Influence of dry operating conditions: observation of oscillations and low temperature CO oxidation over Co_3O_4 and Au/Co_3O_4 catalysts

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The effect of dry operating conditions upon the oxidation of CO over Co_3O_4 and Au/Co_3O_4 has been studied. Under dry conditions (with pretreatment and reaction gases dried at −76°C using molecular sieve traps) oxidation of CO over Co_3O_4 can be observed at temperatures as low as −54°C. However, without sufficient drying Co_3O_4 rapidly deactivates. On the other hand, the Au/Co_3O_4 catalyst is resistant to the presence of moisture even at low temperatures. For both the Co_3O_4 and Au/Co_3O_4 catalytic systems, strong and periodic oscillations in percentage conversion and catalyst bed temperature have been observed.

Keywords: Co_3O_4; gold; CO oxidation; oscillation; moisture effect

1. Introduction

Of the catalytic systems which we have looked at previously for low temperature CO oxidation, the most active are gold supported upon 3d transition metal oxides and the hydroxides of alkaline earths [1–5]. Of these, the Co_3O_4 and Fe_2O_3 systems are the most promising and high percentage conversions have been obtained even at dry-ice temperatures.

Mechanistic studies on these supported gold catalysts have recently been reported by us [5] and interest by other groups on supported gold catalysts is also growing [6–11]. It has been found, that in addition to the low temperature activity shown by supported gold, these catalysts also have the advantageous feature of enhanced activity in the presence of moisture [12]. This is of particular importance for the removal of CO from air under ambient conditions.

In the study of catalysis, however, the role played by water molecules is still unclear. Though the Au/metal oxide system is known to be resistant to water in simple oxides it appreciably deactivates [13]. It has therefore been suggested that

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moisture preferentially adsorbs onto active sites at the metal oxide surface, but as yet direct evidence supporting this hypothesis has not been reported.

It was therefore of interest that, for the Co_3O_4 metal oxide, moisture desorption occurs over four distinct temperature regions. The first of these regions starts between 30 and 180°C [14,15] and under normal operating conditions containing around 3 ppm H_2O, is comparable with the region where the cobalt oxide starts to exhibit high activity.

In this paper we present our initial findings on the behaviour of the Co_3O_4 catalytic system to the low temperature oxidation reaction of carbon monoxide under dried, normal and wet conditions. Comparison with Au/Co_3O_4 under similar conditions is also presented.

2. Experimental

Tricobalt tetraoxide was prepared by a 400°C calcination of the carbonate precipitated from an aqueous solution of $Co(NO_3)_2$. The crystalline nature was confirmed using X-ray diffraction and a BET analysis revealed a specific surface area of 52.1 m^2/g. Catalysts with small gold particles of diameters less than 5 nm were deposited on Co_3O_4 by coprecipitation [1]. For the present studies a 5 at% Au loading has been used with the loading calculated on a $Au/(Au + Co)$ metal basis. The surface area for the Au/Co_3O_4 system was 52.8 m^2/g.

To determine the catalytic behaviour, a fixed-bed reactor shown in fig. 1 was used. The design of this reactor is identical to that used in earlier studies and is able to provide both good temperature stability and reproducibility. In this set-up the mean temperature is measured using a chromel–alumel thermocouple enveloped in glass and set 1 mm into the catalyst bed. Control at low temperatures (± 0.3°C) was achieved by methanol/dry ice mixtures. For higher than room temperatures a standard resistive heater, linked to a computer was used.

Between particles of Co_3O_4 and Au/Co_3O_4 there is an apparent difference in packing density. Therefore, to retain the same catalyst bed length we used two different masses of 150 and 300 mg, respectively. For comparison we have also studied each catalyst twice at 10 000 and 20 000 h^{-1} ml/g-cat space velocities. For both samples the size distribution was within 70–120 mesh.

In the measurement of percentage conversion, a standard reaction gas containing 1% CO and 99% air was used. In all cases pretreatment was for 40 min at 200°C under air. The catalyst was returned to room temperature while still under air and the reaction gas then allowed to enter the cell. Analysis of the effluent gas, for CO and CO_2, was made by gas chromatography, using molecular sieve and active carbon columns. Percentage conversion was recorded after holding the temperature steady for between 30 and 45 min.

