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Hierarchical zeolites as adsorbents for mesosulfuron-methyl removal in aqueous phase

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Bulky organic pollutants such as pesticides and pharmaceutical residues are found in wastewater and are difficult to remove by microporous adsorbents because of their large size. Hierarchical zeolites as potential adsorbents for removal of heavy organic pollutants from aqueous phase are investigated. Hierarchical HMOR and HZSM-5 samples were obtained by post-synthesis desilication by alkaline treatment followed or not by acid leaching of the microporous parent zeolites. The obtained materials have been fully characterized by X-ray diffraction, N_2 physisorption, elemental analysis, pyridine adsorption followed by FTIR. Alkaline treatments lead to a framework desilication creating mesopores with the preservation of the Brønsted acidity. Material adsorption behaviors are studied in pesticide, mesosulfuron-methyl (MM), removal from aqueous phase. For all the materials, adsorption kinetics are well described by a pseudo-second order model indicating that MM molecules are chemisorbed via acido-basic interaction of the neutral form. Sorption isotherms are S-shape isotherms for the parent samples and evolve to more favorable concave isotherms for highly mesoporous samples. Thus hierarchical zeolites exhibit higher sorption rate and capacities than microporous ones. Soft acid leaching treatments carried out after alkaline one help to clean the zeolite porosity from silica debris and to enhance significantly zeolite adsorption efficiency.

1. Introduction

Pesticides and pharmaceutical residues released in environment lead to diffuse water pollution which is an increasingly serious environmental problem. Pesticides can be removed from the environment through chemical techniques such as photocatalysis [1,2], advanced chemical oxidation processes [3,4].... These treatments reduce significantly pesticide concentrations. Nevertheless, a complete mineralization is not always achieved and the resulting reaction by-products may also be toxic and persistent in the environment due to their low degradability degree [4]. The adsorption processes are inexpensive and very effective methods for removing pollutants in the gas and aqueous phases [5–7]. Activated carbons and zeolites are known in the literature to be very efficient adsorbents for organic pollutants [8,9]. However, they are very difficult to regenerate. Zeolites are very efficient microporous adsorbents in which diffusion of bulky molecules is drastically slowed down due to steric hindrances in their narrow micropores network. Mesoporous silica such as MCM-41 or SBA-15 offers larger porosity where no diffusion restriction occurs for bulky molecules. However, organic molecules adsorption in aqueous phase is not efficient since water molecules are preferentially adsorbed due to the high silanol density inside silica mesopores. The grafting of hydrophobic and adsorption active sites is therefore necessary to make these materials more selective adsorbent for organic or inorganic pollutants [10–14]. The resulting hybrid organic–inorganic materials are generally expensive and their synthesis is often time consuming since it requires multiple steps. An alternative to all these materials for the removal of bulky organic pollutants is the use of hierarchical zeolites which contain an auxiliary mesopores network interconnected to the existing microporous framework [15]. A wide variety of bottom-up and top-down methodologies exists to prepare hierarchical zeolites [16]. The simplest one is the top down approach which consists in a post-synthesis dematalation of the microcrystalline parent zeolite sample by alkaline or/and acid treatments [17]. The acid treatment leads to zeolitic framework dealumination and consequently to the decrease in the Brønsted acid site amount [18,19]. Alkaline treatments lead to framework

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desilication without framework aluminum atom extraction [20]. The improvement of molecular diffusion to the Brønsted acid sites in hierarchical zeolites leads to a significant enhancement of their activity and selectivity in various catalytic reactions such as aromatization [21], isomerization [22], alkylation [23], acylation [24]…. In catalysis applications, the resulting mesoporosity of hierarchical zeolites improved the reactants and products diffusion. In adsorption applications, the hierarchical zeolite mesopores can host large guest molecules. Only few works are found in the literature on such use in case of enzyme immobilization [25], metal complex inclusion [26], organic pollutant adsorption [27].

In the present work, we propose to study the removal by adsorption of MM as a model of a bulky organic pesticide. MM is a molecule from the sulfonylurea family (Fig. 1). Compounds from this family are typically used as pesticides [28] and as medical agents in the treatment of diabetes [29]. Similarly to sulfonylurea, MM is a weak acid (pKa = 4.3) and is more persistent in neutral and weakly acid media [30]. These compounds can be found in the natural media and their impact on the human health is not very well known. From a previous study on organically modified mesoporous silica and FAU zeolite [31], MM adsorption in aqueous solution takes place on bridged framework oxygen ($Si—O^-—Al$).

The main purpose of the present study is to compare MM adsorption behavior on different hierarchical zeolites (HMOR and HZSM-5). Hierarchical zeolites will be obtained using alkaline treatments in order to prevent dealumination. The impact of the severity post-synthesis treatment on MM adsorption properties as well as the necessity of a soft acid leaching after desilication treatment will be evaluated through MM adsorption isotherms, kinetics plots and abatement rate determination. A correlation between the accessibility to the Brønsted acid site and the MM adsorption behavior is expected.

