New Approaches to the Preparation of Highly Efficient Chromium-Containing Oxide Catalysts for the Water Gas Shift Reaction

A. A. Khassin^{*a,b*}, T. P. Minyukova^{*a*}, M. P. Demeshkina^{*a*}, N. A. Baronskaya^{*a*}, L. M. Plyasova^{*a*}, G. N. Kustova^{*a*}, V. I. Zaikovskii^{*a*}, and T. M. Yurieva^{*a*}

^a Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia ^b Novosibirsk State University, Novosibirsk, 630090 Russia

> *e-mail: aakhassin@catalysis.ru* Received October 21, 2008

Abstract—It was found experimentally that the solutions of Cr^{3+} nitrate and the nitrates of other metals that are the constituents of Cr-containing catalysts can be prepared by dissolving a corresponding metal (for example, cast iron and electrolytic copper) in a solution of chromic anhydride and nitric acid to reach the quantitative reduction of Cr^{6+} without the formation of nitrogen oxides. Analogously, the oxidation of Fe^{2+} cations to Fe^{3+} coupled with the reduction of hexavalent chromium can be performed. The precipitation of Fe^{3+} , Cr^{3+} , and Cu^{2+} ions at a ratio of Fe : Cr = 9 and a concentration of Cu^{2+} to 20 at % can result in the formation of a partially hydrated oxide with the hydrohematite structure—a dispersed and highly defective oxide structure with a high specific surface area more than 300 m²/g and a higher thermal stability, as compared with the goethite phase (α -FeOOH). The dehydration of hydrohematite occurred at a noticeable rate at temperatures higher than 400°C. Hydrohematite promoted with copper cations exhibited high activity below 400°C; this can decrease the starting temperature of the adiabatic high-temperature WGSR to 300°C or below.

DOI: 10.1134/S002315840906007X

INTRODUCTION

It is well known that the specific catalytic activity of the majority of oxide catalysts correlates with the specific surface area, and the relationship between the catalytic activity and the specific surface area of an oxide is adequately described by a direct proportionality for many catalysts. One of the most well-known procedures for the preparation of oxides with a high specific surface area is the calcination of corresponding hydroxides or hydroxo carbonates at relatively low temperatures to provide only incomplete removal of $OH^{\scriptscriptstyle -}$ and $CO_3^{2\scriptscriptstyle -}$ anions. The structure of these anionmodified oxides contains a considerable amount of defects. In addition to a developed surface, the presence of defects stabilizes cations in a more preferable coordination to increase the mutual solubility of oxides. For example, it provides an opportunity to increase the solubility of Cu^{2+} cations in spinel [1] or zinc oxide [2].

The presence of admixture anions has also a considerable effect on the structure and catalytic properties of catalysts whose active components are metal particles formed as a result of reduction. In particular, the presence of admixture anions stabilizes nanosized metal particles to temperatures at which the complete dehydration of the system occurs. This can be due to the formation of oxo-hydroxo clusters containing support cations on the metal surface (for example, the formation of metal particles of size 4-8 nm stable to sintering up to 650-800°C upon the reduction of mixed oxo-hydroxo compounds of Co-Al, Co-Si, and Ni-Al-Si [3, 4]). In other cases, this was due to the retention of a defect oxide structure, which provided the epitaxial metal-support bond, for example, in catalysts prepared by the reduction of copper chromite or copper-zinc oxide. The epitaxial bond of copper metal and oxide particles was retained up to the temperatures at which the complete dehydration of the support oxide occurred [5, 6]. Note that, in many cases, the role of admixture anions is not limited by an increase in the stability of an active nanodispersed metal phase: the catalytic properties of active metal particles decorated with oxide clusters can be considerably different from the properties of undecorated particles. This phenomenon has been described in many scientific publications, and it is well known as the strong metal-support interaction.

The removal of admixture anions from the oxide structure results in the relaxation of structural defects, exothermal oxide crystallization, and, as a consequence, a dramatic decrease in the specific surface area or, in some cases, in the decomposition of a mixed oxide into individual oxides, that is, in a dramatic change in the catalyst structure. In this context, it seems very important to increase the thermal stability of anion-modified oxides, which are catalysts or catalyst precursors. The stability of admixture anions as oxide constituents can be increased by introducing promoter cations forming stable hydroxo compounds or partially hydrated oxides, such as Mg^{2+} , Al^{3+} , and Zr^{4+} .

The Cr³⁺ cation is one of the most effective promoters, which improve the stability of OH- anions in oxide structural defects. The efficiency of stabilization of hydroxyl groups in the defects of chromium-containing oxides can be illustrated by a special mechanism of reduction of copper cations from well-crystallized copper chromite (CuCr₂O₄), a mixed copper and chromium oxide with the tetragonally distorted spinel structure. The reduction of this compound in a flow of hydrogen is accompanied by only the partial removal of oxygen anions with the formation of water molecules, and it mainly occurs by hydrogen oxidation to protons. The resulting protons are absorbed by the oxide to replace reduced copper cations in its structure as OH⁻ groups, as found recently with the use of neutron inelastic scattering [7]. The structural dehydration of reduced copper chromite, which is accompanied by the formation of chromium oxide and the rupture of an epitaxial bond between copper metal particles and an oxide support, occurs only at temperatures higher than 450°C. The absorption of hydrogen in the course of reduction of copper cations was also observed previously in other copper oxides, for example, containing Zn^{2+} and Al^{3+} cations [8]. However, the steps of hydrogen absorption and dehydration occur at very different temperatures only in the reduction of copper chromite.

The efficiency of catalyst promotion with chromium cations in order to increase the specific activity and thermal stability of catalysts was demonstrated by long-factor experience in the development and operation of Fe-Cr catalysts for high-temperature WGSR, Cu–Zn–Al–Cr catalysts for low-temperature WGSR, Ni–Cr catalysts for hydrogenation, etc. However, along with undoubted advantages, chromiumcontaining catalysts have a number of disadvantages. First of all, this is due to the high toxicity of Cr(VI) compounds, which poses rigid requirements on the preparation of these catalysts: the Cr(VI) content of the catalyst should be no higher than 0.05 wt %. In spite of these requirements, many chromium-containing catalysts are currently manufactured with the use of chromic anhydride as a raw material, in particular, using the wet mixing method. This method cannot ensure the absence of hexavalent chromium in the catalyst and the complete and uniform interaction of chromium cations with other catalyst components (i.e., the formation of a homogeneous oxide system). The procedures used to prepare a homogeneous catalyst mass with the complete inclusion of chromium cations into the mixed oxide structure (coprecipitation of cations and homogeneous supporting-precipitation procedure [9]) imply the use of salts of chromium(III) and other metals, which are catalyst constituents, for example, nitrates, as raw materials. Unfortunately, these raw materials are expensive so that catalysts prepared by coprecipitation cannot compete in factors of price with less expensive but more hazardous catalysts prepared with the use of chromic anhydride.

Because of the above, the preparation of the solutions of Cr^{3+} and other metal (including Fe³⁺, Cu^{2+} , and Ni²⁺, which are catalyst constituents) nitrates from inexpensive and available raw materials is a problem of considerable current interest. In this study, corresponding metals, chromic anhydride, and nitric acid were chosen as these raw materials. In this work, we considered the preparation of nitrate solutions without the release of higher nitrogen oxides and the preparation of catalysts by the coprecipitation of cations from the resulting solutions and studied the catalytic properties of these catalysts. For the Fe–Cr(–Cu) oxo– hydroxide system, the preparation of partially hydrated Fe–Cr oxide with the hydrohematite structure, which exhibited high activity in the range of 300–400°C, was demonstrated.

