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Effect of pretreatment on properties of TS-1/diatomite catalyst for hydroxylation of phenol by H_2O_2 in fixed-bed reactor

Hong Liu [a,b], Guanzhong Lu [a,*], Yanglong Guo [a], Yun Guo [a], Junsong Wang [a]

[a] *Lab for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, China*
[b] *College of Environmental and Chemical Engineering, Shanghai University, Shanghai 200072, China*

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Abstract

The TS-1/diatomite catalyst was prepared for the hydroxylation of phenol with H_2O_2 in the fixed-bed reactor and the effects of pretreatment on the properties of TS-1/diatomite were studied by FT-IR, XRD, UV–vis, ICP-AES, BET surface area and NH_3-TPD techniques. It is shown when the catalyst is pretreated by the KAc, NaAc, NH_4Ac, NH_4Cl or HNO_3 aqueous solution, the framework structure of TS-1 is not destroyed and titanium in the framework is not removed. The surface area of catalyst has no obvious change compared with that of the untreated catalyst. But the extra-framework TiO_2 can be removed partly, which leads to the slight increase of the crystallinity of catalyst and the decrease of acid concentration on the surface of the TS-1/diatomite catalyst. As a result, the activity, selectivity and utilization of H_2O_2 for hydroxylation of phenol are improved. After the TS-1/diatomite catalyst is pretreated by the $NH_3{\cdot}H_2O$, Na_2CO_3 or Na_3PO_4 solution, its framework silicon is dissolved partly in the base solution and the framework structure of TS-1 is destroyed. While the crystallinity and surface area of catalyst decrease and the concentration of acid sites on the surface of catalyst increased slightly. As a result, the catalytic activity of the TS-1/diatomite catalyst for hydroxylation of phenol descended or deactivated completely.

Keywords: TS-1/diatomite; Pretreatment; Phenol; Hydroxylation; Fixed-bed reactor

1. Introduction

Titanium-substituted silicalite-1 (TS-1) with MFI structure was first synthesized by Taramasso and co-workers in 1983 [1]. As a novel catalysis material, TS-1 has received a considerable interest in the past 20 years, because of its unique catalytic properties for the selective oxidation reactions using hydrogen peroxide as the oxidant, such as aromatic hydroxylation [2], epoxidation of alkenes [3], ammoximation of cyclohexanone [4], oxidation of alkanes and alcohols [5] and so on. The preparation and characterization of TS-1 has been investigated in some detail in recent years. Many studies showed that TS-1 pretreated by the suitable aqueous solution has higher activity than the original catalyst [6,7], but the effects of pretreatment on the physicochemical properties of TS-1, especially for the supported TS-1 catalyst, is not yet known unambiguously.

Recently, we have developed the supported TS-1 on diatomite catalyst for the hydroxylation of phenol in the fixed-bed reactor operated continuously [8]. Compared with the batch process, this process has many advantages, such as freedom from tiresome operations (the catalyst filtration and makeup), and operation in large scale. In this paper, the TS-1/diatomite catalyst for the hydroxylation of phenol by hydrogen peroxide was used as a model catalyst and pretreated with different acid, base or salt aqueous solutions. By means of the systematical investigations of the physicochemical and catalytic properties of the pretreated catalyst, the effects of pretreatment on the performance of the supported TS-1 catalyst are discussed.

2. Experimental

2.1. Synthesis of TS-1 and preparation of TS-1/diatomite catalyst

TS-1 ($Si/Ti = 27$, atom) was prepared by hydrothermal synthesis according to the method described in the literature [9], using tetraethylothosilicate (TEOS) as silicon source, tetrabutylorthotitanate (TBOT) as titanium source

* Corresponding author. Fax: +86 21 64253707.
E-mail address: gzhlu@ecust.edu.cn (G. Lu).

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and tetrapropylammonium hydroxide (TPAOH) as template. The mean crystal size of TS-1 is about 0.25 μm measured by scanning electron microscopy (SEM).

