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Negative activation energies in CO oxidation over an icosahedral $Au/Mg(OH)_2$ catalyst

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In the course of our studies on CO oxidation over $Au/Mg(OH)_2$ we have discovered a catalyst which exhibits an apparent negative activation energy when studied under ultra-dry conditions (80 ppb moisture content). A review of current literature suggests that the oxidation of CO may occur by a reaction between CO and OH radicals and not by oxygen as previously thought. Substantial differences in catalytic behaviour between low and high temperature suggest that the reaction is complex and that more than one reaction pathway is present.

Keywords: CO oxidation, gold catalyst, oxidation on gold

1. Introduction

A large variety of catalysts based on Au or Pt exhibit high activity for CO oxidation near room temperature [1–10]. Although many uncertainties surround the active site of these catalysts it is now becoming clear that water, or in some cases hydroxyl groups, play an important role in controlling the reaction. Schryer and co-workers were the first to show the effect of hydroxyl groups in the case of CO oxidation over platinized tin oxides [9,10]. However, as early as 1984 it was shown that in some cases CO oxidation could occur easily in the gas phase in the presence of hydroxyl radicals during flash photolysis [11–13]. In CO oxidation by OH radicals it is now known that there occurs a region in which the apparent activation energy is negative; an effect that arises from constraints in the rotational degrees of freedom within the molecule [11–13]. Until now, however, no negative activation energies have been reported in heterogeneous catalysis of carbon monoxide to CO_2.

Over the last three years we have carried out extensive studies on the $Au/Mg(OH)_2$ catalytic system. This catalyst is of substantial interest to theoreticians due to the specific crystal symmetry required for CO oxidation to take place and the small absolute size of the gold metal particles generated. On average each metal particle contains between 13 and 55 gold atoms, a very small number lying close to the 9–11 atom boundary at which gold can be thought of as charged and molecular. During subsequent studies on this system, a number of unusual phenomena were observed. Through detailed explanations for all the phenomena still remain unclear, sufficient interest was expressed by others that publication of our preliminary results was considered worthwhile.

2. Experimental

In order to produce catalysts with gold in the icosahedral symmetry [14–19], a $Au/Mg(OH)_2$ catalyst (5 wt% Au loading) was fabricated using a modified deposition–precipitation process [1,2]. In this paper the deposition time was extended to three days in order to inhibit the formation of FCC cuboctahedral crystal nuclei. During preparation the $HAuCl_4$ is first added dropwise over a period of 4 h to an aqueous suspension of MgO (Ube Industries Ltd.). The suspension was then mixed thoroughly until equilibrium is reached and after 24 h the temperature raised to 70 °C. After a period of 1 h, magnesium citrate was then slowly added and the resultant $Au/Mg(OH)_2$ precursor washed to remove chlorine. After drying under vacuum the precursor was calcined at 250 °C for 100 min under air.

To obtain the low levels of moisture required for accurate data analysis a specially designed reactor line was constructed from stainless-steel tubing coated with low surface area Cr_2O_3. This coupled with vacuum tight joints at all valves and cell connections allowed the moisture in the gas phase to be reduced to a level of 80 ppb [20].[1] To dry the catalyst, dry air was passed through the catalyst bed at a maximum temperature of 170 °C until the moisture contained in the gas passing through the catalyst bed, at 80 ppb, equalled that entering. At above 180 °C sintering of the $Au/Mg(OH)_2$ catalyst is possible and thus studies at this temperature were avoided. After the moisture levels in the gas inlet and outlet were equal, the gas was then switched from air to the reaction gas of 1% CO in air.

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[1] Though a minimum level of 10 ppb was found possible, stability problems prevent the use of such dry conditions in actual use. Moisture levels were recorded by two independent Hycosmos II Cryogenic optical dew-point-meters, supplied from Osaka Sanso Kogyo Ltd., Japan.

