One-pot catalyst preparation: combined detemplating and Fe ion-exchange of BEA through Fenton's chemistry†

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BEA zeolite has been simultaneously detemplated and Fe-exchanged by treating the parent zeolite with a Fenton's-type reagent (Fe^{3+}–H_2O_2) at low temperature. This *one-pot* process simplifies and speeds up considerably the preparation route. The catalyst shows excellent performance on N_2O decomposition compared to conventionally prepared Fe-BEA.

Zeolites and their post-synthesis modifications are receiving increased interest in the chemical processing industry. They are expected to contribute to improved catalysts and processes, not only in the production route itself (oil refinery, petrochemicals and fine chemicals) but also for cleaning technologies.[1] The abatement of nitrous oxide from the nitric acid industry is nowadays an active field of catalyst development based on zeolites.[2] Due to the presence of NO, Fe-zeolites are the most attractive systems for this in terms of performance, price and risk. Fe-ZSM5 has been studied extensively, but the amount of Fe that can be incorporated by ion exchange (liquid and solid modes) is limited, as it is competing with the formation of inactive FeO(OH). This can happen during the exchange (typically observed in liquid–ion exchange) or after calcination of samples prepared by chemical vapour deposition of $FeCl_3$. The use of a more open zeolite like BEA is therefore more attractive. The crystal size of BEA is smaller and the micropore channels are larger than for MFI-type zeolites. This will facilitate higher exchange levels and thus avoid the formation of Fe-oxides. Fe-BEA has already been tested in N_2O decomposition,[3] but as yet little work has been done on its optimization and on characterisation of the active species.

The preparation of such Fe-zeolite materials usually involves multiple steps: (i) hydrothermal synthesis of the zeolite using organic templates, (ii) detemplating by thermal treatment, (iii) accommodation of the zeolite to the desired form (usually NH_4-form), (iv) incorporation of the Fe (ion-exchange), (v) drying and (vi) calcination. Reducing the number of steps will contribute to an improved and faster synthesis process.

The idea presented in this paper is the combination of the detemplating of the zeolite with the simultaneous incorporation of the iron. This *one-pot* process will simplify the above mentioned steps. To realise this, a strong oxidant is necessary to remove the organic template molecules, and Fe-cations for exchange. Both requirements are met with the *so-called* Fenton's reagent.[4] Fenton's reagent consists of an Fe^{2+} solution of H_2O_2 (10–30 wt%), while Fenton's-type comprises Fe(III)-salts. The mixture is strongly oxidizing by the formation of $OH^{\bullet}$ radicals. Contacting the synthesized zeolite with this reagent leads to a *ready-to-use* catalyst.

The experiments were performed with a commercial BEA zeolite from TOSOH containing the template (HSZ-720KOA, Si:Al = 9.2:1). Thermogravimetric analysis (TGA) shows three major weight losses around 350, 700 and 900 K (Fig. 1-A). The first is due to physisorbed water, while the other two exothermal processes come from the template. Temperatures as high as 900 K are needed to completely remove the template.

An Fe^{3+}–H_2O_2 solution containing the desired amount of Fe to be exchanged was prepared by dissolving ferric nitrate in 30 wt% H_2O_2. The choice of a Fe(III) salt was based on price. The solution was stabilised by cooling down in ice since the propagation of the $OH^{\bullet}$ radicals is very fast, which could increase the temperature tremendously. Then the zeolite (6 g) was stirred with H_2O_2 solution (200 mL) at 333 K. To this suspension, the Fe^{3+}–H_2O_2 solution was added dropwise. The removal of the template was visually observed by the evolution of a dense fog through the coil condenser. The reaction was ended after stirring for 2 h. The suspension was filtered off and the solid dried at 373 K for 2 h. The catalyst is referred to as *one-pot* Fe-BEA. The effectiveness of the detemplation was studied by TGA (Fig. 1-B). The sample only presents one weight loss due to physisorbed water, while those due to the template are missing. Moreover, the amount of water in the sample (~17 wt%) is significantly larger than for the original

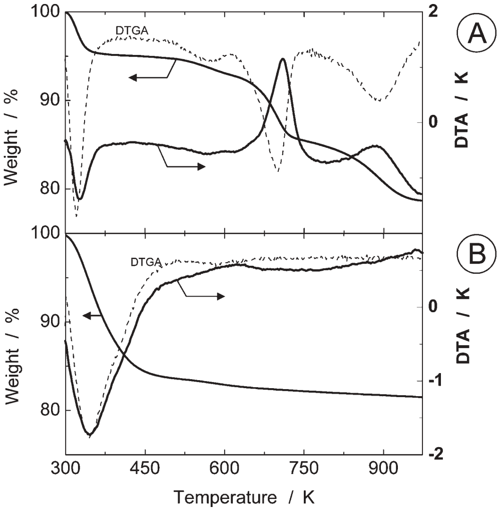

Fig. 1 Thermogravimetric analysis of the (A) parent zeolite and (B) *one-pot* catalyst.

