

POSTSYNTHETIC TREATMENT OF FAU TYPE ZEOLITE WITH ZINC IONS

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ABSTRACT

Faujasite type zeolite has potential as catalyst for methanol-to-olefin (MTO) conversion. In order to enhance its catalytic properties by reducing the intercrystal diffusion path for both reactants and product, nanosized crystals were used and the prepared material was further functionalized by a wet impregnation with zinc ions. The wet impregnation was conducted at room temperature but also under hydrothermal conditions.

Keywords: zinc, faujasite, wet impregnation.

INTRODUCTION

Faujasite type zeolite (FAU) is one of the most studied zeolites because of its application as catalyst in fluid catalytic cracking (FCC) and support for a platinum/palladium in a hydrocracking process. Depending on the Si/Al ratio synthetic FAU is classified as X, if ratio is between 2 and 3, or more widely used and thermally stable Y if ratio is 3 or higher. A large 12-membered ring pores and Brønsted's sites make the FAU type zeolites potential catalyst for the methanol-to-olefins (MTO) conversion [1], but in order to enhance their catalytic properties further modifications are needed. The particle and the pore size play a crucial role in the catalytic performance of material because they are directly related to one of the most common problems of porous solid state catalysts, intercrystal diffusion. In order to facilitate diffusion of both reactants and products we can either reduce the particle size to nanoscale in order to reduce the path to and from the active site or use surfactants in the process of synthesis, such as cetyltrimethylammonium bromide (CTAB), to form mesoporous network through which molecules can move easily. Thus synthesized materials can be further functionalized by the wet impregnation with transition metal salts in order to form larger number of Brønsted's and Lewis's acid sites that serve as the active sites for the MTO catalytic process.

EXPERIMENTAL

The zeolite for post synthetic treatment (HF-22) was isolated from a gel with following composition $8\text{Na}_2\text{O}:0.7\text{Al}_2\text{O}_3:10\text{SiO}_2:160\text{H}_2\text{O}$ adopted from Awala and co-workers [2]. The aluminate (A) and silicate (B) components of reaction gel were prepared separately. Component B was prepared by mixing Ludox-HS 30, sodium hydroxide (Kemika, aq, 33 %) and redistilled water. The resulting suspension was then heated until a clear solution was obtained. To prepare component A, an aluminum wire (99,999 %) was dissolved in a sodium hydroxide solution. Component A was then added dropwise in component B while stirring vigorously. A hydrothermal crystallization was conducted at 120 °C for 70 minutes after aging the reaction gel for 24 hours at room temperature.

HF-Zn1: Previously prepared nanosized FAU zeolite (700 mg) was added in the water solution of zinc nitrate (4 cm^3 , 3 mol dm^{-3}) and stirred. After 45 minutes the crystals were separated from solution and the process was repeated once more. The prepared product was

then washed two times with 40 cm³ of redistilled water and left in a freeze-dryer. The dry product was then calcined at 550 °C.

HF-Zn2: The same procedure was used as described above with the exception that before washing the product with redistilled water the hydrothermal synthesis was conducted at 100 °C for 24 hours.

RESULTS AND DISCUSSION

The XRD patterns of starting material were compared to products isolated after post synthetic treatment. The strong diffraction peaks of zinc oxide at 31.8 °, 34.4 ° and 36.3 ° were not observed which indicates that zinc present in the sample is incorporated in the crystal structure (Figure 1). Minor loss of crystallinity after post synthetic treatment was noticed.

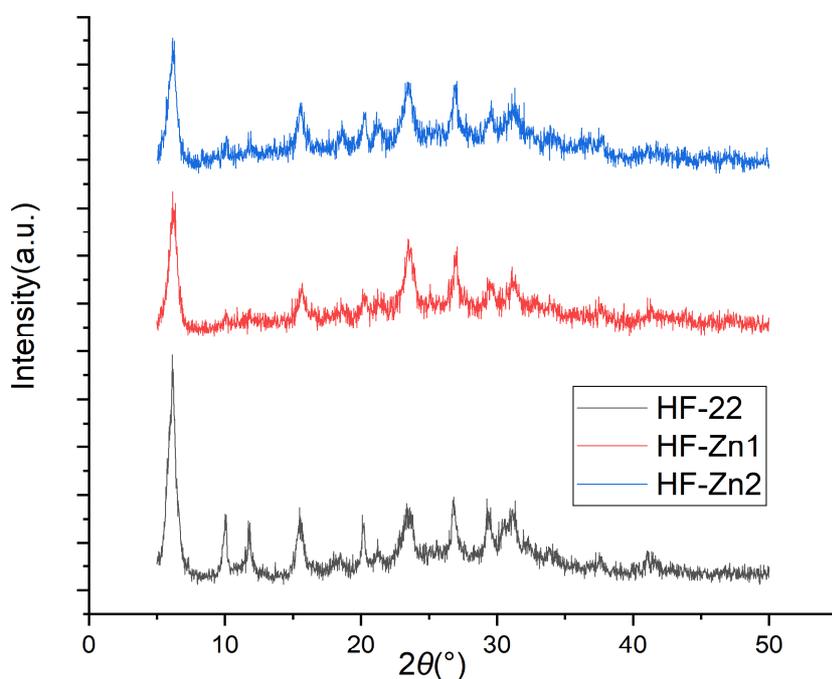


Figure 1. XRD patterns of starting material (HF-22), HF-Zn1 and HF-Zn1.