2. Experimental

2.1. Materials

NH_4^+ form ZSM-5 zeolite was purchased to Zeolyst (Si/Al = 35.6). HMOR zeolite is supplied by Sud Chemie (Si/Al = 35.6). For alkaline, acidic and ionic exchange treatments, sodium hydroxide, hydrochloric acid and ammonium nitrate, respectively were purchased from Sigma–Aldrich and used without further purification.

The H^+ form ZSM-5 zeolite was obtained by NH_4^+ form ZSM-5 zeolite calcination under air (100 mL min^{-1}) at 500 °C for 8 h.

2.1.1. Alkaline treatments

The alkaline treatments were carried out under stirring at temperatures of 60 and 85 °C for 30 min for HZSM-5 and at temperatures of 70 and 90 °C for 120 min for HMOR using a sodium hydroxide solution with a concentration of 0.2 M and with an alkaline solution to zeolite ratio of 30 mL g^{-1}. The solid was recovered by centrifugation (6500 rpm for 10 min), washed by ultrapure water and dried in an oven at 90 °C for 24 h. After alkaline treatment, the zeolite samples were under Na^+ form. In order to recover H^+ form zeolite, three consecutive ammonium exchanges were performed. In each exchange the alkaline treated zeolite powder was contacted with a solution of ammonium nitrate (NH_4NO_3) at a concentration of 2 M (V/m = 10 mL g^{-1}). The mixture was stirred for 4 h at 60 °C. The suspension was filtrated, washed with ultrapure water and dried in an oven at 90 °C for 1 h. In order to recover the H-form modified zeolite, calcination was performed under air (100 mL min^{-1}) at 823 K for 8 h.

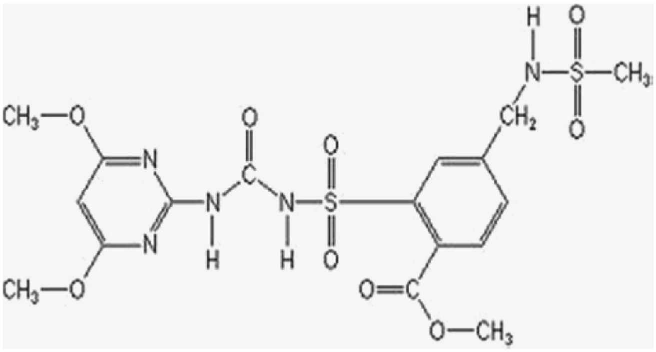

Fig. 1. Mesosulfuron-methyl structure.

2.1.2. Acid treatments

Acid treatments were performed to eliminate extraframework aluminum and/or silica species. Acid treatments were always carried out on H^+ form zeolite. The zeolite powder was stirred with HCl 0.5 M solution at 30 °C for 10 min (V/m = 10 mL g^{-1}). After the treatment, the zeolite sample was recovered by filtration, washed with a large amount of deionized water and oven dried at 120 °C for 24 h.

The sample name and their corresponding post-synthesis treatments are listed in Table 1.

2.2. Physico-chemical characterizations

The global Si/Al ratio was determinate by ICP-OES using a Perkin–Elmer Optima 2000 DV spectrometer.

The zeolite crystallinity was verified by X-ray diffraction using a PANalytical Empyrean diffractometer equipped with a Cu Kα radiation. The signal was recorded for 2θ between 5 and 90° with a recording step of 0.016 every 180 s.

Nitrogen adsorption measurements were performed at −196 °C on gas adsorption system ASAP 2000 (Micromeritics). Prior to measurements, samples were outgassed under secondary vacuum at 350 °C for 12 h. The BET equation was used to calculate the surface area of the samples at relative pressures between 0.01 and 0.30, the different porous volume s (microporous and mesoporous) were determined from α_S-plots using the Jaroniec's non porous silica adsorption isotherm as reference [32]. The mesopore size distribution was obtained from the desorption branch of the N_2 isotherms using Barret–Joyner–Halenda (BJH) approach.

The FT-IR quantification of both Lewis and Brønsted acid site on parent and modified zeolite samples was done by pyridine adsorption at 150 °C followed by FT-IR spectroscopy using a Magna Nicollet FT-IR spectrometer. The amount of Lewis and Brønsted sites were calculated from the integrated area of the PyH^+ and PyL bands at 1545 and 1450 cm^{-1}, respectively. The experimental method was described in details in a previous paper [33].

Table 1
Sample nomenclature and experimental condition for post-synthesis modifications.

Sample name	Conditions of desilication by NaOH (0.2 M)	Conditions of soft acid leaching by HCl (0.1 M)
HZSM-5	–	–
HZSM-5_60	60 °C, 30 min	–
HZSM-5_60_Ac	60 °C, 30 min	30 °C, 10 min
HZSM-5_85	85 °C, 30 min	–
HZSM-5_85_Ac	85 °C, 30 min	30 °C, 10 min
HMOR	–	–
HMOR_70	70 °C, 120 min	–
HMOR_70_Ac	70 °C, 120 min	30 °C, 10 min
HMOR_90_Ac	90 °C, 120 min	30 °C, 10 min