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*I.V.Melian-Cabrera@tnw.tudelft.nl; f.kapteijn@tnw.tudelft.nl zeolite (~5 wt%). This is an indirect proof that microporosity has been developed and water enters into the channels. Microporosity formation was confirmed by high resolution low-pressure Ar physisorption.§ The pore-size distribution, calculated according to the Saito–Foley model[6] applied to the adsorption branch of the isotherm, confirms the presence of microporosity in the *one-pot* catalyst. A pronounced development of a pore-size distribution between 5 and 8 Å with a maximum at 6 Å, characteristic of BEA channels (<100> **12** 6.6 × 6.7** ↔ [001] **12** 5.6 × 5.6*) is observed (Fig. 2).

Simultaneously, Fe is incorporated into the zeolite. ICP analyses (Table 1) confirm that all the Fe is incorporated in the sample, close to its full exchange capacity. The question whether the Fe-exchange takes place after the template removal or simultaneously still remains. Further experimentation is being carried out to clarify this aspect. The Si–Al ratio stays close to the original value (no dealumination or desilication), which indicates that the sample is very stable to such a strong oxidising treatment. Local generation of heat during the template removal could lead to cracks in the zeolite structure. However, no temperature increase was observed during the 2 h synthesis. This is related to the fact that the Fe^{3+}–H_2O_2 solution was added dropwise. XRD analysis (not shown) indicates that the topology and crystallinity of the zeolite remains unchanged.

Based on the results, Fenton's oxidation enables detemplation at very low temperature (333 K). The combined effect can even be achieved at room temperature but the process required more time. By using this technology high-temperature calcinations are avoided. This leads to savings in operational costs (less energy input), and less investment for equipment. As zeolite catalysts are speciality products, the market price of hydrogen peroxide is less critical than is usually the case in the chemical industry. In terms of the zeolite itself, cracks and damages of the structure due to high temperature are minimised.

The sample was tested in N_2O decomposition (Fig. 3) after drying without further calcination. An Fe-BEA reference catalyst was prepared by the conventional ion-exchange method at a pH of 2.5 with the previously calcined zeolite. This sample was calcined at 823 K for 4 h as usually done in order to remove nitrate groups left in the catalyst. A description of the activity test can be found elsewhere.[7] The performance of the *one-pot* sample was superior at all temperatures to the reference catalyst, while the amount of Fe in the latter is even slightly higher (Table 1).

The type of Fe species was characterised by temperature-programmed reduction (TPR) with hydrogen (Fig. 4). The reference sample presents a main peak around 700 K due to Fe-exchanged species into the zeolite matrix. A contribution accounting for *ca.* 13% is due to FeOx species, peak at 850 K.¶

The *one-pot* sample presents different features. First of all, no FeOx species were detected. It is worth mentioning that the hydrolysis of Fe^{3+} and subsequent precipitation requires careful pH control to minimize generation of inactive hydroxide[8,9].

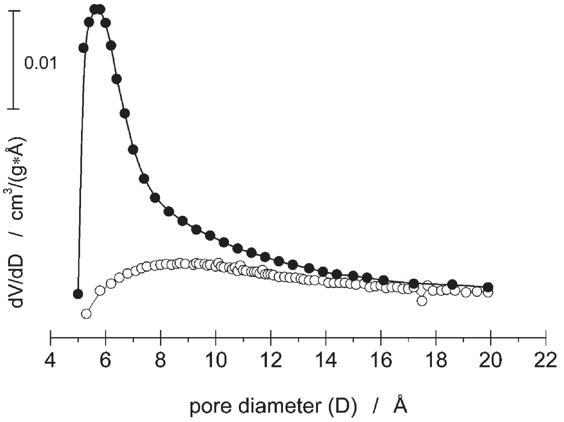

Fig. 2 Saito–Foley adsorption pore-size distribution based on Ar-physisorption: (○) parent BEA zeolite, (●) *one-pot* catalyst.

Table 1 Elemental analysis data (ICP)

System	Fe (wt%)	Exchange level[b] (%)	Si:Al
BEA-TOSOH	58[a]	0.3	12.7:1
Fe-BEA reference	1.74	104	14.0:1
Fe-BEA *one-pot*	1.60	97	12.8:1

[a] in ppm. [b] As Fe/Al*300.

