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Research Note

Solid-state MAS NMR detection of the oxidation center in TS-1 zeolite by in situ probe reaction

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Abstract

In this paper, the oxidation of trimethylphosphine as an in situ probe reaction was performed to monitor the oxidation ability of different Ti species in TS-1 zeolite by ^{31}P MAS NMR spectra, which found for the first time direct evidence about the oxidation center of TS-1 zeolite.
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Since the first report in 1983 [1], TS-1 (titanium–silicalite) zeolite has been a hot topic in the field of catalysis, as TS-1 zeolites have been proven to be a new generation of oxidation catalysts with very high efficiency [2–7]. By using H_2O_2 [1–4], O_2 [5,6], and N_2O [7] as oxidants, selective oxidation of various organic compounds has been realized. The synthesis and reaction performance, especially the characterization of the active centers of the TS-1 zeolite, have attracted the attention of numerous research groups. In order to identify the catalytic active centers of TS-1, different approaches such as XRD, IR, Raman, EXAFS, XANES, XPS, and solid-state NMR have been employed [8–13], some of which have combined with theoretical calculations [12,13]. After many arguments, it is now generally accepted that the active titanium species can be roughly ascribed to the framework Ti of the zeolite, most likely in a tetrahedral coordination. Solid-state NMR is a powerful tool for characterizing the structure of zeolites, with very good ability for gaining information regarding the local structure, geometry, and coordination of the building atoms such as Si and O, or the hetero-substituted atoms such as Al and Ga. However, for titanium in TS-1, it is difficult to conduct $^{47}Ti/^{49}Ti$ NMR directly, due to the quadruple nature of the Ti nucleus, as well as its very low sensitivity and concentration. Meanwhile, as an analogue of the titanium in TS-1, the states of the aluminum in the aluminosilicalite zeolite have yielded interesting information recently by employing two-dimensional ^{27}Al MQ (multiple-quantum) MAS NMR [14–16], combined with the adsorption of probe molecules, such as trimethylphosphine (TMP) and ammonia [16]. Thus, it was verified that even the framework aluminum in aluminum-substituted silicalite zeolites (calcined or dealuminated) has a configuration distribution; i.e., different framework Al sites (for example, tetrahedral aluminum species, tricoordinated aluminum species, and distorted tetrahedral aluminum species) within the zeolite lattice could be resolved by this state-of-art method.

As a counterpart of the aluminum in aluminosilicate, the framework titanium species in titanium-substituted silicalite-1 (TS-1) should also have a distribution. Thus, the questions to be answered are how many kinds of framework Ti sites are there in TS-1, and which site is responsible for the oxidation reactions. Following the pioneer work of Lunsford and other researchers [17–20], we have demonstrated recently by ^{31}P MAS NMR spectra, with trimethylphosphine as a probe, that the coordinate-

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unsaturated framework Ti sites and the distorted tetrahedral Ti sites are the Lewis acid sites of TS-1, whereas the Ti–OH groups such as $Ti(OSi)_3OH$ within the zeolite lattice are associated with the Brønsted acid sites [23]. Therefore, it is possible to discriminate the framework Ti species of different configurations by differentiating the Brønsted or Lewis acid sites observed in ^{31}P MAS NMR spectra of TMP-loaded TS-1. Based on the fact that trimethylphosphine oxide (TMPO) is an excellent probe in distinguishing different acid sites, Lunsford had studied the oxidation of TMP to TMPO in Y-type zeolites [21]. By considering these results and facts, we infer that the oxidation of TMP is indeed a excellent probing reaction for monitoring the oxidation ability of different Ti species in the TS-1 zeolite, thus enabling us to answer the question of which Ti species correspond to the oxidative centers in the TS-1 zeolite. In the present study, this kind of probing oxidation reaction is conducted on both TS-1 and HZSM-5 zeolites, with the hope of finding for the first time direct evidence for the oxidation centers of the TS-1, at least under the conditions employed here.

