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A Novel Method for the Preparation of a Titanium and Boron Containing Zeolitic Material with MFI Structure and its Catalytic Properties

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A new straight forward method, for the preparation of a titanium and boron containing MFI type zeolitic material is presented. Thereby the use of sodium and HF are avoided. The obtained material was characterized by XRD, ^{11}B , ^{29}Si and $^1\text{H} \rightarrow ^{29}\text{Si}$ cross-polarization MASNMR as well as ICP-AES, FT-IR and UV-Vis spectroscopies. This (Ti, B)-MFI zeolite crystallizes rapidly and contains less unwanted extra framework titanium than a reference material synthesized via a known route. Tests with respect to the catalytic properties showed, that this (Ti, B)-MFI zeolite is active in bifunctional catalysis. Phenylacetaldehyde was obtained via the liquid phase epoxidation of styrene followed by epoxide rearrangement of the "in-situ" formed styreneoxide.

1. Introduction

The synthesis of intermediates and fine chemicals is already well established by use of zeolites as acidic catalysts. Since homogeneous catalysts are obsolete in many cases due to their inherent environmental problems, solid acids for heterogeneous catalysis are favorable. Among those zeolites give the advantage of shape selectivity to suppress side reactions¹⁻⁵.

One example of industrial significance is the gas-phase rearrangement of epoxides to the corresponding aldehydes and/or ketones. Many publications indicate their wide potential for industrial applications in the synthesis of *e.g.* pharmaceuticals, fragrances and for food and drug products in general as well as agrochemicals⁶⁻¹⁰.

In the rearrangement of styrene oxides to the corresponding aldehydes, for example the ZSM-5 zeolites and especially the (B)-MFI zeolite is superior to other solid acids and to the homogeneous catalysts. Because of its extremely weak acidic properties and the MFI lattice the formation of by products are efficiently suppressed. They are applicable in the gas phase as well as in the liquid phase^{2,11-13}.

Since the striking discovery of TS-1 by Taramasso *et al.*¹⁴ even liquid phase oxidation reactions using H_2O_2 are performed in the industrially scale. As a result, efforts in the research on zeolitic oxidation catalysts grew tremendously¹⁵⁻²⁰.

In addition, TS-1 is also a capable catalyst in the liquid phase rearrangement of epoxides such as styrene oxides to the corresponding aldehydes. This reaction occurs due to the Lewis-acidity of the TS-1 material. Phenylacetaldehyde was reported to be obtained in H_2O_2 yields of up to 75 % using *t*-butanol as the solvent and a five-fold excess of styrene to get highest possible H_2O_2 conversion²¹.

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TS-1 as an applied catalyst for liquid phase oxidations and (B)-MFI which excels in the rearrangement of epoxides can easily be thought of being combined in one reaction step. Therefore the combination of the benefits of TS-1 and (B)-MFI in a single catalyst would be an interesting challenge.

Trong On *et al.* reported on such a material called TBS-1^{22,23}) which contains both T-atoms, boron and titanium. It is synthesized via a multi step gel preparation in which TiO_2 is precipitated in the first step and brought back to solution in the next. Nevertheless the materials contain rather big amounts of extraframework titanium species. TBS-1 was reported to be active in the liquid phase oxidation of cyclohexene with H_2O_2 in ethanol as the solvent, the consecutive ring opening reaction of the cyclohexene epoxide to the diol with water and with ethanol to form ethers²⁴). Further methods for the synthesis of TBS-1^{25,26}) have been reported with the goal to prevent the use of the costly template TPAOH. These methods suffer from a very low rate of crystallization. They have to be carried out in a multistep synthesis using poisonous and corrosive hydrogenfluoride.

Now we report on a new and more straight forward synthesis method for a titanium and boron containing material with MFI structure so called Ti-BMFI. This method does not use sodium and hydrogen fluoride. Also catalytic tests on the activity in the epoxidation of styrene with H_2O_2 in methanol as a solvent and the consecutive rearrangement to the desirable phenylacetaldehyde were carried out in a "one-pot" reaction.

2. Experimental

The synthesis of the (Ti, B)-MFI materials was performed via two routes once according to Trong On *et al.*²²) (Synthesis I) and the new route (Synthesis II). Both are carried out using TEOS (tetraethoxy-silicate, FLUKA) as silica source, boric acid as the boron source and TEOT (tetraethoxytitanate, Fluka) as titanium source. The template was TPAOH (tetrapropyl-ammonium hydroxide, SACHEM).

