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NICKEL-IRON MAGNETIC COMPOSITES IN THE ETHANOL CONVERSION

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Synthesized nickel - iron magnetic composites and the influence of precursor salts nature on the catalytic activity of the iron oxide in the ethanol conversion has been studied. It revealed that the use of ferric nitrate to produce iron oxide in the iron-nickel composite results in the formation of 20 vol.% hydrogen and 17 vol. % of ethylene, whereas the use of iron acetate leads to the formation of 23vol.% of aromatic hydrocarbons.
***Keywords**: magnetic composites, ethanol, conversion, temperature-programmed reduction.*

INTRODUCTION

Preparation of nano-sized transition metal of the iron group and its mutual two-component systems [1, 2] isone of the most challenging issues. Heightened interest in the subject came from primarily from characteristic features of the magnetic properties of both bulk and fine systems, including high values of the saturation magnetization withina relatively low magnetic field in conjunction with short-timemagnetization reversal together with variations in doping compositions magnitude of the coercive force [3, 4]. For this reason, highly dispersed (andnano-sized) powders of metals of the iron group seem to be rather promising for the production of magnetic materials, including subminiature junctions and elements, magnetic wire, magnetic fluids [5,6]. Also, transition metal (Fe, Co, Ni) nano-phase composites are widely used as catalysts in the utilization of solar energy systems [7], specifically,they are used in the composition of supported catalysts, systems of magnetic recording and storage of information, as well as power sources, etc.

The most popular method of producing nano-particles from magnetite is a liquid phase chemical condensation, which is based on the deposition of bi- and trivalent iron salts by concentrated aqueous ammonia solution [8].

The paper gives weight to the preparation of magnetic composites through the use of impregnation method of bases (carriers) for magnetite on-water absorption. Thus, nickel-iron magnetic composites produced are characterized by their magnetic properties. As a precursor of active components, nickel nitrate, iron nitrate or acetate are used. One of the factors influencing the activity of particle precursors is known to be the nature of salts used.

Hence, the paper focuses on the research into the effect of iron oxide precursor on its state in the composite and catalytic activity in the conversion of ethanol.

EXPERIMENTAL

To synthesize the nickel-iron magnetite, authors used the nitrate $Ni(NO_3)_2 \cdot 6H_2O$ "chem. pure", iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$"chem. pure", iron acetate 4-aqueous $Fe(CH_3COO)_2 \cdot 4H_2O$ and microspheres of oxide alumina gammamodificationγ-Al_2O_3. Composites were prepared through impregnating a carrier (alumina) by incipient wetness. Note that the heat treatment carried out at a temperature 400-500° C within 3 hours.

Test on catalytic activity of magnetic composites in the ethanol conversion has been carried out on an automated flow catalytic unit (FCU-1). The reaction products were identified with the help of the "Chromos GC-1000" apparatus using an absolute calibration method and a thermal conductivity detector.

Research into oxidized forms of the active phase of the magnetic composite made it possible to identify the temperature-programmed reduction of hydrogen (TPR- H_2). TPR has been performed at "101 USGA" installation consisting of gas preparation system with a tubular reactor furnace and a thermal conductivity detector. Hydrogen reduction was carried out by passing the gas mixture (5% H_2 and 95% Ar) through the reactor at 30 ml / min. Linear heating rate was 10^0C / min. Changes in the concentration of hydrogen in the stream has been monitored with the help of a thermal conductivity detector.

RESULTS AND DISCUSSION

It should be noted that the nickel-iron composites displayed their catalytic activity during the conversion of ethanol at a temperature range 200-400^{o}C and space velocity (SV) 30-60 h^{-1}. Figure 1 shows the results obtained at a reaction temperature of 350^{0}C and a SV of 60 hr^{-1} in the composite of 30 wt.% $NiO-Fe_2O_3 / Al_2O_3$.

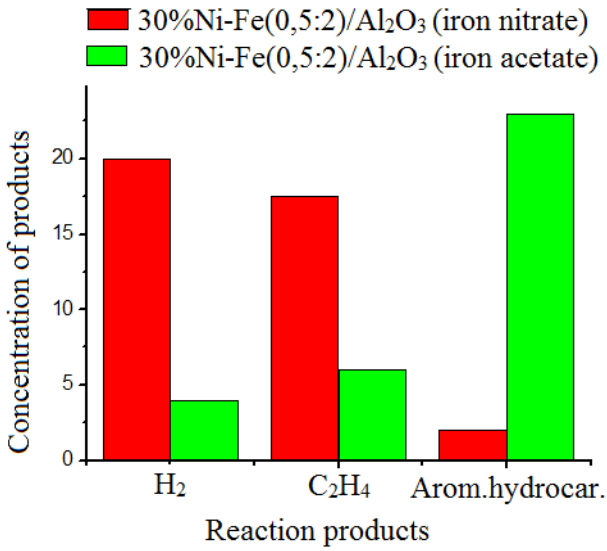

Figure 1. Effect of iron oxide precursor on its activity in the conversion of ethanol