The TS-1/diatomite catalyst was prepared by mixing TS-1 powder calcined with diatomite (TS-1/diatomite = 1/1, wt.), then pressed and crushed to 0.45–0.9 mm.

2.2. Pretreatment of TS-1/diatomite catalyst

8.5 g TS-1/diatomite was placed into a flask and then 25 ml aqueous solution including the pretreatment reagent (HNO_3, KAc, NaAc, NH_4Ac, NH_4Cl, $NH_3{\cdot}H_2O$, Na_2CO_3 or Na_3PO_4) was added. After refluxed at 80 °C for 3 h, the pretreated catalyst was filtered, washed with distilled water, dried at 120 °C and calcined at 550 °C for 6 h in air.

2.3. Characterization of catalyst

X-ray diffraction (XRD) analysis was performed on the Rigaku D/max-2400 diffractometer using CuKα radiation and graphite monochromator. Infrared (IR) spectra were recorded on the Nicolet Nexus FT-IR spectrometer and the catalyst to be measured was ground with KBr and pressed into thin wafers. UV–vis spectra were measured by the Varian Cary-500 spectrometer, in which the diffuse reflectance technique in the range of 200–500 nm was used and $BaSO_4$ was used as the reference. The chemical compositions of the catalyst were determined by ICP-AES (TJAIRIS 1000) after dissolved in the HF–$HClO_4$ solution. The acidity of the catalyst was determined by the NH_3-TPD technique, the rate of temperature programmed is 10 °C/min. The BET surface area of catalyst was determined according to the N_2 adsorption isotherms measured by Micrometrics ASAP 2010.

2.4. Hydroxylation of phenol

The hydroxylation of phenol was carried out in the continuous flow fixed-bed glass reactor (Ø15 mm). Seven grams of catalyst was placed in the isothermal region of reactor, and the mixture of phenol, 30% H_2O_2 and solvent (acetone) was imported from the bottom of reactor by a metric pump. The reaction condition was controlled at 84 °C, phenol/H_2O_2 = 3:1 (mol), phenol/acetone = 1.25:1 (wt.) and WHSV = 8.46 h^{-1}. The concentration of H_2O_2 was analyzed by an iodometric titration. The organic products were analyzed by the PE Autosystem XL chromatograph, in which the flame ionization detector and capillary column (Ø0.32 mm × 25 m) containing 5% methyl benzene silicone were used. The conversion of phenol and the selectivity to product are defined as follows:

$$X_{\text{phenol}} = \frac{n^0_{\text{phenol}} - n_{\text{phenol}}}{n^0_{\text{phenol}}}$$

$$X_{H_2O_2} = \frac{n^0_{H_2O_2} - n_{H_2O_2}}{n^0_{H_2O_2}}$$

$$S_{\text{DHB}} = \frac{n_{\text{CAT}} + n_{\text{HQ}}}{n_{\text{CAT}} + n_{\text{HQ}} + n_{\text{PBQ}}}$$

$$U_{H_2O_2} = \frac{n_{\text{CAT}} + n_{\text{HQ}} + n_{\text{PBQ}}}{n^0_{H_2O_2} \times X_{H_2O_2}}$$

X_{phenol} is the conversion of phenol, $X_{H_2O_2}$ the conversion of H_2O_2, S_{DHB} the selectivity to dihydroxybenzene, $U_{H_2O_2}$ the utilization of H_2O_2, n^0 the initial mole concentration and n the final mole concentration. CAT: catechol, HQ: hydroquinone and PBQ: *p*-benzoquinone.

