DOI: 10.6060/ivkkt.20246708.3t

УДК: 544.473

ВЛИЯНИЕ ТЕМПЕРАТУРНОЙ ОБРАБОТКИ НА СТРУКТУРНО-ФАЗОВЫЙ СОСТАВ НАНЕСЕННЫХ Co-Mo/Al_2O_3 КАТАЛИТИЧЕСКИХ СИСТЕМ

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Методом пропитки в избытке пропиточного раствора и последующей температурной обработки в интервале температур 100-400 °С был проведен синтез нанесенных на активный оксид алюминия γ-модификации каталитических систем на основе переходных металлов (Co, Mo) и исследованы их физико-химические свойства. Отличительной особенностью этих систем было использование в качестве источника молибдена полиоксометалатных комплексов (молибденовые сини), полученных методом механоактивации коммерческого дисульфида молибдена. Носитель был получен высокотемпературной обработкой промышленного порошка псевдобемита AlOOH (ООО «Ишимбайский специализированный химический завод катализаторов»). Такой подход позволяет значительно упростить синтез каталитических систем. При этом используемые реактивы являются общедоступными и производятся на территории Российской Федерации в промышленных масштабах. Полученные системы предполагается использовать в процессах гидроочистки (гидродесульфирование и гидродеазотирование) дизельных фракций. Синтез включал стадию получения пропиточного раствора добавлением навески нитрата кобальта к спиртовому раствору молибденовой сини, и стадию непосредственно пропитки носителя в избытке пропиточного раствора. После пропитки системы подвергались прокалке при различных температурах с целью изучения генезиса активных компонентов и влияния температурной обработки на различные физико-химические свойства. Синтезированные системы были изучены различными физико-химическими методами (РФА, ИК-спектроскопия). Было выявлено, что для полного элиминирования нитрогруппы из состава системы необходима температурная обработка не ниже 400 °С, также показано, что молибденовая синь способна выступать в роли источника Mo.

Ключевые слова: оксид алюминия, полиоксометаллаты, молибденовая синь, гидроочистка, гидродесульфирование

THE INFLUENCE OF TEMPERATURE TREATMENT ON THE STRUCTURAL-PHASE COMPOSITION OF SUPPORTED Co-Mo/Al_2O_3 CATALYTIC SYSTEMS

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Using the method of impregnation in an excess of impregnating solution and subsequent temperature treatment in the temperature range of 100-400 °C, the synthesis of γ-modified catalytic systems based on transition metals (Co, Mo) supported on active aluminum oxide was carried out and their physicochemical properties were studied. A distinctive feature of these systems was the use of polyoxometalate complexes (molybdenum blues) obtained by mechanical activation of commercial molybdenum disulfide as a source of molybdenum. The carrier was obtained by high-temperature treatment of industrial pseudoboehmite powder AlOOH (Ishimbay Specialized Chemical Plant of Catalysts LLC). This approach makes it possible to significantly simplify the synthesis of catalytic systems. At the same time, the reagents and technologies used are publicly available and are produced on the territory of the Russian Federation on an industrial scale. The resulting systems are expected to be used in hydrotreating processes (hydrodesulfurization and hydrodenitrogenation) of diesel fractions. The synthesis included the stage of obtaining an impregnating solution by adding a weighed portion of cobalt nitrate to an alcohol solution of molybdenum blue, and the stage of directly impregnating the carrier in an excess of the impregnating solution. After impregnation, the systems were calcined at various temperatures in order to study the genesis of the active components and the effect of temperature treatment on various physicochemical properties. The synthesized systems were studied using various physicochemical methods (XRD, IR spectroscopy). It was found that to completely eliminate the nitro group from the system, a temperature treatment of at least 400 °C is necessary. It was also shown that molybdenum blue can act as a source of Mo.

Keywords: aluminum oxide, polyoxometalates, molybdenum blue, hydrotreating, hydrodesulfurization

Для цитирования:
Жиров Н.А., Акимов Ал.С., Сударев Е.А., Акимов А.С. Влияние температурной обработки на структурно-фазовый состав нанесенных Co-Mo/Al_2O_3 каталитических систем. *Изв. вузов. Химия и хим. технология*. 2024. Т. 67. Вып. 8. С. 44–49. DOI: 10.6060/ivkkt.20246708.3t.

For citation:
Zhirov N.A., Akimov Al.S., Sudarev E.A., Akimov A.S. The influence of temperature treatment on the structural-phase composition of supported Co-Mo/Al_2O_3 catalytic systems. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2024. V. 67. N 8. P. 44–49. DOI: 10.6060/ivkkt.20246708.3t.

