

SBA-15, MCF and HMS mesoporous silicas modified with iron oxide aggregates as catalysts for selective reduction of NO with ammonia

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Introduction

Nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), generated by fuel combustion processes, belong to one of the major air pollutants. Commercial method used for elimination of NO_x from flue gases emitted by stationary sources (e.g. electric power stations) is based on selective catalytic reduction of nitrogen oxides by ammonia (DeNOx). This technology effectively operates in the temperature range of 250 - 400°C in the presence of the monolithic catalyst based on the V_2O_5 - TiO_2 oxide system. Recently, modified version of the DeNOx process, called Blue-tech, was implemented for elimination of NO_x from gases emitted by diesel engines of heavy trucks. The studies focused on the development of new catalysts for the DeNOx process are still carried out due high volatility of V_2O_5 and relatively narrow temperature range of effective operation of the commercial catalysts.

Mesoporous silica sieves, due to their high surface area and ordered porous structure, seem to excellent materials for catalytic supports. Pure silica mesoporous sieves do not exhibit ion-exchange properties, thus direct application of ion-exchange method for deposition of catalytic active components is in this case limited. However, it is possible to anchor anionic organic molecules on the surface of mesoporous silica, which will be able to generate ion-exchange properties of the modified support. Such strategy for iron oxide species deposition on the mesoporous silica sieves were applied in the presented studies. The obtained materials were tested in the role of the DeNOx catalysts.

Materials and Methods

SBA-15, MCF and HMS mesoporous silica supports were prepared by surfactant directed method. Synthesis methods were presented in [1], [2] and [3]. In the next step thiol (-SH) groups were anchored by reaction of (3-Mercaptopropyl)trimethoxysilane (MPTMS) with surface silanol groups of silica supports. Then, the samples modified with surface -SH groups were treated with a solution of H_2O_2 to oxidase thiol groups to $-\text{SO}_3\text{H}$. Detailed description of this procedure was presented in [4]. In parallel, $[\text{Fe}_3\text{O}(\text{OCOCH}_3)_6 \cdot \text{CH}_3\text{COOH} \cdot 2\text{H}_2\text{O}]\text{NO}_3$ or Fe-III iron cationic complexes were prepared by method reported by Maes et al. [5]. Such complexes was deposited on the modified silica materials by ion exchange method. Finally, the samples were separated from solution by filtration, washed with ethanol, dried and calcined. Textural parameters of the silica samples were determined by low-temperature N_2 adsorption method (3Flex, Micromeritics). Efficiency of surface groups anchoring of the support surface was determined by FT-IR spectroscopy (Nicolet 6700 Thermo), TG-QMS (Mettler Toledo 851°) and chemical analysis (CHNS Vario MICRO Cube microanalyzer). Structure of the samples was examined using XRD (X'Pert APD, Philips) and UV-vis-DRS (Evolution 600, Thermo) methods.

Catalytic tests were performed in a plug flow microreactor system combined with quadrupole mass spectrometer (VG Quartz).

Results and Discussion

Applied method of catalyst preparation resulted in deposition of iron oxide aggregates on the surface of mesoporous silicas. Such modification of mesoporous silica supports resulted in their catalytic activation in the process of selective reduction of NO with ammonia. Examples of the catalytic results, obtained for MCF and SBA-15 modified with iron oxide aggregates, are shown in figure 1. Maximum of NO conversion, at the level of 84-87%, was obtained in the temperature range of 325-350°C. A decrease in NO conversion observed at higher temperatures is caused by side process of ammonia oxidation by oxygen present in the reaction mixture. Moreover, it was shown that catalytic performance of the studied samples

depends on loading of the deposited iron oxide species as well as the porous structure of the silica supports.

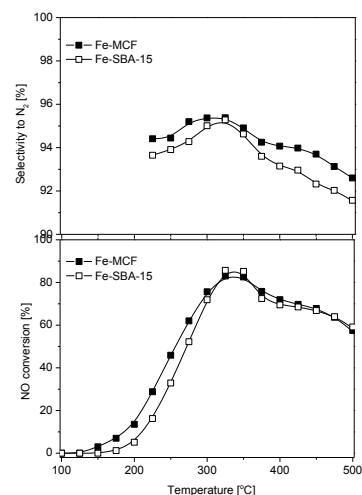


Figure 1. Results of DeNOx tests for mesoporous silicas modified with iron oxide aggregates. Composition of gas mixture: $[\text{NO}] = [\text{NH}_3] = 0.25$ vol. %, $[\text{O}_2] = 2.5$ vol. % and $[\text{He}] = 97$ vol. %.

Significance

New method of iron oxide aggregates deposition on the surface of mesoporous silica supports was reported. Iron modified mesoporous silicas were found to be active and selective catalysts of the DeNOx process.

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