

EFFECT OF METAL CATIONS IN FAU TYPE ZEOLITE ON ACID SITES

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ABSTRACT

Faujasite type zeolite isolated from the gel with a composition of $4\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:158\text{H}_2\text{O}$ after 48 h at 100°C was modified during synthesis using cetrimonium bromide (CTAB), or post-synthetically treated with sodium hydroxide aqueous solution in order to create mesopores. This way prepared material was then wet impregnated using metal salts of magnesium(II), cobalt(II), nickel(II) or zinc(II). The effect of exchanged metal cation on Brønsted and Lewis acid sites was observed using adsorption of deuterated acetonitrile in vacuum IR.

Keywords: FAU, wet impregnation, vacuum IR, mesopores.

INTRODUCTION

Faujasite type zeolite is one of the most widely used types of zeolite. Its 12-member ring cage makes it one of the best catalysts for fluid catalytic cracking (FCC) and support for platinum or palladium in a hydrocracking process. Depending on the Si/Al ratio synthetic FAU is classified as X, if the ratio is between 2 and 3, or Y if the ratio is 3 or higher. High aluminum content in X type zeolite results in a large number of Brønsted's acid sites which often leads to unwanted cyclic byproducts and the formation of coke. In order to avoid this problem, post-synthetic modifications to the zeolite structure are needed. One of the most important factors for solid-state catalysts is the rate of diffusion of molecules through the crystal. Large pores enable easy access of reactants but also the fast removal of products from the active site which reduces a possibility for byproduct formation.

Formation of mesopores is most commonly achieved by etching with alkaline water solution or using mesoporosity template such as CTAB. This way prepared zeolites can then be further modified by wet impregnation with various metal salts. The type of metal and its coordinational preferences can have a huge effect on acid sites in the zeolite framework.

EXPERIMENTAL

The zeolite for post-synthetic treatment (HF2-2) was isolated from a gel with following composition $4\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:158\text{H}_2\text{O}$ [1]. The aluminate (A) and silicate (B) components of reaction gel were prepared separately. Component B was prepared by mixing Ludox-HS 30 and sodium hydroxide (Kemika, aq, 33%). To prepare component A, sodium aluminate was dissolved in a sodium hydroxide solution and water. Component A was then added in component B while stirring vigorously. A hydrothermal crystallization was conducted at 100°C for 48 hours after aging the reaction gel for 18 hours at room temperature. The resulting product was then washed, dried and calcined at 550°C for 6 hours. To get **HF2-2 des30** thus synthesized product was treated with 0.2 mol dm^{-3} sodium hydroxide water solution at 65°C for 30 minutes [2]. The ratio of solid phase to water solution was 1:30. For the synthesis of **HF2-2 24a** the reaction mixture was cooled down after 24 hours and slurry of CTAB in alkaline water (mass ratio CTAB:H₂O=1:1, and pH of the solution same as the one of the reaction gel) was mixed with synthesis gel in the molar ratio $\text{SiO}_2:0.4\text{CTAB}$. After that reaction mixture was returned to the oven for another 24 hours. The product was washed with distilled water, dried and calcined for 10 hours at 550°C .

Wet impregnation: Prepared FAU type zeolites **HF2-2 des30** and **HF2-2 24a** were wet impregnated with the nitrate salts of magnesium(II) (1 mol dm^{-3}), cobalt(II) (1 mol dm^{-3}), nickel(II) (0.5 mol dm^{-3}) and zinc(II) (1 mol dm^{-3}) two times for 40 minutes after which they were thoroughly washed with redistilled water, dried and calcined at 550°C for 6 hours.

RESULTS AND DISCUSSION

The XRD patterns of parent samples were compared and no significant differences were observed (Figure 1). Diffraction patterns of samples after wet impregnation were compared with those of parent samples and the peaks of corresponding metal oxides were not observed.

