Russian Journal of General Chemistry, Vol. 74, No. 5, 2004, pp. 679–683. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 5, 2004, pp. 742–746.
Original Russian Text Copyright © 2004 by Tsyganova, Didenkulova, Shekunova, Aleksandrov.

Oxidation of Carbon Monoxide on Co-, Ni-, and Cu-containing Catalysts Prepared by Pyrolysis of Metal β-Diketonates on Synthetic Foamed Ceramics

E. I. Tsyganova, I. I. Didenkulova, V. M. Shekunova, and Yu. A. Aleksandrov

Research Institute of Chemistry, Lobachevskii Nizhni Novgorod State University, Nizhni Novgorod, Russia

Received January 21, 2002

Abstract—Catalytic systems containing Co, Ni, and Cu composite coatings prepared by gas-phase thermolysis of metal acetylacetonates and hexafluoroacetylacetonates on synthetic foamed ceramics were suggested for oxidation of CO to CO_2. The relative activities of the catalysts and the kinetic and activation parameters of CO oxidation were determined. The catalytic activity depends on the catalyst preparation procedure.

Catalytic oxidation of CO to CO_2 is an efficient procedure for eliminating CO from automobile exhausts and industrial emissions. This study continues a search for new catalytic systems for oxidation of CO to CO_2 supported on synthetic foamed ceramics (SFC) [1, 2].

The catalyst supports were prepared from modified KhIPEK foamed ceramics [TU (Technical Specifications) 5759-010-10657190–97) [3]. The compositions of the supports and data on their moisture saturation are listed in Table 1. All the supports exhibited satisfactory compression strength (6–8 kg cm^{-2}), water resistance, and moisture saturation. Metal coatings were deposited on the supports in a vacuum by chemical vapor deposition (CVD) [4, 5], namely, by gas-phase thermolysis of copper and cobalt acetylacetonates $M(acac)_2$ (M = Cu, Co) and nickel hexafluoroacetylacetonate $Ni(hfacac)_2$. The compositions of the catalysts and conditions of their preparation and subsequent treatment are given in Table 2.

It is known [6, 7] that thermolysis of metal β-diketonates yields coatings of complex composition, containing metals, their oxides, carbides, and free carbon; the coating composition depends on the deposition parameters. For example, the coating prepared by decomposition of $Cu(acac)_2$ at 300°C contains (wt %) 40 Cu, 50 CuO, and 10 polymeric copper chelate. The coatings prepared by thermolysis of $Co(acac)_2$ and $Ni(hfacac)_2$ at 300–700°C contain carbon in the form of metal carbides and free carbon [6, 7].

For comparison, we also give in Table 2 the data for the catalysts prepared on support II by impregnation with copper(II) nitrate and copper(II) acetate solutions, and also by introduction of copper(II) nitrate into the support composition. It is known that decomposition of $Cu(NO_3)_2$ in air yields CuO, and decomposition of $(CH_3COO)_2Cu$ at 300°C, a carbon-containing composite coating [5].

We studied the moisture saturation of the supports and catalysts in time. The moisture saturation of supports I–III annealed at 500°C does not exceed 3.5% in 10 days (Fig. 1). The moisture saturation of catalysts 1–3 is also shown for comparison. The highest moisture saturation in 10 days is shown by catalyst 1 (7.5%), and the lowest, by catalysts 2 and 3 (4.5%).

The catalyst activities were compared under similar conditions in a pulse catalytic system. All the cata-

Table 1. Composition of ceramic supports

Support	Composition of ceramics	r, g cm^{-1}	Water saturation in 10 days, %
I	SFC[a]	0.51	3.5
II	GAZ slime[b]/SFC	0.65	2.5
III	GAZ slime + 10% finely dispersed carbon[c]/SFC	0.68	2.3

[a] Synthetic foamed ceramics of the composition $Fe_3O_4/P_2O_5/B_2O_3$/KhIPEK I [3]. [b] Waste from the electroplating shop of the Nizhni Novgorod Automobile Plant. Content of components, %: 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; and Cl^- 0.9. [c] Finely dispersed carbon of SKT brand.

