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## Kinetic Features of Thermal Decomposition of Cobalt Acetylacetonate and Development of Catalysts for the Oxidation of Carbon Monoxide, Based on the Decomposition Products

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**Abstract**—The kinetic features of thermal decomposition of cobalt acetylacetonate in a vacuum were elucidated, and the volatile thermolysis products were identified. The homogeneous-heterogeneous character of the process was shown. Catalysts for the oxidation of CO to  $CO_2$  were developed on the basis of cobalt acetylacetonate decomposition products and synthetic cellular ceramics, and the kinetic and activation parameters of the oxidation were determined.

In [1] we considered in detail the reactivity of  $\beta$ -diketonates of Group I–VIII metals in thermolysis and the kinetic features and mechanisms of these processes. The use of these compounds for obtaining active phases of metals, oxides, oxycarbides, and metal complexes on the surface of various supports has been described in [2–4].

Proceeeding with systematic studies of the reactivity of metal  $\beta$ -diketonates, we examined in this work the thermolysis of cobalt acetylacetonate  $Co(acac)_2$  in a vacuum under static conditions in the range 513–603 K at the initial pressure of 40– 133 hPa, using a manometric method. The thermolysis of  $Co(acac)_2$  under these conditions is satisfactorily described by a first-order kinetic equation with respect to both current and initial concentrations of the starting compound (Table 1).

The temperature dependence of the first-order rate constant is described by the following equation (E, J mol<sup>-1</sup>):

$$\log k = (2.93 \pm 0.34) - (54.3 \pm 3.6) \times 10^3 / (2.3RT).$$

As a result of the thermolysis at temperatures above 593 K, the reaction vessel walls are coated with a dark opaque film of pyrolytic cobalt. When the thermolysis is carried out in the presence of air in the ratio  $p[Co(acac)_2]:p_{air} = 1:2$ , the rate constant of the thermolysis increases by a factor of 2, whereas the presence of hydrogen does not appreciably affect the rate constant (Table 1). It was shown that the thermo-

lysis of  $Co(acac)_2$  is a complex homogeneous-heterogeneous process. When the decomposition is carried out in a reaction vessel with walls coated by solid products of the  $Co(acac)_2$  thermolysis obtained in the previous experiment, after removal of the volatile thermolysis products by heating in vacuum at 593 K, the rate constant of the  $Co(acac)_2$  decomposition at 513 K increases by a factor of 1.5. The 5.6-fold increase in the heterogeneous factor *S/V* (*S* is the surface area of the vessel and *V* is its volume) decreased the rate constant by a factor of 1.5. A similar

**Table 1.** Kinetic parameters of gas-phase thermolysis of  $Co(acac)_2$  in a vacuum (V 60 ml, S/V 1.8 cm<sup>-1</sup>)

$T, K^{-1}$	$k \times 10^3$ , s <sup>-1</sup>	p <sub>0</sub> , hPa	$p_{\rm f}/p_0$
513	2.6	114	1.8
513 <sup>a</sup>	1.1	110	1.9
518 <sup>b</sup>	6.1	40	2.6
531	3.6	125	2.3
531 <sup>c</sup>	5.5	110	2.4
557	7.7	40	2.6
557 <sup>d</sup>	8.1	40	2.7
578	9.6	137	2.7
593	14.3	30	2.8
593	14.5	133	2.8

<sup>a</sup>  $S/V = 10 \text{ cm}^{-1}$ . <sup>b</sup> Thermolysis in the presence of air (70 hPa).

<sup>c</sup> Thermolysis in the presence of solid thermolysis products from the previous run, heated in a vacuum at 593 K. <sup>d</sup> Thermolysis in the presence of hydrogen (24 hPa).

decrease in the rate constant with increasing S/V was observed in the thermolysis of Ca, Sr, Ba, and V  $\beta$ -diketonates. This may be due to deceleration of the limiting stage of the thermolysis of metal chelates, namely, opening of the chelate ring followed by elimination of the free ligand [5].

