



Fenton chemistry-based detemplation of an industrially relevant microcrystalline beta zeolite. Optimization and scaling-up studies



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ABSTRACT

A mild template removal of microcrystalline beta zeolite, based on Fenton chemistry, was optimized. Fenton detemplation was studied in terms of applicability conditions window, reaction rate and scale up. TGA and CHN elemental analysis were used to evaluate the detemplation effectiveness, while ICP, XRD, LPHR-Ar physisorption, and ^{27}Al MAS NMR were applied to characterize the structure and texture of the resulting materials. The material properties were compared to calcination. By understanding the interplay of relevant parameters of the Fenton chemistry, the process can be optimized in order to make it industrially attractive for scale-up. The H_2O_2 utilization can be minimized down to 15 mL $\text{H}_2\text{O}_2/\text{g}$ (88 °C, 30 ppm Fe), implying a high solid concentration and low consumption of H_2O_2 . When Fe concentration must be minimized, values as low as 5 ppm Fe can be applied (88 °C, 30 mL $\text{H}_2\text{O}_2/\text{g}$), to achieve full detemplation. The reaction time to completeness can be reduced to 5 h when combining a Fe-oxalate catalyst with UV radiation. The protocol was scaled up to 100 times larger its original recipe. In terms of the material's properties, the scaled material is structurally comparable to the calcined counterpart (comparable Si/Al and XRD patterns), while it displays benefits in terms of texture and Al-coordination, the latter with full preservation of the tetrahedral Al.

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1. Introduction

Progress in relevant areas of oil-refining, petrochemistry, fine chemicals and pollution abatement can be attributed to zeolites [1–6]. Zeolites are microporous crystalline aluminosilicates that have many exploitable properties such as adsorption, separation and catalysis. They are typically synthesized at specific conditions with very precise gel compositions [7]. Often hydrothermal conditions are necessary to provoke the nucleation and crystal growth in the presence of mineralizers, such as NaOH, NaAlO_4 or fluoride compounds.

Among the various synthetic approaches, the use of organic structural directing agents (SDA) has been crucial to discovering new zeolites [8–13]. This was possible due to the introduction of quaternary and diquaternary alkyl ammonium compounds, amines, alkylphosphonium salts and phosphazenes, among the most relevant ones. The removal of these SDA molecules is an essential step in order to obtain the final porous network. This step is normally carried out by calcination of the dried gel at temperatures ranging 500 up to 650 °C [3,4]. For the case of ill-crystalline

zeolites, having crystal sizes below 1 μm , such type of calcination is problematic. The inorganic network is unstable, in particular when the Al concentration is high. This is caused by the longer distance of the Al–O bonds that makes it easily to be hydrolysed in the presence of the self-generated steam during calcination. This is the case of beta zeolite [14–16]. Recent advances in beta zeolite synthesis are in the direction of template-free routes and some remarkable examples have been reported [17–19]. However, the current industrial manufacturing process of beta zeolite still involves tetraethyl-ammonium hydroxide (TEA) as SDA; the organic template seems to be crucial to control the crystal growth. However, the removal of the TEA by calcination in zeolite beta is known to have serious drawbacks; the most remarkable is the dealumination with the formation of extra framework species [20–23]. Therefore, it has been a challenge to find alternative routes to detemplate beta zeolite at milder conditions.

Studies on solvent extraction of SDAs by Davis and co-workers reported that successful extraction is limited to the case that the SDA has a smaller size than the pore opening of the zeolite, and secondly, weak interactions with the zeolite framework [24]; in the case of Al-beta zeolite around 50% of the template could be extracted. Solvent extraction applied to a colloidal beta zeolite removed most of the SDA, and ~65% of the microporosity was developed [25]. Cold plasma has been successfully applied to

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nano-sized beta zeolite, with full template removal and structural preservation. The acidic properties, density and strength, for the plasma-derived route were lowered when compared to the calcined route [26]. In parallel to these studies, a mild detemplation method based on highly-oxidizing OH[•] radicals to decompose the SDA of a microcrystalline beta zeolite was proposed by Melián-Cabrera et al. [27–29]. More recently, the approach was extended to a soft MCM-41 [30] and SBA-15 [31]. This methodology has been successfully applied to mesoporous silicates and aluminosilicates [32,33], RUB-18 [34], aluminophosphates [35,36], silicalite-1 colloids, and transparent composite film containing zeolite nanoparticles for organic light emitting devices [37]. A simultaneous detemplation and metal introduction method has been reported as well [38–40]. A simplified route using H₂O₂ in the absence of Fe has been successfully applied to mesoporous silicates such as MCM-56 [41], regeneration of Al-doped ZSM-5 membranes [42], and silicoalumina phosphates (SAPO-34) [36]. Other attempts to generate OH[•] radicals from H₂O₂ were assisted by UV light radiation to detemplate SBA-15 [43], and microwave irradiation over nano-beta particles [44] and AIPO-5 [45].

Fenton chemistry-based detemplation consists of using OH[•] radicals as oxidizing agents to remove the organic templates in zeolites, zeotypes and mesoporous materials. These radicals are normally originated from the catalytic decomposition of H₂O₂ at low temperature, using a Fe salt as catalyst at ppm level, though it can be assisted by UV radiation. In order to make this approach industrially attractive for zeolite activation, there are a number of aspects that require careful consideration. In this work we have carried out systematic studies considering those practical aspects, such as: the influence of relevant parameters on detemplation (temperature, Fe concentration and H₂O₂ utilization), optimization about reducing the utilization of H₂O₂ and Fe concentration, reduction of the reaction time aided by UV irradiation, an scaling-up investigation and the evaluation of relevant properties for the derived scaled-up material. These investigations have been carried out on an industrially relevant zeolite beta.