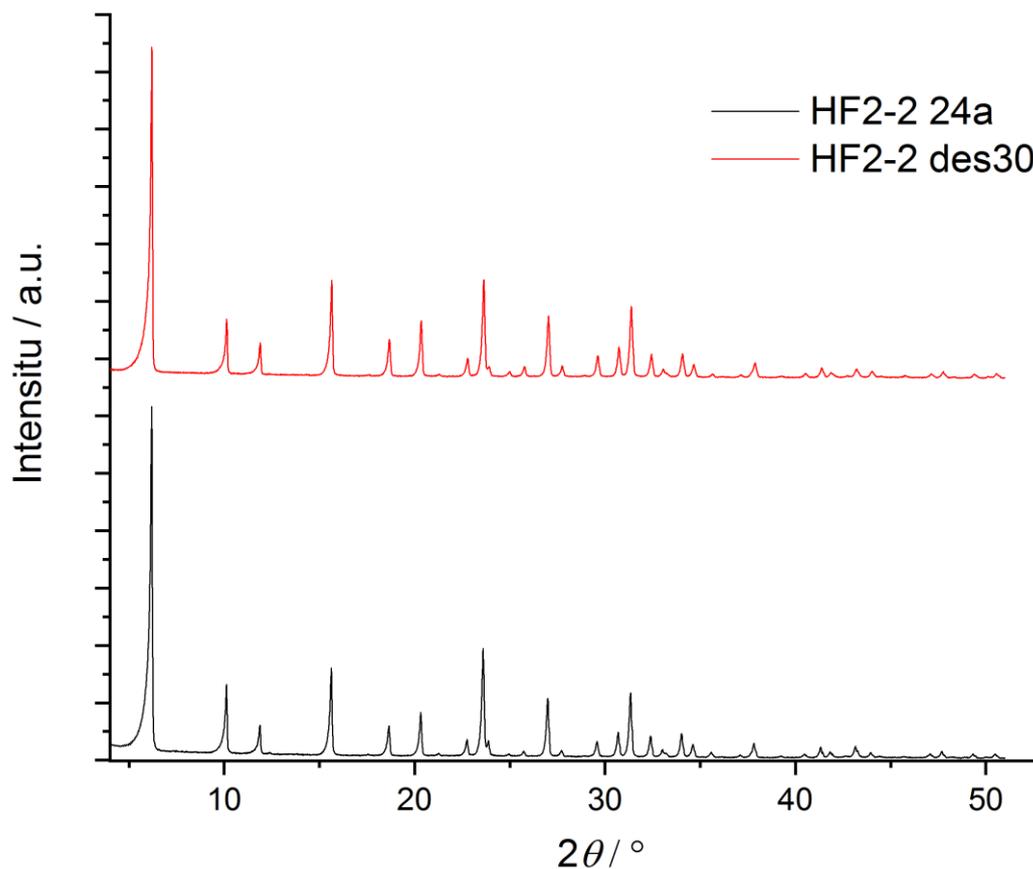


Figure 1. X-ray diffraction patterns of parent samples.

The effect of synthesis with the addition of CTAB compared to post-synthetic treatment with NaOH solution on zeolite morphology was observed using SEM (Figure 2). The difference in morphology after wet impregnation was not observed.

