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Mesoporous MEL, BEA, and FAU zeolite crystals obtained by *in-situ* formation of carbon template over metal nanoparticles

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Here, we report the synthesis and characterization of hierarchical zeolite materials with MEL, BEA and FAU structures. The synthesis is based on the carbon templating method with an *in-situ*-generated carbon template. Through the decomposition of methane and deposition of coke over nickel nanoparticles supported on silica, a carbon-silica composite is obtained and exploited as a combined carbon template/silica source for the zeolite synthesis. The mesoporous zeolite materials were all prepared by hydrothermal crystallization in alkaline media followed by removal of the carbon template by combustion, which results in zeolite single crystals with intracrystalline pore volumes of up to 0.44 cm³/g. The prepared zeolite structures are characterized by XRD, SEM, TEM and N₂ physisorption measurements.

1 Introduction

Zeolites are crystalline inorganic materials with an ordered microporous structure and strong acid sites that are extensively used as heterogeneous catalysts in oil refining and chemical synthesis [1, 2]. Furthermore, zeolites possess high surface areas and large pore volumes and are therefore used in many modern industrial processes related to catalysis, adsorption, and separation, where they provide excellent size- and shape-selectivity [3, 4]. However, the large-scale application of zeolites has still not reached its full potential [5], because zeolite catalysts often suffer from severe diffusion limitations. Since the reactants and products have to diffuse through the micropores in order to reach and leave the active sites, the diffusion in zeolites is often orders of magnitude slower than both molecular and Knudsen diffusion. These diffusion limitations are enhanced for large and bulky compounds that closely match the pore sizes of the zeolites and will inevitably slow down the reaction rate.

Moreover, in some reactions, coke formation enhances these limitations, as the coke deposits block the zeolite micropores, which results in a rapid decrease in catalytic activity [6, 7].

Therefore, several preparative strategies have been developed in the attempt to improve the performance of zeolites in catalysis: the synthesis of zeolites with extra-large pores [8-11], direct synthesis of zeolite nanocrystals [12-17], by exfoliating layered zeolites [18, 19], and by introducing mesopores in the microporous materials through templating

strategies [7, 20 - 22] or demetallation processes [4, 7, 23-25]. Recently, a novel synthesis procedure for the preparation of mesoporous MFI-type material based on the carbon templating method with an *in-situ*-generated carbon template was reported by our group [26]. The mesoporous zeolite crystals combine the shape-selectivity, hydrothermal stability, and high acidity typical for conventional zeolites with highly efficient transport of reactants and products typical for mesoporous materials [7]. The novel synthesis approach has several advantages in comparison with existing carbon templating methods, where relatively complicated preparative strategies involving multistep impregnation procedures are used [27-30]. In the presented approach a cheap and available silica source - silica gel (SiO₂) is used. The carbon template is generated *in situ* by decomposition of methane, which results in the formation of large amounts of coke around the silica supported nickel nanoparticles [26]. The formation of coke over metal nanoparticles is a well-known phenomenon for a range of catalytic reactions that is frequently investigated [31]. For the decomposition of methane, supported nickel nanoparticles are recognized as effective catalysts [32]. In this way, the novel synthesis approach is more cost effective in comparison with the conventional carbon templating approach that relies on relatively expensive starting materials such as carbon black pearls and tetraethyl orthosilicate [7, 27, 28, 30]. The encapsulated carbon is removed by combustion after the zeolite crystallization, which creates mesoporosity in the zeolite crystals. In Fig. 1 a schematic overview of the presented synthesis approach is given.

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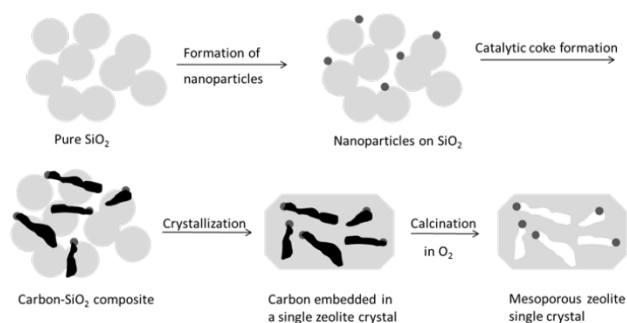


Fig. 1. Synthesis scheme for preparation of mesoporous zeolite single crystals based on the carbon templating method with an *in-situ*-generated carbon template.