EXPERIMENTAL

Catalyst Preparation

P2 pig iron of second category with respect to sulfur, chromic anhydride (CrO₃), copper oxide (CuO), and a solution of nitric acid were used for the preparation of Fe–Cr and Fe–Cr–Cu catalysts. Electrolytic copper, chromic anhydride, zinc oxide, pseudoboehmite, AlOOH, and a solution of nitric acid were used for the preparation of Cu–Zn–Al–Cr-containing samples.

Hydroxo compounds with specified compositions were precipitated from prepared working solutions with a solution of sodium carbonate. The precipitate was washed by decantation. The catalyst mass was dried and calcined in a flow of nitrogen at 200–300°C.

The hydroxo compounds of iron rather than carbonates are formed on precipitation from a solution of iron and chromium nitrates because of hydrolysis. Depending on the composition of this solution and the conditions of precipitation, phase-homogeneous hydroxo compounds with the structures of goethite and hematite (frequently referred to as 2-line ferrihydrite, see the discussion below) or Fe_2O_3 with the hematite structure can be obtained. An analysis of published data on the properties of the hydroxo compounds of iron and procedures for their preparation [10, 11] made it possible to develop procedures for the preparation of iron—chromium and iron—chromium copper hydroxo compounds with the goethite and hydrohematite structures. The preparation of a hydroxo compound with the goethite structure is based on the formation of α -FeOOH upon the oxidative hydrolysis of iron(II). Therefore, in the dissolution of cast iron, conditions were chosen to obtain a solution of a bivalent iron salt, which was subsequently oxidized by precipitation with atmospheric oxygen blown through the solution. To prepare samples with the hydrohematite structure, a solution of trivalent iron nitrate was used. If necessary, copper was introduced into the prepared solutions.

The concentration of chromium(VI) in solutions was determined by chemical analysis (qualitatively, with the use of phenylanthranilic acid as an indicator for chromium or, quantitatively, by titration with Mohr's salt) or spectrometric analysis (based on absorption line intensities at 22 500 and 28 500 cm⁻¹). Extracts from catalysts calcined in a flow of an inert gas were also analyzed. The sensitivity of the used methods to Cr(VI) was $<10^{-3}$ wt %.

Phase analysis was performed on D-500 (Siemens) and D-8 (Bruker) X-ray diffractometers with the use of filtered Cu K_{α} radiation (graphite monochromator in the reflected beam).

The IR spectra were measured in the range of 350–4000 cm⁻¹ using a Bomem MB-102 spectrometer. Catalyst powders were diluted in KBr or CsI matrices and pressed as pellets.

The differential thermal analysis (DTA) of sample dehydration was performed on a Netzsch STA-409 thermal analyzer in a flow of argon at a heating rate of 10 K/min.

The electron-microscopic study of the samples was performed on a JEM-2010 transmission electron microscope (JEOL) (resolution, 1.4 Å; accelerating voltage, 200 kV). The samples were supported onto perforated carbon substrates from alcohol suspensions subjected to ultrasonic dispersion.

Catalytic Tests

The catalytic activity of the samples in the water gas shift reaction was determined in a catalytic flow system over a temperature range of $240-480^{\circ}$ C at a nearatmospheric pressure. The tests were performed in a reaction mixture containing 12 vol % CO, 5.5 vol % CO₂, and 82.5 vol % H₂ at a steam : gas ratio of 0.6– 0.9 on a catalyst fraction of 0.25–0.50 mm mixed with quartz glass of the same particle size in a ratio of 1 : 1 and on heat-conducting catalyst plates as disc segments of size 25 × 2.5 mm (the preparation procedure and testing of heat-conducting catalyst plates was described in detail elsewhere [12]). The weight of the catalyst fraction was varied from 0.05 to 0.50 g. The space velocity of the reaction mixture was varied in the range of $400-40000 \text{ h}^{-1}$.

Before the tests, the catalyst was activated in nitrogen to 200°C at a heating rate of 5 K/min and then in a moist gas mixture at $320-330^{\circ}$ C for 1 h at a heating rate of 2 K/min.

Catalytic Data Processing

The initial catalytic experimental data contained information on the composition of the starting reaction mixture (SRM) and final reaction mixture (FRM) after a flow reactor. The composition of the starting and final reaction mixtures was determined by chromatography with the use of a flame-ionization detector. After separation on a chromatographic column with activated carbon 0.5 m in length, carbon oxides were methanized in a reactor with a commercial Ni–Cr catalyst before analysis.

To evaluate the characteristics of specific catalytic activity (for example, the rate constants of catalytic reactions), it was necessary to chose a kinetic model of the process. A few rate equations have been described in the literature; among them, Eq. (1), which corresponds to the model of a stepwise reaction on the assumption that the rates of the steps of CO oxidation and hydrogen reduction from water are approximately equal, is most accurate and reliable [13]:

$$W = k_{\rightarrow} \left(\frac{P_{\rm CO} P_{\rm H_2O} - K_{\rm p}^{-1} P_{\rm CO_2} P_{\rm H_2}}{A P_{\rm H_2O} + P_{\rm CO_2}} \right).$$
(1)

At the same time, Semenova et al. [14] recommended the use of the following simplified rate equation, which corresponds to first order of reaction with respect to CO, over a wide range including industrial catalyst operation conditions:

$$W = k_{\to} \left(P_{\rm CO} - K_{\rm p}^{-1} \frac{P_{\rm CO_2} P_{\rm H_2}}{P_{\rm H_2O}} \right).$$
(2)

The difference between Eqs. (1) and (2) consists in the factor

$$\left(\frac{P_{\rm H_2O}}{AP_{\rm H_2O} + P_{\rm CO_2}}\right),\tag{3}$$

which depends on the reaction mixture composition, the temperature (because the parameter *A* depends on temperature in accordance with the Arrhenius equation with $E_a = 36.7$ kJ/mol), and the nature of catalysts.

The use of simplified kinetics (2) facilitates data processing, but it can lead to errors for the following two reasons:

(1) The dependence of factor (3) on mixture composition in solving an integral rate equation for a flow reactor (integration over a catalyst bed) is ignored.

(2) The temperature dependence of factor (3) is ignored; because of this, the apparent activation energy is much different from the true activation energy of a rate-limiting step.

An analysis of changes in factor (3) under changes in the composition of the reaction mixture in the region of CO conversion to 40%, which was reached in

| Half reaction | Standard elec- trode potential, V |
|---|--------------------------------------|
| $NO_3^- + 2H^+ + e^- = NO_2 + H_2O$ | 0.775 |
| $NO_3^- + 3H^+ + 2e^- = HNO_2 + H_2O$ | 0.930 |
| $NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$ | 0.957 |
| $2NO_3^- + 10H^+ + 8e^- = N_2O + 5H_2O$ | 1.116 |
| $2NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O$ | 1.244 |

Table 1. Standard electrode potentials of redox reactions with the participation of the nitrate anion

our experiments, demonstrated that the integration of the rate equation over the reactor length ignoring the dependence of factor (3) on the composition of the mixture introduced an error of no higher than 20 rel. % or less than 10 rel. % in the region of high temperatures. On the other hand, the use of accurate kinetics (1) for calculating constants requires experimental data on the concentrations of all components in the starting and final reaction mixtures. Each of these experimental values is determined with an error of ~5–7 rel. %; because of this, the introduced error can be as high as 15%.

The activation energy determined from the true reaction constants, which can be determined from Eq. (1), is considerably different from the apparent activation energy estimated from data using simplified kinetics (2). However, for the purpose of this work, the apparent activation energy at a near-industrial mixture composition rather than the true activation energy of reaction is of crucial importance.

