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Maghemite as a Catalyst for Oxidation of Alcohols with Air

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Abstract—The possibility of using maghemite (γ-iron(III) oxide) as a catalyst for the oxidation of alcohols with atmospheric oxygen has been explored. It has been shown that maghemite is active in the oxidation of benzyl alcohols. In the case of benzyl alcohol, the oxidation leads to benzaldehyde with nearly 100% selectivity. It has been found that the addition of small amounts of basic cocatalysts can substantially increase the yield of the target products.

Keywords: maghemite, oxidation reaction of alcohols
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The oxidation of alcohols is a classical and well-developed method of obtaining carbonyl compounds. The structure of a compound formed by the oxidation of an alcohol depends on whether the alcohol is primary, secondary, or tertiary. The individual and most complicated problem in the oxidation of primary alcohols to aldehydes is the subsequent oxidation of aldehydes to carboxylic acids. This is due to the fact that aldehydes are usually more readily oxidizable than the corresponding alcohols, and it is quite challenging to terminate the reaction at the aldehyde stage. Therefore, optimizing the conditions of the partial oxidation reaction of alcohols is an important scientific and engineering problem. The use of (atmospheric) oxygen in this reaction is the most preferable as it is the cheapest of all possible oxidants. In addition, a situation when undesirable byproducts are not formed whatsoever is theoretically possible in the case of oxidation with oxygen.

In terms of cheapness and availability, the catalysts based on iron oxides appear the most promising, since iron is the cheapest and most available of transition metals. It is known from published data that magnetite indeed exhibits catalytic activity in the oxidation reaction of alcohols [1, 2]. However, magnetite is unfavorable because of its gradual oxidation upon storage in air. This process is especially intense for magnetite samples with a developed surface, i.e., those possessing the highest catalytic activity. Therefore, the investigation of the catalytic activity of trivalent iron oxides (hematite and maghemite), which are stable upon storage in air, might be of significant interest. Maghemite can serve as a catalyst for the oxidation of alcohols with the use of, e.g., hydrogen peroxide [3, 4]. However, there is a lack of information in the literature on the catalytic activity of maghemite in the oxidation reaction of alcohols with air.

It is important that a fast drop in catalyst activity is often observed for heterogeneous catalytic reactions because of the blocking of catalyst surface by nonvolatile byproducts. Another substantial problem is heat release or consumption in the case when the process is accompanied by a significant thermal effect. Situations when the active form of the catalyst is formed in situ (as, e.g., in the Fischer–Tropsch synthesis) are also known. The use of a slurry (three-phase) reactor is promising in all these cases [5, 6]. The application of the slurry technology to alcohol oxidation can hold promise as making it possible to distill off the lower boiling product (aldehyde, ketone) from the reaction mixture and thereby shifting the equilibrium of the reaction to the desired direction. Therefore, in this study, we explored the possibility of implementing the alcohol oxidation process in the slurry reactor mode.

EXPERIMENTAL

Preparation of Catalysts

Magnetite. Magnetite was prepared by coprecipitation from aqueous solutions of $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ in an alkaline medium (11.1 g of $FeSO_4 \cdot 7H_2O$, 21.6 g of $FeCl_3 \cdot 6H_2O$, and 12.8 g of NaOH). The salts of divalent and trivalent iron were mixed at a molar ratio of 1 : 2, respectively. A solution of sodium hydroxide in 40 mL of distilled water was added dropwise to the solution of iron salts in 80 mL of distilled water with constant stirring. The obtained suspension was left to stay for several days in the absence of air. Then the mixture was washed with distilled water until the wash water was clear after adding a $BaCl_2$ solution.

After this, the catalyst was dried on a water bath under vacuum.

Maghemite. Maghemite was prepared by the oxidation of magnetite for 3 h at 200°C in air.

Hematite. Hematite was prepared by precipitating from an aqueous solution of $FeCl_3 \cdot 6H_2O$ with sodium bicarbonate (27.0 g of $FeCl_3 \cdot 6H_2O$ and 8.4 g of $NaHCO_3$). Iron chloride was dissolved in 100 mL of distilled water, and then a solution of sodium bicarbonate in 100 mL of distilled water was added dropwise with constant stirring. After the addition of all the sodium bicarbonate solution and termination of gas evolution, the obtained suspension was held for 6 h at 100°C, and then the precipitate was filtered off, washed six times with distilled water, and dried at 200°C.