TS-1 was synthesized by the hydrothermal method. Using silicate gel as the silicon source, tetraethylorthotitanate (TEOTi) as the titanium source, NH_4OH as the base, and tetrapropylammonium bromide (TPABr) as the template, the reagents were stirred and crystallized at 160–170 °C for 3–5 days. After crystallization the sample was recovered by centrifugation, washed several times with distilled water, and dried in an oven. Occluded TPABr were removed by calcination in air at 833 K for 6 h. XRD and ^{29}Si MAS NMR confirmed that the products had the proper TS-1 structure. XRF elemental analysis displayed that the ratio of Si/Ti was 33, Si/Al was 540, and Si/Na was 643. The aluminum in the resulting TS-1 zeolite probably came from the impurity of the raw material. HZSM-5 was prepared by a similar method, using sodium aluminates instead of tetraethylorthotitanate. The ratio of Si/Al is 40.

By means of a special home-made device [22], the sample was degassed at 673 K in a vacuum (less than 10^{-2} Pa) for 20 h. Adsorption of TMP was performed by exposing the dehydrated sample to saturated TMP vapor at room temperature for 30 min. Excess TMP was removed by evacuation, and then the sample was exposed to air and allowed to oxidize at 343 K for a certain period of time. All spectra were recorded at 298 K after adsorption and oxidation. The ^{31}P MAS NMR spectra were recorded at 161.9 MHz on a Bruker DRX-400 spectrometer. The pulse width was 2.0 µs, and 2048 scans were accumulated with a 2-s recycle delay. Chemical shifts were referenced to 85% H_3PO_4. The WINNMR supplied by the instrument manufacturer was employed for spectral deconvolution using Gaussian–Lorentzian lineshapes.

The curves from (a) to (f) in Fig. 1 show the ^{31}P MAS NMR spectra of the TMP adsorbed on the TS-1 zeolite before (a) and after oxidation in air for different exposure times (b)–(f). Before the occurrence of any oxidation, at least five peaks can be explicitly observed in the ^{31}P MAS NMR spectrum (see Fig. 1a). As reported previously, the resonances at −4.8 and −62.1 ppm in the ^{31}P MAS NMR spectra can be assigned to the protonated and physisorbed TMP, respectively, [17]. The protonated TMP adducts $[(CH_3)_3P\text{–}H]^+$ in the case of TS-1 were identified from TiOH in framework $Ti(OSi)_3OH$ and part of the silanol (SiOH) [23]. The resonance at −59.8 ppm is ascribed to the physisorbed TMP, in which the weakly bonded Na^+ ions have an influence on the chemical shift of the phosphorus [18]. The two peaks at −34.2 and −32.0 ppm are related to the TMP adsorbed on Lewis acid sites [23]. In our previous work, we have confirmed that these two signals are not associated with the aluminum in the framework of the TS-1 zeolite, but are related to the distorted tetrahedral-coordinated titanium species in the framework of the zeolite and the coordinate-unsaturated Ti^{4+} ions, both of which are able to accept electrons transferred from the probe molecule and are thus visible to the ^{31}P MAS NMR [23]. Meanwhile, the ^{31}P MAS NMR spectrum of the HZSM-5 loaded with TMP is shown in Fig. 2a. Only two peaks at −3.7 and −62.1 ppm are observed in the spectrum. A shoulder of the −62.1 ppm peak, which is located at −61.0 ppm, can only be resolved with spectral deconvolution. Similar to TS-1, the peaks at −3.7 and −62.1 ppm can be ascribed to the TMP adsorbed on the

