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Deactivation and regeneration of TS-1/diatomite catalyst for hydroxylation of phenol in fixed-bed reactor

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Abstract

The performance of the TS-1/diatomite catalyst for hydroxylation of phenol was investigated in the fixed-bed reactor. The results show that the activity and the selectivity to product of the TS-1/diatomite catalyst decrease simultaneously with an increase of the reaction time, which indicates that the TS-1/diatomite catalyst has deactivated gradually during the reaction. The deactivated catalyst was characterized by XRD, UV–vis, FT-IR, N_2 adsorption and thermogravimetric analysis techniques. It was found that the crystallinity of TS-1/diatomite catalyst decreased slightly, but the structure of TS-1 zeolite and the content of titanium in the framework were unchanged. Compared with the fresh catalyst, the channels of the TS-1/diatomite catalyst were blocked by the organic byproducts, to result in the obvious decrease in the surface area and pore volume of the deactivated catalyst. The deposited byproducts inside the channels of TS-1/diatomite can be removed by calcining at 550 °C or refluxing with dilute hydrogen peroxide, which makes the performance of the deactivated catalyst recover completely.

Keywords: TS-1/diatomite; Deactivation; Regeneration; Hydroxylation of phenol; Fixed-bed reactor

1. Introduction

Titanium silicalite-1 (TS-1) has attracted much attention last decade because of its unique catalytic properties for the selective oxidations such as aromatic hydroxylation [1], epoxidation of alkenes [2], ammoximation of cyclohexanone [3] and oxidation of alkanes and alcohols [4,5] using hydrogen peroxide as oxidant. The synthesis and characterization of TS-1 have been investigated in some detail in recent years. And that it has also been found [6,7] that the TS-1 catalyst has a short lifetime, but the reason of deactivation and method of regeneration have not yet been investigated systematically, specially in the fixed-bed reactor system.

Recently, we have found that the supported TS-1 on diatomite catalyst had good catalytic performance for hydroxylation of phenol in the fixed-bed reactor operated continuously [8]. Compared with the batch process, this process has many advantages, such as free from tiresome operations (the catalyst filtration and makeup), and operation in large scale. In order to develop the continuous process of phenol hydroxylation catalyzed by TS-1, the deactivation and regeneration of the TS-1/diatomite catalyst used in the fixed-bed reactor were investigated in detail in this paper.

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 described in Ref. [9], using tetraethylorthosilicate (TEOS) as silicon source, tetrabutyorthotitanate (TBOT) as titanium source, and tetrapropylammonium hydroxide (TPAOH) as template. The average crystal size of TS-1 is about 0.25 μm measured by scanning electron microscopy (SEM).

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The TS-1/diatomite catalyst was prepared by mixing TS-1 powder with diatomite ($SiO_2\% \geq 85.0$, $Al_2O_3\% \leq 3.5$, $Fe_2O_3\% \leq 1.5$) homogeneously, TS-1/diatomite = 3/2(wt), then pressed and crushed to 0.45–0.9 mm grains. For the phenol hydroxylation, no catalytic activity of diatomite has been found in the blank experiment.

2.2. Characterization of catalyst

X-ray diffraction (XRD) analysis was performed on the Rigaku D/MAX-2400 diffractometer using Cu Kα radiation and graphite monochromator. 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. Infrared (IR) spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer, and the samples to be measured were ground with KBr and pressed into thin wafers. The BET surface area and pore diameter distribution of the samples were determined according to the N_2 adsorption isotherms measured by Micrometrics ASAP 2010. The thermogravimetry and differential scanning calorimetry (TG-DSC) were operated on the Netzsch STA 409 PC simultaneous thermal analyzer, the heating rate was 10 °C/min.

