

Article

Direct Hydroxylation of Benzene to Phenol over TS-1 Catalysts

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Abstract: We synthesized a TS-1 catalyst to directly hydroxylate benzene to phenol with H_2O_2 as oxidant and water as solvent. The samples were characterized by FT-IR (Fourier Transform Infrared), DR UV-Vis (Diffused Reflectance Ultraviolet Visible), XRD (X-ray diffraction), SEM (scanning electron microscope), TEM (Transmission Electron Microscope), XPS (X-ray photoelectron spectroscopy), ICP (inductively coupled plasma spectrum), and N_2 adsorption-desorption. A desirable phenol yield of 39% with 72% selectivity was obtained under optimized conditions: 0.15 g (0.34 to the mass of benzene) TS-1, 5.6 mmol C_6H_6 , reaction time 45 min, 0.80 mL H_2O_2 (30%), 40.0 mL H_2O , and reaction temperature 70 °C. The reuse of the TS-1 catalyst illustrated that the catalyst had a slight loss of activity resulting from slight Ti leaching from the first run and then kept stable. Almost all of the Ti species added in the preparation were successfully incorporated into the TS-1 framework, which were responsible for the good catalytic activity. Extraframework Ti species were not selective for hydroxylation.

Keywords: benzene; hydroxylation; phenol; TS-1 catalyst

1. Introduction

Phenol is an important chemical widely used in medicine, pesticides, plastics, and so on. The cumene method is the main process for phenol production in current commercial manufacturing, and this method has three steps from benzene to the target product [1–3]. The yield of phenol is not high, with disadvantages of high energy consumption and equipment corrosion. There is also an equimolar amount of acetone formed as a co-product [4,5]. The number of studies on the synthesis of phenol directly from benzene has been increasing, emphasizing environmental friendliness and economic feasibility. The one-step direct hydroxylation of benzene to phenol with hydrogen peroxide, which requires the activation of C–H bonds in the aromatic ring and the subsequent insertion of oxygen, has drawn much attention [6–9]. Several efficient catalysts with high activity and stability have been designed and tested [10–13].

TS-1, a Ti-containing MFI (Mordenite Framework Inverted) structure zeolite, first synthesized in 1983 by Taramasso et al. [14], has been found to display excellent catalytic activity in the oxidation of the aromatic ring, such as aromatic hydroxylation and cyclohexanone ammoxidation [15–18]. A TS-1-catalyzed reaction can proceed under mild conditions with aqueous H_2O_2 as the oxidant so as to satisfy the demand of environmental protection. TS-1 suffers from an intracrystalline diffusion limitation on account of the micropores blocked by the reaction intermediates and by-products, and this limitation is most pronounced for a low temperature liquid phase reaction [19,20]. Thereby, research on TS-1 post-synthesis to extend the pore size has attracted much attention, where the pore-modified TS-1 catalyst may possess the advantage of a micro/mesoporous structure. Hierarchical zeolites possess

both the typical characteristics of zeolites and the properties usually related to amorphous materials, such as a crystalline structure and the presence of larger pores [21]. The practical applications of hierarchical zeolites have been greatly extended, and have become one of the excellent potential strategies to overcome the mass transport limitation in the catalyst [22].

In our previous work, an activated carbon catalyst was found to be efficient for the direct hydroxylation of benzene [23,24]. However, the repeated use of the activated carbon catalyst requires cumbersome treatments, and the yield of phenol was not high enough. The Fe-loaded ZSM-5 catalyst, with N_2O as the oxidant in a hydroxylation reaction, usually had an excellent selectivity to phenol [25]. On hierarchical zeolite material post-treated ZSM-5, N_2O oxidated benzene to phenol with good stability and selectivity [26]. There are some reports of benzene hydroxylation by a Pd-loaded membrane reactor, with H_2 and O_2 gases as co-reactants, which had good selectivity [27–29]. N_2O as an oxidant requires a high reaction temperature, and O_2 as an oxidant usually requires inert gas as a carrier. Therefore, H_2O_2 as a cheap and energy-saving oxidant is widely used in current research. Liya Hu et al. reported that vanadium-containing mesoporous carbon composites displayed superb catalytic activity, but the reuse was not good enough [30]. In the hydroxylation of benzene by the PQ Corporation commercial catalyst TS-PQTM, the conversion of H_2O_2 was 19.4% and the selectivity of the phenol was 92% with an excess use of benzene [31]. The Fe-CN/TS-1 catalysts, with metal chloride as a precursor and a TS-1 zeolite as a support, could oxidize benzene to phenol in a biphasic water- H_2O_2 /acetonitrile medium with visible light irradiation [32,33]. Therefore, the preparation of a catalyst with high catalytic activity and high stability is of great interest.

In the present work, a TS-1 catalyst was synthesized with a modified method and used for benzene hydroxylation to phenol, with H_2O_2 as the oxidant and water as the solvent. Commercial TS-1 and S-1 were also used for comparison.