For reaction conditions described as wet or normal, the pretreatment step was carried out without consideration of the moisture level. Under these conditions, the

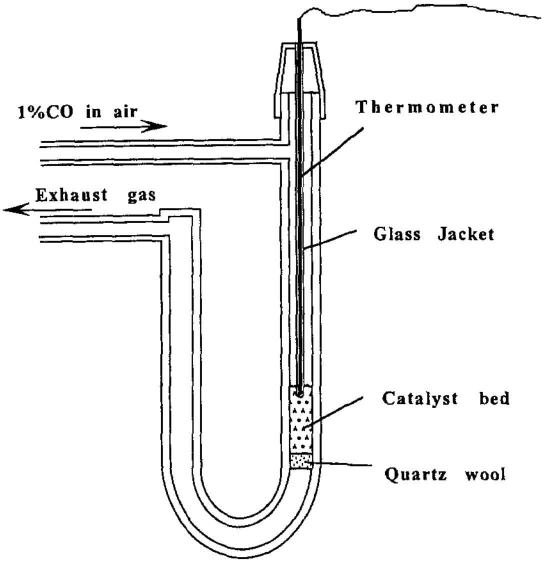

Fig. 1. Diagram of reaction cell used in these studies. Catalyst bed length 3 cm long with the temperature recorded 1 mm into the bed.

moisture entering the reaction vessel during pretreatment was high and typically well in excess of 10 ppm. The reaction gas used for wet conditions was additionally bubbled through a water bed to give a moisture level of 6000 ppm. For normal conditions the reaction gas was taken directly from the cylinder without treatment and contained 3 ppm H_2O.

For dried conditions both the pretreatment and reaction gases were passed through molecular sieve traps cooled at dry ice temperatures. Pretreatment and reaction gases were dried individually and the reaction lines purged thoroughly. This required between 2 and 4 h after which the moisture level was typically measured at 850 ppb. An additional 2 to 3 h was also required to obtain a stable GC response due to the retardation effect experienced by the CO as it passes through the molecular sieve H_2O trap.

All moisture levels given above are for the gas directly before entering the reaction vessel. Detection of moisture from between 0.5 and 10 000 ppb was made using a modified Hycosmo C1202LA cryogenic optical dew point moisture sensor supplied by Osaka Sanso Kogyo Ltd.

3. Results and discussion

The data for wet, normal and dried reaction conditions are presented in fig. 2 as a function of temperature. In all cases the data is shown after pretreatment. The reaction gas was then allowed to enter the reaction cell and the percentage conver-

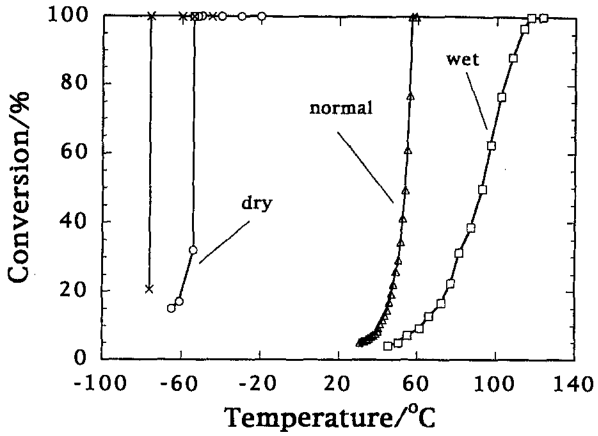

Fig. 2. Conversion profiles for CO oxidation over Co_3O_4, with changes in pretreatment and reaction conditions. Data shown is for (□) wet, (△) normal and (○) dry reaction conditions. Data for Au/Co_3O_4 under normal conditions (×) is shown here for comparison.

sion recorded at room temperature. The temperature was then increased, or decreased, depending upon the initial percentage conversion. In this diagram, the data for Au/Co_3O_4 under normal reaction conditions is shown for comparison.

Looking first at the difference between Co_3O_4 under normal and wet conditions, two curves are obtained separated by some 40°C. When the reaction conditions were changed to dry pretreatment and reaction gases this shift continues and the operating temperature for 50% conversion decreases to −54°C. At this point deactivation of the catalyst is rapid with the percentage conversion decreasing from 100 to 35%. For Au/Co_3O_4 under normal reaction conditions a sharp drop in conversion was only observed near −76°C.

To test the reproducibility of this deactivation temperature, the operating temperature was reduced from room temperature over cooling times ranging three to seven hours (fig. 3). In each case different samples were additionally used, however, between each of the plots the difference in deactivation temperature is only 1.5°C.