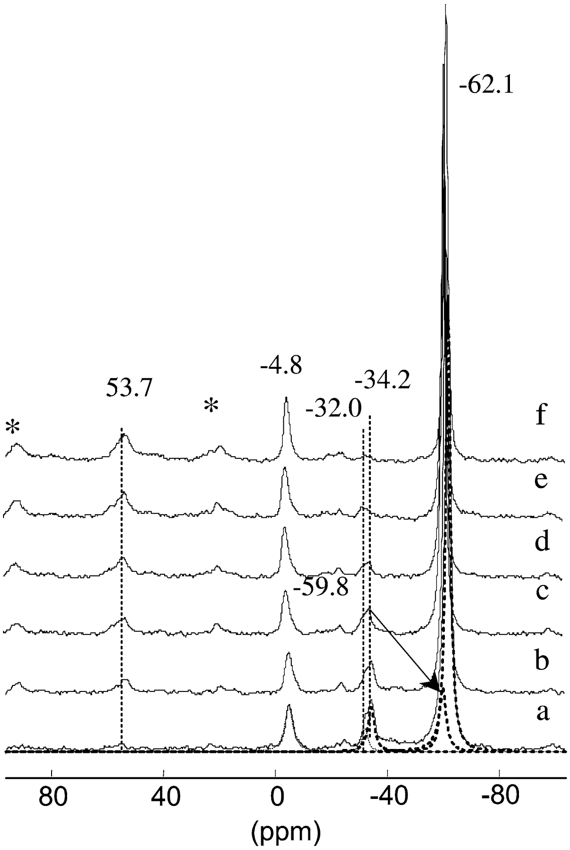

Fig. 1. The change of the ^{31}P MAS NMR spectra of TMP adsorbed on TS-1 zeolite, upon heating for a certain period of time at 343 K after exposure to air: (a) fresh adsorption at room temperature, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, ∗ presents sideband.

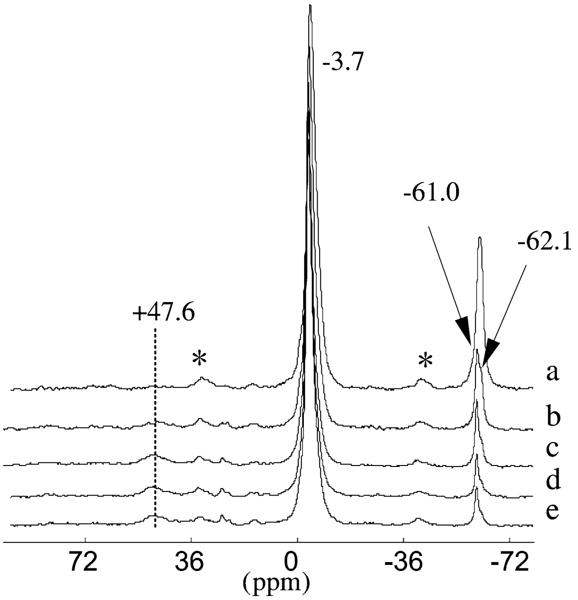

Fig. 2. The change of the ^{31}P MAS NMR spectra of TMP, adsorbed on HZSM-5 zeolite, upon heating for a certain period of time at 343 K after exposure to air: (a) fresh adsorption at room temperature, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, ∗ presents sideband.

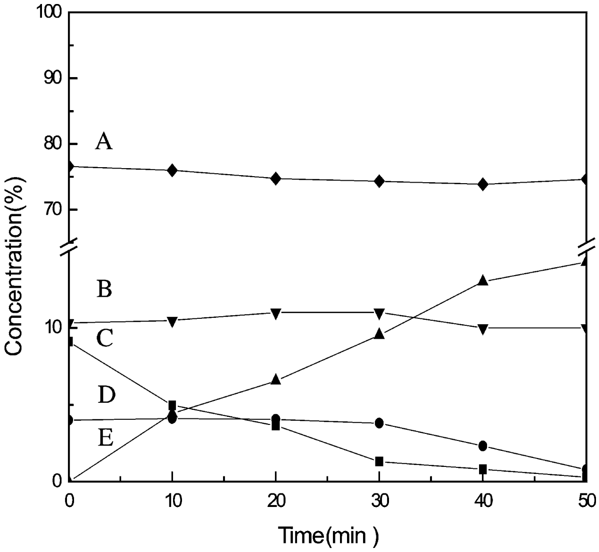

Fig. 3. Concentrations of TMP or TMPO bound to different species adsorbed on TS-1 zeolite in ^{31}P MAS NMR spectra as a function of exposure time. (A) the peak at −62.1 ppm, (B) the peak at −4.8 ppm, (C) the peak at −34.2 ppm, (D) the peak at −32.0 ppm, (E) the peak at +53.7 ppm.

