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Oxidation of Carbon Monoxide on Cr-, Mn-, Fe-, Co-, and Ni-containing Catalysts on a Foamed Ceramic Support

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Abstract—A series of oxide catalytic systems with a new foamed ceramic support were suggested for oxidation of CO with atmospheric oxygen. The activity of the catalysts was studied by the pulse procedure; the reagents were analyzed by gas chromatography. The kinetic parameters of oxidation were determined for each catalyst. The systems were ranked with respect to their activity. The systems developed ensure high conversion of CO (~98%) and show promise for industry.

An efficient way to reduce atmospheric pollution with toxic gases is catalytic oxidation of CO. The majority of catalysts presently used for gas treatment contain platinum-group metals or their mixtures with oxides of variable-valence metals [1]. However, such catalysts are expensive and have some other drawbacks, such as high gasodynamic resistance, low specific surface area, high moisture capacity, etc. Therefore, a search for effective catalysts is still an urgent problem [2–4]. The goal of this work was to develop high-performance catalysts using a synthetic foamed ceramics (SFC) as support and Cr(III), Mn(II), Fe(III), Co(II), and Ni(II) compounds as active substances.

We found that the catalysts show noticeable activity in oxidation of CO in the examined range (300–800°C). The reaction is first-order with respect to CO for each catalyst, as follows from the fact that the conversion α of CO at fixed values of temperature and flow rate of the carrier gas is independent of the CO partial pressure in the sample. The ranges of CO concentrations in which the reaction is first-order are listed in Table 1 for all the tested catalytic systems.

The observed order with respect to CO is consistent with published data according to which it can vary from first to negative (close to zero) depending on reaction conditions [5]. Indeed, in our case for all the tested systems the reaction order with respect to CO decreases with decreasing CO concentration. For example, for the Fe-containing catalyst the observed reaction order decreases from 1 to 0.66 as the CO concentration is decreased from 3.52×10^{-3} to 1.17×10^{-3} M. Apparently, under conditions when the reaction order is less than unity prevails the Langmuir–Hinshelwood mechanism involving oxidation of CO with oxygen adsorbed on the catalyst surface [6]. Carbon monoxide is adsorbed better than oxygen [7], and with increasing CO concentartion it displaces oxygen from the surface and decreases the contribution of the Langmuir–Hinshelwood mechanism. Under these conditions the Mars–van Krevelen mechanism becomes prevailing. This mechanism is characteristic of *d* metal oxides at high temperatures [5] and involves reaction of adsorbed CO with oxygen of the oxide, followed by filling of the resulting vacancy with oxygen from the gas phase.

Determination of the kinetic parameters of the reaction by our procedure [8] is possible if the reaction is first-order and is not influenced by diffusion factors. To check this, for each catalyst we have studied the influence of the carrier gas flow rate on the degree of conversion of carbon monoxide at fixed values of temperature and *m/F* ratio, where *m* is the catalyst weight and *F* is the carrier gas flow rate (Table 1). The CO conversion was independent of the

Table 1. Influence of reaction conditions on the degree of CO conversion[a]

Catalyst no.	Catalyst	*T*, K	*m/F*, g s cm^{-3}	$C_{CO} \times 10^3$, M	α
I	Cr_2O_3/SFC	719	0.5	1.76–5.29	0.18
II	MnO_2/SFC	633	0.37	1.49–5.29	0.65
III	Fe_2O_3/SFC	733	0.5	3.52–5.29	0.12
IV	Co_3O_4/SFC	798	0.5	3.52–5.29	0.13
V	NiO/SFC	798	0.5	2.94–5.29	0.20

[a] The quantity *F* ranged from 1 to 2 cm^3 s^{-1}.