Table 2. Composition of catalysts for oxidation of CO to CO_2; conditions of their preparation and subsequent treatment[a]

Catalyst	Catalyst composition	Metal source	Deposition procedure	Deposition conditions	Metal content, wt %
1	Support I + 3%Co[b]	Co(*acac*)$_2$	CVD	Vacuum, 300°C, 2 h	7.65
2	ositel I + 3%Co 3%Cu[b]	Co(*acac*)$_2$ Cu(*acac*)$_2$	CVD	The same	7.65 10.15
3	Support I + 3%Co 3%Ni[b]	Co(*acac*)$_2$ Ni(*hfacac*)$_2$	CVD	Vacuum, 320°C, 1 h	10.3 19.0
4	Support II + 7.5%Cu[b]	Cu(*acac*)$_2$	CVD	Vacuum, 300°C, 1 h	24.0
5	Support II + 3%Co + 3%Ni[b]	Co(*acac*)$_2$ Ni(*hfacac*)$_2$	CVD	The same	10.3 19.0
6	Support III + 3%Co + 3%Ni[b]	Co(*acac*)$_2$ Ni(*hfacac*)$_2$	CVD	"	10.3 19.0
7	Support II + 7.5%CuO	$Cu(NO_3)_2 \cdot 3H_2O$	Impregnation of support with solution	Air, 20°C C	12.52
8	Support II + 7.5%CuO	$Cu(NO_3)_2 \cdot 3H_2O$	Introduction into support composition	The same	12.52
9	Support II + 7.5%CuO	$(CH_3COO)_2Cu$	Impregnation of support with solution	"	23.0
10	Support I	–	–	–	–
11	Support II	–	–	–	–
12	Support III	–	–	–	–

[a] All the catalysts were annealed in air for 1 h at 600°C. [b] Co-, Ni,-, and Cu-containing coatings consist of metals, their oxides, carbides, and free carbon.

lysts were preliminarily annealed in a reactor for 3 h at 500°C in a helium flow to attain steady catalytic activity. The steady state was attained with all the catalysts after 2–3 inputs of samples of the CO–air mixture into the catalytic system.

The temperature dependences of the conversion of CO to CO_2 on various catalysts are shown in Figs. 2 and 3.

The most active catalysts of CO oxidation to CO_2 are those prepared on supports I and II and promoted with solid metal-containing products of joint thermolysis of mixtures of Co and Cu, or Co and Ni β-diketonates (Table 2). The reaction at these catalysts started even at 115–150°C, and at 250–300°C the conversion was complete. These catalysts are only slightly inferior in activity to the Pd-containing catalyst Pd/SFC on which the reaction started at room temperature and the conversion reached 100% at 100°C [1]. The SFC-supported catalysts can be ranked in the following order with respect to the catalytic activity (with the comparison made at 50% conversion: 2 > 5 > 4 > 3 > 6 > 1.

The supports themselves exhibited a weak catalytic activity. With supports I, II, and III, the reaction started at 200, 450, and 600°C, respectively, and 100% conversion was attained at 800–900°C (Fig. 2). On support I, the most active were composite catalysts 2 (Co–Cu) and 3 (Co–Ni); cobalt-containing catalyst 1 was less active. On support II, composite Co–Ni catalyst 5 was the most active, and copper-containing catalyst 4, the least active. The activity of Co–Ni

