Hierarchization of pure silica LTA zeolite

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Abstract

The effect of base leaching on pure silica ITQ-29 zeolite being the counterpart of LTA zeolite, was investigated. The extent of the desilication process over pure silica zeolite was controlled by partial detemplation followed by silicon extraction. The potential of hierarchically porous ITQ-29 zeolite in environmentally friendly applications concern selective adsorption of organic molecules in aqueous environments. The introduction of additional porosity by desilication process offers full usage of zeolite grains volume without diffusional limitations during the adsorption process.

Keywords: zeolites, hierarchical, desilication.

1. Introduction

The environmentally friendly applications of zeolites in a wide range of process as ion-exchange, separation and heterogeneous catalytic reactions are well known. Zeolite LTA, a small-pore aluminosilicate with large cavities, is typically obtained with low Si/Al ratio assuring its high capacity as shape-selective adsorbent, drying agent or cation exchanger. The catalytic and separation applications of LTA zeolite are however limited to water-free environments because of its high hydrophilicity. Furthermore, the diffusional limitation for different processes c occurs when purely microporous LTA zeolites with large crystal sizes are used. The attempts to improve the suitability of LTA zeolite for applications requiring the higher hydrophobicity, as for an example adsorbing organic molecules preferentially over water, have been made (*Barrer R.M. et al*, *Wadlinger, R.L. et al.*). The solution was delivered by the synthesis of the pure–silica ITQ-29 zeolite of LTA structure offering high hydrophobicity (*Corma A. et al.*), and as silicalite-1 (*Flanigen E.M. et al.*) or pure-silica beta zeolite (*Camblor M.A. et al.*), presenting higher thermal stability over aluminium rich counterpart. What is more, the smaller diamater of micropores of ITQ-29, over silicalite-1 and beta zeolite, gives rise to higher selectivity toward small organic molecules, even in the presence of water or other polar solvents making this zeolite highly attractive adsorbent. The further optimization of ITQ-29 zeolite properties should be focused on a proper balance between microporous environment and the meso/macroporous one improving the diffusion of molecules in zeolite grains. This should not only increase the rate of the process but also assure full availability of internal grains volume. The alkaline treatment of zeolites is a widely applied method for obtaining the hierarchical materials. The desilication process is aimed to increase the external surface area by the creation of secondary porosity. The susceptibility of zeolite towards base treatment is ruled by several parameters, among Si/Al ratio and irregularities/defect sites in the crystal grains are considered as the prominent ones (*Li T. et al.*). The desilication process of MFI zeolites depending on those parameters has been extensively studied. The optimal Si/Al ratio of MFI zeolite for introducing the secondary mesoporosity has been established between 25-50, for higher values the modification of desilication method is required (*Verboekend D. et al.*). It has been also proved that the alkaline leaching process strongly differs for other zeolite structures such as BEA, MOR or FER. Here we report the effect of base leaching on pure silica ITQ-29 zeolite, synthesized in the fluoride medium assuring the essentially free of crystal defects product (*Corma A. et al.*). The extent of the desilication process was controlled by partial detemplation followed by silicon extraction, a method previously successfully applied to BEA (*Pérez-Ramírez J. et al.*) and SSZ-13 (*Wardani M.K. et al.*) zeolites. The attack of hydroxyl ions on siloxane bonds can be effectively hindered by deliberately leaving the organics within the zeolite structure.

2. Experimental

As-ITQ-29 zeolite was synthesized according to the procedure previously described (*Corma A. et al.*). The partial detemplation procedure was performed at 350 (*A1*), 400 (*B1*) and 450 °C (*C1*). The desilication was done with NaOH solution followed by washing, filtration and drying. Finally, all samples were calcined at 700 °C for 6 h (ITQ-29 and deSi ITQ-29 *A2, B2, C2*). XRD patterns were recorded on a PANanalytical Cubix Pro diffractometer equipped with a graphite monochromator operating at 40 kV and 45 mA using nickel-filtered Cu Ka radiation (λ= 0.1542 nm). Textural properties were determined by N_2 adsorption at -196 °C in a Micromeritics ASAP 2000 equipment. FE-SEM (Field Emission Scanning Electron Microscope, Zeiss, Ultra 55) equipped with a Secondary Electron detector (SED) was used to observe the changes in textural properties. Thermogravimetric analysis was measured using a thermal analyzer NETZSCH STA 449 F3 Jupiter under air flow in the range of temperatures from ambient to 800 °C at a temperature ramp of 10 °C·min^{-1}.

