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Synthesis, Characterization and Catalytic Properties of TBS-2 Zeolites†

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Titanium and B co-substituted silicate-2 zeolites were characterized using XRD, FT-IR and NH_3-TPD, and the TBS-2's bifunctional catalytic properties as oxidative and acidic catalysts were investigated using the epoxidation of styrene and rearrangement of styrene oxide.

Co-incorporation of Ti and trivalent metal ions such as B^{3+}, Al^{3+}, Ga^{3+}, or Fe^{3+} in MFI and MEL structures to modify their catalytic properties has been reported recently.[1–6] However, details of the synthesis, characterization and catalytic properties of the co-incorporated zeolites are sparse. In the present work, we report the synthesis, characterization and catalytic properties of TSB-2 zeolites.

The observed XRD patterns for calcined TBS-2 zeolites, which are well crystallized, show no line broadening and match well those of TS-2, BS-2 and S-2, strongly suggest that Ti and B are simultaneously incorporated into the MEL structure. The unit cell volume of TS-2 (Table 1) is larger than that of pure S-2 and consistent with many reports.[7] However, that of TBS-2 is smaller than that of pure S-2 and larger than that of BS-2. This is due to the replacement of the framework Si by the smaller B^{3+} ions, which can cause S-2 framework contraction. A decrease in the unit cell parameters should confirm that boron has been successfully incorporated into the framework of TS-2. The IR bands at 960 and 1380 cm^{-1} are used as fingerprints of Ti and B incorporation into the S-2 framework.[7,8] The absence of any new IR features in TBS-2 other than framework Ti and B bands may indicate that, despite the presence of the two elements in the same crystallites, there are no mixed Ti–O–B sites in the framework.

Increasing the H_2O_2:SiO_2 ratio from 0.13 to 0.26:1 (corresponding to samples 2 and 1) will obviously cause a decrease in the framework B band, but varying this ratio in the range 0.13–0.08 will not affect the two framework bands (samples 2 and 3). However, when increasing B_2O_3:SiO_2 from 0.05 to 0.10:1 (samples 2, 3, 4 and 5) the framework B band is not obviously increased, and the framework Ti band is obviously decreased. Thus, the amounts of H_2O_2 and H_3BO_3 used for efficient incorporation of B and Ti into the S-2 framework must be appropriate, the use of excessive H_2O_2 or H_3BO_3 will obviously inhibit such incorporation. The addition of 10% aq. TMAOH not only avoids serious gelation, but also efficiently enhances the incorporation of boron (samples 6 and 7).

NH_3-TPD was used to measure the acidic properties of these zeolites. The amounts of ammonia desorbed from these zeolites and the maximum temperatures are summarized in Table 1. There is only a desorption peak for the all samples with a desorption temperature range of 383–573 K. The NH_3 uptakes on the greater part of TBS-2 zeolites are higher than on TS-2 and BS-2; the two TBS-2 samples (samples 1 and 5) and BS-2 have lower NH_3 uptakes, which is attributed to the decrease in the framework Ti and B bands in these samples. The maximum temperatures of NH_3 desorption on TBS-2 and BS-2 zeolites are 20–30 K higher than that of TS-2. These results show that all these zeolites have weak acidic properties, and the incorporation of boron in TS-2 can enhance both the number and strength of its acid sites.

In the epoxidation of styrene, TS-2 has slightly higher oxidation activity and selectivity for rearrangement to phenylacetaldehyde than TBS-2, which is due to a higher Ti content in TS-2. The catalytic activity of TBS-2 increases with an increase in its framework Ti content, and the selectivity decreases with an increase in its framework B content. The products comprise 70–80% phenylacetaldehyde, arising from the Lewis acid–catalysed rearrangement of the epoxide,[9] 20–28% benzaldehyde and formaldehyde and about 1.5% phenylethanol, in agreement with the results of Xia *et al.*[10] In order to verify the formation of PhCHO and HCHO, phosphoric acid was added to the epoxidation reaction system. There was obviously an increase in the formation of PhCHO and HCHO. Thus, we propose that their formation is due to the catalysis of Brønsted acid sites produced by the co-ordination of H_2O/H_2O_2 to the Ti and B atoms of TBS-2.[11] In catalytic rearrangement of styrene oxide, TBS-2 is obviously more