2.1 Synthesis I

Gel 1: 95 mmol TEOS was hydrolysed with 35 mmol 25 % TPAOH solution in water. Afterwards 4.75, 9.5, 2.38 mmol boric acid were added, followed by the residual 15 mmol 25 % TPAOH solution. The ethanol formed in the reaction was removed under vacuum.

Gel 2: 3.02 mmol TEOT were precipitated as TiO_2 with 1.03 mmol of water and diluted again with 16.7 mmol of 30 % hydrogenperoxide forming soluble titanium peroxy-species.

The gel 2 was added dropwise to gel 1, stirred over night and filled into a steel autoclave. The pH was 11. Hydrothermal synthesis was performed for 5 days at 175 °C under autogeneous pressure. The composition of the gel was: SiO_2 : 0.03 TiO_2 : 32 H_2O : 0.45 TPAOH: $n \text{ B}_2\text{O}_3$ with $n = (0.05, 0.1, 0.025, 0.02)$. These materials are named TBS-1.

2.2 Synthesis II

In a "one pot" preparation 68.8 mmol of TEOS (Fluka) are mixed with 2.1 mmol of TEOT (Fluka) under stirring. In an argon atmosphere 30.8 mmol of 25 % TPAOH (Sachem) were added carefully under vigorous stirring at 10 °C. Afterwards ethanol was removed by evaporation under vacuum. Under stirring 0.86, 1.72, 3.44 and 6.87 mmol of boric acid diluted in 1 mol water were added. The composition of the gel was: SiO_2 : 0.03 TiO_2 : 32 H_2O : 0.45 TPAOH: $n \text{ B}_2\text{O}_3$ with $n = (0.0125, 0.025, 0.05, 0.1)$. These materials are named Ti-BMFI

2.3 Calcination

The samples were calcined using a gentle method that leaves the boron T-atoms in the framework of the zeolite. The trigonally coordinated intra-framework boron which is formed during standard calcination in air is hydrolyzed by the water formed by the pyrolysis of the template. In order to protect the boron sites in the framework, the boron is kept tetrahedrally coordinated until the template is burned off completely. This is done by a sequence of ion exchanges followed by calcinations in the adequate atmospheres. The technique was described

Table 1 Chemical Composition and Crystallinity in Percent of the Reference Substance TS-1 of the Investigated Materials.

Sample	synth.	% cryst.	Ti/Si gel	Ti/Si as syn.	Ti/Si calcined	B/Si gel	B/Si as syn.	B/Si calcined
TS-1	II	100	0.03	0.022	0.029	0	0.001	0
(B)-MFI	II	123	0	0	0	0.2	0.027	0.025
TBS-1a1	I	102	0.03	0.021	0.028	0.05	0.018	0.015
TBS-1a2	I	98	0.03	0.036	0.031	0.1	0.018	0.021
TBS-1a3	I	95	0.03	0.035	0.030	0.2	0.028	0.024
Ti-BMFI1	II	100	0.03	0.032	0.039	0.1	0.015	0.015
Ti-BMFI2	II	95	0.03	0.033	0.036	0.2	0.020	0.018
Ti-BMFI3	II	97	0.03	0.037	0.041	0.05	0.011	0.012
Ti-BMFI4	II	96	0.03	0.031	0.028	0.025	0.008	0.01
Ti-BMFI5	II		0.03	0.033		0.2	0.025	

by de Ruiter *et al.*^{27,28)}.

2.4 Characterization

XRD measurements were done on a Siemens D5000 diffractometer using Cu K α radiation. Crystallinity was determined via the measurement of the intensity of the d₅₀₁ reflection. Chemical analysis of the zeolitic materials was obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a ICP-AES Spectro Flame D. The thermal analysis were carried out using a Netzsch STA409. All shown DTG-plots were smoothed. The presented FT-IR spectra were recorded on a Nicolet 510P spectrometer using KBr wavers with 1 wt.% of sample.

Diffuse reflection UV-Vis spectra were obtained using a Perkin Elmer Lambda 7 Spectrometer. MASNMR spectroscopy was carried out with a Bruker Avance 500 Spectrometer in a 7 mm ZrO₂ rotor. For ²⁹Si and ¹H \rightarrow ²⁹Si CP-MASNMR tetramethylsilane was used as a standard whereas the contact time for the cross-polarization experiment was 5 ms. ¹¹B-MASNMR spectra were standardized to BF₃ · ET₂O. A spin echo pulse program was applied to suppress the background signal caused by the boronnitride in the probehead.

