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The effect of the structure of Cu–Ti oxide systems obtained by sol–gel synthesis on the nature of catalytic centres and catalytic activity in low-temperature CO oxidation

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It has been shown by X-ray diffraction analysis, EXAFS and XPS methods and in experiments on the low-temperature oxidation of CO that two types of catalytic oxidation centres are formed during sol–gel synthesis of single-phase Cu–Ti oxide systems (0.5–5.0 mass% Cu) based on anatase: the first type involves Cu^+ ions in the [111] crystal planes, while the second type involves Cu^{2+} ions, which isomorphically substitute titanium ions in the [100] planes of TiO_2.

Alkoxo technology is a non-traditional method for the preparation of highly active metal oxide catalysts.[1,2] Analysis of recent literature shows that, although this approach is used rather widely for the directed synthesis of materials for electronics, its application to the synthesis of catalysts is only at the developmental stage.

In the present work we study the effect of the synthesis conditions on the structure, catalytic properties and nature of the active centres in a series of Cu–Ti oxide systems (copper content 0.5–14 mass%) synthesised by the sol–gel method.[†] The oxidation of CO was used as the model reaction because of the high reactivity of this compound and the diversity of its oxidation mechanisms on oxide catalysts.[‡]

Analysis of the results in Table 1 shows that for single-phase Cu–Ti oxides, an increase in copper content from 0.5 to 3 mass% (samples 1–5) decreases the temperature of the start of CO oxidation from 140 °C to less than 100 °C, while the degree of CO conversion at temperatures near 140 °C increases several-fold. When the copper content is increased to 8 mass% (samples 5–7), the CO conversion at 100–140 °C increases. Further accumulation of copper in the Cu–Ti oxide resulted in phase separation and hence a decrease in the catalytic activity of CO oxidation over the entire temperature range. This is evident from the fact that CO conversion on samples 8 and 9, which contained 11 and 14 mass% copper, respectively, was 12–50% of that on samples 5–7.

The data in Table 1 show that a constant copper content in the oxide phase (5 mass%) structure is the factor determining the catalytic activity in oxidation (samples 6 and 10–13). For example, the ratio of degrees of CO conversion on samples 6 and 10, which have the same phase composition (anatase) but different microcrystallite size (13 and 19 nm, respectively), is 4:1 at 100–120 °C. As the temperature is increased, the difference in activity decreases only near 200 °C. The change in phase composition, which manifested itself as the formation of rutile and CuO identified by X-ray diffraction (samples 11–13), led to a decrease in catalytic activity over the entire temperature range, and exhaustive conversion of CO was not reached even at 200 °C.

Pure TiO_2 (sample 14) was inactive in CO oxidation over the temperature range studied and provided a noticeable conversion only at temperatures close to 400 °C. In the presence of CuO (sample 15), exhaustive conversion of CO requires a temperature of 200–210 °C. Of the Cu–Ti oxides obtained, the highest activity was displayed by single-phase systems with empirical formula $Cu_xTi_{1-0.5x}O_2$ (anatase), where $x \leq 0.09$.

The effective activation energy of CO conversion in the low-temperature region (5–7% conversion) and at 150–160 °C (6–10% conversion) was calculated to be 5.6 and 17–19 kcal mol^{-1}, respectively. The latter value is in good accord with that determined for oxides with perovskite structure and corresponds to the activation energy of oxygen in the lattice.[5]

Analysis of data obtained by EXAFS and XPS (Tables 2 and 3) and comparison of ion sizes for titanium and copper makes it possible to make an assumption about the structure of the surface monolayer of the Cu–Ti oxide single-phase systems synthesised. For example, it was shown by XPS that 90% of surface copper is in the 2+ oxidation state, which is characterised by bond energies of 953.0, 943.5–943.0 and 956.0 eV. Only 10% of the modifier is present in the 1+ state with bond energies of 932.5 and 952.5 eV. The main difference between the surface states of the catalytic systems studied is that the ratio of the amounts of chemisorbed oxygen (1s) and Cu^+ ions for specimen 6 was several times higher than that for specimens 10 and 13 with the same copper content (Table 3).

