

## **ACIDITY OF HIERARCHICAL FAU, BEA AND ZSM-5 ZEOLITES**

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### **ABSTRACT**

Three types of zeolites, FAU, BEA and ZSM-5, were subjected to mesopore formation through alkaline treatment. All samples developed significant mesoporosity, while preserving their initial microporous and crystalline structures. Zeolites were characterized using X ray diffraction and low temperature nitrogen adsorption. Acidity of parent and mesoporous samples was evaluated in both gas and liquid phase. The distributions of acid sites' strengths were quantitatively determined by microcalorimetry/volumetry of ammonia adsorption. Differentiation between Bronsted and Lewis sites was performed using IR spectroscopy of pyridine adsorption/desorption experiments. In liquid phase, acidity was evaluated by calorimetry/volumetry of phenylethylamine adsorption. Obtained results revealed different degrees of acidity preservation in the mesoporous samples, compared to the parent ones, within the three investigated zeolitic structures.

Keywords: hierarchical zeolites, acidity, microcalorimetry, pyridine, phenylethylamine.

### **INTRODUCTION**

In recent years, a novel type of zeolites, containing two levels of porosity (i.e. micropores and mesopores) has been attracting scientific attention [1,2]. Introducing mesoporosity into zeolitic structures has proven to increase the range of molecules these materials can interact with, compared to their microporous analogues. Furthermore, improved catalytic performance has been found for different zeolites due to the existence of mesopores in the structures [3,4]. These zeolites, having more than one level of porosity, are named hierarchical.

Mesoporosity in zeolitic structures can be obtained either by synthetic or postsynthetic routes. In this work, we focused on a postsynthetic way of creating mesopores in initially microporous zeolites (FAU, BEA and ZSM-5), and the evaluation and comparison of the acidity in parent and modified structures. For that purpose, we evaluated all the samples using three different techniques: microcalorimetry/volumetry of ammonia adsorption, IR spectroscopy of pyridine adsorption/desorption and liquid state calorimetry/volumetry of phenylethylamine adsorption. To the best of our knowledge, this is the first time calorimetric quantitative data concerning acid sites number and strength in hierarchical zeolites are published.

### **EXPERIMENTAL**

Parent zeolites were obtained from Zeolyst International: FAU (CBV 760, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=60), BEA (CP814E, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=25) and ZSM-5 (CBV 5524G, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=50). Mesopore formation was performed using desilication by alkaline treatment, following the procedures reported in literature [5,6]. ZSM-5 sample was treated with NaOH, (0.2M, 30 min, 338 K). The samples were filtrated, washed and dried at 393 K overnight. An acidic treatment was then performed, (0.1 M HCl, 6h, 298K). Zeolites FAU and BEA were subjected to the identical alkaline treatment, but in the presence of TPABr, a pore directing agent. Both parent and modified samples were converted to their ammonium forms by three-fold ion-exchange

(0.1 M NH<sub>4</sub>NO<sub>3</sub>, 363 K, 1 hour). As prepared materials were filtered, washed, dried at 393 K and finally calcined in air at 773 K for 5 h. The obtained materials were denoted as xP and xM, for the parent and the modified, mesoporous forms, respectively; where x stands for zeolite type, i.e. FAU, BEA and ZSM-5.

The surface pore volumes and pore sizes were measured by nitrogen adsorption at 78 K on a Micromeritics 2010 apparatus, after pre-treatment at 673 K during 4 hours. XRD measurements were performed on a Bruker D5005 powder diffractometer scanning from 2° to 80° (2θ) at a rate of 0.02° s<sup>-1</sup> using a Cu Kα radiation.

Microcalorimetric – volumetric measurements of ammonia adsorption were performed in a heat-flow calorimeter of the Tian-Calvet type (Setaram), linked to a glass volumetric line. The samples were pretreated under vacuum at 673 K prior to adsorption of ammonia in the calorimetric cell maintained at 423 K respectively. Successive small doses of NH<sub>3</sub> were introduced onto the samples until a final equilibrium pressure of 66 Pa was achieved.

FTIR spectra were recorded using an FTIR Bruker IFS-48 Vector 22 spectrometer. A zeolite sample, in the form of a self-supported pellet was placed in a sample holder in an IR cell with CaF<sub>2</sub> windows. Adsorption of pyridine was performed at 373K, after a pretreatment at 673K in vacuum. Following adsorption, the samples were evacuated in vacuum at the desired temperature (373K, 423K, 473K, 573K and 673K), cooled to room temperature and then IR spectra were recorded (100 scans at 2 cm<sup>-1</sup> resolution), using the spectrum of the pretreated zeolite as background.