3. Results and discussion

3.1. Effect of pretreatment on physicochemical properties of TS-1/diatomite

3.1.1. FT-IR

The catalytic performance of TS-1 is related to the amount of Ti in the framework of zeolite. The FT-IR technique is one of the useful tools to characterize framework titanium in zeolite. In the FT-IR spectra of the TS-1/diatomite catalyst (Fig. 1) pretreated with acid, weak basic salts or weak acidic salts (HNO_3, KAc, NaAc, NH_4Ac and NH_4Cl), there are the peak at about 960 cm^{-1}, which indicates that titanium has been incorporated into the framework of zeolite. Reddy and co-workers [10] thought that the relative intensity I_{960}/I_{550} increased linearly with the increase of titanium amount in

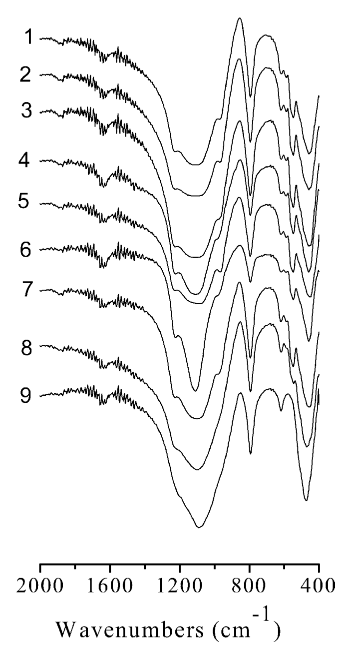

Fig. 1. FT-IR spectra of TS-1/diatomite (1) and the catalyst pretreated with HNO_3 (2), KAc (3), NaAc (4), NH_4Cl (5), NH_4Ac (6), $NH_3{\cdot}H_2O$ (7), Na_2CO_3 (8) and Na_3PO_4 (9).

Table 1
The feature data of FT-IR spectra of TS-1/diatomite pretreated with different aqueous solution

Pretreatment	I_{960}/I_{550}
Untreated	1.03
KAc	1.06
NaAc	1.03
NH_4Ac	1.04
NH_4Cl	1.01
HNO_3 [a]	1.05
$NH_3 \cdot H_2O$ [a]	0.84
Na_2CO_3	0.75
Na_3PO_4	0

[a] Its concentration is 2N, others is 10% (wt.).

Table 2
Chemical composition of TS-1/diatomite analyzed by ICP-AES

Pretreatment	TiO_2 (wt.%)	SiO_2 (wt.%)
Untreated	3.10	96.77
10%Na_3PO_4	3.64	96.23

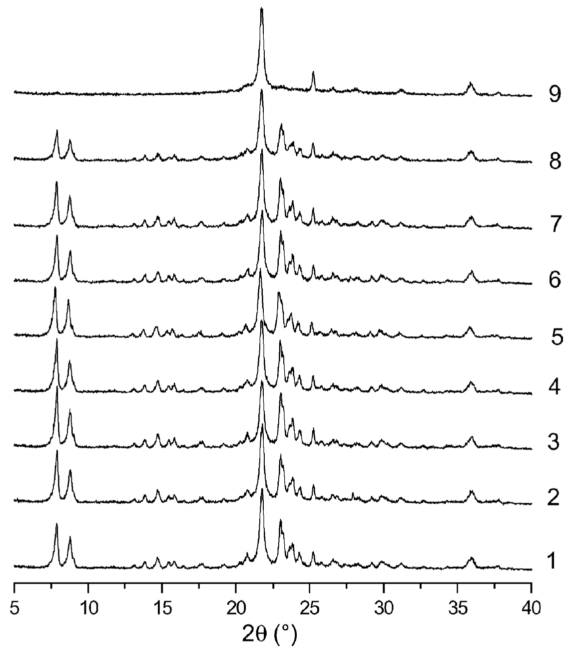

Fig. 2. XRD patterns of TS-1/diatomite (1) and the catalyst pretreated with HNO_3 (2), KAc (3), NaAc (4), NH_4Cl (5), NH_4Ac (6), $NH_3 \cdot H_2O$ (7), Na_2CO_3 (8) and Na_3PO_4 (9).

framework. The results in Table 1 show that I_{960}/I_{550} of the catalyst is not changed obviously after pretreated with acid, weak basic salts or weak acidic salts. This indicates that the number of active titanium site on the catalyst does not reduce. However, when the catalyst was treated with bases ($NH_3 \cdot H_2O$, Na_2CO_3 and Na_3PO_4), its intensity of the absorption peak in 960 cm^{-1} became weak and the relative intensity I_{960}/I_{550} decreased with an increase of the basicity of the pretreatment reagents. After the catalyst was treated by the Na_3PO_4 solution, its peaks in 960 and 550 cm^{-1} disappeared completely and the peak in 450 cm^{-1} shift to high wavenumber. The results above show that the base medium can destroy the framework structure of TS-1.

