

## CHARACTERIZATION OF METAL SPECIES IN METAL-MODIFIED HIERARCHICAL MORDENITE

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### ABSTRACT

Two methods were investigated to synthesize mesoporous mordenite. PXRD showed that the samples made by both methods are crystalline mesoporous material with MOR framework. The transition metal cations Ag and Fe were introduced by the ion exchange method. The introduction was confirmed with EDS and AAS analysis. UV–Vis spectroscopy was applied to identify the silver and iron species in samples.

Key words: zeolite, mordenite, hierarchical, wet impregnation.

### INTRODUCTION

The unique physicochemical properties of the zeolites, such as their controlled acidity, adsorption capacity, ion exchange properties, thermal stability, as well as uniform channels and cavities crystallographically ordered in size and position, determine their effectiveness in catalytic processes. Mordenite is widely used in catalysis, separation, and purification because of its uniform, small pore size, and high internal surface area. Mordenite is a zeolite with two-dimensional pores, as the structure determined by Meier in 1961 showed [1]. The pore system of mordenite consists of main channels of  $6.5 \times 7.0$  Å, which are connected by tortuous pores of  $2.6 \times 5.7$  Å that form the so-called side pockets. Since the latter is too small for most molecules to enter, mordenite is generally regarded as a mono-dimensional zeolite.

The major drawback of mordenite and zeolites, in general, is the limited size of the channels and cavities and the lack of interconnectivity. This imposes diffusional limitations on reactions, limiting their activity, selectivity, and stability [2]. Despite the microporous structure, there are limitations that decrease the efficiency of the zeolite as catalysts. Such limitations can be avoided by creating mesoporous voids. Another important issue in catalysis efficiency is the number of active sites. Its number can be increased with a number of hetero T-atoms within the framework by post-synthesis treatment, such as ion exchange. Metal-modified zeolites being a very suitable substrate for selective catalytic activity.

### EXPERIMENTAL

#### *Synthesis of classical mordenite microcrystals (M-1)*

Zeolite with oxide formula  $20.2 \text{ SiO}_2 \times 4.4 \text{ Na}_2\text{O} \times \text{Al}_2\text{O}_3 \times 173 \text{ H}_2\text{O}$  was prepared by mixing silica and alumina alkaline solutions. The resulting gel was stirred at room temperature for 30 min. The mixture was subsequently transferred to a Teflon-lined stainless steel autoclave. The hydrothermal treatment was carried out for 5 days at 180 °C under static conditions. Autoclaves were cooled down to room temperature, and solid products were filtered off, washed thoroughly with distilled water, and dried overnight at 70 °C. The calcination of the samples was carried out at 550 °C for 10 h ( $2 \text{ °C min}^{-1}$ ) in the air stream. H-form of the sample was obtained by ion exchange with 0.8 M  $\text{NH}_4\text{NO}_3$  at room temperature followed by calcination. Intracrystalline mesoporosity was developed by post-synthesis treatment with 0.2 M NaOH solution followed by ion exchange with  $\text{NH}_4\text{NO}_3$  and calcination in a stream of air.

### One-pot synthesis of mesoporous mordenite (MOR)

The second strategy of mordenite preparation with the same Si/Al ratio was the direct synthesis of hierarchical structure. It was made using a similar procedure with pore generating agent, respectively cetyltrimethylammonium bromide, CTAB. The duration of the synthesis was shortened by 1 day, and the crystallization temperature was lower by 30 °C. H-form of the sample was obtained by ion exchange with 0.8 M NH<sub>4</sub>NO<sub>3</sub> at room temperature followed by calcination.

#### Implementation of Fe and Ag cations

Mono- and bimetallic systems of Ag, Fe, and Ag–Fe were prepared by the ion exchange method in H-form mordenite. For that purpose, slightly acidic solutions of Fe(NO<sub>3</sub>)<sub>3</sub> and AgNO<sub>3</sub> were used. The samples of H-form mordenite were added to the preheated metal salt solution and stirred for 1 hour. After 1 hour the samples were filtered, dried, and the procedure was repeated for another 1 hour. After drying at 90 °C, the samples were calcined at 550 °C in a stream of air.

