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Effect of $(n)SiO_2/(n)B_2O_3$ in the precursor on chemical–physics properties of Ti-ZSM-5 synthesized by gas–solid method

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Abstract

Ti-ZSM-5 samples were successfully synthesized by using B-ZSM-5 with different molar ratios of $(n)SiO_2/(n)B_2O_3$ as the precursors. The gas–solid synthesis included two steps which were deboronation in HCl solution and titanation with $TiCl_4$. The effect of $(n)SiO_2/(n)B_2O_3$ on the incorporation of titanium into the framework was investigated. The synthesized titanium containing samples were thoroughly characterized by XRD, FT-IR, XRF, UV–Vis, Raman, ICP-AES and NH_3 TPD. Propylene epoxidation and phenol hydroxylation properties were also investigated. The results showed that $(n)SiO_2/(n)TiO_2$ in the samples increased with an increase in the $(n)SiO_2/(n)B_2O_3$ in the precursors. The conversion of H_2O_2 increased with the decreasing of $(n)SiO_2/(n)B_2O_3$ or $(n)SiO_2/(n)TiO_2$, and the selectivity to propylene oxide (PO) decreased. Anatase appeared in Ti-ZSM-5 sample synthesized by using B-ZSM-5 with a $(n)SiO_2/(n)B_2O_3$ ratio 100 as the precursor.

Keywords: Ti-ZSM-5; B-ZSM-5; Gas–solid phase isomorphous replacement; Propylene epoxidation; Phenol hydroxylation

1. Introduction

Titanium silicalite-1 (TS-1) belongs to the large and continuously developing family of the MFI type structure materials. It has been noted as one of the very effective catalyst materials in oxidation of many organic compounds at low temperature with dilute hydrogen peroxide solution as an oxidant due to its specific catalytic oxidation properties [1]. For the synthesis of TS-1, there are two methods, hydrothermal method and secondary synthesis or post synthesis. Gas–solid phase isomorphous replacement is a simple method to synthesize TS-1, which avoids the use of expensive template TPAOH. Generally, it is thought that titanium is incorporated into the zeolite framework through the reaction of hydroxyl nests in zeolite with gaseous $TiCl_4$. The more are the hydroxyl nests, the more are the amount of titanium into the framework. TS-1 has been successfully synthesized by this method when B-ZSM-5 was used as the precursor [2]. However, it is not clear whether the amount of titanium incorporated into the framework is in inverse proportion to the $(n)SiO_2/(n)B_2O_3$ in the precursor. In this paper, the chemical–physics properties as well as the propylene epoxidation and phenol hydroxylation properties of the TS-1 samples prepared by gas–solid synthesis with B-ZSM-5 as the precursors were investigated in order to understand the conception of “making nests for titanium atom planting” [3].

2. Experimental

2.1. Sample preparation

The parent B-ZSM-5 materials which had a $(n)SiO_2/(n)B_2O_3$ ratio in the gel varies from 5 to 100 were synthesized by using silicon-sol (aluminium free), NaOH, H_3BO_3, TPABr, and distilled water. The synthesis followed the procedure described in a previous publication [4].

All deboronation treatments were performed in a 300 ml glass reactor equipped with a heater, under vigorous stirring, using 2 mol/L hydrochloric acid aqueous solution. Afterwards the samples were filtered, washed thoroughly, dried at 393 K and calcined in static air at 813 K for 5 h.

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For the titanation step, a desired amount of deboronated and calcined zeolite samples were shaped and put in a vertical quartz tube reactor. The samples in the reactor were calcined again in a nitrogen stream of typically 1.8 L h^{-1} at 723 K for 4 h in order to remove the air and other impurity gas in the samples, after which the temperature was raised to 873 K and a saturator flow (typically 1.8 L h^{-1}) was introduced, saturated with gaseous $TiCl_4$. After 26 h reaction, the samples were purged with nitrogen for 2 h at the same temperature used for titanation to remove all the unreacted titanium chloride species in the samples. Finally, the samples were washed with ethanol thoroughly, dried in static air at 393 K for 2 h, and calcined in air at 813 K for 5 h. The samples synthesized by using B-ZSM-5 with different $(n)SiO_2/(n)B_2O_3$ varying from 5 to 100 as the precursors were noted as S-1, S-2, S-3, S-4 and S-5.