2.3. Hydroxylation of phenol

The hydroxylation of phenol was carried out in the continuous flow fixed-bed glass reactor (Φ15 mm), in which the catalyst was packed in the isothermal region of the reactor. The mixture consisting of phenol, 30 wt.% H_2O_2 and solvent (acetone) was fed by a micro-pump from the bottom of the reactor. The reaction conditions are as follows: catalyst 7.0 g, reaction temperature 84 °C, phenol/H_2O_2 = 3:1(mol), phenol/acetone = 1.25:1(wt), WHSV = 8.46 h^{-1}. The residual H_2O_2 was determined by the iodometric titration. The reaction products were analyzed by the PE Autosystem XL gas chromatograph with flame ionization detector and PE-2 capillary column (25 m × 0.32 mm × 1.0 μm, 5% methyl benzene silicone). The conversion of phenol and H_2O_2, the selectivity to dihydroxybenzene and the utilization of H_2O_2 may be defined as follows:

The conversion of phenol: $X_{\text{phenol}} = \frac{n^0_{\text{phenol}} - n_{\text{phenol}}}{n^0_{\text{phenol}}}$

The conversion of H_2O_2: $X_{H_2O_2} = \frac{n^0_{H_2O_2} - n_{H_2O_2}}{n^0_{H_2O_2}}$

The selectivity to dihydroxybenzene: $S_{\text{DHB}} = \frac{n_{\text{CAT}} + n_{\text{HQ}}}{n_{\text{CAT}} + n_{\text{HQ}} + n_{\text{PBQ}}}$

The utilization of H_2O_2: $U_{H_2O_2} = \frac{n_{\text{CAT}} + n_{\text{HQ}} + 2n_{\text{PBQ}}}{n^0_{H_2O_2} \times X_{H_2O_2}}$

n^0 and n denotes the initial mole fraction and the final mole fraction. CAT, HQ and PBQ represent catechol, hydroquinone and *p*-benzoquinone, respectively.

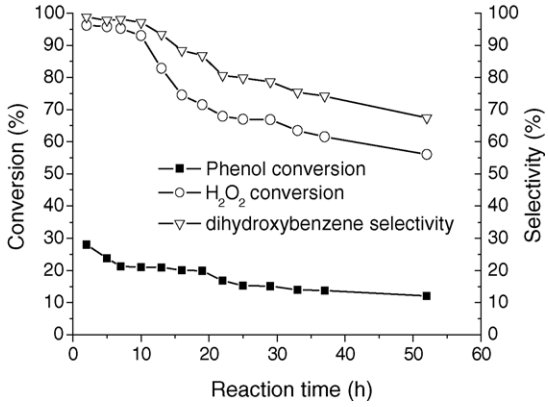

Fig. 1. Conversion of phenol and H_2O_2 and the selectivity to dihydroxybenzene vs. the reaction time.

3. Results and discussion

3.1. Deactivation of the TS-1/diatomite catalyst

Fig. 1 shows the performance of the TS-1/diatomite catalyst for the hydroxylation of phenol in the fixed reactor. The conversions of phenol and H_2O_2 decline significantly with the reaction time. As the reaction time increases from 1 to 52 h, the conversions of phenol and H_2O_2 decrease from 28.1 to 12.0% and 96.3 to 56.0%, respectively. For the selectivity to dihydroxybenzene, it change hardly during the initial 10 h, but after 10 h it declines obviously also. So the TS-1/diatomite catalyst has deactivated gradually during the hydroxylation reaction. The utilization of H_2O_2 also decreases slightly with the reaction time (Fig. 2). With the decrease of phenol conversion over the deactivated catalyst, the amount of H_2O_2 consumed for phenol hydroxylation decrease also, which makes the concentration of H_2O_2 higher, the decomposition rate of H_2O_2 increases linearly with the concentration of H_2O_2 [10]. So the ineffective decomposition of H_2O_2 over the deactivated catalyst becomes more serious. Meanwhile, the high H_2O_2 concentration in the reactor can promote the further oxidation of dihydroxybenzene [8,11], resulting in

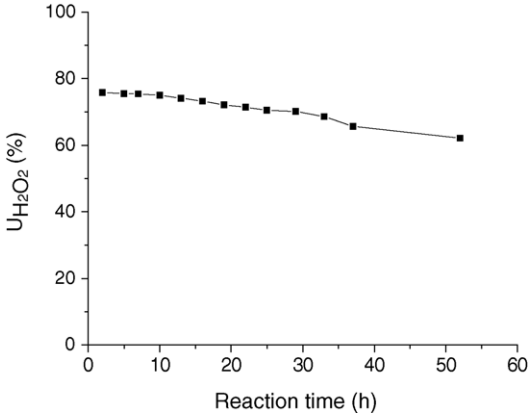

Fig. 2. Utilization of H_2O_2 vs. the reaction time.