The products of the  $Co(acac)_2$  thermolysis in a vacuum were analyzed by mass spectrometry (Table 2). The products of the thermolysis at low degrees of decomposition at 533 K were acetone, carbon monoxide, and hydrogen. As the temperature was increased from 539 to 693 K, the content of hydrogen and carbon monoxide in the products of complete decomposition increased from 10.5 to 42.3% and from 12.0 to 40.05%, respectively, and the content of acetone decreased from 67.1 to 9.8%. This fact suggests that acetone is formed in the initial stages of the decomposition, and then it decomposes on the cobaltcontaining coating. Thus, the pathway of  $Co(acac)_2$ decomposition is similar to that characteristic of other compounds  $M(acac)_n$  (M = Y, Ti, V, n = 3; M = Ca, Sr, Cu, Ba, n = 2 [5]. It is believed that the first stage of the thermolysis of  $M(acac)_n$  is opening of the chelate ring. Then the ligand undergoes a steric rearrangement with migration of the  $\gamma$ -CH proton from a nonactivated ligand to the activated ligand to form free acetylacetone [5].

Comparison of the kinetic stability of  $Co(acac)_2$ and acetylacetonate complexes  $M(acac)_n$  of the metals studied earlier (M = Cu, Ca, n = 2; M = V, Ti, n = 3), decomposing in the gas phase [5], shows that  $Co(acac)_2$  is the least stable with respect to the thermolysis. Using the thermolysis rate constant as the measure of reactivity, we can rank the acetylacetonate complexes studied in the following order with respect to their kinetic stability:  $V(acac)_3 > Ca(acac)_2 >$  $Ti(acac)_3 > Cu(acac)_2 > Co(acac)_2$ .

We used  $Co(acac)_2$  to prepare catalysts I and II for the oxidation of CO to  $CO_2$  by chemical vapor deposition (CVD) of a cobalt-containing coating in a vacuum on synthetic cellular ceramics (SCC) of various compositions. Catalysts III and IV were prepared for comparison by the impregnation of a cellular ceramics with a  $Co(acac)_2$  solution followed by annealing in air at 873 K (Table 3). The coatings obtained by the thermolysis of  $Co(acac)_2$  at 573– 1073 K are composite carbon–metal coatings of complex composition, containing metals, their oxides, carbides, and free carbon [1, 2]. The coatings obtained by the impregnation of synthetic cellular ceramics followed by annealing in air contain cobalt oxides and free carbon.

We have compared the activity of the catalysts

**Table 2.** Composition of gaseous products of cobalt acetylacetonate pyrolysis (mol%) at various temperatures (*T*) and degrees of decomposition ( $\alpha$ )

<i>Т</i> , К	τ, min	α	Н2	H <sub>2</sub> O	СО	CO <sub>2</sub>	CH <sub>3</sub> COCH <sub>3</sub>
533 533 573 693	60 10 10 30	1.0 0.3 0.5	10.5 10.0 8.1 42.3	1.8 2.9 2.5 0.7	12.0 17.9 13.8 40.05	8.6 1.8 10.5 7.0	67.1 67.4 65.1 9.8
693	10	0.8	46.0	0.7	23.0	7.8	22.4

**Table 3.** Composition of catalysts for the oxidation of CO to  $CO_2$ , based on  $Co(acac)_2$  thermolysis products, and conditions of their preparation and treatment

Catalyst	Support	Application technique	Application conditions
Ι	SCC <sup>a</sup>	CVD <sup>b</sup>	Vacuum, 593 K. 2 h
II III	GAZ slime <sup>c</sup> /SCC SCC <sup>a</sup>	CVD <sup>b</sup> Impregnation with Co( <i>acac</i> ) <sub>2</sub> solution in	The same Annealing in air
IV	GAZ slime <sup>c</sup> /SCC	acetone The same	The same

<sup>a</sup> SCC is synthetic cellular ceramics with the composition  $Fe_3O_4/P_2O_5/B_2O_3/KhIPEK$  [6]. <sup>b</sup> CVD is chemical vapor deposition. <sup>c</sup> GAZ slime is the waste from the electroplating production of the GAZ Joint-Stock Company; composition, %:  $Cr^{3+} 0.017$ ;  $Fe^{2+}$ ,  $Fe^{3+} 4.5$ ;  $Mn^{2+} 0.01$ ;  $Zn^{2+} 4.5$ ;  $PO_4^{3-} 22.37$ ;  $P_2O_5$  16.72;  $Cu^{2+} 0.01$ ;  $Ni^{2+} 0.87$ ;  $SO_4^{2-} 0.9$ ;  $Cl^- 0.9$ .

under comparable conditions in a pulse microcatalytic system [7] (Figs. 1, 2). All the catalysts were preliminarily annealed for 3 h at 773 K in a helium flow to achieve a steady catalytic activity.