2.5 Test reactions

Test reactions were performed in round bottom flasks under refluxing conditions and stirring. The sample was dried over molecular sieve 5 Å and analyzed using gas chromatography (GC). GC was carried out using a CS FS-SE-54 60 m column in a

Carlo Erba C1200 chromatograph. The temperature program used was 50 °C, 6 min. isotherm, 5 °C per minute to 270 °C.

3. Results and Discussion

3.1 XRD and Chemical Analysis

Powder diffraction measurements revealed MFI structures of the samples prepared according to the method of Trong On (synthesis I) and according to the new method (synthesis II). No other phases such as anatase, rutile or brookite have been detected. Table 1 gives a summary on the crystallinity and chemical composition of the synthesized samples. The crystallinity is given in percent of the chosen reference sample TS-1. In case of all samples no significant changes in the crystallinity were observed.

The chemical analysis using ICP-AES revealed differences between the incorporation of boron and titanium species into the as-synthesized materials. As seen in Table 1, the titanium to silicon ratio in the synthesis gel was found to be slightly increased by approx. 10 % in the synthesized materials. This can be explained with the higher reactivity of the titanium species compared to the silicon species as well in the aspect of hydrolysis of the TEOS and TEOT as in the consecutive polycondensation. The boron to silicon ratio in the solid materials was found to be ten times less than in the synthesis gel. This is due to the good solubility of boric acid in the mother liquor.

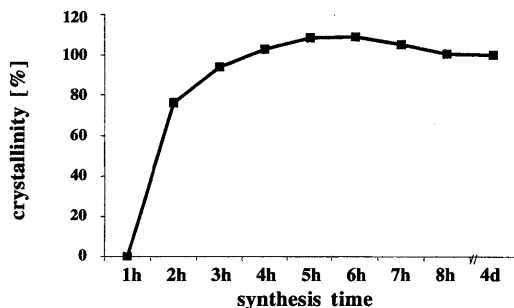


Fig.1 Crystallization of Ti-BMFI-5 (see Table 1).

After calcination via the method described by de Ruiter *et al.*²⁷⁾, the boron to silicon and titanium to silicon ratios did not change evidently.

3.2 Speed of Crystallization

The crystallization of TBS-1 was described to be complete after a minimum of 2 days²³⁾. Earlier investigations with synthesis times of 8 or even 14 days did not yield better crystallinity²⁶⁾. In the example of the synthesis of Ti-BMFI-5 according to the new method, to our surprise the sample showed already 80 % crystallinity compared to the TS-1 reference after a duration of 2 hours (see Table 1). 100 % crystallinity was achieved after 4 hours as shown in Fig.1. The plot shows a maximum of 109 % after 6 h synthesis time. This could be due to a larger amount of very small crystallites compared to the samples obtained after 4 days. No differences in the crystallinity could be observed in the batches carried out in the time frame of 8 hours and 4 days.

3.3 Thermal Analysis

To determine the nature of the organic templates in the as-synthesized materials DTG was carried out. As shown in Fig.2, the template decomposes at two different temperatures of 380 °C and 440 °C. Park *et al.*²⁹⁾ explained the existence of two decomposition temperatures with the existence of two species of TPA⁺ cations. One species is the TPA⁺OH⁻ ion pair which decomposes at lower temperatures, the other one is a charge balancing TPA⁺ ion attached to the isomorphously substituted atom in the zeolite framework. The latter decomposes at higher

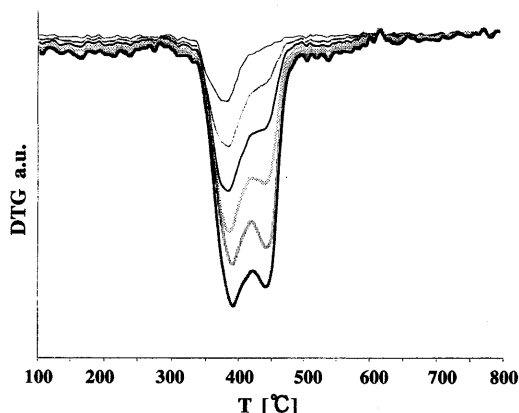


Fig.2 DTG of (Ti, B) MFI Materials with from Top to Bottom Increasing Boron Content. Materials (top to bottom): TS-1, Ti-BMFI-4, Ti-BMFI-3, Ti-BMFI-1, Ti-BMFI-2, B-(MFI).

temperatures.