Oxidation Reaction of Alcohols

The oxidation of alcohols was performed in a three-neck flask equipped with a magnetic stirrer. The catalyst charge was 900 mg, and the amount of an alcohol taken was 0.04 mol. The mixture was heated, air was bubbled through it, and the reaction was carried out until the end of distillation. An experiment with the fractionation on γ-Fe_2O_3 was also carried out. The air bubbling rate was 100 mL/min; a fraction was collected every 35 min.

In addition, a recycling experiment on the oxidation of benzyl alcohol over γ-Fe_2O_3 was carried out. The air bubbling rate was 100 mL/min, and fractions were collected every 30 min. After complete distillation of the fractions, they (except for the samples taken for analysis) were combined and placed into the reaction vessel, and the sequence of operations was repeated.

Gas Chromatographic Analysis

The analysis was performed on a Kristall-Lyuks gas chromatograph equipped with a flame ionization detector. A capillary column with a length of 20 m, an inner diameter of 0.22 mm, and the FFAP phase (poly(ethylene glycol) esterified with nitroterephthalic acid) was used. The stationary phase film thickness was 0.25 μm. Helium was used as the carrier gas. The elution was performed in the isothermal mode at 210°C. The obtained products were analyzed in the form of 10% solutions in ethanol.

For the quantitative measurements, 10% solutions of benzyl alcohol and benzoic acid in ethanol were injected into the chromatograph with a syringe, with the relative sensitivity of the detector to benzyl alcohol and benzoic acid having been determined.

Proton Magnetic Resonance

The ^{1}H NMR spectra were recorded on a Bruker Avance 400 instrument. Deuterated chloroform was used as the solvent.

Magnetic Measurements

The kinetic studies were performed in situ using a vibrating-sample magnetometer. The test samples of a 20 mg weight were placed in the measurement cell of the magnetometer [7] which was a 0.3-cm^3 flow microreactor. The sample of the catalyst under study was fixed between two porous quartz membranes. The flow rate of an inert gas (Ar) was 10 mL/min in all the experiments. The heating was performed at a rate of 10°C/min to a preset temperature, with the change in magnetization being continuously recorded at a frequency of 1 Hz. After reaching the preset temperature, the sample was cooled at a rate of 10°C/min in an Ar flow, and the temperature dependence of magnetization was recorded. The Curie temperature was found as the interception of the tangent to the extremum in the magnetization–temperature curve with the abscissa axis.

X-Ray Diffraction Analysis of Catalysts

The X-ray powder diffraction (XRD) patterns of the initial support and the obtained catalysts were recorded on a Dron-3 diffractometer using cobalt radiation (a wavelength of 0.17903 nm).

RESULTS AND DISCUSSION

Structure of the Catalysts

The X-ray diffraction pattern of initial maghemite is presented in Fig. 1.

XRD analysis was also performed for maghemite after the reaction. It was found that the X-ray diffraction pattern of the sample was slightly different in this case. However, the situation was complicated by the fact that magnetite and maghemite possess very similar X-ray diffraction patterns, and they cannot be reliably distinguished under the conditions when the lines have a noticeable width (like in our case). To understand how the catalyst behaves during the course of the reaction, the Curie temperature was determined for the catalyst samples before and after the reaction. It was found that the Curie temperatures for magnetite and maghemite before the reaction were in agreement with their published values (580 and 675°C, respectively), whereas the Curie temperature for all of the samples after the reaction had a value of about 580°C' i.e., even if maghemite was taken as the catalyst, it transformed into magnetite in the reaction. This finding is confirmed by the fact that all the samples of maghemite and magnetite catalysts after the reaction had a black color characteristic of magnetite (rather

