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Development of a Resource-Saving Technology of Catalysts for Medium-Temperature Conversion of Carbon Monoxide in Ammonia Production

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Abstract—The physicochemical characteristics of modern catalysts for the medium-temperature conversion of carbon monoxide to hydrogen in the production of ammonia were studied by X-ray diffraction, scanning electron microscopy, gas chromatography, and thermogravimetric and laser dispersion analyses. It was shown that, along with iron oxide, the catalysts contained promoter additives of Cr, Cu, Ca, and Mn compounds in a total concentration of 1–9 wt%. The investigated commercial catalysts have a monodisperse porous structure with a pore size of up to 10 nm and a large surface area from 70 to 120 m^2/g. The catalytic activity of the samples was estimated by the conversion of CO in a flow-type plant. At 2.2 MPa and 340 °C it was 89–91%. The drawback of the catalysts was that the condensate contained rather much ammonia (27.6–45.6 mg/L). It was established that using calcium and copper ferrites and nickel oxide as promoters makes it possible to obtain a catalyst that is not inferior in activity to commercial analogs but has a higher selectivity by reducing the ammonia content of the condensate by 20–30%.

Keywords: catalyst, carbon monoxide conversion, activity, selectivity, calcium ferrite, copper ferrite

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At present, due to the increased interest in hydrogen energy, the demand for catalysts and sorbents used in the production of hydrogen and hydrogen-containing gases by hydrocarbon conversion methods is especially great [1, 2]. Ammonia production is critical to the development of many industries. Carbon monoxide conversion is one of the key steps in ammonia production. The main goal of the carbon monoxide conversion process is ensure a maximum yield of hydrogen.

The medium-temperature conversion of carbon monoxide to hydrogen in ammonia production is performed on iron–chromium catalysts. The fraction of iron oxide in such catalysts varies from 85 to 93%, and the fraction of chromium oxide varies from 6.5 to 10% [3]. The active phase of iron–chromium catalysts is Fe_3O_4 formed by preliminary reduction of the contact catalyst. Chromium oxide in iron–chromium catalysts acts as a texture modifier, which in itself is not catalytically active but during process it stabilizes the porous structure of the catalyst to prevent its agglomeration [4].

Enhancement of the efficiency of the main branches of chemical industry is associated with the development and introduction of new catalysts and catalytic processes. The quality and assortment of commercial catalysts are among the main factors determining the level of any industry. Since a significant part of catalysts used in the nitrogen industry is purchased abroad, import substitution and development of domestic production of catalysts are of strategic importance not only for the chemical industry, but also for the economy of the whole country.

The aim of the present work was to perform a comprehensive study of the physicochemical characteristics of modern foreign catalysts for the medium-temperature conversion of carbon monoxide into hydrogen, reveal their advantages and disadvantages, and develop domestic high-performance contact catalysts.

EXPERIMENTAL

The X-ray diffraction (XRD) phase analysis was performed on a DRON-3M diffractometer (CuK_α radication, λ 0.15406 nm, Ni filter). The XRD data were interpreted using MINKRIST and PDF-4 crystallographic databases. Broadening of the XRD peaks allows one to determine changes in the coherent scattering region

Table 1. Physicochemical characteristics of medium-temperature CO conversion in ammonia production

Catalyst	Elemental composition		Surface area, m^2/g	Mechanical strength, MPa	Activity, % (CO conversion at 340°C)
	element	wt %			
C1	Fe	84.0	70	5.0	91.0
	Cr	9.0			
	Cu	3.6			
	Ca	2.8			
	Mn	0.6			
C2	Fe	86.0	120	4.6	90.0
	Cr	8.0			
	Cu	9.5			
	Ca	1.5			
	Mn	1.0			
C3	Fe	89.0	75	4.8	89.5
	Cr	8.0			
	Cu	2.0			
	Ca	1.0			

(CSR) and rms microdeformations. The substructural parameters of the samples were determined by a program that implements harmonic analysis of XRD line profiles. The thermogravimateric analysis (TGA) of the reaction products was performed om a Netzsch STA 449 F3 Jupiter instrument at a heating rate of 5°C min^{-1}. The specific surface areas were determined by the BET method from nitrogen absorption isotherms measured on a Sorbi-MS instrument. The SEM images were obtained on a VEGA 3 TESCAN microscope. The particle size distributions were measured on an Analysette 22 laser particle sizer.

