

Letter

Studies on superoxide O_2^- species on the interaction of TS-1 zeolite with H_2O_2

Qi Zhao^{a,*}, Xin-he Bao^a, Yi Wang^a, Li-wu Lin^a, Gang Li^b, Xin-wen Guo^b,
Xiang-sheng Wang^b

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China

^b Laboratory of Comprehensive Utilization of Carbonaceous Resources, Dalian University of Technology, Dalian 116012, People's Republic of China

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Abstract

The interactions of silicalite-1 (S-1), titanium silicalite-1 (TS-1), Ti-Si gel and anatase with H_2O_2 were investigated by ESR technique. It was found that different Ti- O_2^- species could be formed over TS-1 zeolite and Ti-Si gel, which are dependent on the local structures of Ti atoms. The decay of O_2^- species on these samples depicted that O_2^- species on framework Ti sites are much more unstable than O_2^- species on dispersed extra framework Ti sites. The reaction of O_2^- species with phenol confirmed that O_2^- species on framework Ti sites are highly active. © 2000 Elsevier Science B.V. All rights reserved.

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Recently, titanium silicalite (TS) has attracted much attention due to its outstanding catalytic properties in the oxidation of various organic compounds using H_2O_2 as an oxidant. The reaction mechanisms over TS with H_2O_2 oxidant have stimulated great research interests, but they are still under dispute [1–4]. Notari [1,5] raised a concerted mechanism, in which titanium-peroxide complexes are considered as the active species. However, it could not give a good explanation for some reactions, such as the oxidation of alkanes. Other researchers pro-

posed a free radical mechanism, but this mechanism lacks direct support [1]. Superoxide O_2^- species over metal oxides and zeolitic systems usually act as active species in radical reactions [6,7]. Geobaldo et al. [9] reported that Ti- O_2^- species could be formed in titanium silicalite-1 (TS-1) zeolite in the presence of H_2O_2 . However, few literature discussed whether superoxide O_2^- species could be also formed on dispersed extra framework Ti, and what the roles of different Ti- O_2^- species were in these oxidation reactions. In this article, we have investigated the interactions of TS-1, silicalite-1 (S-1), Ti-Si gel and anatase with H_2O_2 by means of ESR technique, and found that superoxide O_2^-

* Corresponding author. Fax: +86-411-470-9962.
E-mail address: zhaqiqi@ms.dicp.ac.cn (Q. Zhao).

species can be formed on both dispersed extra framework Ti sites and framework Ti sites. The oxidative abilities of Ti-O_2^- species are related to the local structures of Ti atoms.

TS-1 and S-1 zeolites were synthesized using tetrapropylammonium bromide as a template [8]. Ti-Si gel was obtained with the same method as TS-1 but with a short heating time, and was verified by XRD to have an amorphous structure. All the samples were calcined at 813 K for 5 h. The ESR experiments were carried out on a JEOL ES-EDX3 ESR spectrometer at room temperature. The frequency and power of the microwave were 9.230 GHz and 1 MW, respectively. Mn^{2+} cation was taken as an external reference. During the measurements, 0.04-g fresh samples were first saturated with an aqueous solution of H_2O_2 (50 mass%). In order to suppress the effects of polar H_2O molecules, the saturated samples were blotted with filtering paper, and then, were diluted with 0.12-g fresh samples.

The ESR spectra of the samples adsorbed with H_2O_2 are shown in Fig. 1. The adsorbed TS-1 zeolite and Ti-Si gel gave two signals at $g_{zz} = 2.0236$, $g_{yy} = 2.0100$, $g_{xx} = 2.0091$ and $g_{zz} = 2.0270$, $g_{yy} = 2.0100$, $g_{xx} = 2.0091$, which are assigned to superoxide O_2^- anions.

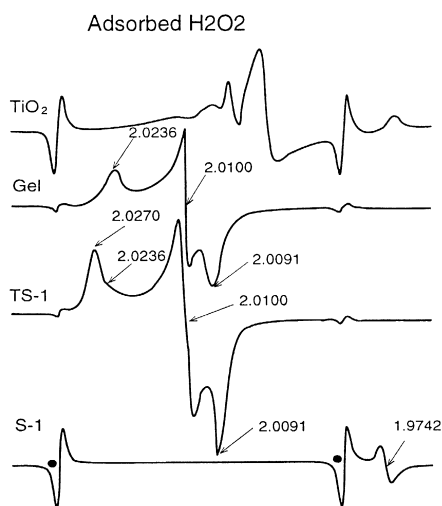


Fig. 1. ESR spectra of samples adsorbed with H_2O_2 (● Mn^{2+} signal).