2. Results and Discussion

2.1. Catalytic Activity Test

2.1.1. Optimization of Reaction Conditions

The effect of reactant concentration. The concentration of hydrogen peroxide was investigated, and the results are shown in Figure 1a. With an increasing concentration of H_2O_2 , the yield of phenol (PH) increased, reached the maximum at the concentration of 0.20 mol/L, and then decreased. The yield of catechol (CAT), hydroquinone (HQ), and benzoquinone (BQ) monotonously increased. The high concentration of H_2O_2 led to the over-oxidation of phenol to dihydroxybenzene (DHB, namely, CAT and HQ) and benzoquinone [34], so the selectivity of the phenol did not change much when the concentration of H_2O_2 was less than 0.20 mol/L. Then, the selectivity of the phenol decreased gradually for the production of more DHB and benzoquinone.

The effect of reaction temperature. The activity of the catalysts was tested at 50 °C, 60 °C, 70 °C, 80 °C, and 90 °C, and the results are shown in Figure 1b. With an increasing reaction temperature, the yield of phenol enhanced, reached a maximum at 70 °C, and then decreased, whereas the yield of DHB increased monotonously. It has been reported that a low temperature is beneficial to restrain the over-oxidation of phenol [35,36]. When the reaction temperature reached 80 °C, the generation of by-products was significantly faster than the generation of phenol, which led to an obvious decrease of selectivity to phenol.

The effect of reaction time. The reaction time was studied in the range of 25–65 min and the results are shown in Figure 1c. The conversion of benzene and the yields of DHB and benzoquinone increased monotonically with time. However, the yield of phenol increased within 45 min and then decreased, and the selectivity of phenol was stable within 45 min and then decreased. A longer reaction time resulted in an increased formation of over-oxidation products [37], which reduced the yield and selectivity to phenol.

The effect of catalyst amount. The mass ratio of TS-1 to benzene was increased from 0.30 to 0.39, and the results are shown in Figure 1d. The yield of phenol increased with the mass ratio of TS-1 to benzene up to 0.38, and the yield of over-oxidation products, DHB and benzoquinone, had the same variation trend. When the mass ratio of TS-1 to benzene was greater than 0.39, the excess catalyst might catalyze the noneffective decomposition of H_2O_2 , which was responsible for the decrease of benzene conversion. Considering the yield and selectivity of phenol, a mass ratio of TS-1 to benzene of around 0.34, namely 0.15 g TS-1, was rational.

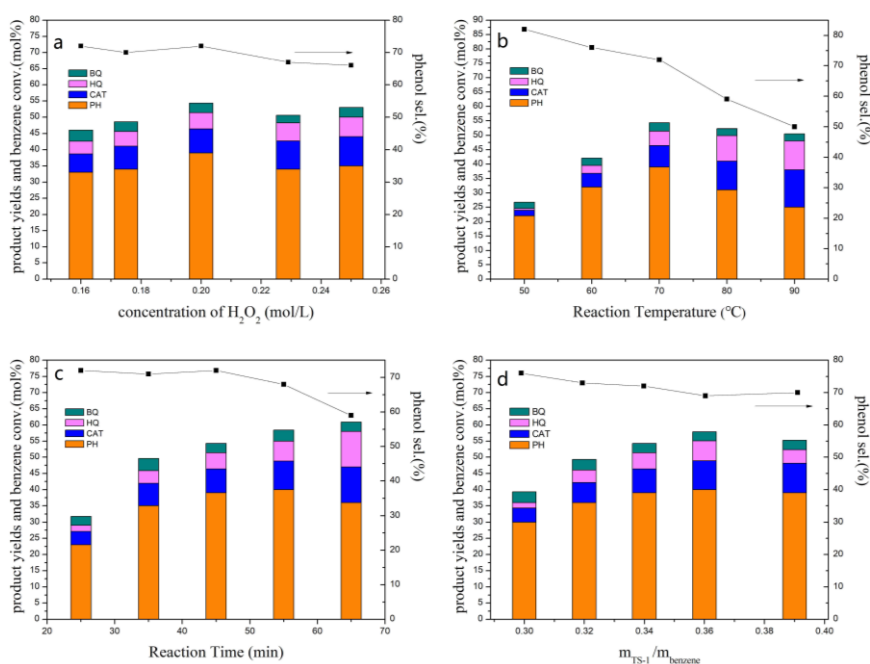


Figure 1. The yield of products, the conversion of benzene, and the selectivity of phenol. Reaction conditions: 5.6 mmol C_6H_6 , 40.0 mL H_2O : (a) The effect of concentration of H_2O_2 , $m_{\text{TS-1}}/m_{\text{benzene}} = 0.34$, reaction time 45 min, reaction temperature 70 $^{\circ}\text{C}$; (b) The effect of reaction temperature, $m_{\text{TS-1}}/m_{\text{benzene}} = 0.34$, reaction time 45 min, 0.80 mL H_2O_2 (30%); (c) The effect of reaction time, $m_{\text{TS-1}}/m_{\text{benzene}} = 0.34$, 0.80 mL H_2O_2 (30%), reaction temperature 70 $^{\circ}\text{C}$; (d) The effect of catalyst amount, 45 min, 0.80 mL H_2O_2 (30%), reaction temperature 70 $^{\circ}\text{C}$.

2.1.2. Recycling of the Catalyst

The stability of TS-1 was tested and the results are shown in Figure 2. After reaction, the catalyst was filtrated and calcined at 550 $^{\circ}\text{C}$ for 10 h. The yield of phenol and the conversion of benzene reduced slightly from the first run to the second, then kept almost invariable in the following runs. The selectivity of phenol kept almost constant in all runs.