In the case of TS-1 the major species found is the ion-pair. The upper plot in Fig.2 shows only a weak shoulder that can be related to the charge balancing TPA⁺ ions. The plot of the (B)-MFI sample (bottom) shows, that in the case of (B)-ZSM-5 the amount of charge-balancing TPA⁺ ions is almost equal to the amount of the ion-pair. The amount of the charge balancing TPA⁺ increases with increasing boron content of the samples. It seems there is no mutual effect of titanium and boron T-atoms in the framework of the zeolite on the decomposing temperature and the ratio of both species of template ions.

3.4 Infrared Spectroscopy

The coordination of boron as a T-atom in the synthesized samples can be examined by FT-IR spectroscopy. In Fig.3, two plots of the same material before and after calcination are shown which are typical for all the discussed boron containing materials. The as-synthesized sample shows a band at 910 cm⁻¹ which is attributed to a framework Si-O-B vibration³⁰⁾. The calcined sample shows the same band and an additional broad banded absorption at 1380 cm⁻¹ which is attributed to trigonally coordinated framework boron³¹⁾. These findings are also relevant for the other synthesized samples.

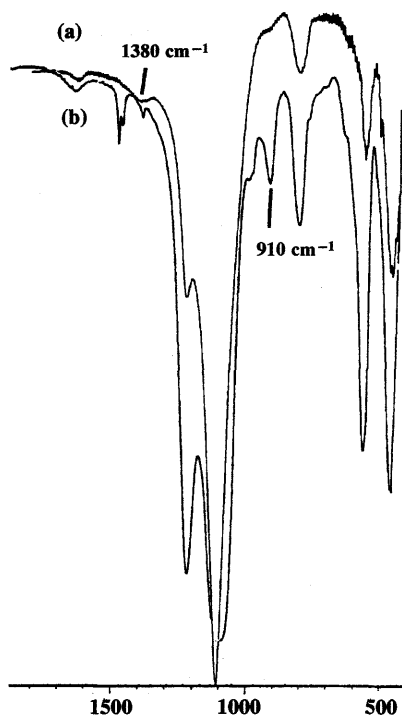


Fig.3 FT-IR Spectrum of Ti-BMFI-2 Calcined (a) and as Synthesized (b).

As synthesized TBS samples contain only tetrahedrally coordinated intra-framework boron which is partially transformed to trigonally coordinated intra-framework boron during calcination. The band at 1380 cm^{-1} is only obtained with TBS samples that were calcined, following the method of de Ruiter *et al.* Otherwise the trigonally coordinated boron is readily hydrolyzed out of the framework by the water formed during calcination²⁸.

3.5 DR-UV Spectroscopy

Diffuse reflectance ultraviolet spectroscopy (DR-UV) was used to probe the existence of framework and non-framework titanium. As an example two materials with the same B/Si ratio namely TBS-1a2 and Ti-BMFI-1 were compared (Fig.4). They were calculated using the Kubelka-Munk function to perform a semi-quantitative analysis³². The band at 47000 cm^{-1} has been assigned to isolated tetrahedrally coordinated framework titanium species³³. The broad banded absorption

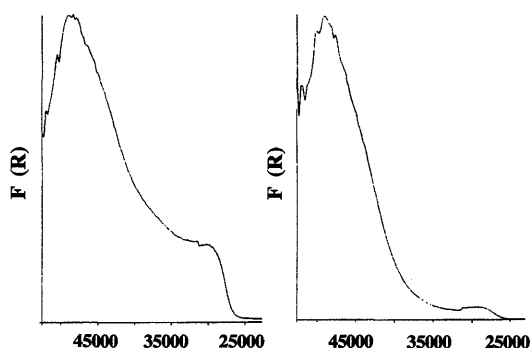


Fig.4 UV-Vis Spectra of Samples TBS-1a2 and Ti-BMFI-1.

between 40000 cm^{-1} and 27000 cm^{-1} has been attributed to anatase³³. The shown spectrum of the sample TBS1-a1, is typical for materials prepared via the route of Trong On *et al.*²². They contain a rather high amount of extraframework titanium as anatase. In comparison to that, the spectra of the Ti-BMFI samples *e.g.* the spectrum of Ti-BMFI-1 (Fig.4) show only a weak shoulder between 40000 cm^{-1} and 27000 cm^{-1} because they contain much less anatase. The same result is found with all synthesized samples. The new materials (Ti-BMFI) contain much less extraframework titanium species than the materials with the same B/Si ratio synthesized according to Trong On *et al.* (synthesis I)²².

