Design of SiO₂ materials with hierarchical structure as promising supports for catalysts

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Abstract. The silicate support with a hierarchical structure based on diatomite and MCM-41 is synthesized. The MCM-41 is formed directly on the surface of diatomite and from the diatomite itself without the use of additional silica precursors. The structure of the synthesized samples is characterized by the low-temperature nitrogen adsorption and scanning electron microscopy (SEM). It was shown that hydrothermal treatment of diatomite with NaOH and cetyltrimethylammonium bromide leads to the partial dissolving of diatomite with self-assembly of MCM-41 fragments inside diatomite pores. The developed approach has demonstrated the opportunity to obtain the supports based on diatomite and MCM-41 that are characterized by a hierarchical structure (macropores of diatomite with size of 10-500 nm and mesopores of MCM-41 with size of 3-4 nm) and a high specific surface area that is promising for their application as supports for catalysts.

1. Introduction

The catalytic non-oxidative propane dehydrogenation (PDH) is a valuable technique for propylene synthesis, and its value is growing globally. Propylene is ranked the second after ethylene in chemical industry by production value. Many significant organic compounds, namely polypropylene, polyacrylonitrile, acrolein, propylene oxide, acryl acid, glycerin, etc., are the products of reactions with propylene [1,2]. Alumina-chromia (CrOₓ/Alₓ2O₃) and platinum-tin (Pt-SnOₓ/Alₓ2O₃) catalysts provide the major commercial catalysts for dehydrogenation of C₃-C₅ alkanes [3,4]. Hexavalent chromium is present in (CrOₓ/Alₓ2O₃) catalyst comprising the main disadvantage of the former due to Cr(VI) toxicity imposing risks during the catalyst exploitation [5]. The bimetallic Pt-Ga combination is promising since both components exhibited activity in the PDH [6]. The main disadvantage of the alumina support is a relatively high acidity that leads to selectivity decreasing and deactivation due to coke formation [7]. The above-mentioned facts demonstrate that the designing of support and PDH catalysts on the basis thereof is a topical direction. The interest to silica supports is attributed to both high surface area and low reaction ability that is important for high selectivity and stability of the catalyst.

Silica supports, namely MCM-41 and SBA-15, possess both high specific surface area and ordered mesoporous (3-8 nm) structure [8,9]. However, the dehydrogenation processes are realized at temperatures of 550-600 °C and characterized by the diffusion limitations. This requires a specific catalyst structure that ensures efficient transport of reagents to the active sites of the catalyst and removal of products from the reaction zone [10]. The materials with a hierarchical porous structure are
promising to solve this challenge by combining a wide pore transport system (mainly, more than 50 nm) and mesopores providing high values of specific surface area of the catalyst [11]. The aim of this study is to develop a silica support with a hierarchical structure based on diatomite and MCM-41. A specialty of the approach is that MCM-41 is synthesized on the surface of diatomite and from diatomite itself without the use of additional silicon oxide precursors [12]. The resulting composite support MCM-41/diatomite is characterized by a bi-porous structure: a system of transported pores of natural diatomite as well as a system of ordered reflected pores of 3–4 nm of the material MCM-41 formed on the diatomite surface.

2. Material and research methods

Synthesis of MCM-41 was carried out from the sodium silicate in an alkaline medium (pH ≈ 12) using cetyltrimethylammonium bromide (CTAB) as a template [13]. The diatomite ("Kvant", Russia), treated with a hydrochloric acid to remove Fe and Al was used to prepare composite supports MCM-41/diatomite. The calculated amount of CTAB was dissolved in a NaOH solution, a weighed portion of diatomite was added to the resulting solution at a constant stirring, and then underwent to hydrothermal treatment. After that, the obtained precipitate was filtered, washed and calcined at 600 °C for 10 hours. The NaOH/diatomite ratio varied from 0.12 to 0.45. The porous structure of the supports was studied by scanning electron microscopy (SEM) using QUANTA 200 3D microscope and low-temperature nitrogen adsorption (−196 °C). Adsorption-desorption isotherms were measured by “3Flex” analyzer (Micromeritics, US) from a relative pressure of p/p° ≈ 10⁻⁶ by fine adjustment of the N₂ portions and precision detecting of the pressure. The samples were outgassed at 200 °C for 2h prior to the analysis. The specific surface area (S_{BET}) was calculated by straightening of the adsorption isotherm in Brunauer–Emmett–Teller (BET) coordinates in the range from 0.05 to 0.20. The pore size distributions were calculated by the BJH-Adsorption method.

3. Results

According to the results of the low-temperature N₂ adsorption, the MCM-41 sample synthesized from the sodium silicate is characterized by the specific surface area of 1080 m²/g and a pore volume of 0.92 cm³/g (Table 1). The isotherm of nitrogen adsorption–desorption for the MCM-41 sample (Figure 1(a, b)) is characterized by a sharp bend in the range of relative pressures of 0.27–0.35 indicating the formation of an ordered structure of mesopores with a diameter of 3–4 nm (Figure 1(c)). The specific shape of the isotherms and a narrow pore size distribution confirms the formation of the material with the MCM-41 structure [14].

