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SYNTHESIS AND PROPERTIES OF MAGNETIC COMPOSITE Fe_3O_4 STABILIZED BY POLYMERS FOR CATALYTIC OXIDATION OF AROMATIC HYDROCARBONS

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ABSTRACT

The present study is aimed at creating catalytic systems based on magnetite (Fe_3O_4) stabilized by polymers (polyvinylpyrrolidone (PVP) and chitosan), for liquid-phase oxidation of organic compounds with gaseous oxygen in order to obtain oxygen-containing compounds that can be used in the production of dyes, synthetic fibers, drugs, and many other petrochemical products. Magnetic composites of Fe_3O_4 stabilized by PVP and chitosan were synthesized by the coprecipitation method. The prepared magnetic composites were studied by physicochemical analysis methods. It was found that surface stabilization with polymers leads to a decrease in the size of magnetite nanocrystallites in nanocomposites. The sizes of the studied composites are less than ~ 10 nm. Mössbauer spectra of the obtained Fe_3O_4, Fe_3O_4/PVP, and Fe_3O_4/chitosan composite catalysts showed the presence of trivalent iron ions in a tetrahedral environment and the presence of Fe^{2+} and Fe^{3+} in an octahedral environment, as well as a doublet spectrum. The possibilities of using magnetite-based composite catalysts for heterogeneous liquid-phase oxidation of para-xylene with oxygen are considered. Based on the analysis of the IR spectra of the final reaction samples, the presence of CH bonds in the aromatic ring and C=C double bonds, as well as valence vibrations of the C=O group of carbonyl compounds and vibrations of the bonds of hydroxyl groups was established. It is shown that the main products of the oxidation reaction of p-xylene are p-toluyl aldehyde and dibutyl phthalate, which can be widely used for basic organic synthesis. The authors concluded that the magnetic composite of the Fe_3O_4/PVP composition can be used to produce oxygen-containing compounds, in particular, toluyl aldehyde and dibutyl phthalate.

Keywords: Oxidation, Catalysts, Aromatic Hydrocarbons, Chitosan, Polyvinylpyrrolidone, P-Xylene.

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INTRODUCTION

Catalytic oxidation of hydrocarbons and other organic compounds with oxygen is one of the most important and widespread reactions of organic synthesis, is of great importance for the national economy, and forms the basis for obtaining various industrially important oxygen-containing products that are used as additives to improve the quality of gasoline fuel and bitumen, as well as in the production of dyes, synthetic fibers, pharmaceuticals, etc.[1-3] Currently, the main tasks facing the oil refining industry are to increase the volume of production of petroleum products, expand their range, and improve the quality of the products. The choice of conditions for such reactions determines not only the economy of the process but also its specificity, that is, the minimum presence of by-products, which is very important from the point of view of environmental protection. Such processes were previously carried out at high pressures and temperatures, but at present there is a clear tendency to implement catalytic oxidation of organic compounds in the liquid phase under "milder" conditions. This contributes to greater specificity of the reaction, requires significantly less energy costs, is most economically advantageous, and eliminates environmental pollution with by-products. Nowadays, the lack of industrial production of oxygen-containing compounds, as well as the insufficient development of technologies for their production, leads to the fact that almost 100% of oxygen-containing compounds for various industries and scientific research used in the Republic of