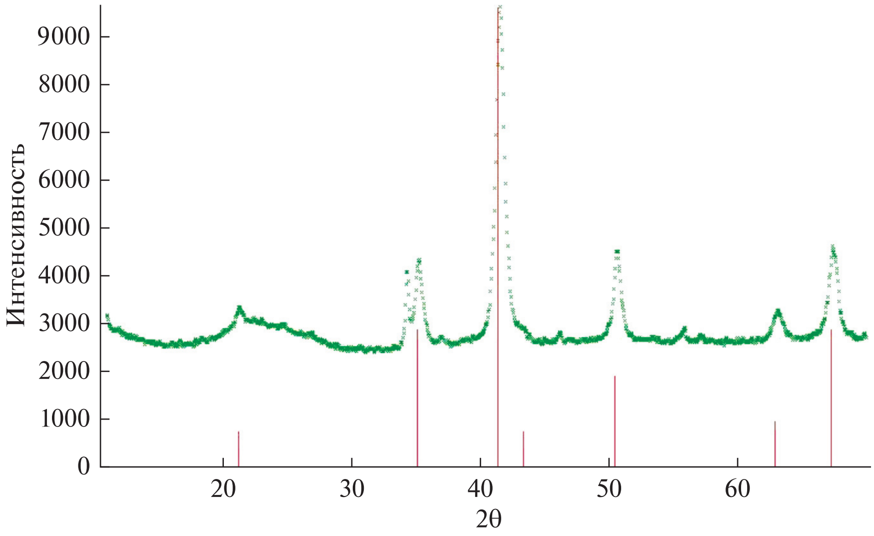

Fig. 1. X-ray diffraction pattern of initial maghemite.

than a reddish brown color of maghemite). Thus, maghemite transforms into magnetite under the reaction conditions.

In our opinion, it is quite an important fact. The matter is that magnetite with a developed surface (and, generally, the higher the specific surface area of a catalyst, the higher its activity) is spontaneously, although relatively slowly, oxidized to maghemite by air. Therefore, the absence of the difference in activity between magnetite and maghemite allows researchers not to raise the question as to how deep magnetite planned for use as a catalyst has been oxidized.

On the other hand, since the medium appears to be more reducing under the reaction conditions than in air, the reverse transformation of magnetite to maghemite seems to occur as well. It can be assumed that maghemite formed from magnetite by reacting with oxygen is the immediate oxidant for an alcohol. The magnetite–maghemite mutual transitions readily occur and are explained by the fact that crystal lattices of these phases are very similar. This behavior allows the system to act as an effective carrier of oxygen onto organic substrates. At the same time, hematite possessing an essentially different crystal lattice exhibited no catalytic activity in this reaction. It should also be noted that after attempting to carry out the benzyl alcohol oxidation reaction with hematite as a catalyst, the latter underwent no changes. It was confirmed by XRD data.

Study of the Alcohol Oxidation Reaction by ^1H NMR Spectroscopy

Proton NMR spectroscopy can be a convenient method for studying the oxidation reaction of alcohols. The oxidation products of primary alcohols, aldehydes, have a characteristic signal, namely, the proton of the formyl group appears at 9–10 ppm. The signal of protons in the α-position to the hydroxylic group at 3–4 ppm is characteristic of a primary alcohol. In the case of secondary alcohols, the oxidation product, ketone, can be distinguished by the line at 2.3–2.5 ppm due to the α-protons to the carbonyl group. The valuable property of ^{1}H NMR spectroscopy is the fact that the area of a signal is directly proportional to the number of protons giving this signal. It is independent of other factors; hence, a ^{1}H NMR spectrum gives not only qualitative, but also quantitative information. Certain difficulties can emerge in the case of identification of the oxidation products of primary aliphatic alcohols, aldehydes, and carboxylic acids, because the signals of the protons of the hydrocarbon radicals appear in the same region in the case of the same structure, and the signal of the carboxylic group at about 12 ppm may not appear. Additional research methods are required in this case. However, this problem does not emerge in the case of oxidation of benzyl alcohols because the *o*-proton signals of the corresponding aldehydes and acids are generally quite much apart. Thus, the signal of the *o*-proton for benzoic acid is at 8.12 ppm versus that at 7.87 ppm for benzaldehyde.

Octanol-1. It was found that the aerobic oxidation of octanol-1 did not occur over our catalysts.

Benzyl alcohol. Benzyl alcohol was the next substrate for oxidation studied in this work. It has been shown that its aerobic oxidation reaction proceeds in the presence of magnetite or maghemite, while hematite exhibits no catalytic activity. The reaction also does not occur in the absence of a catalyst. When using maghemite as a catalyst, the benzaldehyde yield of 18% is achieved as shown in the Experimental section. The reaction does not occur when the temperature in

Table 1. Experiments on the oxidation of benzyl alcohol over maghemite and magnetite catalysts with fractionation. The air flow rate is 100 mL/min and the reaction temperature is 202–203°C

Catalyst	Yield of benzaldehyde
Maghemite	1st portion 8 wt %
Maghemite	2nd portion 2 wt %
Maghemite	3rd portion 8 wt %
Magnetite	1st portion 8 wt %
Magnetite	2nd portion 4 wt %
Magnetite	3rd portion 4 wt %

Table 2. Recycling experiments on the oxidation of benzyl alcohol over maghemite. The air flow rate is 100 mL/min and the reaction temperature is 202–203°C

Cycle number	Yield of benzaldehyde, wt %	Yield of benzoic acid, wt %
1	18	0
2	21	0.4

the reaction vessel is decreased below 200°C. Benzoic acid was not detected among the distillation products.