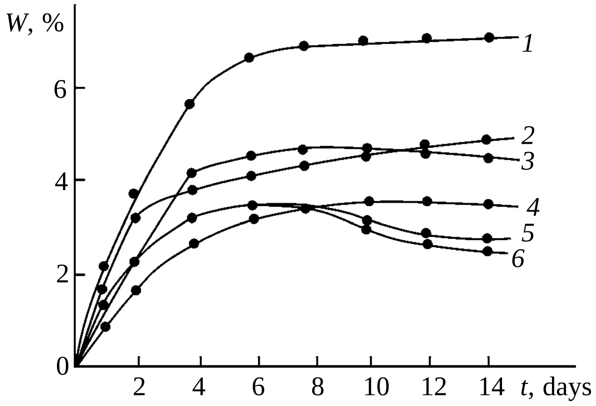

Fig. 1. Moisture saturation (*W*) of catalysts [(*1*) 1, (*2*) 2, and (*3*) 3] and supports [(*4*) I, (*5*) II, and (*6*) II] in time.

catalysts 3, 5, 6 grew with increasing activity of the support: 5 (II) > 3 (I) > 6 (III).

Comparison of the activities of the Co- and Ni-containing catalysts prepared by pyrolysis of β-diketonates of the corresponding metals in a vacuum with the activities of Co_3O_4/SFC and NiO/SFC catalysts prepared by impregnation of support I with solutions of the metal nitrates followed by decomposition [2] showed that the oxide catalysts were less active than the composite carbon-containing catalysts prepared by pyrolysis of metal β-diketonates. For example, at 520°C the conversion on Co_3O_4/SFC and NiO/SFC did not exceed 10–20% [2].

The activity of the Cu-containing catalysts depends on the procedure of their preparation. In Fig. 3, we compare the activities of the Cu-containing catalysts on support II, prepared by different procedures: thermolysis of $Cu(acac)_2$ in a vacuum (4), impregnation of the support with copper(II) nitrate (7) or acetate (9), and introduction of copper(II) nitrate into the composition of support II in the course of its preparation (8). Catalyst 8 was the least active; its activity was even lower than that of straight support II (11). The conversion of CO to CO_2 on catalyst 8 started only at 600°C, against 200°C on sample 11. Catalyst 7 prepared by impregnation of support II with a $Cu(NO_3)_2$ solution followed by annealing at 500°C was more active: The reaction started at 500°C, and 100% conversion was attained at 600°C. The different activities of catalysts 7 and 8, both containing 7.5 wt % CuO, are due to different surface concentrations of CuO. In catalyst 8, CuO is mainly contained in the bulk of the support and in its internal pores, whereas under our experimental conditions only the external surface of the catalyst operates in heterogeneous-catalytic oxidation of CO.

The most active is catalyst 4 prepared by pyrolysis of $Cu(acac)_2$. The similar activity is shown by catalyst 9 prepared by impregnation of the ceramics with a $(CH_3COO)_2Cu$ solution followed by decomposition. This is due to similar composition of the solid phases formed by decomposition of copper acetate and acetylacetonate [5, 6]. Thus, the Cu-containing catalysts can be ranked in the following order with respect to the catalytic activity: 4 > 9 > 7 > 8.

Catalysts 3, 4, 10, and 11 show unusual temperature dependences of the activity, flattening out at 300–500 (for catalysts 3 and 4) or 600–800°C (for catalysts 10 and 11) (Fig. 2). The weak dependence of the CO conversion on temperature may be due to the occurrence of disproportionation [8]:

$$2CO \longrightarrow CO_2 + C.$$

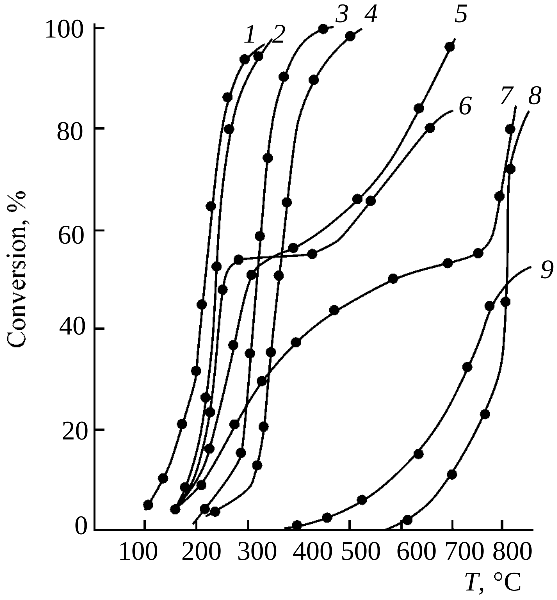

Fig. 2. Comparison of the catalytic activities of catalysts in a pulse system (F 0.5 $cm^3 s^{-1}$, 0.3–0.5-mm fraction). Catalyst: (*1*) 2, (*2*) 5, (*3*) 6, (*4*) 1, (*5*) 3, (*6*) 4, (*7*) 11, (*8*) 12, and (*9*) 10.