3.6 ^{11}B , ^{29}Si and $^1\text{H} \rightarrow ^{29}\text{Si}$ Cross-Polarization MASNMR

Fig.5 displays the ^{11}B -MASNMR spectra of Ti-BMFI-2 before and after calcination. The well known signal at -4.1 ppm in the spectrum of as-synthesized Ti-BMFI2 is attributed to tetrahedrally coordinated boron as a T-atom in a MFI-type zeolite ($\text{B}(\text{OSi})_4$)³⁴⁻³⁶. This supports the findings presented in the section on FT-IR, that boron is incorporated into the framework.

As expected after calcination the signal of the tetrahedrally coordinated boron was found to be shifted to -4.7 ppm and a doublet signal at 6.4 and -0.4 occurred which is attributed to trigonally coordinated boron in the zeolite framework ($\text{B}(\text{OSi})_3$)³⁴. This shows, as already stated in the FT-

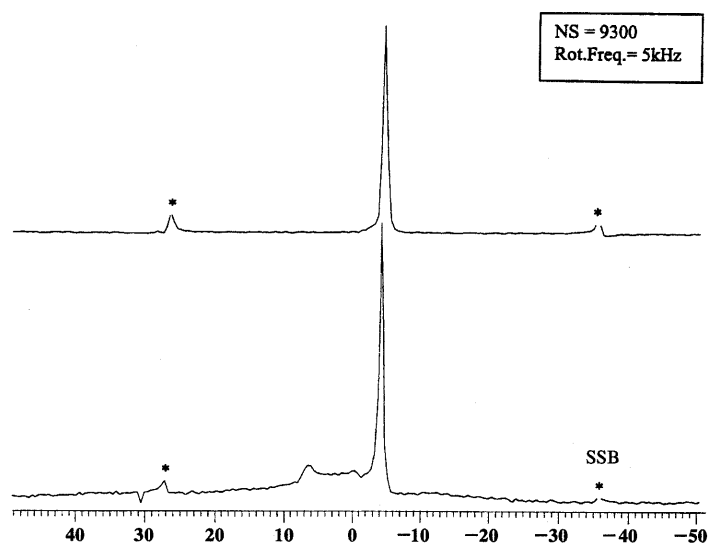


Fig.5 ^{11}B -MASNMR of Ti-BMFI-2; Top: as Synthesized, Below: Calcined.

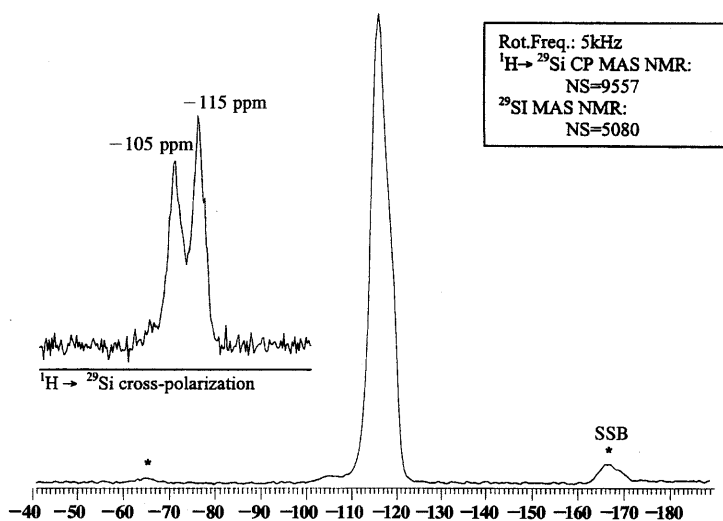


Fig.6 ^{29}Si -MASNMR and $^1\text{H} \rightarrow ^{29}\text{Si}$ CP-MASNMR of Ti-BMFI-2.

