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CHEMICAL KINETICS
AND CATALYSIS

Combined Hydrogenation of Carbon Oxides on Catalysts Bearing Iron and Nickel Nanoparticles

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Abstract—The reaction of the hydrogenation of a mixture of carbon oxides on ultradisperse powder (UDP) catalysts containing Fe and Ni nanoparticles and their bimetallic mechanical mixtures was investigated. It was established that the main reaction product on UDP Ni is methane, while the main products on the bimetallic systems are methane and ethylene. A synergetic effect was observed on the bimetallic catalyst under investigation. It was revealed that the hydrogenation of a mixture of carbon oxides proceeds through the stage of dissociative adsorption of both components, CO and CO_2. The olefin selectivity of the process was explained by the participation of different forms of adsorbed hydrogen ($H_I : H_{II}$) at the catalyst surface. It is assumed that the hydrogenation of carbon oxides on iron–nickel catalysts proceeds either through the jumpover effect or via hydrogen spillover.

Keywords: carbon oxide, carbon dioxide, iron, nickel, nanoparticles, catalysis, hydrogenation.
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INTRODUCTION

Amplification of the anthropogenic effect on nature has led to degradation of the quality of the environment and generated a number of the problems associated with it. Human impact on the atmosphere can be reduced by converting exhaust carbon oxides into useful products.

The numerous syntheses based on carbon oxides and hydrogen are of paramount practical and theoretical interest since they allow us to obtain useful organic compounds from elemental substances. A key role in these reactions is played by catalysis by transition metals that are capable of activating CO, CO_2, and H_2 molecules [1–4]. In the last two decades, a particular type of material has found wide application: ultradisperse powders (UDP). These are assemblies of metal, semiconductor, or dielectric particles whose dimensions lie in the range of 1 to 100 nm due to the uniqueness of many of their physicochemical properties [5–7].

The aim of this work was to investigate the possibility of producing olefins from a mixture of hydrogen and carbon mono- and dioxides, and to determine the influence of the method of production and the characteristics of disperse nickel and iron particles on their activity and selectivity relative to olefins.

EXPERIMENTAL

This work deals with the combined hydrogenation of carbon oxides (CO, 9 vol %; CO_2, 15 vol % in helium) and hydrogen in the component ratios equal to 1 : 2 and 1 : 4.

The hydrogenation of carbon oxides was studied in a flow catalytic unit at atmospheric pressure in a unit temperature range of 573 to 823 K. Analysis of the products was performed by chromatography using a column of stainless steel filled with Poropack Q at 393 K.

Nanopowders (UDP) of nickel were obtained from a nickel wire with a total content of impurities no greater than 0.1 % by evaporation and condensation in a flow of helium.

The phase composition of the catalysts was determined by X-ray diffraction on a DRON-7 diffractometer. It was established that the nickel nanopowder did not contain bulk oxide phases. According to XPES on an XSAM-800 spectrometer with magnesium or aluminum anodes, however, the near-surface layer of nickel catalysts contained nickel oxide. The structure of the particles was investigated by transmission electron microscopy on an EMV-100L apparatus. The nickel particles were multiply doubled polyhedra with a film of nickel oxide on their facets. Particles with diameters above 20 nm were faceted, while smaller ones were spherical. Nickel UDP was mixed with aluminum oxide. The specific surface area determined by low-temperature adsorption of nitrogen by BET was 40 m^2/g, and the mean size of the particles was 40 nm.

Iron UDP was obtained by the plasma–chemical decomposition of a mixture of vapors of metal pentacarbonyls with hydrogen, which served as the carrier and plasma-forming gas. Prior to the decomposition

