Mesoporous MEL – type zeolite single crystal catalysts

Marina Yu. Kustova[a,b,*], Peter Hasselriis[b], and Claus Hviid Christensen[a,b,c]

[a] Department of Chemistry, Building 206, Technical University of Denmark, DK-2800 Lyngby, Denmark
[b] Interdisciplinary Research Center for Catalysis (ICAT), Building 312, Technical University of Denmark, DK-2800 Lyngby, Denmark
[c] Center for Atomic-scale Materials Physics (CAMP), Building 309, Technical University of Denmark, DK-2800 Lyngby, Denmark

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New mesoporous silicalite-2, ZSM-11, and titanosilicalite-2 zeolite single crystals were synthesized by use of carbon particles as a mesopore template. After removal of the carbon particles by combustion, zeolite single crystals with intracrystalline mesopore volumes between 0.31 and 0.44 cm^3/g were isolated. All samples were characterized by XRD, SEM and adsorption measurements. Isomerization and cracking of *n*-hexadecane, and epoxidation of oct-1-ene and styrene were chosen as model test reactions. The mesoporous zeolite single catalysts were generally found to exhibit high activity in these model reactions. The advantage of introducing an intracrystalline mesopore system into zeolite catalysts is attributed to the resulting improvements in the mass transport to and from the active sites. This is particularly important for more bulky reactants, intermediates and products and especially under experimental conditions giving high reaction rates.

KEY WORDS: MEL; zeolite; mesopores; synthesis; carbon; cracking; isomerization; epoxidation.

1. Introduction

Zeolites are crystalline microporous materials that are widely applied in industry for adsorption, separation and catalysis. A multitude of chemical reactions of industrial interest is catalyzed by zeolites, which often exhibit unique properties with respect to both activity and selectivity [1]. Much of the success of zeolites can be attributed to the presence of micropores with well-defined structures. The exact shape and size of the micropores may result in various kinds of shape selectivity [2]. Nevertheless, the sole presence of micropores may in some cases also limit the catalytic performance of zeolite catalysts, particularly when diffusion in the micropores becomes significantly slower than the catalytic reaction [3]. Several different preparative strategies have been attempted to circumvent this problem. One possibility is to increase the pore size of the zeolite, and this approach has led to the discovery of novel zeolites with larger pores (e.g., UDT-1) and also to the discovery of the mesoporous molecular sieves [4–8]. Another possibility is to decrease the crystal size of the zeolites, which is often in the range of 0.5–50 μm. Several synthesis schemes have now been reported to reproducibly allow preparation of a very small (< 50 nm) zeolite crystals [9–13]. Thus, both of the above strategies have already resulted in significant developments in zeolite catalysis. Yet another approach is to introduce mesopores into each individual zeolite crystal, usually done by suitable post-treatments such as dealumination [14] or desilication [15] that lead to partial disintegration of the zeolite crystals. However, during the last few years, it has proven possible to introduce a very high degree of mesoporosity in zeolite crystals in a more controlled manner [16,17]. These mesoporous zeolite single crystals are prepared by nucleating zeolite crystals inside a carbon material so the zeolite crystals grow and partially encapsulate the carbon. After complete crystallization, the carbon is removed by combustion. The resulting zeolite material has been shown conclusively to consist of quite large mesoporous single crystals rather than aggregates of randomly oriented nanosized zeolite crystals [18,19]. Compared to other known methods for introducing mesopores into zeolite crystals, such as dealumination, the present method has numerous advantages. First of all, it appears to be a general method for introducing mesopores into zeolite crystals, independent of their structure and their initial Si/Al ratio, i.e., it can also be applied to high-silica zeolites. Furthermore, the introduction of mesopores can be done without altering the original Si/Al ratio. The mesopore volumes achieved in mesoporous zeolite single crystals are much higher than those obtained by other known methods, and most importantly the size and shape of the mesopores can be directly controlled through the use of different carbon materials [20,21].

