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ABSTRACTS

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Design of Pt-Ga Catalysts Supported on Hierarchical Silica Materials for Propane Dehydrogenation

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The CrO_x/Al_2O_3 (Catofin process) and $Pt\text{-}SnO_x/Al_2O_3$ (Oleflex process) catalysts are the major industrial catalysts used for direct propane dehydrogenation (PDH). The main disadvantage of the alumina support consists in high surface acidity that leads to a decrease in the selectivity and catalyst deactivation due to the coke formation. The growth of propylene market and abovementioned factors prove the need to designing new PDH catalysts. The bimetallic Pt-Ga combination is a promising catalyst system since both components are active in the PDH reaction [1]. Moreover, the gallium additions enhance both the dispersion of platinum particles and the stability of the catalyst system.

The silica support MCM-41 is one of the most studied mesoporous materials and is promising for the preparation of catalysts based on transition metal oxides and/or noble metals [2,3]. However, the PDH is a high temperature diffusion controlled process that requires specific catalyst structure that ensures efficient transport of reagents to the active sites of the catalyst and removal of products from the reaction zone. The materials with a hierarchical porous structure are promising to address this challenge by combining a wide pore transport system (mainly, above 50 nm) and mesopores providing high values of specific surface area of the catalyst [4].

The present study is devoted to development of silica support with a hierarchical structure based on the diatomite and MCM-41 as well as to designing of the Pt-Ga catalysts on the basis thereof for the propane dehydrogenation to propylene.

The MCM-41 was synthesized from sodium silicate in an alkaline medium (pH≈12) using cetyltrimethylammonium bromide (CTAB) as a template. The diatomite (LLC “Kvant”, Russia) was used to synthesize the composite MCM-41/diatomite supports [5]. The $Pt\text{-}Ga/SiO_2$ catalysts were prepared by impregnation method. 9 wt.% gallium and then 1 wt.% platinum were introduced by the incipient wetness impregnation of SiO_2 from the corresponding precursors, i.e., gallium nitrate and H_2PtCl_6 solution. After the impregnation, the catalyst was calcined at 500 °C under air. The structure and chemical properties of the synthesized materials were studied by low-temperature nitrogen adsorption, SEM, XRD, and TPR-H_2 methods.

According to the low-temperature nitrogen adsorption results (Fig. 1a), the sharp increase in the adsorption value in the relative pressure range of 0.3-0.38 is observed for MCM-41/diatomite composite indicating the presence of the ordered MCM-41 structure in the material. A hysteresis loop in the pressure range of 0.95-1.0 also indicates the preservation of the diatomite macroporous structure in the material [4]. Thus, the MCM-41/diatomite composite is characterized by the hierarchical porous structure. Fig. 1b represents the SEM image for diatomite. A layer of amorphous material that may be attributed to the MCM-41 is observed in the diatomite pores for the MCM-41/diatomite composite (Fig. 1c). The XRD results for Pt-Ga catalysts show that the samples are characterized by the amorphous silica and β-Ga_2O_3. The Pt-containing samples are characterized by the presence of metallic Pt particles.

The catalytic activity was investigated in the PDH reaction at 550 °C. According to the results obtained, the Pt-Ga catalysts show higher activity compared to Pt and Ga_2O_3 catalyst (Fig. 1d) that may be attributed to the synergy between Pt and Ga_2O_3 species in the dehydrogenation reaction. The Pt-Ga/MCM-Diatomite catalyst shows the highest activity due to both Pt-Ga synergy and increased surface area of the catalyst.

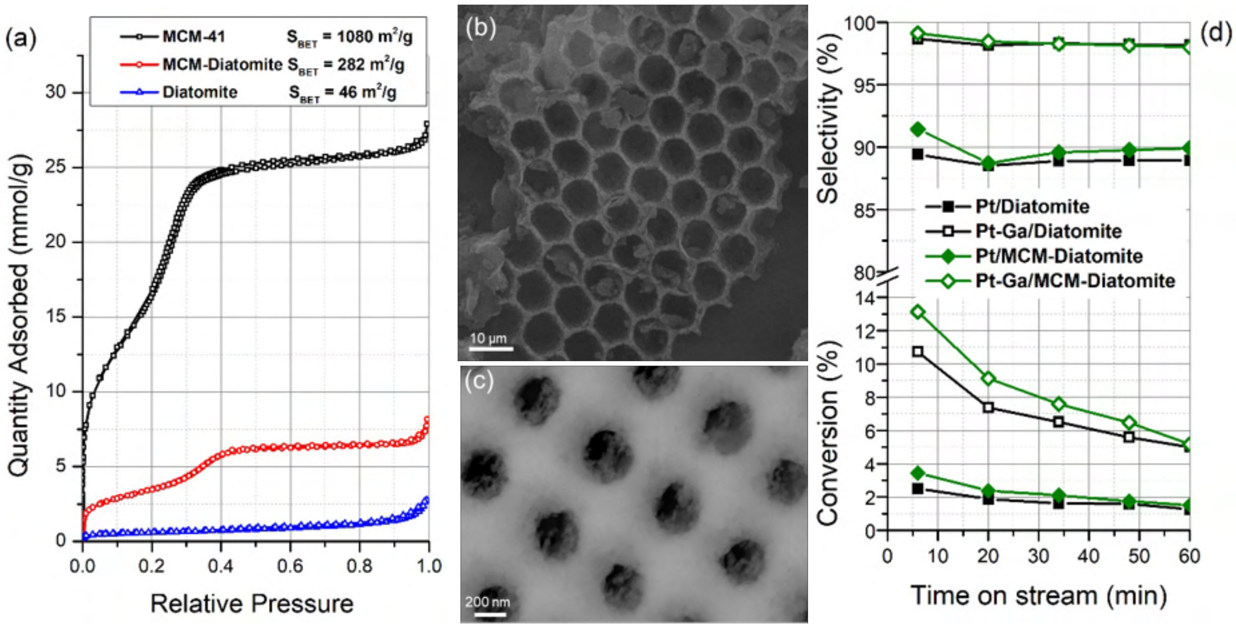

Fig. 1. Nitrogen adsorption-desorption isotherms for synthesized supports (a); SEM images for diatomite (b) and MCM-Diatomite composite (c); catalytic activity in PDH at 550 °C (d).

In summary, it was shown that the synthesized composite support MCM-41/diatomite is characterized by a hierarchical porous structure. The Pt-Ga catalysts supported on MCM-41/diatomite composite is characterized by high activity in the propane dehydrogenation reaction. The effect of Ga addition comprising the increase in the efficiency of Pt catalysts has been shown.

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