to Brønsted acidic protons (SiOH\(_{\text{Al}}\)) and non-acidic silanol groups (SiOH) on ZSM-5 zeolite,\(^{[16]}\) respectively. In addition, the formation of ZnOH groups on ZSM-5(I2) and ZSM-5(I6) can be found by the weak signal at 1.2 ppm.\(^{[17]}\) A slight decline of the acidic protons is observable for ZSM-5(G2), suggesting that most of these protons remain intact. In contrast, the concentration of acidic protons is remarkably reduced on ZSM-5(I2) and ZSM-5(I6) (Table S2). This indicates that most of the Brønsted acidic protons have been replaced by the introduced Zn\(^{2+}\) ions which compensate the negative charges of two neighboring conjugate-base sites (SiO\(^-\)Al) of Brønsted acid sites.

To further characterize the acidity of these zeolites, \([D\text{\textsubscript{5}}]\)pyridine that is a well-established NMR probe to measure the acid property of zeolites was employed.\(^{[18]}\) Since the signals in the single-pulse \(^1\)H MAS NMR spectra are not well resolved (Figure S5), spin-echo \(^1\)H MAS NMR experiments were performed to distinguish different hydroxy groups.\(^{[16]}\) As shown in Figure 2b, the downfield signals at 15.5 and 19.3 ppm can be assigned to \([D\text{\textsubscript{5}}]\)pyridine adsorbed on the acidic protons of ZSM-5 zeolite with different acidic strength; the signals at 8.3 and 6.7 ppm come from the formation of hydrogen bonds between \([D\text{\textsubscript{5}}]\)pyridine and non-acidic SiOH...
groups.[16] Actually, different types of SiOH groups with a chemical shift distribution could contribute to the observed broad signal at 2.3 ppm on H-ZSM-5[16] (Figure 2a). The newly resolved signal at 1.9 ppm is due to the SiOH group inaccessible to pyridine. It is interesting to note that a weak shoulder peak at 13.4 ppm appears in the 1H MAS spectra of [D3]pyridine adsorbed on ZSM-5(12) and ZSM-5(16), but it is absent on ZSM-5(G2) and H-ZSM-5. The existence of this signal is also confirmed by recording the spin-echo 1H MAS NMR spectra of ZSM-5(12) and H-ZSM-5 at high magnetic field (18.8 T) (Figure S6). For [D3]pyridine adsorbed on Brønsted acidic protons of zeolites, pyridinium ion complexes are formed with 1H chemical shifts of 12–20 ppm,[16] and a smaller chemical shift corresponds to a stronger acid strength.[19] Thus, the appearance of the 13.4 ppm signal indicates that the acid strength of a small fraction of Brønsted acid sites is largely increased on ZSM-5(12) and ZSM-5(16), probably due to the interaction of acidic protons and the introduced zinc ions. Although the Hirschler-Plank effect may produce the acidic protons in the preparation of multivalent metal cations modified zeolites,[20] it should be negligible due to the afterwards high temperature calcination of the samples.[21]