Here, the preparation of mesoporous silicalite-2, ZSM-11 and titanosilicalite-2 (TS-2) single crystals is reported for the first time. So far, only mesoporous MFI-type zeolite single crystals have achieved significant attention. In particular, mesoporous ZSM-5 catalysts were shown to exhibit both higher activity and selectivity

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*To whom correspondence should be addressed.
E-mail: mk@kemi.dtu.dk

than conventional ZSM-5 catalysts in the alkylation of benzene with ethene to produce ethylbenzene [22]. Similarly, mesoporous TS-1 was shown to posses improved activity over conventional TS-1 in some catalytic epoxidations [23]. Most recently, it also proved possible to synthesize mesoporous zeolite Y single crystals by use of carbon particles as the mesopore template [24]. This is obviously a very interesting development due to the extensive use of zeolite Y in several large-scale catalytic processes. Mesoporous MEL-type single crystals are also of significant interest as potential catalysts for many industrially important processes. For example, MEL-type zeolites have been used in alkylation, isomerization, and aromatization reactions [25,26]. Furthermore, TS-2 can be used as an efficient catalyst for the epoxidation of alkenes with hydrogen peroxide [27,28]. However, the synthesis of mesoporous MEL-type single crystals is also important to illustrate that the use of carbon as a mesopore template is a generally applicable method in zeolite synthesis.

Isomerization of *n*-hexadecane and epoxidation of oct-1-ene and styrene were chosen as model test reactions for the synthesized zeolite materials. For relatively large substrate molecules, the presence of mesopores should significantly influence the catalyst performance by providing improved mass transport to and from the active sites located within the zeolite crystal.

2. Experimental

2.1. X-ray powder diffraction

X-ray powder diffraction patterns were recorded using CuK_α radiation in the 2θ interval 5–50° using a Philips powder diffractometer.

2.2. Nitrogen physisorption

Nitrogen adsorption and desorption measurements were performed at liquid nitrogen temperature on a Micromeritics ASAP 2000N. The samples were outgassed in vacuum at 200 °C prior to measurement. Total surface area was calculated according to BET method. Meso- and micropore volumes were determined by the BJH method (desorption).

2.3. Scanning electron microscopy

Scanning electron microscopy (SEM) was performed on a Philips XL20 FEG. The calcined zeolite samples were placed on a carbon film and Pt was evaporated onto the sample for approximately 20 min to achieve sufficient conductivity.

2.4. Materials

For synthesis of mesoporous zeolites, carbon black particles (BP-2000) having an average particle diameter of 12 nm and carbon black particles (BP-700) having an average particle diameter of 18 nm (ASTM D-3249), both obtained from Carbot Corporation, were used as inert matrices. Carbon black was dried at 110 °C for 24 h prior to use. All other reagents were of reagent grade and were used without further purifications: Tetraethylorthosilicate (TEOS, 98 wt%, Aldrich), tetraethylorthotitanate (Fluka), tetrabutylammonium hydroxide (TBAOH, 40 wt%, Fluka), ethanol (EtOH, 99 wt%, Aldrich), sodium hydroxide (NaOH, 97 wt%, Riedel-de Haen), sodium aluminate ($NaAlO_2$, 54 wt% Al_2O_3 and 41 wt% Na_2O, Riedel-de Haen), *n*-hexadecane (99 wt%, Aldrich), methanol (MeOH, 97 wt%, Bie & Berntsen), benzene (C_6H_6, 99.5 wt%, Fluka), 1-Octene (97 wt%, Fluka), styrene (99 wt%, Aldrich), hydrogen peroxide (H_2O_2, 35 wt% aqueous, Bie & Berntsen), and distilled water.

2.5. Synthesis of composite carbon/silicalite-2 gel

About 10 g of BP-2000 is dried in an oven (at 110 °C) overnight. In a 200 mL flask, 17.2 g of 40% TPAOH, 2.5 g of H_2O and 15.1 g of EtOH is added with stirring to obtain a homogeneous solution. The dried carbon is impregnated with this solution to incipient wetness. After evaporation of ethanol at room temperature for 12 h, the carbon particles are impregnated with 19.3 g of TEOS. This mixture is left at ambient conditions to hydrolyze overnight. The composition of the resulting synthesis gel is $SiO_2 : 0.2\ TBA_2O : 0.01\ Na_2O : 2\ H_2O$.