According to the above results, the optimal conditions were the following: 5.6 mmol C_6H_6 , 0.80 mL H_2O_2 (30%), 40.0 mL H_2O , reaction temperature 70 $^{\circ}\text{C}$, reaction time 45 min, and 0.15 g TS-1. Under the aforementioned optimized conditions, we obtained a phenol yield of about 39%, with a selectivity of about 72%, and the turn-over frequency (TOF) value reached 73 h^{-1} , which indicated the good catalytic performance of the TS-1 catalyst in the hydroxylation of benzene.

As a comparison, we used commercial TS-1 as a catalyst for the hydroxylation of benzene. We also prepared an S-1 catalyst by the same strategy as for the TS-1 catalyst, with no titanium trichloride addition. The catalytic activity of commercial TS-1 and S-1 was tested under the optimized conditions. The yield of phenol was 17% and the selectivity of phenol was 75% over the commercial TS-1, whereas the yield of phenol over S-1 was low, less than 1%. This indicated that Ti is essential for the hydroxylation reaction, and that the TS-1 prepared in the present work exhibited high activity [38–40].

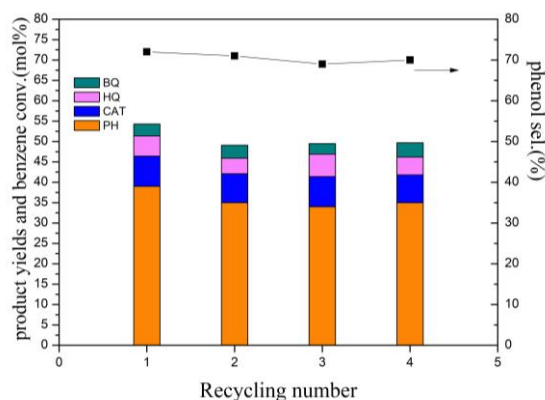


Figure 2. The stability of catalyst. Reaction conditions: $m_{\text{TS-1}}/m_{\text{benzene}} = 0.34$, 40.0 mL H_2O , 5.6 mmol C_6H_6 , reaction time 45 min, 0.80 mL H_2O_2 (30%), reaction temperature 70 °C.

2.2. Characterization of the Catalyst

2.2.1. FT-IR Spectroscopy

The FT-IR spectra of TS-1, used TS-1, and commercial TS-1 are shown in Figure 3. Based on the literature [21,41–45], the band at 550 cm^{-1} was assigned to the asymmetric framework vibration of double five rings and the characteristics of the MFI structure, and the band at 965 cm^{-1} was evidence of the isomorphous substitution of Ti in the TS-1 catalyst framework. As shown in Figure 3, the bands at 553 cm^{-1} and 965 cm^{-1} demonstrate the successful incorporation of Ti into the MFI framework of both the TS-1 catalyst and the commercial TS-1. There was no change in the characteristic peaks of the used TS-1 comparing with the parent TS-1.

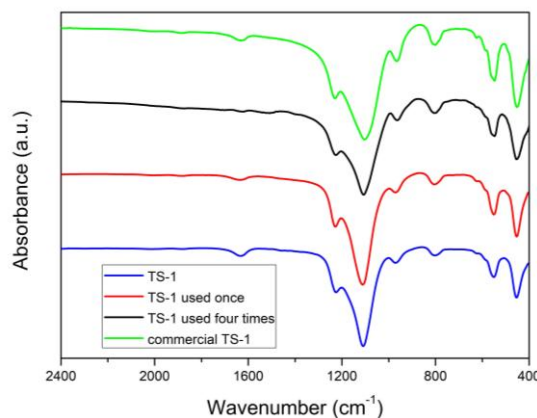


Figure 3. FT-IR spectra of TS-1, used TS-1, and commercial TS-1.

2.2.2. Diffuse Reflectance UV-Vis

The diffuse reflectance (DR) UV-Vis spectra of the TS-1, used TS-1, and commercial TS-1 are shown in Figure 4. Based on the literature [46–48], the absorption band at around 210 nm was the characteristic peak of Ti tetrahedrally incorporated into the framework, and the absorption band at 260–330 nm was assigned to penta- and hexa-coordinated and anatase extraframework Ti species. As shown in Figure 4, the presence of the band at around 210 nm and the absence of bands around 260–330 nm proved that almost all of the Ti species were incorporated in the framework of TS-1. The commercial TS-1 had an obvious absorption band at 260–330 nm, which implied the existence of penta- and hexa-coordinated Ti species and anatase TiO_2 . The framework Ti species had a good catalytic performance; meanwhile,

the extraframework Ti species were usually responsible for the decomposition of H_2O_2 [49,50]. From the DR UV-Vis spectra of used TS-1, no obvious change of absorption bands was observed.

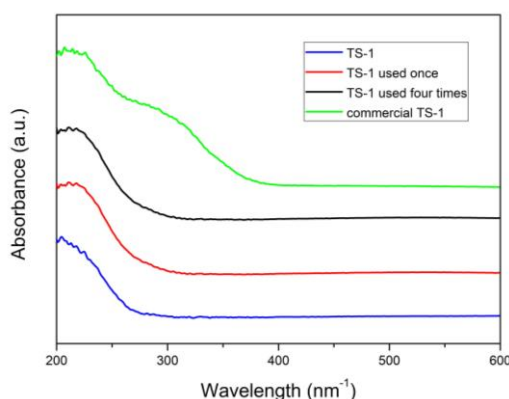


Figure 4. Diffuse reflectance (DR) UV-Vis spectra of TS-1, used TS-1, and commercial TS-1.