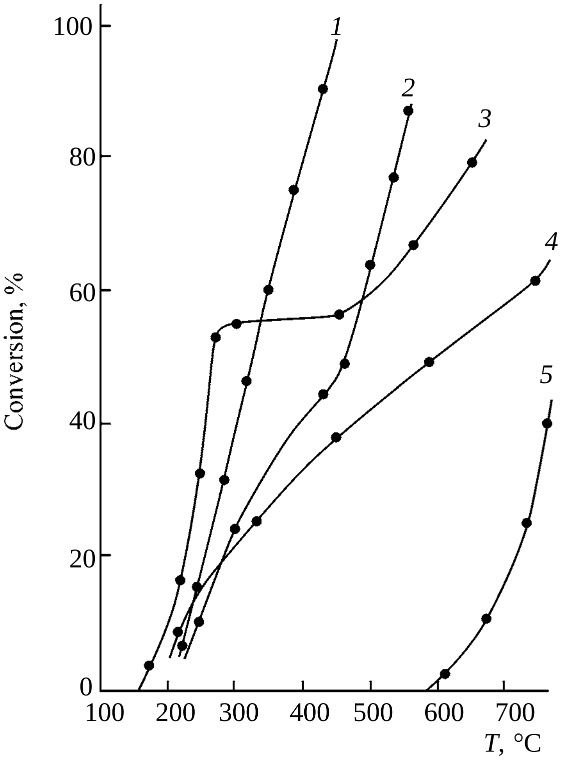

Fig. 3. Temperature dependence of conversion of CO to CO_2 on Cu-containing catalysts prepared by various procedures (F 0.5 $cm^3 s^{-1}$). Catalyst: (*1*) 9, (*2*) 7, (*3*) 4, (*4*) 11, and (*5*) 8.

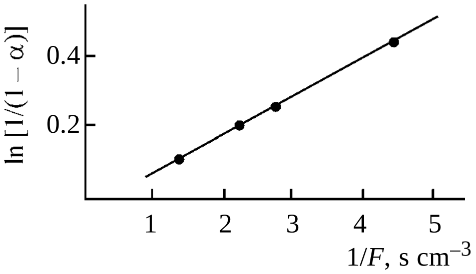

Fig. 4. Plot of CO conversion vs. reciprocal gas flow rate for p_{CO} = 20 mm Hg, T = 237°C.

Catalysts 1, 2, 5, and 6 show a "flash," i.e., a sharp growth of the activity on reaching certain temperature. Apparently, at these temperatures CO oxidation propagates into the bulk by the chain mechanism [9].

Under our experimental conditions, the oxidation of CO to CO_2 had the total reaction order of 1 (Fig. 4).

The conditions of the kinetic experiments and the activation parameters of the heterogeneous-catalytic oxidation of CO on the catalysts studied are given in Table 3. The activation energies suggest that the reaction is kinetically controlled.