## RESULTS AND DISCUSSION

Classical mordenite microcrystals were prepared by hydrothermal synthesis. Parent material (M-1) was obtained after the introduction of mesoporous voids by post-synthesis treatment with 0.2 M NaOH solution followed by ion exchange with NH<sub>4</sub>NO<sub>3</sub> and calcination. The second strategy, respectively one-pot synthesis using CTAB, resulted with slightly less crystalline material corresponds to the structure of mordenite (MOR) (Fig. 1).

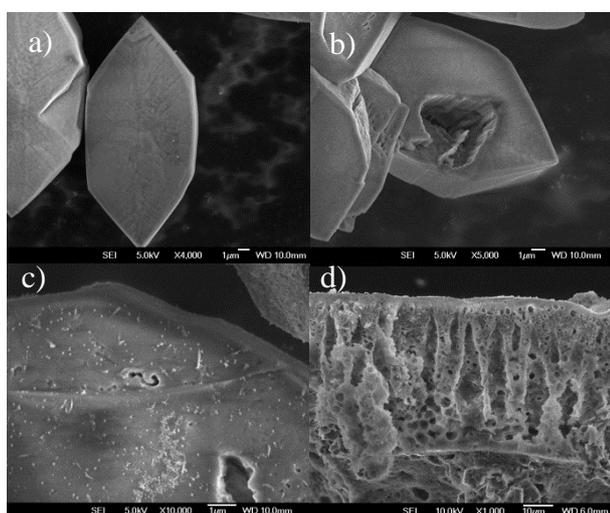


Figure 1. FE-SEM images of a) M-1, b) M-1 after treatment with 0,2 M NaOH (M-1-0.2NaOH) solution, c) surface of M-1+Fe and d) MOR.

Mono- and bimetallic systems of Ag, Fe, and Ag–Fe were prepared by the ion exchange method in H-form mordenite samples. PXRD patterns of parent materials show that the structure corresponds to the structure of mordenite (Fig. 2). Wet-impregnation treatments did not have a significant influence on the crystallinity of the samples. The exchange for metals changed only the intensity of the peaks. The missing peak (020) in the diffractogram of the samples with Ag occurs due to the displacement of H<sup>+</sup> cations, originally located in small mordenite channels, that occur under the action of the wet impregnation procedure. The H<sup>+</sup>

cations leave their site, but Ag<sup>+</sup> cations do not replace them, preferring to settle in the main channel near the entrance to the side pocket.

The exact concentration of metals in all samples was confirmed with AAS analysis. Interesting is the fact that after all post-synthetic treatments the Si/Al ratio remained preserved.

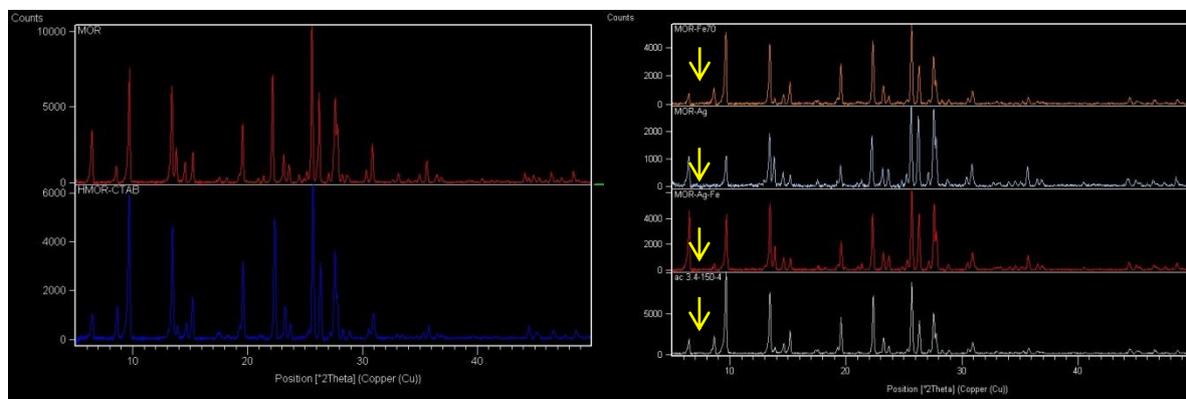


Figure 2. PXRD of parent materials M-1 (blue) and MOR (red) (left); PXRD patterns of wet impregnated MOR with Ag and Fe cations (right).

