



Short Communication

Gas-phase chlorination of aromatics over FAU- and EMT-type zeolites

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ABSTRACT

Three FAU-structure type zeolites (EMC-1, USY and USY without EFAl) with different Si/Al molar ratio and their pure hexagonal analogue, the EMC-2 zeolite (EMT-structure type) were prepared and thoroughly characterized. Their catalytic properties were examined in the non-conventional gas–solid reaction requiring a strong acidity. A deeper focus was paid to the difference in activity/selectivity of these zeolites toward the continuous chlorination of aromatics (nitrobenzene and toluene) using trichloroisocyanuric acid (TCCA, C₃N₃O₃Cl₃) as chlorination agent.

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1. Introduction

Conventional Y zeolite, with a Si/Al molar ratio below 2.5, suffers from the lack of thermal and hydrothermal stabilities. Nowadays for cracking applications, conventional Y zeolite is replaced by a high silica ultra-stable Y zeolite (USY) with Si/Al > 4 [1,2]. Indeed, USY zeolite is produced from dealumination of conventional Y zeolite using two distinct approaches: either by hydrothermal or by chemical treatment [3–6]. Unfortunately, these methods require several post-treatments and are time consuming. This explains the strong interest of a one-step synthesis of high-silica FAU-type zeolites for industrial applications.

High silica FAU-type zeolite can be directly synthesized by using specific structure-directing agents (SDA) in a synthesis hydrogel. Guth and co-workers reported the crystallization of EMC-1 (Elf Mulhouse Chemistry One) by using 15-crown-5 ether [7–9]. Likewise, using the 18-crown-6 ether, they also obtained a pure hexagonal analogue of FAU, the EMC-2 zeolite (EMT-type structure) [7–9]. While FAU structure results from a stacking of faujasite sheets with an inversion center symmetry operation (type ABCABC), in contrast, the EMT structure is obtained by a mirror plane operation between the same sheets (type ABAB). The latter stacking allows the formation of two different types of cage: a large hypercage having a free diameter of 14 Å, and besides a smaller ellipsoid hypocage with inner dimensions of 13 × 7 Å, connected through 12 MR apertures. In EMT-type structure a straight

channel having 12 MR openings parallel to the *c* direction is observed [10].

The catalytic performances of these two zeolite types have been widely studied. Compared to EMC-1 zeolite, EMC-2 zeolite usually allows achieving a higher conversion in *n*-alkane isomerization or cracking reactions [9,11]. Such improved catalytic activity arises from the heterogeneous distribution of aluminum atoms within the framework and the presence of hypercages and hypocages [11]. Indeed, similar performances in the vacuum gasoil cracking were obtained for EMC-1 and USY zeolites in terms of product selectivities and activity. Nevertheless, EMC-2 zeolite led to enhanced performances [12].

Chloroaromatics are valuable reagents for the synthesis of dyes, pesticides or pharmaceuticals. Unfortunately, the conventional industrial methods employed for the chlorination of aromatics produce mixtures of regioisomers, being difficult to separate. Indeed, the utilization of Cl₂ as chlorine source always produces a large quantity of waste. Another disadvantage is the use of toxic acid catalysts such as harmful Lewis acids, which are consumed and need to be neutralized after the reaction. In parallel, strong Brønsted acid catalysts such as H₂SO₄ remain very corrosive and generate a lot of salts as byproducts.

In contrast, TCCA is a non-expensive solid, being frequently used as swimming-pool disinfectant and bleaching agent. It is an efficient chlorine source due to its high chlorine content, which can be up to 45.8% in weight, allowing a priori a higher atomic efficiency than its *N*-chloro analogues [13].

In the present study, we report the catalytic evaluation of these three important zeolites in a non-conventional gas–solid reaction that requires a strong acidity. The continuous chlorination of aromatics such as nitrobenzene and toluene with TCCA has been performed over EMC-1, EMC-2 and USY (with or without EFAl) zeolites.

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2. Experimental

2.1. Reagents

Trichloroisocyanuric acid (98%, Aldrich), toluene (99%, SDS) and nitrobenzene (99%, Merck) were used as received. Four different zeolites exhibiting the faujasite structure: H-USY (Zeolyst CBV500), H-USY without EFAl, H-EMC-1 and the EMT structure (H-EMC-2) were employed.

2.2. Zeolite synthesis

2.2.1. EMC-1 and EMC-2 zeolites synthesis

EMC-1 and EMC-2 zeolites were synthesized in a PTFE-lined stainless steel autoclave using the following molar gel compositions 2.1 Na₂O:10 SiO₂:1 Al₂O₃:0.5 15-crown-5:100 H₂O (EMC-1); 2.1 Na₂O:10 SiO₂:1 Al₂O₃:0.5 18-crown-6:100 H₂O (EMC-2) at 110 °C for 10 days. Sodium hydroxide (99.99 wt.%, Riedel de Haën), colloidal silica (Ludox AS-40, Aldrich), sodium aluminate (57 wt.% Al₂O₃, 40 wt.% Na₂O, Strem Chemicals), 15-crown-5 (98 wt.%, Alfa Aesar), 18-crown-6 (95 wt.%, Alfa Aesar) and distilled water were chemical reagents used in this step. After being filtered, washed with water and dried at 70 °C overnight, the zeolite was calcined at 550 °C during 6 h in order to remove the template.