IR section, that the trigonally coordinated boron was not hydrolyzed and thus not removed from the structure. These results can be generalized for all synthesized, boron containing materials.

^{29}Si -MASNMR of Ti-BMFI2 is shown in Fig.6 revealed a strong signal at -115.8 ppm and a very weak one at -105.7 . The first is attributed to Q^4 silicon ($\text{Si}(\text{OSi})_4$) in a MFI-type zeolite and the latter

one to Q^3 silicon. By $^1\text{H} \rightarrow ^{29}\text{Si}$ cross-polarization technique, the weak signal at -105.7 is assigned to silanol with extremely weak acidic terminal OH groups attached ($\text{Si}(\text{OSi})_3\text{OH}$)³⁷. The cross-polarization technique enhances selectively the signals of silicon atoms which are coupled with protons of hydroxyl groups by dipolar ^1H - ^{29}Si interaction. Again no significant difference between all synthesized materials

was found.

The examined materials do not contain perceivable amounts of lattice faults, since only very low amounts of Q^3 silicon were found in the spectra and no Q^2 silicon.

3.7 Catalytic Test

The materials were tested for their ability to epoxidize styrene to styrene oxide and to rearrange the *in-situ* formed epoxide to phenylacetaldehyde by means of bifunctional catalysis.

Conditions in our experiment were chosen to be close to stoichiometric for the epoxidation. Nevertheless with a slight excess of styrene was used that H_2O_2 does not limit the reaction. Residual H_2O_2 was detected after every test reaction. Methanol was used as a solvent to explore the nucleophilic ring opening reaction of the epoxide to the ethers which occurs parallel to the rearrangement to the aldehyde.

The results of the catalytic tests are shown in Table 2. The TBS-1a materials turned out to be poorly active in the conversion of styrene, so that the yield of phenylacetaldehyde was never found to be higher than 3 % and the yield on dimethoxyphenylethanol (DMPE) formed by the addition of methanol to the epoxide was not higher than 5 %. This can be explained with the high amount of anatase found in these samples by DR-UV because anatase is not active in epoxidation reactions with H_2O_2 ³⁸⁾.

The Ti-BMFI materials showed a higher conversion of styrene of approximately 50 % in average. The selectivities to phenylacetaldehyde were very poor with Ti-BMFI-1. However the highest selectivity of 18 % to phenylacetaldehyde was obtained with Ti-BMFI-4. Taking in consideration the results found with Ti-BMFI-3, a trend is obvious: small amounts of boron improve the selectivity to phenylacetaldehyde in comparison to TS-1 but higher amounts seem to be counterproductive. On the other hand the selectivities to benzaldehyde which is formed via a decarboxylation reaction in small amounts, are very low but ascending with increasing boron content of the samples.

Table 2 Reaction Data from (Ti,B)-MFI Samples and References.

Sample	Styrene Conversion (%)	Select. Phenylacetal. (%)	Select. DMPE (%)	Select. Benzaldehyde (%)
TS-1	83.74	11.22	19.69	2.99
BS-1	32.31	0.00	0.00	0.00
TBS-1a1	33.05	7.41	11.83	5.31
TBS-1a2	12.97	18.12	36.13	21.04
Ti-BMFI1	56.94	1.08	13.21	1.87
Ti-BMFI3	43.40	4.53	7.89	3.02
Ti-BMFI4	50.26	17.97	25.91	5.13

Reaction conditions: 200 mg catalyst, 13, 4 mmol styrene, 12 mmol H_2O_2 30 %, 10 g methanol refluxing, 6 h reaction time.

Some side products are formed. Water can react with the epoxide in the same way as methanol, forming the phenylethanediol which is found only in small amounts (selectivities on styrene of approx. 1 %). It was therefore not listed in Table 2. As reported for the liquid phase rearrangement of styrene oxide over H-ZSM-5 catalysts, polymerization of the styrene occurs in all tests³⁹⁾. Suppression of the polymerization by inhibitors like hydroquinone or 4-tert-butylcatechol fails because they are quickly oxidized by H_2O_2 . Therefore no inhibitors were used. The polymers represent the strongest fraction of products. Anyhow the selectivities to the polymers were not listed in Table 2, because they were determined by gravimetric methods. Since no other products than the mentioned were detected by GC and no gaseous products were found, the mass balance could be closed with the estimation, that the polymers represent the remaining masses.