The catalytic activities of the samples in the steam CO conversion process were determined in a PKU-2 flow reactor under a pressure of 2.2 MPa. The starting gas mixture contained CO (10.0 vol %), CO_2 (10.0 vol %), H_2 (55 vol %), and He (25 vol %). Steam was fed with an Aquilon Stayer pump to a steam/gas ratio of 0.6. The gas mixture was fed to a catalyst with a volume rate of 5000 h^{-1}. The gas mixtures before and after reaction, as well as the condensates were analyzed on a Crystal Lux gas chromatograph. Mechanochemical synthesis of calcium and copper ferrites was performed in a VM-4 laboratory roller–ring vibratory mill by the procedure described in [1].

RESULTS AND DISCUSSION

Technical development in chemical industry is impossible without the creation of new technologies for the production of raw materials and products. The progress in this area is associated with the widespread use of catalysts. At present ammonia production industry in Russia is generally based on the use of foreign catalysts. Analysis of the catalyst market showed that the share of domestic catalysts does not exceed 10%.

The main reason for such state of things is the suspension of the development of new types of domestic catalysts. Among foreign catalysts, the most widely used are those produced by JCJ (Great Britain), Haldor Tope (Denmark), Sūd Chemie (Germany), and others. The results of the determination of the chemical composition and physicochemical characteristics of foreign catalysts are presented in Table 1.

The energy dispersive analysis showed that the catalysts, along with iron and chromium compounds, contain calcium, copper, and manganese compounds. It is obvious that chromium and calcium oxides play the role of texture promoters, which prevent agglomeration of iron oxide particles and increase the thermal stability of the catalyst. As known, similar properties, specifically ability to stabilize the structure of catalysts, are also characteristic of magnesium and aluminum oxides.

However, to ensure high conversions, known iron–magnesium and iron–aluminum catalysts require high temperatures. The role of structural promoters in such contact catalysts is played by copper and manganese oxides. The latter oxides also have a positive effect on the catalytic activity.

Steam conversion of CO occurs in an intradiffusion region. Therefore, during the preparation of the catalysts, it is necessary to obtain the optimal pore structure, which would reduce the intradiffusion retardation of intradiffusion inhibition and increase the degree of utilization

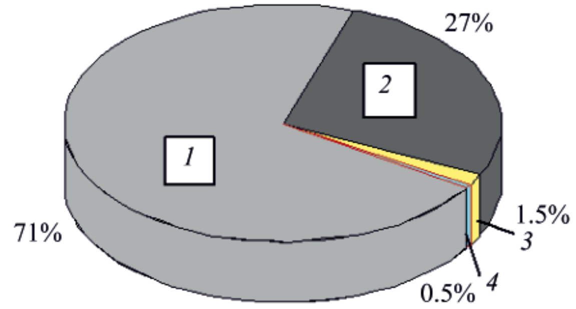

Fig. 1. Contents of admixtures in the condensate in a large ammonia production plant: (*1*) NH_3; (*2*) CH_3OH; (*3*) amines; and (*4*) formates.