Furthermore, this novel synthesis method allows preparation of mesoporous zeolites with desirable acidity, which is challenging in the case of the conventional carbon templating method [33].

Here, we report the recent progress on the synthesis and characterization of mesoporous zeolites with MEL, BEA and FAU structures using an *in-situ*-generated carbon template obtained by decomposition of methane over nickel nanoparticles. The results demonstrate that our synthetic strategy is general and opens up for simple and cost-effective synthesis of several important industrial zeolite catalysts in mesoporous form.

2 Experimental

2.1 X-ray Powder Diffraction

X-ray powder diffraction patterns were recorded in transmission mode using Cu-K α radiation from a focusing quartz monochromator and a Huber G760 Guinier camera in the 2θ interval 5–60°.

2.2 Nitrogen Physisorption

Nitrogen adsorption and desorption measurements were performed at liquid nitrogen temperature on a Micromeritics ASAP 2020. The samples were outgassed in vacuum at 200°C during 18 h prior to measurement. Total surface area was calculated according to the BET method. Total- and micropore volumes were determined by the BJH method (desorption branch) and *t*-plot method respectively.

2.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed on Quanta 200 ESEM FEG operated at 10 kV, with the calcined zeolite samples placed on a carbon film and Au was evaporated onto the samples for 5 seconds to achieve the sufficient conductivity.

2.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was performed on a FEI Tecnai microscope operated at 200 kV with the samples dispersed directly on holey carbon grids.

2.5 Materials

All reagents were of reagent grade and used without further purifications: tetrabutylammonium hydroxide (TBAOH, 40 wt%, Sigma-Aldrich), tetraethylammonium hydroxide (TEAOH, 35 wt%, Sigma-Aldrich), silica gel (SiO₂, Davisil Grade 62, pore size 150 Å, 60–200 mesh, Sigma-Aldrich), sodium hydroxide (NaOH, 97%, VWR), sodium aluminate (NaAlO₂, 54 wt % Al₂O₃ and 41 wt % Na₂O, Riedel-de Haen), aluminium nitrate (Al(NO₃)₃·9H₂O, Riedel-de Haen), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Sigma-Aldrich), methane gas (CH₄, AGA), forming gas (10% H₂/N₂, AGA), argon gas (Ar, AGA) and distilled water.

2.6 Zeolite Synthesis

2.6.1 Preparation of Ni-containing silica-carbon composite

material. The silica-carbon composite was prepared by the following procedure. 0.15 g of Ni(NO₃)₂·6H₂O was dissolved in 1.73 g of water. 1.50 g of SiO₂ was impregnated with this solution to incipient wetness. The resulting material was dried overnight at room temperature and then reduced in a flow of 10% H₂/N₂ (with a ramp of 20 °C /min) at 600 °C for 4 hours, followed by calcination in a flow of Ar until temperature was fallen to 550 °C. Then the obtained materials were subjected to CH₄ flow at 550 °C for 8 hours.

2.6.2 Synthesis of Ni-containing mesoporous MEL-type zeolite.

The mesoporous Ni-containing Na-ZSM-11 material was prepared according to the following procedure. In a 100 ml flask, 3.16 g of H₂O, 0.14 g of NaOH and 0.21 g of Al(NO₃)₃·9H₂O were added with stirring and mixed with the Ni-containing silica-carbon composite obtained above (2.6.1). Then, 3.18 g of TBAOH was added to this mixture. The composition of the resulting synthesis gel was 1 Al₂O₃ : 91 SiO₂ : 9.1TBA₂O : 6.5 Na₂O : 1055 H₂O. The final composite material was placed in a Teflon beaker inside a stainless steel autoclave, containing 15 g of water to produce saturated steam, heated to 175 °C and kept there for 24 h. Then, the autoclave was cooled to room temperature, the product was washed with deionized water (1 l) and filtered by suction. Finally, the product was dried at 90 °C for 10 h, and the organic template and the carbon were removed by controlled combustion in air in a muffle furnace at 550 °C for 24 h.

