Room Temperature Oxidation of Carbon Monoxide Catalyzed by Hydrous Ruthenium Dioxide**

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The catalytic oxidation of carbon monoxide to carbon dioxide at room temperature and atmospheric pressure is a key process for respiratory protection and industrial air purification. Examples where it is used include safety devices for mining industry, space technology, and deep sea diving; removal of CO in flue gases; the stabilization of carbon dioxide lasers; and fuel cells.[1] Numerous studies were therefore performed to improve the catalytic oxidation of carbon monoxide at low temperatures, typically less than 100 °C. It was found that noble metals such as Au, Ag, Pd, Pt, and Ru supported on various metal oxides can catalyze the oxidation of CO in the range of 30–75 °C.[2] Similar results were reported for gold catalysts supported on MnO_x, Fe_2O_3, Co_3O_4, NiO, and CuO.[3] However, most of these metal catalysts can not be applied practically in humid air since the presence of water induces anodic corrosion. For this reason many attempts have been made to use mixed metal oxides as possible substitutes for the precious metals. One of the best known is hopcalite[4] ($CuMn_2O_4$), which is the active component of various technical devices. Further examples are SnO_2/CuO gels[5], Mn/Ag composite oxides,[6] Cu/Zn oxides,[7] and supported $PdCl_2/CuCl_2$ catalysts.[8] Herein we report that a simple binary oxide, hydrous ruthenium(IV) oxide, is an efficient catalyst for the low-temperature oxidation of carbon monoxide by humid air. Although this oxide has been widely used as a catalyst for the photo and thermal oxidation of water to O_2,[9, 10] no report on CO oxidation under the corresponding mild reaction conditions could be found in the literature. These experimental conditions differ significantly from very recent findings in which CO is oxidized at the RuO_2 (110) crystal surface at about 600 K. Heating to a higher temperature reconstitutes the surface.[11]

Figure 1 displays conversion versus time curves for the room-temperature oxidation of CO (0.8 vol %) in undried air catalyzed by $RuO_2 \cdot x H_2O$ powder spread onto a glass plate carrier. Almost 40 % of the CO was converted into CO_2 after 20 min. The stability of the catalyst is demonstrated by the negligible change in activity upon multiple use. In situ IR spectroscopy on the reaction revealed the presence of an isosbestic point, which suggests a clean oxidation reaction occurs.

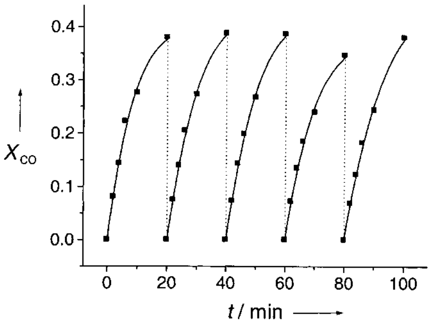

Figure 1. Five successive cycles for the room temperature oxidation of CO in the presence of $RuO_2 \cdot x H_2O$ (dried at 150 °C) in undried air. The dotted lines correspond to the readjustment of the CO concentration (0.8 vol % in air) after the previous run.

To investigate the dependence of activity on the heating treatment, a series of $RuO_2 \cdot x H_2O$ samples were dried at various temperatures and their catalytic activity was tested at 21 ± 1 °C in a CO/O_2 mixture with a partial pressure ratio ($p(CO)/p(O_2)$) of 1/1 (Table 1). The untreated sample contained 82 wt % of water and exhibited almost negligible activity. When it was dried in ambient air, its initial rate increased from 0.1 to 5.3 mL min^{-1}. The highest initial rates of 80–90 mL min^{-1} and conversions of 42–46 % (after 10 min) were observed when the samples were dried at 150–250 °C; in these cases the powders contained 9–10 wt % of H_2O. When the samples were dried at 450 or 600 °C the water content decreased sharply to 0.6 % and the activity was almost as low as for the highly hydrous sample. This large decrease in the activity may arise from partial decomposition or a decrease in the specific surface area caused by the process of sintering and crystallization.[9] The initial rate of 71 mL min^{-1} for a sample loaded on silica gel at low coverage ($RuO_2 \cdot x H_2O/SiO_2 = 3/10$ (wt/wt)) almost matches that of the unsupported catalyst dried at 150 °C. This result may be attributed to the large surface area of silica gel (340 m^2 g^{-1}), which provides a higher concentration of catalytic sites.

Table 1. Dependence of the initial rate of reaction (v_0 [mL min^{-1}]) and CO conversion (X_{CO} [%]) after 10 min[a] on the water content (x_{H_2O} [wt %]), after various drying times t and different temperatures T; $p(CO)/p(O_2) = 1/1$.

T [°C]	t [h]	x_{H_2O} [wt %]	v_0 mL min^{-1}	X_{CO} [%]
RT[b]	1.5	82	0.1	0.1
21	15[c]	33	5.3	2.9
60	12	16	75	36
150	4	10	82	46
250	10	9	90	42
450	0.5	2	1.1	0.7
600	2	0.6	0.9	0.6

[a] Based on the amount of CO_2 produced. [b] Highly hydrous sample, 1.5 h of exposure to ambient air after filtering off. [c] Dried in air.

