

Oxygen Enhanced Hydrogen Exchange and Hydrogenation over Supported Gold Catalysts

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Addition of oxygen during the reaction was found markedly to accelerate the rates of H₂-D₂ exchange and hydrogenation of propene over highly dispersed gold catalysts supported on silica or magnesia.

The ability of metallic gold to catalyse hydrogen exchange and hydrogenation reactions is relatively low compared with group 8 metals.¹⁻³ Thus activated hydrogen atoms must often be supplied *via* an external source, *e.g.* with a radiofrequency discharge.^{4,5} Supported gold surfaces, however, are found to display significant catalytic activity for reactions involving hydrogen^{6,7} or oxygen.⁸⁻¹⁰ Recent results with highly dispersed supported gold surfaces include the hydrogenation of alkenes,¹¹⁻¹⁴ the reduction of NO,^{15,16} and the oxidation of alkenes.¹⁷ The nature of the active sites and the mechanism of hydrogen activation on these catalysts have not been clarified yet. Bond *et al.*^{12,14} have reported that the rate of pent-1-ene hydrogenation over Au/SiO₂ markedly depended on the concentration of Au on the silica support. The increase in Au dispersion, even though its concentration decreased, led to an unusually high activity per unit weight of metal in the hydrogenation. Chambers and Boudart³ reported the effect of added oxygen in the hydrogenation and dehydrogenation of cyclohexene, where the introduction of a small amount of oxygen was found to decrease markedly the production of cyclohexane and to increase the selectivity of the reaction for benzene formation. It was suggested that the oxygen consumed the adsorbed hydrogen to favour the dehydrogenation path. Similar results were reported by Inami *et al.*¹⁸ in the case of the dehydrogenation of butane.

In the study of H₂-D₂ exchange and C₃H₆ hydrogenation reactions over Au/SiO₂ and Au/MgO catalysts with various metal loadings we have found a novel effect of added oxygen

on the reaction rate. The effect was unusually dependent on the gold dispersion. Inhibition of HD or propane formation was observed over the 5-0.1 wt% Au catalysts, whereas a marked acceleration effect was observed over catalysts with less than 0.05 wt% Au. We report a study of this novel phenomenon in connection with the mechanism of hydrogen activation over supported Au catalysts.

The catalysts (5, 0.5, 0.1, 0.05, and 0.025 wt% Au) were prepared by impregnation of SiO₂ (Aerosil) or MgO (Merck) with an aqueous solution of HAuCl₄ (Nakarai Chemicals, Spec. Pure).¹⁴ After drying at 393 K for 48 h in air, 1 g of the catalyst was placed in a U-shaped reaction vessel connected to a closed gas circulation system, heated very slowly in an atmosphere of 26 kPa of H₂ up to 573 K, and kept at this temperature for 12 h. The colour of the 5 wt% Au/SiO₂ catalyst was reddish-brown, and the mean particle size was estimated to be 200-250 Å by X-ray diffraction (x.r.d.). The 0.05 and 0.025 wt% catalysts were mauve (Au/SiO₂) or pale pink (Au/MgO) in colour, as reported in the literature.^{14,15} Their mean particle size could not be estimated by x.r.d. because no distinct diffraction peaks were detected.

H₂-D₂ exchange and C₃H₆ hydrogenation reactions were carried out at 423 K in the same closed gas circulation system. The products were analysed by mass spectrometry and gas chromatography with a thermal conductivity detector.

Figure 1 shows the effect of oxygen (2.7 kPa) addition in the middle of a run; the formation of HD or propane stopped completely in the case of the 5 wt% Au/SiO₂ catalyst. Rapid

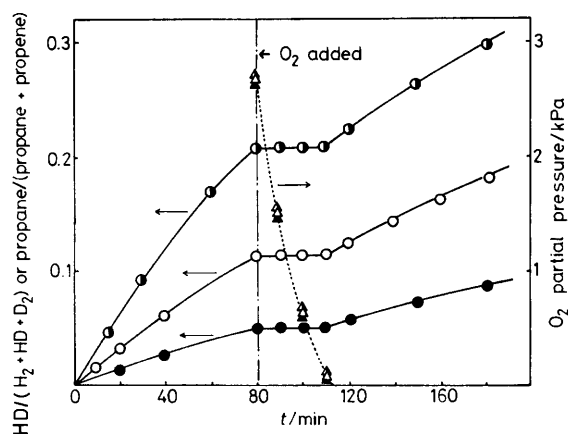


Figure 1. The effect of oxygen addition on $\text{H}_2\text{-D}_2$, $\text{C}_3\text{H}_6\text{-H}_2$, and $\text{C}_3\text{H}_6\text{-D}_2$ reactions over 5 wt% Au/SiO_2 (1 g) at 423 K: \circ propane formed in $\text{C}_3\text{H}_6\text{-H}_2$ reaction; \bullet propane formed in $\text{C}_3\text{H}_6\text{-D}_2$ reaction; \circ HD formed in $\text{H}_2\text{-D}_2$ exchange reaction; broken line: partial pressure of oxygen during \triangle $\text{C}_3\text{H}_6\text{-H}_2$, \blacktriangle $\text{C}_3\text{H}_6\text{-D}_2$, and \blacktriangle $\text{H}_2\text{-D}_2$ reactions, respectively.