On S-1 and anatase adsorbed with H_2O_2 , these resonances could not be observed (the lines in the spectrum of the anatase originate from the impurities). Because the UV-Vis spectra (not shown in this paper) of fresh TS-1 zeolite and Ti-Si gel have indicated that there is no anatase phase in the samples and superoxide O_2^- anions are usually stabilized at positive cationic sites [1,2,9,10], it can be concluded that superoxide O_2^- species in adsorbed TS-1 and Ti-Si gel located on framework Ti sites and dispersed extra framework Ti sites. The signal at $g_{zz} = 2.0236$, $g_{yy} = 2.0100$, and $g_{xx} = 2.0091$ in Ti-Si gel is attributed to O_2^- species on dispersed extra framework Ti sites. The spectrum of adsorbed TS-1 zeolite shows a strong O_2^- signal ($g_{zz} = 2.0270$, $g_{yy} = 2.0100$, $g_{xx} = 2.0091$) with a weak signal associated with O_2^- species on dispersed extra framework Ti sites. Since Ti atoms are incorporated into the framework of TS-1 zeolite, the strong signal is soundly assigned to O_2^- species on framework Ti sites and the weak one is assigned to O_2^- species on dispersed extra framework Ti sites. The two O_2^- signals present different g_{zz} values but the same g_{xx} and g_{yy} values. According to the formula of $g_{zz} = g_e + 2/(\lambda, \text{spin-orbit coupling constant of oxygen}; \Delta, \text{crystal field stabilization energy})$, the magnitude of g_{zz} component of O_2^- species is sensitive to cationic crystal field [2,10,11]. The larger g_{zz} value from O_2^- species on framework Ti reflects that the distance between O_2^- and framework Ti site is longer than that between O_2^- and dispersed extra framework Ti sites [11]. This means that the former is more active than the latter.

The decays of O_2^- species on adsorbed TS-1 zeolite and Ti-Si gel are shown by the ESR spectra in Fig. 2. On TS-1 adsorbed with H_2O_2 , the intensity of O_2^- signal on framework Ti gradually decreases with time. After 5.5 h, there is only a weak signal of O_2^- on dispersed extra framework Ti sites. On adsorbed Ti-Si gel, the intensity of the signal of O_2^- species on dispersed extra framework Ti decreased slowly to 30% after 20 h. On both TS-1 and Ti-Si gel,

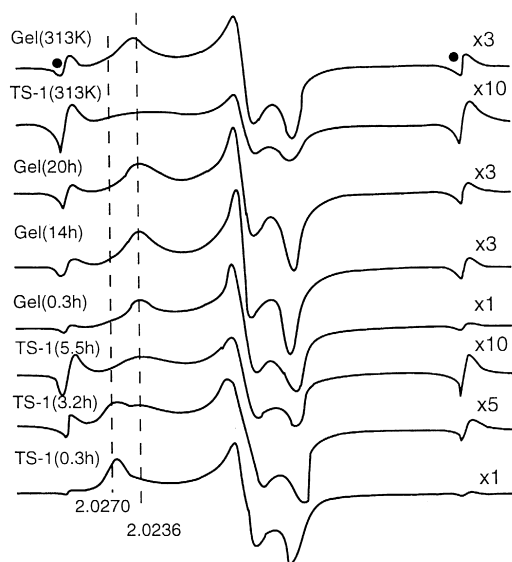


Fig. 2. ESR spectra of TS-1 and Ti-Si gel adsorbed with H_2O_2 at different times and of those heated for 5 min at 333 K (● Mn^{2+} signal).

the signal of O_2^- species on extra framework Ti can still be observed even after heating at 313 K (usual reaction temperature) for 5 min (as shown in Fig. 2). This indicates that O_2^- species on

dispersed extra framework Ti are much more stable than those on framework Ti sites. Our reaction results [12] have demonstrated that the former does not catalyze the decomposition of H_2O_2 . Compared with Ti-Si gel, the local structures of framework Ti atoms in TS-1 zeolite do not easily change. Thus, the repulsion originated from Ti-O-Si bonds on O_2^- species on framework Ti are larger than those on Ti-Si gel, which makes O_2^- species away from framework Ti sites and activate O_2^- species. The O_2^- species on dispersed extra framework Ti is very stable and has no oxidative ability due to the shorter distance between O_2^- species and Ti sites. This is consistent with the g_{zz} values of the corresponding O_2^- signals.