2.6. Synthesis of composite carbon/ZSM-11 gel

About 10 g of BP-2000 is dried in an oven (min 110 °C) overnight. In a 200 mL flask, 17.2 g of 40% TPAOH, 2.5 g of H_2O and 0.2 g of $NaAlO_2$ is added and heated briefly with stirring until a clear solution is obtained. After cooling to room temperature 15.1 g of EtOH is added with stirring to obtain a homogeneous solution. The carbon is impregnated with this solution to incipient wetness. After evaporation of the ethanol at room temperature for 12 h, the carbon particles are impregnated with 19.3 g of TEOS. This mixture is left to hydrolyze overnight. The composition of the resulting synthesis gel is $1Al_2O_3 : 100SiO_2 : 20\ TBA_2O : 1\ Na_2O : 200\ H_2O$.

2.7. Synthesis of composite carbon/titanosilicate-2 gel (TS-2 (BP-2000) and TS-2 (BP-700))

About 10 g of BP-2000 or 10 g of BP-700 were dried in an oven (min 110 °C) overnight. In a 200 mL flask, 17.2 g of 40% TPAOH, 2.5 g of H_2O and 15.1 g of EtOH is added and with stirring to obtain a homogeneous solution. The dried carbon is impregnated with this solution to incipient wetness. After evaporation of the ethanol at room temperature for 12 h, the carbon particles are impregnated by a mixture of 19.3 g of

TEOS and 0.2 g of TEOTi. This mixture is left to hydrolyze overnight. The composition of the resulting synthesis gel is 1 TiO_2 : $100SiO_2$: 20 TBA_2O : 200 H_2O.

2.8. *Crystallization and isolation of MEL-type zeolites*

After hydrolysis, the impregnated carbon black is introduced into a 300 mL teflon beaker which is placed in the stainless steel autoclave containing 100 ml of water to produce saturated steam. The autoclave is heated very slowly (0.05 °C/min) to 180 °C and kept there for 72 h. After the autoclave has cooled to room-temperature, the product is suspended in water, filtered by suction, resuspended in water, and filtered again. This is repeated four times. Then the product is dried at 110 °C for 10 h. The carbon black is removed by controlled combustion in air in a muffle furnace at 550 °C for 18 h. In this way, a white material is obtained which by chemical analysis is shown to contain less than 0.5 wt% of carbon.

2.9. *Catalyst preparation*

Mesoporous H-ZSM-11 is prepared by ion-exchanging Na-ZSM-11 (2 g) with 1 M aqueous NH_4NO_3 (60 ml) at 80 °C two times. The filtered NH_4-ZSM-11 is washed with 80 °C deionized water (1 L) after each exchange and allowed to dry in air. Then the ion-exchanged product was heated in air at 350 °C for 5 h to produce H-ZSM-11.

2.10. *Catalytic experiments*

2.10.1. *Cracking and isomerization of n-hexadecane*

The catalytic conversion of *n*-hexadecane is carried out in 60 mL stirred Parr batch autoclave. 0.5 g of catalyst is added to the autoclave under inert atmosphere. Then 18 ml of *n*-hexadecane is added. The drive belt is set to 250 rpm whereafter the reactor was gradually heated to 280 °C and left at that temperature for 18 h. After reaction, the batch autoclave is cooled to room temperature. In order to identify unreacted feed together with isomerized and cracked products, the resulting reaction mixture is analyzed by an Shimadzu Gas Chromatograph GC-9A equipped with a Flame Ionization Detector (FID) and an NicolTH Fused Silica capillary column (15 m * 0.53 mm ID * 0.5 μm).

2.10.2. *Epoxidation of oct-1-ene and styrene with hydrogen peroxide*

The epoxidation reaction is carried out in an inert atmosphere (N_2) in a closed round-bottomed glass reactor fitted with a condenser, thermometer and a rubber septum. 100 mg of catalyst is dried *in situ* in a flow of nitrogen for two hours at 200 °C. After cooling to 60 °C, a reaction mixture containing 7.5 mL of methanol, 200 μl of benzene (GC internal standard) and 1.17 mL of oct-1-ene (or 0.86 mL styrene) is prepared and injected through the septum. The reaction is started by adding 130 μl of 35% hydrogen peroxide mixed with 0.2 mL of methanol. The reaction is followed by gas chromatography using a HP5 column. All products are identified by comparison with retention times of reference compounds.