Flow experiments. An important characteristic of the performance of a catalyst system is its turnover number (TON), which illustrates the on-stream stability of the catalyst. To understand how the amount of the oxidation substrate affects the catalyst activity, we performed experiments on the oxidation of benzyl alcohol in the flow mode.

As is seen from Table 1, the yield of benzaldehyde is not high; however, it slightly depends on time. Here, benzoic acid was not detected in any of the distillates.

Recycling experiments. Recycling is one of the most important operations in industrial organic chemistry, which makes it possible to increase the yield of the target product. We carried out several experiments in the recycle mode to understand whether the yield of the target product could be increased by this means.

For the maghemite catalyst, the yield of benzaldehyde is 18% in the first cycle and 21%, in the second cycle, i.e., recycling at least does not reduce the product yield. Benzoic acid (the *o*-proton at 8.1 ppm) is not detected in the 1st cycle, and its amount in the 2nd cycle is about 2% of benzaldehyde.

It was shown in the previous experiments that the test catalysts were active in the aerobic oxidation of benzyl alcohol. However, the question whether this oxidation proceeds by the radical or ionic mechanism remained unclear. Apparently, the carbanionic mechanism is almost impossible in the presence of proton-donating compounds (benzyl alcohol, water); therefore, two possibilities remained, namely, radical and carbocationic mechanisms. On the other hand, it is clear that the carbocationic mechanism is also almost impossible if there are no acid sites with any noticeable strength on the catalyst surface. To clarify this question, experiments with 1-phenylethanol (PhEtOH) were performed. Like benzyl alcohol, this alcohol is capable of forming a benzyl-type cation; however, unlike the benzyl cation, this cation is extremely prone to proton elimination to form styrene. This reaction occurs in the presence of almost all somehow strong acids. Therefore, if such sites are present on the catalyst surface, noticeable amounts of styrene should be detected among the products.

The results of oxidation of 1-phenylethanol over our catalysts are presented in Table 3. As is seen from Table 3, phenylethanol is oxidized in the presence of magnetite or maghemite (Fig. 2) (in addition to the signal of the α-proton of phenylethanol at 4.87 ppm, the signal of acetophenone α-protons at 2.61 ppm is also present). However, styrene becomes the main component of the obtained distillate, and its amount exceeds by an order of magnitude the amount of formed acetophenone. This indicates that there are acid sites of sufficient strength on their surface, and the oxidation can occur via both mechanisms.

Experiments on Alcohol Oxidation over a Catalyst in the Presence of Trioctylamine

To clarify how important is the role of surface acid sites in the oxidation of phenylethanol, we added 100 μL of tri-*n*-octylamine to the reaction mixture (maghemite was used as the catalyst). First, trioctylamine possesses high basicity and can effectively interact with acid sites, and second, its boiling point is very high and it is for sure that this additive will not be distilled off during the reaction and not contaminate the product.

It was found that the yield of acetophenone increased fivefold and the yield of styrene decreased twofold in this case. This clearly indicates that the surface acid sites not only do not promote the oxidation reaction, but even inhibit it. Therefore, in this case, the oxidation also proceeds via the radical mechanism. An experiment was also carried out. on the oxidation of benzyl alcohol over maghemite in the presence of trioctylamine In this case, the yield of benzaldehyde increases at least fourfold, thereby fully confirming the above conclusion.

