

A significant enhancement of catalytic activities in oxidation with H₂O₂ over the TS-1 zeolite by adjusting the catalyst wettability†

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Hydrophilic TS-1 (H-TS-1) with rich hydroxyl groups, which were confirmed by ²⁹Si and ¹H NMR techniques, exhibits much higher activities in the oxidation than conventional TS-1. This phenomenon is strongly related to the unique features of high enrichment of H₂O₂ on H-TS-1.

The microporous titanosilicate zeolite of TS-1 with MFI-type framework structure has been widely used in liquid-phase oxidation using H₂O₂ as a clean oxidant, which is considered a significant breakthrough in the fields of zeolites and catalysis.^{1–3} Considering the great importance of the TS-1 zeolite, a further improvement of the catalytic activities has been extensively investigated. For example, recent results show that the hydrophobic TS-1 zeolite is favorable for increasing catalytic activities in the oxidation, because the hydrophobic titanosilicate surface could adsorb and enrich the organic hydrocarbon substrates, leading to high catalytic activities.⁴

On the other hand, it is also accepted that the first step in the oxidation with H₂O₂ over the TS-1 zeolite is the activation of H₂O₂ by Ti species.⁵ Therefore, it is also important to enrich H₂O₂, another substrate in the oxidation, to nearby the Ti species, which could effectively improve the activities.⁶ According to this idea, a relatively hydrophilic TS-1 zeolite has been rationally synthesized. As we expected, the hydrophilic TS-1 zeolite is more active in the oxidation with H₂O₂ than the conventional TS-1 zeolite.

As a model of oxidation, 1-hexene oxidation with H₂O₂ was chosen because of the great importance of the 1,2-epoxyhexene product in industry.⁷ Interestingly, it is observed that over the conventional TS-1 catalyst (C-TS-1) both 1-hexene and H₂O₂ concentrations are very sensitive to the activity (Fig. S1, ESI†), suggesting that the enrichment of both reactants in the

microporous titanosilicate catalysts could effectively improve the activity.

In this work, we have synthesized the relatively hydrophilic TS-1 zeolite (H-TS-1) from dimethyl dimethoxy silane (DDS) in the starting gel. After crystallization of H-TS-1, the methyl groups were introduced into the zeolite framework. After calcination at 550 °C to remove the organic template, the methyl groups were transformed into hydroxyl groups. These samples were designated as H-TS-1-*x*, where *x* stands for the percentage of the DDS/SiO₂ (total silica) molar ratio in the starting gel (Scheme S1, ESI†).

Fig. S2 (ESI†) shows XRD patterns of various TS-1 samples, exhibiting good crystallinities associated with typical MFI structure. Fig. S3 (ESI†) shows SEM images of these samples, confirming the high crystallinities. Notably, H-TS-1-5, H-TS-1-7.5, H-TS-1-10, and H-TS-1-20 have crystal sizes of 298, 307, 500, and 1170 nm, which are obviously larger than that (212 nm) of C-TS-1. N₂ sorption isotherms (Fig. S4, ESI†) show that all H-TS-1-*x* samples give very similar sorption isotherms to that of C-TS-1, giving a typical feature of crystalline microporous structure. These samples exhibit similar Si/Ti ratios (52–60), microporous sizes (0.53–0.54 nm), and surface areas (403–435 m² g^{−1}), as presented in Table S1 (ESI†). UV-visible spectroscopy shows that the H-TS-1-*x* samples have a strong peak near 220 nm, which is related to the 4-coordinative Ti species in the framework of the TS-1 zeolite (Fig. S5, ESI†).

Fig. 1 shows ²⁹Si and ¹H MAS NMR spectra of C-TS-1 and H-TS-1-7.5 samples. Both samples exhibit strong signals at −113 and −116 ppm in the ²⁹Si spectra (Fig. 1A), which are associated with typical Si(OSi)₄ species. However, the signal at −103.5 ppm, assigned to the Si species functionalized by hydroxyl groups, is stronger in the spectrum of H-TS-1-7.5 (Fig. 1A-a) than that of C-TS-1 (Fig. 1A-b).^{6a,8} Upon deconvolution and integration of the ²⁹Si MAS NMR spectra, the molar ratio of hydroxyl-attached Si can be obtained as 3.5% and 7.6% for C-TS-1 and H-TS-1-7.5, respectively. Furthermore, ¹H MAS NMR spectroscopy (Fig. 1B) shows that both samples exhibit obvious signals at 1.7 and 2.0 ppm, which are attributed to the Si–OH species in the samples. Notably, H-TS-1-7.5 (Fig. 1B-a) has stronger signals than C-TS-1 (Fig. 1B-b), demonstrating that H-TS-1-7.5 has more rich hydroxyl groups than C-TS-1.

