Unusual Promotion of the Dehydrogenation Activity of Supported Platinum by Mercury in Low Concentration

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Mercury is found to *increase* the rate at which oxide-supported platinum catalyses the dehydrogenation of cyclohexene at 423 K in concentrations several orders of magnitude lower than that at which promoters normally operate.

Poisons of metal surfaces are generally adsorbed strongly thereon;[1] mercury is an early example of such a poison[2] and is notable because it is available in a monatomic form. Its enthalpy of adsorption on group 8 metal surfaces is high[3] (*i.e.* -109 kJ mol^{-1}) and it is often necessary to protect metal catalyst surfaces using gold or low temperature traps. There is a substantial body of evidence[4] acquired over many years to show that the adsorption of mercury on the surface of group 8 metals reduces their ability to catalyse alkene hydroisomerisation, alkene–alkyne hydrogenation, and benzene hydrogenation. This loss of activity has been attributed[5] to site blocking, where the atomic radius of Hg (0.147 nm) is larger than that for Pt (0.138 nm). Often the activity decreased to zero at an Hg surface coverage of about 70% and could result from Hg atoms isolating the group 8 metal surface atoms into ensembles too small to be active. However, the effect could also result from Hg donating a 6s electron to the d-band of the group 8 metal, thereby reducing the number of d-band vacancies. It is also known that Hg additions reduce the coverage of hydrogen on such metal surfaces[6] and this would also reduce the overall hydrogenation rate. Equally although Pt-catalysed hydrocarbon reactions appear to take place readily,[7] the rate of cyclohexane dehydrogenation increases at stepped surfaces of high Miller index and it is possible that additions of Hg disrupt the group 8 metal surface and *increase* the number of such sites. In addition bulk acceptance of mercury by the group 8 metal can result in alloy formation.[4,8]

Here a series of bimetallic Pt–Hg heterogeneous catalysts have been produced by adding low concentrations of Hg from the monoatomic gas phase to the supported Pt surface. On such surfaces it has been shown that Hg can adsorb in two different energetic states.[9] Highly dispersed bimetallic catalysts are finding increasing use as heterogeneous catalysts; thus in cyclohexane dehydrogenation Os–Cu, Ru–Cu, and Pd–Au show higher activity than the pure metals.[10] This may be due to their higher intrinsic activity or their decreased rate of poisoning by the accumulation of carbonaceous residues; notable cases of the latter situation are Pt–Sn and Pt–Re catalysts.[11] If Hg can decrease the hydrogenation activity of Pt surfaces with explanations based upon changes in properties of surface ensemble, surface disruption, electronic changes, and rates of accumulation of carbonaceous residues, then it was judged that Hg additions might *increase* the dehydrogenation activity of the same Pt surfaces.

Silica-(Aerosil 200), alumina-(Aluminium Oxide C), and titania-(Titanoxid P25) supported Pt catalysts were prepared by impregnation of the oxide supports (Degussa Chemicals) with aqueous solutions of hexachloroplatinic acid (Johnson Matthey, Specpure) using the incipient wetness technique. Table 1 lists their compositions after drying and reduction and also the average Pt particle sizes estimated by extrapolation of hydrogen chemisorption isotherms at 295 K to zero pressure (where it was assumed that each surface Pt atom adsorbed one H atom and each m^2 of Pt surface contained 1.12×10^{19} Pt atoms). *X*-Ray photoelectron spectra of reduced silica- and titania-supported catalysts all showed Pt 4d$_{5/2}$ peaks at 2 eV above that expected for the zero-valent metal (316 eV) but this was taken to imply problems of charging rather than Pt in a positive oxidation state.

Cyclohexene is an interesting reactant since it may readily be dehydrogenated or hydrogenated depending upon the prevailing temperature.[12] The purity of a sample (Aldrich Chemicals) was established by gas chromatography (flame ionisation detector, f.i.d.) to be 99.87%. Gaseous H_2 (BOC, 99.9% purity) and white spot N_2 (BOC) were used from cylinders without further purification. The gas mixture being studied was saturated with cyclohexane at a known vapour pressure and temperature and then flowed at a constant rate (200 ± 1 cm^3 min^{-1}) through a microcatalytic reactor held in a thermostat (273—313 ± 0.1 K) containing 10—25 mg of