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Kazakhstan are produced abroad. In world practice, the most commonly used technology is one in which hydrocarbon oxidation is carried out at elevated temperatures (180-220°C) and pressure (1.0-2.0 MPa), which requires a large amount of energy and at the same time this method is low-selective.[4-8] Liquid-phase catalytic oxidation of organic substances using molecular oxygen as an oxidizer is used to obtain a number of oxygen-containing substances, especially in the case of compounds that are unstable at high temperatures of vapor-phase processes. Some of the industrially important oxygen-containing compounds are toluyl alcohol, aldehyde, benzoic acid, and its salts and esters, dimethyl terephthalate are widely used in production as industrial raw materials and intermediate compounds in fine organic synthesis. They are obtained by liquid-phase oxidation of p-xylene and catalytic oxidation of toluene with atmospheric oxygen in the presence of catalysts.[9,10] A perspective method for producing oxygen-containing compounds is the process of heterogeneous catalytic oxidation, characterized by the simplicity of separating the catalyst from the reaction products and the possibility of its reuse, which is especially important in industry. Despite the obvious advantages of heterogeneous catalysts, such as ease of separation from reaction products and the possibility of reuse, their application in the oxidation of hydrocarbons is still at the research and development stage. Therefore, the development of low-temperature oxidation of aromatic hydrocarbons to the corresponding oxygen-containing compounds is promising, since high-value products are obtained from relatively inexpensive raw materials. The most economical and environmentally friendly method is the liquid-phase oxidation of hydrocarbons with oxygen using nanocatalysts based on metals of variable valence, and the ideal oxidizers from the point of view of "ecological" purity are oxygen, hydrogen peroxide since the product of their reduction is water. The oxygen molecule in gaseous, solid, and liquid states is paramagnetic and has a fairly high dissociation energy (5.08 eV).[11-16] A simplified diagram of the liquid-phase oxidation of para-xylene (p-xylene) is shown in Fig.-1.

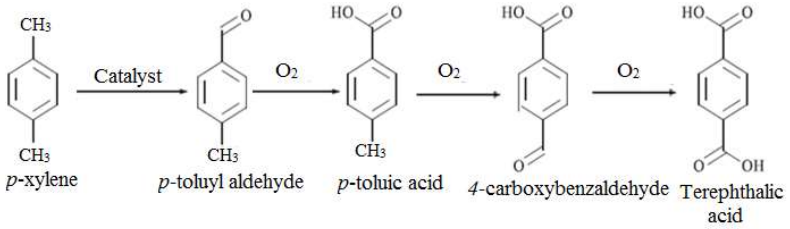


Fig.-1: Scheme of Oxidation of p-xylene in the Presence of Catalysts

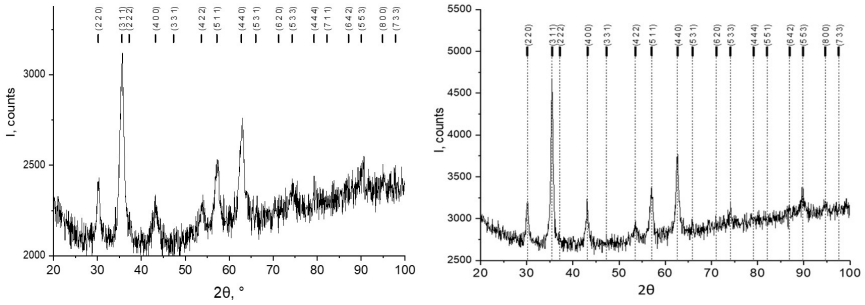
Success in solving the problems of technological use of molecular oxygen is determined by the properties of metals that have electrons on donor d-orbitals and provide oxygen activation due to its coordination. Magnetic composites stabilized by polymers containing iron play a key role in oxygen binding and activation. When O_2 is bound, a two-electron reduction usually occurs, leading to the formation of peroxo-intermediates.[13-19]As shown by quantum chemical calculations, the heme-oxygen bond and binding in Fe(III)–OO–R complexes depend significantly on the spin.[13,15-20] A strong iron-oxygen bond is obtained with a low spin (S = ½), and a weak bond with a high spin (S = 5/2) in peroxo complexes, which is confirmed by Raman and EPR spectra.[14,19-24] In recent years, metal complexes fixed on a polymer matrix have been used as catalysts to obtain oxygen-containing substances. Such systems have the advantages of homogeneous and heterogeneous catalysts and are promising for the catalytic oxidation of alkyl aromatic substances in the liquid phase. A perspective direction of research in this area is the development of catalysts obtained by applying complexes of variable valence metals to polymer matrices. When using a natural polymer matrix as a substrate, helps to reduce the harmful impact of this industry on the environment.[24-29] Highly effective magnetic composites based on polyvalent metals immobilized on a polymer matrix are environmentally friendly and allow the oxidation of aromatic hydrocarbons to be carried out under mild conditions, as well as to carry out processes without initiators at a sufficiently high rate even at low temperatures and atmospheric oxygen pressure. This work aims to develop catalytic systems based on magnetite Fe_3O_4 immobilized on a polymer matrix (polyvinylpyrrolidone (PVP) and chitosan) for the oxidation of p-xylene and to determine the possibility of using the obtained catalytic samples in this reaction; to determine the characteristics of the obtained magnetic composites using physicochemical research methods.

