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ПЕРСПЕКТИВЫ РАЗВИТИЯ ФУНДАМЕНТАЛЬНЫХ НАУК

Сборник научных трудов
XVII Международной конференции студентов, аспирантов
и молодых ученых

РОССИЯ, ТОМСК, 21 – 24 апреля 2020 г.

Том 2. Химия

PROSPECTS OF FUNDAMENTAL SCIENCES DEVELOPMENT

Abstracts
XVII International Conference of Students
and Young Scientists

RUSSIA, TOMSK, April 21 – 24, 2020

Volume 2. Chemistry

DESIGNING SiO_2 MATERIALS WITH HIERARCHICAL STRUCTURE AND Pt-Ga CATALYSTS ON THEIR BASIS FOR PROPANE DEHYDROGENATION

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РАЗРАБОТКА SiO_2 МАТЕРИАЛОВ С ИЕРАРХИЧЕСКОЙ СТРУКТУРОЙ И Pt-Ga КАТАЛИЗАТОРОВ НА ИХ ОСНОВЕ ДЛЯ ДЕГИДРИРОВАНИЯ ПРОПАНА

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Аннотация. *В данной работе проведен синтез силикатного носителя с иерархической пористой структурой на основе диатомита и MCM-41. Особенностью синтеза является то, что MCM-41 образуется непосредственно на поверхности диатомита и из самого диатомита, без использования дополнительных предшественников оксида кремния Исследование пористой структуры полученного носителя проводили методом низкотемпературной адсорбции азота (–196 °С), для изучения структуры поверхности материала был использован метод сканирующей электронной микроскопии (СЭМ). Показано, что разработанный подход позволяет получать носители на основе диатомита и MCM-41, характеризующиеся иерархической структурой и высокими значениями удельной поверхности.*

Introduction. The catalytic non-oxidative propane dehydrogenation (PDH) is a valuable technique to propylene synthesis, and its value is elevating all over the globe. Propylene is the second place after ethylene in chemical industry by production value. Many significant organic compounds, namely polypropylene, polyacrylonitrile, acrolein, propylene oxide, acryl acid, glycerin etc, are products of reactions with propylene [1]. Alumina-chromia (CrO_x/Al_2O_3) and platinum–tin ($Pt\text{-}SnO_x/Al_2O_3$) catalysts provide the major commercial catalysts for C_3-C_5 alkanes dehydrogenation. Hexavalent chromium is present in (CrO_x/Al_2O_3) catalyst and this is the main disadvantage of former due to toxicity of Cr (VI), which poses a risk while catalyst exploitation [2]. The abovementioned facts demonstrate that designing of catalysts for propane dehydrogenation is actual issue.

Design of dehydrogenation catalysts based on silica support is a relevant investigating area. Silica support, namely MCM-41 and SBA-15, has a high specific surface area and an ordered mesoporous (3-8 nm) structure [3]. However, dehydrogenation processes is realized at temperatures of 550-600 °C and characterized by the diffusion limitation. This requires a specific catalyst structure that ensures efficient transport of reagents to the active centers of the catalyst and removal of products from the reaction zone. The materials with a hierarchical porous structure are promising to solve this problem due to combining a wide pore transport system (mainly more than 50 nm) and mesopores, providing high values of the specific surface area of the catalyst.

The aim of this study is to develop a silicate support with a hierarchical structure based on diatomite and MCM-41, and to design of Pt-Ga catalysts based on this support for the dehydrogenation of propane to propylene. A specialty of the approach that is MCM-41 synthesized on the surface of diatomite and diatomite itself without the use of additional nitric oxide precursors [4]. The resulting composite support MCM-41/diatomite is characterized by a biporous 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 onto the surface of diatomite.

Research methods. The synthesis of MCM-41 was carried out from sodium silicate in an alkaline medium (pH ≈ 12) using CTAB (cetyltrimethylammonium bromide) as a template [5]. The diatomite treated with a hydrochloric acid (OOO "Kvant", Russia) was used preliminarily solution for the preparation of. 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 with 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 obtained composite supports were used for the preparation of Pt-Ga catalysts. The porous structure of the supports was studied by the low-temperature nitrogen adsorption (–196 °C) and scanning electron microscopy (SEM).