UV-Vis spectroscopy was applied to identify the silver and iron species. UV-Vis spectroscopy identify the silver and iron cationic species (Fig. 3). The peak with a maximum around 210 nm, and the shoulder around 220 nm correspond to the Ag<sup>+</sup> electronic transitions of isolated silver ions located on the ion exchanged sites of the mordenite framework. The other observed bands are attributed to the small silver cationic clusters. In the case of samples with iron, the spectra show a band with a maximum centered at 270 nm, which is attributed to oxygen-to-iron charge transfer of isolated Fe<sup>3+</sup> ions in tetrahedral coordination. Additionally, two more contributions took place; 340 nm, which is related to octahedral Fe cations in oligomeric clusters of the Fe<sub>x</sub>O<sub>y</sub> type inside the mordenite channels, and 470 nm, corresponding to the Fe<sub>2</sub>O<sub>3</sub> particles located on the external surface of mordenite crystals [3]. Those particles on the external surface of M-1 are visible on FE-SEM images (see Fig. 1).

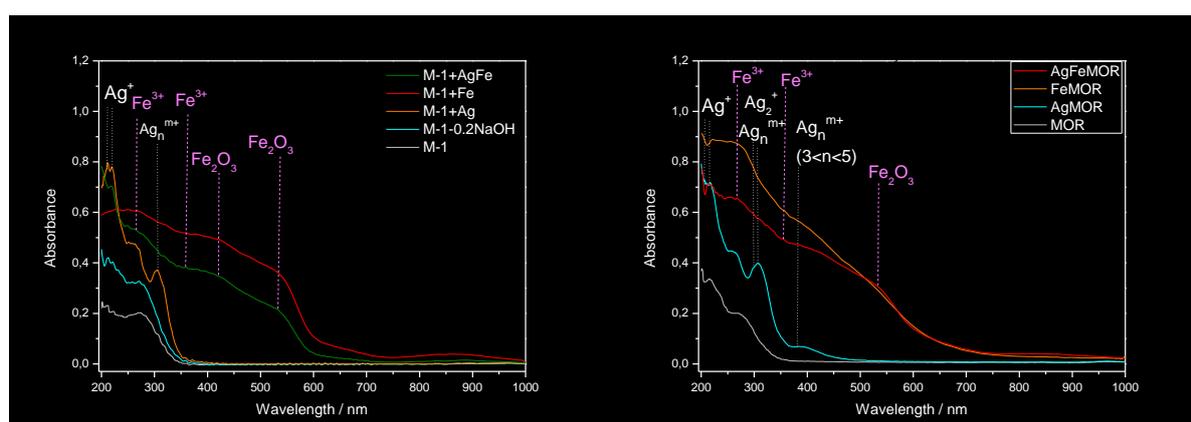


Figure 3. UV-Vis spectra of the M-1 samples (left) and MOR samples (right) in a wavelength range of 200 nm to 1000 nm

Due to the usually specific behaviour of the Ag and Fe cations under the light, photostability was confirmed by exposing the samples to radiation in the wavelength range of 200 to 1000 nm.

## **CONCLUSION**

Samples of mordenite were prepared by a feasible method, which is suitable for application in industrial production. Introduction of mesoporous voids (hierarchical structure of the crystals) was obtained by post-synthesis treatment with 0.2 M NaOH solution or using the mesoporous template (CTAB) during catalyst synthesis. That resulted in micro- and mesoporous mordenite crystals. The second part of the post-synthesis treatment was done using wet impregnation with slightly acidic salts solutions. The content of all cations is confirmed by EDS and AAS analysis. Identification of the silver and iron species was also made using UV-Vis spectroscopy. In the M-1 samples, different morphology of the iron oxide was deposited on the crystal surface, while in the MOR samples this was not the case.

## **REFERENCES**

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