According to EXAFS data, each surface copper ion is surrounded by six oxygen ions and the length of the Cu–O bonds on the surface is 1.95 Å (Table 2). Only one longer interatomic distance was observed, namely, Cu–Me (Me = Ti or Cu), $R = 3.04$ Å, which coincides with the distance in the anatase lattice. Table 3 illustrates the two possible variants of the model consistent with the results obtained. One of the models regards the Cu–Ti distance of 3.04 Å as the interatomic distance in the first coordination sphere of Cu^{2+} and describes TiO_2 modified with copper (anatase). The other model, which uses the Cu–Cu distance of 2.99 Å, describes the copper dimer in the CuO phase. The coordination number of copper was estimated as 1 in both models. Probably, the first model is preferable, since a study of the charge state by the static magnetic susceptibility method showed that copper is present in its single-phase oxides as isolated paramagnetic Cu^{2+} ions (d^9).

Thus, analysis of the experimental data makes it possible to make an assumption about the structure of the surface monolayer of the Cu–Ti oxide single-phase systems synthesised. The Cu^{2+} ions can isomorphically substitute Ti^{4+} ions in microcrystallite planes; the difference between the ionic radii (0.72 and 0.68 Å, respectively) can cause defects in the crystal lattice.

[†] Copper stearate, $Cu(C_{17}H_{35}COO)_2$, and titanium tetrabutoxide, $Ti(OBu^n)_4$, were used as precursors.

[‡] A mixture of CO with air (0.5 vol.%) was used in the catalytic experiment. The experiments were carried out in a flow-through U-shaped quartz reactor (inner diameter 4 mm) with a stationary catalyst layer (particle size 0.1–0.25 mm). The specimen amount was 0.5 cm^3, the gas volume velocity was 50000 h^{-1}, and the temperature range was 50–400 °C. The composition of the gas mixture at reactor inlet and outlet was analysed chromatographically on a column with Porapak Q (inner diameter 2 mm, length 1.5 m). The concentration of CO in the flow was determined on a Riken Fine IR-550A gas analyser.

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Table 1 Structural characteristics of Cu–Ti oxides synthesised and their catalytic activity in the oxidation of CO (0.5 vol.%) with atmospheric oxygen at a volume velocity of 50000 h^{-1}.[a]

Sample no.	Phase composition, empirical formula	Copper content (mass%)	Crystallite size/nm	Specific surface area[b]/ m^2 g^{-1}	Conversion of CO (±1%) at temperature (°C)					
					100	120	140	150	170	200
1	Anatase $Cu_{0.006}Ti_{0.997}O_{2+\delta}$	0.5	50	120	0	0	1	3	7	16
2	Anatase $Cu_{0.01}Ti_{0.99}O_{2+\delta}$	1.1	42	120	8	19	22	26	32	49
3	Anatase $Cu_{0.02}Ti_{0.99}O_{2+\delta}$	2.2	28	118	16	39	61	72	86	100
4	Anatase $Cu_{0.02}Ti_{0.99}O_{2+\delta}$	2.5	—	118	20	62	91	97	100	100
5	Anatase $Cu_{0.03}Ti_{0.98}O_{2+\delta}$	3.1	13	118	55	94	100	100	100	100
6	Anatase $Cu_{0.06}Ti_{0.97}O_{2+\delta}$	5.0	13	118	49	89	100	100	100	100
7	Anatase $Cu_{0.09}Ti_{0.95}O_{2+\delta}$, CuO (traces)	8.1	14	110	56	92	100	100	100	100
8	Anatase 80%, rutile 9%, CuO 11%	11.1	46	80	7	21	46	66	90	100
9	Anatase 50%, rutile 36%, CuO 14%	14.1	35	70	9	28	60	74	84	96
10	Anatase $Cu_{0.06}Ti_{0.97}O_{2+\delta}$	5.1	19	110	12	22	53	73	93	100
11	Anatase, CuO (traces)	5.0	25	100	2	8	15	20	40	92
12	Anatase 23%, rutile 73%, CuO 4%	5.1	86	90	2	8	17	25	62	96
13	Anatase (traces), rutile 95%, CuO 5%	5.1	90	30	1	3	5	7	18	92
14	Anatase	0.0	122	120	0	0	0	0	0	0
15	CuO	80.0	—	—	0	0	0	7	40	98

[a]The phase composition and mean crystallite size were determined on a DRON-3M diffractometer with filtered CuKα irradiation. Identification of crystalline phases was performed according to X-ray diffraction data for pure compounds published by ASTM.[3] The mean crystallite size was calculated from the half-widths of the [200] and [400] lines for anatase using the Sherer equation.[4] The half-width $MgAl_2O_4$ at 1600 °C was used as a standard. [b]Determined by the BET method with nitrogen as the sorbate.

The Cu^+ ions (0.93 Å) can only be connected through bridging oxygen above the plane surfaces. The elevation of singly-charged copper above the surface allows it to coordinate a large quantity of weakly bound oxygen (Table 3), which is highly reactive even at low temperatures (100–140 °C).