3. Results and Discussion

The analysis of XRD patterns (Fig. 1) of parent and modified samples, both partially detemplated (ITQ-29, *A1*, *B1*, *C1*) and base leached (deSi ITQ-29), confirm the formation of ITQ-29 zeolite and its full stability upon applied treatments. The well-resolved and intensive peaks evidence the highly crystalline structure of all samples. The degree of partial detemplation was assessed based on TG and DTG curves (Fig. 1). The degree of detemplation was gradually increased upon temperature raising. The detemplation of samples was varying from 56 to 14% of the original amount of organic template. As expected the higher content of organic residue led to less extensive desilication process and higher preservation of zeolite sample. The generation of pores can be observed on FE-SEM micrographs proving that high amount of macropores was generated upon alkaline treatment (Fig. 1). The slight mesopores formation with a diameter between 10-20 nm followed by a slight drop in the microporous area was observed for ITQ-29 (A2) sample (Table 1). The mesopores and macropores are preferentially created on external surfaces of zeolite grains, while the interior is protected. Further optimization of leaching procedure should provide the higher secondary mesoporosity development accompanied by full crystallinity perseveration.

Table 1. Textural parameters of studied samples.

	S_{BET} m^2/g	S_{micro}[a] m^2/g	V_{micro}[a] cm^3/g	V_{meso}[b] cm^3/g
ITQ-29	637	626	0.31	0.02
deSi ITQ-29 (A2)	576	562	0.28	0.03

[a] *derived from t-plot method*
[b] *derived from BJH method*

4. Conclusions

The partial detemplation procedure followed by alkaline leaching can assure the controlled leaching of silicon from ITQ-29 zeolite and full crystallinity preservation. Further optimization is required for the higher content of mesoporosity instead macroporosity in zeolite grains. Nevertheless, the obtained materials present interesting textural properties and are potentially attractive for further sorption studies of organic molecules in water containing systems.

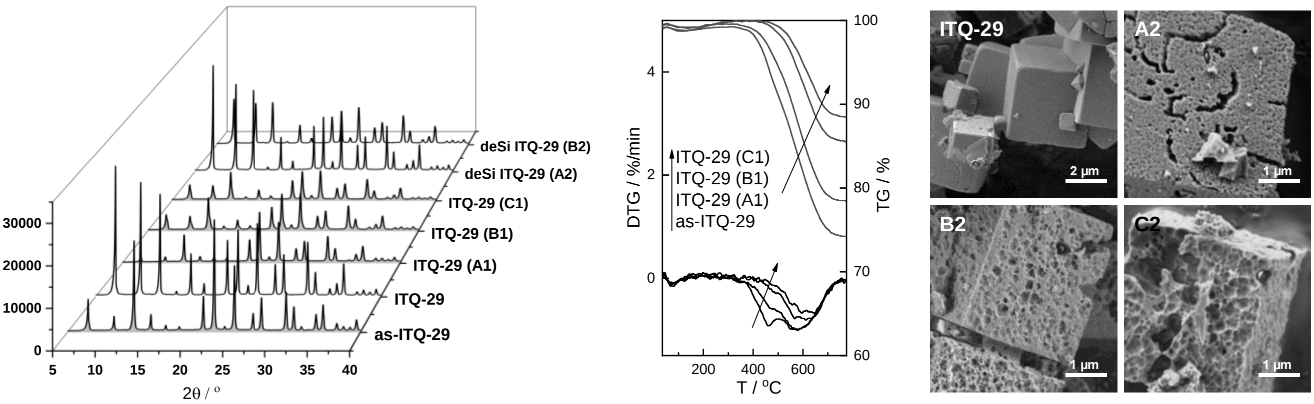

Figure 1. (*Left*) XRD patterns, (*middle*) TG&DTG curves and (*right*) FE-SEM micrographs of studied samples.

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