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The percentage of CO converted was calculated by directly reading the amount of CO_2 produced, or the amount of CO remaining in the exhaust gas.

Structural analysis of the supported gold was carried out by a process called Debye function analysis as described in detail in [1,2,21,22] and references therein. This involves background subtraction of the X-ray diffraction signal of the $Mg(OH)_2$ support from the $Au/Mg(OH)_2$ catalyst. Analysis of the obtained difference spectra, which in this case corresponds to the supported gold particle, is then carried out by careful modelling of the X-ray scatter. Normally this involves calculation of the X-ray spectra from computer derived three-dimensional gold clusters (typically closed shell structures are used) which are then compared directly with the actual experimental data.

3. Results

As seen from DFA analysis of the X-ray difference spectra (figure 1) at between temperatures of -120 and 170 °C the size of the gold nanoparticle prepared on $Mg(OH)_2$ is exceptionally small. In contrast to our previous papers, the crystal structure appears to be dominated by (111) face icosahedral gold particles of approximately 0.8 nm size. In previous studies the mean particle size of gold supported on $Mg(OH)_2$ was approximately from 1.0 to 1.2 nm, suggesting that elongation of the deposition time is benificial in creating smaller, more well defined particles on the support. From calculation, approximately 90% of the gold atoms present are located at the surface, of which only half are considered available for reaction; the lower half of the particle being in contact with the support. A further difference with previous work is that, in this particular study, no direct evidence was found for FCC cuboctahedral gold on the $Mg(OH)_2$. This is presumably due to the changes in preparation described above. However, one must note that as the DFA analysis involves a semi-continuous analysis of the size distribution, the presence of small traces of FCC cuboctahedral gold (perhaps less than 10%) cannot totally be discounted. A slight difference in the spectra at high b values from theory also appears to suggest, but again could not prove, an interaction of the X-rays with asymmetric gold clusters, i.e., those containing insufficient gold atoms to form closed shell structures [16]. Aside from an apparent reduction in the Au–Au bond distance from 0.281 to 0.279 nm between temperatures of 150 and -120 °C, there was also no apparent change in the diffraction pattern obtained from the $Au/Mg(OH)_2$ catalyst and consequently the structure of the gold, under reaction conditions and within the temperature range of interest, is thought to be stable.

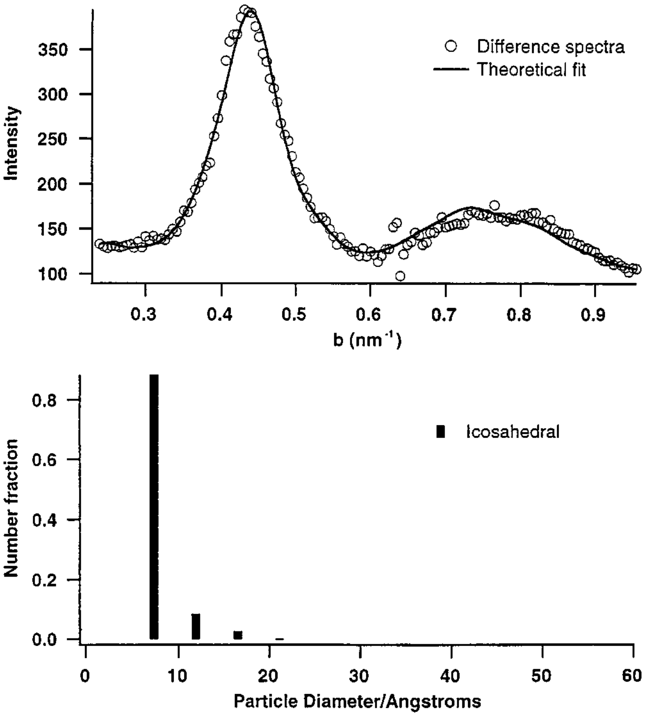

Figure 1. Debye function analysis of the X-ray difference spectrum (upper diagram) for a four month old $Au/Mg(OH)_2$ catalyst after subtraction of the X-ray signal of the pure $Mg(OH)_2$ support. Results indicate the presence of predominantly icosahedral gold particles. The lower diagram shows the number fraction of particles present. No change in crystal structure was observed in cooling the catalyst from 170 to -120 °C.