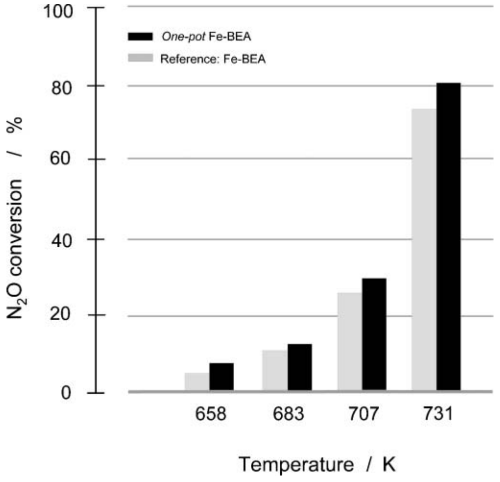

Fig. 3 Performance of the catalysts in N_2O decomposition. Conditions: 4.5 mbar N_2O in He at 3 bar total pressure and W/F_{N_2O} = 895 kg s mol^{-1}.

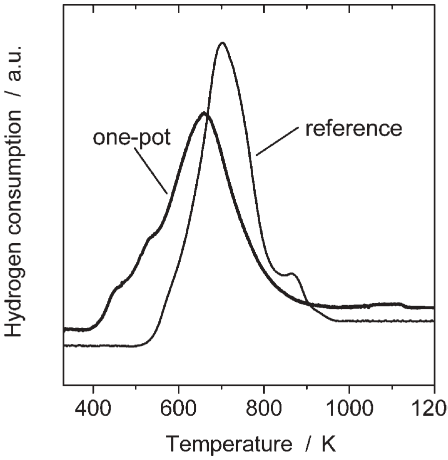

Fig. 4 Temperature-programmed reduction profiles. Conditions: 7% H_2 in Ar, heating rate: 10 K min^{-1}.

However, the new procedure circumvents this drawback and therefore controlling pH *via* inorganic acid addition is not necessary. This can be related to the fact that Fenton's reaction generates H^+ from the reduction of Fe^{3+}/Fe^{2+}. Such redox cycle takes place *locally* inside the channels during detemplation and avoids the hydrolysis. Secondly, the Fe-species reduce at lower temperature than the reference catalyst. This correlates with the activity performance. Since the rate-determining step in N_2O decomposition is the oxygen removal from the Fe sites, the higher the reducibility of Fe the better the performance.

Summarizing, application of Fenton's-type reagent to a BEA zeolite containing the organic template proves to be efficient for the combined detemplating and full Fe-exchange. $OH^{\bullet}$ radicals are able to oxidize the template at low temperature. Simultaneously, Fe-cations are exchanged into the zeolite matrix leading to very active species for N_2O decomposition. The advantages of the method are the reduction in time and steps in the preparation route as well as an improved performance in N_2O decomposition. The increased reducibility of the Fe-species correlates well with the performance in N_2O decomposition. Additionally, this method avoids high temperature calcination of the zeolite (both for detemplating and catalyst activation prior to the reaction) which minimises the cracks in the structure.

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Notes and references

§ Accurate measurements of micropore size distribution are preferentially carried out using Ar adsorption at 87 K, as being more inert than N_2 (quadrupolar moment of N_2 enhances the interaction with the heterogeneous surface, leading to a more difficult discrimination between zeolites with different pore sizes).[5]

¶ Although a pH of 2.5 was employed, Fe(III)-hydrolysis was extensive. This probably occurs inside the channels. Electrostatic restrictions of the microchannels induce water dissociation and therefore hydrolysis.

1 *Zeolites for Cleaner Technologies*, ed. M. Guisnet and J.-P. Gilson, Imperial College Press, London, 2002, Catalytic Science Series, vol. 3.
2 J. Pérez-Ramírez, F. Kapteijn, K. Schöffel and J. A. Moulijn, *Appl. Catal., B*, 2003, **44**, 117.
3 M. Mauvezin, G. Delahay, B. Coq, S. Kieger, J. C. Jumas and J. Olivier-Fourcade, *J. Phys. Chem. B*, 2001, **105**, 928.
4 H. J. H. Fenton, *J. Chem. Soc. Abstr.*, 1894, **65**, 899.
5 J. C. Groen, L. A. A. Peffer and J. Pérez-Ramírez, *Microporous Mesoporous Mater.*, 2003, **60**, 1.
6 A. Saito and H. C. Foley, *Microporous Mater.*, 1995, **3**, 531.
7 J. Pérez-Ramírez, R. J. Berger, G. Mul, F. Kapteijn and J. A. Moulijn, *Catal. Today*, 2000, **60**, 93.
8 M. Wark, W. Lutz, G. Schulz-Ekloff and A. Dyer, *Zeolites*, 1993, **13**, 658.
9 J. S. Kim, L. Zhang and M. A. Keane, *Sep. Sci. Technol.*, 2001, **36**, 1509.