It is known that non-bridging Me=O bonds in the surface oxide polyhedra of some transition metals can undergo excitation under conditions of thermal treatment, forming reactive anion radicals, which can subsequently dissociate.[6,7] It should also be noted that the catalytic activity of perovskites ABO_3 in oxidation was proved to depend on the energy of the metal–oxygen bond in the anion.[8–10] Even a small weakening of the B–O bond resulted in a sharp decrease in the overall rate of CO oxidation at low temperatures. In the case of our catalysts, it is most likely that a similar effect was observed in $Cu_xTi_{1-0.5x}O_2$ single-phase systems, in which defects appeared on crystallite faces due to the deformation of the anatase lattice, as described above. Replacement of titanium ions with Cu^{2+} ions partially weakens the bonds of chemisorbed oxygen with the surface; this weakening manifests itself as a decrease in CO oxidation temperatures even at a low copper content in Cu–Ti oxides (Table 1).

Comparative analysis of catalytic and structural data allows us to assume that the surface of the catalysts synthesised contains two types of active centres: low-temperature (100–140 °C) and high-temperature ones (140–200 °C). Probably, the former centres involve Cu^+ ions, whereas the latter ones contain Cu^{2+} ions, which isomorphically replace a fraction of the titanium ions in the first monolayer of anatase.

A comparison of degrees of CO conversion at 120 and 200 °C for samples 2 and 3 (Table 1) shows that the ratio of contributions of the low- and high-temperature centres is *ca.* 0.6, provided that they are totally involved in oxidation and taking into account the increase in the reaction rate with increase in temperature (from 120 to 200 °C). At higher copper content in single-phase systems (specimens 4–7), total oxidation occurs at 140 °C, *i.e.* it involves the low-temperature centres only.

Table 2 EXAFS results for the coordination environment of copper ions in the structure of $Cu_{0.06}Ti_{0.97}O_2$ (anatase) for the two possible models.

Model	Type of bond	Interatomic distance/Å	Effective coordination number	Debye–Vallera factor	*R* factor
1	Cu–O	1.95	6.20	2.6	26.9
	Cu–Ti	3.04	0.74	2.4	
2	Cu–O	1.95	6.20	2.6	26.4
	Cu–Cu	2.99	0.72	2.3	

Figure 1(*a*) shows a possible structure for the transition complex during the oxidation of CO on the low-temperature centres of Cu-substituted anatase according to the Rideal–Eley mechanism, reactions (1)–(3).[11] The elevation of isolated Cu^+ ions above the plane surface favours the formation of local areas of increased concentration of weakly bound non-bridging oxygen, which is easily activated at temperatures as low as 100–120 °C. XPS data indicated an increased ratio of concentrations of reactive surface oxygen and Cu^+ ions on specimen 6 (anatase) (Table 3).

$$Cu^+\text{---}O + CO_{gas} \longrightarrow Cu^+\text{-------}O\text{-----}CO \qquad (1)$$

$$Cu^+\text{-------}O\text{-----}CO \longrightarrow Cu^+\text{---}[\ ] + CO_2 \qquad (2)$$

$$2Cu^+\text{---}[\ ] + O_2 \longrightarrow 2Cu^+\text{---}O \qquad (3)$$

$$Cu^{2+}\text{---}O + CO_{ads} \longrightarrow Cu^{2+}\text{-------}O\text{---}CO \qquad (4)$$

$$Cu^{2+}\text{-------}O\text{---}CO \longrightarrow Cu^{2+}\text{---}[\ ] + CO_2 \qquad (5)$$

$$2Cu^{2+}\text{---}[\ ] + O_2 \longrightarrow 2Cu^{2+}\text{---}O \qquad (6)$$

As the temperature is increased, the process involves ever more high-temperature active centres containing Cu^{2+} ions, where CO chemisorption becomes possible [Figure 1(*b*)]. This enables the Langmuir–Hinshelwood mechanism, reaction (4), to occur.[11] When CO_2 formed desorbs from the catalytic surface, an oxygen vacancy is formed on the catalyst surface, reaction (5). This vacancy can activate oxygen that comes from the gas phase, reaction (6). As noted above, at temperatures near 200 °C the differences in catalytic activity of CuO and oxide systems containing over 1 mass% copper almost level off. This indicates that the –Cu–O– fragment participates in reactions (4)–(6) in all cases: on a modified anatase surface (samples 3–6

Table 3 Composition (atom.%) of the surface of Cu–Ti oxide catalysts containing 5 mass% copper (samples 6, 10 and 13) according to XPS data.