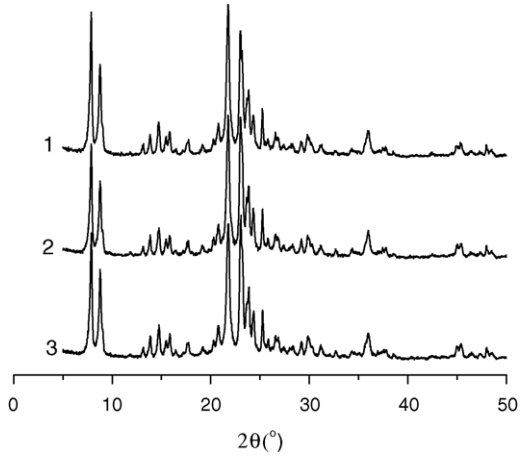

Fig. 3. XRD patterns of the TS-1/diatomite catalysts.

the decrease of the selectivity to dihydroxybenzene over the deactivated catalyst.

3.2. Characterization of catalysts

In order to investigate the reasons of deactivation, the fresh catalyst (sample 1) and the catalysts used for 25 and 52 h (sample 2 and sample 3, respectively) were characterized.

The XRD patterns of the fresh and used catalysts were shown in Fig. 3. All the samples have the typical MFI structure and their crystallinities are changed hardly as shown in Table 1. It indicates that the framework structure of TS-1 zeolite is not destroyed during the hydroxylation of phenol.

It has been found that the catalytic performance of TS-1 zeolite is related to the amount of Ti in its framework [10]. UV–vis and FT-IR techniques are usual tools to characterize framework titanium. The UV–vis spectra of all the samples (Fig. 4) have two absorption peaks, one at 210 nm can be attributed to tetra-coordinated titanium inside the frameworks and another at 330 nm can be attributed to anatase TiO_2 [10,12]. Compared with the fresh catalyst, the peak intensity at 210 and 330 nm of the used catalysts has no obviously change. This suggests that titanium-framework in the catalyst does not lose during the phenol hydroxylation.

The IR spectra in Fig. 5 show that all the samples have the absorption peak at about 960 cm^{-1}. This is indicative of titanium incorporated into the zeolite framework, even though the assignment of this absorption band is subject to discussion. Reddy and co-workers [11] thought that the relative intensity (I_{960}/I_{550}) of the absorption peaks at 960 and

Table 1
Data of XRD and FT-IR spectra of the TS-1/diatomite catalysts

Catalyst	Usage state	Relativity crystallinity (%)	I_{960}/I_{500}
1	Fresh	100	0.746
2	Used for 25 h	99	0.749
3	Used for 52 h	95	0.743

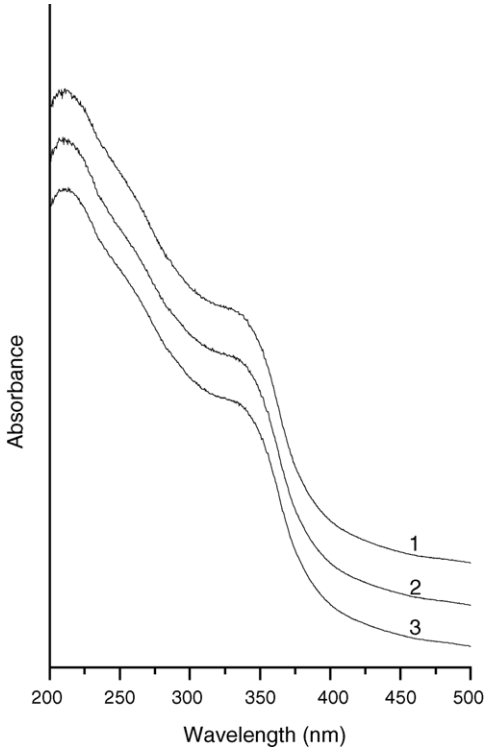

Fig. 4. UV–vis spectra of the TS-1/diatomite catalysts.

