Synthesis of Aluminosilicate Composites with Magnetic Properties

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In this work, we propose a procedure for the synthesis of magnetic materials based on commercial zeolites of the ZSM-5 type and the oxide form of aluminosilicate SIRALOX 40/490. The synthesized composites were characterized by various physicochemical methods. In particular, it was shown for the first time that the introduction of magnetite nanoparticles into aluminosilicate sorbents results in the blocking of acid sites. It has been established that the specific surface area and the nature of the porosity of the initial sorbents do not undergo critical changes in the course of synthesis, which also suggests a slight change in their sorption properties. Using electron microscopy, the average size of magnetite particles formed in the pores of sorbents was determined to be within 55-65 nm. The high content of iron in composites (in the composition of magnetite) determines their good magnetic characteristics, which allows them to be quickly and completely separated from the liquid phase by means of an external magnetic field. The synthesized magnetic composites can be used as sorbents or supports for the synthesis of magnetically recoverable heterogeneous catalytic systems, which can significantly reduce the cost and facilitate the regeneration and reuse procedure.

1. Introduction

In the development of new industrial catalysts, most often, preference is given to heterogeneous catalytic systems, which have an important advantage - the relative ease of separation from the reaction mass for subsequent regeneration and reuse (Ndolomingo et al., 2020). At the same time, the existing methods for separating heterogeneous catalysts from the reaction mass (filtration, centrifugation, decantation, etc.) are very laborious, time-consuming and are associated with inevitable losses of the catalyst (Rossi et al., 2021), especially if its particles have a small size and density (Goesmann, 2010). These problems can be solved by imparting magnetic properties to catalyst particles (Polshettiwar et al., 2011). This strategy has been used by many researchers (Rossi et al., 2012). Magnetic separation of the catalyst has at least the following set of advantages: fast and efficient separation (the process of separating the catalyst by a magnetic field takes seconds or minutes; the catalyst is completely separated); low energy consumption of the process (either a permanent magnet or an electromagnet is used); the catalyst remains inside the reactor. Therefore, after removing the reaction mixture and introducing a new portion of the substrate into the reactor, the process can be resumed with minimal time costs; catalyst losses are minimal; magnetic catalysts exhibit their properties only in the presence of a magnetic field, so there are no additional requirements for the storage, handling, and use of such catalytic systems; sampling and separation of the product are greatly simplified if the reaction takes place in an inert atmosphere; the consumption of solvents is minimized; waste generation is minimized; the process is easily scaled from laboratory to industrial volumes; magnetic properties can be imparted to any catalysts (based on enzymes, metals, solid acids, etc.) (Rossi et al., 2021).

In recent years, magnetic catalysts have been successfully used in olefin exchange, azide-alkyne cycloaddition, oxidation (Wang, 2014), hydrogenation (Zhang et al., 2013), biomass processing (Kannapu et al., 2020), in particular, for the conversion of cellulose and inulin (Sulman et al., 2020), etc.

There are several methods for the synthesis of magnetic nanoparticles in porous materials, on which the active phase of the catalyst is then immobilized, corresponding to the task (hydrolysis, hydrogenation, oxidation, etc.). These methods include the coprecipitation method, microemulsion method, sol-gel method, aerosol and laser pyrolysis, and hydrothermal method (Tran et al., 2021). The composition of magnetic carriers mainly includes metals (Fe, Co, Ni), alloys (FePt, CoPt), iron oxides (FeO, Fe_2O_3, Fe_3O_4), or spinel ferrites MFe_2O_4 (M = Co, Mn, Cu, Zn) (Zhang et al., 2012). Among them, magnetite (Fe_3O_4) is an ideal and most widely used support in catalysis due to its low cost and eases of preparation (Hyeon, 2003). Fe_3O_4 nanoparticles can be quite easily obtained in a solvothermal system as a result of a reduction reaction between $FeCl_3$ and ethylene glycol (Deng et al., 2005). However, magnetic particles are not very stable. They are sensitive to oxidation and agglomeration and may also exhibit undesirable chemical activity (Wei et al., 2011). To solve these problems, the modification of magnetic particles using coatings or stabilizing ligands, such as silica, polymers, carbon, etc., is used. (Baig, 2014).

Magnetic catalysts are being actively developed and used in many areas; they have great potential in heterogeneous catalysis (Kannapu et al., 2020). However, they are not yet used on an industrial scale for a number of reasons. First, the synthesis of magnetic metal nanoparticles and metal oxides often requires expensive precursors and uses toxic organic solvents, which greatly limits large-scale production (Zhang et al., 2019).

