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INTRODUCTION OF TRANSITION METAL CATIONS (Co^{2+} and Zn^{2+}) INTO DEALUMINATED NaY ZEOLITE OBTAINED BY CITRIC ACID TREATMENT

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Abstract

Aluminum ions were extracted from the framework of the faujasite type zeolite NaY (Si/Al=2.4) by citric acid treatment. Dealuminated CoY and ZnY zeolites of high cobalt and zinc content were prepared by replacing sodium ions with Co^{2+} and Zn^{2+} in dealuminated Y zeolites, with increased framework Si/Al ratio. Chemical and XRD analyses of zeolites were performed and the FTIR-ATR spectra were recorded. The results of physicochemical analyses are discussed in terms of unit cell (u.c.) composition.

Introduction

Framework dealumination is an important method to improve catalytic properties of zeolites. Dealumination treatment process extracts Al atoms from tetrahedral positions in the zeolite framework and converts them to octahedral, amorphous aluminum oxide (extraframework aluminium species), which often remains in the pores of zeolite. Transition-metal-exchanged zeolites are key materials for catalysis and adsorption. Framework Si/Al ratio dictates the amount of transition-metal cations that can be exchanged into zeolite, and therefore the active site density. The aim of presented work was to obtain dealuminated Y zeolites of relatively high cobalt and zinc content through a relatively simple procedure. Chemical, XRD and FTIR-ATR data are presented for these products.

Experimental

The zeolite used in this work was NaY(SK-40) faujasite sample with the u.c. formula $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]$. Zeolites with different Si/Al framework ratios were prepared by citric acid treatment [1]. Relative crystallinity was estimated from the XRD patterns that were recorded with a XRD Phillips PW 1050 instrument (20 mA, 34 kV, 2.5°/min), by means of comparison of (1 1 1) peak intensities of the dealuminated samples to the reference NaY zeolite. The sodium form of the dealuminated Y zeolite samples was transformed into different cation forms (CoY and ZnY) by ion exchange procedure, using 0.5M solutions of $CoCl_2$ and $ZnCl_2$. All samples were microwave digested in aqua regia and analyzed for Na, Co, Zn, Al and Si content by atomic emission spectroscopy (Perkin-Elmer ICP/6500). Infrared attenuated total reflection (ATR) spectra were recorded on a Nicolet 380 FT-IR spectrometer (4000-400cm^{-1}). The lattice cell constants were calculated using FullProf Suite software.

Results and Discussion

According to literature date, in the process of dealumination of faujasite type zeolites (f.e. thermochemical treatment of NH_4Y in steam [2] and treatment of NaY with $SiCl_4$), dealuminated zeolites appear as the proton modification, HY. The method presented in this paper provides preparation of dealuminated Co^{2+} and Zn^{2+} exchanged Y zeolites without their conversion to protonated Y form.

Chemical analysis showed that the content of total (framework and extraframework) aluminum decreased from 8.6% (NaY) to 5.4 % (NaY-D) and the content of sodium decreased from 7.3 % (NaY) to 3.6 % (NaY-D). XRD patterns of regular NaY and the obtained dealuminated zeolites are shown in Fig. 1.

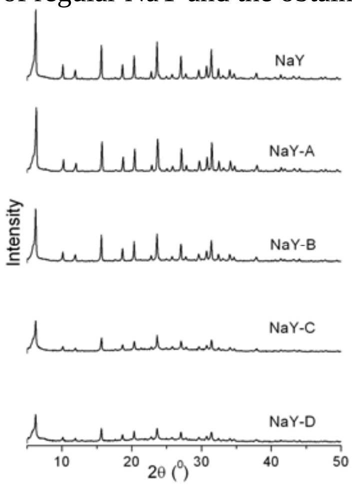

Fig.1. X-Ray diffraction patterns of zeolites: NaY, NaY-A, NaY-B, NaY-C and NaY-D

The peak positions in the observed XRD patterns of the dealuminated samples remained unchanged. The structure of zeolite is not essentially destroyed during the treatment with citric acid solution of low concentration, 0.01 M for NaY-A and 0.02M for NaY-B. The treatment with 0.03 M (NaY-C) and 0.04 M (NaY-D) citric acid solution lead to the collapse of zeolite lattice. The estimated relative crystallinity of NaY-A was 95%, NaY-B - 81%, NaY-C - 61% and NaY-D - 40%. The calculated lattice cell constants for the starting NaY and the dealuminated zeolites with high estimated crystallinity (NaY-A and NaY-B) were 2.4642, 2.4594 and 2.4576 nm, respectively. The decrease of the u.c. size is the consequence of the increasing Si/Al ratio during the dealumination of zeolite [3].