Because of this, in this work, we used simplified kinetic model (2) and characterized the specific activity of catalysts in the WGSR by the apparent rate constant of the forward reaction, which was evaluated with consideration for the reversibility of reaction assuming first order with respect to CO in accordance with the equation

$$k_{\rightarrow} = \ln \left(\frac{C_{\rm CO-humid} - C_{\rm CO-eq}}{C_{\rm CO-FRM} - C_{\rm CO-eq}} \right) \frac{1}{\tau}, \, s^{-1}, \qquad (4)$$

where $C_{\text{CO-moist}}$ is the mole fraction of CO in the humid initial reaction mixture, $C_{\text{CO-FRM}}$ is the mole fraction in the reaction mixture at the reactor outlet, and $C_{\text{CO-eq}}$ is the equilibrium mole fraction of CO at the reaction temperature.

RESULTS AND DISCUSSION

Preparation of the Nitrate Solutions of Cr^{3+} and Other Metals That Are Catalyst Constituents (Fe^{3+} , Cu^{2+} , and Ni^{2+})

Dissolution of metals in the solutions of nitric acid and chromic anhydride. It is well known that, in the reactions of iron metal, nickel metal, or copper metal with nitric acid, the metal is oxidized to the state M^{2+} with the formation of a corresponding nitrate solution and gaseous nitrogen compounds in accordance with the reactions

 $2M+6HNO_{3} \longrightarrow 2M(NO_{3})_{2}+NO_{2}\uparrow + NO\uparrow + H_{2}O; (I)$ $3M+8HNO_{3} \longrightarrow 3M(NO_{3})_{2}+2NO\uparrow + 4H_{2}O; (II)$ $4M+10HNO_{3} \longrightarrow 4M(NO_{3})_{2}+N_{2}O\uparrow + 5H_{2}O; (III)$ $5M+12HNO_{3} \longrightarrow 5M(NO_{3})_{2}+N_{2}\uparrow + 6H_{2}O; (IV)$ $4M+10HNO_{3} \longrightarrow 4M(NO_{3})_{2}+NH_{4}NO_{3}\uparrow + 3H_{2}O. (V)$

In this case, reaction (I) occurs through the formation of nitrous acid

 $M + 3HNO_3 \rightarrow M(NO_3)_2 + HNO_2 + H_2O$, (VI) which decomposes with the formation of higher nitrogen oxides by reaction (VII) or is further reduced to result in the occurrence of the process in accordance with overall reactions (II)–(V).

$$2HNO_2 \rightarrow NO^{\uparrow} + NO_2^{\uparrow} + H_2O.$$
 (VII)

A decrease in the concentration of nitric acid and the reaction temperature resulted in a decrease in the rate of reaction (VII) and a further decrease in the oxidation state of nitrogen. In this connection, a metal can be dissolved to nitrate without the formation of higher nitrogen oxides by properly choosing the temperature and nitric acid concentration.

Note that iron is converted into corresponding Fe^{2+} salts only under the action of dilute inorganic acids. Under the action of 13 wt % HNO₃, iron metal forms a mixture of iron(II) and iron(III) nitrates, whereas concentrated nitric acid (25–30 wt %) reacts with iron on heating in accordance with the equations

 $Fe + 4HNO_3 = Fe(NO_3)_3 + NO\uparrow + 2H_2O;$ (VIII) $Fe + 6HNO_3 = Fe(NO_3)_3 + 3NO_2\uparrow + 3H_2O.$ (IX)

Table 1 summarizes the standard electrode potentials of the corresponding half-reactions of nitrogencontaining anion reduction [15].

It is well known that nitrous acid is oxidized to nitric acid in the presence of an oxidizing agent in the system; for example, this occurs in the presence of hydrogen peroxide:

$$NO_2^- + H_2O_2 = NO_3^- + H_2O_2$$
 (X)

It is also well known that the standard electrode potential of the half-reaction

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$$
 (XI)

is 1.333 V versus the standard hydrogen electrode. Comparing this value with potentials in Table 1, we note that the reduction of chromium coupled to the oxidation of HNO_2 to NO_3^- is thermodynamically more preferable than the formation of gaseous nitrogen oxides even at a very low concentration of dichromate anions. Thus, we believe that the dichromate anion is an efficient oxidizing agent for the nitrite anion in accordance with the reaction

$$3 \text{ HNO}_2 + \text{Cr}_2 \text{O}_7^{2^-} + 5 \text{ H}^+$$

= 2 Cr³⁺ + 3 NO₃⁻ + 4 H₂O. (XII)

KINETICS AND CATALYSIS Vol. 50 No. 6 2009

Consequently, a metal can be dissolved in a solution of nitric acid and chromic anhydride in accordance with the overall reaction

$$3M + H_2Cr_2O_7 + 12HNO_3$$

= 3M(NO_3)_2 + 2Cr(NO_3)_3 + 7H_2O (XIII)

to obtain a solution of M^{2+} and Cr^{3+} nitrates without the formation of nitrogen oxides.

Note that the redox reaction between a metal and the dichromate anion does not occur at a noticeable rate in the absence of nitric acid (for example, in a solution of acetic acid and chromic anhydride). That is, nitric acid is a catalyst for the interaction of a metal with the dichromate anion. The catalytic cycle of overall reaction (XIII) consists of two redox steps. At initial step (XIV), the oxidation of a metal in an acidic medium is accompanied by the reduction of the $NO_3^$ anion (see also reaction (VI)):

$$M + NO_3^- + 3H^+ \longrightarrow M^{2+} + HNO_2 + H_2O_2$$
 (XIV)

At the second step, which is described by Eq. (XII), nitrous acid reduces the chromium of the dichromate anion to Cr^{3+} to be oxidized to the nitrate ion and to close the catalytic cycle.

Our experiments on the dissolution of nickel metal and copper metal in a solution of nitric acid and chromic anhydride demonstrated that the rate of reaction (XIII) was much higher than the rate of metal dissolution in reactions (I)-(V) at sufficiently low values of pH (lower than -0.5) and a low temperature (e.g., at room temperature). Thus, Fig. 1 shows experimental data on the cationic composition of solution upon the complete dissolution of copper metal powder in a solution of nitric acid and chromic anhydride at a constant solution temperature of 22°C. The concentration of nitric acid was varied from 8 to 17.5 wt %. The initial amounts of chromic anhydride and copper metal strictly corresponded to the stoichiometry of reaction (XIII), that is, Cu : Cr = 3 : 2. Upon completion of the reaction, the concentrations of Cu^{2+} and Cr^{3+} cations and $Cr_2O_7^{2-}$ anions in solution were determined. Figure 1 shows the results as the dependence of the $3Cr^{3+}/(2Cu^{2+}-3Cr^{3+})$ ratio on the pH of solution.

The above ratio between the concentrations of cations in the final solution corresponds to the ratio of the amount of copper (n_{Cu}) dissolved by reaction (XIII) to the amount of copper dissolved without the participation of chromic anhydride, that is, by reactions (I)–(V):

$$\frac{n_{\mathrm{Cu},(13)}}{n_{\mathrm{Cu},(1-5)}} = \frac{n_{\mathrm{Cu},(13)}}{n_{\mathrm{Cu},\Sigma} - n_{\mathrm{Cu},(13)}}$$

$$= \frac{3/2n_{\mathrm{Cr},(13)}}{n_{\mathrm{Cu},\Sigma} - 3/2n_{\mathrm{Cr},(13)}} = \frac{3[\mathrm{Cr}^{3+}]}{2[\mathrm{Cu}^{2+}] - 3[\mathrm{Cr}^{3+}]}.$$
(5)

It can be clearly seen that, at pH < -0.5, more than 95% of dissolved copper was oxidized by the reduction of hexavalent chromium. In this case, note that the

KINETICS AND CATALYSIS Vol. 50 No. 6 2009

 $3[Cr^{3+}]/(2[Cu^{2+}] - 3[Cr^{3+}])$

Fig. 1. Dependence of the ratio between the concentrations of Cr^{3+} and Cu^{2+} cations in solution on the pH of a solution of nitric acid and chromic anhydride.

release of higher nitrogen oxides was not observed in the course of dissolution. This fact can be explained by a low steady-state concentration of nitrous acid, which is an intermediate in overall reaction (XIII).