Figures 1 and 2 show that the oxidation of CO with oxygen in the presence of catalysts I and II obtained by CVD proceeds in a complex oscillatory mode with a hysteresis in an "anti clockwise" direction when the conversion of CO into  $CO_2$  was different at increasing and decreasing temperatures. The occurrence of the hysteresis is attributed to the critical phenomena and the possibility of autooscillations [8], and also to local overheating of active centers and low thermal conductivity of the porous support [9].

An "anticlockwise" hysteresis was also observed with catalysts III and IV prepared by impregnation with a  $Co(acac)_2$  solution, but oscillatory phenomena

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**Fig. 1.** Comparison of the activities of catalysts I and III on an SCC support in a pulse system ( $F \ 0.5 \ \text{cm}^3 \ \text{s}^{-1}$ , fraction 0.3–0.5 mm). Sample: (1, 2) CO/O<sub>2</sub> 1/8 and (3, 4) CO without O<sub>2</sub>. Catalyst: (1, 4) I and (2, 3) III.

were not observed. The catalysts catalysts are ranked in the following order with respect to their catalytic activity: II > I > III > IV (the comparison was carried out using the ascending curve at 50% conversion). Catalyst II had the highest activity; the conversion on it started at 373 K, and 80% conversion was attained at 623 K. Catalysts III and IV were less active.

The catalyst  $\text{Co}_3\text{O}_4/\text{SCC}$  obtained by impregnation of synthetic cellular ceramics with a solution of cobalt(III) nitrate, followed by annealing [10], is much inferior in the activity to catalysts I–III. The conversion of CO to  $\text{CO}_2$  on it is 13% at 798 K.

The conversion on catalyst II at 373–573 K and on catalyst IV at 423–723 K depends only slightly on temperature (Fig. 1), apparently because of the occurrence of disproportionation [8].

$$2CO \longrightarrow CO_2 + C_2$$

The experimental conditions and parameters of heterogeneous catalytic oxidation of CO on the catalysts under study are given in Table 4. The activation energies show that the reaction is kinetically controlled.



**Fig. 2.** Comparison of the activities of catalysts II and IV on a GAZ slime/SCC support (F 0.5 cm<sup>3</sup> s<sup>-1</sup>, fraction 0.3–0.5 mm). Sample: (I, 2) CO/O<sub>2</sub> 1/8 and (3, 4) CO without O<sub>2</sub>. Catalyst: (I, 3) II and (2, 4) IV.

To determine the mechanism of the reaction on catalysts I–IV, we carried out the oxidation of CO to  $CO_2$  both in the presence and in the absence of oxygen in the reaction mixture. The activation parameters of the oxidation decrease in the case of catalysts I–III and increase in the case of IV. Table 5 shows the ratio of conversions ( $\alpha_2/\alpha_1$ ) at various temperatures ( $\alpha_1$  is the conversion of CO to  $CO_2$  in the presence of  $O_2$ , when  $O_2$  and CO are adsorbed on active centers of the catalyst and react with each other;  $\alpha_2$  is the conversion in the absence of  $O_2$ , when the oxidant is the crystal lattice). The contribution of the second pathway increases with temperature for catalysts I and III and decreases for catalysts II and IV.

## EXPERIMENTAL

Crystalline Co(*acac*)<sub>2</sub> (mp 482 K) was synthesized according to [3]. Found, %: C 46.7; H 5.65; Co 23.0. M 257. C<sub>10</sub>H<sub>14</sub>CoO<sub>4</sub>. Calculated, %: C 46.69; H 5.45; Co 22.96; O 24.9. M 257.

The kinetics of the thermal decomposition of  $Co(acac)_2$  was studied by the manometric method [11]. The rate of the thermal decomposition was determined from an increase in the total pressure

**Table 4.** Conditions of kinetic experiments and activation parameters of catalytic oxidation of CO to  $CO_2$  on cobalt-containing catalysts (*F* 0.5 cm<sup>3</sup> s<sup>-1</sup>, CO/O<sub>2</sub> ratio 1/8)<sup>a</sup>