From analysis of CO oxidation under different moisture levels (figure 2) the catalytic behaviour of the icosahedral $Au/Mg(OH)_2$ catalyst under (a) normal ambient moisture levels (10 000 ppb in the gas inlet and outlet) and (b) under conditions where the catalyst has been dried (80 ppb) exhibit almost mirror images of each other. At the highest temperatures studied, close to 170 °C, we find that for normal ambient conditions water acts as a promoter in the CO oxidation reaction. This is in agreement with previous work carried out on gold catalyst. However, as the temperature is reduced, the promotion effect weakens, until at close to 50 °C, water becomes a poison. This result was independent of whether the catalyst was cooled or heated (see figure 2), indicating, as explained later, that the observed effect is not due to secondary effects such as water build-up during study. At the same time the activity (which we measured by both the amount of CO_2 produced and the amount of CO reacted) showed an unexpected increase at temperatures below 100 °C. From a logarithmic plot of conversion against reciprocal temperature we calculate the activation energy to be negative 10 $kJ\,mol^{-1}$ under dry conditions (80 ppb), and 22.5 $kJ\,mol^{-1}$ under normal moist conditions (figure 3). For dry conditions, at temperatures greater than 100 °C the activation energy is 17.0 $kJ\,mol^{-1}$. All data was obtained using a space velocity of 400 000 $ml\,h^{-1}\,g\text{-cat}^{-1}$ with the catalyst comprising of 0.01 g of $Au/Mg(OH)_2$ catalyst diluted in 0.30 g inert quartz powder. All activation energies were obtained at conversions of less than approximately 20%.

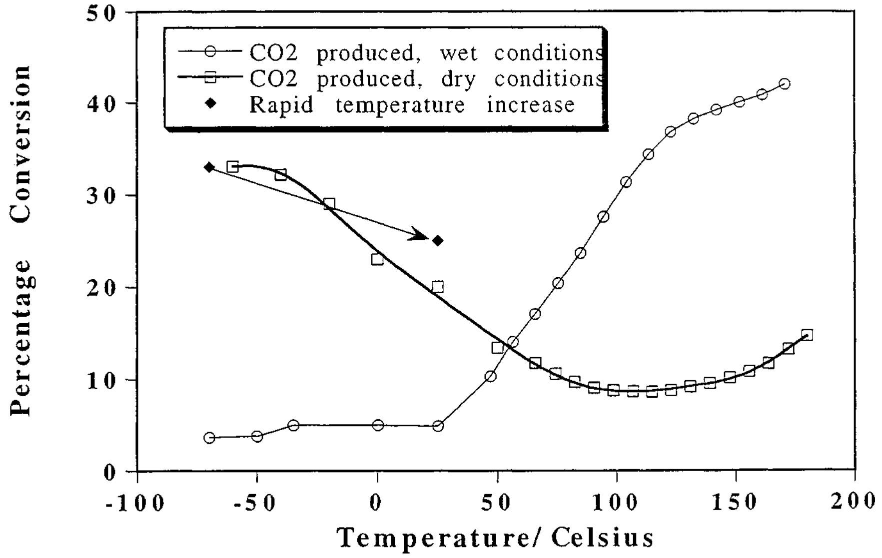

Figure 2. Effect of moisture removal on the conversion of CO to CO_2. Percentage conversions for dry operation conditions were measured over a continuous period of one month. Analysis was carried out in both temperature decreasing and increasing modes, and at random. Data above 180 °C was not taken due to the possibility of gradual coalescence of the nanometer size gold at elevated temperatures.