To reduce the operating temperature below −54°C, for Co_3O_4, it was found necessary to rapidly cool the system at much higher rates. This can be done, for example, by the direct cooling of the catalyst in dry ice methanol. This is shown in fig. 4 where the percentage conversion for both Au/Co_3O_4 and Co_3O_4 catalysts are presented directly from the point of immersion. In this figure, percentage conversions have been obtained under dry conditions at two space velocities (10 000 and 20 000 h^{-1} ml/g-cat) and within 20 min of pretreatment.

Considering first only the Au/Co_3O_4 catalyst, the time observed for deactivation (around 100 min) compares favorably with data which we have already published [16]. In this diagram we have defined the deactivation time as being only the time required for the conversion to falls below 100%. This is generally easier to define than the time required to reach steady-state.

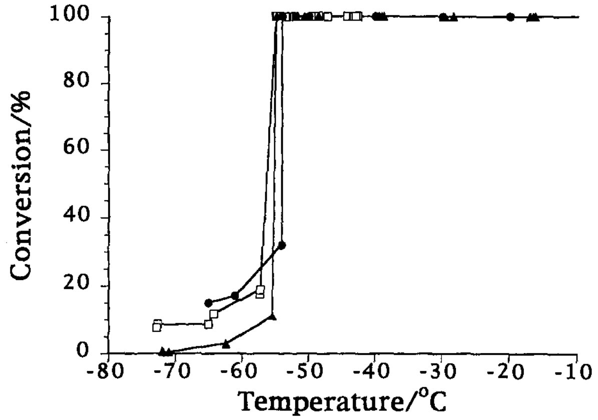

Fig. 3. Reproducibility of low temperature behaviour for 150 mg Co_3O_4, under dry operating conditions, with catalyst cooled slowly over periods ranging from 3 to 7 h.

By decreasing the space velocity by half, from 20000 to 10000 h^{-1} ml/g-cat, the time from immersion to loss of 100% conversion increases from 45 to around 100 min (a factor of 2.2). The Co_3O_4 metal oxide catalyst, identified by black and clear circles, shows similar behaviour to that of Au/Co_3O_4 and between the two flow-rates the difference in deactivation time is comparable at 2.3.

From these time ratios the difference between Au/Co_3O_4 and Co_3O_4 therefore appears quite small. However, as can be clearly seen in the times required before visible deactivation of the catalyst takes place, there is an apparent contradiction in the results. In all studies which we have so far carried out, we found consistently that the time required for deactivation was always less for Au/Co_3O_4 than for

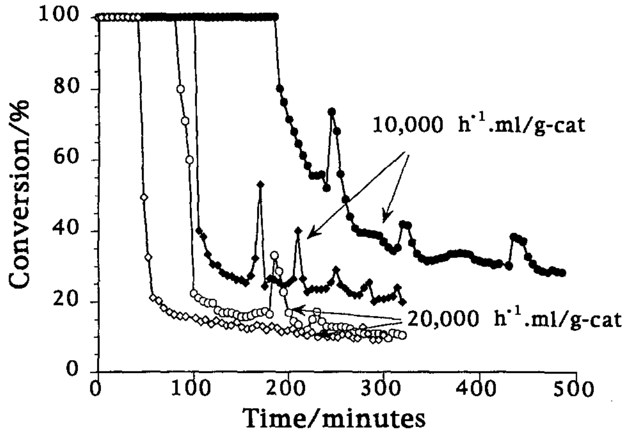

Fig. 4. Conversion profiles, as a function of time, for CO oxidation operated at −76°C under dry conditions. Data is shown for 300 mg Au/Co_3O_4 (◆ and ◇) and 150 mg Co_3O_4 (● and ○). In each case black symbols represent a space-velocity of 10000 h^{-1} ml/g-cat and open symbols 20000 h^{-1} ml/g-cat.