EXPERIMENTAL

Magnetite nanocrystals stabilized with polyvinylpyrrolidone (PVP), M_w = 10,000, and chitosan-based on magnetite were obtained by chemical coprecipitation of the divalent and trivalent iron ions in an alkaline solution.[5,22,23] Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, analytical grade), iron (II) sulfate hexahydrate ($FeSO_4 \cdot 6H_2O$, analytical grade), and ammonium hydroxide (25% NH_4OH, analytical grade) were used. The prepared catalytic samples were examined by a complex of physical and chemical research. The diffraction patterns were measured in the Bragg-Brentano geometry in the angle range 2θ = 15-100°. The average crystallite size was calculated using the Debye-Scherrer formula $D=K\lambda/\beta\cos\theta$, where K is the Scherrer constant, λ is the X-ray wavelength, β is the peak width at half maximum, and θ is the Bragg diffraction angle. The textural properties of the composites were obtained by analyzing the adsorption-desorption isotherms of N_2 at -196.15°C, obtained on a Quantachrome NOVATOUCH LX4 adsorption analyzer equipped with long cells with a flask and an outer diameter of 9 mm. The reaction products were analyzed by gas chromatography with mass spectrometric detection (7890A/5975C), as well as IR spectroscopy. Conditions of chromatographic analysis: sample injection temperature 240°C, splitless. [23]

RESULTS AND DISCUSSION

The phase state of magnetic composites based on magnetite stabilized by PVP (Fe_3O_4/PVP) and chitosan (Fe_3O_4/ chitosan) was studied. It was found that the main phase formed during chemical coprecipitation is represented by magnetite Fe_3O_4, the diffraction pattern of Fe_3O_4 nanoparticles stabilized by polymers is close to the standard pattern of crystalline magnetite. Figure-2 shows the X-ray diffraction pattern of the obtained Fe_3O_4/PVP and Fe_3O_4/ chitosan composites. The characteristic diffraction peaks designated by indices (220), (311), (400), (422), and (511) can be well correlated with the structure of cubic spinel Fe_3O_4.[5,28,30] The peaks and their relative intensities confirm that the obtained composite represents a single phase with a spinel structure, the unit cell parameter a = 0.83564 nm and a = 0.83635 nm, respectively (space group Fd-3m).



a b

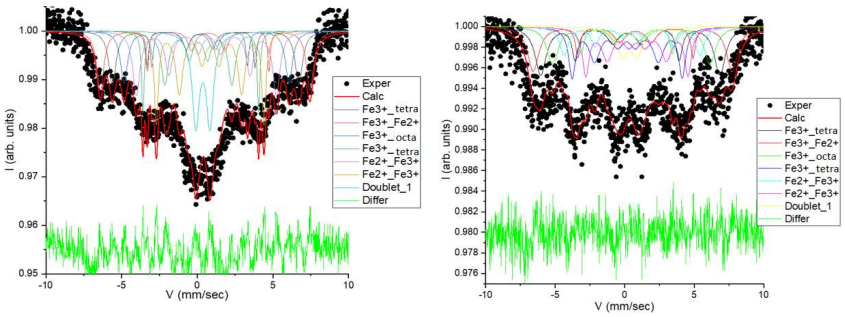
Fig.-2: Results of X-ray Diffractometry of Magnetic Composites Fe_3O_4/PVP (a), Fe_3O_4/Chitosan (b)

The characteristic peaks for Fe_3O_4 did not change, and only the intensity and width of the peaks changed after the application of PVP and chitosan, which shows that the crystal structure of the modified nanoparticles did not change. The results of the X-ray structural analysis of the obtained magnetic composites are given in Table-1.

