Hierarchical porous ZSM-5 zeolites prepared using non-templating method as catalysts for DeNOx processes

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Introduction

ZSM-5 is one of most common and widely used zeolites. It was recognized as active catalyst, especially in petroleum industry (catalytic cracking of hydrocarbons, gasoline conversion, aromatization and cyclization of hydrocarbons), mostly due to the presence of strong acidic sites in its structure. Despite this great advantage the applicability of ZSM-5 is limited due to the small pore size (< 2 nm) and therefore the accessibility of the channels is limited. This phenomenon is obvious for reactants and products that are too large to fit into the micropores, however also for reactants smaller than the micropore diameter, the diffusion limitations can occur.

The improvement of the ZSM-5 zeolite properties by generation of mesopores in its structure is important due to the possible optimization of a large number of the catalytic processes. That is why recently a lot of research is put into development of the new synthesis routes of combined materials with micro- and mesoporosity, so-called hierarchical materials with properties of ZSM-5 zeolite.

In the undertaken research mesoporous ZSM-5 zeolite was prepared using so called non-templating method [2]. The obtained materials were modified with copper by ion-exchange method and physicochemical characterized (N_2 sorption, XRD, TGA, IR-DRIFT, UV-vis-DRS, ICP). The impact of mesopores in the ZSM-5 structure on the catalytic reactions was examined in N_2O decomposition and selective reduction of NO with ammonia.

Materials and Methods

The synthesis of mesoporous ZSM-5 zeolite started with preparation of gel according to the recipe described in [3] for high alumina ZSM-5. The resulting slurry after 24 h of aging at 423 K (containing nanoseeds of ZSM-5 zeolite) was acidified in a different proportions of concentrated HCl per 10 mL of the nanoseeds slurry. Subsequently, the acidified solutions were hydrothermally treated at 423 K for 7 days, yielding a micro-mesoporous materials denoted as *ZSM-5/meso/xml*, where x is the amount of used HCl. The slurry aged without acidification was used for the synthesis of conventional microporous ZSM-5 zeolite, denoted as *ZSM-5*.

The Na-forms of the obtained samples were modified with Cu by ion exchange method.

Results and Discussion

The obtained materials were characterized by low temperature N_2 sorption (using 3Flex v1.00, Micromeritics). The textural parameters of Na^+ forms of ZSM-5, ZSM-5/meso/1ml and ZSM-5/meso/2ml are given in **Table 1**. The acidified samples possess higher external surface areas and volumes of meso and macropores in comparison to the ZSM-5 sample. An increase in these values took place at the expense of their microporosity (micropore volume and surface area decreased in comparison to the ZSM-5 sample).

Table 1. Textural properties of the samples determined from N_2-sorption measurements

Sample code	S_{BET} /$m^2 \cdot g^{-1}$	Micropore area /$m^2 \cdot g^{-1}$	External surface area /$m^2 \cdot g^{-1}$	Micropore volume /$cm^3 \cdot g^{-1}$	Meso+macropore volume /$cm^3 \cdot g^{-1}$
ZSM-5	411	366	45	0.139	0.049
ZSM-5/meso/1ml	344	267	77	0.104	0.082
ZSM-5/meso/2ml	314	245	69	0.096	0.071

The results of XRD analysis (performed using Bruker D2 Phaser) are presented in **Figure 1**. Both ZSM-5/meso/1ml and ZSM-5/meso/2ml exhibit reflexes characteristic of ZSM-5.

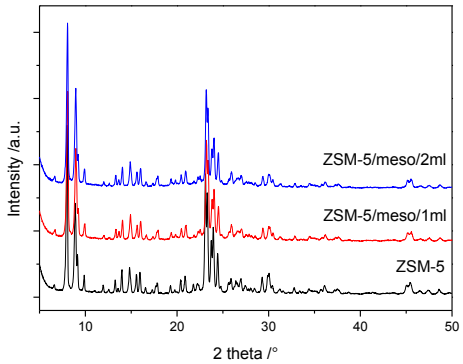

Figure 1. XRD diffractograms of ZSM-5, ZSM-5/meso/1ml and ZSM-5/meso/2ml

Significance

The physico-chemical characterization of the obtained samples showed that non-templating method resulted in synthesis of the micro-mesoporous material with properties of ZSM-5 zeolite. The samples modified with Cu were found to be active catalysts in N_2O decomposition and selective reduction of NO with ammonia.

References

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This work was supported by the National Science Center under grant no. DEC-2011/03/N/ST5/04820 and by the Foundation for Polish Science MPD Programme co-financed by the EU European Regional Development Fund.