TiO_2 powder, which consists mainly of the anatase and to a lesser extent of the rutile modification, was chosen as another support because of its nontoxicity and the fact that RuO_2 has a rutile structure. A further advantage of TiO_2 is that it adheres firmly to the surface of the glass plate carrier. It is thus possible to use the catalyst repeatedly under exactly the same conditions. We therefore investigated in this system the oxidation of CO in the temperature range of 22–79 °C using a mixture of CO and O_2 with a partial pressure ratio of 1/1 (Figure 2a). The activation energy (E_a) was determined as 8.6 kcal mol^{-1} from the temperature dependence of the initial

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[**] L.Z. is indebted to the Alexander-von-Humboldt-Stiftung for a fellowship.

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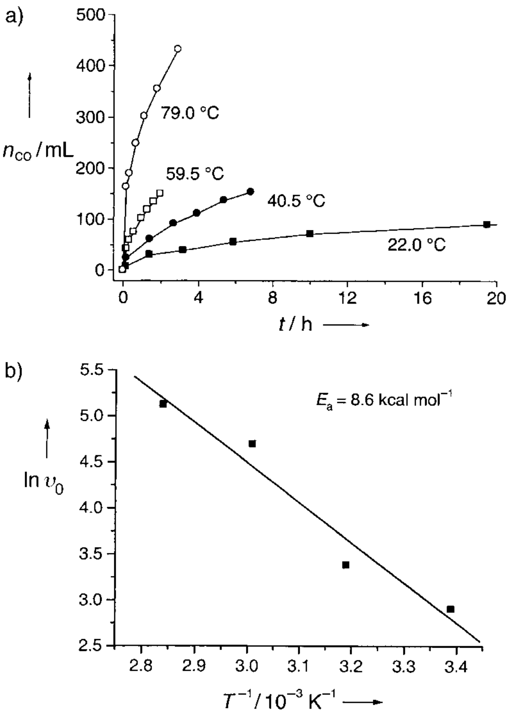

Figure 2. Temperature-dependence of the CO oxidation when catalyzed by TiO_2-supported $RuO_2 \cdot xH_2O$ (dried at 200°C); $p(CO)/p(O_2) = 1/1$. a) The turnover–time curve, n_{CO} = CO consumption; b) The Arrhenius plot, where v_0 is the initial rate of the reaction.

rate (Figure 2b). This value is much lower than the ones reported for other metal oxides such as Cu_2O (13.9 kcal mol^{-1}), CuO (16.7 kcal mol^{-1}), and Fe_2O_3 (26.4 kcal mol^{-1}).[12, 13] This lower value may explain the higher activity of the hydrous ruthenium oxide at room temperature.

Table 2 presents the effect of the composition of the CO/O_2 mixture on the rate of CO oxidation at room temperature with a catalyst dried at 150°C. It is evident that the initial reaction rate increases steadily with increasing partial pressure of CO.

Table 2. CO oxidation rates v_0 and conversion X[a] at different CO/O_2 partial pressure ratios.

CO/O_2	1/11.5	1/4	1/1.5	1/0.89	1/0.56	1/0.16
v_0 [mL min^{-1}][b]	5.4	12	56	84	113	150
X [%][c]	18	19	29	33	36	20

[a] From the disappearance of CO. [b] Initial rate. [c] After 6 min.

The catalyst is quite active with respect to CO conversion over the whole range of CO/O_2 ratios with an optimum value at a partial pressure ratio ($p(CO)/p(O_2)$) of about 1/0.56. In the three experiments where CO is in excess of O_2 the reaction proceeded violently, accompanied by red fire flashing at the surface of the catalyst powder. However, at the highest CO partial pressure ratio of 1/0.16 the activity decreased within several minutes, possibly as a consequence of the reduction of the Ru^{IV} species to lower oxidation states by CO. This proposal might explain the decrease in the conversion of CO into CO_2 observed at this high CO partial pressure. Generally, the high activity, good stability at low CO partial pressures, and tolerance towards humidity makes this material a promising catalyst for CO removal. Examples for practical applications are fuel cells, air filters, antipollution paints, and various environmental safety devices.

Experimental Section

Triply distilled water (30 mL) was added to $RuCl_3 \cdot nH_2O$ (439 mg, 41% Ru) with stirring. The solution was kept for 30 min before the pH value was adjusted 4.5–5.0 by the slow addition of 2 M NaOH. Subsequent stirring of the mixture for another 30 min was followed by the addition of further 2 M NaOH until pH 6 was reached and precipitation of $RuO_2 \cdot xH_2O$ occurred. After stirring the mixture for a further 60 min the solution was finally adjusted to pH 7.0 to complete the process. Thereafter stirring was continued for another 60 min and the solution was refluxed at 100°C for 2 h. The black precipitate was filtered off and washed 10 times with water. Water contents were calculated from the weight loss after annealing. SiO_2- or TiO_2-supported catalysts were prepared by sonication of the corresponding suspension containing hydrous RuO_2. After drying the samples for more than 2 days at 60°C, $RuO_2 \cdot xH_2O/SiO_2$ (3/10 (wt/wt))) was heated for 4 h at 150°C, and $RuO_2 \cdot xH_2O/TiO_2$ (3/10 (wt/wt)), coated on the glass plate, was heated for 20 min at 200°C in an air stream. Oxidation of CO was carried out in a closed reaction system (total volume of 2435 mL) containing the catalyst powder cast onto a heatable glass plate (4 × 4 cm) and fitted with a membrane pump for gas circulation and a gas cell with KBr windows for IR measurement. A total pressure of 1 atm of the reactant gases (CO/O_2 or CO/air) was maintained in all experiments. The production of CO_2 and the decrease of CO were monitored from the changes in the IR absorption, after calibration with the pure gases.

Received: April 11, 2000 [Z14969]

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