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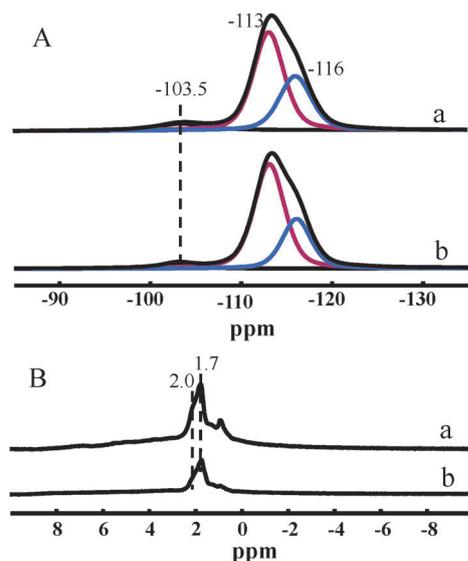


Fig. 1 (A) ^{29}Si and (B) ^1H MAS NMR spectra of (a) H-TS-1-7.5 and (b) C-TS-1 samples.

When a water droplet was brought into contact with the surface of the C-TS-1 zeolite, the contact angle was measured to be 17° . In contrast, the water droplet contact angles were much smaller on the H-TS-1- x samples (Fig. S6, ESI †). For example, the contact angle is lower than 5° on H-TS-1-7.5, indicating its relatively hydrophilic surface as compared with C-TS-1. This conclusion is strongly supported by the IR spectra of the samples in the region of $3100\text{--}3700\text{ cm}^{-1}$ associated with adsorbed water, as well as the water adsorption capacities (Fig. S7, ESI †). These results are reasonably attributed to the presence of rich hydroxyl groups on the framework of H-TS-1- x samples, compared with C-TS-1.

Fig. 2 shows dependences of the reaction rate on H_2O_2 concentration over C-TS-1 and H-TS-1-7.5 catalysts in the oxidation of 1-hexene. Very clearly, at the same H_2O_2 concentration the reaction rate over H-TS-1-7.5 is always higher than that over C-TS-1. More importantly, at relatively low H_2O_2 concentration ($C_{\text{H}_2\text{O}_2} < 0.33\text{ mol L}^{-1}$), the reaction rate (r_0) over C-TS-1 obviously decreased with the H_2O_2 concentration, giving the reaction kinetic order at about 0.71 (Fig. S1, ESI †). In contrast, under the same

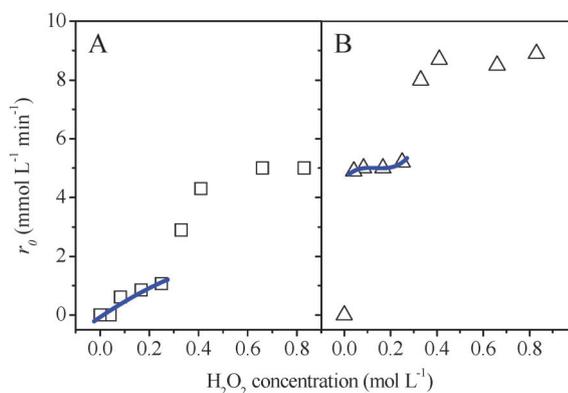


Fig. 2 Dependences of the catalytic rate (r_0) on H_2O_2 concentration over (A) C-TS-1 and (B) H-TS-1-7.5 catalysts.

conditions, the influence of H_2O_2 concentration on r_0 over the H-TS-1-7.5 catalyst is little, giving the reaction kinetic order at only 0.11 (Fig. S8, ESI †). These results suggest that the H-TS-1-7.5 catalyst with more hydroxyl groups could efficiently enhance catalytic activities in epoxidation of 1-hexene, compared with C-TS-1.