Table 3. Conditions of kinetic experiments and activation parameters of the catalytic oxidation of CO to CO_2 (F = 0.5 $cm^3\,s^{-1}$, CO/O_2 ratio 1.8)[a]

Catalyst	Temperature range, °C	T, °C (α 50%)	log k_0	E_a kJ mol^{-1}
1	255–408	400	9.47 ± 1.2	120.96 ± 3.67
			3.45 ± 0.52	70.35 ± 2.11[b]
2	150–250	215	3.46 ± 0.53	70.35 ± 8.70
3	250–700	300	1.19 ± 0.18	16.30 ± 2.15
4	185–632	260	1.77 ± 0.18	24.66 ± 2.77
5	210–350	240	6.62 ± 0.11	69.0 ± 2.42
			0.86 ± 0.13	27.21 ± 1.92[b]
6	220–450	320	4.64 ± 0.14	55.89 ± 1.40[c]
			4.20 ± 0.11	50.12 ± 1.17[d]
7	250–645	460	2.40 ± 0.05	34.61 ± 3.97
8	630–800	775	4.72 ± 0.32	105.5 ± 1.37
9	240–458	340	4.36 ± 0.70	53.60 ± 7.15
10	220–630	625	2.09 ± 0.18	47.82 ± 2.88
			4.53 ± 0.05	104.71 ± 1.00[b]
11	700–840	810	1.89 ± 0.09	28.05 ± 0.92
			5.84 ± 0.08	128.28 ± 1.59[b]
12	450–880	800	5.59 ± 0.48	121.70 ± 3.99

[a] F is the carrier gas flow rate. [b] Air-free CO sample. [c] Ascending branch of the hysteresis loop. [d] Descending branch of the hysteresis loop.

Composite Co–Ni catalyst 6 showed the "counterclockwise" hysteresis, with different degrees of conversions of CO to CO_2 measured in the course of heating and cooling. There is no common opinion in the literature about the nature of the hysteresis. Berman and Margolis [10] attribute it to the occurrence of critical phenomena and possible autooscillations, and Subbotin *et al.* [11], to local overheating of the active centers and low thermal conductivity of the porous support. On Co–Ni catalyst 5, no hysteresis was found even at the CO content in the sample increased by a factor of 2 (from 20 to 40 mm Hg). At higher CO concentration, the temperature of the reaction onset increased from 150 to 200°C, and the temperature of 100% conversion, from 200 to 600°C.

To elucidate the mechanism of CO oxidation to CO_2, we performed experiments on catalysts 1 and 5 both in the presence and in the absence of oxygen (Table 4). It is seen that the conversion of CO to CO_2 in the presence of oxygen ($CO : O_2 = 1 : 8$) is higher. In the absence of oxygen in the gas phase, CO is oxidized with the lattice oxygen. With catalysts 1 and 5, below 240°C, the reaction occurs only in the presence of oxygen (Langmuir–Hinshelwood mechanism), with adsorption of O_2 and CO on active centers and their reaction with each other, whereas above 290°C the Rideal–Ealy mechanism becomes operative, involving the lattice oxygen [12]. The contribution of the second pathway grows with temperature. The CO conversion is independent of the number of successively input samples (up to 10 samples), which confirms the assumption that CO is oxidized with the lattice oxygen. The activation parameter of the CO oxidation on catalysts 1 and 5 in the absence of oxygen in the gas phase are listed in Table 3. In both cases, the activation parameters were lower than those in the presence of oxygen.

EXPERIMENTAL

The catalyst supports based on KhIPEK ceramics were prepared according to TU (Technical Specifications) 5759-010-10657190–97 [3] by introducing various additives into the systems. The water resistance tests were performed by boiling the ceramics in water for no less than 12 h, and the moisture saturation tests, by placing a finely ground sample in a desiccator containing water on the bottom (100% humidity) at room temperature. The moisture saturation was calculated by the formula $\Delta m/m$, where Δm is the weight gain of the sample in time τ, and m is the initial weight. Catalysts 1–6 were prepared with ceramic samples I, III, and III annealed for 1 h at 500°C (0.3–0.5-mm fraction) using definite weighed

Table 4. Temperature dependence of the CO conversion to CO_2 in the presence (α_1) and in the absence (α_2) of oxygen in the gas phase

T, °C	Catalyst 1			T, °C	Catalyst 5		
	α_1, %	α_2, %	α_2/α_1		α_1, %	α_2, %	α_2/α_1
450	90	2	1/45	290	94	2.13	1/44
500	100	4	1/25	355	100	5.38	1/19
550	100	6	1/17	445	100	7.3	1/14
600	100	10	1/10	670	100	12.0	1/8
650	100	25	1/4	740	100	12.9	1/8

portions of metal acetylacetonates $M[CH_3C(O)CH \cdot C(O)CH_3]_2$ (M = Co, Cu). In the case of the Ni-containing catalyst, nickel hexafluoroacetylacetonate $Ni[CF_3C(O)CHC(O)CF_3]_2$ was taken.