2.2. Characterization

X-ray powder diffraction (XRD) was performed on a D/max-2400 diffractometer using the Cu *K*α radiation. Relative crystallinity of samples was calculated by comparing the sum of the peak intensities of $2\theta = 7.8^\circ$, 8.8°, 23.2°, 23.8° and 24.3° in the XRD patterns. The crystallinity of B-ZSM-5 sample calcined at 813 K was assumed to be 100%. Fourier-transform infra-red spectra (FT-IR) were taken on a Nicolet-5DX spectrometer at room-temperature. Before measurement, zeolite samples were grounded with KBr and pressed into thin wafers and dried at 393 K for 1 h in air. UV–Vis spectra were recorded on a Shimadzu V-550 in the range of 190–400 nm using the diffuse reflectance technique. The blank board was used as the reference. XRF analysis were taken on a SRS-3400 X-ray fluoroscope from Bruker Co. NH_3 temperature programmed desorptions were recorded on a Chembet 3000 chemical adsorber from Quantachrom Co. Raman spectra were recorded on a Jobin Yvon U-1000 Raman spectrometer. ICP-AES were taken on a Plasam-Spec-I (Leem Labs, USA) spectrometer.

2.3. Reaction test

The epoxidation of propylene was carried out in a stainless-steel reactor which was immersed into a bath temperature-controlled at the required temperature. Typically, 0.2 g of calcined catalyst, 33.6 ml of the mixture of H_2O_2 and methanol were fed into the reactor. Then propylene was charged at constant pressure (0.4 MPa). The mixture was heated at 333 K under magnetic agitation for 60 min. The residual H_2O_2 was checked by iodometric titration. The product of the reaction was analyzed on a GC-8A gas chromatography using a flame ionization detector and a capillary column (40.0 m × 0.25 mm) containing polyethylene glycol 20 M as the stationary phase. Propylene oxide (PO) was the target product, and propylene glycol (PG) and its mono-methyl ethers (MME) were the by-products. The result of the reaction was given using these criteria:

$$x_{H_2O_2} = \frac{n^0_{H_2O_2} - n_{H_2O_2}}{n^0_{H_2O_2}} \times 100,$$

$$e_{H_2O_2} = \frac{n_{PO} + n_{MME} + n_{PG}}{n^0_{H_2O_2} \times x_{H_2O_2}} \times 100,$$

$$s_{PO} = \frac{n_{PO}}{n_{PO} + n_{MME} + n_{PG}} \times 100,$$

$$s_{MME} = \frac{n_{MME}}{n_{PO} + n_{MME} + n_{PG}} \times 100,$$

$$s_{PG} = \frac{n_{PG}}{n_{PO} + n_{MME} + n_{PG}} \times 100.$$

The hydroxylation of phenol (PHE) was carried out in a glass reactor which was immersed into a bath temperature-controlled at the required temperature. In a typical run, 0.4 g of calcined catalyst, 4 g phenol, 8.7 ml acetone and 1.5 ml H_2O_2 aqueous solution were fed into the reactor. The mixture was heated under magnetic agitation for 6 h. The product of the reaction was analyzed on a GC-8810 gas chromatography using a flame ionization detector and a capillary column (15.0 m × 0.25 mm) containing SE-54 as the stationary phase. Catechol (CAT) and hydroquinone (HQ) were the main products, and *para*-benzoquinone (PBQ) was the by-product. The result of the reaction was given using the criteria as follows:

$$x_{PHE} = \frac{n^0_{PHE} - n_{PHE}}{n^0_{PHE}} \times 100,$$

$$s_{HQ} = \frac{n_{HQ}}{n_{HQ} + n_{CAT} + n_{PBQ}} \times 100,$$

$$s_{CAT} = \frac{n_{CAT}}{n_{HQ} + n_{CAT} + n_{PBQ}} \times 100,$$

$$s_{PBQ} = \frac{n_{PBQ}}{n_{HQ} + n_{CAT} + n_{PBQ}} \times 100.$$

3. Results and discussion

3.1. Characterization of Ti-ZSM-5 from gas–solid synthesis

The XRD patterns (Fig. 1) and FT-IR spectra (Fig. 2) indicate that all the Ti-ZSM-5 samples remain the MFI structure after titanation. The relative crystallinity of S-1 to S-5 were 87.9, 82.2, 96.2, 87.1 and 100%, respectively. After gas–solid phase isomorphous replacement, the relative crystallinity decreased to about 90%, compared with the parent B-ZSM-5. The XRD peak at 24.4° of S-5 split into two peaks, which indicates the transformation from orthorhombic system to monoclinic system. The splitting in S-5 is not due to the titanation because the peak at 24.4° has been split into two peaks in B-ZSM-5 ($SiO_2/B_2O_3 = 100$) precursor. The peak at 25.4° of S-5 shows the appearance of anatase TiO_2.