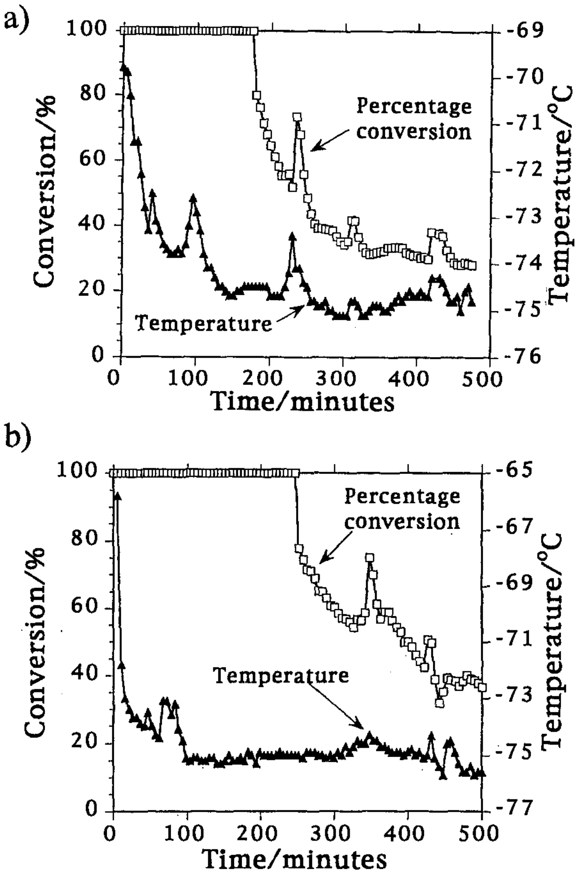

Fig. 5. Oscillations in (▲) temperature and (□) percentage conversion for (a) 150 mg of Co_3O_4 at 10 000 and (b) 300 mg of Au/Co_3O_4 at 5 000 h^{-1} ml/g-cat space velocities. In Au/Co_3O_4 a reduced space velocity is used to show the decrease in oscillation frequency.

Co_3O_4. Additionally, when the Au/Co_3O_4 catalyst was cooled slowly, we failed to observe any signs of deactivation at temperatures near −54°C. For these studies the longest cooling cycle attempted was between 6 and 7 h.

The observation that Co_3O_4 deactivates at higher temperatures than Au/Co_3O_4, but takes longer to show signs of deactivation when directly immersed in a dry ice/methanol bath appears difficult to explain. The decrease in conversion of CO, over Co_3O_4, when the temperature was gradually decreased from room temperature, may be ascribed to a slow accumulation of water molecules at the surface and that this accumulation does not cause deactivation in Au/Co_3O_4. However, such an explanation does not readily explain the absence of time dependency in studies where the cooling rate was varied between 3 and 7 h.

In experiments carried out at dry ice temperature (−76°C), with the catalyst directly immersed soon after pretreatment, we consider that the decrease in percentage conversion may be caused mainly by the accumulation of carbonate intermediates on the surface. Since the total exposed area of metal oxide in the Au/Co_3O_4 system is less than for Co_3O_4 the time required to deactivate the surface by these carbonate intermediates should decrease. The decomposition of these carbonate species is also considered to be the rate determining step in the oxidation of CO at low temperatures [5].

A second feature of interest in these diagrams is the presence of periodic oscillations in the percentage conversion seen at low temperatures. These oscillations appear in the region where the percentage conversion is lower than 40% and therefore where heat transfer problems are usually considered to be less serious. Oscillations can also be seen in the catalyst bed temperature, fig. 5, and extend into the 100% conversion region.

Oscillations in the signal intensity and temperature of the catalyst bed may be explained by a number of models. We, however, believe that the most probable explanation is the intermittent decomposition of carbonate intermediates at the catalyst surface. Other models under consideration related to the Pt-based system [17–22], which explain oscillations either through changes in surface morphology or by coupled heat and mass transfer limitations. Further work is now required to determine the cause and to determine how the process occurs in the absence of a noble metal.

4. Conclusions

In summary, we would like to emphasize three main points from this work.

Firstly, in agreement with previous observations we have determined Au/Co_3O_4 is not appreciably influenced by the presence of moisture. Further work is required, but it is considered that the contact region between gold and metal oxide is the most probable adsorption and reaction site. At this site the CO is then able to interact with the metal oxide (in the presence of moisture) by using the Au particle as a pathway to the surface.

Secondly, without the use of gold and by drying the pretreatment and reaction gases, CO oxidation is observed over the Co_3O_4 metal oxide at temperatures as low as −54°C. The higher temperature range of 30–58°C, under normal conditions, is believed to be a consequence of a simple competition between moisture and CO molecules for the same adsorption sites upon the Co_3O_4 surface. Sufficient drying of the catalyst therefore allows a number of these sites to become available for the adsorption of carbon monoxide, allowing oxidation to then take place. The increase of the temperature for 50% conversion to 93°C under wet conditions is in agreement with this model.

Thirdly, under dried conditions we have observed, at temperatures as low as −76°C, a number of sharp oscillations in plots of both the percentage conversion and the catalyst bed temperature.

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