Cata- lyst	Tempera- ture range, K	<i>T</i> , K (α 50%)	log k <sub>0</sub>	$E_{\rm a}$ , kJ mol <sup>-1</sup>
I	528-681	673	$9.47 \pm 1.20$	120.96±3.67 <sup>b</sup>
	653–550	603	$7.10 \pm 0.30$	$87.69 \pm 2.93^{\circ}$
	681–946	973	$3.45 \pm 0.52$	$70.35 \pm 2.11^{d}$
II	548-613	593	$11.96 \pm 1.08$	$137.94 \pm 2.8^{b}$
	601–538	588	$12.20 \pm 0.80$	$139.19 \pm 2.6^{\circ}$
	627–943	_	$0.85 \pm 0.13$	$27.21 \pm 1.92^{d}$
III	668-811	768	$5.03\pm0.30$	$76.45 \pm 4.02^{b}$
	758–628	698	$7.12 \pm 0.12$	$97.89 \pm 2.30^{\circ}$
	678–906	898	$3.80 \pm 0.20$	$67.34 \pm 2.93^{d}$
IV	548-883	838	$1.83 \pm 0.10$	$32.69 \pm 3.76^{b}$
	903-573	783	$2.50 \pm 0.16$	$37.87 \pm 2.09^{\circ}$
	759–943	_	$4.46 \pm 0.16$	$88.24 \pm 2.51^{d}$
	1			

<sup>a</sup> *F* is the flow rate of the carrier gas. <sup>b</sup> Ascending branch of the hysteresis. <sup>c</sup> Descending branch of the hysteresis. <sup>d</sup> CO sample without oxygen.

**Table 5.** Temperature dependence of CO conversion to  $CO_2$  in the presence  $(\alpha_1)$  and in the absence  $(\alpha_2)$  of oxygen

Catalyst	<i>T</i> , K	α <sub>1</sub> , %	α <sub>2</sub> , %	$(\alpha_1/\alpha_2) \times 100\%$
I	673	51	1	2
	773	15	4	27
	873	90	10	11
II	573	20	2	10
	673	82	5	6.1
III	673	12	4	33.3
	773	60	17	28.3
	873	98	50	51
IV	773	20	2	10
	873	80	4	5

during the reaction. The kinetic curves were constructed as dependences of the degree of reagent conversion  $\alpha$  on time  $\tau$ :  $\alpha = f(\tau) \{\alpha = (p_{\tau} - p_0)/(p_f - p_0) [p_{\tau}, p_0, \text{ and } p_f \text{ are, respectively, current pressure at$  $time <math>\tau$ , initial pressure of the reagent calculated by the equation pV = mRT/M (*p* is pressure; *V*, volume of reaction vessel; *m*, weighed portion of the reagent; *M*, molar weight of the reagent; *R*, universal gas constant; and *T*, temperature), and final pressure of decomposition products  $p_f$ ]. To characterize the Co(*acac*)<sub>2</sub> reactivity in the thermolysis, we used rate constants calculated by the first-order equation  $-\ln(1 - \alpha) = k\tau$ . 1649

The first order of the thermolysis was proved by the fact that the rate constant is independent of the  $Co(acac)_2$  initial concentration. The rate constant was calculated at low conversions (up to 25–30%), which allowed us to neglect the influence of decomposition products on the kinetics of the main process. The activation energy and the preexponential factor were calculated by the Arrhenius equation  $k = k_0 e^{-E/RT}$ using the least-squares method.

The mass-spectrometric analysis of the thermolysis products was carried out on an MI-1305 mass spectrometer at the energy of ionizing electrons of 70 eV, emission current of 1.5 mA, and room temperature of the ion source and inlet system.

The catalyst supports were prepared on the basis of KhIPEK ceramics according to TU (Technical Specifications) 5759-010-10657190–97 [6] by introducing various additives into the system.

To prepare catalysts I and II, we used samples of synthetic cellular ceramics (SCC) annealed for 1 h at 773 K (fraction 0.3–0.5 mm). For this purpose, 0.26 g of Co(*acac*)<sub>2</sub> on 2 g of the support was placed in a 60-ml glass ampule, which was evacuated and heated for 2 h at 573 K. Catalysts III and IV were prepared by impregnating samples of cellular ceramics with a solution of Co(*acac*)<sub>2</sub> in acetone [0.206 g of Co(*acac*)<sub>2</sub> in 2–5 ml of acetone on 2 g of the support]. The solvent was evaporated at room temperature, and then the catalysts were kept for 1 h at 773 K in a muffle.

The kinetics of heterogeneous catalytic oxidation of CO to  $CO_2$  was studied using a pulse version of the gas-chromatographic method [7]. The conversion was calculated from the  $CO_2$  peaks using calibration. The technique of the kinetic measurements is described in [12].

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