If we consider processes occurring with the participation of nitrous acid, the concentration ratio shown in Fig. 1 corresponds to the ratio of the rate of reduction of the dichromate ion by reaction (XII) to the sum of the rates of nitrous acid decomposition by reaction (VII) and interaction with copper metal, which leads to transformations described by reactions (II)–(V). The reduction of dichromate occurs with the participation of protons; consequently, its rate depends on the pH of solution, whereas the rate of decomposition of nitrous acid is independent of pH. Consequently, the above ratio would be expected to increase with decreasing pH. This is obviously supported by data in Fig. 1. In accordance with our experimental data, the dependence on the pH of solution is expressed by the relationship

 $\log \{3 [Cr^{3+}]/(2[Cu^{2+}] - 3[Cr^{3+}])\} = -0.37 - 3 \text{ pH.}(6)$ The third order of reaction (XII) with respect to the concentration of H⁺ in solution may be indicative of the mechanism of this step; however, currently available data are insufficient to hypothesize this mechanism.

The results obtained show that the solutions of nitric acid and chromic anhydride are promising for the preparation of Cr^{3+} and other metal nitrate solutions by interactions accompanied by the release of nitrogen oxides in an insignificant amount. Another important test for the applicability of this method to the preparation of the stock solutions of nitrates consists in the completeness of the reaction of hexavalent chromium.

Note that, if the starting metal is taken in an excess, the occurrence of reaction (XIII) results in the com-



Fig. 2. The temperature dependence of the rate constant of the forward reaction in the Arrhenius coordinates for Cu–Zn–Al–Cr catalysts prepared by (1) coprecipitation and (2) mixing. Reaction conditions: 12% CO and 5.5% CO₂ in the dry initial reaction mixture; steam/gas = 0.9; and P = 1.5 atm.

plete reduction of hexavalent chromium because the thermodynamic equilibrium is strongly shifted to the formation of a solution of Cr^{3+} and M^{2+} nitrates and the standard Gibbs potential of reaction at 25°C is very high $(-\Delta_{(13, Ni)}G_{298}^0 > 900 \text{ kJ/mol})$. We failed to detect hexavalent chromium in solution using available analytical techniques. After completion of conversion in accordance with reaction (XIII), the subsequent dissolution of the remaining metal occurred by reactions (I)–(V) in accordance with chosen conditions (nitrate anion concentration, pH, and temperature).

Oxidation of Fe^{2+} cations to Fe^{3+} in the solutions of nitric acid and chromic anhydride. The oxidation of iron metal in a solution of weak nitric acid under conditions that prevent the formation of higher nitrogen oxides occurs only to the oxidation state of Fe^{2+} . The further oxidation of Fe^{2+} to Fe^{3+} can be performed by interaction with air in accordance with the reaction

 $2Fe^{2+} + 1/2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + H_2O.$ (XV) However, the dichromate anion can also be used as

However, the dichromate anion can also be used as an oxidizing agent:

$$6Fe(NO_3)_2 + H_2Cr_2O_7 + 12HNO_3$$

= 6 Fe(NO_3)_3 + 2Cr(NO_3)_3 + 7H_2O. (XVI)

Analogously to reaction (XIII), reaction (XVI) occurs rapidly, and the standard affinity is high $(-\Delta_{16}G_{298}^0 = 325.3 \text{ kJ/mol})$; this provides the complete interaction of Fe²⁺ and hexavalent chromium.

Thus, the use of chromic anhydride as an oxidizing agent in a solution of nitric acid allows us to dissolve copper, nickel, or iron and to obtain the solutions of Cr^{3+} and corresponding metal (Cu^{2+} , Ni^{2+} , or Fe^{3+}) nitrates without the formation of a detectable amount of nitrogen oxides. The solution of chromic anhydride and nitric acid can also be used for the oxidation of the Fe^{2+} nitrate to the Fe^{3+} nitrate and the preparation of a solution of $Cr(NO_3)_3$ and $Fe(NO_3)_3$. Nitric acid is a catalyst for the interaction of metals or Fe^{2+} cations with the dichromate anion. A decrease in pH considerably increases the contribution of reaction (XIII) to metal oxidation. This method for the preparation of nitrate solutions for the subsequent preparation of catalysts has a number of serious advantages:

(1) The use of inexpensive and available raw materials—a metal, chromic anhydride, and nitric acid.

(2) The absence of considerable nitrogen oxide emissions.

(3) The complete reduction of hexavalent chromium.

(4) The low concentrations of sulfur and other impurities. The concentrations of impurities depend on the purity of the metal used. For example, P2 pig iron of first and second category with respect to sulfur contains no more than 0.02 wt % sulfur, which completely meets all of the requirements imposed on iron-containing catalysts.

Because of these advantages, methods for the preparation of catalysts with the use of nitrate solutions, for example, a coprecipitation method, can be implemented on a commercial scale.

Cu–Zn–Al–Cr Catalyst Prepared by Coprecipitation for the Low-Temperature Conversion of CO

Figure 2 clearly illustrates that a coprecipitation method is preferable to a wet mixing method, which is commonly used in industrial practice for the preparation of catalysts for the low-temperature conversion of CO (such as the NTK-4 catalyst). This figure shows the temperature dependence of the rate constants of reactions measured in the kinetic region for a Cu–Zn-Al-Cr catalyst prepared by coprecipitation from a solution of nitrates and an analog of a commercial Cu–Zn-Al-Cr catalyst prepared by mixing. The samples were calcined at 350°C in an inert gas flow.

From Fig. 2, it follows that the catalyst prepared by coprecipitation was more active than the catalyst prepared by mixing by a factor of 1.5-2.5. This is most likely due to the complete involvement of chromium and copper in the composition of a mixed oxide and the homogeneous phase composition of the catalyst.

Fe-Cr and Fe-Cr-Cu Catalysts Prepared by a Coprecipitation Method for the High-Temperature WGSR

Preparation conditions, including temperature, the pH of the mother liquor, the Fe^{3+}/Fe^{2+} ratio in the initial nitrate solution, and precipitate aging conditions and time, affect the phase composition and



Fig. 3. Diffraction patterns of the catalyst samples (*1*) FeCr-1, (*2*) FeCrCu-2, and (*3*) FeCrCu-3 and (*4*) a commercial Fe–Cr–Cu catalyst for high-temperature WGSR and the model diffraction patterns of (*5*) (ICDD 00-033-0664) hematite α -Fe₂O₃ and (*6*) (ICDD 00-029-0713) goethite α -FeOOH structures.

structure of the precipitate prepared by the interaction of a solution of Cr^{3+} and iron nitrates with a solution of sodium carbonate. It was found that catalyst samples containing three oxo hydride phases with various degrees of Fe–Cr oxide hydration can be obtained by varying preparation conditions. To study the structure and catalytic properties of these phases, we prepared three corresponding phase-homogeneous samples FeCr-1, FeCr-2, and FeCr-3 with the cationic ratio Fe³⁺ : Cr³⁺ = 90 : 10 and analogous samples with the cationic ratio Fe³⁺ : Cr³⁺ : Cu²⁺ = 88 : 8 : 4. Figures 3 and 4 show the diffraction patterns and IR spectra of samples. Note that the diffraction patterns and IR spectra of Fe–Cr samples and corresponding Fe–Cr– Cu samples promoted with copper are very similar.