550 cm^{-1} in the IR spectra increases linearly with an increase of the amount of titanium-framework. The results in Table 1 shows, after the catalyst is used for 25–50 h, the change of I_{960}/I_{550} in their IR spectra is not obvious, that is to say, the amount of active titanium-framework does not decrease. This is consistent with the result of UV–vis (Fig. 4).

The results above signify that deactivation of the TS-1/diatomite catalyst does not ascribe to change of the framework structure of zeolite or decrease of the amount of titanium-framework in TS-1.

The adsorption isotherm of the TS-1/diatomite catalyst is a typical Langmuir IV adsorption isotherm as shown in

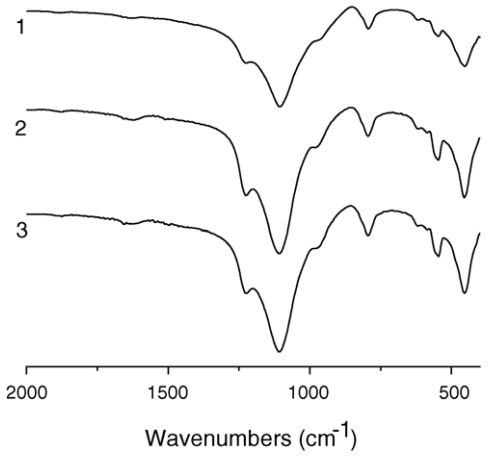

Fig. 5. FT-IR spectra of the TS-1/diatomite catalysts.

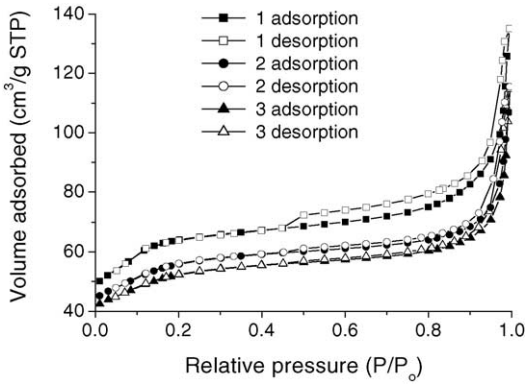

Fig. 6. N_2 adsorption isotherms of the TS-1/diatomite catalysts.

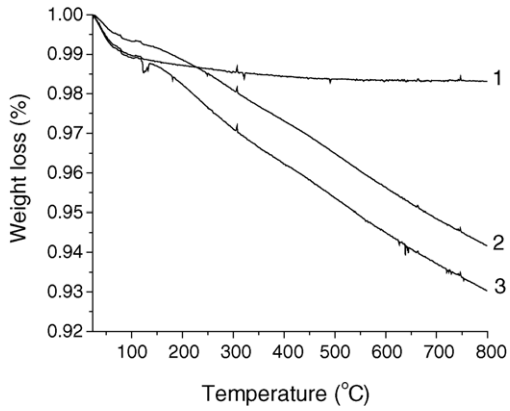

Fig. 8. TG curves of the TS-1/diatomite catalysts.

Fig. 6. When the relative pressure $p/p_0 < 0.45$, the branch of desorption overlaps completely the adsorption branch. When $p/p_0 > 0.45$, a H1 type of hysteresis loop appears according to IUPAC classification [13]. This implies that the TS-1/diatomite catalyst has a wide range of pore size distribution, which agrees with the results in Fig. 7. Besides the micropores provided by TS-1 zeolite, there are many macropores in the TS-1/diatomite catalyst. These macropores are contributed by the support or formed in the molding process by pressing.