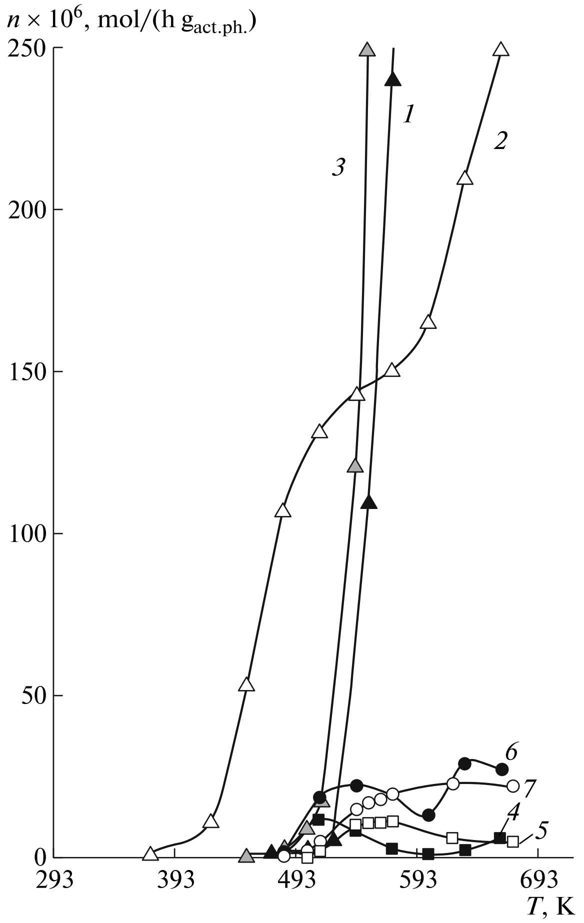

Fig. 1. Temperature dependence of the yield of hydrocarbons upon performing the reaction of hydrogenation in the ratio of $(CO + CO_2) : H_2 = 1 : 4$. (*1*) CH_4 on Ni/Al_2O_3; (*2*) Fe/Al_2O_3; (*3*) $Fe–Ni/Al_2O_3$; (*4*) C_2H_6 on Fe/Al_2O_3; (*5*) $Fe–Ni/Al_2O_3$; (*6*) C_2H_4 on Fe/Al_2O_3; (*7*) $Fe–Ni/Al_2O_3$.

of Fe pentacarbonyl, the required amount of aluminum oxide was placed into the plasma chemical reactor. The immediate matrixing of the metallic particles in the carrier during their formation led to the iron particles being fixed on the carrier.

X-ray studies revealed the presence of α and *g* phases of iron; FeO, Fe_3O_4, and Fe_2O_3 oxides in powders; and trace amounts of Fe_3C and free carbon. Chemical analysis of the iron powders showed that they contained up to 3% of free carbon and up to 2% of bound carbon, and were ~80% metal. According to the transmission electron microscopy data, the powders contained both separate particles and their agglomerates. The smallest particles (2–5 nm) were not faceted and formed large agglomerates. Particles with the sizes of 5–15 nm had fair faceting, while the larger particles with sizes of 15–25 nm were clearly faceted. The specific surface of iron-containing catalysts defined by the low-temperature adsorption of nitrogen by BET measured ~30 m^2/g, while the mean size of the particles was 20 nm.

All of the investigated monometallic catalysts were 5% Fe or Ni, while bimetallic catalysts were 10% active phase.

Before catalytic experiments, the catalyst samples were subjected to reductive processing in a hydrogen flow at 573 K and a bulk velocity of hydrogen of 1.5–2.0 l/h. In the gas phase, we registered methane, CO, and CO_2, due to the presence of carbon and oxygen-containing particles adsorbed during the production and storage of the samples. Attempts to completely remove the abovementioned particles from the sample surface were futile, although the yield of methane upon reduction decreased.

RESULTS AND DISCUSSION

Performing the reaction of hydrogenation by mixing carbon oxides at the ratio of $(CO : CO_2) : H_2 = 1 : 2$ and 1 : 4 on Ni UDP, Fe UDP, and their equivalent mixtures showed that the main product was methane (Fig. 1), the formation of which began at 403 K and increased as the temperature grew. In performing the reaction on iron-containing samples, were we detected ethylene and ethane among the reaction products along with methane (Fig. 1).

The qualitative and quantitative compositions of the products, along with the values of the calculated activation energies of methane formation and the preexponential factor logarithm, are listed in the table. From the table it follows that the addition of an equivalent amount of nickel to iron nanopowders substantially enhanced the specific catalytic activity (SCA) relative to the conversion of carbon oxide to methane and ethane: on the bimetallic catalyst, the maximum yield of hydrocarbons was several times higher than the amount of CH_4 obtained on samples containing only iron nanoparticles. Enhancement of the logarithm of the preexponential factor in the Arrhenius equation when performing the reaction in a dearth of hydrogen indicates a rise in the number of catalytically active centers of the surface, i.e., a synergetic effect was observed. The 28% increase in olefin selectivity (Fig. 2) in the range of low temperatures was also worthy of note.

