

Oxidation of Carbon Monoxide on Carbon-Supported Metal Oxides

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Introduction

Many investigations have been concerned with the catalytic oxidation of carbon monoxide by metal oxides but relatively few when the oxides are supported on activated carbons. Commercial carbons have been modified by operations of outgassing, heating or specific burn-offs. The present studies, however, are concerned with metal oxides on these materials using only air or nitrogen in dynamic flow systems as the preconditioning process.

Carbon Dioxide from Activated Carbons

The carbon dioxide contained in granular activated carbons was removed by passing a flow of nitrogen through the sample contained in a vertical 2-cm tube with downward flow at the temperature of the experiment. A aliquot of the effluent was passed through a non-dispersive carbon dioxide analyses for on-line measurements and through a carbon monoxide analyzer when CO was present.

An example (Figure 1) shows the removal of carbon dioxide from a coal-base carbon in a flow of nitrogen at 80°C. The results are similar to chromatograph behavior with the important exception that the carbon particles are large (1.3 to 0.7 mm diameter) and baseline steady states may be more rapidly attained. No carbon monoxide was detected in this experiment.

A second example (Figure 2) followed the rapid desorption of adsorbed carbon dioxide in a flow of nitrogen (2 L/min) at the indicated temperatures. Previously, a mixture of carbon dioxide in nitrogen (2000 ppm) was passed through the sample for about 10 minutes; nitrogen at the same flow was then rapidly introduced and the resulting concentration of carbon dioxide determined. An analogous procedure with the empty container is shown in which the baseline concentration was attained in less than 2 minutes. There is only a small temperature effect on the removal of the carbon dioxide. Although a flow of

nitrogen does not completely desorb the carbon dioxide, it does permit the experiment to reach a reproducible baseline at a given temperature, flow and initial concentration.

Oxidation of Carbon Monoxide

The oxidation of carbon monoxide has been followed using the above pretreatment for the metal oxide supported on activated carbon. An example with a commercial whetlerite (Cu, Cr and Ag oxides on a coal-base activated charcoal) is shown in Figure 3. Steady-state concentrations of both

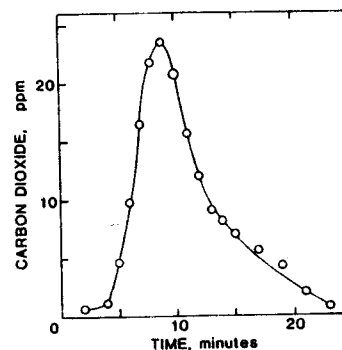


Fig. 1 Removal of CO₂ from activated carbons in flow of nitrogen at 80°C (6025).

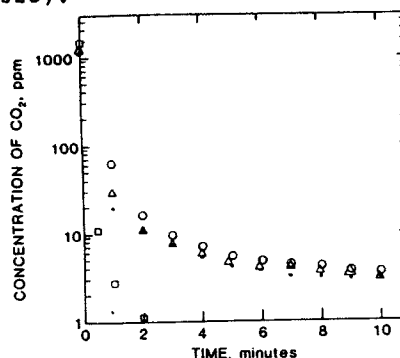


Fig. 2 Desorption of adsorbed CO₂ into a Flow of Nitrogen (Run 6017); O 23°, Δ 44°, ● 56°, □ empty container.

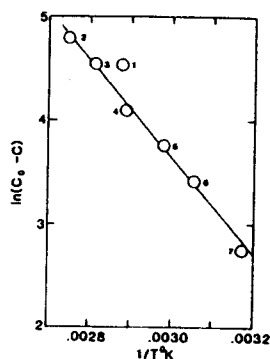


Fig. 3 Catalytic Oxidation of CO based on the disappearance of CO (Run 6016), $\Delta H = 9.7$ Kcal

carbon dioxide and carbon monoxide were attained between 42 and 90.5°C. A plot of the CO removed as a function of $1/T^\circ K$ gave a heat of activation of 9.7 kcal/mole. The low heat is attributed to the desorption of the carbon dioxide formed at the catalytic sites of oxidation.

An important variation in the observed CO oxidation was found with different samples of the catalyst. Plots of the carbon dioxide formed as a function of the carbon monoxide lost showed linear plots of different slopes. If the reaction produces 1 CO₂ and consumes 1 CO, the reaction is stoichiometric with slope 1 (Fig. 4, line A). If two CO molecules produce only 1 CO₂, the slope is 2 (Fig. 4, line B). Many examples have found for behavior in agreement with A, B or in between.

Laboratory Catalysts

A number of catalysts have been prepared using ammoniacal copper carbonate or ammoniacal copper and chromium carbonates supported on a coal-base activated carbon. Copper alone is not very active at temperatures below 100°C (Fig. 5), but copper and chromium impregnations oxidize CO as low as 50°C (Fig. 6).

Conclusions

The oxidation of CO to form CO₂ was observed to range with different catalysts from a mole ratio CO/CO₂ of 2 to 1, depending on the catalyst preparation. The mole ratio is linear with temperature in the range in which the carbon support has thermal stability with respect to oxidation. A preparation using copper plus chromium is more reactive below 100°C than those containing copper alone.

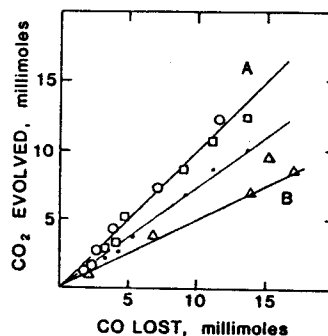


Fig. 4 Mass balance between carbon dioxide found and carbon monoxide lost on a commercial whetlerite.

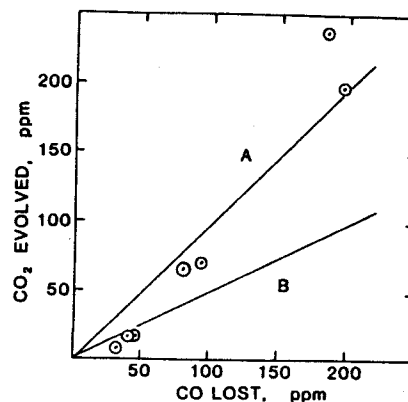


Fig. 5 Oxidation of CO by CuO catalyst supported on activated carbon; note temperature range 144- 294°C (6024).

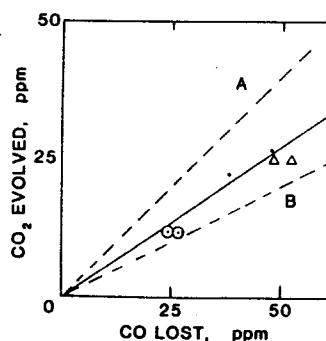


Fig. 6 Oxidation of CO by Cu-Cr oxide catalyst supported on activated carbon - note temperature range 50-72°C (6023).