On SEM images of starting material and samples HF-Zn1 and HF-Zn2 which underwent post synthetic treatment, significant change of morphology and crystal size was not observed (Figure 2). From the EDS spectra of HF-Zn1 and HF-Zn2 (Table 1) it is visible that substitution of sodium ions with zinc ions was complete, but amount of present zinc ions is larger than necessary for charge compensation which indicates that some of the ions may be incorporated in aluminosilicate framework. It is also observed that samples that were hydrothermally processed after wet impregnation contain larger amounts of zinc ions than samples that were not.

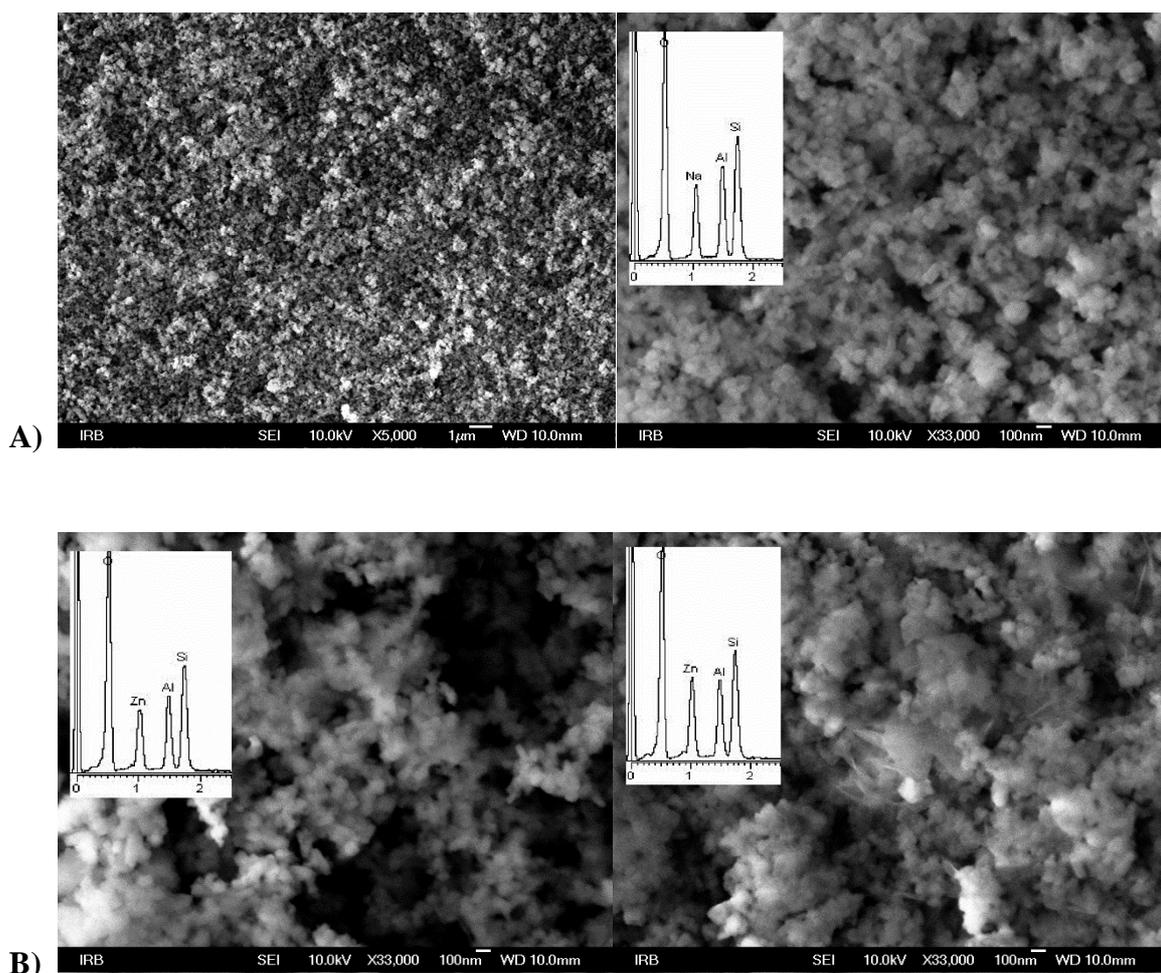


Figure 2. SEM images of: A) starting material B) HF-Zn1 (left) and HF-Zn2 (right).

Table 1. Results of EDS measurements.

Element	mas.% (HF-22)	Element	mas.% (HF-Zn1)	mas.% (HF-Zn2)
O	51.13	O	47.19	44.48
Na	11.35	Zn	18.15	21.37
Al	13.70	Al	12.54	12.65
Si	23.82	Si	22.12	21.50

CONCLUSION

After post synthetic treatment changes in the crystal size and morphology were not observed. Wet impregnation in combination with hydrothermal processing proved to be effective method of implementing zinc ions in the crystal structure of FAU type zeolite and thus enhancing its catalytic properties.

ACKNOWLEDGEMENT

This work was supported by Croatian Science Foundation, project IP-2016-06-2214.

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