Figure 1 shows that over the nickel-iron composite synthesized from iron nitrate ethylene and hydrogen is formed in the reaction products. The use of iron acetate as a precursor of the iron oxide catalyzes ethylene oligomerization reaction to produce aromatic hydrocarbons.

Effect of iron oxide precursor on phase changes in the composition has been examined by the TPR method. Note that TPR is an informative method for the analysis of oxidized forms of samples analyzed. Figure 2 shows the spectra of 30 wt.% $NiO\text{-}Fe_2O_3$ / Al_2O_3 synthesized from various iron salts.

The use of ferric nitrate as a precursor for 30 wt.% $NiO\text{-}Fe_2O_3$ / Al_2O_3catalyst is illustrative that the spectrum of TPV sample consists of three peaks with temperatures of 425, 570 and 780°C (Figure 2, spectrum 1). According to the literature [9], in case of application of iron oxides there is consistent recovery of $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$. The first peak can be attributed to the transition of $Fe_2O_3 \rightarrow Fe_3O_4$ (magnetite Fe_3O_4 is iron magnetite). The peak at 570°C corresponds to the formation of FeO ($Fe_3O_4 \rightarrow FeO$). Shoulder at 780°C can be attributed to the formation of metallic iron and / or iron aluminate.

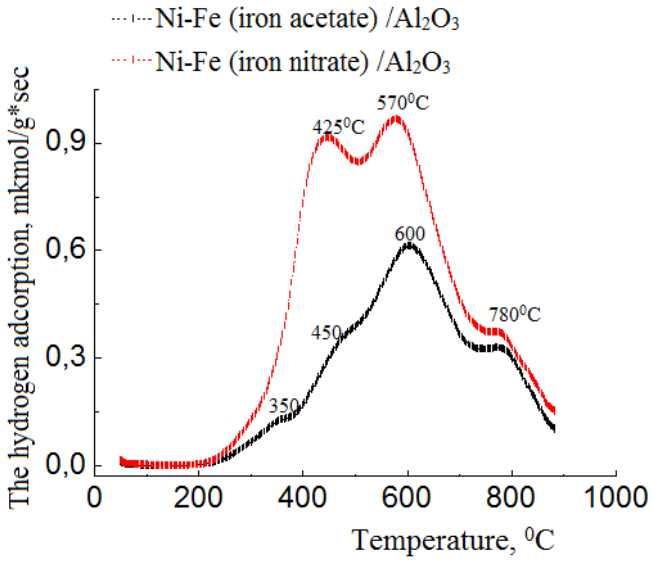

Figure 2.TPR spectra of 30 wt. % $NiO\text{-}Fe_2O_3$ / Al_2O_3synthesized from various iron salts

In case of 30 wt.% $NiO\text{-}Fe_2O_3$ / Al_2O_3 synthesized from iron acetate, there is rise in hydrogen absorption. Application of iron acetate as a precursor gives rise to a peak at 350°C, which relates to nickel oxide [10]. The emergence of a new phase in the low temperature area may catalyze the formation of aromatic hydrocarbons from ethanol. The peak with a maximum at 600° C is in line withpossible reduction of iron ions in the composition $NiFe_2O_4$.

The change of phase composition of magnetite under the influence of the reaction medium has been studied. Figures 3 and 4 show the TPR spectra of magnetite of 15 wt.% Fe_2O_3 / $Al_2O_3$and 30 wt.% $NiO\text{-}Fe_2O_3$ / Al_2O_3before and after the study into the ethanol conversion reaction, at 200-400°C range of temperatures.

