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# Relationship between the Catalytic Properties of the Products of the Oxidative Thermolysis of Certain Complexes and the Porous Structures of Samples in the Oxidation Reactions of Volatile Organic Compounds

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**Abstracts**—The rate of the gas-phase oxidation of ethanol, 2-propanol, acetone, ethyl acetate, dioxane, and benzene with atmospheric oxygen is studied on surfaces of bimetallic oxide catalysts Co–Fe, Cu–Fe, Cr–Co, and Ni–Fe, prepared via thermal decomposition of double complex compounds in air. It is found that the rate of oxidation of volatile compounds depends on the volume of the transient pores in the catalyst sample. The rate of oxidation on the same catalyst at 350°C depends on the nature of the substance in the order: acetone > ethyl acetate > ethanol > propanol > dioxane, benzene.

**Keywords:** volatile organic substances, thermolysis product of binary complex compounds, rate constant of catalytic oxidation, transient pore volume

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## INTRODUCTION

Protecting the planet's atmosphere from pollution is a major problem that has long attracted the attention of the scientific community [1]. Volatile organic compounds (VOCs) from different industrial and domestic sources occupy an important place among environmental pollutants. The gas-phase catalytic oxidation of VOCs has been recognized as one of the most effective ways of combating these pollutants [1–4]. The catalysts used in these processes are noble metals (NMs) supported on carriers and the oxides of such transition metal as chromium, manganese, and copper. Due to the high cost of NMs, the cheaper transition metals are receiving increased attention. It is known that bimetallic catalysts based on the latter exhibit better catalytic properties than monometallic catalysts, and even than ones based on NMs [5, 6]. Being a simple molecule, ethanol is well suited for model experiments to study surfaces and thus catalytic oxidation reactions [2]. In [7], the catalytic properties of the products of the thermolysis of double complex compounds (DCCs) of metals of the first transition series in air were studied in the reaction of ethanol oxidation with atmospheric oxygen in a gas stream. The product samples were classified according to composition, specific surface area, pH point of zero charge, concentration of surface OH groups, and the oxida-

tion rate constants of ethanol at 350°C. It was found that the magnitude of the rate constants lay in the range of  $(1-6.5) \times 10^{-5} \text{ s}^{-1}$ , depending on the nature of the catalyst and the gas flow rate. The results obtained in [7] also forced us to give special attention to the porous structure of catalyst samples.

In this work, we continue our study to find a correlation between the rate of oxidation of VOCs and the porous structure of bimetallic oxides obtained via the oxidative thermolysis of DCC. Five of the 13 samples studied in [7], three of which displayed maximum activity and two, minimum activity, in the oxidation of ethanol at 350°C, were selected for more detailed study. In addition, the dependence of the rate of ethanol oxidation on temperature was studied for three samples. For all of the samples, the number of VOCs was expanded to include isopropanol, acetone, ethyl acetate, benzene, and dioxane. Here we studied one possible reactions: the oxidation of VOCs to carbon dioxide. In [4], it was shown that in the presence of manganese oxides, ethyl acetate is completely oxidized to CO<sub>2</sub>. Since dioxane is an isomer of ethyl acetate C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, it is interesting to compare the rate of oxidation of both isomers.