Adsorption of phenylethylamine (PEA) was studied using a previously established procedure [7]: typically, 50 mg of zeolite was added to an appropriate amount of adsorbate solution and mixed in a sealed flask during 2 h at 303 K. The two phases were separated by centrifugation (Minispin from Eppendorf, 13400 RPM, 1 hour). Equilibrium adsorbate concentrations were determined by Shimadzu UV-1650PC spectrophotometer and the adsorbed amounts were calculated from the difference between the initial and equilibrium concentrations. Liquid calorimetry measurements were performed in a differential heat flow reaction calorimeter (TITRYS, from Setaram) equipped with a stirring system. The calorimeter was linked by capillary tubes to a system for liquid injection (PHD 2000, Harvard Apparatus). Successive pulse injections of adsorbate solutions were sent to the sample in 2 h time intervals. The temperature of the calorimetric cell was maintained at 303 K.

## RESULTS AND DISCUSSION

Alkaline treatment resulted in mesopore development in all three investigated zeolites, Table 1. Furthermore, microporous structure was almost completely preserved in ZSM-5-M and BEA-M samples while, in FAU-M, a decrease in microporous volume was detected.

Table 1. Textural properties of parent and mesoporous ZSM-5, FAU and BEA zeolites

Sample	V <sub>pore</sub> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>a</sup>	V <sub>micro</sub> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>b</sup>	V <sub>meso</sub> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>c</sup>	S <sub>meso</sub> (m <sup>2</sup> g <sup>-1</sup> ) <sup>b</sup>	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> ) <sup>d</sup>
ZSM-5-P	0.236	0.144	0.085	65	365
ZSM-5-M	0.449	0.138	0.389	137	470
FAU-P	0.647	0.359	0.257	205	953
FAU-M	1.301	0.289	0.991	625	1219
BEA-P	0.748	0.199	0.531	230	637
BEA-M	1.127	0.190	0.902	328	751

<sup>a</sup> Volume measured at p/p<sup>0</sup>=0.98, <sup>b</sup> t-plot method, <sup>c</sup> BJH method, <sup>d</sup> BET method

For all investigated zeolites, increases in BET surface, mesoporous surface and volume was observed, compared to the parent analogues. XRD patterns showed that crystalline structures were preserved after alkaline treatment in all hierarchical samples.