2.2.3. X-ray Diffraction

The XRD patterns of TS-1, used TS-1, S-1, and commercial TS-1 are shown in Figure 5. The characteristic diffraction peaks at 2θ of 7.9° , 8.8° , 23.1° , 23.9° , and 24.4° proved that the TS-1, S-1, and commercial TS-1 had a well-crystallized MFI structure [51–55]. No significant diffraction peak was observed at 2θ of 25.4° for all of the samples, which indicated the absence of crystalline TiO_2 . Although the DR UV-Vis spectra of commercial TS-1, shown in Figure 5, showed the presence of extraframework TiO_2 species, the XRD patterns with no obvious peak at 25.4° indicated that the extraframework TiO_2 species might be highly dispersed with a very small size in commercial TS-1 [56]. The highly dispersed TiO_2 increased the contact with H_2O_2 , increasing the decomposition of H_2O_2 [50]. This might be the reason why the commercial TS-1 had inferior catalytic activity in the hydroxylation of benzene under the conditions tested in the present work. From the XRD patterns of the used catalysts, there was no obvious change in characteristic diffraction peaks, which showed that the catalyst structure retained its original patterns.

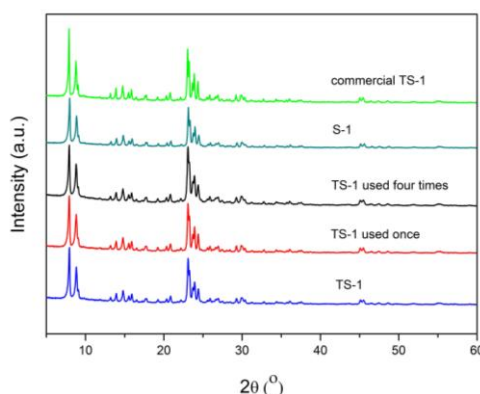


Figure 5. XRD patterns of TS-1, used TS-1, S-1, and commercial TS-1.

2.2.4. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

The SEM images are shown in Figure 6. The SEM images demonstrated that the TS-1 was uniform. The particles of TS-1 were rough-surface spheres of an average size of about 100–150 nm. The particle size of commercial TS-1 was much larger than that of TS-1: about 500–600 nm. The size of some particles was very big, which revealed the nonuniformity in size of commercial TS-1. The agglomeration of

commercial TS-1 was distinct, indicating an uneven distribution of catalyst particles. The TS-1 used four times after calcination displayed a similar morphologic structure to its parent TS-1.

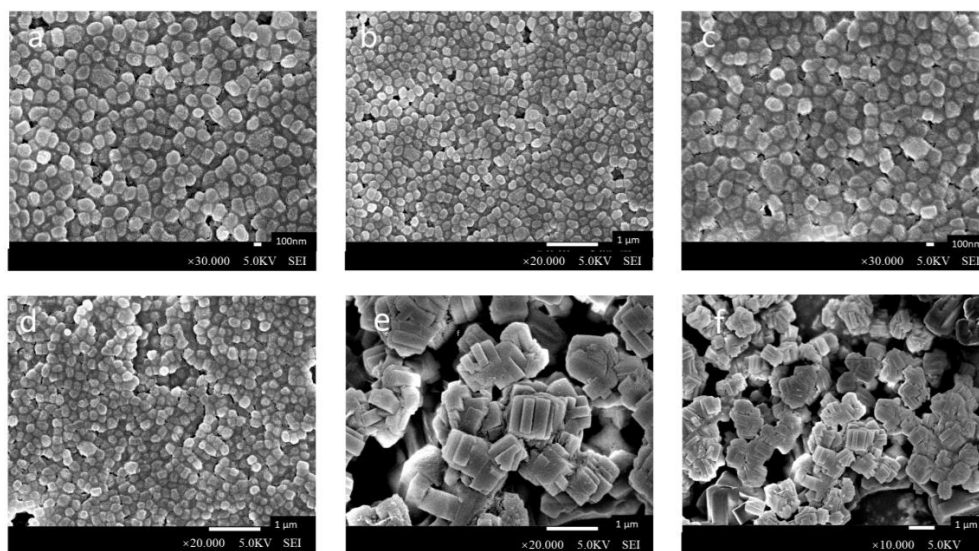


Figure 6. SEM images of TS-1 (a,b), TS-1 used four times (c,d), and commercial TS-1 (e,f).

The TEM images of TS-1, used TS-1, S-1, and commercial TS-1 are shown in Figure 7. From the high resolution TEM images, it could be observed that the particles of TS-1 had an obvious hierarchical structure and a rough surface. The particles of TS-1 consisted of sponge-like irregular aggregates with a size that approached 100–150 nm [39,57]. The TEM images of S-1 showed that S-1 had a less-hierarchical structure and a slightly larger particle size relative to the TS-1. The commercial TS-1 also had a hierarchical structure, but the particle size and shape was nonuniform. The particles of commercial TS-1 were irregular with no specific shape. In combination with the SEM images, the commercial TS-1 had a much larger particle size than the TS-1 prepared in present work, which went against the diffusion of the reactant and products [41]. The TEM images of the reused catalyst indicated that the catalysts still retained a shape resembling the parent TS-1, which showed a stability of morphology.