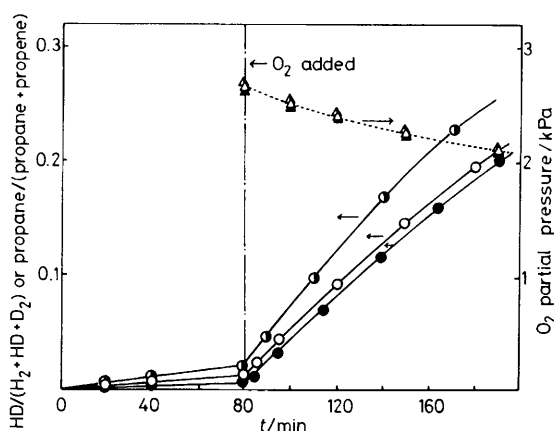


Figure 2. The effect of oxygen addition in $\text{H}_2\text{-D}_2$, $\text{C}_3\text{H}_6\text{-H}_2$, and $\text{C}_3\text{H}_6\text{-D}_2$ reactions over 0.05 wt% Au/SiO_2 (1 g) at 423 K. For symbols see Figure 1.

formation of water as well as a trace amount of CO_2 was then observed. When all oxygen in the gas phase had been consumed, the formation of HD or propane resumed with a similar rate as before. The hydrogenation of propene showed a large kinetic isotope effect. The $\text{C}_3\text{H}_6\text{-H}_2$ reaction was 2–3 times faster than the $\text{C}_3\text{H}_6\text{-D}_2$ reaction. No such isotope effect was observed in the $\text{H}_2\text{-O}_2$ and $\text{D}_2\text{-O}_2$ reactions (broken line in Figure 1). Similar results were obtained over the 0.5 and 0.1 wt% Au/SiO_2 catalysts.

The behaviour of the 0.05 wt% catalyst was completely different, as shown in Figure 2. In the absence of oxygen, the rate of HD or propane formation was much slower than that over the 5 wt% catalyst; the specific rate seemed to be proportional to the metal loading. Addition of oxygen, however, increased the rates of both reactions by 10–30 times. The rates attained were comparable to those on the 5 wt% catalyst. The rate of water formation was nevertheless

very slow, and no isotope effect was observed in the $\text{C}_3\text{H}_6\text{-H}_2$ and $\text{C}_3\text{H}_6\text{-D}_2$ reactions. The acceleration effect was proportional to the partial pressure of O_2 up to 3–4 kPa. At higher oxygen pressures, the effect was almost independent of the partial pressure.

To obtain information on the nature of the adsorbed oxygen species on Au, $^{16}\text{O}_2\text{-}^{18}\text{O}_2$ exchange reactions were carried out over both 5 and 0.05 wt% Au/SiO_2 catalysts at 423 K, but no mixed isotopic species $^{16}\text{O}^{18}\text{O}$ was detected during several hours on both catalysts. $\text{H}_2\text{-D}_2\text{-}^{16}\text{O}_2\text{-}^{18}\text{O}_2$ and $\text{C}_3\text{H}_6\text{-H}_2\text{-}^{16}\text{O}_2\text{-}^{18}\text{O}_2$ reactions were also investigated. No $^{16}\text{O}^{18}\text{O}$ was detected during the reaction, although rapid formation of water was observed on 5 wt% Au/SiO_2 and marked acceleration was observed on 0.05 wt% Au/SiO_2 catalysts. These results suggest that on the Au surface at 423 K, oxygen molecules are not dissociatively chemisorbed but behave as a peroxy-like adsorbed species, which enhances the dissociation of hydrogen molecules. Over the 5 wt% catalyst, water is swiftly formed from this surface complex, which, we suppose, inhibits the recombination of dissociated hydrogen or the hydrogenation of adsorbed propene. Over the 0.05 wt% catalyst, water formation from this intermediate is for some reason rather difficult, which makes the enhancement of hydrogen recombination or hydrogenation possible.

Although, as we mentioned above, we could not determine the Au particle sizes on catalysts with lower loadings, the experimental finding that only the 0.05 and 0.025 wt% catalysts exhibited this enhancement effect suggests that the Au particle size is closely connected to this phenomenon. Similar peroxy-like surface structures may be formed on highly dispersed Au surfaces through the interaction with oxygen in the support material,¹⁹ suggesting a possible mechanism of hydrogen activation on supported Au catalysts.

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