The structure of samples FeCr-1 and FeCrCu-1 is similar to the structure of α -Fe₂O₃ (hematite). According to published data [16], peaks at 324, 462, 561, and 633 cm⁻¹ observed in the IR spectra are characteristic of α -Fe₂O₃, and the positions of the X-ray diffraction lines of sample FeCr-1 closely correspond to data given in the ICDD database for hematite and somewhat shifted to greater angles for the sample promoted with copper. This is unambiguously related to the decrease in the unit cell parameters due to the presence of Cu²⁺ cations in the oxide structure. Note that the commercial catalyst for the high-temperature WGSR is a mixed Fe-Cr-Cu oxide with the hematite structure and with a considerably greater admixture of a spinel phase than that in sample FeCrCu-1, and it contains a graphite phase introduced into the catalyst to facilitate pelletization.

The samples FeCr-2 and FeCrCu-2 have the structure of α -FeOOH (goethite). In the IR spectrum,



Fig. 4. IR spectra of catalyst samples: (*1*) FeCr-1, (*2*) FeCrCu-2, and (*3*) FeCrCu-3.

absorption bands at 289, 370 (shoulder), 416 (shoulder), 472, 617 (shoulder), 893, and 806 cm⁻¹ were observed; they are consistent with published data [17] on the IR spectrum of goethite. Absorption bands at 1336, 1384, 1465, and 1633 cm⁻¹ are related to the vibrations of CO_3^{2-} and NO_3^{-} ions and the deformation vibrations of water. A shift in the positions of diffraction maximums and difference from data (ICDD 00-029-0713) on intensity distribution should be associated with the presence of Cr^{3+} and Cu^{2+} cations in the structure.

The structure of samples FeCr-3 and FeCrCu-3 is essentially different from the structures discussed above. These samples are poorly crystallized. The diffraction patterns are described by two broad diffusion lines in the range of 20 angles of 25° –49° and 55° –70° with maxima at $2\theta_1 = 35.0^\circ \pm 0.1^\circ$ and $2\theta_2 = 61.6^\circ \pm$ 0.1°. Two halos in the diffraction pattern can characterize a two-layer hexagonal packing of anions, in the octahedral or tetrahedral voids of which cations are arranged. Correspondingly, in factors of a hexagonal system, the indices (002) and (110) can be ascribed to the diffraction maximums; on this basis, the following unit cell parameters can be calculated: $a = 2.98 \pm$ 0.01 Å and $c = 5.04 \pm 0.01$ Å. According to the closest packing rule [18], the closest hexagonal packing of ions has the ratio $\frac{c}{c} = 1.63$. For the test sample, this ratio is 1.69, which suggests a disorder in the layers of this structure.

The IR spectra of these samples exhibited absorption bands at wavenumbers of 330, 462, 578, 710 (shoulder), and 920–930 cm⁻¹, which are close to absorption bands reported by Wolska [19] for the structure of a partially hydrated Fe³⁺ oxide—hydrohematite. The spectra also contained absorption bands in the region of 1340–1540 cm⁻¹ due to the vibrations of CO_3^{2-} , OH⁻, and NO₃⁻ anions and an absorption band at 1630 cm⁻¹ corresponding to the deformation vibrations of water.

The physicochemical properties of iron oxides with the hematite and goethite structures are well studied (e.g., see [11]). It is well known that hematite is reduced to the Fe(Fe,Cr)₂O₄ oxide with the magnetite structure under the reaction conditions of the WGSR [20, 21]. At a low steam/gas ratio, the further reduction of iron cations with the formation of carbide is also possible; this is extremely undesirable in factors of a catalytic process because it results in the formation of hydrocarbons in the Fischer–Tropsch synthesis. Promotion with chromium and copper cations increases the stability of the oxide with the magnetite structure and thus the stability of the catalyst for hightemperature WGSR to fluctuations in the composition of the initial reaction mixture.

A structure disordered with respect to the cationic sublattice was also observed in a number of studies; based on IR spectra, we attributed this structure to the partially hydrated oxide $Fe_{2+x}O_3(OH)_{3x}$ (hydrohematite). It was ascribed to the $Fe_5HO_8 \cdot 4H_2O$ ferrihydrite nanostructure [22, 23]. Evidently, in these publications, two-line ferrihydrite is considered; this is a nanomaterial with a crystallite size smaller than 2 nm, whose X-ray diffraction patterns [24, 25] are fully consistent with the X-ray diffraction patterns of samples FeCr-3 and FeCrCu-3.

Note that two-line ferrihydrite should not be confused with the mineral ferrihydrite [26, 27], which has six X-ray diffraction lines and hence is referred to as six-line ferrihydrite. Recently, Michel et al. [28] proposed the structure of this mineral, which contains 80% iron cations in an octahedral coordination and 20% in a tetrahedral coordination, corresponding to the stoichiometry $Fe_{10}O_{14}(OH)_2$. A detailed review of experimental data and proposed interpretations [11] makes it possible to clearly distinguish between these two phases, which historically have the same name. In this context, note that, more recently, Chukhrov [29], who is the author of the initial factor *ferrihydrite*, proposed the factor protoferrihydrite for two-line ferrihydrite; however, the latter factor has not received wide acceptance although it has been used in other publications. To exclude terminological confusions and taking into consideration the absence of a strict stoichiometry from the two-line ferrihydrite phase (according to Wolska [19], the degree of oxide hydration can vary over a wide range), we assume that hydrohematite is the most correct factor to determine the structure under discussion, as proposed by Wolska. This factor reflects the essence of the discussed phase as a highly defect structure stabilized by admixture OH^- anions, in which the local environment of Fe^{3+} cations is close to that characteristic of the hematite structure.

Electron-microscopic data additionally justified this interpretation of the hydrohematite structure. Figure 5 shows a high-resolution electron micrograph of sample FeCrCu-3 thermally treated at 400°C for 2 h in an atmosphere of argon. According to thermal analysis data, which will be discussed below, the dehydration of the hydrohematite phase at this temperature occurred at a rate that provided the removal of only a portion of admixture OH⁻ groups for 2 h. To the right of the micrograph, Fourier filtration data are given for the micrograph of regions marked in the left figure and having the hematite and hydrohematite structures, respectively. From a comparison between the figures, it is evident that, on the one hand, these structures are related to each other and, on the other hand, they are different, as manifested itself in the high imperfection of hydrohematite.

The particle size was estimated from X-ray diffraction data using the Scherrer formula [30]

 $\left(D = \frac{n\lambda}{\beta\cos\theta}\right)$; it was found that the size of coherent scattering regions in the direction [002], that is, the

nanoparticle thickness, was ~14 Å, and the size of coherent scattering regions in the direction [110], that is, the layer length was also ~14.5 Å. Thus, the primary particle of a coherent scattering region consisted of ~3 unit cells in thickness and ~5 unit cells in length.

These particles can have an uncompensated charge; therefore, they strongly retained adsorbed H_2O , OH^- , CO_3^{2-} , and other groups on their surface to prevent sintering and to facilitate ordering.

The calcination of Fe-Cr and Fe-Cr-Cu oxo hydroxides results in dehydration and the formation of a phase with the hematite structure. Figure 6 shows data obtained by in situ X-ray diffraction under conditions of the calcination of sample FeCrCu-2 in a flow of argon. From these data, it follows that the decomposition of goethite promoted with copper and chromium cations occurs at a temperature of 200°C or higher, and it is accompanied by the formation of a phase with the hematite structure. It follows from thermal analysis data, which are shown in Fig. 7, that the dehydration of the hydrohematite structure occurs at much higher temperatures, although this structure is much more imperfect. The onset of dehydration at a heating rate of 10 K/min was detected at a temperature of about 400°C, and a maximum rate of dehydration was observed at 580°C. In this case, the dehydration of hydrohematite was exothermic as a consequence of a considerable structure relaxation, whereas the goethite structure was converted into hematite in the course of an endothermic process. These data are consistent with published data [22-24] on the high



Fig. 5. (left) Electron micrograph of sample FeCrCu-3 thermally treated in Ar at 400°C for 1 h. (right) Results of the Fourier filtration of micrograph regions corresponding to the (top) hematite and (bottom) hydrohematite structures.