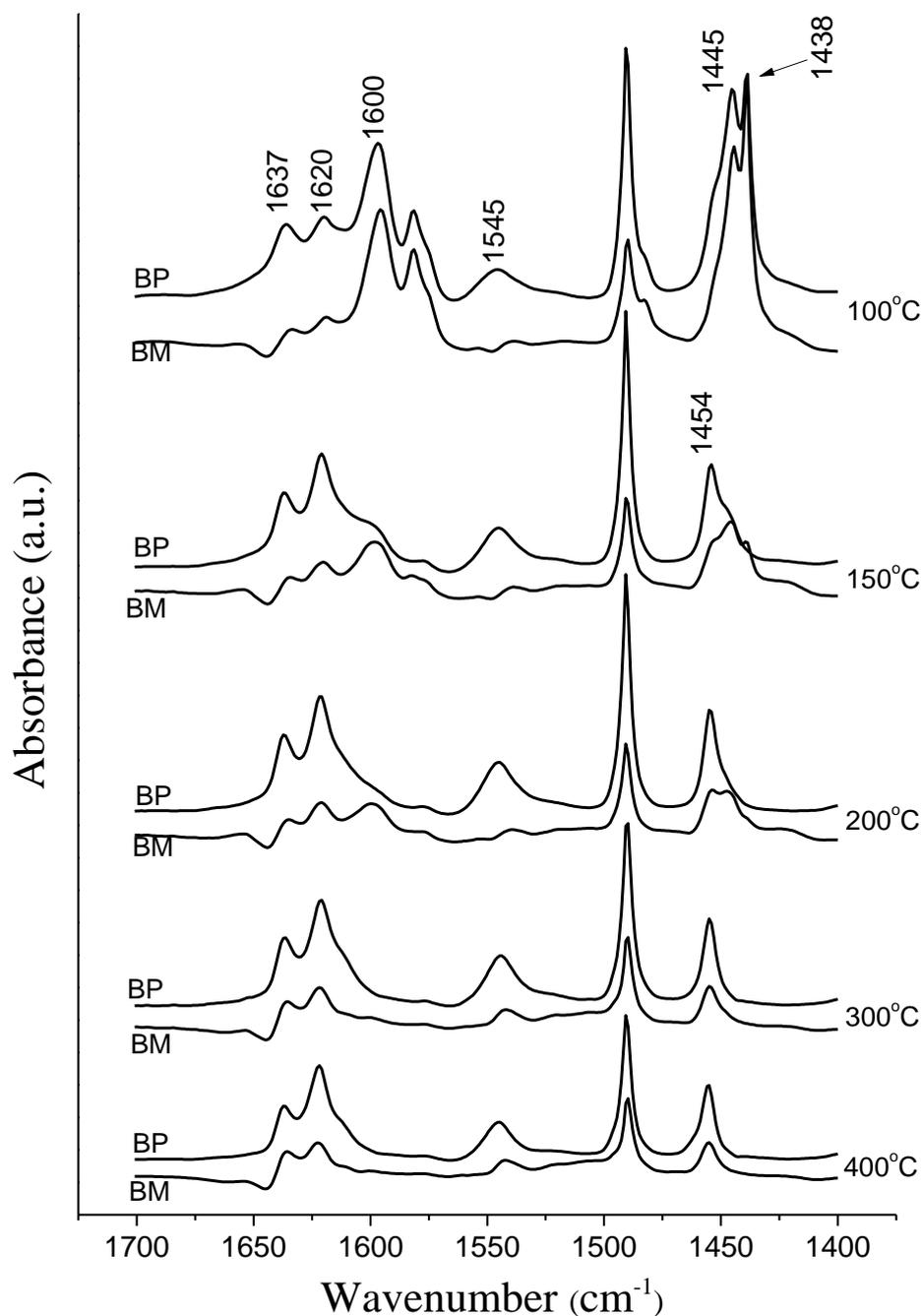


Figure 1. Infrared spectra of pyridine recorded after adsorption and desorption on beta zeolite samples at different temperatures

Microcalorimetric/volumetric measurements of ammonia adsorption revealed that different zeolitic structures reacted differently to the alkaline treatment, in terms of acidity preservation. In the case of ZSM-5 samples, only a slight decrease in acidity was detected, and the distributions of strength of the acidic sites for ZSM-5-P and ZSM-5M are almost the same [8]. Hence, for ZSM-5, no significant changes in total acidity were detected. FAU and

BEA zeolites, however, seem to be more sensitive to base leaching, since their acidity was changed. This was especially pronounced for FAU, where the largest decrease in differential heats of ammonia adsorption was measured.

FTIR of pyridine adsorption/desorption revealed that the largest decrease in acidity as a whole could be attributed to Bronsted acidity diminishing. This decrease in Bronsted acidity is much more pronounced for BEA (Fig. 1) and FAU samples than for ZSM-5. IR spectra also showed that the nature and strength of Lewis sites had changed for mesoporous samples, compared to the parent ones. It can be inferred that alkaline treatment leads to alteration of the distribution of strengths of Lewis acid sites, as well as to formation of new ones.

Liquid state acidity, estimated through PEA adsorption, was compared to the results obtained in gas phase experiments. The results from these two methods can be regarded as complementary. Acidity changes obtained from gas and liquid phase differ and express the different surface conditions in the experiments. Ammonia adsorption is performed in previously evacuated system, while in liquid phase the samples are in contact with water prior to adsorbate administering, and the acid sites interact with water molecules. This makes having results from both acidity estimation methods a more complete view of the sample's acidity and the possibility to correlate them to zeolite's catalytic and adsorptive properties in either gas or liquid phase.

## CONCLUSION

Introduction of mesopores in zeolites via alkaline treatment can affect the acidity of the starting material. Among the investigated samples, FAU sample's acidity was altered the most while, in ZSM-5, acid sites number and strength were almost completely preserved. The dominant relative reduction of acidity was observed for Bronsted sites, in all samples. Redistribution of Lewis acid sites strengths was detected, as well new Lewis acid sites formation.

## ACKNOWLEDGEMENT

This work was supported by Ministry of Education, Science and Technological Development, Republic of Serbia; grant No 172018.

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