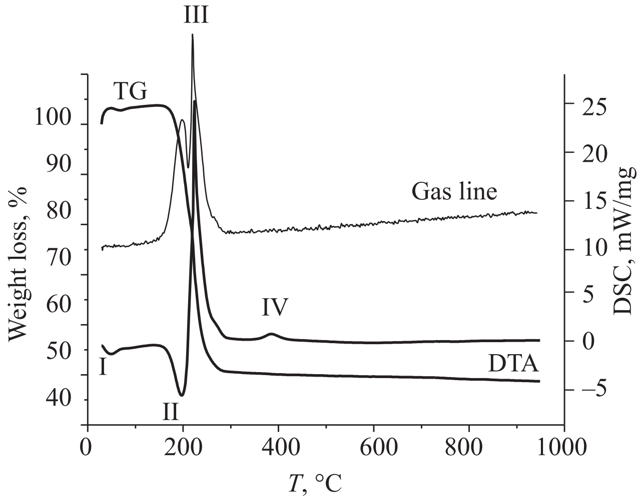

Fig. 2. DTA curves of iron(III) oxalate calcined in air.

of the inner surface. Therefore, the activity of the catalyst will be affected not only by the dispersion of iron oxide and the shape of grains, the inner working surface of which depends on the conditions of catalyst formation.

Electronic microscopy showed that all the tested catalysts consist of aggregates of iron oxide particles up to 20 µm in diameter (50–60%) and have monodisperse porous structure with an effective pore diameter of up to 10 nm. The commercial medium-temperature contact catalysts feature large surface areas ranging from 70 to 120 m^2/g (Table 1).

Testing the catalytic activity of the commercial catalysts under a pressure of 2.2 MPa showed that they all ensured high CO conversions. The highest CO conversion of 89–91% (Table 1) was obtained at 340°C. Along with activity, an important characteristic of the catalysts is their selectivity. The case in point is that steam condensate should be recycled, because this reduces costs for water pretreatment and desalination. As a rule, the recycling of the condensate improves the quality of water and thus ensures more reliable operation of boiler units. However, the condensate can be recycled only if it contains no more than 15 mg/L of admixtures. According to our results, the ammonium content of the condensate was 27.6–45.6 mg/L.

It was found that ammonia is the main component (up to 86.5%) of the condensates obtained with the tested commercial catalysts. The other components include alcohols (3.7%), amines (6.7%), as well as formates, acetates, and oxalates (a total of 3.6%) (see Fig. 1). It was thus concluded that the catalyst performance can be improved by introducing, at the stage of medium-temperature CO conversion, promoting additives to prevent ammonium formation. The other admixtures are also undesirable, but these compounds are formed in much larger amounts in the low-temperature CO conversion on copper catalysts, and, therefore, to reduce their formation should be the issue to deal with in optimizing low-temperature catalysts fir CO conversion.

To obtain catalysts for the medium-temperature conversion of CO in the production of ammonia, finely dispersed iron oxide with a surface area of at least 70–80 m^2/s is required.

One of the technologies of the production of iron oxide for catalysts makes use of thermal decomposition products of iron oxalates. Iron oxalate has a low decomposition temperature (<300°C), which allows low-temperature synthesis of a highly dispersed iron oxide. Despite a significant number of studies on the thermal decomposition of metal oxalates have been reported, there are no publications on the mechanochemical synthesis (MCS) of iron oxalate as a precursor for producing iron oxide (Fig. 2).

In the present work we studied the oxidation of iron-containing powders in oxalic acid solutions. It was shown that 90% of iron metal powder dissolved in 30% $H_2C_2O_4$ after 30-min ultrasonication at 22 kHz.