2. Experimental

2.1. Materials

Stabilized hydrogen peroxide (30 wt.% H₂O₂ in H₂O), nitric acid, (65 wt.%, for analysis EMSURE[®] ISO) and ammonia solution (25 wt.%, pro analysi) were purchased from Merck. Non-stabilized hydrogen peroxide (30 wt.% H₂O₂ in H₂O) was purchased from Sigma–Aldrich. Fe(NO₃)₃·9H₂O (98%, metal basis, denoted as Fe^{III}-nitrate) and (NH₄)₃[Fe(C₂O₄)₃]·3H₂O (pure, denoted as Fe^{III}-oxalate) were supplied by Riedel-de-Haën. NH₄-templated beta zeolite (HSZ-930A) were purchased from TOSOH Corporation.

2.2. Detemplation protocols

2.2.1. Calcination

The general calcination procedure was carried out in a LT9/11 Nabertherm box furnace. The samples were loaded in porcelain crucibles in shallow bed configuration, heated from 30 to 550 °C at 5 °C/min and held at 550 °C for 6 h.

2.2.2. Fenton chemistry-based detemplation

2.2.2.1. Standard experiment. 0.5 g of raw zeolite was mixed with the desired amount (15 mL) of 30% H₂O₂ (stabilized or non-stabilized); non-stabilized was used for temperatures ≤70 °C and stirred until the mixture was homogeneous. Then, the chosen concentration of Fe was adjusted. In the standard experiment 30 mg Fe/kg (referred as ppm) was used. This concentration was

obtained by adding 65 μL of a stock solution (5 g Fe^{III}-nitrate or 5.28 g Fe^{III}-oxalate in 100 mL of deionised water). The pH was adjusted to 4 using diluted HNO₃. The flask containing the reaction mixture was submerged in a pre-heated oil bath at the desired temperature (79 °C in this case) and it was maintained for 24 h under stirring and refluxing to prevent evaporation. The solid was separated by centrifugation, washed with deionised water and dried overnight at 80 °C in a stove oven. In other cases, the pH of the resulting mixture was below 4 and it was adjusted using a diluted NH₃ solution.

2.2.2.2. Optimization studies. For the optimization studies, temperature was evaluated from room temperature to 90 °C, the Fe concentration from 0 to 60 ppm, and H₂O₂ utilisation from 10 to 90 mL/g. The influence of the H₂O₂ type was investigated using stabilized and non-stabilized H₂O₂. The pH was adjusted with either diluted HNO₃ or NH₃ depending on the applied Fe ppm and H₂O₂ utilization. For the evaluation of the dominant parameters, boundary conditions were selected according to Table 1.

2.2.2.3. Kinetic study. In the time-dependency pseudo-kinetic study, Fe^{III}-nitrate and Fe^{III}-oxalate were used as precursors; the concentration was fixed at 30 and 60 ppm and reaction times ranged from 1 to 20 h. Individual experiments were performed for each reaction time. A water-bath was used to keep the reaction temperature constant at 70 °C.

2.2.2.4. Photo-Fenton. The experiments assisted with UV-light (5.5 W Hg lamp) were performed in a commercial set-up (Aceglass, 7880-60) which was modified for this purpose. The preparation of the reaction mixture follows the same procedure than the standard protocol detailed above. In this case, two Fe sources were employed: Fe^{III}-nitrate and Fe^{III}-oxalate. The reaction time was ranged between 1 and 8 h.

2.2.2.5. Scale-up experiment. 16.67 g of zeolite were mixed with 500 mL of stabilized H₂O₂ and 2.166 mL of Fe^{III}-nitrate stock solution (5 g Fe^{III}-nitrate in 100 mL of deionised water), and the standard protocol described above was followed.

2.3. Characterization

Thermogravimetric analyses (TGA) were carried out in a Mettler-Toledo (TGA/SDTA851e) analyser using a flow of synthetic air of 80 mL/min (NTP). Typically, 5–10 mg of sample was loaded in a 70 μL α-Al₂O₃ crucible and the temperature was increased from 30 to 900 °C at 10 °C/min. Blank curve correction using an empty crucible was subtracted.

CHN elemental analyses were carried out in a EuroVector 3000 CHNS analyzer. All analyses were done in duplicate to check sample heterogeneity; the standard deviation was below 2 wt.%. Approximately 2 mg of sample were accurately weighed in a 6-digit analytic balance (Mettler-Toledo). The samples were burned at 1800 °C in the presence of an oxidation catalyst and decomposed into CO₂, H₂O and N₂. These gases were then

Table 1
Detemplation conditions corresponding to the experimental design.

| Parameters | H1 | H2 | H3 | H4 |
|---|----|----|----|----|
| P ₁ : Detemplation temperature (°C) ^a | 88 | 88 | 70 | 70 |
| P ₂ : H ₂ O ₂ utilization (mL/g) | 30 | 10 | 30 | 10 |
| P ₃ : Iron concentration (ppm) | 60 | 0 | 0 | 60 |
| Detemplation level (η ^{TGA} , %) | 99 | 19 | 25 | 37 |

^a The resolution of the Hadamard matrix is carried out using absolute temperature.

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