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Oxidation of CO on Mn-Containing Catalysts Prepared by Pyrolysis of Metal β-Diketonates on Synthetic Ceramic Foam

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Abstract — New catalytic systems for oxidation of CO to CO_2 were developed. These systems are based on composite Mn, Mn–Ni, and Mn–Cu coatings and are prepared by gas-phase thermolysis of metal β-diketonates on a ceramic foam support. The relative activity of the new catalytic systems was examined. The kinetic and activation parameters of the oxidation of CO on these catalysts were determined.

Catalytic oxidation of CO to CO_2 is an efficient way of rendering harmless gaseous exhausts from automobile transport and industrial enterprises. It was shown previously [1–4] that Mn-containing catalysts are active in conjugate oxidation–reduction of a mixture of nitrogen oxides and CO. Therefore, proceeding with systematic studies of catalytic systems prepared by vacuum thermolysis of transition metal β-diketonates on synthetic ceramic foam [5–8], we studied the catalytic activity of Mn, Mn–Ni-, and Mn–Cu-containing catalysts in oxidation of CO to CO_2.

The catalyst supports were prepared from KhIPEK synthetic ceramic foam (SCF) [TU (Technical Specifications) 5759-010-10657190–97] [9].

Onto synthetic ceramic foam of various compositions, we deposited solid metal-containing products by gas-phase vacuum thermolysis of metal β-diketonates: Mn and Cu acetylacetonates M(*acac*)$_2$ and Ni hexafluoroacetylacetonate Ni(*hfacac*)$_2$. The composition of the catalysts and the conditions of their preparation are given in Table 1.

Thermolysis of metal β-diketonates yields composite coatings containing metals, their oxides, carbides, and free carbon; the coating composition depends on the deposition parameters [10]. Vacuum pyrolysis of Cu(*acac*)$_2$ at 300–400°C yields metallic Cu in a mixture with a nonstoichiometric oxide. Pyrolysis of Ni(*hfacac*)$_2$ yields NiO containing up to 1 wt % C. Pyrolysis of Mn(*acac*)$_2$ yields highly pure ultradispersed (200–500 Å) manganese oxides [11].

Table 1. Composition of catalysts for oxidation of CO to CO_2 and conditions of their preparation

Catalyst no.	Catalyst composition	Metal source	Deposition conditions[a]	Metal source content, wt %
1	Support I[b] + 3% Mn[c]	Mn(*acac*)$_2$	400°C, 1 h	12.1
2	Support I + 3% Mn[c] + 3% Cu[c]	Mn(*acac*)$_2$ Cu(*acac*)$_2$	350°C, 1 h	12.1 9.53
3	Support I + 3% Mn[c] + 3% Ni[c]	Mn(*acac*)$_2$ Ni(*hfacac*)$_2$	400°C, 1 h	12.1 17.4
4	Support II[d] + 3% Mn[c]	Mn(*acac*)$_2$	400°C, 1 h	12.1
5	Support II + 3% Mn[c] + 3% Cu[c]	Mn(*acac*)$_2$ Cu(*acac*)$_2$	350°C, 1 h	12.1 9.53
6	Support II + 3% Mn[c] + 3% Ni[c]	Mn(*acac*)$_2$ Ni(*acac*)$_2$	400°C, 1 h	12.1 17.4

[a] The coatings were deposited by gas-phase thermolysis in a vacuum. [b] Support I: synthetic ceramic foam of the composition $Fe_2O_3/P_2O_5/B_2O_3$/KhIPEK I [9]. [c] Mn-, Mn–Cu-, and Mn–Ni-containing coatings consist of metals, oxides, carbides, and free carbon. [d] Support II: GAZ slime/SCF [GAZ slime is a waste from the electroplating production of the Nizhni Novgorod Automobile Plant (GAZ)], wt %: Cr^{3+} 0.017; Fe^{2+}, Fe^{3+} 4.5; Mn^{2+} 0.01; Zn^{2+} 4.5; PO_4^{3-} 22.37; P_2O_5 16.72; Cu^{2+} 0.01; Ni^{2+} 0.87; SO_4^{2-} 0.9; Cl^- 0.9.