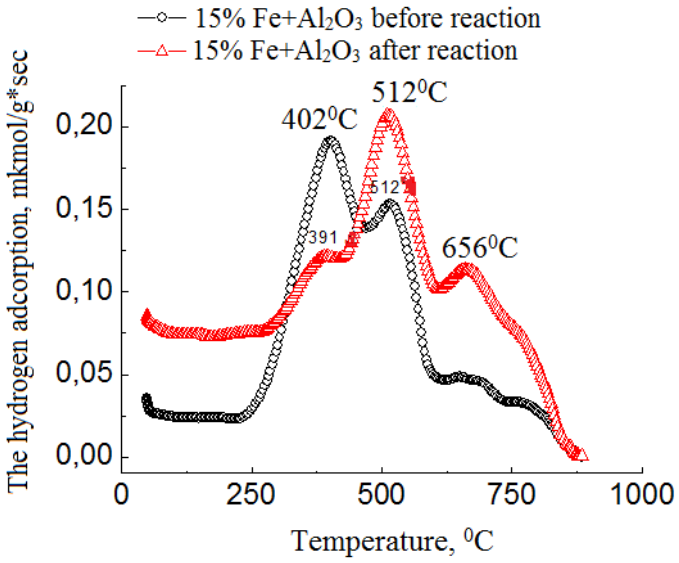

Figure 3.TPR spectra of 15 wt.%Fe_2O_3 / Al_2O_3composite

On the TPR range of 15 wt.% Fe_2O_3 / Al_2O_3 before reaction, four peaks are observed with maxima at 402, 512, 656 and 760^{0}C. The presence of peaks at 402, 512 and 656^{0}C faces the transition of $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$. Following the reaction under the influence of ethanol the nature of TPR spectra changes. The intensity peak pertinent to the Fe_3O_4 phase falls down while the intensity of FeO phase peak grows.

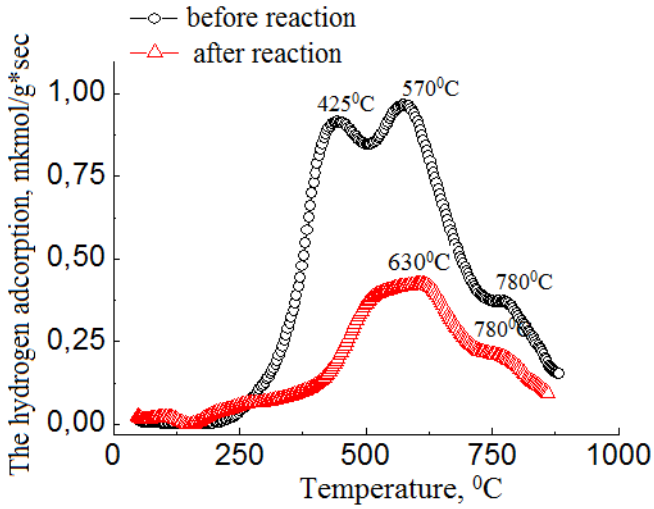

Figure 4.TPR spectra of 30 wt.% NiO-Fe_2O_3 / Al_2O_3composite

With the introduction of the nickel into iron composite, temperature maximum peak (T^1_{max}=402^{o}C, T^2_{max}=512^{o}C) shifts to higher temperature area (T^1_{max}=425^{o}C, T^2_{max}=570^{o}C), which may testify to the presence of dispersed particles. After the ethanol conversion reaction over the magnetite 30 wt.%NiO-Fe_2O_3 / Al_2O_3, there arise two peaks with maxima at 630 and

780°C. The changing the nature of the TPR spectrum NiO-Fe_2O_3 / Al_2O_3 composite after its research in ethanol conversion reaction indicates that a new phrase is formed under the influence of the reaction medium, which is active in the conversion of ethanol.

Thus, the study into the influence of a precursor (ferric nitrate and acetate) of iron oxide on catalytic changes of magnetic nickel-iron composites showed that the use of iron nitrate leads to the formation of 20 vol.% hydrogen and 17 vol.% ethylene. Application of iron acetate to produce iron oxide in the iron-nickel composite results in the formation of 23 vol.% aromatics. This is due to the formation of a new phase in the low-temperature (T_{max} = 350° C) area of TPR. TPR method determined that in case of iron oxide backed by aluminum oxide there can be observed consistent recovery: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$ and increased dispersion of composite particles with the addition of nickel oxide.

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НИКЕЛЬ - ЖЕЛЕЗНЫЕМАГНИТНЫЕ КОМПОЗИТЫ В КОНВЕРСИИ ЭТАНОЛА

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Синтезированы никель-железные магнитные композиты. Изучено влияние природы используемых солей предшественников на каталитическую активность оксида железа в конверсии этанола. Определено, что использование нитрата железа для получения оксида железа в составе никель-железного композита приводит к образованию 20 об.% водорода и 17 об.% этилена, тогда как применение ацетата железа - к образованию 23 об.% ароматических углеводородов.

Ключевые слова: *магнитные композиты, этанол, конверсия, термопрограммированное восстановление.*

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