Preparation and Chemisorption Properties of a Supported Rhodium Catalyst approaching Atomic Dispersion

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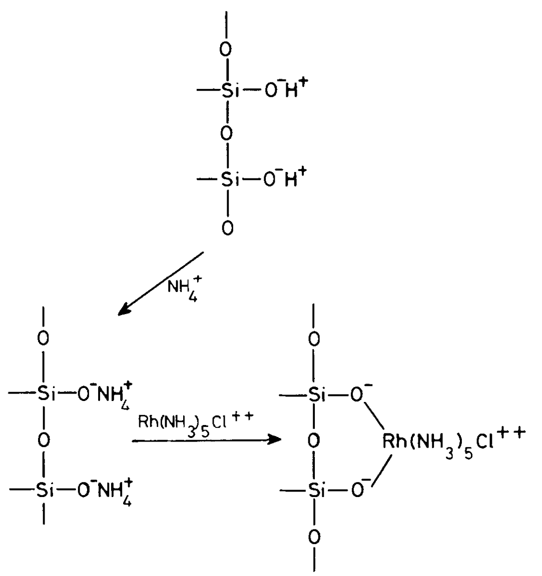
Highly-dispersed rhodium on silica characterised by H_2 and CO adsorption is capable of chemisorbing CO_2 at room temperature in the presence of surface hydrogen.

Preparation of highly-dispersed supported metal catalysts offer unique approaches in exploring some of the interesting topics in catalysis. Structure sensitivity of adsorption and surface reactions on metals has been investigated in terms of particle size effects in the critical size range (often below 5 nm) where large changes occur in the relative concentrations of surface atoms with different co-ordination numbers.[1] There is currently a rapid development in the area of transition metal clusters in order to understand how and to what extent the deviation of electronic structure from the two extremes (*i.e.*, a single atom and bulk) affect the chemical reactivity of the cluster.[2] Approach to atomic dispersion is a 'homogenisation' of heterogeneous catalyst which is one way to study the relationship between homogeneous and heterogeneous catalysis.[3]

The recent success in preparing high-dispersion Rh/SiO_2 catalysts by ion exchange[4] suggested possibilities further to increase the dispersion through careful considerations of relevant factors.

In order to remove trace amounts of metal contaminants, the support SiO_2 (Davison 62), was treated with a 5 M HCl solution (ACS reagent), filtered, washed with pure water and dried in vacuum at room temperature. Then it was mixed with a 30% NH_4OH solution where cation exchange took place



Scheme 1. Formation of precursor.

between the surface protons of the support and the ammonium ions (Mixture A). A dry sample of $[Rh(NH_3)_5Cl]Cl_2$ (Pfaltz and Bauer) was dissolved in a 15% NH_4OH solution (Mixture B). Metal loading of 1 wt% was chosen such that there is about 100 times higher concentration of protons on SiO_2 (as estimated from BET surface area) compared to that of total rhodium atoms introduced. Mixture B was slowly added to Mixture A (0.05 $cm^3 s^{-1}$) while stirring at 343 K to effectively exchange the ammonium ions with the rhodium amine complex ions, thus forming the probable precursor described in Scheme 1. During the exchange, the pH was adjusted to 10 which assured 100% uptake of rhodium as indicated by the absence of the metal in the filtrate after washing the precursor with pure water.

The vacuum-dried precursor was decomposed in oxygen (99.98%). The minimum temperature required for total decomposition was 723 K. This was determined by measuring the weight loss of the precursor which progressively increased with temperature until no further loss was observed. The oxidised rhodium was reduced in flowing hydrogen (LDC/ Milton Roy H_2 generator, Pd-diffused) at 673 K while gradually raising the hydrogen pressure to atmospheric. This is the temperature at which the temperature-programmed reduction curve completed as measured by following a standard procedure with 5% H_2/Ar mixture and a thermal conductivity detector. The temperature for complete desorption of chemisorbed hydrogen was also 673 K. This was confirmed by observing maximum uptake of hydrogen at room temperature after evacuation at 673 K. Further increase in evacuation temperature up to 693 K did not increase the uptake.

Chemisorption capabilities of the catalyst made above were studied in a glass system equipped with double liquid nitrogen traps backed by a diffusion pump system (with CONVALEX 10 oil) which resulted in a 10^{-8} torr (1 torr = 133.322 Pa) vacuum. This pressure is sufficiently low to create a very clean metal surface after reduction and evacuation at 673 K.[5] The static adsorption cell system with precision pressure transducer (DATAMETRICS 590) was minimised in volume (7 cm^3) to maximise system sensitivity and minimise contamination. The amount chemisorbed on rhodium was determined at room temperature by taking the difference between two adsorption isotherm curves obtained in sequence and extrapolated to zero pressure where the second curve was obtained after evacuation following the completion of the first curve so as to remove the physisorbed species on the metal and the support. The first curves for H_2 and CO behaved as Langmuir-type isotherms. The results were H/Rh = 1.82 and CO/Rh = 1.94 which are the number of hydrogen atoms and CO chemisorbed against the total number of rhodium atoms in the sample taken. The very high adsorption stoicheiometry for hydrogen suggests the possibility of dominant population of sites where two hydrogen atoms are bonded to one rhodium atom. The stoicheiometry for CO implies formation of rhodium gem-dicarbonyl as indicated by the appearance of twin peaks for symmetric and antisymmetric stretching modes in the i.r. spectrum when the rhodium particle size becomes very small.[6] Although it is sometimes argued that the appearance of the twin peaks may be due to the presence of rhodium oxides as a result of incomplete reduction during the catalyst preparation, this is unlikely in our case since the completion of reduction is carefully confirmed as explained above. This information together with high-resolution electron microscopy (JEOL 200 CX) studies† indicate that the rhodium clusters are much less than 1 nm in size.