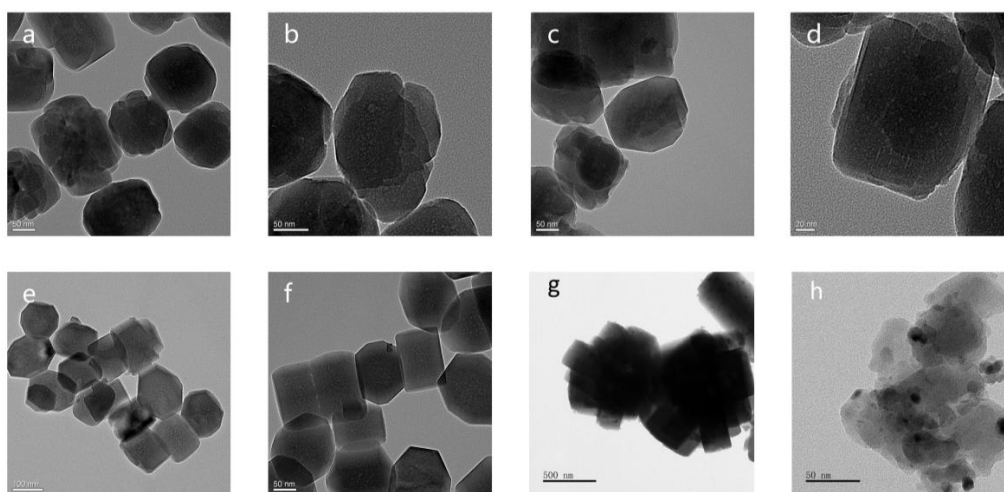


Figure 7. TEM images TS-1 (a,b), TS-1 used four times (c,d), S-1 (e,f), and commercial TS-1 (g,h).

2.2.5. Inductively Coupled Plasma (ICP) and X-ray Photoelectron Spectroscopy (XPS)

The XRF analysis showed that TS-1 only had Si, Ti, and O elements, without potassium and sodium, from the template of tetrapropylammonium hydroxide (TPAOH). ICP was performed to analyze the Ti content of the catalyst. A pretreatment using HF to dissolve Si in a Teflon vessel was applied, then aqua regia was used to dissolve all of the elements after the evaporation of HF. The liquid mixture was analyzed by ICP to quantify the content of Ti. The Ti content of the TS-1 catalyst was detected to be 1.13 wt.%, and the Ti content of the commercial TS-1 was detected to be 4.80 wt.%. The Ti $2p_{3/2}$ spectra are shown in Figure 8. The peak at the binding energy (BE) at around 460 eV belonged to the tetrahedral Ti in the framework, and the peak at the BE at 458 eV turned out to be the extraframework Ti in the catalyst [58–62]. As shown in Figure 8, the single peak at the BE at 460 eV of the TS-1 catalyst demonstrated that almost only framework Ti species existed. The obvious peak at 458 eV of the commercial TS-1 belonged to the extraframework TiO_2 . Table 1 lists the surface Ti content percentage detected by XPS. The content of surface Ti species was far less than the total Ti species for TS-1 and commercial TS-1, suggesting that the content of surface Ti species was much less than the bulk content. The TS-1 catalyst almost only had framework Ti species on the surface: about 0.21 wt.%. It was clear that the majority of Ti species of the commercial TS-1 dispersed in the extraframework—about 0.92 wt.%—and the contribution at 460 eV from framework Ti species was 0.34 wt.%, which was more than the TS-1 catalyst. As shown in Table 1, the surface Ti content of the TS-1 kept almost stable in consecutive runs. This might be the reason for the stable activity of the catalyst. Based on the literature [49,50], the extraframework TiO_2 was responsible for the decomposition of H_2O_2 . Although the commercial TS-1 contained more content of surface framework Ti species than the TS-1, the amount of extraframework Ti species was also significant. Thus, the decomposition of H_2O_2 on commercial TS-1 might be serious, resulting in a low yield of phenol.

