



Beneficial changes in coke properties with alkaline treatment on aluminum-rich mordenite



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ABSTRACT

The impact of the textural properties of mordenite zeolites on the growth and toxicity of coke formed at 350 °C during propene transformation is investigated. The addition of intracrystal mesopores by alkaline treatment to a unidimensional zeolite is a simple tool for changing its classical deactivation mode, pore blocking, to a mode more usual on zeolites with a three-dimensional framework, poisoning. This change requires that the zeolite possess a high hierarchy factor, as a result of severe alkaline conditions generating a lot of intracrystal mesopores. Desilication treatment removes part of the Brønsted acid sites and generates extra-framework aluminum species that can block access to the protonic sites and/or enhance their strength, which increases the coking rate. A mild acid leaching is enough to dissolve them. The presence of a few mesopores is sufficient to enhance the access of oxygen to coke, which favor its combustion.

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1. Introduction

In many industrial processes catalyzed by zeolite materials, coke formation is unfortunately ineluctable [1,2] and leads to the deactivation of acid sites, either by blocking access to them or by poisoning them [3–5]. Coke formation follows a shape-selective process reminiscent of the manufacture of a ship in a bottle [6]. Its retention in pores and/or on external surfaces mainly depends on reaction temperature and zeolite framework [7]. Mordenite (MOR) zeolite, used in important industrial processes such as alkylation [8] and hydro-isomerization [9] reactions, is a large-pore zeolite with 12-membered ring (MR) pore channels of 0.67 × 0.70 nm interconnected by 8-MR pores of 0.34 × 0.48 nm [10] (side pockets, SP). As most organic molecules cannot enter through SP, MOR zeolite can be considered as a one-dimensional pore system in which mass transport is limited by *single file diffusion* [11]. This particular feature of one-dimensional diffusion (called *tunnel shape selectivity*) explains the high selectivity to coke for MOR zeolite as well as its main mode of deactivation by pore blocking [3].

The creation of additional porosity in MOR zeolite by postsynthesis treatments (dealumination or desilication) is a simple and efficient tool for mitigating its deactivation by coking. Dow

Chemical was able to circumvent the coking problem that occurs in cumene synthesis by making “three-dimensional” MOR zeolites through dealumination treatments 25 years ago [12,13]. The generation of mesopores allowed retarding the ability of coke to block access to the active sites. In addition, coking mitigation is accentuated by using an aluminum-poor MOR zeolite (Si/Al = 70) [14]. Indeed, the initial rate of coke formation is proportional to the concentration of protonic sites [15]. Hence, the formation of mesopores to make an acid catalyst resistant to coking is all the more important in the case of aluminum-rich zeolites. The design of hierarchical zeolite catalysts requires the development of mesoporosity while the intrinsic porosity is preserved [16]. Desilication by alkaline treatment leads to zeolite (e.g., MOR) samples with a high mesopore surface area, while a large number of protonic active sites are preserved. Lin et al. [17] observed during benzene alkylation of diolefin-containing dodecene for linear alkylbenzene synthesis (LAB) a considerable increase of catalyst stability after desilication treatment of very acidic MOR zeolites (Si/Al = 7.2 and 13.1). The improved stability of hierarchical zeolites is attributed to the enhanced diffusivity of oligomer byproducts and coke precursors. The presence of mesopores in the vicinity of the Brønsted acid sites limits the zeolite deactivation, owing to faster desorption of products and coke precursors [18–20] that inhibits their growth into coke. This enhancement of stability is related to a decrease in the apparent deactivating effect of the coke, the toxicity (Tox), which corresponds to the number of active sites deactivated per

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one molecule. In the case of MOR zeolite, coke is extremely toxic, since one molecule located in a large channel is enough to block the access of the reactant molecules to all the acid sites located in this channel; the acid sites made inaccessible to the reactant molecules appear to be deactivated. On the other hand, with hierarchical MOR zeolites, new access to the acid sites is created, which decreases the coke toxicity. In methanol conversion into hydrocarbons, dealumination of HMOR zeolites, which make the pore system quasi-three-dimensional, decreases the coke toxicity more than 10 times [21]. The deactivation mode changes from pore blocking on HMOR to poisoning on hierarchical mordenite.

The aim of this study is to evaluate the impact of the hierarchization of an aluminum-rich MOR zeolite ($\text{Si}/\text{Al} = 10$) on the time evolution of the coke properties in terms of chemical composition, content, formation rate, location (micropores, mesopores), toxicity, and removal by combustion, and also the changes in the acidic and textural properties of the catalysts. The coking reaction will be carried out by microgravimetry under a high pressure of olefins ($P_{\text{propene}} = 1 \text{ bar}$) in order to simulate industrial operation.