2.6.3. Synthesis of Ni-containing mesoporous BEA-type zeolite.

The mesoporous Ni-containing Na-Beta material was prepared according to the following procedure. In a 100 ml flask, 0.08 g of NaOH, 1.74 g of H₂O, 0.17 g of NaAlO₂ and 4.25 g of TEAOH were added with stirring until a clear solution was obtained. After that, the Ni-containing silica-carbon composite obtained above (2.6.1) was impregnated with this mixture. The composition of the resulting synthesis gel was 1 Al₂O₃ : 28 SiO₂ : 5.6 TBA₂O : 2.4 Na₂O : 278 H₂O. The final composite material was introduced into a stainless steel autoclave, containing 15 g of water to produce saturated steam, heated to 140°C and kept there for 144 h. Then, the autoclave was cooled to room temperature, the product was washed with deionized water (1

l) and filtered by suction. The zeolite was dried at 90°C for 10 h, and the organic template and the carbon were removed by controlled combustion in air in a muffle furnace at 550 °C for 24 h.

2.6.4. Synthesis of Ni-containing mesoporous FAU-type zeolite. The synthesis of mesoporous FAU-type crystals was based on the recipe from the patent by Christensen et al. Example 9 [34]. In a typical synthesis procedure, the freshly prepared chemicals were used: sodium silicate (200 g/l SiO₂), sodium aluminate solution (240 g/l Al₂O₃), sodium hydroxide solution (400 g Na₂O/l). The mesoporous NaY material was prepared using seed gel according to the following procedure. Seed gel was made by the followed recipe: in 100 ml flask 9.3 ml of sodium aluminate solution (240 g/l Al₂O₃), 19.97 ml of sodium hydroxide solution (400 g/l Na₂O) and 50 ml of sodium silicate (200 g/l SiO₂) were added slowly with stirring. After that the mixture was left for 4 hours. Synthesis gel was prepared by the followed procedure: in 100 ml flask 4.4 ml of sodium aluminate solution (240 g/l Al₂O₃), 2.35 ml of sodium hydroxide solution (400 g/l Na₂O) and 5.46 ml of sodium silicate (200 g/l SiO₂) were added slowly with stirring. After that, the Ni-containing silica-carbon composite obtained above (2.6.1) and 0.48 ml of seed gel was added slowly. The mixture was left for 1 hour with stirring. The composition of the resulting synthesis gel was 1 Al₂O₃ : 7 SiO₂ : 5 Na₂O : 85 H₂O. Then the gel was introduced into a stainless steel autoclave, containing 15 g of water to produce saturated steam, heated to 100°C and kept there for 18 h. Then, the autoclave was cooled to room temperature, the product was washed with deionized water (1L) and filtered by suction. The zeolite was dried at 90°C for 10 h, and the carbon template was removed by controlled combustion in air in a muffle furnace at 550°C for 24 h.

2.6.5. Synthesis of reference conventional zeolite materials. All conventional materials MEL, BEA and FAU were synthesized the same way as the corresponding mesoporous materials using 1.5 g of pure SiO₂ instead of the Ni-containing silica-carbon composite described above (2.6.1).

3. Results and Discussion

All X-ray powder diffraction (XRPD) patterns were obtained after the zeolite synthesis and subsequent combustion of the organic template and/or the carbon material. XRPD patterns for the conventional- and mesoporous ZSM-11, Beta and Zeolite Y zeolites are shown in Fig. 2. Based on these data, all obtained zeolites are concluded to be highly crystalline structured materials.