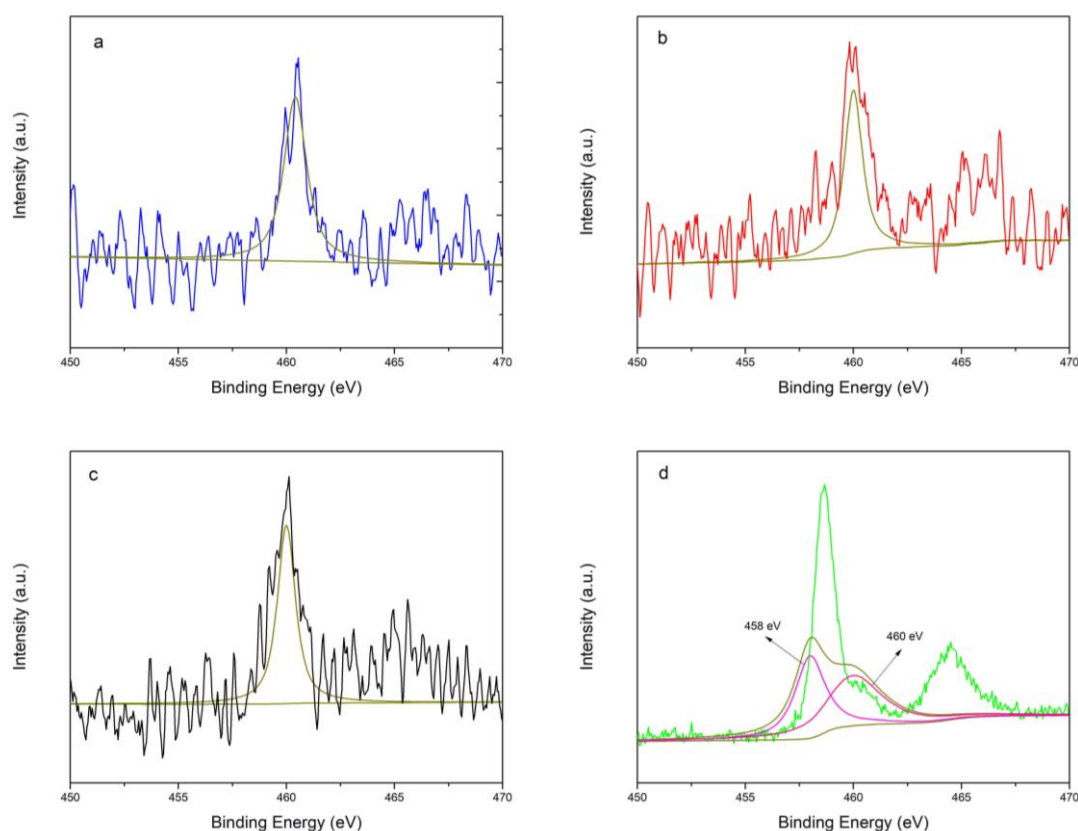


Figure 8. XPS spectra of TS-1 (a), TS-1 used once (b), TS-1 used four times (c), and commercial TS-1 (d).

Table 1. Surface Ti content of catalysts.

Sample	458 eV (wt.%)	460 eV (wt.%)	Total (wt.%)
TS-1	-	0.21	0.21
TS-1(used once)	-	0.26	0.26
TS-1(used four times)	-	0.26	0.26
commercial TS-1	0.92	0.34	1.26

The resulting filtrate after reaction was analyzed by ICP to detect the leaching of Ti. The amount of the leaching of Ti in the first run was 0.12 wt.%, and then almost no leaching of Ti species was detected. As no obvious change in the morphology of TS-1 was observed, the leaching of Ti was the reason for the reduction of the activity of the catalyst from the first run to the second.

2.2.6. N₂ Adsorption-Desorption Isotherms and Pore Size Distribution Curves

The N₂ adsorption-desorption isotherms of TS-1, used TS-1, S-1, and commercial TS-1 are shown in Figure 9a. The gentle uptake at $P/P_0 < 0.05$, and almost no adsorption at intermediate relative pressures, suggested the presence of micropores. The existence of a hysteresis loop at $P/P_0 > 0.9$ could be attributed to the interparticle adsorption within the voids formed between the catalyst particles, which indicated that the samples consisted of both microporous and mesoporous channels [19,42,63]. The commercial TS-1 showed a type-I isotherm, typical of microporous material, and the hysteresis loops in the nitrogen isotherm indicated the existence of minority mesopores [38,64,65]. The pore size distribution curves showed that the pore size of the TS-1 was concentrated at 15–18 Å, and mesopores existed obviously, as shown in Figure 9b. The commercial TS-1 displayed a sharp distribution of pore width at 15 Å. Table 2 lists the textural parameters of the samples. The TS-1 catalyst had a relatively large adsorption average pore size of 23.0 Å and a Brunauer–Emmett–Teller (BET) surface area of 476 m²g^{−1}. The commercial TS-1 had a smaller adsorption average pore size of 17.0 Å and a BET surface area of 411 m²g^{−1}. The TS-1 catalyst had a greater microporous volume and mesoporous volume than the commercial TS-1, and the commercial TS-1, with a microporous volume of 0.084 cm³g^{−1}, was much smaller than the TS-1 catalyst of 0.17 cm³g^{−1}, which might be caused by the extraframework Ti species.

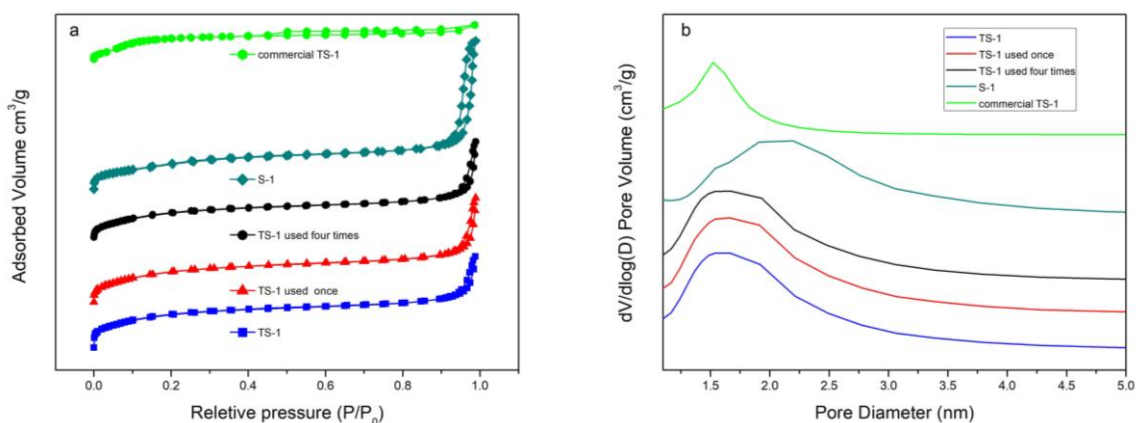


Figure 9. N₂ adsorption-desorption isotherms (a) and pore diameter distribution (b) of TS-1, used TS-1, S-1, and commercial TS-1.