The ratio of saturated and unsaturated hydrocarbons in the hydrogenation products was determined mainly by the amount of atomic hydrogen, which was able to migrate to the active centers of the surface, and by the structure of these centers [4, 8]. Upon the adsorption of hydrogen on metals able to dissolve it, there is a possibility that two forms will emerge on the surface [8, 9], one of which is associated only with one metal atom (H_I) while the other (H_{II}), being strongly adsorbed, is associated with several atoms. The formation of hydrocarbons occurs through the stage of the formation of active carbon; however, the olefin selec-

Qualitative and quantitative compositions of the products of hydrogenation of the mixture of carbon oxides at 623 K, the values of apparent activation energies of methane formation, and the logarithms of the pre-exponential factor

Catalyst	$(CO + CO_2) : H_2$	$n \times 10^6$, mol/(h $g_{act.ph.}$)			E_a, kJ/mol	$\ln K_0$
		CH_4	C_2H_4	C_2H_6		
Fe/Al_2O_3	1 : 2	110	6.35	0.72	57	2.90
	1 : 4	208	29.3	2.35	58	3.74
Ni/Al_2O_3	1 : 2	406	–	–	54	5.69
	1 : 4	605	–	–	121	15.5
$Fe\text{-}Ni/Al_2O_3$	1 : 2	300	28	13	87	9.83
	1 : 4	1448	12	6	71	5.96

Note: n is the yield of SCA products, E_a is the activation energy of methane formation.

tivity of the process is likely to be determined by the ratio of $H_I : H_{II}$ at the catalyst surface. An increase in the hydrogen concentration in the H_{II} form apparently enhances the yield of olefins.

Chromatographic analysis of the content of CO and CO_2 in the course of the reaction for all catalysts showed that at room temperature in the first 20 min of contact there was intensive adsorption of the mixture of carbon oxides with reduced surface. As time went on and the temperature gradually rose to 513 K, the amount of carbon oxides in the gaseous phase retained almost unchanged (Fig. 3).

As the temperature rose to the catalytic temperature ($T = 513$ K), it is natural to assume that the active carbon particles at the sample surface resulting from the dissociative adsorption of both carbon mono- and dioxides [1–3, 8] began to interact with hydrogen at low temperatures via the reactions

for CO: $CO \longrightarrow C_{ads} + O_{ads},$

for CO_2: $CO_2 \longrightarrow CO + O_{ads}$ (1)

$CO \longrightarrow C_{ads} + O_{ads}$ (2)

leading to the formation of methane, which was desorbed into the gas phase. The possibility arises from adsorption of carbon oxides at the vacant active centers, and the amount of CO and CO_2 in the gas phase is correspondingly reduced.

The shape of the curves that describe the temperature dependences of the content of carbon oxides in the reaction mixture both when performing the reaction in stoichiometric amounts and in a dearth of hydrogen did not differ appreciably for the studied catalysts, due probably to the involvement in the reaction of only carbon particles resulting from dissociative adsorption in the range of non-catalytic temperatures.

The mechanical mixing of ultradisperse powders of iron and nickel led to an increase in the content of carbon dioxide in the mixture (Fig. 3), due possibly to the reaction of CO disproportionation [8]: $2CO \longrightarrow CO_2 + C$.

A comparison of the experimental and literature data allows us to assume that there are several types of active centers on the surface of the bimetallic sample. One of these (presumably iron), on which hydrogen is adsorbed predominantly in molecular form [9, 10], is responsible for the formation of CH_2-radicals. On others (nickel) their hydrogenation to methane with atomic hydrogen takes place. In the opinion of the authors of [9], a weakening of Me–CO and Me–CO_2 bonds leads to an increase in olefin selectivity; at the same time, these bonds become stronger in passing from iron to nickel [9, 10].

The rise in the catalytic activity of nickel upon the addition of iron could be associated either with the diffusion of weakly bonded hydrogen (H_I) along the catalyst surface from Fe particles to Ni particles [4, 11–13] or with the jumpover effect when CH_2 radicals forming on iron centers are transferred to nickel through the gas medium, where their subsequent hydrogenation to methane with atomic hydrogen (H_I) occurs and ethylene is formed on iron [13, 14]. This could explain the increase in the catalytic activity of