Fig. 6. Data of in situ X-ray diffraction on the calcination of sample FeCrCu-2 in a flow of argon at the following temperatures: (1) 20, (2) 130, (3) 200, (4) 250, and (5) 300° C.

stability of unpromoted hydrohematite. Promotion with Cr^{3+} and Cu^{2+} cations did not exert a considerable effect on the range of temperatures at which the dehydration of oxo hydroxides occurred. However, unlike the dehydration of unpromoted hydrohematite [24], we did not detect the intermediate formation of γ -Fe₂O₃ (maghemite).

Catalytic Properties of Fe–Cr and Fe–Cr–Cu Oxo Hydroxides in the WGSR

Table 2 summarizes the specific surface areas of Fe–Cr and Fe–Cr–Cu oxo hydroxides determined by the BET method for the samples calcined at 200°C in an atmosphere of argon.



Fig. 7. Thermal analysis data for the decomposition of samples in an atmosphere of argon: (*1*) FeCrCu-2 and (*2*) FeCrCu-3. Heating rate: 10 K/min.

The catalytic activity of Fe-Cr catalysts correlates well with the specific surface area of the oxide. The introduction of copper increases the activity of all of the catalysts; however, the effect of copper promotion is much higher for catalysts with the hydrohematite structure. Thus, the activity of catalyst FeCrCu-3 is higher than the activity of catalyst FeCrCu-1 by one order of magnitude. Taking into account electronmicroscopic data, we assume that this is due to a high concentration of defects accessible to gas-phase molecules, in which admixture copper cations are stabilized. It is likely that these copper cations are active sites at temperatures of 300 and 330°C. However, note that we did not study the nature of active copper sites and this problem is of considerable interest for future studies.

An increase in the cooper content of Fe–Cr–Cu samples to 7, 12, and 20 at % under the preparation conditions of sample FeCrCu-3 at the ratio Fe/Cr = 9 : 1 resulted in an increase in the specific activity of the catalyst. In this case, note that, according to XRD and IR-spectroscopic data, an increase in the copper

content did not cause the formation of phases other than oxo hydroxide with the hydrohematite structure. Figure 8 shows the results of catalytic activity tests at 300, 330, and 450°C depending on the copper content of hydrohematite. From these data, it can be clearly seen that, in the range to 12% copper, the rate constant of forward reaction of the WGSR (k_{\rightarrow}) linearly depended on (moreover, was directly proportional to) the amount of introduced copper in the temperature range of 300–330°C. Only upon the introduction of 20% copper, a considerable decrease in the specific activity with respect to a linear trend was observed.

The activity of catalysts at 450° C nonlinearly depended on the amount of copper introduced into the catalyst composition; it is likely that it was only indirectly related to the copper content through the effect of the copper content on the oxide structure formed after the dehydration of hydrohematite at elevated temperatures. After long-term calcination at 450° C, the hydrohematite structure was converted into a hematite-type structure. In this case, the diffraction pattern of the oxide formed in a sample con-

| Sample | Structure and copper content, at % | Specific surface area S_{BET} , m ² /g | Rate constant of the forward reaction of the WGSR k_{\rightarrow} , s ⁻¹ | | | |
|----------|------------------------------------|--|--|-------|-------|--|
| | | | 300°C | 330°C | 450°C | |
| FeCr-1 | Hematite, 0 | 67 | 0.2 | 1.0 | 21 | |
| FeCrCu-1 | Hematite, 4 | 75 | 1.0 | 2.2 | 60 | |
| FeCr-2 | Goethite, 0 | 147 | 1.8 | 3.9 | 56 | |
| FeCrCu-2 | Goethite, 4 | 167 | 2.2 | 7.0 | 73 | |
| FeCr-3 | Hydrohematite, 0 | 310 | 2.2 | 5.5 | 62 | |
| FeCrCu-3 | Hydrohematite, 4 | 295 | 14 | 24 | 127 | |

Table 2. Experimental data on the specific surface areas of the test catalysts and on the activity of these catalysts in the WGSR

taining 4% copper was different from that of hydrohematite in only a decrease in the cell parameter (a = 8.383 Å, as compared with 8.396 Å for α -Fe₂O₃ according to published data [31]). However, in the samples with high copper concentrations, a tetragonal distortion of the hematite structure was observed, which manifested itself in the splitting of the [400] reflection into two ([400] and [004]). The lattice parameters of the tetragonally distorted structure for the sample containing 20 at % copper were a = 8.444 Å and c = 8.372 Å.

Difference in the dependence of the activity of catalysts on copper content in the regions of low temperatures (300-330°C) and elevated temperatures (450°C) suggests that the seam conversion of CO occurs at different active sites in different temperature ranges. The temperature dependence of catalytic activity was studied in detail for a hydrohematite sample containing 7 at % copper. To provide an isothermal catalytic bed, this catalyst was tested in a structured reactor with an increased thermal conductivity of the catalyst bed, which was reached by introducing the catalyst mass into heat-conducting composite plates 25 mm in diameter and 2.5 mm in thickness. The procedure for the preparation of heat-conducting composite catalysts as plates, the characterization of their thermal conductivity and efficiency, and the procedures of testing were described in detail elsewhere [12]. Figure 9 shows data on the catalytic activity (expressed in factors of the apparent rate constant of forward reaction) of the catalyst with the hydrohematite structure containing 7 at % copper in the course of a continuous series of experiments performed for 150 h. These data indicate that the steady-state occurrence of the reaction was reached in 15-20 h after increasing the reaction temperature. Henceforth, all of the discussed values that characterize the activity of catalysts are given for steady-state reactions. Figure 9 also indicates that the activity of the catalyst at low temperatures (330°C) decreased many times after heating the catalyst to 460°C in a reaction atmosphere. The temperature dependence of the catalytic activity of the catalyst with the initial hydrohematite structure after performing the catalytic reaction in the region of temperatures to 480°C was studied in another series of continuous tests with a total duration of 275 h. Table 3 summarizes the initial experimental data and the calculated apparent rate constants of forward reaction; they support the conclusion on a change in the catalytic properties of the catalyst after operation in the temperature range of $460-480^{\circ}$ C.

Figure 10 shows data in the Arrhenius coordinates on the steady-state activity of the above catalyst over the entire temperature range as the temperature was gradually increased to 480° C followed by a decrease in the reaction temperature. This figure also shows the temperature dependence of the steady-state activity of a commercial Fe–Cr–Cu catalyst with the hematite structure (copper content of 2.8 at %).



Fig. 8. Dependence of the activity of catalysts with the hydrohematite structure on the copper content at various reaction temperatures: (1) 310, (2) 330, and (3) 450°C. Catalyst grain size: 0.14-0.25 mm.

From Fig. 10, it follows that the temperature dependence of the steady-state rate constant is complicated. The rate constant depends only slightly on temperature in the range of 310–420°C; the apparent activation energy can be estimated at 10 ± 2 kJ/mol. Above 420°C, the apparent activation energy has a significantly larger value of 54 ± 4 kJ/mol. The catalyst kept at 480°C for 15 h or longer exhibited a lower catalvtic activity, and the temperature dependence of its activity over the entire test temperature range obeyed the Arrhenius equation with activation energies close to the activation energy observed for the commercial catalyst (~60 kJ/mol). Taking into account the above results, including the effect of copper content on the catalytic activity of copper-containing catalysts with the hydrohematite structure, we can explain data shown in Fig. 10 in the following manner:

(1) In the region of temperatures to $400-420^{\circ}$ C, the hydrohematite structure is stable (at least, the rate of dehydration is low so that the conversion of hydrohematite into hematite does not occur within the experiment time of about 100 h). The activity of the copper-promoted catalyst with the hydrohematite structure depends on copper-containing sites. It is likely that the reaction proceed by a concerted mechanism [32].