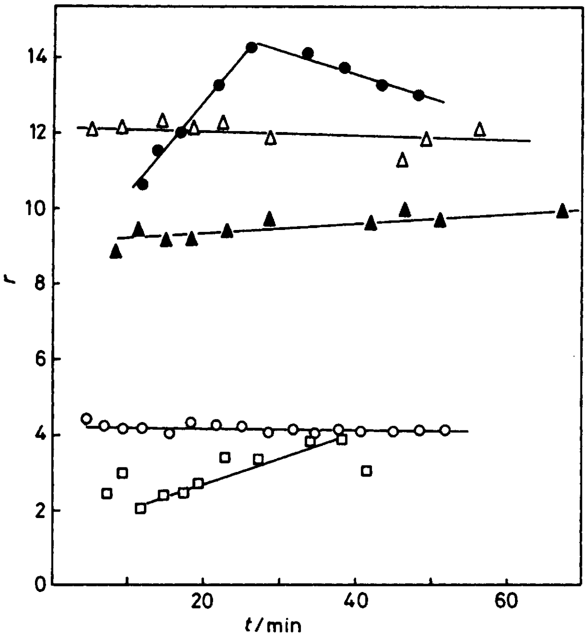

Figure 1. Rate, r, of dehydrogenation of cyclohexene (molecules) converted per g of catalyst per min × 10^{-19}) over 3% Pt/SiO_2 at 400 K (□) and 423K (○, △, ▲, and ● containing 0, 17, 86, and 144 p.p.m. of Hg respectively).

catalyst. A gas sampling valve then fed samples of constant volume to an f.i.d. gas chromatograph (Pye Unicam GCD) fitted with a 10% dibutyl phthalate-coated Poropak Q (80—100 mesh) column. In measurements of hydrogenation activity the reduced catalyst was first flushed with N_2 at 500 K and then reduced in H_2 (101 kPa; 20 cm^3 min^{-1}; 0.5 h) at the same temperature; it was then allowed to cool to the reaction temperature and the reactant mixture (1.7 kPa of cyclohexene; 10.1 kPa of H_2 and N_2 balance; 200 cm^3 min^{-1}) was introduced and analysed as a function of time. In all cases the rate of hydrogenation of cyclohexene decreased with increase in reaction time, and turnover numbers were then calculated by dividing observed rates at 25—30 min reaction time by the monolayer extent of hydrogen chemisorption. Mercury was added in known amounts from N_2 immediately prior to catalytic measurements and was not found to be desorbed during such measurements. In the dehydrogenation of cyclohexene, reduction of catalysts in H_2 at 500 K was followed by purging in N_2 at the same temperature (400 or 423 K) at which the reactant stream (1.7 kPa of cyclohexene in N_2 at 10 cm^3 min^{-1}) was introduced and the reaction followed chromatographically. For the dehydrogenation reaction the effect of the addition of mercury was studied at 423 K. Dehydrogenation activities were stable with time unlike those for hydrogenation but again rates of reaction and turnover number were measured at about 30 min reaction time. Figure 1 and Table 1 show the results.

Rates for cyclohexene hydrogenation for each catalyst increased as the temperature rose from 295 to 313 K with an activation energy (30 kJ mol^{-1}) and turnover number (14—0.1 molecules $site^{-1}$ s^{-1}) consistent with earlier results.[12,13] However, the results for dehydrogenation of cyclohexene are rather more noteworthy and surprising. First, in the absence of mercury the activity of each catalyst is stable with time (to 60 min) and increases as the temperature rises from 400 to 423 K. Secondly, as the mercury is added in low concentrations the dehydrogenation activity increases and in some cases passes through a maximum similar to that seen previously[14] as Au was added to Pt(111) catalysing cyclohexane dehydrogenation, although this was only at the relatively high atomic concentration of 50% Au. Turnover numbers (0.2—0.001 molecules $site^{-1}$ s^{-1}) were lower than for hydrogenation but are not entirely meaningful until the actual number and nature of active sites after Hg additions have been determined.

Table 1. Rates, r, of cyclohexene dehydrogenation (molecules converted per g of catalyst per min × 10^{-19}) at 30 min reaction time.

Catalyst	Average Pt particle size /nm	T/K	p.p.m. of Hg	r
3%Pt/SiO_2	7.8	400	0	3.37
		423	0	4.15
		423	17	11.93
		423	86	9.72
		423	144	14.16
3%Pt/TiO_2	5.7	423	0	5.57
		423	17	9.35
		423	144	5.50
1.5%Pt/Al_2O_3	1.4	423	0	6.45
		423	26	12.28

That the activity of a supported metal surface is increased by mercury in itself is notable. That it should do so at a relative concentration of less than 17 Hg atoms per million atoms (*i.e* with possibly only one surface atom in 5000 being Hg) is remarkable. This makes one wonder as to the causes of this promotion and the role of long-range electronic effects or structural dislocations. Bearing in mind the size of the Pt crystallites in these catalysts (see Table 1) it may be that not every crystallite has Hg added. These points are the subject of further study and additional information on this unusual promotional effect will be reported. The results may illuminate the validity of electronic and ensemble explanations of catalysis of hydrocarbon reactions on alloys.[15]

Received, 20th December 1984; Com. 1782

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