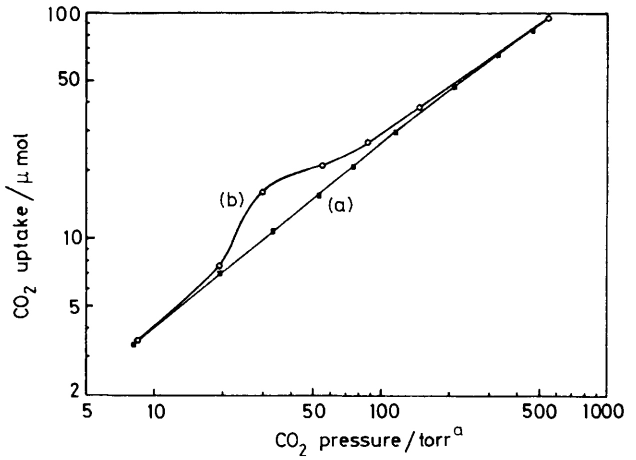


Figure 1. CO_2 Adsorption isotherms at room temperature for 1.047% Rh/SiO_2. (a); after reduction and evacuation at 673 K. (b); after H_2 adsorption at 760 torr followed by evacuation at room temperature.

Adsorption isotherms for CO_2 were measured at room temperature. The uptake of CO_2 increased almost linearly with pressure which is typical for physisorption processes [curve (a), Figure 1]. The isotherm measured immediately after evacuation was almost exactly the same as the first one which indicates negligible amount of chemisorbed CO_2. However, the CO_2 isotherm obtained in the presence of chemisorbed hydrogen at saturation coverage behaved differently. The CO_2 uptake started to increase and deviate rapidly from curve (a) near 20 torr, went through a peak and gradually rejoined curve (a) [curve (b), Figure 1]. Pressure decrease in the cell was noticeably slower for this process (*i.e.*, longer time to approach equilibrium) compared to individual adsorption of CO_2.

Thus, surface hydrogen seems to assist the chemisorption of CO_2 even at room temperature. Such an enhanced adsorption

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† A sample of the catalyst was ultrasonically dispersed in ethanol and deposit-dried on a gold grid with perforated carbon film. Transmission electron micrographs indicated that the Rh clusters are less than 1 nm since particles in the range of 0.5 to 1 nm were finally observed after increasing the reduction temperature to 973 K which caused the clusters to sinter and become larger.

was not observed with a Rh/SiO_2 catalyst having low Rh dispersion (H/Rh = 0.228 corresponding to about 5 nm), although in this case H_2 and CO_2 were coadsorbed at 373 K.[7] Interaction of transition metal complexes with CO_2 and H_2 indicate increased bond strength of CO_2 by hydrogen where CO_2 is bound to a metal atom through the carbon–oxygen double bond (*i.e.*, bidentate structure) instead of through the carbon atom alone.[8] Furthermore, this kind of co-ordination has the highest probability of splitting CO_2 into CO and O as observed by field emission microscopy[9] or as predicted by *ab-initio* valence-bond calculations.[10] The highly dispersed rhodium may possess surface sites capable of forming such a binding state. On the other hand, the total number of chemisorbed CO_2 obtained by taking the difference of the two curves in Figure 1 is about one-half of the total hydrogen atoms initially present. This suggests a possibility of the water-gas shift reaction in the form:

$$CO_2 + 2H \rightarrow CO + H_2O$$

Detection of CO by i.r. spectroscopy would be appropriate for future study. It also means that the number of CO_2 adsorbed per surface rhodium atom is large, that is $CO_2/Rh = 1.82/2 = 0.91$.

The free energy change of this hydrogen-assisted reaction is -379 kJ mol^{-1} compared to $+28.0$ kJ mol^{-1} for the gas-phase reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

The tremendous reduction power created by the rhodium–hydrogen system, due to the large positive free energy of H compared to zero free energy of H_2 at 298 K, turns a thermodynamically unfavourable reaction into a very favourable one. The high number of available H atoms per CO_2 coming from the gas-phase may be helpful in increasing the reaction probability too. In relation to the CO_2 methanation activity, an i.r. spectral study[11] shows that the turnover frequency (number of methane molecules formed per surface rhodium atom per second) increases as the rhodium particle size becomes smaller, regardless of the type of support used. This implies an intrinsic particle size effect for this reaction.

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