Table 1 Results of XRD, IR and NH_3-TPD for TBS-2 zeolites

	TBS-2 Samples			XRD results[a]	Framework IR band intensity[b]			NH_3-TPD	
No.	*x*	*y*	*z*	V/Å^3	550 cm^{-1}	960 cm^{-1}	1380 cm^{-1}	T_m/K	NH_3 uptake
1	0.0	0.050	0.26	5343.2	2.12	0.59	0.02	468	0.15
2	0.0	0.050	0.13	5352.1	2.40	0.77	0.17	486	0.37
3	0.0	0.050	0.08	5349.5	2.19	0.75	0.17	489	0.36
4	0.0	0.075	0.10	5333.7	2.06	0.78	0.20	489	0.41
5	0.0	0.100	0.12	5314.6	2.06	0.49	0.17	485	0.26
6	0.2	0.075	0.12	5212.6	2.22	0.64	0.44	491	0.47
7	0.1	0.075	0.12	5239.5	2.31	0.55	0.25	483	0.36
TS-2	0.0	0.000	0.10	5448.7	2.20	1.03	—	465	0.30
BS-2	0.0	0.050	0.00	5214.1	2.62	—	0.32	491	0.12
S-2	0.0	0.000	0.00	5384.0	2.60	—	—	—	—

[a]Measured by a Siemens D-500 diffractometer with Cu-Kα radiation (λ = 1.54051 Å). [b]Measured by a Nicolt 510P FT-IR spectrometer; band intensity (cm)/800 cm^{-1} band intensity (cm).

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Table 2 Results of epoxidation of styrene and rearrangement of styrene oxide over TBS-2 zeolites

	Contents		Epoxidation of styrene[a]		Rearrangement of styrene oxide[b]	
Sample	Si:Ti	SiO_2:B_2O_3	Conv. (mol%)	$PhCH_2CHO$ Sel. (%)	Conv. (mol%)	$PhCH_2CHO$ Sel. (%)
BS-2	—	66.7	0	—	37.6	96.2
TBS-2(1)	78.9	546.7	7.1	78.0	46.3	98.3
TBS-2(7)	75.8	85.3	7.4	70.9	72.8	97.9
TBS-2(3)	62.1	125.6	8.2	75.4	91.4	98.5
TBS-2(4)	58.4	106.5	8.9	72.1	99.3	99.2
TS-2	45.2	—	10.7	78.2	56.2	96.8
TBS-2(4)	58.4	106.5	12.1[c]	51.6[c]	99.5[d]	79.6[d]

[a] Styrene (2.08 g), 30% aq. H_2O_2 (2.28 g), acetone (10 ml), catalyst (0.2 g), reaction temperature 333 K and time 5 h. Besides phenylacetaldehyde, 20–28% benzaldehyde and formaldehyde, and 1.5% phenylethanol were obtained. [b] Styrene oxide (1 ml), acetone (7 ml), catalyst (0.1 g), reaction temperature 333 K and time 5 h. Besides phenylacetaldehyde, a small amount of benzaldehyde ($\leqslant$3.8%) was obtained. [c] 48.4% Benzaldehyde and formaldehyde were obtained by adding 0.25 ml of 85% aq. phosphoric acid to the epoxidation reaction system. [d] 20.4% Benzaldehyde and formaldehyde were obtained by adding 1.14 g of 30% aq. H_2O_2 to the rearrangement reaction system.

active and slightly more selective than TS-2, which is attributed to the greater number and stronger Lewis acid sites in TBS-2.

Experimental

The synthesis of TBS-2 was as follows: titanium tetrabutoxide (0.172 g) was added to water (5.0 g), giving a white precipitate (hydrous titanium oxide). 30% aq. H_2O_2 was added to dissolve the oxide (solution 1). Solution 2 was prepared from 11.6 g of 10% aq. TBAOH and 10% aq. TMAOH was added to TEOS (4.76 g). A solution containing boric acid in water (10 g) was then added to solution 2. Stirring of 2 was maintained at 353 K for 2 h. Finally, solution 1 was added dropwise to solution 2. The molar composition of the reaction mixture was $0.2\ TBAOH–xTMAOH–1.0SiO_2–0.02TiO_2–yB_2O_3–zH_2O_2–50H_2O$. The crystallization was done statically at 448 K for 4 d. The solid obtained was filtered off, washed with water, dried at 393 K for 2 h, and calcined at 813 K for 16 h in air.

NH_3-TPD was carried out from 373 to 723 K with a heating rate β of 8 K min^{-1} and with N_2 (30 ml min^{-1}) as carrier gas. The NH_3 uptake was determined using TCD by comparing with the integrated area of a known volume of NH_3.

The epoxidation of styrene or rearrangement of styrene oxide was performed under vigorous stirring in a three-necked glass flask equipped with a condenser and thermometer. The reaction products were analysed by GC on a SE-54 capillary column with a FID.

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