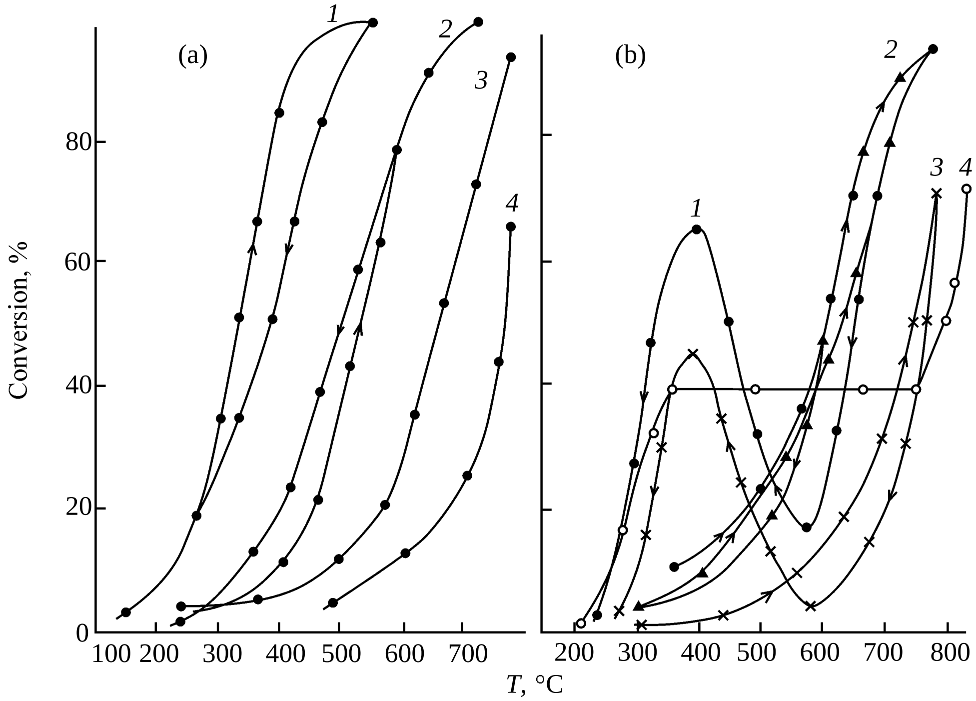

Fig. 1. Comparison of the catalytic activities of the catalysts in a pulse system with CO containing O_2. Support: (a) I and (b) II; *F* 0.5 $cm^3 s^{-1}$; fraction 0.3–0.5 mm; *m*/*F* 1.3 g s cm^{-3}. Catalyst: (a) (*1*) 2, (*2*) 1, (*3*) 3, and (*4*) straight support I; (b) (*1*) 6, (*2*) 5, (*3*) 4, and (*4*) straight support II.

The catalytic activity of the catalysts was evaluated in a pulse microcatalytic system under comparable conditions. All the catalysts were preliminarily heated in the reactor at 500°C for 3 h in a helium flow to attain the stationary catalytic activity. The system reached a steady state after two or three admissions of a CO–air mixture into the microcatalytic system. The temperature dependences of the conversion of CO into CO_2 are shown in Figs. 1 and 2.

With respect to the catalytic activity on support I (Fig. 1a), the catalysts can be ranked in the following order (comparison for 50% conversion in the ascending hysteresis branch): 2 > 1 > 3. The Mn–Cu-containing catalyst was the most active: The conversion of CO to CO_2 started at 100°C, and 100% conversion was attained at 550°C. This catalyst exhibited a “clockwise” hysteresis. The Mn- and Mn–Ni-containing catalysts were less active. The Mn-containing catalyst showed a “counterclockwise” hysteresis, and the Mn–Ni-containing catalyst, no hysteresis. The activity of straight support I was considerably lower than that of the metal-containing catalysts.