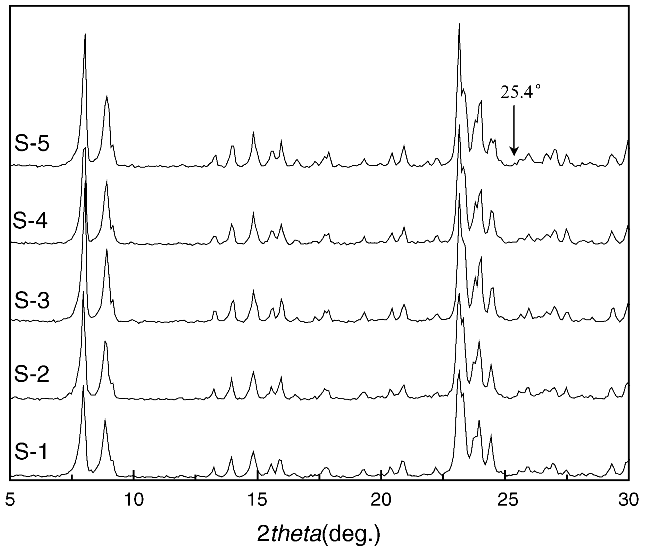

Fig. 1. XRD patterns of Ti-ZSM-5 synthesized by using B-ZSM-5 with different $(n)SiO_2/(n)B_2O_3$ as the precursors.

Fig. 2 exhibits that obvious vibration peaks appear at 960 cm^{-1} which can be attributed to the incorporation of Ti^{4+} into the zeolites framework after titanation. The vibration bands at 550 and 1250 cm^{-1} show the maintenance of pentasil-type of the Ti-ZSM-5 samples. The intensity of 960 cm^{-1} peaks increases with the decreasing of $(n)SiO_2/(n)B_2O_3$ in the precursors. This indicates that the amount of active centre titanium (Ti^{4+}) incorporated into the framework increases with the increases in the amount of boron in the precursors.

The UV–Vis spectra (Fig. 3) exhibit peaks at 212 nm which can be attributed to charge transfer of oxygen 2*p* electron in exited state to the empty 3*d* orbital of framework Ti^{4+}. The active centre Ti^{4+} exists in tetrahedral structure. The shoulder peaks at 240–250 nm may involve the isolated Ti^{4+} in octahedral environment [5]. The peak at 330 nm shows that the amount of extra-framework titanium species, anatase TiO_2, has a sharp increase when the $(n)SiO_2/(n)B_2O_3$ increases to 100.

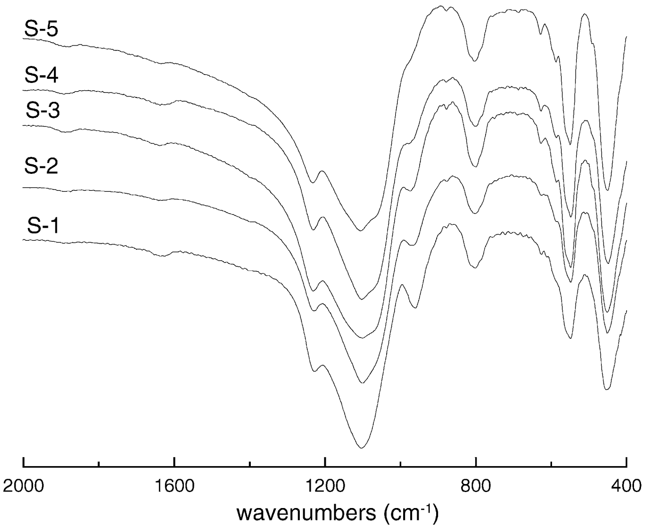

Fig. 2. FT-IR spectra of Ti-ZSM-5 synthesized by using B-ZSM-5 with different $(n)SiO_2/(n)B_2O_3$ as the precursors.