Zeolites should be noted among the list of available materials with excellent sorption and mechanical properties for the synthesis of sorbents and heterogeneous catalysts. Currently, there are a significant number of reports on the synthesis of magnetic zeolites (Yang et al., 2018). Quite a few methods have been proposed for the synthesis of such materials, for example, by mixing magnetite nanoparticles with zeolites (Yamaura, 2013), adding Fe_3O_4 nanoparticles to the gel directly during zeolite synthesis (Cao et al., 2008), etc. There are also known disadvantages of magnetic zeolites, which often are determined by the method of their synthesis: incomplete encapsulation of magnetic nanoparticles in zeolite (Liu et al., 2013), and insufficiently pronounced magnetic properties (Belviso et al., 2015). In this regard, it is important to improve the methods for synthesizing composites based on zeolites with strong magnetic properties, as well as to study their critical properties.

In this work, we propose a procedure for the synthesis of magnetic materials based on commercial zeolites of the ZSM-5 type and the oxide form of aluminosilicate SIRALOX 40/490. The results of analyzes of the synthesized materials by various physicochemical research methods are also presented.

2. Experimental

2.1 Materials

As a basis for the synthesis of magnetic materials, commercial zeolites of the ZSM-5 type (ZSM-5-CVM, ZSM-5-Acros) and the oxide form of silica-alumina hydrates SIRALOX 40/490 were used, the characteristics of which are given in Table 1. $FeCl_3 \cdot 6H_2O$, $CH_3COONa \cdot 3H_2O$, EtOH (95 %), and ethylene glycol were purchased from ChimMedService (Russia) and used as received.

Table 1: Characteristics of initial sorbents

Sample	Producer	SiO_2/Al_2O_3
ZSM-5-CVM	LLC Component, N. Novgorod, Russia	40
ZSM-5-Acros	Acros, Switzerland	400-570
SIRALOX 40/490	Sasol Germany GmbH, Hamburg, Germany	40/60

2.2 The magnetic materials synthesis

In an optimized form, the procedure for the synthesis of magnetic materials is as follows. 1.8 g of $FeCl_3 \cdot 6H_2O$ are dissolved in 30-35 mL of 95 % ethanol. 1.0 g of initial sorbent powder is added to the obtained solution, thoroughly mixed, and left for 10–15 min. After the specified time, a weighed portion of $CH_3COONa \cdot 3H_2O$ powder weighing 2.7 g is added to the solution and stirred until it is completely dissolved. The mixture is dried at a temperature of 50-60 °C, periodically stirring with a glass rod, until the ethanol is completely removed. The resulting dry powder is moistened with ethylene glycol (drop by drop) until a slurry is obtained. The sample is placed in a quartz tube, the internal volume of which is purged several times with an inert gas (nitrogen or argon). The tube is heated in a furnace to 300 °C and maintained at this temperature for 5 h in a weak current of inert gas. At this temperature, iron acetate decomposes to form magnetite (Laurikėnas et al., 2016). At the end of the synthesis, the tube with the sample is cooled to room temperature. The synthesized sample is washed with distilled water to remove particles with unsatisfactory magnetic properties and reagent residues until the wash water becomes clear. A neodymium magnet is used to separate the sample. After that, the sample is washed three times with ethanol and dried in an oven at a temperature of 50-60 °C.

2.3 Characterisation

The specific surface area and porosity of the magnetic materials and the initial sorbents were determined by low-temperature nitrogen adsorption using a Beckman Coulter SA 3100 surface analyzer (Coulter Corporation, USA). The texture characteristics of the samples were calculated by mathematical processing of nitrogen adsorption isotherms in accordance with the Brunauer-Emmett-Teller (BET), Langmuir, and de Boer-Lipens (t-plot) models. The study of samples by NH_3 chemisorption was carried out using a Chemosorb 4580 gas chemisorption analyzer (Micrometrics, Norcross, GA, USA). TEM images were obtained at an accelerating voltage of 80 kV using a JEOL JEM1010 electron microscope. ImageJ software was used to estimate the size of the nanoparticles. Elemental analysis of the catalyst was performed on a VRA-30 analytical X-ray spectrometer (Zeiss Jena, Germany). Magnetic measurements were performed on a vibration magnetometer VIBRACh (TvSU, Russia).

