Room temperature detemplation of zeolites through H_2O_2-mediated oxidation†

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Detemplation of zeolite beta has been successfully achieved at low temperature by controlled oxidation of the template using H_2O_2 and catalyzed by traces of Fe^{3+}. With this approach, unlike calcination, the pristine structure of the material is well preserved; no extra-framework aluminium is formed.

The remarkable properties of zeolites make new breakthroughs possible on improved and cleaner processes for fuels and chemicals.[1] The synthesis of zeolites usually involves the presence of structure-directing agents (*e.g.* quaternary ammonium salts), to form the crystalline Si–Al–M oxides. There exist validated protocols based on seeds, from which the crystals grow under hydrothermal conditions. In this way the use of the organic template is minimized. However, for large pore zeolites the presence of template/s is still required to obtain a good crystallinity. This is the case for zeolite beta (BEA). BEA is of special interest because of its twelve-ring pore structure. The pores are large enough to accommodate commercially interesting hydrocarbons, allowing catalytic reforming, alkylation, dewaxing, cracking and synthesis of ETBE and MTBE. Furthermore, it has shown high activity in inorganic conversions, such as selective reduction of NO_x,[2] and the decomposition of N_2O.[3]

After hydrothermal synthesis the template has to be removed by calcination at high temperature. The oxidation generates a lot of heat (thermal shock), which produces structural inhomogeneities such as inclusions, voids and cracks. The evolution of steam—from the template oxidation—combined with the high temperatures produce the *self steaming* (also known as *in situ* steaming) of the sample. Aluminium is extracted to extra-framework positions as previously reported by solid state NMR.[4,5] The major disadvantage of detemplating by calcination is that the *structure* of the final material is affected by the conditions employed. This is especially the case for BEA, since not being rather crystalline implies less stability. It was reported that after *deep bed* calcination only one-fourth of the aluminium atoms remained in the BEA framework.[4] Therefore, the calcination conditions (temperature, heating rate, bed configuration, *etc.*) of BEA are tremendously important. If not carefully controlled it may lead to irreproducible batches and less-defined properties of the samples.

Here we present a new approach for mild detemplating of zeolites, based on liquid-phase H_2O_2 oxidation. It is particularly interesting for large pore zeolites where the template is required

during synthesis. Small pore matrices develop large crystals and the outlined approach is less meaningful as they possess high stability, so are less affected by calcination.

The experiments were performed with a commercial beta (BEA) zeolite from TOSOH Corp. (Japan) containing the template (their reference HSZ-720KOA, Si/Al = 9.2, crystalline size based on SEM < 0.1 µm). Thermo-gravimetric analysis (TGA) of the sample shows three defined weight losses at 350, 700 and 900 K (Fig. 1-left). The first is due to physisorbed water, while the other two exothermal steps come from the burning-off of the template. The complete removal of the template requires temperatures as high as 900 K.

No detemplation was observed when using only aqueous solutions of H_2O_2 both in acid/basic media, even at high concentrations (30 vol.%). It is known that the presence of some metal cations (especially Fe^{3+}/Fe^{2+}) enhances the oxidizing potential of H_2O_2 by catalyzing the formation of $OH^•$ radicals. This is known as Fenton's chemistry[6] and it is used in wastewater technology to remove organic waste.[7]