To understand the role of the hydroxyl groups in the reaction, we have measured the adsorption of H_2O_2 on H-TS-1-7.5 and C-TS-1 catalysts (Scheme S2, ESI †). As a result, it was found that the H_2O_2 reactant in the reaction can be significantly enriched in H-TS-1-7.5 because of its superior wettability for water.^{6a} For example, the H_2O_2 concentration in the pores of H-TS-1-7.5 is about 10.8 times of that in the reaction liquor, while this value is only 2.7 on the C-TS-1 catalyst. On the other hand, the H-TS-1-7.5 and C-TS-1 catalysts exhibit similar wettability to 1-hexene (another reactant in the reaction, Fig. S6, ESI †), giving similar contact angles of 1-hexene on the catalyst surface. As a result, 1-hexene adsorption tests (Fig. S9, ESI †) show that the H-TS-1-7.5 and C-TS-1 catalysts have similar adsorption capacity for 1-hexene. These results indicate that the introduction of hydroxyl groups in the H-TS-1-7.5 catalyst does not influence the adsorption of 1-hexene, but greatly enriches the H_2O_2 concentration. This phenomenon leads to a significant enhancement of the catalytic activities, in good agreement with the reactant enrichment in carbon nanotubes⁹ and porous polymer catalysts.¹⁰

Table 1 presents the catalytic data in oxidation of 1-hexene, hexane, and phenyl alcohol over various catalysts. In the 1-hexene oxidation, the C-TS-1 catalyst is catalytically active, giving the 1-hexene conversion of 21.2% (TON of 132.3, entry 1 and Fig. S10, ESI †). Very interestingly, H-TS-1-5 and H-TS-1-7.5 catalysts show much higher activities at 32.4 and 35.0 (TON of 213.8 and 243.6, entries 2 and 3 and Fig. S10, ESI †), which is reasonably assigned to the enrichment of H_2O_2 concentration in the catalysts. These results indicate that increasing the hydrophilicity of TS-1 could efficiently improve its catalytic activities. However, when a large amount of hydroxyl groups existed in the catalyst, the H-TS-1-20 catalyst exhibits a low conversion of 12.5% (TON of 85.5, entry 5), compared with C-TS-1. In consideration of the similar wettability of 1-hexene on the TS-1 samples (Fig. S6 and S9, ESI †), this phenomenon might be related to their distinguishable crystal size of the H-TS-1-20 catalyst of 1120 nm, which is much larger than that of C-TS-1 (220 nm). Larger crystal sizes have stronger limitation of mass transfer in the reaction process, giving lower catalytic activities.¹¹ Moreover, when the external active sites are poisoned by bulky molecules of 2,4-dimethylquinoline, the H-TS-1-7.5 catalyst still shows much higher conversion of 1-hexene (33.3%, entry 7) than the C-TS-1 catalyst (18.7%, entry 6), which indicates that the higher activity of H-TS-1-7.5 than C-TS-1 should have originated from the internal active sites in the micropores, rather than those in the external surface.

Similarly, the enhancement of the catalytic activities over TS-1- x catalysts with rich hydroxyl groups is also extended to the oxidation of n -hexane and benzyl alcohol (entries 8–14). In the n -hexane oxidation, H-TS-1-5 and H-TS-1-7.5 exhibit much higher conversion (23.8 and 27.9%, entries 9 and 10, TON of 78.5 and 97.1, Fig. S10, ESI †) than C-TS-1 (16.0%, entry 8, TON of 49.9, Fig. S10, ESI †). In addition, it is also found that the H-TS-1- x catalysts have higher 2- and 3-hexanone selectivity (71.0–85.0%, entries 9–12) than the C-TS-1 catalyst (66.0%, entry 8).