2.2.2. H-USY without EFAl

H-USY zeolite has been chemically modified to evaluate the role of its Lewis acidity in the chlorination reaction. H-USY zeolite (200 mg) was dispersed in a 0.1 M solution of Na₂H₂-EDTA (17.4 mL, 2 eq.). The mixture was heated at 62 °C and stirred for 24 h. The solution was then filtered, washed with distilled water and exchanged with a solution of NH₄NO₃. Finally, the zeolite was calcined in static air at 550 °C overnight. All extra-framework aluminum (EFAl) species were completely removed from pristine FAU material [14,15].

2.3. Characterization of the zeolites

X-ray diffraction patterns of the different samples were recorded using a PANalytical MPD X'Pert Pro diffractometer operating with Cu K α radiation ($\lambda = 0.15418$ nm) equipped with an X'Celerator real-time multiple strip detector. The size and the morphology of the crystals were determined by scanning electron microscopy (SEM) using a Philips XL 30 FEG microscope or a JEOL FEG 6700F microscope. Nitrogen adsorption/desorption isotherms were measured using a Micromeritics ASAP 2420 apparatus. The specific surface area (S_{BET}) and microporous volume (V_{micro}) were calculated using the BET and t -plot methods, respectively. The Si/Al molar ratios of the zeolites were determined using the X-Ray Fluorescence (Philips, Magic X). H/D exchange isotope technique was used to determine the number of Brønsted acid sites present in the different solid acids [16–19].

2.4. Continuous chlorination process

All the chlorination reactions were performed in a gas flow system with a cylindrical glass reactor [15]. The dry nitrogen flow was set to 100 mL/min and 20 mL/min for nitrobenzene and toluene, respectively. The reactions were carried out by diluting the catalytic bed (TCCA and the acid catalyst) in an amorphous silica matrix (Silica Grace) to set the same height for all catalytic beds. To investigate the influence of the solid acid structure on its catalytic performance, the experiments were conducted at iso-site conditions. Indeed, all the catalytic tests were performed by keeping a constant number of Brønsted acid sites for the catalysts, which was set to 0.44 mmol H⁺ for nitrobenzene chlorination (0.41 mmol H⁺ for toluene).

Table 1 presents the Si/Al molar ratio and the number of Brønsted acid sites for the different catalysts used for the chlorination reaction.

The solid acid catalyst, trichloroisocyanuric acid (0.15 mmol for nitrobenzene; 0.51 mmol for toluene) and silica matrix (17 mmol, 1 g) were blended closely by grinding. The mixture was then transferred into the cylindrical reactor and the reactor was fixed to the setup. The catalytic bed was first dried under dry N₂ flow at 150 °C for 30 min to desorb the water present in the void volume of the zeolite. Then, nitrobenzene or toluene was supplied in its gaseous state by sweeping a dry N₂ flow through a stripping reactor containing the aromatic liquid. This continuous gas–solid process was operated during 5 h for nitrobenzene and 3 h for toluene in a dry N₂ flow. The products were trapped at –196 °C and analyzed by gas chromatography (HP 5890 Series II). The degree of conversion and the selectivity toward the different products were calculated by taking into account the response factor of the substrate (nitrobenzene or toluene) and those from the products (mono- and dichlorinated aromatics) through the use of an external standard (styrene).

3. Results and discussion

3.1. Characterization of the zeolites

The crystallinity and purity of the samples were checked by XRD. According to these patterns, pure crystalline FAU and EMT-type zeolites have been obtained for EMC-1, USY and EMC-2 materials (Fig. S1).

The SEM micrographs given in Fig. 1 reveal the shape of zeolite particles. Both USY and EMC-1 zeolite crystals exhibit characteristic pyramidal shape of about 0.5–1 μm and 1–2 μm for USY and EMC-1, respectively. In contrast, EMC-2 zeolite (EMT-type) crystals exhibit a regular hexagonal platelet morphology of 2 μm . As expected for microporous solids, typical type I nitrogen adsorption isotherms were observed (Fig. S2). The associated Brunauer–Emmett–Teller (BET) surface area, microporous volume and external surface of the two synthesized zeolites and commercial USY zeolite are reported in Table 2.

3.2. Catalytic experiments

Fig. 2 presents the nitrobenzene conversion and the selectivity in monochlorination products for the four catalysts. It is important to mention that blank experiments with the Na-zeolite forms and the amorphous silica matrix were performed. No activity at all could be detected. Though the zeolites possessed different Si/Al ratio, thus variations in their densities of acid sites (Table 1), the catalyst mass has been adjusted to guarantee iso-site conditions.

It is noteworthy that the H-EMC-2 zeolite exhibits a nearly 30% higher performance with respect to pristine H-USY zeolite, i.e.; 51% versus 39%. Likewise, the selectivity toward mono-chlorination was 100% for the former H-EMC-2 zeolite, being thus higher than those obtained with the H-EMC-1 (95%) catalyst. Among the products formed, the meta-chloronitrobenzene was always found as major isomer, i.e.; >90% with respect to the ortho- and para-chloronitrobenzene, as a priori expected for the nitro electron attracting group. The selectivity toward monochlorination was drastically reduced over the H-USY zeolite

Table 1
Chemical composition and Brønsted acidity of as-prepared zeolites.

Zeolite	Si/Al	Brønsted acid sites [mmol/g]
H-USY	2.9	3.90
H-EMC-1	4.0	4.63
H-EMC-2	4.0	4.36
H-USY without EFAl	6.2	3.18
H-ZSM-5	25	1.04

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