(2) In the region of temperatures higher than 420° C, hydrohematite is dehydrated to hematite. This structure is also thermodynamically stable in the region of low temperatures; therefore, a decrease in the temperature below 400° C does not lead to the recovery of the initial degree of oxide hydration. Iron cations are the active sites of this catalyst at which the WGSR occurs with a higher activation energy most likely by a stepwise mechanism [33].

 k_{\rightarrow}, s^{-1} 460°C 10 9 440°C 8 320°C 380°C 400°C 420°C 7 6 5 $\overline{\mathbf{v}}$ $\sim \infty$ 4 3 2 330°C 1 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 Time on stream, h

Fig. 9. The temperature dependence of the apparent rate constant of forward reaction of the WGSR for the Fe–Cr–Cu catalyst with the hydrohematite structure containing 7 at % copper.

The observed activation energies are lower than the corresponding values known for the WGSR on Fecontaining catalysts ($E_a \approx 90 \text{ kJ/mol}$ on Fe-containing catalysts [33]). This may be explained by the effect of diffusion limitations in catalytic tests on grains with a characteristic size of ~ 2.5 mm. According to published data [34], the efficiency is 35–60% for heat-conducting plates. However, the occurrence of diffusion limi-

| T, °C | V _{SRM} , nl/h (NTP) | τ, s | Composition of the wet initial reaction mixture, vol % | | $C_{\rm CO}^{\rm equil}$, | Composition of the reaction mixture after the reactor, vol % | | CO conversion, | k_{\rightarrow}, s^{-1} | |
|-------|-------------------------------------|-------|--|-----|----------------------------|--|------|-----------------|---------------------------|------|
| | | | H ₂ O | СО | CO ₂ | vol % | СО | CO ₂ | 70 | |
| 320 | 50.2 | 0.119 | 38.7 | 7.4 | 3.5 | 0.89 | 4.78 | 6.2 | 35.6 | 4.4 |
| 310 | 50.6 | 0.120 | 38.4 | 7.4 | 3.4 | 0.78 | 5.10 | 5.7 | 31.5 | 3.6 |
| 350 | 49.8 | 0.114 | 37.5 | 7.5 | 3.5 | 1.23 | 4.67 | 6.3 | 38.1 | 5.3 |
| 380 | 49.9 | 0.109 | 37.9 | 7.4 | 3.4 | 1.60 | 4.41 | 6.3 | 40.1 | 6.6 |
| 480 | 49.8 | 0.095 | 37.7 | 7.4 | 3.5 | 3.16 | 5.23 | 5.6 | 29.4 | 7.6 |
| 460 | 49.8 | 0.097 | 37.6 | 7.4 | 3.4 | 2.82 | 5.31 | 5.5 | 28.3 | 6.3 |
| 440 | 49.6 | 0.100 | 37.4 | 7.6 | 3.4 | 2.54 | 5.57 | 5.4 | 26.7 | 5.1 |
| 420 | 49.6 | 0.103 | 38.1 | 7.5 | 3.4 | 2.23 | 5.72 | 5.2 | 24.0 | 4.0 |
| 400 | 44.6 | 0.118 | 31.1 | 8.3 | 3.8 | 1.90 | 6.55 | 5.5 | 20.8 | 2.7 |
| 380 | 50.2 | 0.108 | 38.3 | 7.6 | 3.5 | 1.67 | 6.37 | 4.7 | 16.6 | 2.2 |
| 350 | 49.8 | 0.114 | 38.2 | 7.4 | 3.4 | 1.22 | 6.54 | 4.3 | 12.1 | 1.37 |
| 330 | 48.9 | 0.120 | 37.4 | 7.3 | 3.4 | 0.96 | 6.63 | 4.1 | 9.7 | 0.98 |

Table 3. Results of the tests of the catalytic activity of the catalyst with the hydrohematite structure containing 7 at % copper depending on temperature obtained in the course of a continuous series of experiments for 350 h*

* The catalyst was tested as heat-conducting plates (see the text); the order of rows in the table corresponds to the sequence of temperature changes in the course of tests; tests were performed to reach a steady-state course of reaction at each temperature.



Fig. 10. The temperature dependence of the apparent steady-state rate constant of forward reaction of the WGSR for (*I*) the Fe–Cr–Cu catalyst with the hydrohematite structure containing 7 at % copper and (*2*) the commercial Fe–Cr–Cu catalyst containing 2.8 at % copper. The tests were performed in the following orders: (*I*) 310–320–330–340–420–440–440–480°C and (*I*) 480–460–440–420–400–380–350–330°C.

tations in the course of the experiment has no crucial effect on the above conclusions.

CONCLUSIONS

The above experiments demonstrated that the solutions of Cr³⁺ nitrate and the nitrates of other metals that are the constituents of Cr-containing catalysts can be prepared by dissolving a corresponding metal (such as cast iron and electrolytic copper) in a solution of chromic anhydride and nitric acid. Nitric acid is a catalyst for the redox reaction between a metal and the dichromate anion with the formation of M^{2+} (Fe³⁺ in the case of iron) and Cr³⁺ cations. Under conditions of this catalytic reaction, the steady-state concentration of nitric acid in solution is very low; this determines the low rate of side reactions of metal oxidation with nitric acid to form nitrogen oxides. A decrease in the pH of solution results in an increase in the rate of the catalytic reaction between the metal and the dichromate anion and, consequently, in an increase in the fraction of the metal dissolved in the target reaction, as compared with the fraction of the metal dissolved without the participation of the dichromate anion. Analogously, the oxidation of Fe^{2+} cations to Fe^{3+} coupled with the reduction of hexavalent chromium can be performed.

The proposed method for the preparation of nitrate solutions is characterized by the complete interaction of a metal or Fe^{2+} cation with the dichromate anion; the residual concentration of Cr^{6+} in solution is no higher than 10^{-3} wt %; that is, the fraction of reduced chromium is higher than 99.95%. In addition, the amount of nitrogen oxides released in the course of metal dissolution is lower by two orders of magnitude

than that in the absence of chromic anhydride. The resulting solutions are characterized by high purity in factors of sulfur determined by the sulfur content of the initial raw materials (the S/Fe weight ratio is no higher than 2×10^{-4} with the use of grey cast iron of first and second category with respect to sulfur). Moreover, it is of importance that it is inexpensive, as compared with the price of individual nitrates, in combination with practical usability.

The precipitation of Fe³⁺, Cr³⁺, and Cu²⁺ cations in the ratio Fe/Cr = 9 at a concentration of Cu²⁺ to 20 at % can result in the formation of a partially hydrated oxide with the hydrohematite structure—a disperse and highly imperfect oxide structure with an ordered anionic sublattice and the absence of an order in the cationic sublattice observed by X-ray diffraction. The hydrohematite phase is characterized by a high specific surface area of >300 m²/g and a higher thermal stability, as compared with the phase of goethite, α -FeOOH. The dehydration of hydrohematite occurs at a noticeable rate at temperatures higher than 400°C.

Hydrohematite promoted with copper ions exhibits high activity in the region of temperatures lower than 400° C. The activity of Fe–Cr–Cu hydrohematite is proportional to the amount of copper introduced into the catalyst, whereas it is likely that copper cations are the active sites of the catalyst. After the dehydration of hydrohematite, which occurs at a noticeable rate at temperatures higher than 400° C, the activity of the catalyst decreases and the catalyst approaches catalysts with the hematite structure in its catalytic properties. After dehydration, the activity is restricted to the sites characteristic of Fe–Cr catalysts over the entire temperature range.