Table 1 Catalytic activities and selectivities in oxidation of 1-hexene, hexane, and benzyl alcohol over various catalysts^a

Entry	Substrate	Catalyst	Conv. (%)	Selectivity (%)	Others ^a
1 ^b	1-Hexene	C-TS-1	21.2	97.0	3.0
2 ^b	1-Hexene	H-TS-1-5	32.4	98.5	1.5
3 ^b	1-Hexene	H-TS-1-7.5	35.0	97.8	2.2
4 ^b	1-Hexene	H-TS-1-10	25.3	98.0	2.0
5 ^b	1-Hexene	H-TS-1-20	12.5	99.0	1.0
6 ^b	1-Hexene	C-TS-1-poisoned ^c	18.7	97.9	2.1
7 ^b	1-Hexene	H-TS-1-7.5-poisoned ^c	33.3	97.5	2.5
8 ^d	Hexane	C-TS-1	16.0	66.0	34.0
9 ^d	Hexane	H-TS-1-5	23.8	74.2	25.8
10 ^d	Hexane	H-TS-1-7.5	27.9	72.6	27.4
11 ^d	Hexane	H-TS-1-10	16.1	71.0	29.0
12 ^d	Hexane	H-TS-1-20	2.0	85.0	15.0
13 ^e	Benzyl alcohol	C-TS-1	17.6	>99.0	
14 ^e	Benzyl alcohol	H-TS-1-7.5	35.5	>99.0	

^a The C₆ alcohols, ketones, and some others. ^b Reaction conditions: 60 °C, 4 h, 0.05 g of catalyst, 10 mL of methanol, 10 mmol of 1-hexene, 10 mmol of H₂O₂. ^c 1 mmol of 2,4-dimethylquinoline into the reaction mixture. ^d Reaction conditions: 60 °C, 4 h, 0.1 g of catalyst, 10 mL of methanol, 10 mmol of cyclohexane, 20 mmol of H₂O₂. ^e Reaction conditions: 80 °C, 4 h, 0.05 g of catalyst, 3 mL of water, 5 mmol of phenyl alcohol, 10 mmol of H₂O₂.

This feature might be related to that the presence of rich hydroxyl groups on H-TS-1-*x* catalysts is favorable for the adsorption of 2- and 3-hexanol, re-oxidizing to 2- and 3-hexanone products. Similar to the phenomenon observed in the oxidation of 1-hexene, the H-TS-1-20 catalyst exhibits very low activity in the oxidation of *n*-hexane (conversion at 2.0%, entry 12, TON of 6.8, Fig. S10, ESI[†]), which might also be related to the bulky crystal size of H-TS-1-20. In the oxidation of benzyl alcohol, the H-TS-1-7.5 catalyst exhibits much higher conversion (35.5%, entries 14) than C-TS-1 (17.0%, entry 13). These results suggest wide applications of the H-TS-1-*x* catalysts in a series of catalytic oxidation with H₂O₂ in the future.

Fig. S11 (ESI[†]) shows a dependence of catalytic data in 1-hexene conversion and 1,2-epoxyhexene selectivity on reaction time over the H-TS-1-7.5 catalyst in a fixed-bed reactor. Very importantly, the H-TS-1-7.5 catalyst always retains much higher 1-hexene conversion than the C-TS-1 catalyst for a long time (100 h). These results confirm that the H-TS-1-7.5 catalyst has stable high activity, which offers a good opportunity for potential industrial applications of the highly active H-TS-1-7.5 catalyst in the future (Fig. S12, ESI[†]).

In summary, the TS-1 zeolite with rich hydroxyl groups (H-TS-1-*x*) was rationally designed and successfully synthesized by introducing methyl groups into the zeolite framework, followed by calcination to transform methyl groups to hydroxyl groups.

The obtained H-TS-1-7.5 catalyst shows a significant enhancement of catalytic activities in oxidation of hexene, hexane, and benzyl alcohol, compared with the conventional TS-1 catalyst. This phenomenon is reasonably related to the presence of hydroxyl groups in the H-TS-1-7.5 catalyst, which efficiently enrich the concentration of H₂O₂ in the micropores. Considering the wide applications of the TS-1 catalyst in industrial processes, a significant enhancement of catalytic activities by adjusting the catalyst hydrophilicity would be of great importance for the production of fine chemicals in the future. The method in this work would open a new door for developing more alternative active catalysts, such as hydrophilic ZSM-5 catalysts (Fig. S13–S16, ESI[†]).

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