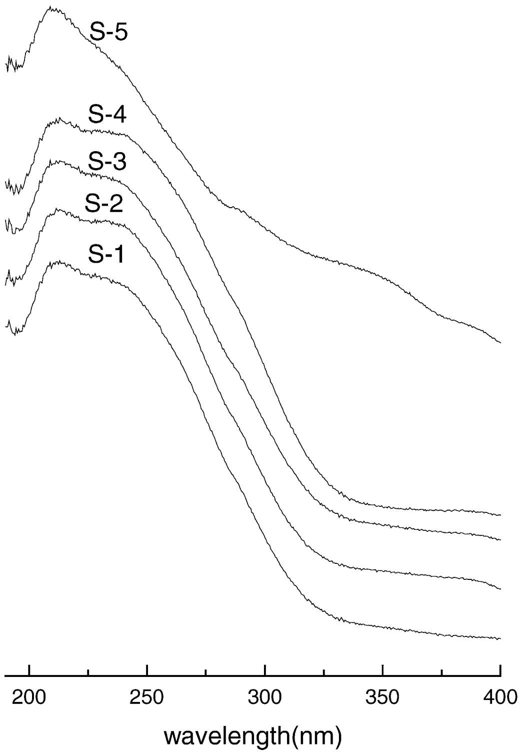

Fig. 3. UV–Vis spectra of Ti-ZSM-5 synthesized by using B-ZSM-5 with different $(n)SiO_2/(n)B_2O_3$ as the precursors.

Raman spectroscopy is a sensitive technique for making certain whether there is anatase TiO_2 specie in zeolite samples. In order to confirm the result of XRD and UV–Vis analysis, the Raman spectra of S-4 and S-5 were taken (Fig. 4). The spectra show that there is anatase TiO_2 in S-5 (band at about 145 cm^{-1} [6,7]).

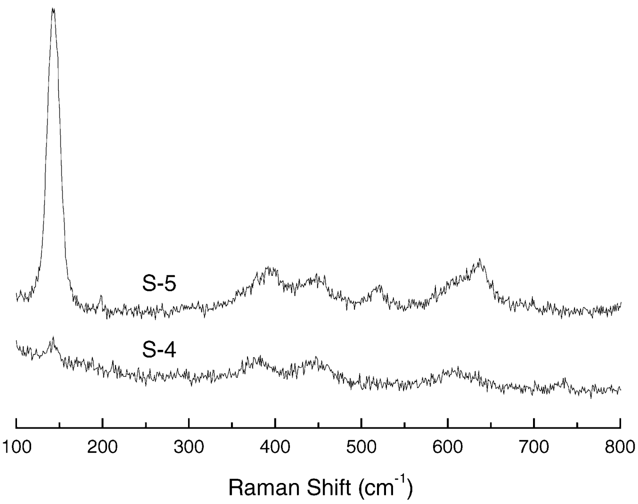

Fig. 4. Raman spectra of samples S-4 and S-5.

Table 1
XRF analysis of Ti-ZSM-5 synthesized by using B-ZSM-5 with different $(n)SiO_2/(n)B_2O_3$ as the precursors

Sample	$(n)SiO_2/(n)B_2O_3$ (in the gel, mol/mol)	SiO_2/Al_2O_3 (mol/mol)	SiO_2/TiO_2 (mol/mol)	$TiO_2/TiO_2 + SiO_2$ (10^{-2} mol/mol)
S-1	5	788.5	41.8	2.34
S-2	10	1178.3	44.3	2.21
S-3	20	1587	51.9	1.89
S-4	50	>2000	63.8	1.54
S-5	100	>2000	94.8	1.04
S-anatase	–	86.63	41.7	2.34

S-anatase: Ti-ZSM-5 samples containing a large amount of anatase TiO_2.

Table 1 lists the elemental composition of Ti-ZSM-5 synthesized by using B-ZSM-5 with different $(n)SiO_2/(n)B_2O_3$ in the precursors. From the table it can be seen that $(n)SiO_2/(n)TiO_2$ in the samples increases with an increase in the $(n)SiO_2/(n)B_2O_3$ in the precursors. This indicates that the more is the amount of boron in the precursor the more hydroxyl nests after HCl treatment, and the more is the amount of titanium incorporated into the framework after titanation treatment. This indicates that the amount of Ti incorporated into the zeolite samples during the titanation step can be controlled by adjusting the amount of boron in the precursors.

3.2. *Epoxidation of propylene and hydroxylation of phenol over Ti-ZSM-5 prepared by gas–solid synthesis*

Table 2 lists the propylene epoxidation properties of Ti-ZSM-5 synthesized by using B-ZSM-5 with different $(n)SiO_2/(n)B_2O_3$ as the precursors. It can be seen in Table 2 that the catalytic activity ($x_{H_2O_2}$) and the H_2O_2 efficiency ($e_{H_2O_2}$) of the samples increase with the decreasing of $(n)SiO_2/(n)B_2O_3$ or $(n)SiO_2/(n)TiO_2$. It can be attributed to that more Ti^{4+} in the framework provides more active centres to catalyze the reaction of propylene with dilute H_2O_2. Moreover, this paper gives better catalytic activity and efficiency of H_2O_2 of gas–solid synthesized Ti-ZSM-5 in the epoxidation of propylene than previous reports [8].