Since the production rate of radicals depends very much on the concentration of Fe, this has to be carefully controlled since it can lead to uncontrolled run-away preparations. Addition of very small concentration of Fe^{3+} (500 ppm Fe) in 30% H_2O_2 allowed full detempletion at room temperature (*ca.* 298 K) overnight. As the Fe was partially retained–exchanged in the final sample the concentration of Fe in solution was minimized to 20 ppm while the temperature was increased to 353 K to kinetically compensate the drop in Fe concentration. Detemplation was achieved after 16 h. The concentration of Fe in the resulting solid was below
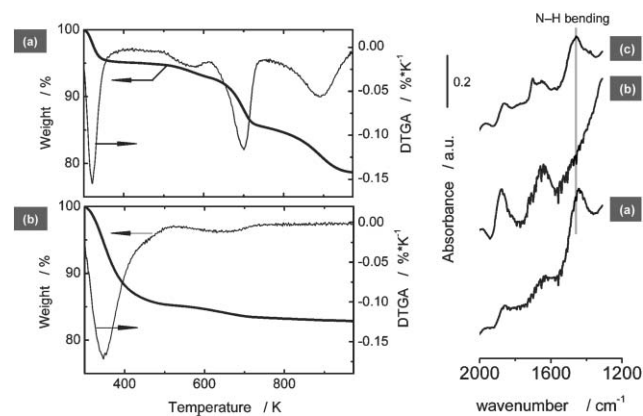
Fig. 1 (Left) Thermogravimetric analysis of the (a) parent zeolite and (b) *detemplated via* H_2O_2 oxidation. (Right) DRIFT spectra of (a) reference NH_4-form BEA, (b) 923 K-calcined zeolite and (c) *detemplated*.
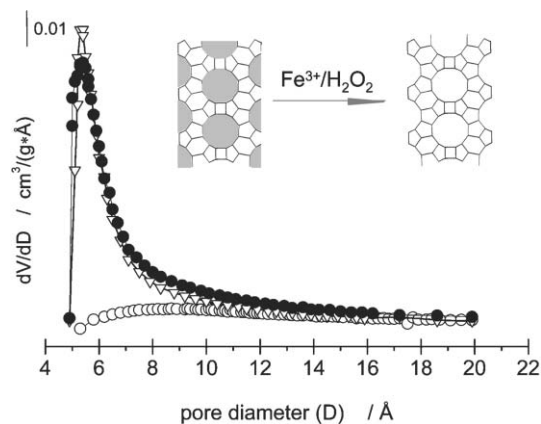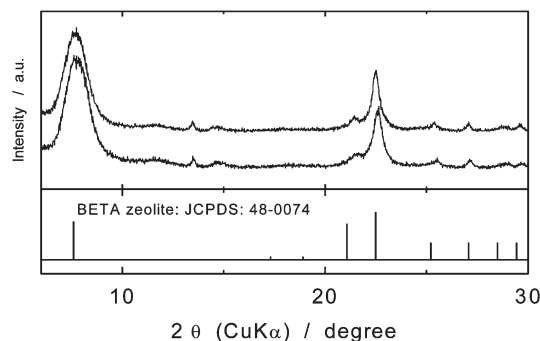
400 ppm and can be considered an impurity. Commercial zeolites exhibit these amounts of Fe. This sample was taken for characterisation afterwards. As indicated in Fig. 1-left (b), the template's weight losses are missing, and the sample contains much more physisorbed water than the starting material with template. This indirectly proves that the sample has developed *porosity*. The porosity created was analyzed by high-resolution low-pressure Ar physisorption. The pore-size distribution was calculated according to the Saito–Foley model[8] applied to the adsorption branch of the isotherm. It shows the presence of microporosity in the *detemplated* sample (Fig. 2). A pronounced development of pores between 5 and 8 Å with a maximum at 6 Å was detected, which is characteristic of BEA channels (<100> **12** 6.6 × 6.7** ↔[001] **12** 5.6 × 5.6*). The sample was compared with a reference material. A commercial NH_4-form beta zeolite (Zeolyst CP814-E) was measured as well. As indicated, the pore size distributions coincide. This comparison also suggests that the NH_4 groups of the template (tetrapropyl-ammonium) are not oxidized under treatment by OH· radicals and remain in the sample. This was confirmed by IR analysis of the samples (Fig. 1-right). The detemplated sample presents the N–H bending absorption at 1451 cm^{-1} characteristic of NH_4 groups. This information confirms that template is oxidized through the tetrapropyl chains while the ammonium groups remain at the Brønsted sites of the framework. These NH_4^+ groups are released at 600–700 K (as indicated in the DTGA curve).

XRD analysis (Fig. 3) indicates that the topology and crystal-linity of the zeolite remains unchanged. The Si/Al ratio stays close to the original value (no dealumination or desilication), which indicates that the sample is very stable to the oxidising treatment.

