Metal-ion zeolites obtained by chemical and mechanochemical methods as Fenton-like catalysts for health applications

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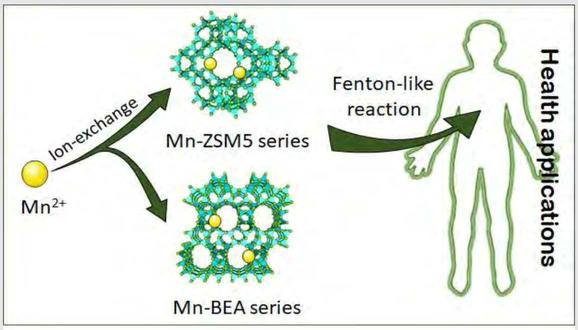

One of the critical steps for the development and health applications of inorganic nanoparticles is to exhibit high efficiency without inducing toxicity. In this work, metal-ion zeolites were developed to be used as Fenton-like catalysts for health applications. ZSM-5 and BEA zeolites were modified through chemical and mechanochemical methods to obtain nanomaterials with tuned particle size and texture. Characterization data showed that the modified materials kept the crystal structure although some textural modifications occurred. Upon Mn^{2+}loading, the catalytic behavior was evaluated by Fenton-like reaction using physiological and mild acidic conditions (37 ºC, pH=7.4 and 6.4 and 50 µM H_2O_2), since these conditions are relevant to various pathological environments. MnBEA series showed the best results by Fenton-like reactions, revealing the great potential of metal-zeolite nanomaterials for health applications.

Introduction

Zeolites are inorganic materials with high thermal and mechanical stability, organized porosity, and intrinsic acidity [1]. These nanomaterials have been widely used as adsorbents and catalysts. In addition, they present a high stability in biological environments making them good candidates for medical and healthcare applications [2,3]. The development of these nanomaterials as heterogeneous catalysts for health applications is appealing, since some pathological conditions exhibit mild acidity and overproduction of hydrogen peroxide (H_2O_2), important characteristics for the Fenton reaction [4]. However, some limitations as the crystal size and acidity cause some constraints [5]. So, the design of zeolite nanomaterials through chemical methods, such as desilication, or mechanochemical is a possible strategy to produce nanomaterials with optimized properties to transport and react in biological medium, envisaging further application for biomedical purposes.

The aim of this work is to modify ZSM-5 and BEA zeolites by chemical and mechanochemical methods for optimize the catalytic behavior of Mn-ion zeolites by Fenton-like reactions through physiological and mild acidic experimental conditions for future medical applications.

Methods

Commercial powder zeolites, from Zeolyst International, ZSM5 (Si/Al=15) and BEA (Si/Al=12.5) were submitted two types of treatments: i) chemical, and ii) mechanochemical using a ball mill. The chemical modification consisted in an alkaline treatment with NaOH (0.6 or 0.1 M for ZSM5 and BEA, respectively), at 65 ºC for 30 min, followed by an acid treatment with HCl (0.1 M) at 70 ºC for 3 h. The solids were recovered by centrifugation, dried, and calcined at 550 ºC overnight under air flow. The samples were named ZEO_[NaOH]D for the alkaline treated samples, followed by "AT" for acid treated materialsThe mechanochemical procedure was made in a shaker mill (VWR Star-Beater). The materials were ~~and~~ milled for the required time and frequency using five 3 mm steel balls. The samples were labeled as ZEO_*F*_*t*, where *F* is the frequency (Hz) and *t* is the milling time (min). Structural characterization of the pristine and modified zeolites was made through the X-ray diffraction patterns obtained in 2θ range between 5 and 40° in a Pan'Analytical PW3050/60X'Pert PRO. Textural analysis was achieved by low temperature N_2 adsorption isotherms (Micromeritics ASAP 2010) obtained after a previous treatment at 300 °C for 3h under vacuum. Particle size distribution was evaluated by light scattering experiments (Malvern, Master3000) and TEM microscopy using JEOL JEM-2100-HT (Cryo & Tomography) working with an accelerating voltage of 200 kV. To conduct the TEM analysis, a drop of an aqueous dispersion of the sample was placed onto a 400-mesh copper grid coated with carbon film. The grid was then dried under vacuum before being viewed under the microscope. The metal ion (Mn^{2+}) was introduced on the zeolite nanomaterials by ion exchange method (1 mM of Mn^{2+}) using a procedure describe in [2]. The metal ion zeolite catalysts were evaluated using methylene blue (MB) as model molecule by Fenton-like reaction in a semi-batch reactor at atmospheric pressure under stirring using physiological and mild acidic conditions: $T = 37$ °C, pH = 7.4 and 6.4, $[H_2O_2] = 50$ µM, $t_r = 90$ min. The reactor was loaded with methylene blue solution (5 ppm) and the catalyst dose was 400 mg L^{-1}.

Results

The Mn-ion zeolites nanomaterials were prepared with ZSM5 and BEA as pristine zeolites, and with the modified zeolite nanomaterials by chemical and mechanochemical treatments.