3. Results and discussion

3.1. *X-ray powder diffraction*

X-ray powder diffraction patterns for mesoporous MEL-type zeolites are shown in figure 1. These patterns were obtained after the the zeolite synthesis and subsequent combustion of the carbon black material. It is seen that all samples contain exclusively highly crystalline MEL-type structured material [25,26].

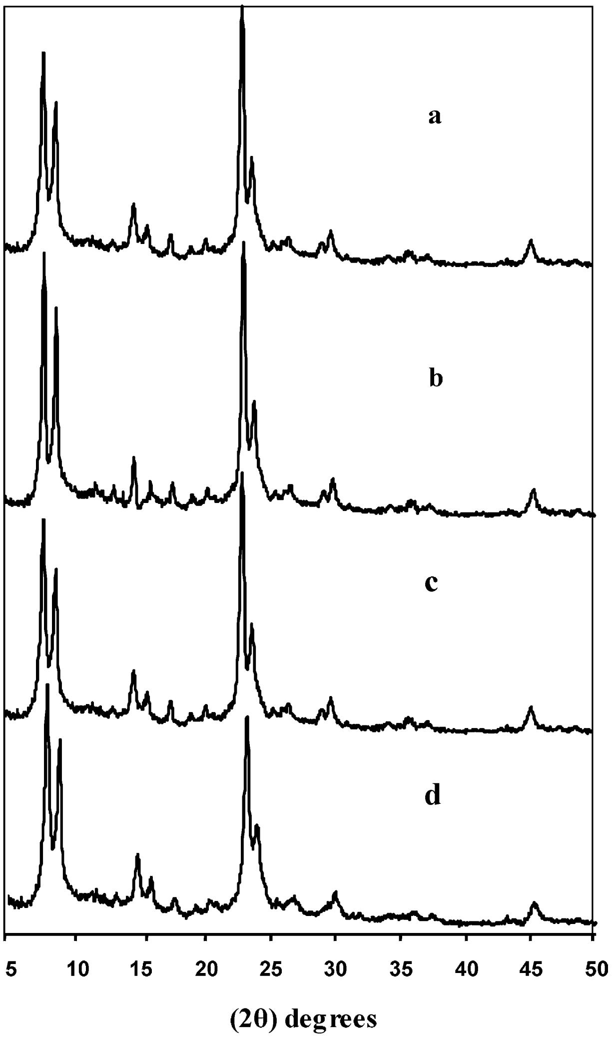

Figure 1. XPRD patterns of (a) silicalite-2 synthesized with BP-2000, (b) Na-ZSM-11 synthesized with BP-2000, (c) TS-2 synthesized with BP-2000, (d) TS-2 synthesized with BP-700.

3.2. Nitrogen physisorption

In figure 2, the nitrogen adsorption and desorption isotherms of the zeolites after combustion of the carbon are given. The isotherms of all samples contain a hysteresis loop at relative pressures higher than $p/p_0 = 0.4$. In table 1, the BET surface areas and micro- and mesopore volumes of all samples are given.

The use of different carbon sources enables one to vary the physical properties of the resulting Ti-containing MEL-type zeolites. The comparison of adsorption characteristics of TS-2 obtained using BP-700 and BP-2000 as carbon sources (figure 2 and table 1) indicates that the use of BP-700 provides a zeolite with higher porosity. In case of TS-2 (BP-2000), a small amount of amorphous material could also be present. The presence of such an amorphous phase might either be a result of incomplete crystallization or of a slight thermal decomposition of the Ti-containing zeolite during the combustion of carbon matrix.