The blank test using BS-1 showed no activity in the epoxidation and rearrangement although polymerization of the styrene was observed. TS-1 was used as a reference material. Using our TS-1 as catalyst the conversion of styrene was higher than 80 % mainly due to polymerisation. 12 % selectivity to phenylacetaldehyde and 20 % selectivity to DMPE were found as well as 3 % to benzaldehyde (see Table 2).

It can be concluded that the Ti-BMFI materials give better catalytic results in comparison to the TBS-

1a materials and to the reference substance TS-1.

4. Conclusions

A new method for the synthesis of a titanium and boron containing material with MFI structure, free of sodium and HF has been found. It is more straight forward than the known methods^{22,25,26}. The synthesis gel can be prepared in a single flask by adding the titanium source (TEOT) to the silicon source (TEOS) instead of the initial precipitation of TiO₂ out of TEOT followed by the dilution of TiO₂ using H₂O₂. The crystallization is complete after the very short time of less than 8 h (Ti-BMFI5). All of the titanium was found in the solid phase and DR-UV revealed much less extra-framework titanium than in the samples prepared according to Trong On *et al.*²².

FT-IR showed the presence of tetrahedrally coordinated boron before and trigonally coordinated boron after calcination of all examined boron containing samples so that the boron is considered to be in the framework.

¹¹B-MASNMR studies confirm these considerations. Two different boron sites were detected in the calcined materials. One is determined as trigonally coordinated boron and the second as a tetrahedrally coordinated species, the both in a MFI-type zeolite framework.

²⁹Si and ¹H→²⁹Si CP-MASNMR measurements show, that all examined materials contain low amounts of terminal non-acidic silanol groups and no detectable defect sites.

As mentioned in the introduction Neri *et al.*²¹ report on high yields of phenylacetaldehyde based on H₂O₂ using TS-1 as a bifunctional catalyst for the liquid phase epoxidation and consecutive rearrangement of the oxide as described above. Comparing the results of our work and with results obtained in reference²¹ however makes no sense as the reaction conditions are completely different. Neri *et al.* applied high excesses of the organic substrate and therefore based the yields on the more valuable hydrogen peroxide.

The new Ti-BMFI materials were found to

be active in the bifunctional catalysis of epoxidation and rearrangement of styrene and nucleophilic ring opening with methanol, respectively. Small amounts of boron give better selectivities to phenylacetaldehyde and DMPE compared to the samples that contain large amounts of boron and compared to TS-1 which is reported to be a suitable catalyst for this type of reaction²¹.

The catalytic performance of the Ti-BMFI materials was also higher compared with the TBS-1a samples due to less catalytically inactive extraframework titanium.

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References

- 1) H. van Bekkum, E. M. Flanigen, and J. C. Jansen (Editors), Introduction to Zeolite Science and Practice, Vol.58, Elsevier, Amsterdam (1991).
- 2) W. F. Hölderich and H. van Bekkum, in Introduction to Zeolite Science and Practice, H. van Bekkum, E. M. Flanigen, and J. C. Jansen (Editors), Elsevier, Amsterdam (1991) p.631.
- 3) W. F. Hölderich, *Appl. Catal. A*, **194**, 487 (2000).
- 4) R. A. Sheldon and R. S. Downing, *Appl. Catal. A*, **189**, 163 (1999).
- 5) K. Tanabe and W.F. Hölderich *Appl. Catal. A*, **181**, 399 (1999).
- 6) A. Liebens, C. Mahaim, and W. F. Hölderich, *Stud. Surf. Sci. Catal.*, **108**, 587 (1997).
- 7) P. J. Kunkeler, J. C. van der Waal, J. Bremmer, B. J. Zuurdeeg, R. S. Downing, and H. van Bekkum, *Catal. Lett.*, **53**, 135 (1998).
- 8) R. A. Sheldon, J. A. Elings, S. K. Lee, H. E. B. Lempers, and R. S. Downing, *J. Mol. Catal. A*, **134**, 129 (1998).
- 9) C. Meyer, W. Laufer, and W. F. Hölderich, *Catal. Lett.*, **53**, 131 (1998).
- 10) A. Liebens, W. Laufer, and W. F. Hölderich, *Catal. Lett.*, **60**, 71 (1999).
- 11) W. F. Hölderich and N. Goetz, in Proceedings of the 9th International Zeolite Conference, Montreal, R. van