Brønsted acid sites of the HZSM-5 and the physisorbed TMP, respectively, while the peak at −61.0 ppm is assigned to the TMP bound to another kind of Lewis acid sites [17–20,24]. It should be noted that no peak at around −30 to −45 ppm is observed in the case of HZSM-5. The origin of the Lewis acid sites of aluminosilicates having chemical shifts in this region has been discussed in our previous work. They may come from coordinate-unsaturated framework aluminum species such as tricoordinated framework aluminum or octahedral framework aluminum which is three coordinated in nature [16]. Our observation proves that the framework aluminum ions are much more stable with respect to the framework Ti ions during thermal treatment (for removing the template), while only calcination at a higher temperature or hydrothermal treatment can result in the formation of the peaks corresponding to the distorted or coordinate-unsaturated framework aluminum at −30 to −45 ppm.

As oxygen was leaked into the sample, the physisorbed TMP (−62.1 ppm) on the HZSM-5 was oxidized (Fig. 2b), while the TMP bound to another kind of Lewis acid sits at −61.0 ppm was not easily oxidized. As a result, by increasing the exposure time (Fig. 2b–2e), the physisorbed TMP peak disappeared, leaving the Lewis acid peak at −61.0 ppm to be the dominant one. Spectral deconvolution suggests that the intensity of the Lewis acid peak also decreases, but it is far less apparent than that of the physisorbed species. Only under a more rigorous condition, i.e., by further extending the oxidation time or using a higher oxidation temperature, can the TMP bounded to Lewis acid sites be thoroughly oxidized. Interestingly, the intensity of the peak corresponding to the TMP-Brønsted site adducts (−3.7 ppm) remains almost unchanged during the oxidation reaction, as shown in Fig. 2. This implies that the Brønsted centers of HZSM-5 are not able to react with oxygen. At the same time, a new broad resonance at +47.6 ppm, which is assigned to the physisorbed TMPO, appears [21], indicating that TMP was transformed into TMPO, but still attached to the zeolite (Fig. 2b–2e). We need to point out that the oxidation of different TMP species is actually a competition process. Only the oxidation of that kind of TMP which is adsorbed on the sites that have the capability to catalyze the oxidation of TMP exhibits a faster rate than the oxidation of the geometrically easily accessible physisorbed TMP. Therefore, for HZSM-5, the experimental methodology used here was unable to demonstrate the potential ability of the Al site to serve as oxidation centers. At the same time, we also found the peaks centered at +24.0 and +12.0 ppm in the spectra, which have been disputed for a long time. The peak at +24.0 ppm has been assigned to TMP adsorbed to an especially strong Lewis acid site, or a complex between TMP and an unidentified soft acid, $[(CH_3)_3P\text{–}H]^+$, or inadvertent oxygen exposure [25–27]. Recently, Haw et al. considered that the peak at +27.0 ppm was due to $P(CH_3)_4{}^+$, formed in a reaction that consumes a Brønsted site at the highest loading of TMP [28].