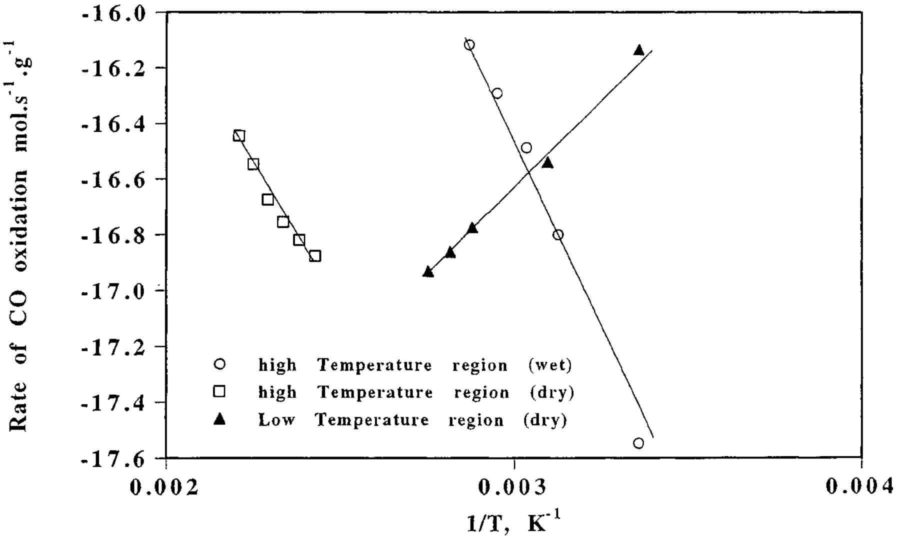

Figure 3. Logarithmic reaction rate of CO oxidation over an icosahedral $Au/Mg(OH)_2$ catalyst as a function of reiprocal temperature. Data was taken four months after catalyst preparation. Conditions refer to ambient wet (10 000 ppb), and dry 80 ppb moisture contents in the gas phase.

4. Discussion

The observation of increasing catalytic activity with decreasing temperature appears at first to logically suggest the possibility of some structural changes in the $Au/Mg(OH)_2$ catalyst. In many cases phase transition can occur in materials that may result in the formation of a phase that is more active than the one that it precedes. However, moisture may also play a role and thus three explanations for the negative gradient of the reaction curve are initially possible. These are:

(1) A phase transition in either the gold of the $Mg(OH)_2$ to a structure that is catalytically more active. This, however, appears unlikely, especially in the absence of any observable changes in the diffraction pattern of either the gold, or the $Mg(OH)_2$ support; other than that which one would normally expect for the thermal contraction of the crystal lattice.

(2) A structural change in the surface adsorbed species to a geometry that is energetically more favourable, and catalytically more active. As a possibility this is more difficult to discount. However, analogous to the solid–solid phase transition, it is reasonable to say that any structural modification within surface adsorbed molecules, must naturally be governed by the laws of thermodynamics. Thus as the number of species involved at the surface is small, it is unlikely that substantial or large variations in temperature would be required to force a change from one physical state to another. In the experimental study we note that the observed

temperature range over which the activity increases is quite large. Starting first at near 100 °C and stretching down to -70 °C, whereupon, at atmospheric pressures, the carbon dioxide produced proceeds to solidify on the surface. For a phase transition, such temperature ranges are extremely large. We therefore consider that it is extremely unlikely that the effect is due to thermal modification of the surface adsorbed species.

(3) A gradual build-up of moisture. If one takes into account the extreme dryness of the gas under which the catalyst is being studied, it would appear reasonable to assume that even a small trace amount of water, perhaps invisible to the observer, could result in a substantial modification of the catalyst surface being studied. In addition, this effect would, presumably, become more intense, at colder temperatures, leading to sharp unpredictable changes in the observed activity. As a result of this distinct possibility, additional studies were carried out in both heating and cooling modes, as well as by taking activity points at random to ensure that the results are independent of time and thus moisture build-up. In all experiments that we carried out no evidence was found for any time dependency, other than that which could be easily ascribed to CO_2 dry ice formation at close to its freezing point. We therefore conclude, within reasonable doubt, that the results were not influenced by any artifacts in the experimental set-up or design.