3. Results and discussion

Four samples of magnetic composites were synthesized according to the procedure indicated in section 2.2, which were marked as: Fe_3O_4-ZSM-5-CVM; Fe_3O_4-ZSM-5-Acros; Fe_3O_4-SIRALOX 40/490, and Fe_3O_4-SIRALOX 40/490_1. The Fe_3O_4-SIRALOX 40/490_1 sample differed from the others in that during its synthesis, the masses of iron chloride and sodium acetate were reduced by half. To assess the iron content in the synthesized samples, their elemental analysis was carried out, the results of which are shown in Table 2.

Table 2: Elemental analysis results

Sample	Fe content, wt %	Sample	Fe content, wt %
Fe_3O_4-ZSM-5-CVM	15.6	Fe_3O_4-SIRALOX 40/490	14.6
Fe_3O_4-ZSM-5-Acros	17.7	Fe_3O_4-SIRALOX 40/490_1	8.9

It is shown that the proposed method can be used to obtain magnetic composites with an average iron content of about 16 wt %. A small scatter of values (within 3-4 wt %) is apparently due to the nature of the porosity of the initial samples of aluminosilicates. A twofold decrease in the weights of iron chloride and sodium acetate did not lead to a proportional decrease in the iron content in the Fe_3O_4-SIRALOX 40/490_1 sample, which may indicate a certain "saturation" of the sorbent surface with magnetite particles formed during synthesis. However, this fact still needs further research. Table 3 shows the results of studying the synthesized magnetic composites by the method of low-temperature nitrogen adsorption.

Table 3: Results of the study of the initial sample of the HPS and the catalyst by the method of low-temperature nitrogen adsorption

Sample	BET	Langmuir	t-plot	
	S_{BET}, m^2/g	S_L, m^2/g	S_t, m^2/g	V, cm^3/g
ZSM-5-CVM	289	352	36[1]; 253[2]; 289[3]	0.114
ZSM-5-Acros	375	436	170[1]; 202[2]; 372[3]	0.093
SIRALOX 40/490	436	402	-[1]; -[2]; 452[3]	-
Fe_3O_4-ZSM-5-CVM	185	211	63[1]; 123[2]; 186[3]	0.055
Fe_3O_4-ZSM-5-Acros	231	262	114[1]; 116[2]; 230[3]	0.053
Fe_3O_4-SIRALOX 40/490	322	292	-[1]; -[2]; 339[3]	-
Fe_3O_4-SIRALOX 40/490_1	335	290	-[1]; -[2]; 377[3]	-

[1] - specific surface area as calculated by the t-plot model; [2] - specific surface area of micropores; [3] is the total specific surface area; S_L - specific surface area (Langmuir model); S_{BET} - specific surface area (BET model); S_t - specific surface area (t-plot); V is the volume of micropores.

As can be seen from the obtained data, the introduction of magnetite particles into the composition of sorbents leads to a decrease in the specific surface area, on average, by 100–150 m^2/g. In the case of zeolites having a microporous character, a decrease in the volume of micropores is observed, approximately by a factor of two, which is probably due to the blockage of micropores by magnetite particles. A comparison of the nitrogen sorption-desorption curves for the initial samples of sorbents and magnetic composites based on them (Figure 1) shows that the nature of the carrier porosity does not change during synthesis: samples based on ZSM-5 have a pronounced microporous character, and samples based on SIRALOX 40/490 - mesoporous. An analysis of data on the pore size distribution (not shown) showed that the nature of the pore distribution also does not change during the synthesis of magnetic composites. This suggests that the introduction of magnetite particles