The high activity of the Fe–Cr–Cu catalyst with the hydrohematite structure in the region of temperatures lower than 350–400°C can decrease the starting temperature of an adiabatic process of high-temperature WGSR to 300°C or lower.

However, note that the dehydration of hydrohematite is an exothermic process; consequently, it is thermodynamically favorable at lower temperatures. In this context, to evaluate the operation stability of a catalyst for the WGSR in the region of temperatures lower than 400°C, the kinetics of dehydration of hydrohematite should be studied in detail, and the results of these studies will be published elsewhere.

ACKNOWLEDGMENTS

This work was performed at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences in 2005–2008; it was supported in part by OAO AZKIOS. We are grateful to Cand. Sci. (Eng.) I.D. Reznichenko, M.I. Tselyutina, O.M. Posokhova, and L.G. Volchatov (OAO AZKIOS) for helpful discussions, constructive criticism, and thorough examination of the results of laboratory studies a portion of which is considered in this paper. A.A. Khassin acknowledges the support of the Russian Science Support Foundation.

REFERENCES

- Minyukova, T.P., Plyasova, L.M., Yurieva, T.M., Litvak, G.S., and Ketchik, S.V., *Kinet. Katal.*, 1989, vol. 30, no. 2, p. 415.
- 2. Yurieva, T.M., *React. Kinet. Catal. Lett.*, 1983, vol. 23, no. 3, p. 267.
- Khassin, A.A., Yurieva, T.M., Kaichev, V.V., Bukhtiyarov, V.I., Budneva, A.A., Paukshtis, E.A., and Parmon, V.N., *J. Mol. Catal. A: Chem.*, 2001, vol. 175, nos. 1–2, p. 189.
- Khassin, A.A., Yurieva, T.M., Kaichev, V.V., Zaikovskii, V.I., Demeshkina, M.P., Minyukova, T.P., Baronskaya, N.A., Bukhtiyarov, V.I., and Parmon, V.N., *Kinet. Katal.*, 2006, vol. 47, no. 3, p. 420 [*Kinet. Catal.* (Engl. Transl.), vol. 47, no. 3, p. 412].
- 5. Plyasova, L.M., Solovyeva, L.P., Krieger, T.A., Makarova, O.V., and Yurieva, T.M., *J. Mol. Catal. A: Chem.*, 1996, vol. 105, p. 61.
- Yurieva, T.M., Plyasova, L.M., Zaikovskii, V.I., Minyukova, T.P., Bliek, A., van den Heuvel, J.C., Davydova, L.P., Molina, I.Yu., Demeshkina, M.P., Khassin, A.A., and Batyrev, E.D., *Phys. Chem. Chem. Phys.*, 2004, vol. 6, no. 18, p. 4522.
- Khassin, A.A., Yurieva, T.M., Plyasova, L.M., Kustova, G.N., Jobic, H., Ivanov, A., Chesalov, Yu.A., Zaikovskii, V.I., Khassin, A.V., Davydova, L.P., and Parmon, V.N, *Ross. Khim. Zh.*, 2008, vol. 52, no. 1, p. 32.
- Trunov, V.A., Sokolov, A.E., Lebedev, V.T., Smirnov, O.P., Kurbakov, A.I., Heuvel, J., Batyrev, E., Yurieva, T.M., Plyasova, L.M., and Torok, G., *Phys. Solid State*, 2006, vol. 48, no. 7, p. 1291.
- Dillen, J.A, Geus, J.W, Hermans, L.A, and van der Meijden, J., *Proc. 6th Int. Congr. on Catalysis*, London, 1976, p. 677.
- 10. Schwertmann, U. and Cornell, R.M., *Iron Oxides in Laboratory*, New York: VCH, 1991, p. 137.
- 11. Jambor, J.L. and Dutrizac, J.E., *Chem. Rev.*, 1998, vol. 98, p. 2549.
- Baronskaya, N.A., Minyukova, T.P., Sipatrov, A.G., Demeshkina, M.P., Khassin, A.A., Dimov, S.V., Kozlov, S.P., Kuznetsov, V.V., Terentiev, V.Ya., Khristolyubov, A.P., Brizitskiy, O.F., and Yurieva, T.M., *Chem. Eng. J.*, 2007, vol. 134, p. 195.

- 13. Shchibrya, G.G., Morozov, N.M., and Temkin, M.I., *Kinet. Katal.*, 1965, vol. 6, no. 6, pp. 1057, 1115.
- 14. *Spravochnik azotchika* (Nitrogen Engineer's Handbook), Moscow: Khimiya, 1986, p. 147.
- 15. http://www.chem.msu.ru/rus/handbook/redox/.
- The Sadtler Infrared Spectra Hanbdook of Minerals and Clays, Ferraro, J.R., Ed., Philadelphia: Sadtler Research, 1982.
- 17. *Mineralspektren*, Moenke, H., Ed., Berlin: Akademische, 1962, Spectrum 2.29.
- 18. Belov, N.V., *Struktura ionnykh kristallov i metallicheskikh faz* (Structure of Ionic Crystals and Metallic Phases), Moscow, 1947.
- 19. Wolska, E., Z. Kristallogr., 1981, vol. 154, p. 69.
- 20. Baranski, A., Lagan, M., Pattek, A., and Reizer, A., *React. Kinet. Catal. Lett.*, 1980, vol. 15, p. 285.
- 21. Spitzer, R.H., Manning, F.S., and Philbrook, W.O., *Trans. Met. Soc. AIME*, 1966, vol. 236, p. 725.
- 22. Mitov, I., Paneva, D., and Kunev, B., *Thermochim. Acta*, 2002, vol. 386, p. 179.
- 23. Oliveira, A.C., Marchetti, G.S., and Do Carmo Rangel, M., *J. Therm. Anal. Calor.*, 2003, vol. 73, p. 233.
- 24. Eggleton, R.A. and Fitzpatrick, R.W., *Clays Clay Miner.*, 1988, vol. 36, p. 111.
- Drits, V.A., Sakharov, B.A., Salyn, A.L., and Manceau, A., *Clays Clay Miner.*, 1993, vol. 28, p. 185.
- 26. Chukhrov, F.V., Zvyagin, B.B., Gorshkov, A.I., Ermilova, L.P., and Rudnevskaya, E.S., *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1971, no. 1, p. 3.
- Chuckrov, F.V., Zvyagin, B.B., Gorshkov, A.I., Yermilova, L.P., and Balashova, V.V., *Int. Geol. Rev.*, 1973, vol. 16, p. 1131.
- Michel, F.E., Ehm, L., Antao, S.M., Lee, P.L., Chupas, P.J., Liu, G., Strongin, D.R., Schoonen, M.A.A., Phillips, B.L., and Parise, J.B., *Science*, 2007, vol. 316, no. 5832, p. 1726.
- 29. Chukhrov, V.F., Chem. Geol., 1973, vol. 12, p. 67.
- 30. Guinier, A., *Theorie et technique de la radiocristallographie*, Paris: Dunod, 1956.
- Michael, F.E., Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 1984, vol. 40, no. 9, p. 1491.
- 32. Yurieva, T.M., Boreskov, G.K., and Gruver, V.Sh., *Kinet. Katal.*, 1969, vol. 10, no. 4, p. 862.
- 33. Boreskov, G.K., Yurieva, T.M, and Sergeeva, A.S., *Kinet. Katal.*, 1970, vol. 11, no. 6, p. 1476.
- 34. RF Patent 2281805, 2006.

KINETICS AND CATALYSIS Vol. 50 No. 6 2009