In the case of the TS-1, on the contrary, the TMP resonance at −34.2 ppm is the first one to decrease after the sample is exposed to oxygen at 343 K for 10 min, and a new resonance at +53.7 ppm assigned to TMPO bound to Lewis acid sites appears in the spectrum (Fig. 1b) [18]. Ten minutes later, 46% of the TMP which corresponds to the peak at −34.2 ppm have been converted to the Lewis-bound TMPO at around +53.7 ppm, while there are no obvious changes in the signal intensities of other species. Fig. 3 depicts the concentration (%) of TMP or TMPO bound to different species recorded in the ^{31}P MAS NMR spectra as a function of exposure time. The -34.2 ppm signal decreases with the increase of the exposure time and disappears absolutely 40 min later (Fig. 3). In contrast, the peak at $+53.7$ ppm assigned to the TMPO bound to Lewis acidic sites increases with more oxygen leakage into the sample. At the same time, we also found that the protonated TMP remains almost intact during the process, suggesting that the $Ti(OSi)_3OH$ group is unable to catalyze the oxidation of TMP under the present experimental conditions. After exposure to air for 30 min, the intensity of the peak at -32.0 ppm also decreases, which indicates that the TMP species bound to another kind of Lewis acid sites begins to be oxidized. 50 min later, almost all of the Lewis-bound TMP (at -32.0 and -34.2 ppm) have been oxidized completely, but the physisorbed TMP, including Na^+-coordinated TMP, remains constant. Therefore, the results indicate that among the different species of the TMP adsorbed on TS-1 zeolite, the Lewis-bound TMP is the easiest to be attacked by oxygen. Based on the results of Lunsford et al., the capacity of the oxidation of Lewis-bound TMP is similar to that of the Na^+-coordinated TMP in Na–Y zeolite (without Ti, the Lewis acid sites come from defected aluminum) [18]. However, in the present study, there are almost no oxides of TMP arising from the Na^+-coordinated TMP, even all of the Lewis-bound TMP have been oxidized. This indicates that these kinds of Lewis sites (distorted tetrahedral framework Ti sites and coordinately unsaturated framework Ti sites such as tricoordinated framework Ti) are the oxidation centers of the TS-1, which are favorable sites in the competitive oxidation process. For the two kinds of Lewis acid sites observed in the ^{31}P MAS NMR, the one at -34.2 ppm is more active in the oxidation reaction. Previously, albeit there is no direct evidence, several groups had successfully deduced that Lewis acid sites are oxidation centers as well, because they observed that Lewis acid sites were the only sites associated with the titanium species [29,30]. However, it was reported by us that there exists a distribution of the titanium species in TS-1; i.e., there are titanium-related Brønsted sites as well [23]. In the present study, by conducting in situ oxidation reactions of TMP adsorbed on TS-1 and HZSM-5 zeolites via ^{31}P solid-state MAS NMR spectra, we have for the first time clearly shown that among the various framework titanium species (such as the $Ti(OSi)_3OH$ group, the distorted tetrahedral Ti species and the coordinately unsaturated Ti sites like tricoordinated Ti), only those which correspond to the Lewis acid sites are the active oxidation centers of TS-1, at least specifically for this reaction under current conditions.[2]