Table-1: Results of X-ray Structural Analysis of the Obtained Magnetic Composites

Sample	Phase	a, nm	c, nm	Concentration, %	X-ray density, g/cm^3	Space group
Fe_3O_4/PVP	Fe_3O_4 – spinel (Magnetite)	0.83564	-	100	5.271	Fd-3m
Fe_3O_4 / chitosan	Fe_3O_4 – spinel (Magnetite)	0.83635	-	100	5.257	Fd-3m

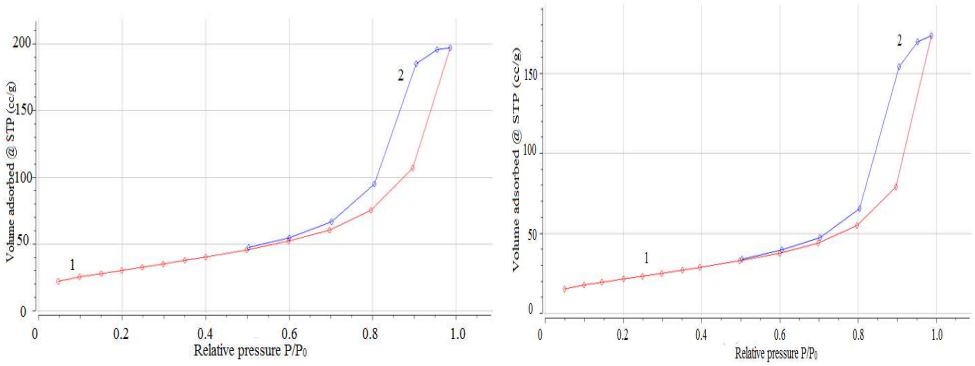
We have also studied the Mössbauer spectroscopy of magnetite Fe_3O_4, the results of which confirmed the structure of Fe_3O_4.[24] Figure-3 shows the Mössbauer spectra of the obtained composite catalysts Fe_3O_4/PVP (a), Fe_3O_4 / chitosan (b) and the parameters corresponding to the trivalent iron ions in the A and B sublattices.



a b

Fig.-3: Mössbauer Spectra of Magnetic Composites Fe_3O_4/PVP (a) and Fe_3O_4/Chitosan (b) at Room Temperature

In the Mössbauer spectra of the obtained composite catalysts Fe_3O_4/PVP and Fe_3O_4 / chitosan, the presence of trivalent iron ions in a tetrahedral environment and the presence of Fe^{2+} and Fe^{3+} in an octahedral environment is noted, and there is also a doublet spectrum. It is seen that the sextets with a smaller isomer shift relative to α-Fe and higher values of the effective hyperfine magnetic field belong to the ^{57}Fe nuclei in tetrahedral positions of the magnetic composites, while the sextets with higher isomer shift values and a lower effective hyperfine magnetic field belong to the ^{57}Fe nuclei in octahedral positions. In the sublattice, the iron cations are in two oxidation states Fe^{2+}, and Fe^{3+} in the octahedral environment, the isomer shift value is significantly higher and the effective magnetic fields are significantly lower than for magnetite. This can be explained by the fact that the sizes of the composites under study are less than ~ 10 nm. The doublet parameters included the isomer shift and quadrupole splitting.[29-31] The N_2 adsorption isotherms for Fe_3O_4/PVP(a) and Fe_3O_4/chitosan are shown in Fig.-4. It can be seen from Fig.-4 that the magnetic composites exhibit typical type IV isotherms with type H_2 hysteresis, according to the classification established by IUPAC. This type of isotherm is determined by mesoporous materials.[29,32]



a b

Fig.-4: N_2 isotherms: 1- adsorption, 2- desorption, for Fe_3O_4/PVP (a) and Fe_3O_4/Chitosan (b)

The results of the study of the textural properties are presented in Table-2. Fe_3O_4 /PVP has the most developed surface compared to Fe_3O_4 /chitosan. It is evident that magnetite stabilized with PVP allows obtaining a material with an insignificant decrease in the surface area.[33-38] At the same time, some decrease in the unit cell parameter is noted, as evidenced by the calculations of the lattice parameter. Probably, the decrease in the crystallite sizes can be associated with the formation of magnetite clusters on the surface of PVP, which prevents their agglomeration into larger particles. The area of magnetite stabilized with chitosan is significantly reduced, and the value of the lattice parameter also decreases. Apparently, the decrease in the surface area of the synthesized composite material compared to magnetite may be due to the formation of particles on the surface of magnetite.