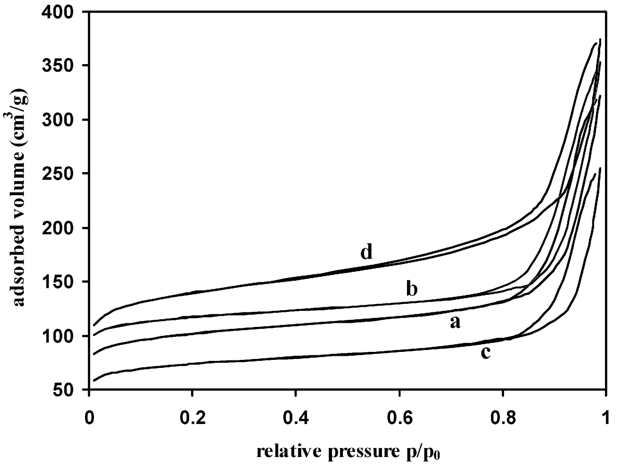

Figure 2. Nitrogen adsorption and desorption isotherms of (a) silicalite-2 synthesized with BP-2000, (b) Na-ZSM-11 synthesized with BP-2000, (c) TS-2 synthesized with BP-2000, (d) TS-2 synthesized with BP-700.

Table 1
Nitrogen adsorption data of the mesoporous zeolites samples after combustion of carbon matrix

Zeolite	C-source[a]	V_{micro} (cm^3/g)[b]	V_{meso} (cm^3/g)[b]	BET area (m^2/g)[c]
TS-2	BP-700	0.13	0.44	477
ZSM-11	BP-2000	0.13	0.40	397
Silicalite-2	BP-2000	0.10	0.39	347
TS-2	BP-2000	0.07	0.31	253

[a] BP-700 = Black Pearls 700: carbon black pellets, BP-2000 = Black Pearls 2000: carbon black pellets.

[b] Calculated by BJH method (desorption).

[c] Calculated by BET method.

3.3. Scanning electron microscopy

The results of scanning electron microscopy (SEM) for the mesoporous zeolite single crystals after combustion of the carbon are shown in figure 3. All the samples