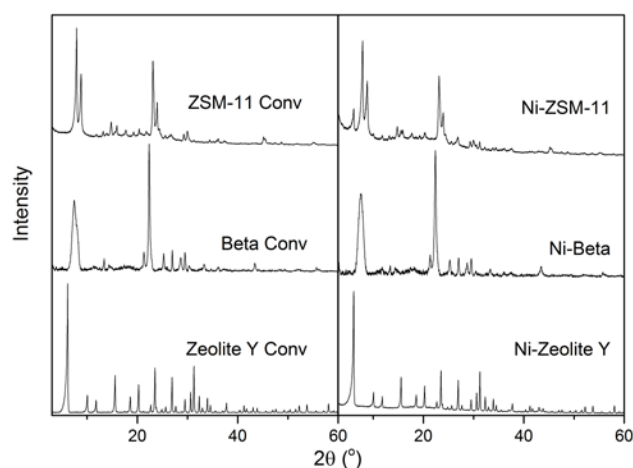


Fig. 2. XRPD patterns of mesoporous ZSM-11, Beta, and Zeolite Y-type materials.

In Fig. 3, the nitrogen adsorption and desorption isotherm of the conventional- and mesoporous ZSM-11, Beta and Zeolite Y materials after combustion of the organic template and/or carbon are shown. In Table 1, the BET surface areas and pore volumes of the obtained ZSM-11, Beta and Zeolite Y samples are summarized. According to the IUPAC classification of physisorption isotherms [35], all prepared mesoporous zeolites have Type IV isotherms. The isotherms contains a hysteresis loop at relative pressures higher than $p/p_0 = 0.4$, which is indicative for mesoporosity. Moreover, the hysteresis loop has an upward curvature at relative pressures above 0.8. This upward curvature indicates the presence of cylindrical mesopores which are connected to the external surface area [35]. The pore size distribution of the prepared materials, are presented in the supplementary materials. It is apparent from Fig. 3 and Table 1 that mesoporous ZSM-11 and Beta zeolite samples obtained by novel method using *in-situ*-generated carbon template have standard pore volumes and are characterized by large surface areas [28, 30]. However, mesoporous Zeolite Y sample has a rather moderate degree of

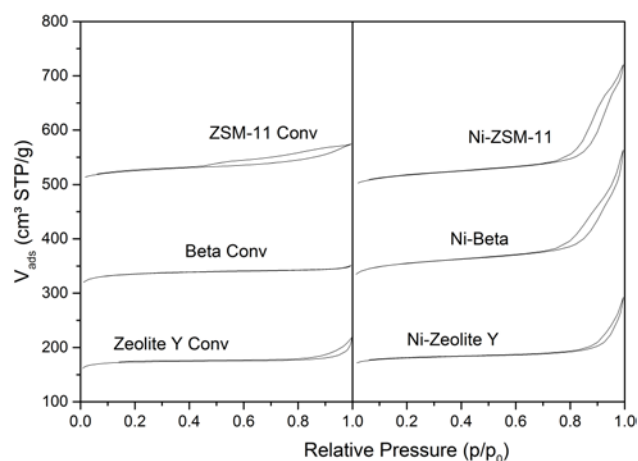


Fig. 3. Nitrogen adsorption and desorption isotherms of the mesoporous Ni-containing ZSM-11, Beta and Zeolite Y-type materials.

Table 1. Nitrogen physisorption and elemental analysis data.

Zeolite	Conv/ Meso	V_{micro}^a (cm^3/g)	V_{total}^b (cm^3/g)	S_{BET}^c (m^2/g)	Si/Al ratio ^d
Ni-ZSM-11	meso	0.13	0.41	397	88
ZSM-11	conv	0.14	0.22	409	88
Ni-Beta	meso	0.18	0.44	522	24
Beta	conv	0.22	0.27	553	22
Ni-Zeolite Y	meso	0.32	0.34	853	4.4
Zeolite Y	conv	0.33	0.35	886	4.6

^aCalculated by *t*-plot method; ^bCalculated by BJH method;

^cCalculated by BET method; ^dDetermined by ICP

mesoporosity [34] and as it is shown in our previous work [26], it can be improved by varying process parameters in 2.6.1. The different and a quite moderate degree of mesoporosity in Zeolite Y compared to ZSM-11 and Beta could be due to the much different procedure for the preparation of the synthesis gel. As synthesized, Zeolite Y has poor thermal/hydrothermal stability due to the high content of Al and Na in the structure. Therefore, the parent zeolite Y is subjected to a series of modifications (stabilization) such as ion exchange followed by steam calcination to impart both acidity and stability into the structure. These modifications of zeolite Y are relatively complicated, since the framework of zeolite Y has to be partially destroyed in order to remove large amounts of Na and Al. Therefore, the introduction of even moderate degree of mesoporosity during the synthesis could improve the ability for the ion exchange of Zeolite Y and thus lead to an improved and more stable ion exchange process on industrial scale. Moreover, it is seen from Table 1 that by using the presented synthesis method it is possible easily to obtain mesoporous zeolite crystals with desirable acidity (matching the acidity of conventional materials), which is challenging in the case of the conventional carbon templating method [33].