The results in Table 2 show that the content of silicon in the catalyst has been reduced after pretreated in the 10% Na_3PO_4 solution, that is to say, the silicons in the TS-1 frameworks have dissolved partly in the pretreatment solution, leading to destructing of the TS-1 frameworks.

3.1.2. XRD

The XRD spectra of the catalysts are shown in Fig. 2 and their crystallinities were estimated by the intensity changes of five characteristic diffraction peaks ($2\theta \approx 7.8^\circ$, 8.8°, 23.1°, 23.8° and 24.4°) of the MFI zeolite. The results in Fig. 2 show that all the samples behave the typical MFI structure except the catalyst pretreated with Na_3PO_4 and have the peak at $2\theta \approx 25.3^\circ$ of the anatase TiO_2 phase. Yasuyuki and co-workers [11] thought that the relative intensity $I_{25.3}/I_{24.4}$ increases with an increase of the TiO_2 amount in the extra-framework. After the catalyst was pretreated with HNO_3, KAc, NaAc, NH_4Ac or NH_4Cl, its relative intensity $I_{25.3}/I_{24.4}$ in the XRD spectra decreased slightly (Table 3), but the peak intensity at $2\theta \approx 24.4^\circ$ attributed to the framework titanium was not changed obviously (Fig. 2). This demonstrates that the anatase TiO_2 in an extra-framework can be removed partly by acid, weak basic salts or weak acidic salts, but the titanium in frameworks cannot be removed by pretreatment. Compared with the untreated catalyst, the crystallinity of catalyst treated with HNO_3, KAc, NaAc, NH_4Ac or NH_4Cl increased slightly. This further confirms that some anatase TiO_2 in an extra-framework has been eliminated. However, the crystallinity of catalyst treated with the $NH_3 \cdot H_2O$ or Na_2CO_3 solutions decreased, and the intensity of peak in $2\theta \approx 24.4^\circ$ became weak. In the XRD pattern of the catalyst treated with Na_3PO_4, no characteristic peaks of the MFI structure were found and its relative crystallinity was 0%.

Table 3
The feature data of XRD spectra of TS-1/diatomite pretreated with different aqueous solution

	Pretreatment								
	Untreated	KAc	NaAc	NH_4Ac	NH_4Cl	HNO_3 [a]	$NH_3 \cdot H_2O$ [a]	Na_2CO_3	Na_3PO_4
$I_{25.3}/I_{24.4}$	1.07	0.97	0.99	1.01	1.02	1.04	1.20	1.30	∞
Relative crystallinity (%)	100	117	103	105	103	103	96.4	65.1	0

[a] Its concentration is 2N, others is 10% (wt.).

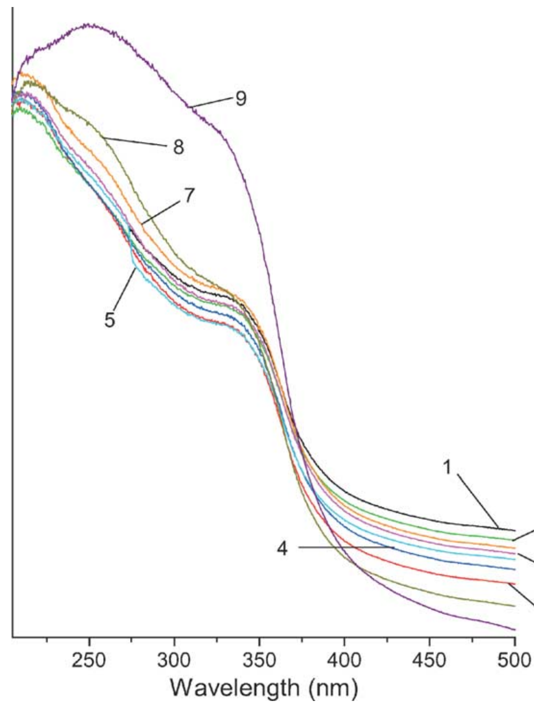

Fig. 3. UV–vis spectra of TS-1/diatomite (1) and the catalyst pretreated with HNO_3 (2), KAc (3), NaAc (4), NH_4Cl (5) NH_4Ac (6), $NH_3{\cdot}H_2O$ (7), Na_2CO_3 (8) and Na_3PO_4 (9).