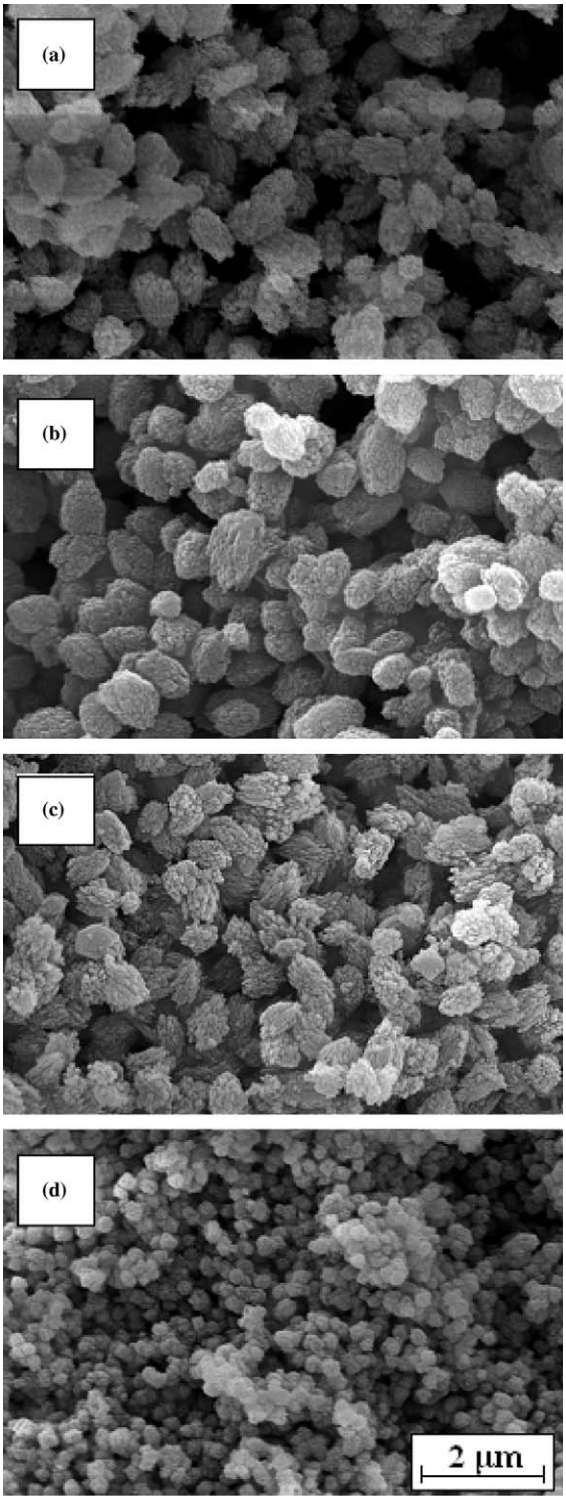

Figure 3. SEM images of (a) silicalite-2 synthesized with BP-2000, (b) Na-ZSM-11 synthesized with BP-2000, (c) TS-2 synthesized with BP-2000, (d) TS-2 synthesized with BP-700 after removal of carbon materials.

appear to be highly crystalline. Moreover, the average crystal size as determined from SEM is almost the same for the different samples, except for the mesoporous zeolite crystals of TS-2 (BP-700), which contains mesoporous zeolite crystals smaller than all the other samples. The smaller crystal size of TS-2, (BP-700) can be attributed to the use of another carbon source than for the others materials.

The presence of non-crystallographic intracrystalline mesopores is clearly visible in the images just as the high mesoporosity and the relatively large average pore size of the mesoporous zeolite single crystals. These mesoporous zeolites crystals are unique in the sense that they contain interconnected micropores and mesopores inside each individual single crystal.

3.4. *Cracking and isomerization of n-hexadecane*

As a test reaction for mesoporous HZSM-11 and silicalite-2, we have chosen the cracking and isomerization of the long chain alkane, *n*-hexadecane.

In table 2, the catalyst performance in terms of conversion of *n*-hexadecane is listed. These results were compared with data obtained for microporous HZSM-5 catalysts, which are known to be among the more active catalysts for the acid-catalyzed cracking and isomerization of alkanes [29]. The low activity obtained for silicalite-2 can be attributed to the absence of aluminum in the framework of the zeolite and the resulting very low acidity. In our case, the conventional zeolite contain far more acid sites than the mesoporous zeolites, therefore, it could be expected to be a better cracking catalyst compared to the mesoporous samples. However, in the catalytic conversion of *n*-hexadecane, the mesoporous HZSM-11 is far more active than the conventional HZSM-5 zeolites. Obviously, there is a pronounced effect of the presence of mesopores in the catalyst, which can be attributed to a considerably shorter diffusion path within the zeolite crystal than in the case of conventional zeolite catalysts. This is particularly important for reactions that involve reactants as large as *n*-hexadecane.

3.5. *Epoxidation of oct-1-ene and styrene with hydrogen peroxide*

The catalyst TS-2 (BP-700) was shown to be active in the epoxidation of simple olefins with hydrogen peroxide. The course of reaction of the straight-chained oct-1-ene is depicted in figure 4.

Table 2
Catalyst performance in *n*-hexadecane conversion

Catalyst	Si/Al ratio	Conversion (%)
Mesoporous silicalite-2	–	2
Mesoporous HZSM-11	100	94
Conventional HZSM-5	85	38

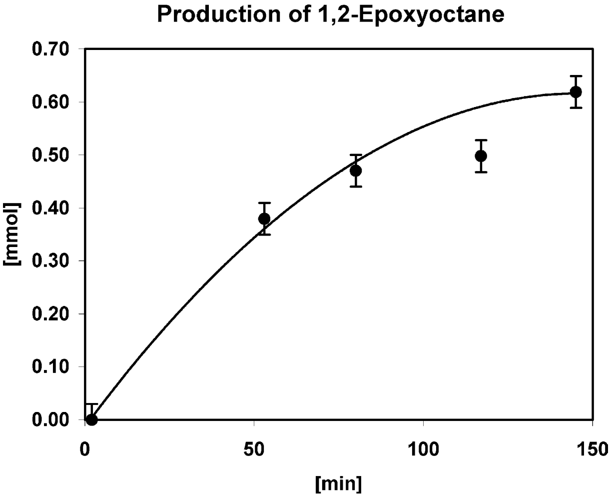

Figure 4. Catalytic production of 1,2-epoxyoctane by reaction between H_2O_2 and oct-1-ene. Reaction conditions: 60 °C, oct-1-ene 7.5 mmol, H_2O_2 1.5 mmol, cat. 0.1 mg, methanol 8 mL. No side products were produced.