CONCLUSIONS

As a result of the experiments done, the following conclusions can be drawn:

(1) It has been shown that under the slurry reactor conditions, maghemite is active in the oxidation reaction of benzyl alcohols with atmospheric oxygen. Ali-

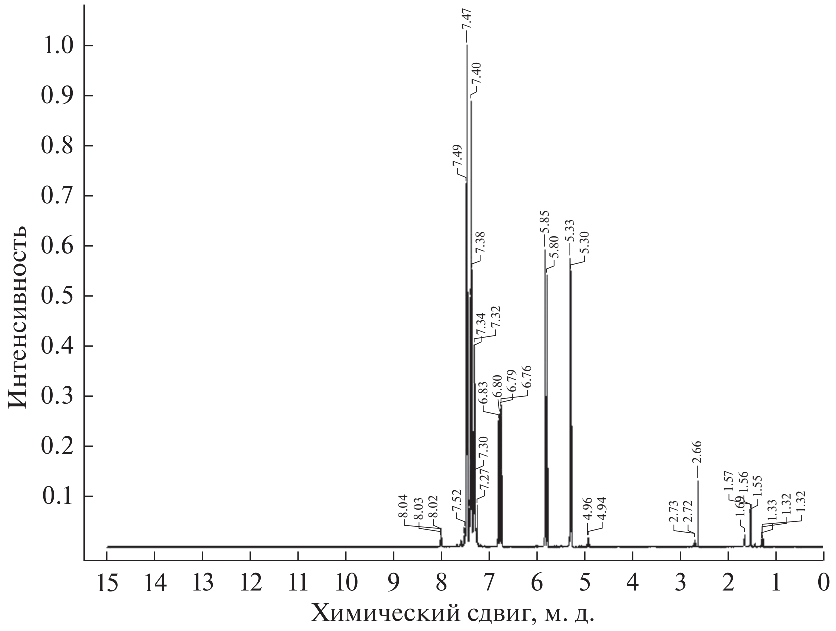

Fig. 2. ^{1}H NMR spectrum of acetophenone with maghemite as a catalyst.

phatic alcohols are not oxidized under the studied conditions.

(2) It has been found that unlike magnetite and maghemite, hematite does not exhibit catalytic activity under the studied conditions. This is apparently associated with the fact that crystal structures of magnetite and maghemite are very similar, allowing these oxides to act as an active oxygen carrier. Apparently, we deal with the standard Mars—van Krevelen mechanism in this case, where magnetite is the reduced form and maghemite is the oxidized form. At the same time, a significant difference of the hematite crystal lattice from the crystal lattice of magnetite substantially complicates the transitions between the oxidized and reduced forms of the catalyst.

(3) Apparently, the reaction follows the radical chain mechanism. The presence of acid sites on the surface is undesirable because it leads to a decrease in the yield of the target product (benzaldehyde) and occurrence of side reactions. It has been shown that the negative action of the acid sites of the catalyst surface can be to a significant extent prevented by the addition of basic substances (trioctylamine) to the system.

(4) The studied catalysts exhibit high benzaldehyde selectivity. In the vast majority of cases, further oxidation products (benzoic acid or its derivatives) are not formed during the reaction.

Table 3. Experiments on the oxidation of 1-phenylethanol over different catalysts. The flow rate of air is 100 mL/min

Catalysts	*T*, °C	Yield of acetophenone, wt %	Yield of styrene, wt %
Fe_2O_3	219–223	2	95
Fe_3O_4	202–203	3	93

Table 4. Experiments on the oxidation of alcohols with admixed trioctylamine over maghemite as the catalyst. The air flow rate of is 100 mL/min

Alcohols	Reaction *T*, °C	Yield of product, wt %
1-PhEtOH + trioctylamine	202	16 (acetophenone), 44 (styrene)
Benzyl alcohol + trioctylamine	205–210	56 (benzaldehyde)

REFERENCES

1. M. Shaikh, M. Satanami, and K. V. S. Ranganath, Catal. Commun. **54**, 91 (2014).
2. M. Shaikh, M. Sahu, P. K. Gavel, and K. V. S. Ranganath, Catal. Commun. **64**, 18 (2015).
3. F. Shi, M. K. Tse, M. M. Pohl, et al., Angew. Chem., Int. Ed. Engl. **46**, 8866 (2007).
4. C. Kamonsatikul, T. Khamnaen, P. Phiriyawirut, et al., Catal. Commun. **26**, 1 (2012).
5. M. V. Kulikova and S. N. Khadzhiev, Pet. Chem. **57**, 1173 (2017).
6. M. V. Kulikova, O. S. Dement'eva, A. E. Kuz'min, and M. V. Chudakova, Pet. Chem. **56**, 1149 (2016).
7. P. A. Chernavskii, B. S. Lunin, R. A, Zakaryan, et al., Instrum. Exp. Tech. **57**, 78 (2014).

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