- Ballmoos (Editor) Butterworth-Heinemann USA 309 (1993).
- 12) W. F. Hölderich, N. Götz, L. Hupfer, R. Kropp, H. Theobald, and B. Wolf, Pat. 0228675, BASF AG (Ludwigshafen, DE)(1990).
- 13) W. F. Hölderich and U. Barsnick, in *Fine Chemicals through Heterogeneous Catalysis*, H.v. Bekkum and R. Sheldon (Editors), VCH Weinheim (2001) p.217.
- 14) M. Taramasso, G. Perego, and B. Notari, Pat. US 4,410,501 Snamprogetti S.p.A. (Milan, IT)(1983).
- 15) R. Millini, G. Perego, D. Berti, W. O. Parker Jr., A. Carati, and G. Belussi, *Microporous and Mesoporous Materials*, **35-36**, 387 (2000).
- 16) W. Adam, R. Kumar, T. I. Reddy, and M. Renz, *Angew. Chem.*, **108**(8), 944 (1996).
- 17) P. B. Venuto, *Stud. Surf. Sci. Catal.*, **105**, 175 (1996).
- 18) R. S. Drago, S. C. Dias, J. M. McGilvray, and A. L. M. L. Mateus, *J. Phys. Chem. B*, **102**, 1508 (1998).
- 19) G. Bellussi and M. S. Rigutto, *Stud. Surf. Sci. Catal.*, **85**, 177 (1994).
- 20) B. Notari, *Stud. Surf. Sci. Catal.*, **37**, 413 (1988).
- 21) C. Neri and F. Buonomo, Pat. US 4,495,371 ANIC S.p.A. (Palermo, IT)(1985).
- 22) D. Trong On, S. Kaliaguine, and L. Bonneviot, *J.Catal.*, **157**, 235 (1995).
- 23) D. Trong On, L. Le Noc, and L. Bonneviot, *J. Chem. Society, Faraday Trans.*, **92**, 1031 (1996).
- 24) M. P. Kapoor, D. Trong On, E. T. Galiott, and S. Kaliaguine, *Catal. Lett.*, **43**, 127 (1996).
- 25) M. Shibata, J. Gerard, and Z. Gabelica, *Stud. Surf. Sci. Catal*, **105**, 242 (1997).
- 26) M. Shibata and Z. Gabelica, *Microp. Mater.*, **11**, 237 (1997).
- 27) R. de Ruiter, K. Pamin, A. P. M. Kentgens, J. C. Jansen, and H. van Bekkum, *Zeolites*, **13**, 128 (1993).
- 28) R. de Ruiter, *Dissertation*, TU-Delft, The Netherlands (1992).
- 29) Y. K. Park, K. Y. Park, and S. I. Woo, *Catal. Lett.*, **26**, 169 (1994).
- 30) J. Wong, *J. Elect. Soc.*, **127**, 62 (1980).
- 31) G. Coudurier, *J. Catal.*, **108**, 1 (1987).
- 32) W. Schmidt, in *Optische Spekt.*, VCH Weinheim. (1994) p.316.
- 33) A. Zecchina, G. Spoto, S. Bordiga, A. Ferrero, G. Petrini, G. Leofanti, and M. Padovan, in *Zeolite Chemistry and Catalysis*; P. A. Jacobs, N. I. Jaeger, L. Kubelkova, and B. Wichtelova (Editors) Elsevier Amsterdam (1991) p.251.
- 34) K. F. M. G. J. Scholle and W. S. Veeman, *Zeolites*, **5**, 118 (1985).
- 35) Z. Gabelica, J. B. Nagy, P. Bodart, and G. Debras, *Chem. Lett.*, 1059 (1984).
- 36) Z. Gabelica, G. Debras, and J. B. Nagy, *Stud. Surf. Sci. Catal.*, **19**, 113 (1984).
- 37) M. M. Hunger, J. Kärger, H. Pfeifer, J. Caro, B. Zibrowius, M. Bülow, and R. Mostowicz, *J. Chem Soc. Faraday Trans.*, **83**, 3459 (1987).
- 38) C. B. Khouw, H. Dartt, X. Li, and M. E. Davis, *ACS Symp. Series*, **523**, 273 (1993).
- 39) K. Smith and M. Al-Shamali, in 12th International Conference on Zeolites; M. M. J. Treacey (Editor), Material Research Society, Warrendale 3 (1999) p.228.