At the same time, the selectivity to propylene oxide (s_{PO}) decreases with the decreasing of $(n)SiO_2/(n)B_2O_3$. S-1 exhibits low selectivity to PO in the epoxidation of propylene with dilute H_2O_2, while S-5 exhibits high selectivity to PO. The low selectivity to PO is attributed to the acidity of Ti-ZSM-5 from the residual boron and the silicon hydroxyls. Fig. 5 shows the NH_3 TPD analysis of samples S-1 and S-5. It can be calculated that the acidity of S-1 is 14 times than that of S-5. The ICP-AES analysis shows that the amount of residual boron of S-1 (0.085 wt.%) is 12 times than that of S-5 (0.0071 wt.%). Then it can be concluded that most of the acid sites in the samples were resulted from the residual boron.

XRD pattern and Raman spectrum of S-5 show that more crystalline anatase phase appears in the sample, however, the H_2O_2 efficiency does not decrease too much compared with that of samples 3 and 4. It seems that the anatase TiO_2 with high crystallinity has less or no side effect on decomposing hydrogen peroxide. In order to prove the concept, Ti-ZSM-5 samples contain much anatase TiO_2 were synthesized and used to catalyze the epoxidation of propylene with dilute H_2O_2. Fig. 6 shows the XRD pattern of the sample. The elemental composition and epoxidation properties are listed in Tables 1 and 2 (marked as S-anatase). From the figure and the tables it can be seen that the aluminium existing in the framework resulted in the dramatic increase in the amount of anatase TiO_2 and decrease in the amount of framework titanium (Ti^{4+}). The acid sites came from the aluminium decreased the selectivity to PO, while the anatase TiO_2 ex-

Table 2
Epoxidation properties of Ti-ZSM-5 synthesized by using B-ZSM-5 with different $(n)SiO_2/(n)B_2O_3$ as the precursors

Sample	$x_{H_2O_2}$ (%)	$e_{H_2O_2}$ (%)	s_{PO} (%)	s_{MME} (%)	s_{PG} (%)
S-1	97.50	98.52	47.02	50.63	2.35
S-2	93.10	95.00	53.63	43.17	3.20
S-3	87.50	88.81	65.66	32.34	2.00
S-4	79.84	88.09	75.64	24.36	0
S-5	66.13	85.40	89.15	10.85	0
S-anatase	55.00	91.41	5.30	94.70	0

Reaction conditions: $T = 333$ K, $t = 60$ min, the concentration of H_2O_2 0.54 mol/L, propylene pressure 0.4 MPa, amount of catalyst 5.95 g/L, solvent methanol. S-anatase: Ti-ZSM-5 samples containing a large amount of anatase TiO_2.

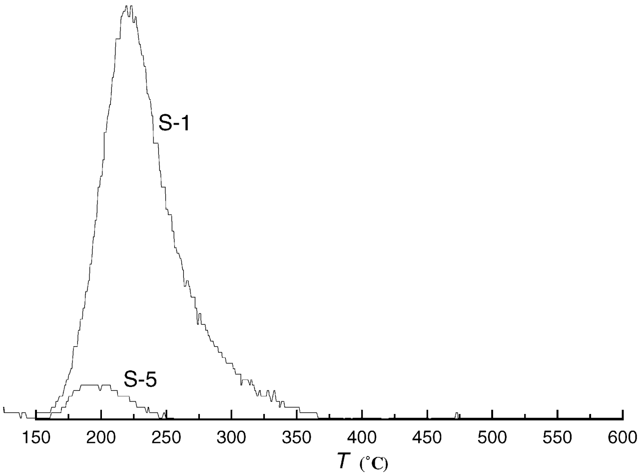

Fig. 5. NH_3 TPD analysis of samples S-1 and S-5.