Previously we studied the activity of Mn-containing catalysts prepared by impregnation of support I with an aqueous solution of Mn(III) orthophosphate, followed by thermolysis in a helium atmosphere at 700°C [12, 13]. The resulting catalyst MnO_2/SCF (3% Mn in terms of metal) at 360°C and *m*/*F* 0.37 g s cm^{-3} (where *m* is the catalyst weight and *F*, flow rate of the carrier gas) afforded 65% conversion of CO to CO_2. Thus, this catalyst was more active than the Mn–Cu-containing catalyst prepared in this study. The catalyst MnO_2/SCF + V_2O_5 prepared using a vanadium-modified ceramic foam was less active [12]. On this catalyst, the conversion of CO to CO_2 at 600°C was as low as 23%. The Mn-containing catalysts prepared by impregnation of synthetic ceramic foam with potassium permanganate, $K_2O \cdot MnO_2$/SCF, showed a high activity. The amount of the active phase (in terms of Mn) varied from 6 to 30%. The activity of these catalysts depended on the amount of the introduced Mn in a complex fashion, being the highest with 14% Mn. On this catalyst, the conversion of CO to CO_2 started at 200°C, and 100% conversion was reached at 400°C (at *m*/*F* 0.5 g s cm^{-3}) [12]. A high activity was also shown by Mn-containing cobaltites $MnCo_2O_4/\gamma\text{-}Al_2O_3$ prepared by impregnation of the support with the nitrates; the content of the active Mn phase was 20%. The 100% conversion of CO to CO_2 was attained at 170°C [1].

The dependence of the conversion of CO to CO_2 in the presence of oxygen with catalysts on support II

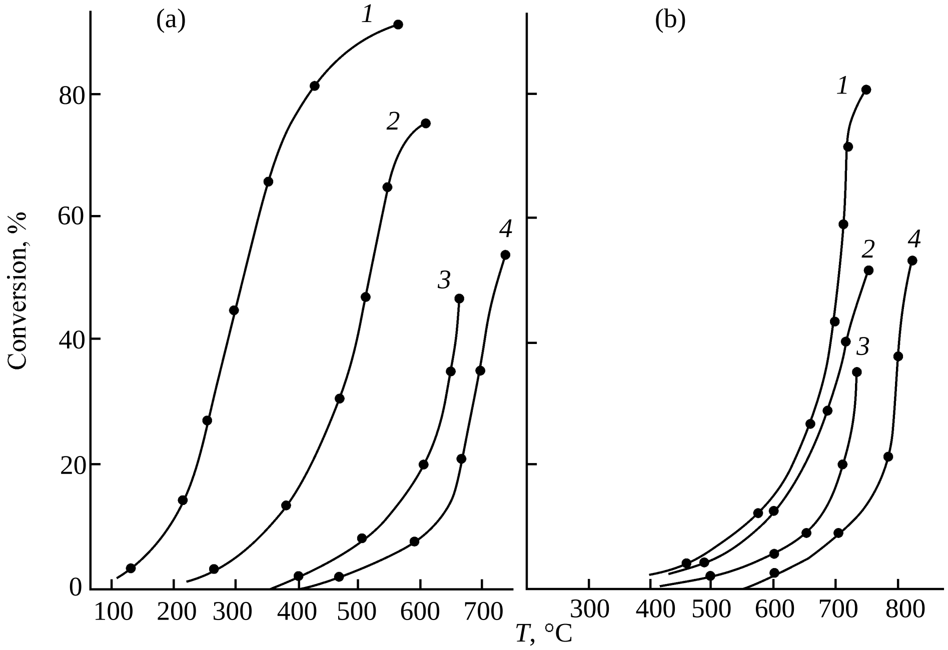

Fig. 2. Comparison of the catalytic activities of the catalysts in a pulse system with oxygen-free CO. Support: (a) I and (b) II; **F** 0.5 $cm^3 s^{-1}$; fraction 0.3–0.5 mm; *m*/*F* 1.3 g s cm^{-3}. Catalyst: (a) (*1*) 2, (*2*) 1, (*3*) 3, and (*4*) straight support I; (b) (*1*) 5, (*2*) 6, (*3*) 4, and (*4*) straight support II.

is shown in Fig. 1b. The conversion curves have a complex oscillating character with a “clockwise” hysteresis. The conversion of CO to CO_2 on straight support II starts at 200°C, at 300°C it reaches 40%, remaining on this level up to 700°C, after which it starts to increase again. The independence of the conversion of CO to CO_2 from temperature in the range 300–750°C may be due to the occurrence of disproportionation: $2CO \rightarrow CO_2 + C$. The catalysts can be ranked in the following order with respect to their activity (for 50% convesion, ascending branch): 6 > 5 > 4 > straight support II. The Mn- and Mn–Cu-containing catalysts on support I are more active than those on support II.

The oxidation of CO to CO_2 under the examined conditions is in total a first-order reaction [5].