into the composition of aluminosilicates will have an insignificant effect on the nature of their sorption properties, although it is obvious that a slight decrease in the sorption capacity of magnetic sorbents will still be observed.
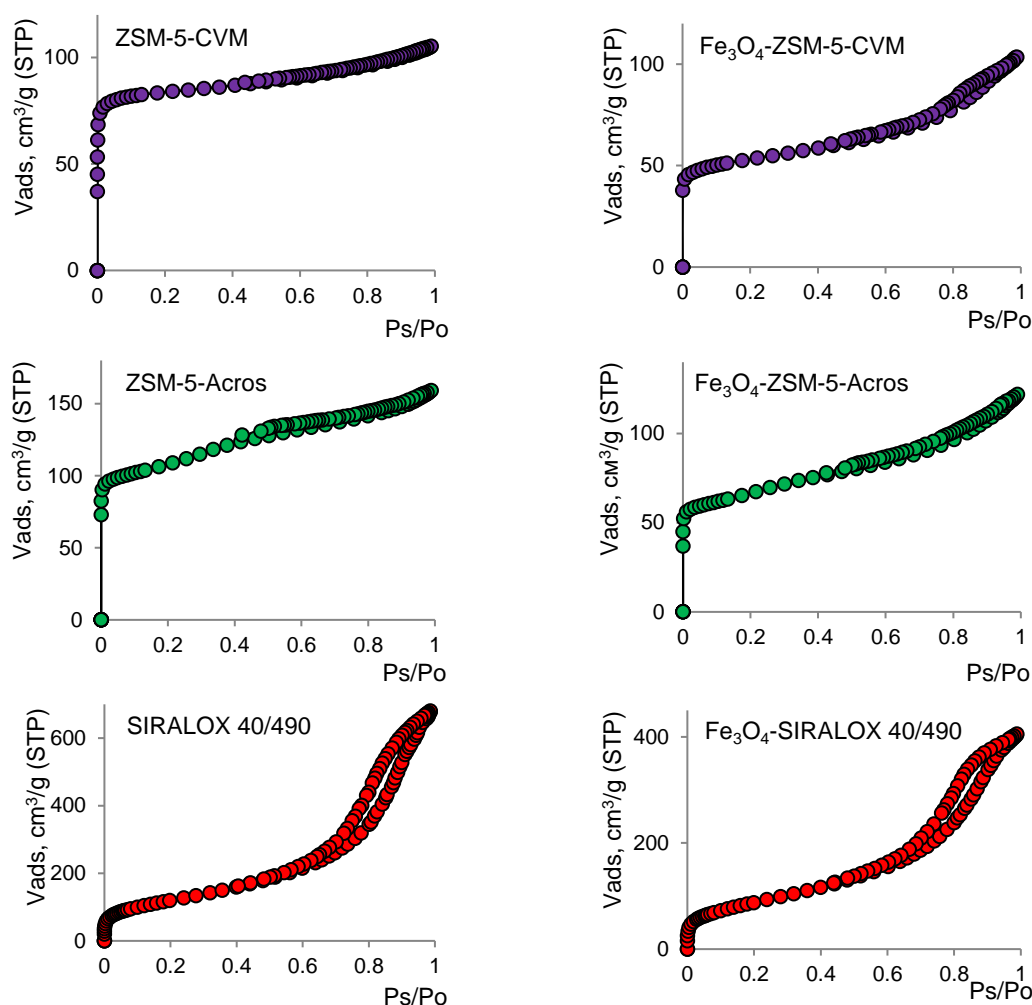

Figure 1: Nitrogen sorption-desorption curves for initial sorbent samples and magnetic composites based on them

To estimate the number of acid sites on the surface of the initial and magnetic sorbents, an ammonia chemisorption study was carried out, the results of which are shown in Table 4. As can be seen from the data in the table, the ZSM-5-CVM sample has the maximum number of acid sites on the surface, and the ZSM- 5 Acros. In all cases, when magnetite particles are introduced into the composition of the initial sorbents, a significant decrease in the number of acid sites is observed, as well as a shift in the temperature maxima of ammonia desorption. The decrease in the number of acid cents for different materials occurred to an unequal degree. After the introduction of magnetite particles into the composition of the sorbents, the number of acid centers on the surface of ZSM-5-CVM decreased by approximately 3 times; on the surface of SIRALOX 40/490 - 4 times; c on the surface of ZSM-5-Acros - 14 times. It is obvious that the formed magnetite particles block part of the acid sites, which is clearly seen in the example of SIRALOX 40/490: as the iron (magnetite) content increases, the number of acid sites decreases (Tables 2 and 4). A sharp decrease in the number of acid sites on the surface of ZSM-5-Acros can be explained by their initial small amount (6-20 times less compared to other sorbents) and their almost complete blockage by magnetite particles.