The ratios of the supports and promoting additives are given in Table 1. A sample of support with additions of metal β-diketonates was placed in a 60-ml glass ampule, which was evacuated and placed in an oven heated to the required temperature. The decomposition conditions optimized in [6, 7] were chosen. The resulting catalysts were annealed in air for 1 h at 600°C. The procedure for preparing catalysts by impregnation with solutions of metal nitrates and acetates is given in [1, 2].

The kinetics of the heterogeneous-catalytic oxidation of CO to CO_2 was studied by gas chromatography in the pulse mode [1]. The conversion was calculated from the CO_2 peaks, with preliminary calibration. The procedure of the kinetic experiments is described elsewhere [13].

REFERENCES

1. Aleksandrov, Yu.A., Tsyganova, E.I., Shekunova, V.M., Ivanovskaya, K.E., and Vorozheikin, I.A., *Zh. Obshch. Khim.,* 2001, vol. 71, no. 1, p. 46.
2. Aleksandrov, Yu.A., Vorozheikin, I.A., Ivanovskaya, K.E., and Tsyganova, E.I., *Zh. Obshch. Khim.,* 2001, vol. 71, no. 6, p. 881.
3. Aleksandrov, Yu.A., Tsyganova, E.I., and Kaloshina, N.N., RU Patent 2 091 348, 1997, *Byull. Izobret.,* 1997, no. 27, p. 280.
4. Razuvaev, G.A., Gribov, B.G., Domrachev, G.A., and Salamatin, B.A., *Metalloorganicheskie soedineniya v elektronike* (Organometallic Compounds in Electronics), Moscow: Nauka, 1972, p. 311.
5. Gribov, B.G., Domrachev, G.A., Zhuk, B.V., Kaverin, B.S., Kozyrkin, B.I., Mel'nikov, V.V., and Suvorova, O.N., *Osazhdenie plenok i pokrytii razlozheniem metalloorganicheskikh soedinenii* (Deposition of Films and Coatings by Decomposition of Organometallic Compounds), Moscow: Nauka, 1981.
6. Dyagileva, L.M. and Tsyganova, E.I., *Zh. Prikl. Khim.,* 1996, vol. 69, no. 2, p. 177.
7. Tsyganova, E.I. and Dyagileva, L.M., *Usp. Khim.,* 1996, vol. 65, no. 4, p. 334.
8. Panich, N.M., Pirogova, G.N., and Korosteleva, R.N., *Izv. Ross. Akad. Nauk, Ser. Khim.,* 1999, no. 4, p. 698.
9. Orlik, S.N., *Katal. Katal.,* 1987, no. 25, p. 1.
10. Berman, A.D. and Margolis, L.Ya., *Probl. Kinet. Katal.,* 1981, no. 18, p. 48.
11. Subbotin, A.N., Gudkov, B.S., Yakerson, V.N., Chertkova, S.V., Golosman, E.Z., and Kozyreva, G.V., *Zh. Prikl. Khim.,* 2001, vol. 74, no. 9, p. 1463.
12. Orlik, S.N., Vysochenko, V.G., and Martsenyuk, M.G., *Dokl. Akad. Nauk SSSR,* 1980, vol. 253, no. 4, p. 915.
13. Aleksandrov, Yu.A., Tsyganova, E.I., Ivanovskaya, K.E., and Vorozheikin, I.A., *Zh. Obshch. Khim.,* 2002, vol. 72, no. 1, p. 17.