To provide direct experimental evidence on the spatial proximity/interaction between various protons and zinc species, 1H-[67Zn] S-RESPDOR solid-state NMR experiments were performed on ZSM-5(12) and ZSM-5(16). Under 67Zn irradiation, the 1H signal of protons that are in close proximity to 67Zn atoms will be modulated by 1H–67Zn dipolar interaction. The difference spectrum (ΔS) is obtained by subtracting the 1H spectrum with 67Zn irradiation (S) from that without 67Zn irradiation (S0), in which only the protons having dipolar interactions with Zn atoms can be observed. The accuracy and robustness of the measurements were confirmed by the control experiments on ZSM-5(12) (Figure S7a). In the difference spectra (Figure 3a), the 1H signals from SiOH (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. Figure 3b shows the 1H-[67Zn] S-RESPDOR signals build up curves (ΔS/S0) versus recoupling time for the two samples. A ΔS/S0 value expressed as (S0−S)/S0 (S and S0 represent the signal intensity with and without dipolar dephasing, respectively) is used to describe the degree of 1H–67Zn dipolar dephasing, characterizing the dipolar interaction and spatial proximity between protons and Zn atoms. The recoupling time for acidic proton and ZnOH to reach the maximum dipolar dephasing is approximately 12 ms and 7.2 ms, respectively, while the ΔS/S0 of SiOH group keeps increasing. This indicates that the three hydroxy groups experience different degrees of dipolar interactions with Zn atoms. The longer maximum recoupling time for acidic proton as compared to ZnOH suggests that the 1H–67Zn internuclear dipolar interaction between acidic proton and zinc species is slightly weaker than that in ZnOH. The close spatial proximity between Zn2+ ion and acidic proton probably lead to the observed strong interaction. As the ΔS/S0 of silanol group increases even after 14 ms recoupling time, it may be located farther away from zinc species. This indicates that the silanol group is less affected by the zinc modification, in consistent with the above 1H MAS NMR results. The approximate 1H–67Zn nuclear distances between the three types of protons and zinc atoms were extracted from both analytical formula and numerical simulations on the 1H-[67Zn] S-RESPDOR dephasing data of ZSM-5(16) (see Figure S8–S11 and the details in Supporting Information), which provides structural information on these moieties. The internuclear 1H–67Zn distance is 2.70–3.34 Å for acidic proton, 2.43–2.86 Å for ZnOH and 5.06–5.42 Å for SiOH (Table S3).

The activity of the Zn-modified zeolites was evaluated by [D3]methane H/D exchange reaction which was monitored with in situ solid-state 1H MAS NMR spectroscopy (Fig-
ure S12). ZSM-5(12) and ZSM-5(16) catalysts exhibit a similar activity, much higher than that of ZSM-5(G2) and parent H-ZSM-5 (Figure S13). As demonstrated by Kramer et al.,[23] methane H/D exchange on acidic zeolites is determined by the acid strength, a stronger acidity resulting in a higher H/D exchange rate. Thus, the Brønsted acid sites with enhanced acid strength found by our $^1$H MAS NMR on ZSM-5(12) and ZSM-5(16) are most likely responsible for their distinct activity. The lower and comparable H/D exchange activity of ZSM-5(G2) and H-ZSM-5 implies that the ZnO particles on ZSM-5 have little contribution to the reaction. This is probably due to the lacking of strong interactions between ZnO particles and Brønsted acidic protons. The methane H/D exchange experiment was also performed on a ZSM-5(16) sample treated by acid-washing. Interestingly, its H/D exchange activity remains almost unchanged compared to the parent ZSM-5(16) (Figure S14). The acid-washed ZSM-5(16) was also analyzed by $^{67}$Zn NMR. Unfortunately, the low signal to noise ratio and resolution did not allow us to quantify the different zinc species even after 60 h signal accumulation (Figure S15a). This is likely due to the significant elimination of the Zn species by the acid treatment. UV/Vis spectroscopy was alternatively used, which confirmed that most of the ZnO particles and a small fraction of Zn$^{2+}$ ions had been removed by the acid treatment (Figure S15b). Since the H/D exchange activity does not change much, it can be concluded that only the Zn$^{2+}$ ions having interaction with zeolite framework dictate the activity. Further $^1$H MAS NMR kinetics analysis shows that ZSM-5(12) and ZSM-5(16) have a similar activation energy of ca. 74 kJ mol$^{-1}$ for the H/D exchange reaction (Figure S16), much lower than that (ca. 120 kJ mol$^{-1}$) on parent H-ZSM-5.[7b,23a] This indicates that the activity of the two Zn-modified samples is promoted by the same kind of active sites which are constituted by Zn$^{2+}$ ions and Brønsted acid sites. It is noteworthy that the concentration of Zn$^{2+}$ ions determined by $^{67}$Zn NMR on ZSM-5(16) is approximately twofold (2:1:1) of that on ZSM-5(12) (Table S1). Thus, only a fraction of the Zn$^{2+}$ ions is involved in the interaction with Brønsted acid sites, forming the synergic active sites.