Investigation of the decomposition products by simultaneous thermal and XRD phase analysis showed that the thermoanalytical curves contained 2 endo- and 2 exothermic effects. In the temperature range 120–190°C, a two-stage dehydration process took place:

$$FeC_2O_4 \cdot 2H_2O \xrightarrow{-0.5H_2O} FeC_2O_4 \cdot 1.5H_2O \xrightarrow{-1.5H_2O} FeC_2O_4.$$

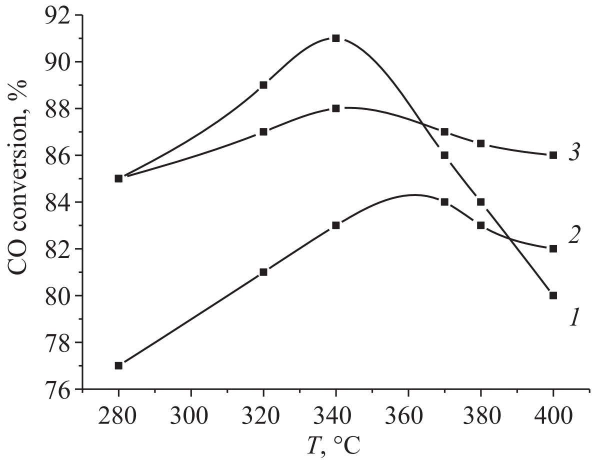

Fig. 3. Temperature dependences of CO conversion on different catalysts: (*1*) $CuFe_2O_4$; (*2*) $Ca_2Fe_2O_5$; (*3*) iron oxide catalyst with calcium ferrite, copper ferrite, and nickel oxide promoters.

Further on, in the temperature range 200–320°C, the decomposition of anhydrous iron oxalate leading to $FeCO_3$ followed by conversion of the latter to γFe_2O_3 with elimination of CO and CO_2 is observed:

$$FeC_2O_4 \xrightarrow{-CO} FeCO_3 \xrightarrow{-CO_2} \gamma\text{-}FeC_2O_4.$$

The surface area of the resulting γ-Fe_2O_3 reaches 80 m^2/g.

At present abundant published evidence is available on ferrites of the spinel structure and perovskites, which are actively studied due to their unique physical and chemical properties [4]. Such members of this class of compounds as calcium and copper ferrites act as highly active and selective catalysts in medium-temperature steam CO conversion [4–8]. We recently employed mechanochemical activation to prepare highly disperse calcium and copper ferrites and considerably decrease the temperature of the subsequent thermal treatment [9].

It was found that calcium ferrite showed the highest catalytic activity in the range 360–400°C. The conversion of carbon monoxide to hydrogen was 87–84%. Copper ferrite was the most active at lower temperatures (300–350°C). The conversion of CO on the copper ferrite–promoted catalyst reached 87–92.5% (Fig. 3).

The selectivity of calcium and cooper ferrites in medium-temperature CO conversion was found to be poor: the reaction gave a lot of ammonia.

As known, all catalysts lose catalytic activity and selectivity and degrade during service. The problem of the service life of structures which have acquired enhanced reactivity due to mechanochemical activation is of great importance.

Thus, our study has demonstrated the possibility of the preparation of catalysts of medium-temperature CO conversion in ammonia production, using calcium and copper ferrites as promoters. Calcium ferrite enhances the catalytic activity at high temperatures and copper ferrite, at low temperatures. To decrease ammonium production, small nickel oxide additives are recommended [10].

CONCLUSIONS

The physicochemical characteristics of foreign catalysts for medium-temperature CO conversion in ammonium production were studied. It was shown that the high catalytic activity of the studied contact catalysts is explained by the presence of a highly dispersed iron oxide and Cr, Cu, Ca, and Mn compounds as promoters. In addition, commercial catalysts are mostly composed of 20-μm aggregates (50–60%) and have a developed monodisperse porous structure with an effective pore diameter of up to 10 nm. The surface area of the catalysts reaches 70–120 m^2/g.

The disadvantage of commercial catalysts is the low selectivity with respect to ammonia: the condensate contains 27.6–45.6 mg/L of ammonia. It was found that the use of the highly disperse iron oxide obtained by dissolution of iron metal in oxalic acid and subsequent thermal treatment and calcium and copper ferrites and nickel oxide as promoters provides a catalyst that compares in activity with commercial analogs, and, at the same time, the ammonium content of the condensate can be decreased by 20–30% [10].

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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