**Table 1.** Porous structures of the samples

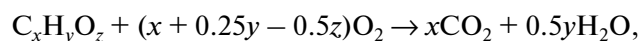
Sample	Starting DCC	$T_{\text{DCC}}$ , °C	$S_{\text{BET}}$ , m <sup>2</sup> /g	$V_{\Sigma}$ , des., cm <sup>3</sup> /g	$V$ , des. ( $d = 300\text{--}15$ nm), cm <sup>3</sup> /g	$S$ ( $d = 300\text{--}15$ nm), m <sup>2</sup> /g	$V$ , des. ( $d = 5\text{--}10$ nm), m <sup>3</sup> /g	$S$ ( $d = 5\text{--}10$ nm), m <sup>2</sup> /g
1	[Cr(ur) <sub>6</sub> ][Co(NO <sub>2</sub> ) <sub>6</sub> ]	250	15.76	0.0396	0.0223	2.35	0.002	1.46
			14.85	0.0347	0.0196	2.08	0.002	1.70
2	[Cr(ur) <sub>6</sub> ][Co(NO <sub>2</sub> ) <sub>6</sub> ]	450	43.92	0.1348	0.0650	8.63	0.061	18.34
3	[Co(NH <sub>3</sub> ) <sub>6</sub> ][Fe(CN) <sub>6</sub> ]	350	48.98	0.1745	0.0954	11.09	0.039	21.37
			39.66	0.1722	0.1145	14.73	0.026	20.89
4	[Co(NH <sub>3</sub> ) <sub>6</sub> ][Fe(CN) <sub>6</sub> ]	450	46.62	0.170	0.097	12.89	0.035	20.00
5	[Cu(pn)] <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub> · 8H <sub>2</sub> O	300	29.64	0.1232	0.0840	9.06	0.017	9.50
			17.09	0.086	0.063	7.50	0.01	5.50
6	[Ni <sub>3</sub> (pn) <sub>6</sub> ][Fe(CN) <sub>6</sub> ] <sub>2</sub> · 6H <sub>2</sub> O	440	27.24	0.070	0.0224	2.21	0.029	15.00

$T_{\text{DCC}}$  is the thermolysis temperature of DCC.

## EXPERIMENTAL

DCCs with the composition [Co(NH<sub>3</sub>)<sub>6</sub>][Fe(CN)<sub>6</sub>], [Cr(ur)<sub>6</sub>][Co(NO<sub>2</sub>)<sub>6</sub>], [Cu(pn)]<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub> · 8H<sub>2</sub>O, [Ni<sub>3</sub>(pn)<sub>6</sub>][Fe(CN)<sub>6</sub>]<sub>2</sub> · 6H<sub>2</sub>O were used as the initial compounds for preparing bimetallic products via thermolysis. The synthesis and thermal decomposition of these compounds under different conditions were described in [8–11]. Thermolysis was performed in air inside a SNOL-7.2/1100 box furnace in quartz boats. Samples were identified via chemical analysis and X-ray diffraction (XRD). The stoichiometric composition of the samples was determined from the results of elemental analysis. Prior to analysis, the samples were dissolved in a mixture of acids (HCl and H<sub>2</sub>SO<sub>4</sub>) and the content of metals in the resulting solution was determined via atomic absorption using an AAnalyst 400 analyzer. The porous structure of these samples was investigated via low temperature nitrogen adsorption using a Tristar 3020 apparatus. Table 1 shows the values obtained for the total pore volume ( $V_{\Sigma}$ , des.); the transient pore volume ( $V$ , des. for  $d = 300\text{--}15$  nm); and specific surface area  $S$  with respect to transient pores, derived from the desorption branch of the nitrogen adsorption isotherm. Ethanol dried via distillation over CaO [12] (density of the resulting alcohol, 0.792 g/cm<sup>3</sup>), was used along with commercial isopropanol, acetone, ethyl acetate, dioxane, and benzene of analytical grade.

Only the full oxidation reaction of organic compounds (ethanol, isopropanol, acetone, ethyl acetate, benzene, and dioxane) was controlled in our experiments, using the equation



and CO<sub>2</sub> was determined as a final product, although the possibility of formation of the products of partial oxidation was not excluded.

Catalytic testing was performed using a laboratory setup [7] consisting of a Nabertherm RT 50-250/11 tubular furnace and a 31 mL tubular quartz reactor (diameter, 15 mm) inserted in it. Catalyst samples weighing 100 mg were placed in quartz boats in the heating zone of the reactor. Atmospheric oxygen was used both as the oxidant, and as the carrier gas for VOCs. Gas–vapor mixtures were obtained by letting air flow at a certain rate through an evaporator held at room temperature, in which about 0.5 g of a VOC were placed. The experiments were performed until most of the VOC had evaporated (at room temperature), which determined the duration of each experiment. The evaporator was weighed before and after each experiment. To obtain comparable data, the oxidation reaction was performed at 350°C.