Representative results of SEM for the conventional and mesoporous ZSM-11, Beta and Zeolite Y zeolites after combustion of the carbon template are shown in Fig. 4. From the SEM images it can be seen that all samples are highly crystalline and that crystals of uniform size are obtained. The average crystal size of both conventional and mesoporous zeolites determined from SEM images in Fig. 4 and are about 3 μm for ZSM-11, 1 μm for Beta and 0.5 μm for Zeolite Y.

The major difference between the conventional and mesoporous ZSM-11 and Beta zeolite crystals, is the presence of non-crystallographic intracrystalline mesopores resulting in the high porosity. The conventional zeolite ZSM-11 has the typical coffin-shape intergrown crystals, and the conventional Beta material has the typical rounded-cube shape. From the SEM images of the mesoporous ZSM-11 and Beta zeolites, it can be seen that the crystals have shapes typical for the mesoporous single crystals. The conventional and mesoporous crystals of Zeolite Y materials look very similar due to rather moderate degree of mesoporosity in the mesoporous sample.

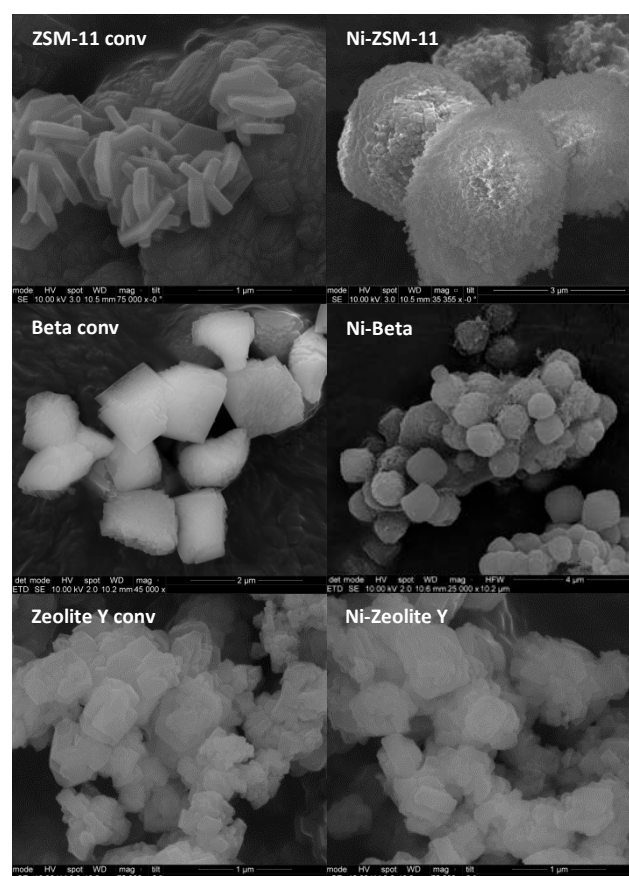


Fig. 4. SEM images of conventional and mesoporous ZSM-11, Beta and Zeolite Y-type materials.

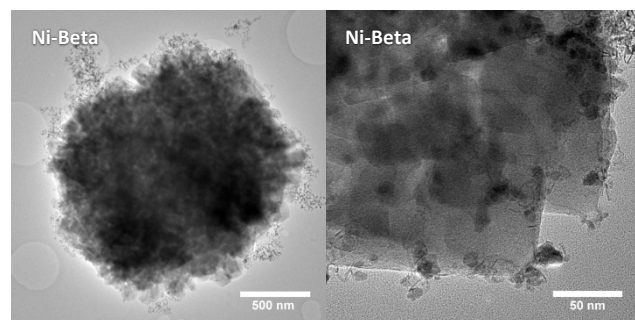


Fig. 5. TEM images of mesoporous Beta-type materials.