The average size of particles and morphologies of pristine zeolites were analyzed by TEM, as shown in the Figure 1.

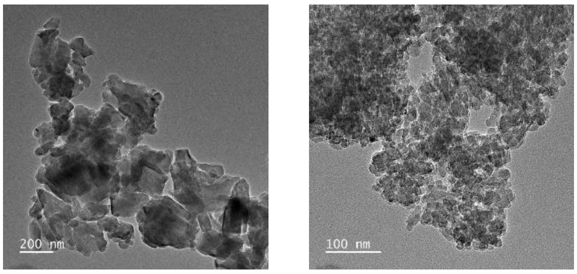

Figure 1. TEM images of pristine zeolites: ZSM5 (left) and BEA (right).

The two different commercial zeolites, ZSM5 and BEA display different average particle sizes. ZSM5 zeolite exhibits irregular particles, with large aggregates, medium and small particles (308, 115 and 30 nm, respectively), and BEA show small particles with an average size of 20 nm, which form large aggregates.

The crystallinity and textural parameters of the pristine and chemically modified materials are presented in Table 1 revealing that the crystal structures of the zeolites were kept but some loss of crystallinity occurs, especially in the case of BEA series. The textural parameters show the development of microporosity, especially in the case of ZSM5 series.

All these samples were submitted to ion exchange procedure with the same concentration of Mn^{2+} for obtain Mn-ion zeolite catalysts. Figure 2 shows the results obtained with these catalysts for the Fenton-like reaction using MB as probe molecule. The data show that the MB was degraded under physiological and mild acidic conditions in the presence of Mn-ion zeolite catalysts. The degradation of the MB molecule by Fenton-like reaction at pH = 7.4 was achieved (data not shown) and the best catalytic results were obtained with the Mn-ion BEA series. However, as expected, the degradation was enhanced in the pH = 6.4 with $[H_2O_2] = 50$ µM at 37 ºC. It must be noted that there is a significant difference between the MnZSM5 and the MnBEA series, as all the catalysts prepared with BEA series samples are more efficient in degrading the MB molecule. In fact, both MnBEA_0.1D and MnBEA_0.1D/AT are very active under mild acidic conditions (pH = 6.4 and H_2O_2 = [50 μM]). In fact, with these samples total MB degradation was achieved while in the case of ZSM5 derived catalysts the maximum degradation attained was only 60%.

Table 1. Crystallinity and textural parameters of starting and chemically modified samples.

Sample	$C_{XRD}{}^{a}$ (%)	$V_{micro}{}^{b}$ ($cm^3\ g^{-1}$)	$V_{meso}{}^{c}$ ($cm^3\ g^{-1}$)	$A_{ext}{}^{b}$ ($cm^2\ g^{-1}$)
ZSM5	100	0.15	0.07	43
ZSM5_06D	65	0.12	0.29	78
ZSM5_06D/AT	64	0.11	0.20	106
BEA	100	0.14	0.53	250
BEA_01D	53	0.08	0.52	203
BEA_01D/AT	47	0.08	0.56	205

[a]Crystallinity percentage using parent zeolites as reference material; [b]V_{micro} and A_{ext} quantified through the application of f α_s method; [c]$V_{meso}= V_{total} - V_{micro}$ where V_{total} corresponds to the amount of N_2 adsorbed a $p/p^0 \approx 0.95$

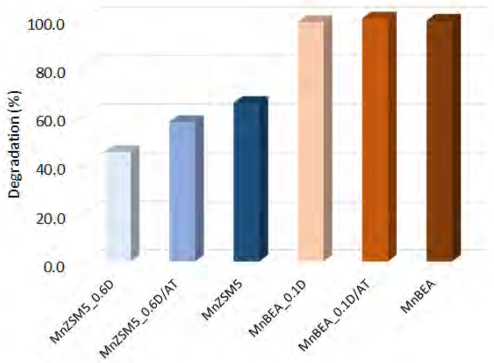

Figure 2. Degradation efficiency of the Mn-ion catalysts prepared with the pristine zeolites and the modified nanomaterials by chemical methods. Conditions of reaction: 25 mL buffer solution pH 6.4 MB (5 ppm); 10 mg catalyst; H_2O_2 = [50 μM], t = 90 min and T = 37 ºC.

The control with the pristine zeolites and in the presence of the physiological and mild acidic conditions are not enough to trigger the reaction, which confirm that the reaction occurs by a typical Fenton process.

The study will continue testing the catalysts prepared with mechanochemically modified samples that preserved more than 80 % of the crystallinity of the starting sample.

Conclusions

Chemical and mechanochemical methods were utilized to obtain several Mn-zeolite nanomaterials, which were tested for their ability to degrade MB using the Fenton-like reaction at mild acidic and physiological conditions. All the Mn-zeolite nanomaterials displayed catalytic activity under these experimental conditions, indicating their potential as Fenton-like catalysts for health applications

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