On the obtained catalysts Fe_3O_4 / PVP and Fe_3O_4 / chitosan, the oxidation of para-xylene was studied under optimal conditions. The installation and implementation of the process of liquid-phase oxidation of hydrocarbons using the oxidation of phenol as an example is well described in previous works.[5,24,28] The results of the reaction products of chromatographic analysis with mass spectrometric detection are given in Table-3.

Table-2: Textural and Structural Parameters of Magnetic Composites

Sample	Parameters			
	$S_{specific}$, m^2/g	V_{pore}, cm^3/g	Average crystallite size according to Scherrer, nm (311)	Lattice parameter, nm
Fe_3O_4	111	0.28546	16.12868	0.83665
Fe_3O_4/PVP	106	0.28372	9.89182	0,83564
Fe_3O_4 / chitosan	78	0.25749	8.797442	0.83635

Table-3: Results of para-Xylene Oxidation on Fe_3O_4/PVP Catalyst According to Chromatographic Analysis Data.

No	Retention time, min	Compounds	Probability of identification, %	Percentage content, %
1	3.69	Benzene, 1,3-dimethyl-	94.9	2.63
2	11.77	Acetic acid	97.0	31.70
3	17.85	Benzaldehyde, 4-methyl-	98.0	29.68
4	30.44	2-(p-Tolylmethyl)-p-xylene	91.0	1.64
5	34.15	Benzaldehyde, 4-[(2-methylphenyl)methoxy]-	82.0	2.25
6	34.48	1,2-Benzenedicarboxylic acid, bis(2-methyl propyl) ester	94.0	0.47
7	35.64	Phthalic acid, butyl hept-4-yl ester	86.0	0.30
8	36.83	Dibutyl phthalate	98.0	30.85
9	40.45	1,4-Benzenediol, 2,5-dimethyl-	92.0	0.45

The data of chromatographic analysis show that the main products of the paraxylene oxidation reaction are p-tolu aldehyde and dibutyl phthalate.[39-49] The IR spectrum of the reaction product reveals oscillations of the bonds of hydroxyl groups, stretching vibrations of the C=O groups of carbonyl compounds, and the presence of CH and double C=C bonds in the aromatic ring. A broadened band is observed in the region of 2,915-2,843 cm^{-1}, which includes stretching vibrations of the ch bonds of the methylene and methyl groups. Based on the chromatographic analysis data of the final reaction product, it can be concluded that the magnetic composite of the Fe_3O_4/PVP composition can be used to obtain oxygen-containing compounds, in particular, toluyl aldehyde and dibutyl phthalate.

CONCLUSION

Magnetic composites of Fe_3O_4 and catalysts based on it stabilized by polyvinylpyrrolidone (PVP) and chitosan were obtained. Rietveld refinement of Fe_3O_4/PVP confirms that they have a pure spinel cubic structure without any additional phases with the Fd-3m space group. According to the X-ray diffraction results, the magnetic composites are a single phase with a spinel structure, the unit cell parameter a = 0.83564 nm and a = 0.83635 nm, and the average crystallite size according to Scherrer (311) is 9.89182 and 8.797442, respectively (space group Fd-3m). Stabilization of the surface by polymers leads to a decrease in the size of magnetite crystallites in nanocomposites. Oxidation of paraxylene under optimal conditions on the synthesized magnetic composites was studied. The results of chromatographic analysis of the final reaction product allow us to conclude that the studied magnetic composite Fe_3O_4/PVP can be used to obtain oxygen-containing compounds, in particular, toluyl aldehyde, dibutyl phthalate, which are widely used for basic organic synthesis.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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