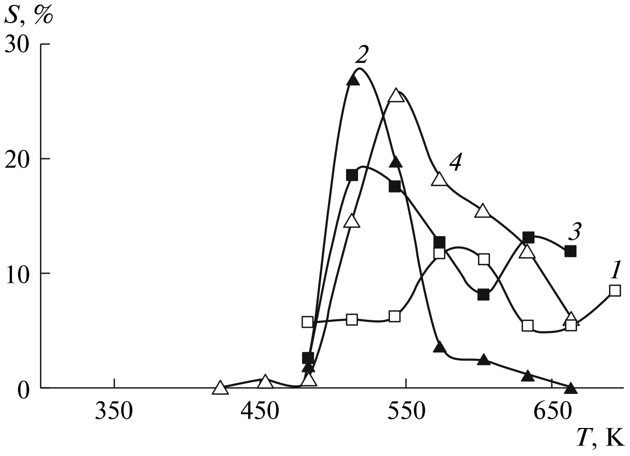

Fig. 2. Total olefin selectivity (S, %) at $(CO + CO_2) : H_2 = 1 : 2$ on Fe/Al_2O_3 (*1*), $Fe–Ni/Al_2O_3$ (*2*); at $(CO + CO_2) : H_2 = 1 : 4$ on Fe/Al_2O_3 (*3*), $Fe–Ni/Al_2O_3$ (*4*).

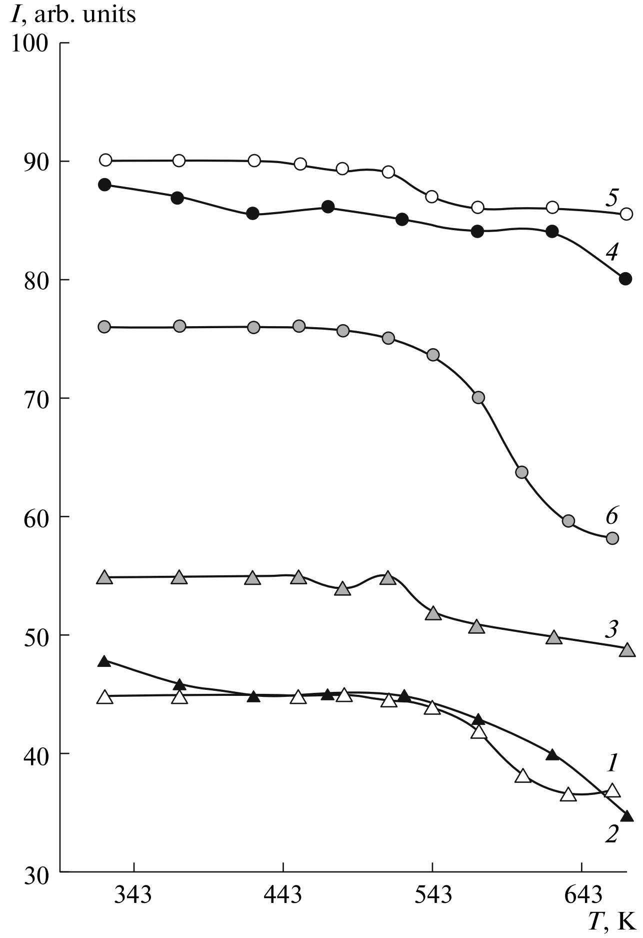

Fig. 3. Content of carbon mono- and dioxides in the near-surface layer during hydrogenation at $(CO + CO_2) : H_2 = 1 : 4$. (*1*) CO on Ni/Al_2O_3; (*2*) Fe/Al_2O_3; (*3*) Fe–Ni/Al_2O_3; (*4*) CO_2 on Ni/Al_2O_3; (*5*) Fe/Al_2O_3; (*6*) Fe–Ni/Al_2O_3.

the bimetallic iron–nickel sample, as compared to pure UDP nickel.

CONCLUSIONS

In studying the reaction of hydrogenation of a mixture of carbon oxides on ultradisperse powdered catalysts containing Fe and Ni nanoparticles and their mechanical mixture, it was established that the main product on UDP Ni is methane, while the main products on bimetallic systems are methane and ethylene. Based on the obtained results and the literature data, we may suggest the following course of the process that proceeds during the studied reaction. The olefin selectivity of the process is likely to be determined by the ratio $H_I : H_{II}$ at the surface catalyst. An increase in hydrogen concentration in the H_{II} form enhances the yield of olefins. Hydrogenation of the mixture of carbon oxides proceeds through the stage of dissociative adsorption of both components. Hydrogenation of carbon oxides on iron–nickel catalysts proceeds either via the jumpover effect or through hydrogen spillover. The removal of hydrogen in (H_I) form from the iron surface leads to an increase in strongly bonded hydrogen (H_{II}) and, as a result, to the growth in the olefin selectivity. On the explored bimetallic catalyst, we observed a synergetic effect (a rise in selective catalytic activity over that of monometallic catalysts).

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