INTRODUCTION

Currently, oil refining to obtain high-quality motor fuels and other petroleum products is impossible without the use of catalytic processes [1-3]. This is dictated by both high operational requirements and significantly tightened environmental standards. Also, the widespread use of processing processes using catalysts is due to a decrease in quality and significant weighting of the extracted raw materials [4, 5]. Most of the catalysts are imported, and therefore the development of domestic highly efficient catalysts for various hydroprocesses (including hydrotreating) is an extremely urgent task. The most commonly used are supported catalysts, in which transition metals (Co, Ni, Fe) act as active components, with a promoting agent (Mo, W) [6]. Such systems have proven themselves to be quite active, while maintaining this activity over a long service life, which quite fully meets industrial requirements. Aluminum oxide of the γ-modification is widely used as a support [7], since it also has a developed specific surface area and porosity, as well as acceptable physical and mechanical properties [8]. It is produced on an industrial scale [9] and is an easily accessible reagent. Thus, the goal of the work was the synthesis of supported bimetallic catalytic systems, in which the active components are Co promoted by Mo, and the carrier is γ-Al_2O_3.

EXPERIMENTAL PROCEDURE

Aluminum oxide (γ-Al_2O_3) was chosen as the support for our catalytic systems due to its optimal balance between its availability and physicochemical properties. Industrial pseudoboehmite powder - AlOOH, produced by Ishimbay Specialized Chemical Plant of Catalysts LLC, was used as the starting material for obtaining the carrier. To obtain γ-Al_2O_3, pseudoboehmite underwent heat treatment in a muffle furnace at T = 550 °C for 4 h [10]. To prepare the impregnating solution, $Co(NO_3)_2{\cdot}6H_2O$ (c.p) was used as a Co-containing component in an amount of 3% wt. (in terms of metal), which was dissolved in an alcohol solution of molybdenum blue [11]. Molybdenum blue was synthesized according to an original method using a pre-mechanically activated MoS_2 precursor [12]. The synthesis of Co-Mo-containing systems was carried out by impregnating the carrier according to moisture capacity [13], after which it was kept for 24 h, dried at room temperature, and then heat treated in the range from 100 to 400 °C. A sample obtained at room temperature without heat treatment acts as a point of comparison for studying the genesis of precursors of active components.

Below is the matrix of synthesized samples (Table).

Table

Matrix of experiments

***Таблица.* Матрица экспериментов**

Name	(K-1)	(K-2)	(K-3)	(K-4)	(K-5)
Treatment temperature, °C	25	100	200	300	400

Subsequently, the catalytic systems processed at different temperatures were studied using IR spectroscopy and X-ray phase analysis (XRD). Infrared spectra were recorded on a Nicolet 5700 IR-Fourier spectrometer (USA) in the frequency range 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. Solid samples for surveying were prepared according to standard methods by pressing tablets of 3 mg of the powder under study with 300 mg of KBr. X-ray phase analysis was carried out on a D8 Discover powder diffractometer (USA) in the 2Θ angle range from 15 to 86°.

RESULTS AND DISCUSSION

The phase composition depending on the processing temperature of the synthesized systems is presented in Fig. 1 and 2. The initial system (Fig. 1) is represented by the carrier phase (γ-Al_2O_3), as well as a Co-containing component ($Co(NO_3)_2{\cdot}6H_2O$) [14-16]. Unmarked reflections correspond to impurity phases of various oxide Fe-containing structures that are part of the initial reagent (namely, cobalt nitrate). With increasing calcination temperature, gradual elimination of water of crystallization and decomposition of nitrate to oxide occurs [17]. Complete decomposition occurs after treatment at 400 °C. Also, with increasing temperature, the reflections of impurity phases become less intense.

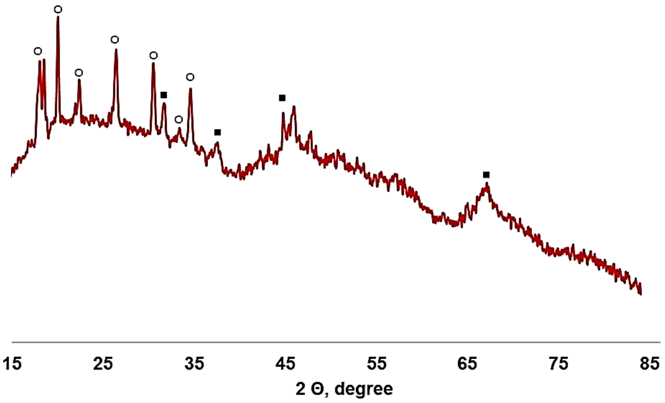

Fig. 1. Phase composition of the original system K-1 (▪ PDF 00-120-0015 γ-Al_2O_3; ○ PDF 12-0572 $Co(NO_3)_2{\cdot}6H_2O$)

Рис. 1. Фазовый состав исходной системы К-1 (▪ PDF 00-120-0015 γ-Al_2O_3; ○ PDF 12-0572 $Co(NO_3)_2{\cdot}6H_2O$)