Acknowledgments

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References

[1] B. Notari, Stud. Surf. Sci. Catal. 37 (1989) 413.
[2] M.G. Clerici, Appl. Catal. 68 (1991) 249.
[3] B. Kraushaar, J.H.C. Van Hooff, Catal. Lett. 1 (1988) 81.
[4] G. Perego, G. Bellusi, C. Corno, M. Taramasso, S. Nagishi, H. Tominaga, J. Chem. Soc., Chem. Commun. (1990) 467.
[5] G.X. Lu, H.X. Gao, J.H. Suo, S.B. Li, J. Chem. Soc., Chem. Commun. (1994) 2423.
[6] S.V.N. Raju, T.T. Upadhya, S. Ponrathnam, T. Daniel, A. Sudalai, Chem. Commun. (1996) 1969.
[7] L.V. Pirutko, A.K. Uriarte, V.S. Chernyavsky, A.S. Kharitonov, G.I. Panov, Micropor. Mesopor. Mater. 48 (2001) 345.
[8] D. Gleeson, G. Sankar, C.R.A. Catlow, J.M. Thomas, G. Spanoç, S. Bordiga, A. Zecchina, C. Lamberti, Phys. Chem. Chem. Phys. 2 (2000) 4812.
[9] C. Li, G. Xiong, J.K. Liu, P.L. Ying, Q. Xin, Z.C. Feng, J. Phys. Chem. B 105 (2001) 2993.
[10] A. Labouriau, T.J. Higley, W.L. Earl, J. Phys. Chem. B 102 (1998) 2897.
[11] C. Lamberti, S. Bordiga, A. Zecchina, G. Artioli, G. Marra, G. Spano, J. Am. Chem. Soc. 123 (2001) 2204.
[12] S. Bordiga, A. Damin, F. Bonino, A. Zecchina, J. Phys. Chem. B 106 (2002) 9892.
[13] C.A. Hijar, R.M. Jacubinas, J. Eckert, N.J. Henson, P.J. Hay, K.C. Ott, J. Phys. Chem. B 104 (2000) 12157.
[14] J.A. Van Bokhoven, A.L. Roest, D.C. Koningsberger, B. Miller, J.T. Nachtegaal, A.P.M. Kentgens, J. Phys. Chem. B. 104 (2000) 6743.
[15] C.A. Fyfe, J.L. Bretherton, L.Y. Lam, Chem. Commun. (2000) 1575.
[16] D. Ma, X. Han, S. Xie, X. Bao, H. Hu, S.C.F. Au-Yeung, Chem.—Eur. J. 8 (2002) 162.
[17] J.H. Lunsford, W.P. Rothwell, W.X. Shen, J. Am. Chem. Soc. 107 (1985) 1540.
[18] J.H. Lunsford, P.N. Tutunjian, J. Chu, E.B. Yeh, D.J. Zalewski, J. Phys. Chem. 93 (1989) 2590.
[19] D.J. Zalewski, P.J. Chu, P.N. Tutunjian, J.H. Lunsford, Langmuir 5 (1989) 1026.
[20] B.Y. Zhao, H.J. Pan, J.H. Lunsford, Langmuir 15 (1999) 2761.
[21] L. Baltusis, J.S. Frye, G.E. Maciel, J. Am. Chem. Soc. 108 (1986) 7119.
[22] W. Zhang, D. Ma, X. Liu, X. Liu, X. Bao, J. Chem. Soc., Chem. Commun. (1999) 1091.
[23] J. Zhuang, Z. Yan, X. Liu, X. Liu, X. Han, X. Bao, Catal. Lett. 83 (2002) 87.
[24] W. Zhang, X. Han, X. Liu, X. Bao, J. Mol. Catal. A 194 (2003) 107.
[25] D.J. Coster, A. Bendada, F.R. Chen, J.J. Fripiat, J. Catal. 140 (1993) 497.
[26] J.H. Lunsford, H. Sang, S.M. Campbell, C.H. Liang, R.G. Anthony, Catal. Lett. 27 (1994) 305.
[27] T. Riemer, D. Spielauer, M. Hunger, G.A.H. Mekhemer, H. Knozinger, J. Chem. Soc., Chem. Commun. (1994) 1181.
[28] J.F. Haw, J. Zhang, K. Shimizu, T.N. Venkatraman, D.P. Luigi, W.G. Song, D.H. Barich, J.B. Nicholas, J. Am. Chem. Soc. 122 (2000) 12561.
[29] A. Bittar, A. Adnot, A. Sayari, S. Kaliaguine, Res. Chem. Intermed. 18 (1992) 49.
[30] G. Sastre, A. Corma, Chem. Phys. Lett. 302 (1999) 447.

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[2] With a few exception, the majority of the partial oxidation reactions of TS-1 zeolite are conducted in an aqueous environment. However, it is almost impossible to do the solid-state NMR under such conditions. Whether the current conclusion holds generally needs a further investigation, but we can say that Lewis acid centers are the oxidation centers of TS-1, at least under the present conditions.