3.1.3. UV–vis

The UV–vis spectroscopy is one of technologies to detect sensitively TiO_2 outside the framework of zeolite. Fig. 3 shows that, the UV–vis spectra of all the catalysts except one treated by the Na_3PO_4 solution have two absorption peaks, one at 210 nm attributed to tetra-coordinated titanium inside the frameworks and another one at 330 nm attributed to anatase TiO_2 [12,13]. The peak at 270–280 nm have not been observed in all the spectra, i.e., there is no hexa-coordinated titanium species (e.g., hydrated oligomeric TiO_x) in the catalysts. After the catalysts was treated with the HNO_3, KAc, NaAc, NH_4Ac or NH_4Cl solution, the intensity of the absorption peak at 330 nm decreased, which indicates that some TiO_2 located at the extra-framework can be removed by pretreatment. These results are in agreement with the results obtained by XRD. In the UV–vis spectrum of the catalyst treated with Na_3PO_4, there are two absorption peaks at 330 and 249 nm, the latter is a new absorption peak. At 210 nm no absorption peak can be observed. The results above confirm further after the TS-1/diatomite is pretreated by the base solution, the framework structure of TS-1 would be destroyed.

3.1.4. BET surface area

Table 4 shows that the BET surface area of catalyst treated with HNO_3, KAc, NaAc, NH_4Ac or NH_4Cl is almost the same as that of the untreated catalyst. But, after the catalyst was treated with the $NH_3{\cdot}H_2O$, Na_2CO_3 or Na_3PO_4 solution, its BET surface area decreased obviously, in which one pretreated with the Na_3PO_4 solution has a lowest surface area, 95.3 m^2/g. This shows also that the framework structure of TS-1 is destructed gradually during its boiling in the base solution.

Table 4
BET surface area of TS-1/diatomite pretreated with different aqueous solution

Pretreatment	S_{BET} (m^2/g)
Untreated	196.5
KAc	199.8
NaAc	198.2
NH_4Ac	193.7
NH_4Cl	199.4
HNO_3 [a]	194.1
$NH_3{\cdot}H_2O$ [a]	184.1
Na_2CO_3	140.0
Na_3PO_4	95.3

[a] Its concentration is 2N, others is 10% (wt).

3.1.5. NH_3-TPD

The TPD spectra of NH_3 adsorbed on catalyst are shown in Table 5. After the catalysts were pretreated with the aqueous solution of KAc, NaAc, NH_4Ac, NH_4Cl or HNO_3, the acid strength (the top peak temperature) on the surface of the TS-1/diatomite catalyst changed hardly, but the acid amount (the peak area) decreased slightly. This is attributed to some extra-framework TiO_2 and impurities to be removed. When the catalyst was pretreated by bases solution of Na_2CO_3 and Na_3PO_4, the strength and amount of acid sites on the surface of catalyst increased slightly. It is known that the framework silicon of TS-1 is dissolved partly in the base solution and the relative amount of TiO_2 in the catalyst increases (Table 2), which leads to the increase of acid sites on the surface of the TS-1/diatomite catalyst. Another reason is that the framework destruction of TS-1 causes changing of acid sites on the surface of catalyst.