For a quantitative determination of the synergic active sites, the $^1$H-$^{67}$Zn S-RESPDOR experiment provides a feasible approach. The maximum $\Delta S/S_0$ value reflects the fraction of the total acidic protons involved in the synergic active sites. Analysis of the build-up curve gives rise to a maximum $\Delta S/S_0$ value of ca. 3.7% and 7.8% for ZSM-5(12) and ZSM-5(16) respectively. Considering the residual acidic protons on H-ZSM-5 and the scaling factor (86–100%) of the $^1$H dephasing fraction, the concentration of the synergic active sites is calculated to be 3.8–4.4 and 3.9–4.5 μmol g$^{-1}$ for ZSM-5(12) and ZSM-5(16) respectively (Table 1 and Supporting Information for details). The almost same density of synergic active sites on ZSM-5(12) and ZSM-5(16) is in line with their similar methane H/D exchange activity.

Finally, we can rationalize the high activity of Zn-modified ZSM-5 catalysts in the methane H/D reaction by considering the active sites synergy. The enhanced acidity can be attributed to the spatial proximity/interaction between the Zn$^{2+}$ ions and the acidic protons of ZSM-5. Because of the smaller electronegativity of Zn atom than H atom, the local electron density on the bound site is increased, accordingly leading to a decline of the electron density on the oxygen atoms around Brønsted sites in close proximity,[24] which would weaken the interaction between the bridging oxygen and the acidic proton and thus enhance the acidity of Zn-modified zeolites.

In summary, we have presented the first spectroscopic evidence on the spatial proximity/interaction between the Zn$^{2+}$ ions and Brønsted acid sites on Zn-modified ZSM-5 zeolites, which generates a synergic effect for methane C–H bond activation. The $^1$H–$^{67}$Zn 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. The results show implications of $^{67}$Zn NMR and $^1$H–$^{67}$Zn double-resonance NMR techniques in the identification and determination of active sites as well as structural elucidation of the interfaces on the supported catalysts where the interactions between different active sites play a critical role in various heterogeneous catalytic reactions.

### Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grants 21210005, 21473245, 21573278, 21611130104, and 21623311) and IR-RMN-THC Fr-3050 CNRS, Institut Chevreul (FR 2638), Ministère de l’Enseignement Supérieur et de la Recherche, Région Nord-Pas de Calais, CPER, FEDER, and PRC CNRS-NSFC.

### Keywords

- active sites · C–H bond activation · solid-state NMR spectroscopy · synergic effects · zinc-modified zeolite

### How to cite


Angew. Chem. 2016, 128, 16058–16062

---

**Table 1:** Concentration of Brønsted acid sites and synergic active sites on ZSM-5(12) and ZSM-5(16).

<table>
<thead>
<tr>
<th>Samples</th>
<th>SiOHAl [μmol g$^{-1}$]</th>
<th>Maximum dephasing fraction [%]$^a$</th>
<th>Synergic active sites [μmol g$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5(12)</td>
<td>91</td>
<td>3.7</td>
<td>3.8–4.4$^b$</td>
</tr>
<tr>
<td>ZSM-5(16)</td>
<td>45</td>
<td>7.8</td>
<td>3.9–4.5$^b$</td>
</tr>
</tbody>
</table>

$^a$ The maximum dephasing fraction (AS/$S_0$) of SiOHAl obtained from the build-up curve of $^1$H–$^{67}$Zn S-RESPDOR NMR spectra. $^b$ Calculated by multiplying the concentration of SiOHAl by the maximum dephasing fraction and then divided by the abundance of zinc-67 isotope (89.6%) and the scaling factor (86–100%) of the $^1$H dephasing fraction.

学霸图书馆 (www.xuebalib.com) 是一个“整合众多图书馆数据库资源，提供一站式文献检索和下载服务”的24小时在线不限IP图书馆。

图书馆致力于便利、促进学习与科研，提供最强文献下载服务。

图书馆导航：
图书馆首页  文献云下载  图书馆入口  外文数据库大全  疑难文献辅助工具