The gas–air flow (rate, ~15 L/h) was created by a water-jet pump connected to the outlet of the system. The gas stream leaving the reactor passed through a Drechsel bottle containing a titrated solution of carbonate-free NaOH (~0.2 M), in which the formed CO<sub>2</sub> was absorbed. The quantity of CO<sub>2</sub> was determined via titration with 0.1 M HCl solution using two indicators (methyl orange and phenolphthalein) [13]. The air entering the system upstream of the first reactor was passed through a Drechsel flask with 5 M NaOH solution and then one with concentrated sulfuric acid for cleaning and drying [7]. The average concentration of VOCs in the gas stream was (2.0–2.5) × 10<sup>-4</sup> mol/L. The maximum degree of VOC conversion at a flow rate of about 15 L/h reached 60% in 3 h.

According to [14, p. 377], the above system can be considered (as discussed in [7]) to be one in which the reaction proceeds in a laminar flow in a plug flow reactor (i.e., a closed system). The rate of the reaction was monitored from the amount of the accumulated final product, which was used to calculate conversion  $p$  of the initial material. In order to have apparent rate

constant  $k$  as a value that allows to compare the results of catalytic tests, we used the equation for a reaction of the first order in a closed system [14]:

$$t_{p\%} = (-2.303/k)\log(1-p/100),$$

where  $t_{p\%}$  is the interval of time in which the degree of conversion reaches  $p\%$ .

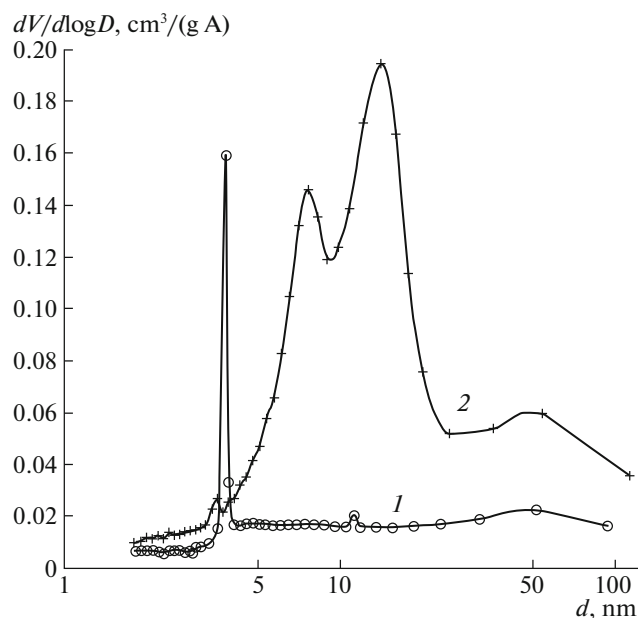
The characteristics of the studied samples are listed in Table 1 and the figure; the averaged values of the rate constants of catalytic oxidation of VOCs are given in Tables 2 and 3. The values of standard deviation are given for the constants.

## RESULTS AND DISCUSSION

Table 1 includes the volumes found using porograms for transient pores and the volumes of the largest micropores with sizes accessible to the studied molecules of VOCs ( $\geq 5$  nm), along with the specific surfaces areas related to those of the pores. The values of the equivalent radii of the molecules (calculated from the molar volume by assuming the molecules were spherical) were, nm: benzene, 0.70; isopropanol, 0.67; dioxane, 0.70; acetone, 0.66; ethyl acetate, 0.73; and ethanol, 0.61.

Samples 1, 3, and 5 serve as examples of the reproducibility with which the studied samples were prepared. The smallest pore volumes and lowest  $S_{\text{BET}}$  were, along with the surfaces of transient pores, found for sample 1 (Fig. 1). It can be seen that it has micropores in a very narrow range, a small surface area, and low volume of transient pores. The porous structure of samples 2–4 is very similar to the characteristics of samples 5 and 6, and it is slightly inferior to the characteristics of 2–4. For the studied samples, the pore volumes and the specific surfaces corresponding to them generally differ by 150–200%, except for samples 1 and 5. The pore structure depends on the nature of the initial complex and the conditions of thermolysis, which were quite similar to one another.