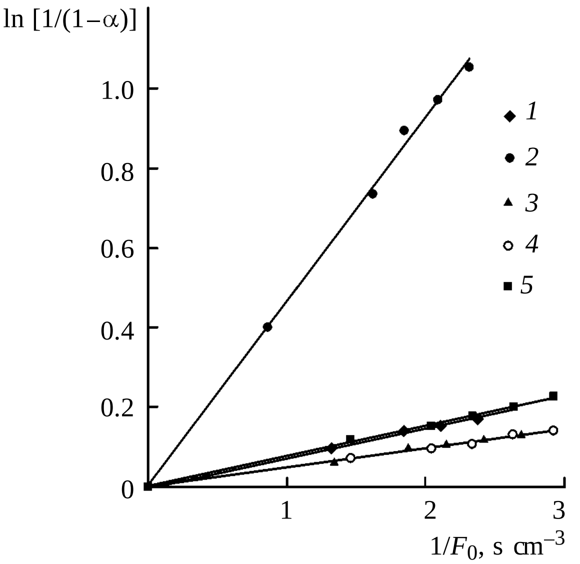

Fig. 1. Conversion of CO as a function of the carrier gas flow rate: (*1*) catalyst **I**, *m* 0.5 g, *T* 719 K; (*2*) catalyst **II**, *m* 0.5259 g, *T* 633 K; (*3*) catalyst **III**, *m* 0.5 g, *T* 733 K; (*4*) catalyst **IV**, *m* 0.5 g, *T* 798 K; and (*5*) catalyst **V**, *m* 0.5 g, *T* 798 K.

gas flow rate in the examined range, which allows the influence of diffusion in this range to be neglected.

To determine the total reaction order, we examined the influence of the carrier gas flow rate on the degree of CO conversion at fixed values of the catalyst weight and temperature (Fig. 1).

The linear plots obtained in the $\ln[1/(1-\alpha)]$–$1/F_0$ coordinates suggest the total first order of the reaction. That is, the reaction order with respect to oxygen under these conditions is zero.

To determine the activation parameters of the reaction, we studied the temperature dependence of the degree of CO conversion. The results are given in Fig. 2 and Table 2.

Table 2. Temperatures corresponding to indicated conversions of CO on various catalysts

Catalyst no.	*T*, K, for indicated α			
	0.25	0.50	0.75	0.98
I	741	800	854	950
II	610	624	636	656
III	785	846	901	998
IV	837	907	971	1087
V	810	868	921	1112

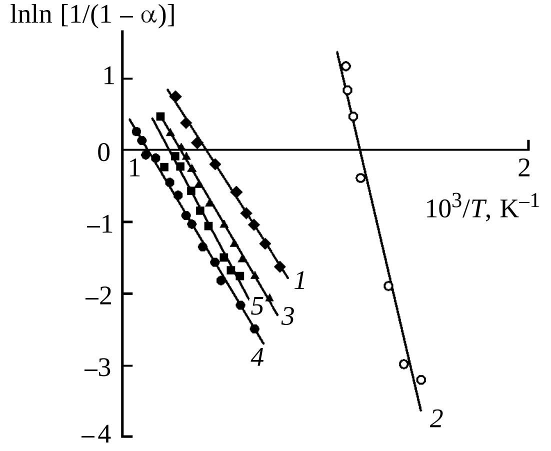

Fig. 2. Temperature dependence of the CO conversion: (*1*) catalyst **I**, *m/F* 0.5 g s cm^{-3}; (*2*) catalyst **II**, *m/F* 0.37 g s cm^{-3}; (*3*) catalyst **III**, *m/F* 0.5 g s cm^{-3}; (*4*) catalyst **IV**, *m/F* 0.5 g s cm^{-3}; and (*5*) catalyst **V**, *m/F* 0.5 g s cm^{-3}.

From the above data, using the relation

$$\ln\ln[1/(1-\alpha)] = -E_a^{app}/(RT) + \ln[k_0^{app}Rm\cdot 273/F_0],$$

where *R* is the universal gas constant and $F_0 = 273F/T$, we calculated the apparent activation energy E_a^{app} and the apparent preexponential term in the Arrhenius equation k_0^{app}.