Table 4: The temperature of desorption peaks and the amount of ammonia adsorbed from the sample surface

Sample	t, °C	NH_3, mmol/g	ΣNH_3, mmol/g
SIRALOX 40/490	260	0.331	0.331
	250	0.193	
Fe_3O_4-SIRALOX 40/490_1	410	0.050	0.256
	650	0.013	
Fe_3O_4-SIRALOX 40/490	245	0.085	0.085
ZSM-5-CVM	320	0.722	1.238
	575	0.516	
Fe_3O_4-ZSM-5-CVM	350	0.427	0.427
ZSM-5-Acros	275	0.041	0.057
	490	0.016	
Fe_3O_4-ZSM-5-Acros	210	0.004	0.004

As an example, Figure 2(a) shows micrographs of magnetite particles on the surface of ZSM-5-CVM. According to TEM data, the average size of magnetite particles in the Fe_3O_4-SIRALOX 40/490 sample was 54±5 nm; in the Fe_3O_4-ZSM-5-CVM sample, 63±5 nm; in the Fe_3O_4-ZSM-5-Acros sample – 58±5 nm.
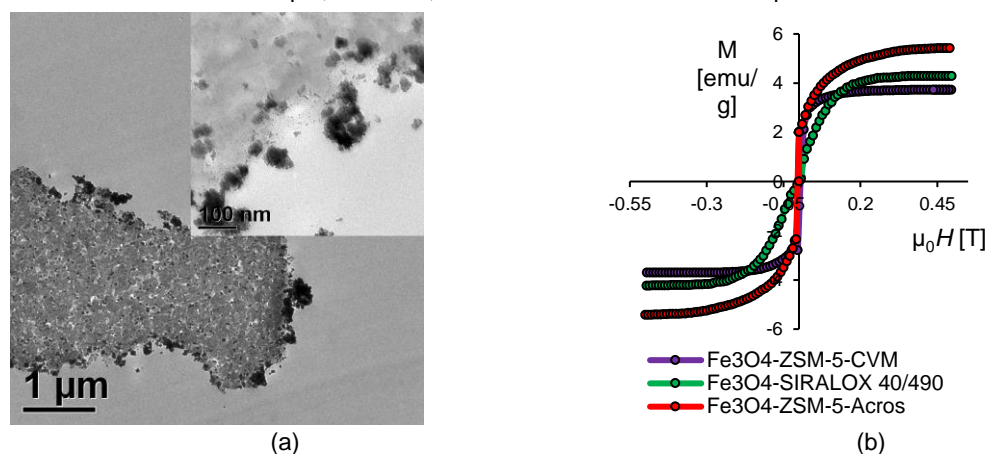

Figure 2: (a) *Magnetite particles on the surface of zeolite ZSM-5-CVM*, (b) *Isothermal magnetization curves of magnetic composites*

During the study, the magnetic properties of the synthesized materials were characterized. Figure 2(b) shows isothermal (20 °C) magnetization curves. The saturation magnetization of Fe_3O_4-ZSM-5-Acros turned out to be maximum and amounted to about 5.5 emu/g. The Fe_3O_4-SIRALOX 40/490 and Fe_3O_4-ZSM-5-CVM samples had approximately the same saturation magnetization values, 4.2 and 3.7 emu/g. Due to such indicators, magnetic sorbents are very sensitive to an external magnetic field and quickly and completely separate from the liquid phase using a permanent magnet.

4. Conclusions

Based on the results of this work, the following conclusions can be drawn. A procedure for the synthesis of magnetic composites based on commercial aluminosilicate materials: ZSM-5 and SIRALOX 40/490 zeolites, which can be used as sorbents or supports for the synthesis of heterogeneous catalytic systems, was proposed. It has been shown that the specific surface area and the nature of the porosity of the initial sorbents do not undergo critical changes, which also suggests a slight change in their sorption properties. It has also been found that when magnetite nanoparticles are introduced into the composition of sorbents, acid sites are blocked on the surface. On the one hand, this may be undesirable, for example, in the synthesis of bifunctional catalysts for which the presence of such sites is an important characteristic; on the other hand, it may have a positive effect in processes where the effect of acid sites is negative. Using electron microscopy, the average size of magnetite particles formed in the pores of sorbents was determined to be within 50-70 nm. The high dispersion of magnetic particles and the high content of iron (in the composition of magnetite) determine the good magnetic characteristics of the synthesized composites, which allow them to be quickly and completely separated from the liquid phase by means of an external magnetic field. The synthesized magnetic composites can be used as

sorbents or carriers for the synthesis of heterogeneous catalytic systems. The nature of the starting materials (aluminosilicates) and magnetic particles (magnetite) provides ample opportunities for the modification and functionalization of the proposed magnetic composites.

Acknowledgments

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