The results of transmission electron microscopy for the mesoporous Beta-type zeolites after combustion of the carbon are shown in Fig. 5. It is easily possible to see the mesoporous zeolite crystal, which clearly features some brighter areas distributed all over. These brighter areas are the mesopores created by removal of the carbon. The sponge-like appearance of the crystal is typical for this kind of mesoporous single crystal materials obtained by using excess of a zeolite gel as described in details by Jacobsen et al. [27]. The nickel particles incorporated into the zeolite catalyst have an average particle size of 6 nm as it is determined from TEM images. It was shown previously [30, 36], that using the standard carbon templating synthesis procedure in alkaline media it is possible to get only nanosized Beta material. Here, we show that the use of novel synthesis procedure based on the carbon templating method with an *in-situ*-generated carbon template allowed us to obtain mesoporous zeolite Beta single crystal materials. TEM images of the mesoporous Ni-ZSM-11 zeolite are presented in the supplementary material.

4. Conclusions

In conclusion, the preparation of mesoporous ZSM-11, Beta and Y-type zeolite single crystals modified with Ni-nanoparticles based on the carbon templating method with an *in-situ*-generated carbon template is reported for the first time. The obtained zeolite materials combine high crystallinity with an intracrystalline mesopore system with pore volume of up to 0.44 cm³/g. Compared to existing carbon templating procedures, this method does not rely on the availability of special and expensive chemicals, only on the mesoporous silica that are used widely and can be obtained easily by precipitation. Moreover, we show that the use of novel synthesis procedure based on the carbon templating method with an *in-situ*-generated carbon template allowed us to obtain mesoporous zeolite Beta in alkaline media. Thus, with this novel and simple preparation method, it will be possible that mesoporous zeolites with incorporated nickel nanoparticles could find use in industrial applications.