The reaction was stopped after 2.5 h. At this time the reaction had reached 41% completion (based on theoretical amount of H_2O_2 consumed assuming 100% selectivity). The epoxide selectivity was 100% during the entire reaction. On other titanosilicates, such as TS-1 this reaction is also fast and quite selective (up to 91%), although usually some side products, such as glycols or glycol methyl ethers are observed [30,31]. In our case, no side products were observed.

In addition to oct-1-ene, the simple olefin styrene was also used in the epoxidation reaction. The electron-withdrawing capability of the aromatic ring opens the possibility of other reaction pathways and side products. On titanosilicates, the most common side products are: phenylethanol formed by isomerization of styrene epoxide, benzaldehyde from C=C bond cleavage and in methanol solution, also 2-methoxy-2-phenylethanol is formed through methanolysis [32–34]. In table 3, activity and selectivities for both 1-octene and styrene epoxidation reactions are listed.

As mentioned, epoxidation of oct-1-ene was 100% selective. In epoxidation of styrene, the main product was the epoxide with a selectivity of 55%. Only the above-mentioned side products were observed. The reaction rate of styrene was lower than that of oct-1-ene. This is mainly attributed to chemical reactivity differences between these two reactants. The styrene epoxidation reaction was continued for up to 4.5 h and a small decline in epoxide selectivity was observed. Table 4 compares the data from epoxidation of styrene in this work with results on similar catalysts and reaction condition prepared by other researchers.

Table 3
Epoxidation efficiency of the mesoporous TS-2 (BP-700) catalyst on two different substrates

Substrate	Epoxide (mmol)	Selectivity (%)			
		Epoxide*	Benzaldehyde	Phenylethanal	2-methoxy-2-phenylethanol
Styrene	0.09	55	21	10	14
Oct-1-ene	0.62	100	–	–	–

Reaction conditions: 60 °C, alkene 7.5 mmol, aqueous H_2O_2 1.5 mmol, cat. 0.1 mg, methanol 8 mL, 2.5 h.
**Epoxide*: Styrene oxide or 1,2-Epoxyoctane.

Table 4
Comparison of epoxidation efficiency with literature values

Catalyst	Solvent	Temperature (°C)	Reaction time (h)	Conversion (% of theoretical)	S_{Epoxide} (%)	Source
TS-2[a]	Methanol	60	4.5	9.7	42	This work
TS-2	Acetone	40	12	57	7	[33]
TS-1	Methanol	60	6	88.8	0.6	[34]
TS-1	Acetone	60	3	20.2	4.2	[32]

[a] mesoporous TS-2.

The selectivities given in table 4 are not directly comparable as the conversions are different in each case. In our work, the final conversion was 10% after 4.5 h. The nearest point of comparison is a TS-1 catalyst where acetone was used as solvent. In this case the selectivity was 4.2 at 20% conversion [32]. It would seem, though, that our mesoporous TS-2 has a somewhat higher selectivity towards the epoxide. The overall activity is lower using the TS-2 catalyst, but one obviously has to take in to account the reaction times listed in table 4. The main product from TS-1 is phenylethanal and this catalyst is also included in a patent by Neri *et al.* in a process for oxidizing styrene and derivates into phenylaldehydes [35].

4. Conclusions

Silicalite-2, ZSM-11 and titanosilicalite-2 were synthesized for the first time in the presence of a carbon matrix. After combustion of the carbon, pure mesoporous zeolite single crystals with MFI-type structure were obtained. The presence of mesopores was confirmed by adsorption measurements and SEM analysis.

The synthesized mesoporous HZSM-11 catalyst were found to reveal extraordinarily high activity in the cracking of *n*-hexadecane, even in comparison with conventional microporous catalysts. The significantly improved conversions of mesoporous catalysts is explained by the considerably improved mass transport within the zeolite crystal than in the case of the conventional zeolite catalysts.

The mesoporous TS-2 (BP-700) catalyst also showed good performance in the epoxidation of oct-1-ene and styrene, especially with regards to selectivity.

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