It is very important is to investigate the *structure* of the framework upon the oxidation. The Al–O bonds can be easily hydrolysed and are therefore the weakest spots in the framework. Solid state ^{27}Al MAS NMR is very sensitive to changes in coordination of Al nuclei. In Fig. 4, several spectra are compiled. The starting BEA containing the template (Fig. 4-a) displays only one resonance band at *ca.* 50 ppm due to tetrahedrally coordinated

Fig. 3 Powder X-ray diffractograms of parent BEA (bottom) and detemplated (top).
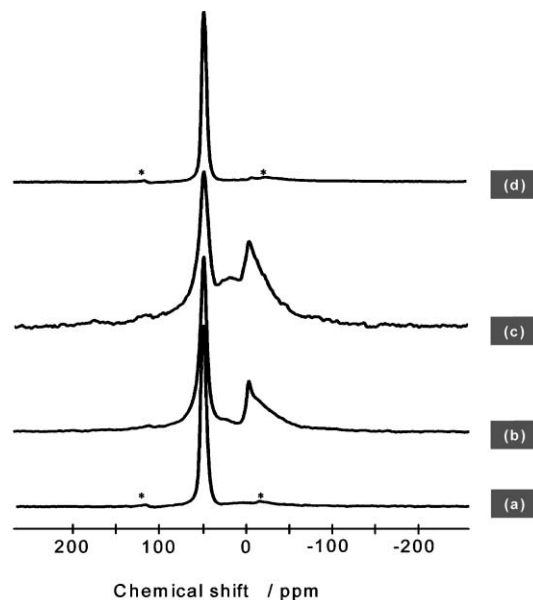
Fig. 4 ^{27}Al MAS NMR spectra of (a) parent BEA zeolite, (b) 923 K-calcined sample in *shallow bed* and (c) under *deep bed* conditions and (d) *detemplated* sample.

Al, characteristic of framework zeolitic species. In spectra (b) and (c) the sample was calcined at 923 K at shallow and deep bed configurations respectively.§ For both cases a large contribution of extra-framework Al (octahedrally coordinated at −2 ppm) is clearly detected. In the case of deep bed a pentacoordinated contribution is additionally seen around 20 ppm. The degree of *self steaming* in this sample is considerable, corresponding to *ca.* 60% of Al atoms. In deep beds the evolved steam is much more retained than in shallow beds. The result is that calcination extracts Al from the structure, and depending on the amount of sample employed for calcination (*i.e.* different bed lengths) this leads to different degree of *self steaming*. However, the *detemplated* sample *via* H_2O_2-oxidation (Fig. 4-d) does not show any extra-framework Al species. All the aluminium remains tetrahedrally coordinated. Therefore, the presented approach on detemplating preserves the virgin structure of the zeolite and leads to very well-defined materials. Ozonation has been reported for mesoporous materials to be an effective method for detemplating.[9,10] However, shrinkage

Fig. 2 Saito-Foley adsorption pore-size distribution based on Ar-physisorption: (○) parent BEA zeolite containing the template (no porosity observed), (▽) commercial NH_4-form BEA (●) *detemplated* sample.

(*i.e.* loss of surface area) is observed. By applying UV radiation this could be minimized. Our approach does not require UV radiation and is thus a much simpler technology, and likely less expensive.

Summarizing, BEA is efficiently detemplated at room temperature by H_2O_2-assisted oxidation and catalyzed by Fe^{3+}. The method is simple to apply and it can be implemented *in situ* after the hydrothermal synthesis in the reactor vessel. The method saves time and equipment since slow calcinations in rotary calciners can be avoided. Particularly interesting is that the method preserves the pristine structure of the zeolite without extraction of aluminium from the framework, leading to very well defined materials. The approach allows a very controlled preparation of atomically engineered materials with a defined site environment. The method can be extensively applied to other matrices. For small pore matrices diffusional limitations can play a major role but for mesoporous materials it is very simple.

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Notes and references

§ For shallow and deep bed configurations an *L/D* of 0.02 and 0.33 was employed, where *L* is the bed depth and *D* the diameter of the calcination plate. Calcination was carried out in a convection oven under static air.

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