Reactions with negative activation energies, though rare, have been noted with high frequency in some specific bimolecular reactions. Benson and co-workers [11–13] in particular have contributed much to the understanding of negative activation energies and have shown that

$$OH^* + CO \rightarrow H^* + CO_2$$

proceeds through radical HOCO species.

Normally, most studies involving the reaction of OH with CO involve the use of flash photolysis, indicating that to form the OH radical the gold must in some way strongly interact with the OH located on the surface of the $Mg(OH)_2$ support during formation of the intermediate. Interestingly, we have found from a review of the literature that a Au_{13} cluster contains precisely the correct number of electrons to be considered a radical cluster [23], an effect which is subsequently lost in larger particles. As the apparent activation energies are high and negative under dry conditions, we therefore assume in accordance with Mozurkewich and Benson that, if the reaction does indeed involve radicals (this assumption being still relatively untested), the reaction with gold must involve substantial loss of many rotational and vibrational degrees of freedom. We also assume, due to the need for restricted rotational and vibrational modes to generate the apparent negative activation energy, that binding between the CO, OH and Au species is probably quite strong.

Epling et al. [24] have previously shown the presence of numerous hydroxyl groups in Au supported catalyst. However, in this previous work analysis was very preliminary and it is not possible to determine the origin of these hydroxyl groups or where they reside on the surface. This aside, and given the fact that the increase in activity at low temperatures appears most strongly upon extreme drying of the catalyst, it seems reasonable to describe the catalytic oxidation of CO as occurring through the direct interaction of CO with hydroxyl radicals present at the interface between the gold and $Mg(OH)_2$. Such that

$$Au/Mg\cdots OH^* + CO \rightarrow Mg + H^* + CO_2$$

In this way the negative gradient of the activation curve could reasonably be explained by correlation to the gas-phase reaction.

AuO(OH) type species have also been observed in an interesting though unfortunately slightly inconsistent paper on Au/Fe_2O_3 by Finch et al. [25]. In the paper by Finch, an apparent error occurs in the lack of discussion over why metallic gold and heamatite species appear in only the lowest and highest concentration studied, that is in the 1.05 and 2.69 at% Au-loaded catalyst, but no metallic gold appear in the ^{197}Au Mössbauer spectra at 2.35 at%. Similar problems also occur in the XRD derived data in the same paper. Though ultimate care must be taken when comparing dissimilar systems, *especially in gold catalysis*, its is quite plausible that a AuO(OH) species, as proposed by Finch et al., may exist at the interface between the gold particle and the support. This species then results in subsequent oxidation of the CO leading to the desired formation of CO_2. It should, however, be noted that to date negative activation energies have only been observed in the $Au/Mg(OH)_2$ system despite attempts to repeat the observation on Au/TiO_2 and Au/Fe_2O_3. The behaviour of CO oxidation appears more or less identical under dry and wet conditions for both the TiO_2 and Fe_2O_3. Attempts to extend results obtained for $Au/Mg(OH)_2$ to other systems would thus appear to be unwise at the present moment.

5. Conclusions

In this paper we have shown that simple bimolecular reactions over $Au/Mg(OH)_2$ are highly complex. Previous results have shown that not only must one consider the symmetry of the gold particle (icosahedral gold particles are active over $Mg(OH)_2$, whereas for TiO_2 FCC cuboctahedral gold particles are preferred) but also that the reaction can proceed through several different pathways. In attempts to study catalytic reactions over gold it would appear that numerous parameters must now be reanalysed and clearly at this point the influence of moisture must be more carefully determined, especially if the true inherent activity of the $Au/Mg(OH)_2$ catalyst is to be calculated.

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