The FTIR-ATR spectra of regular CoY and ZnY and dealuminated CoY-A, CoY-B, ZnY-A and ZnY-B are shown in Fig. 2. Framework sensitive structural bands [4] due to the asymmetric Si-O and Al-O stretching within the tetrahedra at 950-1050 cm^{-1},

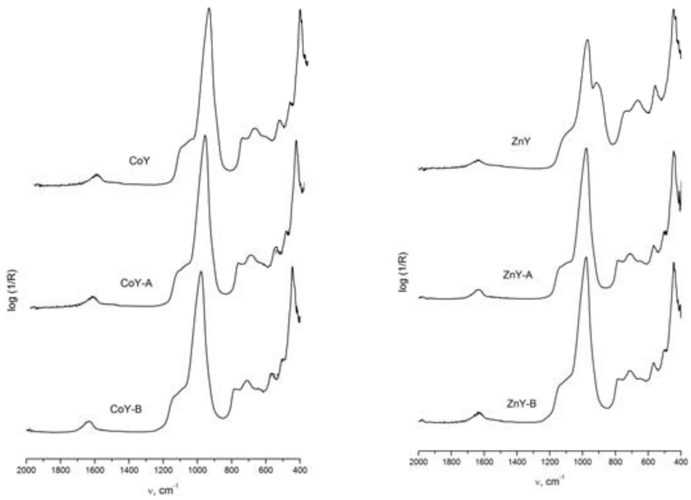

Fig.2. FTIR-ATR spectra of starting and dealuminated CoY and ZnY

symmetric stretching between tetrahedra at 750-820 cm^{-1}, and double six-membered oxygen ring at 500-650 cm^{-1} occur in the spectra of dealuminated CoY and ZnY with the same intensity as in the spectra of regular CoY and ZnY. The frequencies of these bands are very sensitive to the Si/Al framework ratio and with decrease in Al content, i.e. increase in Si content, the bands are shifted to higher frequencies [5]. In our spectra of the dealuminated cation-exchanged zeolites, the frequencies are always higher than in the spectra of regular CoY and ZnY. Using the frequencies of these three bands and the equations given in Refs. [6] the number of framework Al atoms per unit cell in dealuminated CoY and ZnY was calculated. The number of Si atoms per unit cell after dealumination was calculated using the equation N(Si) = 192 - $N(Al_{Framework})$ [6]. Subsequently, the framework Si/Al ratio in dealuminated CoY and ZnY samples was calculated. These data are listed in Table 1, as well as the percent content of Co and Zn determined by chemical analysis.

Table 1. Chemical composition of starting and dealuminated CoY and ZnY

zeolite	% extraframework Al	Framework Al mol/ u.c.	Si mol/ u.c.	Si/Al	% Co	% Zn
CoY	-	56	136	2.4	7.4	
CoY-A	8.2	45	147	3.3	6.5	
CoY-B	7.9	43	149	3.5	5.3	
ZnY	-	56	136	2.4		7.6
ZnY-A	8.2	45	147	3.3		7.1
ZnY-B	7.9	43	149	3.5		5.6

Conclusion

NaY (Si/Al=2.4) was modified by citric acid treatment into highly crystalline NaY-A (95%) and NaY-B (81 %) dealuminated forms with increased framework Si/Al ratio (3.3 and 3.5, respectively). FTIR-ATR spectra of dealuminated CoY and ZnY confirmed that the introduction of Co^{2+} and Zn^{2+} has no adverse effect on the stability of the basic zeolite framework. The number of framework aluminum and silicon, the percent of exchanged Co and Zn and the Si/Al framework ratio in the obtained dealuminated zeolites were calculated.

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