

Mesopore – Beta zeolites modified with Fe, Cu and Co: Preparation, characterization and catalytic activity in N₂O decomposition and selective reduction of NO with ammonia

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Introduction

Mesoporous zeolites are hierarchical porous materials with two types of pore systems (below 2 nm and between 2-50 nm) and properties of crystalline and acidic zeolites. The presence of mesopores in the structure increases the accessibility of the internal surface of zeolite particles, facilitating the mass transport to and from the active centers. Elimination of the diffusion limitations is of big scientist interest, due possible efficiency increase of the industrial catalytic processes [1].

Mesoporous zeolites can be obtained by different routes such as: desilication, dealumination, decreasing of the zeolite crystals size, or template methods (e.g. carbon black, carbon nanotubes, polymers beads are used as templates). In the presented work the modern technique called *non-templating method*, which does not require any template to mesopores generation [2, 3]. Such approach is preferable from both environmental and economic point of view.

The mesoporous Beta zeolite as well as conventional Beta zeolite (as the reference sample) were exchanged with Fe, Cu and Co and physicochemical characterized (N₂ sorption, XRD, TGA, IR-DRIFT, UV-vis-DRS, ICP). In the next step the obtained samples were tested as catalysts in two processes: N₂O decomposition and selective reduction of NO with ammonia.

Materials and Methods

The synthesis of mesoporous Beta zeolite started from the preparation of gel with the following molar composition SiO₂ : 0.024 Al₂O₃ : 0.612 TEAOH : 0.200 HCl : 21 H₂O. The resulting slurry, after 24 h of aging at 423 K (containing nanoseeds of Beta zeolite), was acidified in a proportion of 5 mL of concentrated HCl per 18 mL of the nanoseeds slurry. Subsequently, the acidified solution was hydrothermally treated at 423 K for 72 h, yielding a micro-mesoporous material denoted as *Beta/meso*. The slurry aged without acidification was used for the synthesis of second series of the samples (conventional microporous Beta zeolite) denoted as Beta. The H-forms of the obtained samples were modified with Fe, Cu and Co by ion exchange method.

Results and Discussion

The obtained materials were characterized by low temperature N₂ sorption (using 3Flex v1.00, Micromeritics). The textural parameters of H⁺ forms of the Beta and Beta/meso samples are given in **Table 1**. The acidified sample possess higher BET and external surface area, as well as volume of meso and macropores in comparison to the H-Beta sample. An

increase in these values took place at the expense of microporosity (micropore volume and area decreased in comparison to the Beta sample).

Table 1. Textural properties of the samples determined from N₂-sorption measurements

Sample code	S _{BET} /m ² ·g ⁻¹	External surface area /m ² ·g ⁻¹	Micropore area /m ² ·g ⁻¹	Micropore volume /cm ³ ·g ⁻¹	Meso+macropore volume /cm ³ ·g ⁻¹
H-Beta	710 ± 1	89	622	0.242	0.191
H-Beta/meso	745 ± 2	368	377	0.159	1.278

The results of N₂O decomposition are presented in **Figure 1**. The samples activity depends on the introduced transition metal and the following order of their activation effect: Co>Cu>Fe was observed. The N₂O conversion over the most active Co-modified sample started at about 598 K and reached 100% at about 773 K.

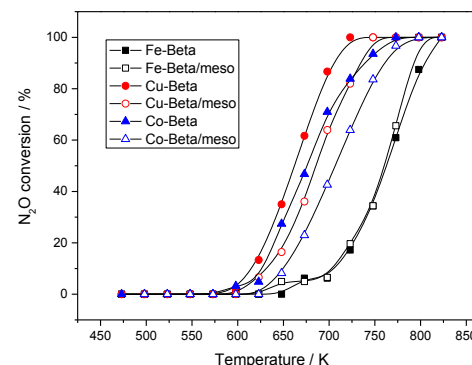


Figure 1. Temperature dependence of N₂O conversion. Conditions: 5000 ppm N₂O; He as balancing gas; total flow rate of 50 ml/min; weight of catalyst - 0.1 g

Significance

The physico-chemical characterization of the obtained samples showed that non-templating method resulted in successful synthesis of the micro-mesoporous materials with properties of Beta zeolite. The Beta and Beta/meso samples modified with Fe, Cu and Co were found to be active catalysts in N₂O decomposition and selective reduction of NO with ammonia.

References

- Čejka, J. *Catalysis Reviews* **2007**, 49, 457
- Rutkowska, M.; Chmielarz, L.; Macina, D.; Piwowarska, Z.; Dudek, B.; Adamski, A.; Witkowski, S.; Sojka, Z.; Obalová, L.; Van Oers, C.; Cool, P. *Applied Catalysis B: Environmental* **2014**, 146, 112

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