3.2. Effect of pretreatment on catalytic performance of TS-1/diatomite

The results in Table 6 show that the pretreatment agents affect greatly the performance of catalyst for the hydroxy-

Table 5
NH_3-TPD data of TS-1/diatomite pretreated with different aqueous solution

Pretreatment	Top peak temperature (°C)	Peak area (a.u./g)
Untreated	125	486
KAc	129	348
NaAc	130	405
NH_4Ac	128	441
NH_4Cl	124	482
HNO_3 [a]	125	378
$NH_3{\cdot}H_2O$ [a]	134	400
Na_2CO_3	124–176	703
Na_3PO_4	124–178	654

[a] Its concentration is 2N, others is 10% (wt.).

Table 6
Effect of pretreatment reagent on catalytic performance of TS-1/diatomite

Pretreatment	X_{phenol} (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)	$U_{H_2O_2}$ (%)	CAT/HQ
Untreated	24.8	95.3	96.5	67.5	1.04
KAc	25.7	95.7	97.8	70.5	0.91
NaAc	25.9	96.4	98.0	70.3	0.87
NH_4Ac	25.1	95.4	97.8	69.0	0.87
NH_4Cl	25.0	96.5	98.1	67.5	0.86
HNO_3[a]	25.0	96.0	98.2	67.9	0.86
$NH_3{\cdot}H_2O$[a]	22.5	90.8	95.7	66.5	1.15
Na_2CO_3	11.4	81.3	85.8	41.0	2.28
Na_3PO_4	0.32	96.0	0	0	∞

[a] Its concentration is 2N, others is 10% (wt.). Reaction condition: phenol/H_2O_2 = 3/1(mol), phenol/acetone = 1.25/1(wt.), WHSV = 8.46 h^{-1}, 84 °C. CAT: catechol, HQ: hydroquinone, DHB: dihydroxybenzene.

lation of phenol. The activity, selectivity and efficiency in utilization of H_2O_2 were improved over the catalyst pretreated by the HNO_3, KAc, NaAc, NH_4Ac or NH_4Cl solution, and the amount of hydroquinone in products increased obviously, which should be studied further. When the catalyst was treated with the base ($NH_3{\cdot}H_2O$, Na_2CO_3 and Na_3PO_4) solution, the catalytic activity, selectivity and efficiency in utilization of H_2O_2 decreased with increasing of basicity of the pretreatment agent. Using the catalyst treated with the strong base Na_3PO_4 solution, the hydroxylation of phenol was almost completely blocked and no objective products formed, but the decomposition of H_2O_2 occurred continually. Some impurities and extra-framework TiO_2 can be formed unavoidably in the catalyst prepared, and these impurities and extra-framework TiO_2 can promote the decomposition of H_2O_2 and affect the acidity on the surface of catalyst and the performance of catalyst for the hydroxylation of phenol [14].

The results above show that, the extra-framework TiO_2 in TS-1/diatomite may be removed by pretreated with the HNO_3, KAc, NaAc, NH_4Ac or NH_4Cl solution, which causes the increase of the activity, selectivity and efficiency in utilization of H_2O_2 for the hydroxylation of phenol. When the base solution is used to treat the catalyst, the framework silicon may be dissolved partly to lead to the decrease or loss of the framework titanium and the catalytic performance of the TS-1/diatomite catalyst, and this deactivation of the catalyst is irreversible.

4. Conclusion

After the TS-1/diatomite catalyst is pretreated with aqueous solution of KAc, NaAc, NH_4Ac, NH_4Cl or HNO_3, its framework structure is not destroyed and titanium in the framework is not removed and its surface area changes hardly, but some extra-framework TiO_2 could be removed partly, which leads to the slight increase of the crystallinity of catalyst and the amount decrease of acid sites on the surface of catalyst. As a result, the activity, selectivity, utilization of H_2O_2 and the HQ/CAT ratio of product for hydroxylation of phenol are improved. When the TS-1/diatomite catalyst is pretreated by a base solution, the framework silicon of catalyst is dissolved partly and the framework structure of TS-1 is destroyed, causing the decrease of the crystallinity and surface area of catalyst and the increase of acid sites on the surface of catalyst. As a result, the catalytic activity of the TS-1/diatomite catalyst for hydroxylation of phenol descended or deactivated completely.

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