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Notes and references

- 1 A. Corma, *Chem. Rev.*, 1995, **95**, 559.
- 2 C. Martínez, A. Corma, *Coord. Chem. Rev.*, 2011, **255**, 1558.
- 3 J. Cejka, G. Centi, J. Perez-Pariente, W. J. Roth, *Catal. Today*, 2012, **179**, 2.
- 4 V. Valtchev, G. Majano, S. Mintova, J. Pérez-Ramírez, *Chem. Soc. Rev.*, 2013, **42**, 263.
- 5 M. Hartmann, *Angew. Chem. Int. Ed.*, 2004, **43**, 5880.
- 6 C. H. Christensen, K. Johannsen, E. Törnqvist, I. Schmidt, H. Topsøe, C. H. Christensen, *Catal. Today*, 2007, **128**, 117.
- 7 K. Egeblad, C. H. Christensen, M. Kustova, C. H. Christensen, *Chem. Mater.*, 2008, **20**, 946.
- 8 M. E. Davis, C. Saldarriaga, C. Montes, J. Garces, C. Crowder, *Nature*, 1988, **331**, 698.
- 9 C. C. Freyhardt, M. Tsapatsis, R. F. Lobo, K. J. Balkus, Jr., M. E. Davis, *Nature*, 1996, **381**, 295.
- 10 A. Corma, M. J. Diaz-Cabanas, J. L. Jorda, C. Martinez, M. Moliner, *Nature*, 2006, **443**, 842.
- 11 R. Simancas, D. Dari, N. Velamazán, M.T. Navarro, A. Cantín, J.L. Jordá, G. Sastre, A. Corma, F. Rey, *Science*, 2010, **26**, 1219.
- 12 L. Tosheva, V. Valtchev, *Chem. Mater.*, 2005, **17**, 2494.
- 13 R. Chal, C. Gerardin, M. Bulut, S. van Donk, *Chem. Cat. Chem.*, 2011, **3**, 67.
- 14 X. Zhang, D. Liu, D. Xu, S. Asahina, K. A. Cychosz, K. V. Agrawal, Y. A. Wahedi, A. Bhan, S. A. Hashimi, O. Terasaki, M. Thommes, M. Tsapatsis, *Science*, 2012, **336**, 1684.
- 15 W. Chaikittisilp, Y. Suzuki, R. R. Mukti, T. Suzuki, K. Sugita, K. Itabashi, A. Shimojima, T. Okubo, *Angew. Chem.*, 2013, **125**, 3439.
- 16 H. Awala, J.-P. Gilson, R. Retoux, P. Boullay, J.-M. Goupil, V. Valtchev, S. Mintova, *Nature Mater.*, 2015, **14**, 447.
- 17 R. Martínez-Franco, C. Paris, M. E. Martínez-Armero, C. Martínez, M. Moliner, A. Corma, *Chem. Sci*, 2016, DOI: 10.1039/C5SC03019F).
- 18 A. Corma, V. Fornes, S. B. Pergher, Th. L. M. Maesen, J. G. Buglass, *Nature*, 1998, **396**, 353.
- 19 S. Maheshwari, E. Jordan, S. Kumar, F. S. Bates, R. L. Penn, D. F. Shantz, M. Tsapatsis, *J. Am. Chem. Soc.*, 2008, **130**, 1507.
- 20 D. P. Serrano, J. M. Escola, P. Pizarro, *Chem. Soc. Rev.*, 2013, **42**, 4004.
- 21 K. Na, G. A. Somorjai, *Catal. Lett.*, 2015, **145**, 193.
- 22 J. Mielby, J. O. Abildstrøm, F. Wang, T. Kasama, C. Weidenthaler, S. Kegnæs, *Angew. Chem. Int. Ed.*, 2014, **53**, 12513.
- 23 M. S. Holm, K. Egeblad, P. N. R. Vennestrøm, C. G. Hartmann, M. Kustova, C. H. Christensen, *Eur. J. Inorg. Chem.*, 2008, 5185.
- 24 P. N. R. Vennestrøm, M. Grill, M. Kustova, K. Egeblad, L. F. Lundegaard, F. Joensen, C. H. Christensen, P. Beato, *Catal. Today*, 2011, **168**, 71.
- 25 K. Na, M. Choi, R. Ryoo, *Micropor. Mesopor. Mater.*, 2013, **166**, 3.
- 26 J. O. Abildstrøm, M. Kegnæs, G. Hytoft, J. Mielby, S. Kegnæs, *Micropor. Mesopor. Mater.*, 2015, DOI: 10.1016/j.micromeso.2015.12.015 .
- 27 C. J. H. Jacobsen, C. Madsen, J. Houzicka, I. Schmidt, A. Carlsson, *J. Am. Chem. Soc.*, 2000, **122**, 7116.
- 28 M. Yu. Kustova, P. Hasselriis, C. H. Christensen, *Catal. Lett.*, 2004, **96**, 205.
- 29 M. Kustova, K. Egeblad, K. Zhu, C. H. Christensen, *Chem. Mater.*, 2007, **19**, 2915.

- 30 K. Egeblad, M. Kustova, S. K. Klitgaard, K. Zhu, C. H. Christensen, *Micropor. Mesopor. Mater.*, 2007, **101**, 214.
- 31 A. K. Rovik, S. K. Klitgaard, S. Dahl, C. H. Christensen, I. Chorkendorff, *Appl. Catal. A*, 2009, **358**, 269.
- 32 S. Takenaka, S. Kobayashi, H. Ogihara, K. Otsuka, *J. Catal.* , 2003, **217**, 79.
- 33 M. Yu. Kustova, A. L. Kustov, C. H. Christensen, *Stud. Surf. Sci. Catal.*, 2005, **158**, 255.
- 34 C. H. Christensen, K. Zhu, M. Kegnæs, K. Egeblad, US Patent 7824657, 2010.
- 35 C.N. Satterfield, *Heterogeneous Catalysis in Industrial Practice, 2nd ed.*, McGraw-Hill, New York, 1991, 132.
- 36 I. Schmidt, C. Madsen, C.J.H. Jacobsen, *Inorg. Chem.*, 2000, **39**, 2279.