2. Experimental

2.1. Materials

Hierarchical zeolites were prepared from a commercial MOR zeolite (Clarian) through alkaline treatment using an aqueous sodium hydroxide solution as described previously in Ref. [22]. To obtain different degrees of hierarchization, moderate and severe conditions were used: $[\text{NaOH}] = 0.2 \text{ M}$, 70°C , and $[\text{NaOH}] = 0.4 \text{ M}$, 85°C , respectively. The samples are referred to as MOR-al(0.2/70) and MOR-al(0.4/85). These alkaline treatments were performed for 2 h, using a liquid/solid ratio of 30 mL/g. Following the concentration of silicon in the treatment solution shows that Si extraction mainly occurs during the first hour (see the Supporting Information, Fig. S1). The dissolution of the amorphous fragments trapped in micropores during the alkaline treatments was carried out by mild acid leaching: $[\text{HCl}] = 0.5 \text{ M}$, 30°C , 10 min. The two resulting materials are named MOR-al(0.2/70)ac and MOR-al(0.4/85)ac. Table 1 summarizes the conditions of the different treatments and reports for each of them the synthesis yield drawn from the weight loss of raw material. In contrast to acid leaching, the alkaline treatments, especially the more severe, led to high material losses and hence a low synthesis yield (ca. 60%).

The protonic form of the zeolite was obtained after three consecutive exchanges of the treated material with 2 M of NH_4NO_3 at a ratio of 20 cm^3 per gram of zeolite. The exchange was carried out at 60°C for 4 h. After a careful washing up to pH 7, the solid was calcined under air flow (100 mL/min/g of zeolite) at 550°C for 5 h.

2.2. Characterization methods

The chemical composition of the materials was measured by X-ray fluorescence (XRF). X-ray diffraction (XRD) data were acquired

on a PANalytical (X'Pert Pro MPD) diffractometer over the 2θ range $5\text{--}50^\circ$ using $\text{Cu K}\alpha$ radiation ($\lambda = 154.05 \text{ pm}$). A Micromeritics ASAP 2000 gas adsorption analyzer was used for nitrogen sorption measurements. Prior to measurement, samples were outgassed at 90°C for 1 h and 350°C for 10 h. Specific surface areas were determined from the BET equation. The total pore volume corresponds to the nitrogen volume adsorbed at $P/P_0 = 0.96$, and the t -plot method was used to discriminate micropores from mesopores. The size distribution of mesopores was estimated by the BJH method. Coked samples were outgassed at 90°C for 1 h and then at 150°C for 1 h to avoid coke elimination. The FT-IR measurements were carried out using a Nicolet 750 Magna FTIR 550 spectrometer (resolution 2 cm^{-1}). The fresh and spent zeolites were pressed into thin wafers and activated in situ in the IR cell under secondary vacuum (10^{-6} mbar) at 350°C overnight and 150°C for 1 h, respectively. The zeolite acidity was measured by adsorption of pyridine followed by infrared spectroscopy. The concentrations of Brønsted and Lewis acid sites were calculated from the integrated area, after pyridine adsorption at 150°C , of the protonated and coordinated pyridine bands at 1545 and 1450 cm^{-1} , respectively, and using extinction coefficients given in Ref. [23].

Catalyst regeneration was studied with a SDT Q600 TA thermogravimetric analyzer coupled with a GA Hiden Analytical mass spectrometer, by heating up to 900°C ($20^\circ\text{C}/\text{min}$) under a 100 mL/min (O_2 10%/He) flow.

2.3. Kinetics of coke deposition

The kinetics of coke formation was described using a microbalance (Sartorius 4433 electrobalance) at 350°C under 1 bar of propene. Before introduction of the coking agent, the zeolite was pretreated under secondary vacuum (10^{-6} kPa) at 350°C for 10 h.

2.4. Coke extraction and characterization

The molecules trapped in zeolite pores were recovered after digestion of the spent catalyst (500 mg) using a concentrated hydrofluoric acid solution (51 vol%, 10 mL) at room temperature for 20 min. The low temperature of HF treatment and the short contact of the acid solution with the coke components allow avoiding some change in coke composition. One fraction of coke was recovered through liquid–liquid extraction using 20 mL of CH_2Cl_2 . The other fraction, insoluble in this solvent, led to black particles that can be totally collected by simple filtration.

The soluble coke fraction obtained after CH_2Cl_2 evaporation was analyzed and quantified by GC-MS (Thermoelectron DSQ) and GC-FID (Agilent), respectively. The soluble and insoluble coke fractions were also characterized by MALDI-TOF MS on a Brüker Autoflex Speed mass spectrometer in a reflectron positive mode where ions were generated by a 337 nm wavelength nitrogen laser. Samples preparation, analysis, and calibration methods were done following the same methodology as described in Ref. [24].

3. Results

3.1. Characterization of materials

The main physicochemical properties of parent and desilicated zeolites are summarized in Table 2 (the characterizations were already presented and discussed in Ref. [22]). The parent MOR zeolite is constituted of crystals with a size between 100 and 500 nm [22]. The crystals are strongly aggregated and the void between them can be assimilated to intergranular mesopores ($V_{\text{meso}}^{\text{inter}} = 0.06 \text{ cm}^3/\text{g}$). To obtain a significant creation of intracrystal mesopore volume, severe alkaline conditions are required (0.4 M

Table 1
Conditions and synthesis yield of acid leaching and alkaline treatment.

	Agent		
	Acid	Alkaline	
	HCl	NaOH	NaOH
Concentration (M)	0.5	0.2	0.4
Temperature ($^\circ\text{C}$)	30	70	85
Time (h)	0.5	2	2
Synthesis yield (%)	99	86	62

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