After the catalyst is used for 25 or 52 h (such as catalyst 2 or catalyst 3), its catalytic activity has decreased obviously (Fig. 1), and its adsorption capability, hysteresis loop, surface area and pore volume decline significantly (Table 2 and Fig. 6) in comparison with the fresh catalyst. The total surface area and total pore volume of the catalyst 3 used for 52 h has decreased about 18.4 and 16.5%, respectively. And its micropore surface area and micropore volume has decreased about 19.7 and 19.1%, respectively. This indicates that the channels of the TS-1/diatomite catalyst have been blocked seriously, and the micropores are blocked more easily than the macropores.

In order to investigate the deposition inside the channels of catalyst, the fresh and the used catalysts were characterized by TG/DSC. As seen from Fig. 8, the weight loss of about 1.3 wt.% occurs at <200 °C for the fresh catalyst, which is mainly attributed to desorption of H_2O from the catalyst surface. For the used catalysts, the weight loss occurs incessantly at whole rang of <800 °C. The total weight loss of sample 2 and sample 3 at <800 °C is about 6 and 7%, respectively, and the weight loss of sample 2 and sample 3 at <200 °C are only 1–1.5%. In the DSC curves shown in Fig. 9, two exothermal peaks at 400–600 °C of the sample 2 and sample 3 are attributed to thermal decompo-

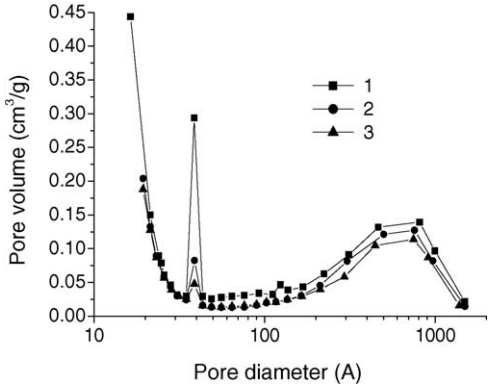

Fig. 7. Pore size distribution of the TS-1/diatomite catalysts.

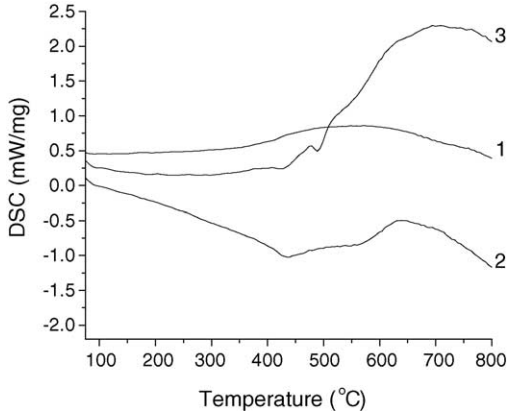

Fig. 9. DSC curves of the TS-1/diatomite catalysts.

Table 2
BET surface area and pore volume of the TS-1/diatomite catalysts

Catalyst	Usage state	S_{BET} ($m^2\ g^{-1}$)	$S_{Micropore}$ ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	$V_{Micropore}$ ($cm^3\ g^{-1}$)
1	Fresh	222.5	119.5	0.2022	0.0524
2	Used for 25 h	194.1	102.1	0.1706	0.0451
3	Used for 52 h	181.6	95.9	0.1688	0.0424

Table 3
Performances of the regenerated catalysts for hydroxylation of phenol

Catalyst	Usage state	Regeneration condition	X_{phenol} (%)	$X_{H_2O_2}$ (%)	S_{DHB} (%)	$U_{H_2O_2}$ (%)	Cat/HQ
1	Fresh		28.1	96.3	98.8	75.8	0.86
3	Used for 52 h		12.0	66.0	67.4	62.1	2.50
4	Regenerated	Calcined, 550 °C/5 h/air	27.8	95.9	98.4	75.2	0.89
5	Regenerated	Refluxed, 5(wt)% H_2O_2/70 °C/4 h	27.4	93.2	99.0	76.3	0.82
6	Regenerated	Refluxed, acetone/50 °C/5 h	18.5	77.0	88.1	68.9	1.32
7	Regenerated	Treated in situ, 10(wt)% H_2O_2–acetone/84 °C/4 h, in fixed-bed reactor	18.9	88.5	89.1	65.0	1.51