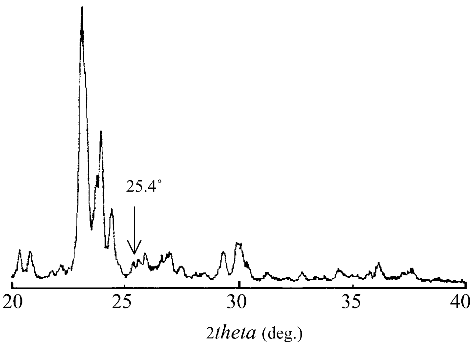

Fig. 6. XRD spectrum of Ti-ZSM-5 samples (S-anatase) containing a large amount of anatase TiO_2.

isting had less or no effect on the H_2O_2 efficiency. The activity of the sample containing a large amount of aluminium is low because of less available active centres (Ti^{4+}).

The phenol hydroxylation properties of Ti-ZSM-5 synthesized by using B-ZSM-5 with different $(n)SiO_2/(n)B_2O_3$ as the precursors are listed in Table 3. The results show that the samples have relatively lower activity in the hydroxylation of phenol (x_{PHE}) with dilute H_2O_2 than the standard TS-1 [9], while in the epoxidation of propylene, some of them show high activity. This can be attributed to the crystalline particles size of the samples. The SEM imagines indicate that the Ti-ZSM-5 samples have the crystalline particles with about 5 μm size. Because of the influence of diffusion [10], the phenol hydroxylation activity of the samples was low. Moreover, the local environment of titanium in Ti-zeolite prepared by gas–solid synthesis seems to be different from that in TS-1 synthesized by the classical method. A ^{29}Si MAS NMR study has proved this view [11]. It can also be seen from Table 3 that less amount of catalyst resulted in a higher selectivity to *para*-benzoquinone (s_{PBQ}), which is attributed to an over-oxidation of hydroquinone in the presence of an excess of H_2O_2. So, suitable amount of catalyst favors the formation of dihydroxybenzenes (hydroquinone and catechol).

Table 3
Phenol hydroxylation with H_2O_2 over Ti-ZSM-5 synthesized by using B-ZSM-5 with different $(n)SiO_2/(n)B_2O_3$ as the precursors

Sample	x_{PHE}	s_{CAT}	s_{HQ}	s_{PBQ}
S-1	19.2[a]	46.8	47.9	5.3
	10.1[b]	56.9	23.2	19.8
	7.8[c]	67.5	7.5	25.0
S-4	8.1[b]	60.5	21.0	18.5
S-5	0.9[b]	88.7	11.3	0
[9]	12.8[d]	47.3	42.6	10.1
	25.5[e]	60.8	29.4	9.8
[12]	4.0[a]	–	–	–
[13]	5.5[a]	–	–	–

Reaction conditions: solvent Me_2CO, $T = 353\,K$, $n(PHE)/n(H_2O_2) = 3$, $n(Me_2CO)/n(PHE) = 2.7$, $t = 6\,h$.

[a] $m(cat)/m(PHE) = 10.0\%$.

[b] $m(cat)/m(PHE) = 5.0\%$.

[c] $m(cat)/m(PHE) = 2.5\%$.

[d] Crsytal size: 1.0 μm × 2.0 μm × 6.0 μm.

[e] Crystal size: 0.1 μm.

Compared with previous reports [12,13] of the application of gas–solid synthesized Ti-ZSM-5 samples to the phenol hydroxylation, S-1 and S-4 exhibit relatively higher catalytic activity. One of the reasons for it is that the framework boron is easier to be removed from the framework than framework aluminium. With less hetero-atoms residual, more titanium can be incorporated into the zeolite framework. Furthermore, the acidity from the residual boron is weaker than that from residual aluminium. Less and weaker acid sites on the surface of Ti-containing zeolites, less side effect of phenol protonation, which hindered the electrophilic reaction of phenol hydroxylation. In a word, more active sides and fewer strong acid sites resulted in the higher phenol hydroxylation activity.

From the above results, it can be concluded that the low catalytic properties of S-5 in phenol hydroxylation can be attributed to the less amount of available active centres (Ti^{4+}).

4. Conclusions

From the above-mentioned results, it can be concluded that it is possible to adjust the amount of framework titanium by varying the $(n)SiO_2/(n)B_2O_3$ in the gel during the synthesis of the precursors, B-containing zeolites, e.g., from 5 to 100.

The amount of titanium incorporated into the framework is in inverse proportion to the $(n)SiO_2/(n)B_2O_3$ in the precursor.

When the $(n)SiO_2/(n)B_2O_3$ is high and less silicon hydroxyls available, the excessive Ti^{4+} not incorporated into the framework will bind to the framework surface and exists as the anatase form after the gas–solid reaction.

The acidity from the hetero-atom, residual boron, causes the decrease of the catalytic selectivity to PO.

Acknowledgements

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