Table 2. Structural properties of the samples.

Sample	S_{BET} (m^2g^{-1})	V_{mic} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	Φ_p^a ($\text{\AA}$)
TS-1	476	0.17	0.16	23.0
TS-1(used once)	480	0.17	0.17	23.4
TS-1(used four times)	460	0.16	0.16	23.1
S-1	458	0.16	0.31	36.8
commercial TS-1	411	0.084	0.11	17.0

The maximum molecule radius of benzene, phenol, catechol, hydroquinone, and benzoquinone was 5.0 Å, 5.7 Å, 5.7 Å, 6.5 Å, and 5.5 Å, respectively (calculated value from Gaussian 09). The Ti species of the samples were mainly distributed within pores detected by XPS, so the added benzene could be adsorbed well in the hydrophobic catalyst channel [61]. The TS-1 catalyst with a relatively large pore size and pore volume permitted many more benzene molecules to react with as many Ti active sites as possible, and the products could leave simultaneously, which greatly accelerated the reaction rate. However, the larger pore size provided sufficient space for phenol over-oxidation to DHB and benzoquinone [66], which led to a decrease in the selectivity of phenol. The pore volume and pore size of the commercial TS-1 was relatively small, which might inhibit the adsorption of benzene and the diffusion of products. Consequently, the other benzene molecules could not enter into the blocked channel simultaneously, resulting in a decrease in catalytic activity.

The TS-1 reused three times almost had no changes in the N_2 adsorption-desorption isotherms and the pore size distribution curve. From the textural parameters of the used TS-1, the values of the BET surface area, pore volume, and adsorption average pore size had almost no changes compared with the parent TS-1. The N_2 adsorption-desorption isotherms and pore size distributions of S-1 are shown in Figure 9, and the textural parameters are listed in Table 2, which indicated that the pore size was mainly distributed in the mesoporous range [67], and the adsorption average pore width of S-1 was around 40.8 Å.

According to the characterization of the samples, almost all of the Ti species of the TS-1 catalyst entered into the framework without post-treatment. S-1 had a similar structure to the TS-1 catalyst without Ti species. The commercial TS-1 contained Ti species, but the majority of them were located at the extraframework, and had some structural differences from the TS-1 catalyst. Based on the results of the catalytic activity, it was evident that the framework Ti species were the active sites for the hydroxylation of benzene. The TS-1 catalyst with a relatively large pore size and pore volume permitted the benzene molecules to react with most of the Ti species within the pores, which shortened the reaction time. The amount of extraframework TiO_2 dispersed on the surface of the commercial TS-1 was more than that of the framework Ti species, which might decrease the catalytic activity by an ineffective decomposition of H_2O_2 .

3. Experimental Section

3.1. Materials

The tetraethyl orthosilicate, isopropanol, sodium chloride (NaCl), hydrogen peroxide (H_2O_2 , 30%), benzene, phenol, chlorobenzene, and ethyl ether were purchased from Chengdu Kelong Chemical Regent Co., LTD., Chengdu, China. The tetrapropylammonium hydroxide (TPAOH, 25%) was obtained from Shanghai Drfinechem Fine Chemicals Co., LTD., Shanghai, China. The titanium trichloride (TiCl_3 , 15–20 wt.%) came from the Tianjin Damao Reagent factory. The catechol (CAT, 99%), hydroquinone (HQ, 99%), and benzoquinone (BQ, 99%) were obtained from TCI, Shanghai, China. The commercial TS-1 was acquired from Nanjing XFNANO Materials Tech Co., LTD., Nanjing, China. All of the materials were used directly without further purification.

3.2. Methods

3.2.1. Catalyst Preparation

The TS-1 catalyst was prepared by a hydrothermal synthesis method which was similar to that in our previous work [32]. Namely, 20 g of isopropanol was first dropwise added into 45 g of tetraethyl orthosilicate with stirring, followed by the addition of 20 g of water. After stirring for 30 min, 60 g of aqueous solution of TPAOH (20%) was dropwise added to the mixture. Then, 3.5 g of titanium trichloride (15.0 wt.%) diluted by 10 g of H₂O was dropwise added to the mixture, and was then replenished with 60 g of water. Then, we heated the solution in a water bath at 55 °C for 1 h and at 77 °C for 7 h. In this heating step, water was dropwise added continuously to keep the total volume invariable. During the whole process, a magnetic stirring apparatus was used to keep the solution mixed well. The resulting solution was cooled down, kept overnight, and crystallized. The crystallization was carried out in a PTFE-lined stainless steel autoclave at 175 °C for 7 days. The white solid product was filtered and washed with deionized water and dried at 80 °C for more than one day. The dried white product was calcined at 550 °C for 10 h to remove the template (TPAOH). Finally, the TS-1 catalyst was obtained.