In order to elucidate the roles of Ti-O $_2^-$ species, we further investigated the effect of adsorption of phenol. Fig. 3 shows the corresponding ESR spectra. After phenol in an acetone solution was dropped into TS-1 adsorbed with H_2O_2 , the lines from O_2^- species on framework Ti disappeared and a new intense signal with $g = 2.0070$ and 2.0036 near g_e ap-

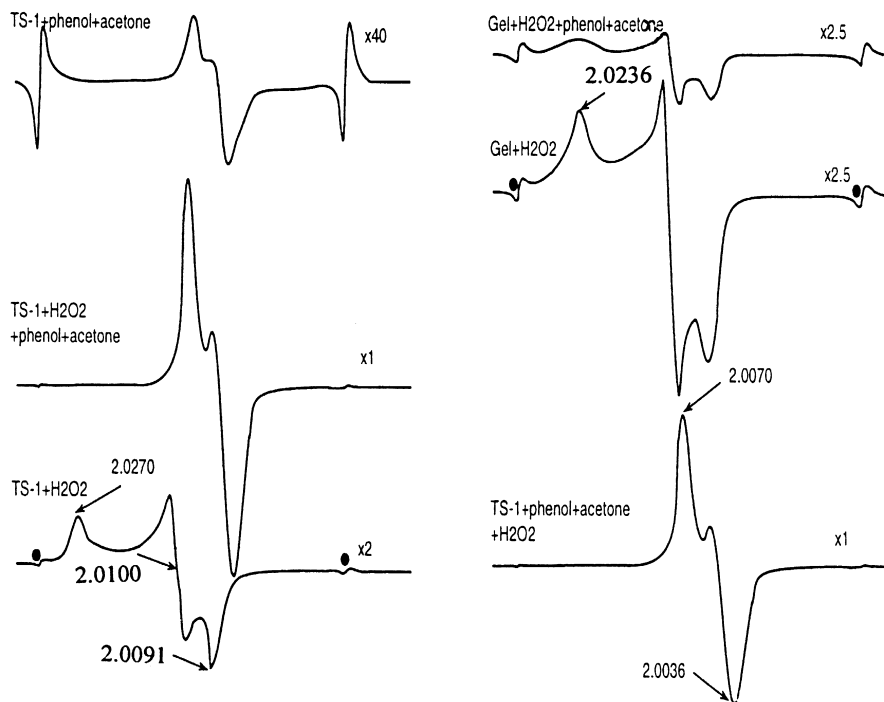


Fig. 3. ESR spectra of TS-1 and Ti-Si gel adsorbed with reactants (● Mn^{2+} signal).

peared. However, the spectrum of fresh TS-1 adsorbed with phenol only gave a very weak signal with $g = 2.0070$ and 2.0036 . After H_2O_2 was added subsequently, the intense signal was restored again. It is well known that O_2^- species can abstract H atom from hydrocarbon and form an organic free radical [6,12]. Gilbert et al. [13] reported that O_2^- species could get H from phenoxy compound and form a phenoxy free radical in the oxidation reaction. Therefore, it is reasonable to attribute the signal with $g = 2.0070$ and 2.0036 to the phenoxy radicals. The phenoxy radical signal increased with the decrease of O_2^- on framework Ti, which suggested that the O_2^- species are the active species and the reaction takes place with the free radical mechanism. On Ti–Si gel adsorbed with H_2O_2 and phenol, no phenoxy radical signal was found, which indicated that the O_2^- on dispersed extra framework Ti has little oxidation ability.

In conclusion, we found that O_2^- species can be generated on both framework Ti sites and highly dispersed extra framework Ti sites. The O_2^- species on framework Ti sites are active species and those on dispersed extra framework

Ti sites show no oxidative ability. The effects of the structures of zeolite and gel on $Ti-O_2^-$ species are reflected by the g_{zz} components of the O_2^- signals in ESR spectra. The appearance of the phenoxy radical with the disappearance of O_2^- species framework Ti sites provided a direct support for the free radical mechanism.

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