All rate constants of VOC oxidation were determined at 350°C. Table 2 confirms the correctness of our choice of temperature. It can be seen that the ethanol oxidation reaction starts only at 250°C. A sharp increase in its rate is observed as the temperature rises to 300°C, after which it remains constant within the error of determination up to 500°C. This profile of the rate's temperature dependence is typical for the gas-phase oxidation of VOCs [1–4].



Differential porograms of samples (1) 1 and (2) 2.

Table 3 shows the apparent rate constants for VOCs. The dependence of oxidation rate on the nature of VOCs for all of the studied catalysts is generally the same: acetone > ethyl acetate > ethanol > isopropanol > benzene > dioxane. It can be seen that it is easier to oxidize VOCs containing carbonyl and carboxyl groups. The reaction most sensitive to the nature of the catalyst is that of the oxidation of benzene; the one least sensitive is that of dioxane, due possibly to the cyclic structure of dioxane containing no multiple bonds. The rate the latter reaction is not affected by minor differences in the structure of the samples. Within the margin of error, the rates of ethanol and isopropanol oxidation can be considered identical, and they depend very little on the nature of the catalyst sample. The faster the reaction proceeds, the more noticeable the differences in the rate for different samples.

Sample 2 should be recognized as the one most active, since it has the greatest volume of pores with diameters of about 8–20 nm (figure, Table 1). In addition, it is the only example that yields fairly high and constant results in the oxidation of benzene. The assumption made in [7] that the volume of transient pores and the specific surface area corresponding to

**Table 2.** Temperature dependence of the rate of ethanol oxidation ( $K_1 \times 10^5, \text{s}^{-1}$ ) at temperatures of 250–500°C

Sample	250°C	300°C	350°C	400°C	450°C	500°C
1	~0.3	$5.5 \pm 0.2$	$5.4 \pm 0.2$	$5.8 \pm 0.3$	$5.2 \pm 0.3$	$5.6 \pm 0.2$
3	~0.3	$4.2 \pm 0.3$	$4.2 \pm 0.5$	$5.6 \pm 0.2$	$5.6 \pm 0.4$	$5.5 \pm 0.4$
5	~0	$5.2 \pm 0.2$	$5.0 \pm 0.1$	$5.0 \pm 0.1$	$5.9 \pm 0.2$	$6.0 \pm 0.7$

**Table 3.** Rate constant values for VOCs oxidation ( $K_1 \times 10^5, \text{s}^{-1}$ ) for samples 1–6 at 350°C

VOC	1	2	3	4	5	6
Ethanol	$5.5 \pm 0.1$	$5.3 \pm 0.4$	$5.1 \pm 0.8$	$3.3 \pm 0.1$	$5.2 \pm 0.2$	$4.2 \pm 0.2$
Isopropanol	$5.0 \pm 0.4$	$5.0 \pm 0.4$	$4.6 \pm 0.2$	$5.2 \pm 0.2$	$4.9 \pm 0.3$	$3.8 \pm 0.3$
Ethyl acetate	$7.8 \pm 0.6$	$8.2 \pm 0.4$	$7.0 \pm 0.4$	$6.2 \pm 1.2$	$6.0 \pm 0.2$	$6.9 \pm 0.4$
Dioxane	~2.7	$2.7 \pm 0.2$	~2.0	~2.6	~2.3	~2.2
Acetone	$15.3 \pm 1.4$	$17.7 \pm 0.7$	$16.6 \pm 0.8$	$13.5 \pm 1.1$	$16.3 \pm 0.4$	$16.9 \pm 0.6$
Benzene	~2.4	$4.6 \pm 0.3$	~0.1	0	~0.3	~0.4

them determine their catalytic activity in the studied reaction was largely confirmed. The reason for the fairly high activity of sample 1 is not entirely clear; its surface area is due mainly to micropores (figure). Our assumptions are indirectly confirmed by the authors of [1–4] agreeing that the rate of VOC oxidation is not associated with the total value of the specific surface area (which in those works lay the range of 25 to 110 m<sup>2</sup>/g), probably because the rate does not correlate with the porous structure of the catalyst samples.

In the future, we intend to expand the range of catalytically active samples by examining their porous structure and using such VOCs as acetone, benzene, and dimethylformamide.

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