Components	Sample no.		
	6	10	13
Ti^{4+}	20.66	21.32	22.80
Cu^+	2.76	6.14	5.86
O_{total}	76.57	72.53	71.33
$O_{lattice + H_2O}$	63.09	60.48	61.07
O_{ads}	13.48	12.06	10.27
O_{ads}/Cu^+	4.90	1.90	1.70

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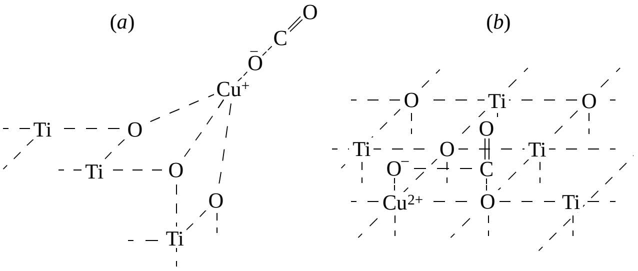

Figure 1 Possible structures of transition surface complexes during CO oxidation on low- (*a*) and high-temperature (*b*) active centres of Cu–Ti oxide single-phase systems.

and 10), in the presence of coarsely-dispersed CuO phase in the mixed oxide (samples 7–9 and 11–13) and on CuO (sample 13) and on CuO (sample 15).

The activation of oxygen probably occurs due to dissociative adsorption, and its surface reactive forms can be attached to copper ions, reaction (3).

It was found that in the low-temperature region, in which activation of chemisorbed CO does not yet occur, the rate of CO oxidation increases (curve *1* in Figure 2) as copper is accumulated in modified anatase $Cu_xTi_{1-0.5x}O_2$ (samples 2–7). On the other hand, the plot of CO conversion per 1 g atom of copper has a maximum at about 3.5 mass% of the modifying metal (curve *2* in Figure 2). Thus, it is not only saturation of the system by the modifying metal that plays a role in the formation of the structure and catalytic activity in the low-temperature region. It is known that weakly bound, readily activated oxygen is concentrated on crystal lattice defects, and the oxidation rate grows as the number of such accumulations involving Cu^+ ions increases (curve *1* in Figure 2). In turn, the inflection of curve *2* at copper content above 3.5% may be caused by the formation of $\{–Cu–O–\}_n$ fragments, which are nuclei of the CuO phase.

Thus, we have shown that the concentration of copper used as a metal modifier affects the structure of oxide systems and hence the catalytic activity in CO oxidation. If the concentration of copper in a Cu–Ti oxide does not exceed 8 mass%, single-phase systems with empirical formula $Cu_xTi_{1-0.5x}O_2$ ($x \leq 0.09$) in the anatase modification are formed. In this case, Cu^+ ions build on the oxide TiO_2 polyhedra in the [111] plane through bridging oxygen, whereas Cu^{2+} ions isomorphically substitute the titanium surface atoms in the [100] plane. If the copper content in the oxide system exceeds 8 mass%, the oxide contains more than one phase, *i.e.* TiO_2 (anatase and rutile) and CuO. Single-phase systems are characterised by catalytically active centres of two types: low-temperature (110–140 °C) involving Cu^+ ions and high-temperature (140–200 °C) involving Cu^{2+} ions.

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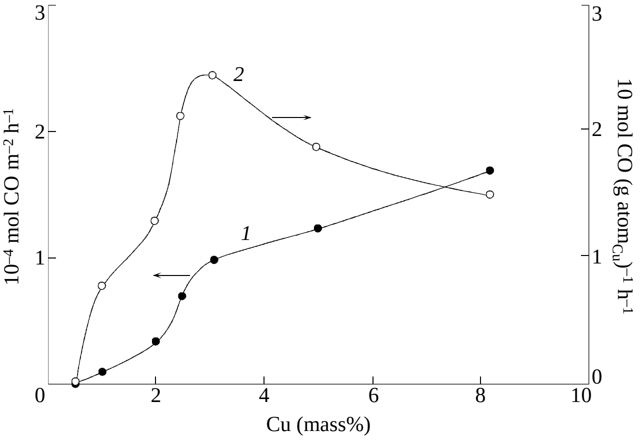

Figure 2 Oxidation rate (mol CO m^{-2} h^{-1}) (curve *1*) and conversion on 1 g atom of copper [mol CO (g $atom_{Cu}$)$^{-1}$ h^{-1}] (curve *2*) in the CO oxidation with air oxygen. The volume velocity was 50000 h^{-1}.

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