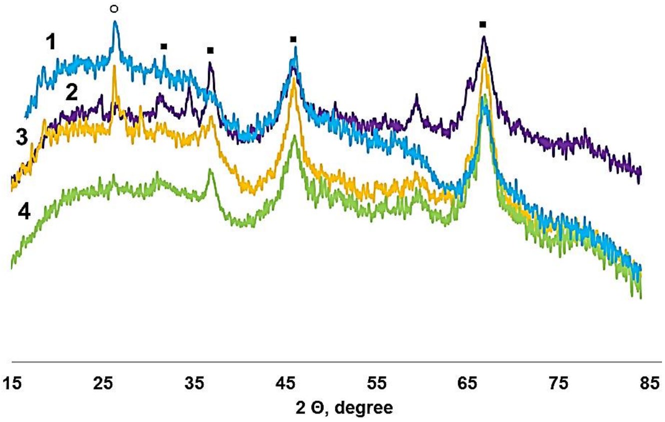

Fig. 2. Phase composition of heat-treated systems (▪ PDF 00-120-0015 γ-Al_2O_3; ○ PDF 12-0572 $Co(NO_3)_2{\cdot}6H_2O$, 1, 2, 3, 4 – samples K-2, K-5, K-3 и K-4 respectively)

Рис. 2. Фазовый состав термообработанных систем (▪ PDF 00-120-0015 γ-Al_2O_3; ○ PDF 12-0572 $Co(NO_3)_2{\cdot}6H_2O$,
1, 2, 3, 4 – образцы К-2, К-5, К-3 и К-4 соотвественно)

The obtained IR spectra (Fig. 3) are in good agreement with the XRD results, there are absorption bands (a.b.) of Al-O and O-H bonds of surface hydroxyl groups, the band common to all systems in the region of 3400 cm^{-1} belongs to the stretching vibrations of the OH group adsorbed water molecules [18]. We can also assume the presence of Mo-O and O-Mo-O bands, which characterize the deposition of molybdenum oxide structures [19], however, their extremely low intensity (due to low concentration) does not allow them to be confidently identified and requires additional research. The absorption bands of the K-5 sample in the region of 950-1200 cm^{-1} belong to the oxide structures of cobalt [20].

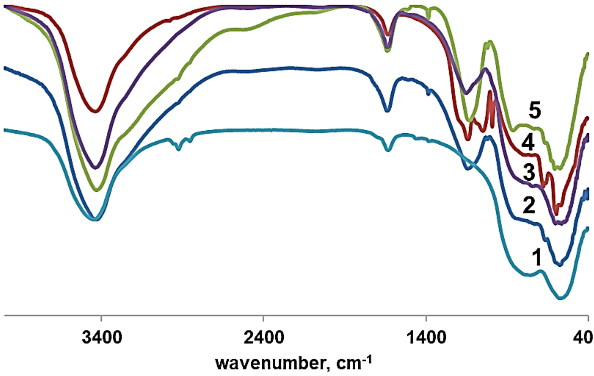

Fig. 3. IR-spectra of synthesized systems (1- γ-Al_2O_3, 2,3,4,5 – K-3, K-4, K-5, K-2 respectively)
Рис. 3. ИК-спектры синтезированных систем (1- γ-Al_2O_3, 2,3,4,5 – K-3, K-4, K-5, K-2 соответственно)

Previous studies have shown that the use of blue as an impregnating solution leads to a decrease in the diameter of the pore space and the specific surface area, based on which the successful application of active components to the surface can be indirectly confirmed. According to the results of the same studies, the pore space is represented precisely by mesopores, which facilitates the access of middle distillate fraction molecules to the active centers, while the absence of micropores leads to rational dispersion of the active components on the carrier.

Applied systems of similar composition were tested during the hydrodesulfurization of a model compound in an autoclave with stirring. The system was converted into the active form by gas-phase sulfidation in a mixture of H_2S+H_2; a solution of dibenzothiophene (DBT) in hexadecane served as a model compound. Based on the test results, the rate constant = 0.53 h^{-1} and the DBT conversion were calculated, which amounted to 86%. Thus, we can assume that the synthesized Co-Mo/Al_2O_3 systems will exhibit catalytic properties in the proposed processes.

CONCLUSIONS

Thus, Co-Mo/γ-Al_2O_3 catalytic systems were synthesized and studied, it was shown that molybdenum blues can be used as a Mo-containing reagent, and the genesis of changes in the composition of systems depending on temperature treatment was also studied. It was found that in order to completely eliminate the nitro group from the nitrate composition, the calcination temperature should be at least 400 °C. The absence of obvious reflections of oxide compounds of molybdenum and cobalt in the diffraction patterns is apparently due to their low concentration and high dispersity. Based on the results of IR spectroscopy, characteristic absorption bands of aluminum oxide were discovered; the presence of absorption bands of the oxide structures of the active components is possible, however, as in the case of diffraction patterns, the low concentration does not allow them to be identified with confidence. For this reasons additional research must be carried out.

ACKNOWLEDGMENT

The work was carried out within the framework of the state task of the Institute of Chemical Sciences of the Siberian Branch of the Russian Academy of Sciences, funded by the Ministry of Science and Higher Education of the Russian Federation.

The authors gratefully acknowledge to the Center for Collective Use " Tomsk Scientific Center of SB RAS".

The authors declare the absence a conflict of interest warranting disclosure in this article.

Работа выполнена в рамках государственного задания ИХН СО РАН, финансируемого Министерством науки и высшего образования Российской Федерации.

Авторы выражают благодарность Томскому региональному центру коллективного пользования ТНЦ СО РАН.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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Поступила в редакцию 29.02.2024
Принята к опубликованию 22.04.2024

Received 29.02.2024
Accepted 22.04.2024