Results. According to the method of low-temperature nitrogen adsorption, the specific surface area of 1080 m^2/g and a pore volume of 0.92 cm^3/g are characteristics of the MCM-41 sample obtained from sodium silicate. The isotherm of nitrogen adsorption–desorption for sample MCM-41 (Fig. 1a) is characterized by a sharp bend in the range of relative pressures of 0.3–0.35, indicating the formation of an ordered structure of mesopores with a diameter of 3-4 nm (Fig. 1b). The nitrogen adsorption–desorption isotherm for the original diatomite sample is characterized by a hysteresis loop within relative pressures of 0.9–1.0, which indicates the presence of wide mesopores and macropores in the sample. The specific surface area of diatomite is of 46 m^2/g and a pore volume (measured by nitrogen adsorption) of 0.09 cm^3/g.

Table 1

Textural characteristics of the studied samples according to nitrogen adsorption data

Sample	S_{BET}, m^2/g	V_{pore}, cm^3/g	D_{pore}, nm	$W_{1/2h}$, nm
Diatomite	46	0,09	7,94	-
NaOH/diatomite = 0.12	282	0,28	4,02	0,73
NaOH/diatomite = 0.18	357	0,33	3,73	0,51
NaOH/diatomite = 0.27	457	0,41	3,65	0,45
NaOH/diatomite = 0.36	482	0,45	3,78	0,44
NaOH/diatomite = 0.45	632	0,54	3,65	0,42
MCM-41	1080	0,92	3,39	0,31

The MCM-41/diatomite composites samples are characterized by a regular increase in the specific surface area from 282 m^2/g 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 from the pressure range of 0.95-1.0 is also indicated to preserve the macroporous structure of diatomite in the material. It can be observed from Fig.1b that, for MCM 41/diatomite samples, narrow pores with a diameter of 3-4 nm are typical, as for MCM 41.

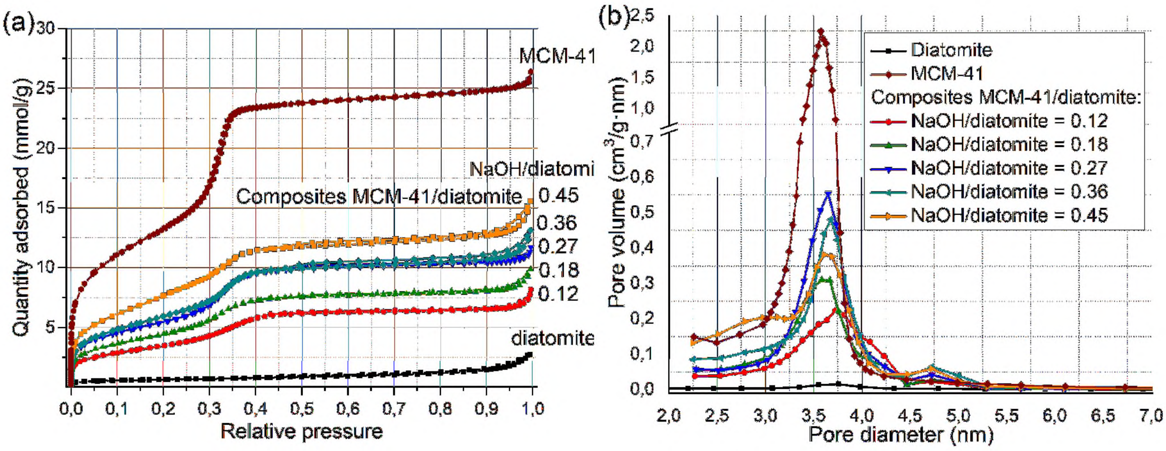

Fig. 1. Nitrogen adsorption-desorption isotherms (a) and BJH pore diameter distribution (b) of the obtained samples

Conclusion. Finally, the developed approach is demonstrated ability to obtain supports based on diatomite and MCM-41 that characterized by a hierarchical structure. The series of Pt-Ga catalysts was obtained on the basis of the supports, their structure, state, distribution of Pt and Ga, the catalytic properties of the propane dehydrogenation will be studied.

Acknowledgements: This work was supported by the Grant of Russian Fund for Basic Research (Grant № 19-43-700008 р_а).

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