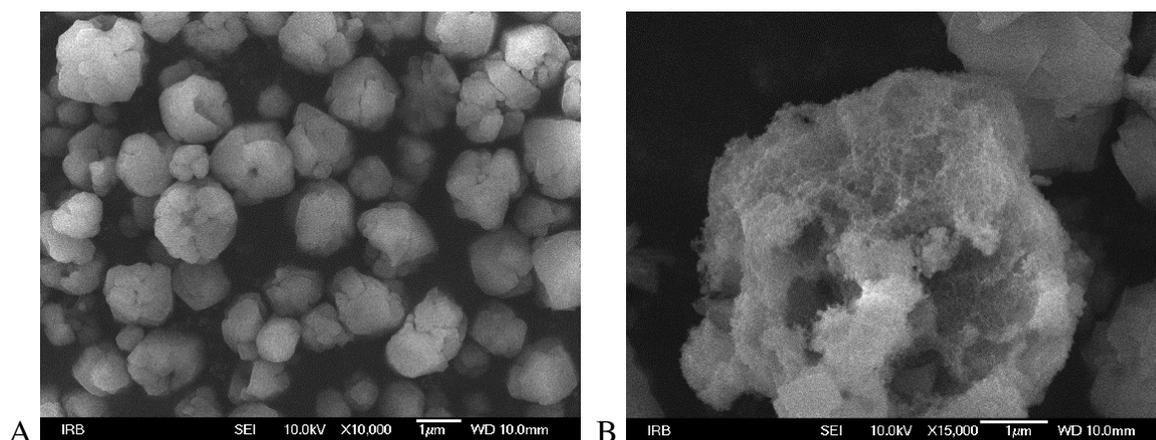


Figure 2. SEM images of HF2-2 24a (A) and HF2-2 des30 (B).

Vacuum IR spectra after adsorption of deuterated acetonitrile (Figure 3) show that in 24a series Co(II) sample has the highest intensity of peak at 2306 cm^{-1} (Lewis acid sites) followed by Mg(II).

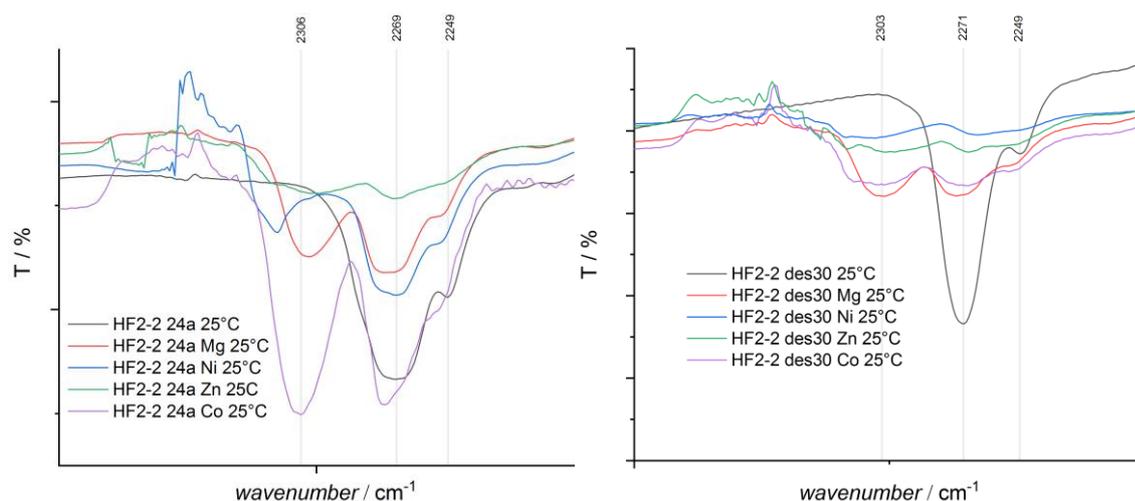


Figure 3. Vacuum IR spectra of deuterated acetonitrile adsorbed on parent and wet impregnated FAU type samples at 25°C .

The sample wet impregnated with Ni(II) shows a shifted peak at 2316 cm^{-1} which indicates a different type of Lewis acid sites compared to other metals. The intensity of a peak at 2269 cm^{-1} (silanol acid sites) is similar for parent and Co(II) sample, while those of Ni(II) and Mg(II) are a bit lower. Sample wet impregnated with Zn(II) has low intensity of both acetonitrile adsorption peaks.

All samples in des30 series show decrease in the intensity of peak at 2271 cm^{-1} after wet impregnation. The peaks at 2303 cm^{-1} are relatively weak in the case of Co(II) and Mg(II) and extremely weak for Ni(II) and Zn(II).

CONCLUSION

In all samples the differences in vacuum IR spectra after deuterated acetonitrile adsorption were observed, while XRD patterns and SEM images don't indicate any structural or morphological differences. The intensity of Lewis' acid site peaks for 24a series of samples follows in order Co>Mg>Ni>Zn, while for the des30 series it is Mg>Co>Zn>Ni. This indicates that the method of sample preparation partially also contributes to the integration of the cations in the framework after wet impregnation.

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