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ABSTRACTS

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Bimetallic Pt-Ag/MCM-41 Catalysts for 4-Nitrophenol Reduction to 4-Aminophenol

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Supported Pt catalysts are widely used in various types of reduction reactions, including selective reduction of aromatic nitrocompounds into corresponding amines. The introduction of the second component (e.g., less expensive Ag) to Pt that can improve the catalytic properties of the supported metal catalysts due to the appearance of the synergistic effects between the metals is widely discussed in the literature [1, 2]. The using of mesoporous structured materials, such as MCM-41, as a support may be one of the approaches to form small-sized bimetallic Pt-Ag particles. Their structure comprises ordered hexagonal packing of open cylindrical pores with a diameter of 3-4 nm that can act as "nanoreactors" for the formation of bimetallic Pt-Ag particles.

The aim of this work was to synthesize the MCM-41-supported bimetallic Pt-Ag catalysts with different metal ratios and to establish the effect of the interaction of the supported components on the physical-chemical characteristics, catalyst reactivity in TPR-H₂, and catalytic properties in the 4-nitrophenol reduction to 4-aminophenol.

The MCM-41 support was synthesized by the hydrothermal method from industrial sodium silicate (SiO₂/Na₂O≈3) with the CTAB addition as a template [3]. The prepared MCM-41 was characterized by high specific surface area (1134 m²/g) and a narrow pore size distribution (3.6 nm). Bimetallic catalysts were prepared by sequential incipient impregnation with aqueous solutions of H₂PtCl₆ and AgNO₃ of appropriate concentrations. During the synthesis, the MCM-41 support was impregnated with H₂PtCl₆ solution, dried and calcined at 500 °C to remove chlorine in order to avoid the formation of insoluble AgCl.

The synthesized Pt catalysts (Pt/MCM-41 sample and reference samples 0.5Pt/MCM-41 and 0.2Pt/MCM-41) were reduced in a 10% H₂/Ar mixture at 500 °C. The obtained 0.5Pt/MCM-41 and 0.2Pt/MCM-41 catalysts were impregnated with AgNO₃ solution dried and calcined at 600 °C (0.5 Pt-0.5Ag/MCM-41 and 0.2Pt-0.8Ag/MCM-41). Thus, a series of mono- and bimetallic catalysts (Ag/MCM-41, Pt/MCM-41, and Pt-Ag/MCM-41) with a mass content of metals of 4.71 wt% was obtained.

Table 1. Metal content and textural characteristics of the prepared support and catalysts on the basis thereof.

Sample	w (Pt), wt.%	w (Ag), wt.%	S _{sp} (BET), m ² /g	V _{pore} , cm ³ /g
MCM-41	-	-	1134	1.14
Ag/MCM-41	-	4.71	906	0.85
Pt/MCM-41	4.71	-	855	0.61
0.2Pt-0.8Ag/MCM-41	1.48	3.23	824	0.60
0.5Pt-0.5Ag/MCM-41	3.06	1.65	820	0.60

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The textural characteristics of the Pt-Ag/MCM-41 catalysts were investigated by low-temperature N₂ adsorption. It was shown that with an increase in the Pt content, the specific surface area (S_{sp}) of the samples decreased to up to 855 m²/g for Pt/MCM-41 sample. For Ag/MCM-41 catalyst, S_{sp} was 906 m²/g. The Pt-Ag/MCM-41 catalysts were characterized by close S_{sp} values of 820-824 m²/g and the average pore diameter d_{pore} of 3.4 nm calculated using the BJH-desorption method.

The reactivity of the samples was investigated by the TPR-H₂ method. The preoxidized samples of mono- and bimetallic catalysts were reduced in 10% H₂/Ar mixture to up to 600 °C at a rate of 10 rpm. The reduction of the Pt/MCM-41 catalysts occurred in the range of 25-200 °C with a maximal H₂ consumption at 88-90 °C (reduction of dispersed Pt oxides) and in the range of 200-500 °C with maxima at 320 and 410-420 °C (reduction of oxidized states of platinum bonded to the substrate surface). The reduction of Ag/MCM-41 catalyst was observed in the temperature range of 0-150 °C. The reduction of bimetallic Pt-Ag/MCM-41 catalysts occurred up to 200 °C with a maximum at 130 °C. No hydrogen absorption was observed in the high-temperature region. A change in the profile and a shift in the H₂ consumption maximum indicate the presence of contact between the metals and the formation of bimetallic particles.

The bimetallic Pt-Ag/MCM-41 catalysts as well as monometallic Pt/MCM-41 and Ag/MCM-41 samples were investigated in the 4-nitrophenol reduction to 4-aminophenol at room temperature and atmospheric pressure using NaBH₄ as a reducing agent. The increased activity for bimetallic Ag-Pt catalysts was observed in comparison with the monometallic Ag/MCM-41 and Pt/MCM-41 catalysts.

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