The nitrogen adsorption–desorption isotherm for the original diatomite sample is characterized by a hysteresis loop within the relative pressures of 0.9–1.0, which indicates the presence of wide mesopores and macropores in the sample. Figure 1(d) demonstrates the presence of wide transport pores with a diameter of 10–100 nm. The specific surface area of diatomite is 46 m²/g and a pore volume (measured by nitrogen adsorption) is 0.09 cm³/g (Table 1).

Table 1. Textural characteristics of the studied samples according to the nitrogen adsorption data.

| Sample              | S_{BET}, m²/g | V_{pore}, cm³/g | D_{pore}, nm | W_{1/2h}, nm | Yield, % |
|---------------------|---------------|-----------------|--------------|--------------|----------|
| Diatomite           | 46            | 0.09            | -            | -            | -        |
| NaOH/diatomite = 0.12 | 282           | 0.28            | 4.02         | 0.73         | 85       |
| NaOH/diatomite = 0.18 | 357           | 0.33            | 3.73         | 0.51         | 74       |
| NaOH/diatomite = 0.27 | 457           | 0.41            | 3.65         | 0.45         | 59       |
| NaOH/diatomite = 0.36 | 482           | 0.45            | 3.78         | 0.44         | 49       |
| NaOH/diatomite = 0.45 | 632           | 0.54            | 3.65         | 0.42         | 35       |
| MCM-41              | 1080          | 0.92            | 3.39         | 0.31         | -        |
The MCM-41/diatomite composite samples are characterized by a regular increase in the specific surface area from 282 m$^2$/g to up to 632 m$^2$/g with an increase in the NaOH/diatomite ratio (Table 1). On the isotherms of composite supports, a sharp increase in the adsorption value in the relative pressure range of 0.3-0.38 is observed, which indicates the presence of the MCM-41 structure in the material, and a hysteresis loop in the pressure range of 0.95-1.0 also indicates the preservation of the macroporous structure of diatomite in the material. It can be observed from Figure 1(c) that for the MCM 41/diatomite samples the narrow pores with a diameter of 3-4 nm are typical as for the MCM-41. Thus, the shape of the isotherms and the corresponding pore size distributions for the MCM-41/diatomite indicate the formation of materials with the hierarchical structure, namely, fragments of silica with MCM-41 structure with pores of 3-4 nm located inside the macropores of diatomite.

Figure 1. Nitrogen adsorption-desorption isotherms (a, b) and BJH pore size distributions (c, d) for the synthesized samples

Figure 2(a) represents the changes in the volumes of pores and yield of synthesis as a function of NaOH/diatomite ratio in the samples. The increasing of NaOH/diatomite ratio leads to the increasing of volume of pores from 0.09 to 0.54 cm$^3$/g and to the decreasing of yield. The decreasing of composite yield was calculated as a mass ratio of MCM-41/diatomite composite to the mass of initial diatomite, and its decreasing is attributed to the diatomite dissolution under basic conditions and the formation of the homogeneous solution of sodium silica. The MCM-41/diatomite composite samples are characterized by a regular increase in the specific surface area from 282 m$^2$/g to up to 632 m$^2$/g with an increase in the NaOH/diatomite ratio (Figure 3(b)), the pore diameter decreases from 4 to up to 3.65 nm.
Figure 2. Changes in the volume pores, yield (a) and specific surface area, diameter of pores (b) of materials as a function of NaOH/diatomite ratio in the samples

Figure 3 demonstrates the microstructures of the raw diatomite and MCM-41/diatomite composites. The initial diatomite powder (Figure 3(a)) mainly consists of the disc-shaped and cylindrical structures, and numerous pores are clearly visible indicating high porosity and a relatively large specific surface area of diatomite [15]. However, Figure 3(b) shows that there were some impurities on the surface of the crude diatomite that are attributed to the features of the diatomite treatments during its recovery and cleaning.

Figure 3. SEM images of: (a-b) raw diatomite and (c-d) MCM-41/diatomite composites
Figure 3(c-d) demonstrates the obtained MCM-41/diatomite composites. The morphology of the porous structure is basically retained after the modifying and the pores are clogged to varying degrees, therefore. The layer of amorphous material, probably MCM-41, is observed in pores of diatomite. Thus, the formation of hierarchical material is observed on the SEM images: the formation of highly porous amorphous silica inside macropores of diatomite. The structure of diatomite was not destroyed in hydrothermal conditions.

4. Conclusions
The studies of the SiO$_2$ materials with the hierarchical structure have been presented in this paper. The performed studies revealed that the obtained MCM-41/diatomite composite supports were characterized by the hierarchical porous structure. The effect of alkali amount on the yield for the obtained supports occurred. The yield decreased with the increasing alkali amount. Likewise, with an increase in the NaOH/diatomite ratio, a regular increase in the specific surface area from 282 m$^2$/g to up to 632 m$^2$/g was observed. Thus, the developed approach demonstrated the opportunity to obtain the supports based on diatomite and MCM-41 that are characterized by the hierarchical structure. These materials are promising as supports for the catalysts (including the processes of dehydrogenation of light paraffins) because of the open porous structure and high surface area.

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