The conditions of the kinetic experiments and the activation parameters of the heterogeneous-catalytic oxidation of CO in the presence of oxygen on the examined catalysts are listed in Table 2. The activation energies suggest the kinetic control of the reaction.

To determine the mechanism of oxidation of CO to CO_2, we studied the oxidation of oxygen-free CO on all the catalysts (Fig. 2). For this process, the catalysts on support I (Fig. 2a) are ranked in the following order (for 50% conversion): 2 > 1 > 3 > support I. This order is similar to that observed with CO containing O_2. However, in the absence of CO the catalyst activities decrease, and the conversion curves shift toward higher temperatures by 100–200°C compared to the oxidation of CO in the presence of O_2. The Mn–Cu-containing catalyst appeared to be the most active under these conditions: The CO conversion on this catalyst started at 200°C, and 50% conversion was attained at 400°C.

On support II (Fig. 2b), the conversion of CO to CO_2 in the absence of O_2 drastically decreased, and 10% conversion was attained only at 550–700°C. The catalysts are ranked in the order (for 10% conversion) 5 > 6 > 4 > straight support II. Thus, the Mn–Cu-containing catalyst was the most active under these conditions also. Oscillation phenomena and hysteresis were observed on none of the catalysts under these conditions. Thus, the activity of Mn-containing catalysts in the absence of O_2, when CO is oxidized by the lattice oxygen, is determined by the nature of the support, as in the case of the Zr-, Fe-, Cr-, Ni-, and Cu-containing catalysts [8]. The catalytic activity of straight supports I and II in the absence of O_2 is very low and approximately equal (≤5% conversion at 700°C). Support I contains metal oxides that readily release lattice oxygen in the oxidation of CO to CO_2, whereas support II mainly consists of metal salts that

Table 2. Conditions of kinetic experiments and activation parameters of catalytic oxidation of CO to CO_2 (F 0.5 $cm^3 s^{-1}$, CO/O_2 ratio 1/8)

Catalyst no.	Temperature range, °C	T, °C (α 50%)	$\log k_0$	E_a, kJ mol^{-1}
1	200–690	540	4.33±0.09	68.34±1.76[a]
	650–200	507	3.13±0.14	48.95±1.84[b]
2	140–450	335	2.67±0.07	36.83±0.84[a]
	507–190	385	3.06±0.28	40.34±2.88[b]
3	200–780	670	3.18±0.13	60.53±2.09[c]
4	200–750	725	1.59±0.58	38.41±4.14[c]
5	327–700	620	2.47±0.07	44.77±1.09[a]
	700–330	570	3.46±0.23	62.70±3.76[b]
6	300–700	615	2.73±0.17	48.07±2.38[c]

[a] Ascending hysteresis branch. [b] Descending hysteresis branch. [c] No hysteresis.

Table 3. Conditions of kinetic experiments and activation parameters of catalytic oxidation of oxygen-free CO to CO_2

Catalyst no.	Temperature range, °C	T, °C (α 50%)	$\log k_0$	E_a kJ mol^{-1}
1	365–675	635	3.73±0.25	50.45±3.39
2	192–540	425	3.81±0.24	46.11±1.42
3	435–763	775	4.95±0.86	104.46±3.55
4	500–800	725	2.94±0.09	69.01±1.55
5	400–750	700	5.24±0.74	98.98±3.25
6	375–750	750	3.44±0.42	70.35±3.55

do not exhibit such a property. The activation parameters of oxidation of CO to CO_2 under these conditions are given in Table 3. The activation energies are typical of kinetically controlled reactions.

EXPERIMENTAL

Supports based on KhIPEK ceramics were prepared according to TU 5759-010-10657190–97 [9] by introducing various additives. Prior to catalyst preparation, the ceramic samples (fraction 0.3–0.5 mm) were annealed for 1 h at 500°C. A definite portion of a metal β-diketonate (for support : promoting additive ratios, see Table 1) was added to the support, the sample was placed in a 60-ml glass ampule, and the ampule was evacuated and placed in an oven heated to the required temperature, which was chosen taking into account the optimal conditions of thermolysis of metal β-diketonates [10]. The catalysts obtained were annealed in air at 600°C for 1 h.

The kinetics of heterogeneous-catalytic oxidation of CO to CO_2 was studied by the pulse version of the gas-chromatographic method [5]. The conversion of CO was calculated from the CO_2 peaks by the calibration method. The procedure for kinetic measurements is described in [5].

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