Thus, the temperature dependence of the apparent rate constant k^{app} (product of the true rate constant and the CO adsorption coefficient, mol atm^{-1} g^{-1} s^{-1} [8]) has the following forms (for catalyst designations, see Table 1):

$$\log k^{app} = (0.110\pm0.004) - (3.835\pm0.095)\times1000/T,$$
for catalyst **I**

$$\log k^{app} = (12.183\pm0.926) - (10.378\pm0.768)\times1000/T,$$
for catalyst **II**

$$\log k^{app} = (0.246\pm0.005) - (4.171\pm0.084)\times1000/T,$$
for catalyst **III**

$$\log k^{app} = (-0.166\pm0.004) - (4.122\pm0.082)\times1000/T,$$
for catalyst **IV**

$$\log k^{app} = (0.602\pm0.048) - (4.607\pm0.345)\times1000/T.$$
for catalyst **V**

Comparison of the apparent rate constants allows the tested catalysts to be ranked in the following order with respect to activity:

$$MnO_2/SFC \gg Cr_2O_3/SFC > Fe_2O_3/SFC$$
$$\geq NiO/SFC > Co_3O_4/SFC.$$

At temperatures above ~1000 K, NiO/SFC and Co_3O_4/SFC change places.

The compensation effect in oxidation of CO on catalysts with the foamed ceramic support is illustrated in Fig. 3. Presumably, the mechanism of CO oxidation is similar on these catalysts. The isokinetic temperature Θ for the catalysts of this group is 520 K.

Comparison with published data [6] allows the developed systems to be classed with catalysts of moderate activity.

The results of this work show that synthetic foamed ceramics is a promising support for catalysts of CO afterburning, along with widely used alumina and silica.

EXPERIMENTAL

As support we used synthetic foamed ceramics belonging to the class of variable-composition heteropoly compounds [9]. The specific surface area of the fraction 0.1–0.4 mm was about 900 $m^2 g^{-1}$. The active substances [chromium(III) nitrate, manganese(II) phosphate, iron(III) sulfate, cobalt(II) nitrate, and nickel(II) nitrate] were applied as described in [4] in the amount of 6.24×10^{-4} mol of metal per gram of support. The prepared catalysts were dried in air at 100°C and then calcined at 700°C in a helium flow. The activities of the catalysts were evaluated with a pulse microcatalytic unit according to [8]. The reagents were analyzed with a Tsvet-106 chromatograph equipped with a thermal conductivity detector and a 3000 × 3-mm column packed with SKT carbon. The carrier gas was helium. The volume of the sample (CO–air mixture) was 1.38 cm^3. The oxidation parameters were varied in the following ranges: temperature 300–800°C; content of CO and O_2 in the sample 2.0–11.8 and 20.6–18.5 vol %, respectively; catalyst weight m 0.37–1.0 g; carrier gas flow rate F 60–120 $cm^3 min^{-1}$. The kinetic measurements were made after attaining the steady-state activity of the catalysts (after conversion of 5–6 samples).

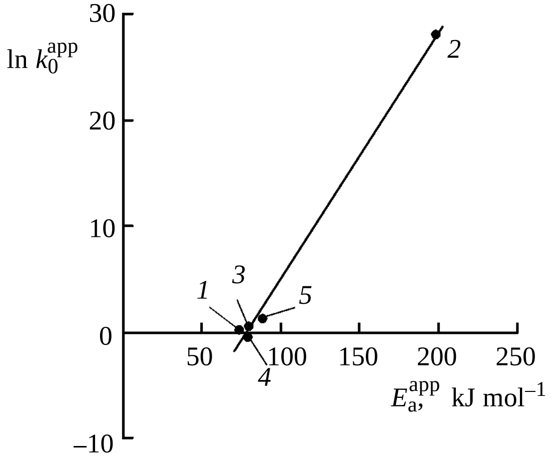

Fig. 3. Compensation effect in CO oxidation on catalysts with the foamed ceramic support: (*1*) Cr_2O_3, (*2*) MnO_2, (*3*) Fe_2O_3, (*4*) Co_3O_4, and (*5*) NiO.

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