Cat: Catechol; HQ: Hydroquinone.

sition of the organic compounds deposited on the catalyst surface. For the fresh catalyst (sample 1), no exothermal peak in the DSC curves can be found. The results above show that, there are many organic compounds deposited inside the channels of the used catalysts and the amount of deposition increases with an increase of the reaction time.

There are side reactions in the catalytic hydroxylation of phenol, such as an oxidation of dihydroxybenzenes to quinones, and its oxidation to large molecular products even to tar. These large molecular byproducts or tar could deposit on the catalyst surface and block the catalyst channels, to result in the deactivation of the TS-1/diatomite catalyst.

3.3. Regeneration of the deactivated catalyst

In order to develop an economic phenol hydroxylation process catalyzed by the TS-1/diatomite catalyst, it is necessary to regenerate efficiently the deactivated catalyst to enhance the lifetime of the TS-1/diatomite catalyst. Four kinds of regeneration methods were used to regenerate the deactivated catalyst, their results are shown in Table 3.

The results show interestingly that catechol becomes a dominant product (e.g. Cat/HQ = 2.50) over the deactivated catalyst 3, which is similar to the situation of radical catalytic hydroxylation of phenol, that is, catechol is mainly formed on the external surface of TS-1. If helping to the effect of the channel constraints, hydroquinone formation prevails at the internal catalytic sites as presented by Tuel et al. [14]. On the other hand, as the organic byproducts deposit mostly inside the channels or the pore mouths of the deactivated catalyst that has been confirmed above, hydroquinone formation is confined to result in the increase of the ratio of catechol/hydroquinone in the products.

By calcination at 550 °C in air or refluxing with 5 wt.% H_2O_2, the performance of the deactivated catalyst can be recovered completely, and its surface area and pore volume are completely recovered also (Table 4). It indicates further that the deactivation of the TS-1/diatomite catalyst is attributed to the deposition of the organic byproducts on the catalyst surface and inside the channels of the catalyst, and its deactivation is reversible and regenerative. In both regeneration methods above mentioned, the refluxing method with dilute H_2O_2 may make the organic byproducts deposited inside the channels breakdown oxidized by H_2O_2. Using the methods of refluxing with acetone or treating in situ with the mixture of H_2O_2 and acetone in the fixed-bed reactor, the performance of the deactivated catalysts cannot be recovered completely (Table 3), and its surface area and pore volume cannot be brought back also (Table 4).

Table 4
BET surface area and pore volume of the TS-1/diatomite catalysts

Catalyst	S_{BET} ($m^2\ g^{-1}$)	$S_{Micropore}$ ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	$V_{Micropore}$ ($cm^3\ g^{-1}$)
1	222.5	119.5	0.2022	0.0524
4	233.4	122.6	0.1907	0.0538
5	243.4	127.9	0.2087	0.0561
6	201.3	106.3	0.1802	0.0462

4. Conclusions

The TS-1/diatomite catalyst will be deactivated during the hydroxylation of phenol by H_2O_2 in a fixed-bed reactor, and the catalytic activity and selectivity to products decrease with an increase of reaction time. But the crystallinities of the TS-1/diatomite catalyst have changed a little, and the framework structure of TS-1 zeolite and the amount of titanium in the framework have not changed. Compared with the fresh catalyst, the BET surface area and pore volume of the deactivated catalyst decrease significantly, and the channels of the TS-1/diatomite catalyst are blocked by the organic by-products deposited on the catalyst surface, resulting in the reversible deactivation of the catalyst. The deposition on the TS-1/diatomite catalyst can be removed by calcining at 550 °C in air or refluxing with dilute hydrogen peroxide, which can recover completely the performance of the TS-1/diatomite catalyst for phenol hydroxylation.

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