3.2.2. Catalyst Characterization

The X-ray diffraction (XRD) measurements were performed on an Empyrean Diffractometer (PANalytical B.V., Almelo, The Netherlands) with a Cu-K α radiation source. The data over a 2 θ scanning range from 5° to 60° were collected at a step size of 0.02°. The surface morphology of the samples was characterized by scanning electron microscopy (JSM-7500F, JEOL, Tokyo, Japan) set at 5 kV. Transmission electron microscopy images of the samples were performed on an FEI company Tecnai G220 Twin instrument (FEI, Hillsboro, OR, USA) at an acceleration voltage of 200 kV. DR UV-Vis spectra of the samples were obtained with a Hitachi U-4100 spectrometer (Hitachi, Tokyo, Japan) equipped with a reflectance attachment. BaSO₄ was used as the reference. Fourier transform infrared (FT-IR) spectra of the samples were collected at a 2 cm⁻¹ resolution on a Nicolet Nexus 670 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an MCT detector. N₂ adsorption-desorption isotherms of TS-1 were measured at 77 K on a Micromeritics Tristar 3020 instrument (Micromeritics, Atlanta, GA, USA). The catalysts were degassed at 300 °C under vacuum for 2 h before N₂ adsorption-desorption. The Brunauer–Emmett–Teller (BET) method was applied to obtain the surface areas. The Barrett–Joyner–Halenda (BJH) method was applied to obtain pore volumes and average pore diameters. Inductively coupled plasma (ICP) was used to analyze the Ti content of the samples and was performed on a VG PQExCell instrument (TJA, Boston, MA, USA). X-ray photoelectron spectroscopy (XPS) was performed on an AXIS Ultra DLD (KRATOS) spectrometer (Shimadzu, Kyoto, Japan).

3.2.3. Catalytic Activity Test

The reaction was carried out in a 50 mL flask with the integration of a reflux condenser. In a typical run, a certain amount of catalyst was added, then 5.6 mmol benzene, 40 mL deionized water, and 0.80 mL H₂O₂ (30%) were introduced into the reaction flask in order. The flask was heated to 70 °C to proceed the reaction for 45 min.

After the reaction system was cooled to room temperature, the resulting mixture was separated by filtration. NaCl was added into the filtrate until saturation, then the salt-added liquid was extracted by ethyl ether for four times. Standard substances were employed to test the extraction rate. A certain amount of standard substance was dissolved in a given volume of water, and the same extraction procedure as that for the extraction of products was used. Then, the obtained standard substance contained in ether solution was analyzed by GC to get the extraction rate of the substance. The extracted liquid phase was identified by GC-MS (Agilent, 5973 Network 6890N, Santa Clara, CA, USA)

and quantified by GC (a Fuli 9750 equipped with a Flame Ionization Detector (FID) and a DB-5 column) using chlorobenzene as an internal standard.

The yield and selectivity of the products, including phenol (PH), catechol (CAT), hydroquinone (HQ), benzoquinone (BQ), and DHB (CAT + HQ) were calculated as the following:

$$\begin{aligned}\text{Yield of phenol (mol \%)} &= \frac{\text{Mole of amount of phenol}}{\text{Initial mole amount of benzene} \times \text{extraction rate (extraction rate of phenol 72\%)}} \\ \text{Yield of catechol (mol \%)} &= \frac{\text{Mole of amount of catechol}}{\text{Initial mole amount of benzene} \times \text{extraction rate (extraction rate of catechol 72\%)}} \\ \text{Yield of hydroquinone (mol \%)} &= \frac{\text{Mole of amount of hydroquinone}}{\text{Initial mole amount of benzene} \times \text{extraction rate (extraction rate of hydroquinone 65\%)}} \\ \text{Yield of benzoquinone (mol \%)} &= \frac{\text{Mole of amount of benzoquinone}}{\text{Initial mole amount of benzene} \times \text{extraction rate (extraction rate of benzoquinone 95\%)}} \\ \text{Selectivity (\%)} &= \frac{\text{Mole amount of phenol}}{\text{Mole amounts of phenol + DHB + BQ}} \\ \text{Conversion of benzene (\%)} &= \frac{\text{Mole amount of phenol + DHB + BQ}}{\text{Initial mole amount of benzene}} \\ \text{TOF of phenol (h}^{-1}\text{)} &= \frac{\text{Mole of amount of phenol}}{\text{Mole amount of Ti} \times \text{reaction time (h)}}\end{aligned}$$

4. Conclusions

In summary, TS-1 as the catalyst for the hydroxylation of benzene had effective catalytic activity under mild reaction conditions. Under the optimized conditions, the yield of phenol reached 39% and the selectivity of phenol reached 72%. The process of reaction was simple and fast, with a short reaction time, only 45 min, and a low concentration of H₂O₂ of about 0.20 mol/L. The TS-1 catalyst almost only had framework Ti species, which were the active sites for the hydroxylation of benzene. The surface-dispersed extraframework TiO₂ contributed to the decrease of catalytic activity. The relatively large pore size might enhance the reaction rate. The TS-1 catalyst showed a relatively good reusability, as there was only a slight decrease from the first run.

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