# Adsorption of [$^{14}$C]Acetylene and [$^{14}$C]Ethylene on Supported Metal Catalysts: Relevance to the Selective Hydrogenation of Acetylene

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*Summary* The adsorption of [$^{14}$C]acetylene and [$^{14}$C]ethylene on supported palladium, rhodium, and iridium catalysts occurs irreversibly at 298 K in two distinct stages: a non-linear primary region, followed by a linear secondary region; hydrogenation catalysis is associated with the secondary region and separate sites are involved in the adsorption of [$^{14}$C]acetylene and [$^{14}$C]ethylene, and the relevance of these observations to the selective hydrogenation of acetylene is briefly discussed.

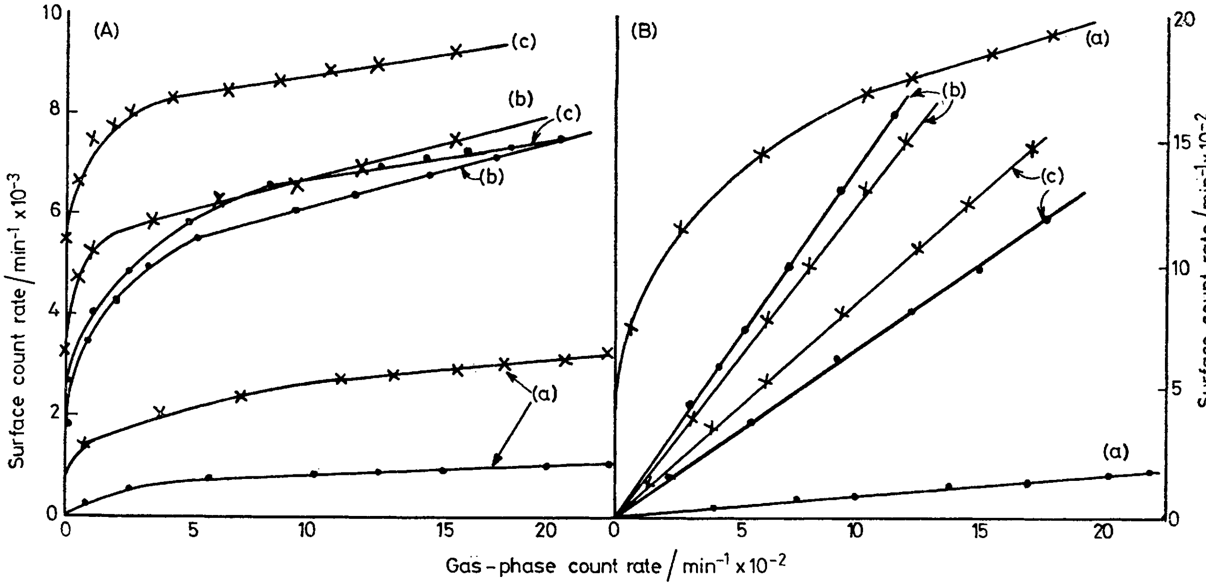

FIGURE. The adsorption of acetylene (×) and ethylene (●) on freshly reduced (A) and constant activity (B) catalysts, for 0·10 g Pd–$SiO_2$ [curves (a)]; 0·20 g Rh–$SiO_2$ [curves (b)], and 0·51 g Ir–$SiO_2$ [curves (c)].

In the hydrogenation of acetylene catalysed by supported metals it is generally assumed that the acetylene and the product ethylene are adsorbed at the same surface sites, although in the hydrogenation of buta-1,3-diene over supported metals[1] and of propadiene over similar catalysts[2] it has been suggested that the sites responsible for at least some alkane formation may be distinct from those at which alkene is formed. The selectivity for ethylene formation is considered to be a consequence of the ability of the more strongly adsorbed acetylene to (a) displace and (b) prevent the subsequent readsorption of the product ethylene.[3,4] Wells[4] has also suggested that occluded hydrogen in the metal may be of importance in determining the observed selectivity. We have observed that with silica-supported palladium, rhodium, and iridium and alumina-supported palladium catalysts ethylene adsorption and hydrogenation can occur in the presence of acetylene in the gas phase.

On freshly reduced catalysts the adsorption isotherms for [$^{14}C$]acetylene and [$^{14}C$]ethylene are of a similar form to those reported previously,[5] consisting of a non-linear primary region and a linear secondary region (Figure A).

However, on active catalysts which after 20—30 reactions with non-radioactive acetylene had been 'run-in' to a constant hydrogenation activity, the isotherms showed a reduced ($C_2H_2$ on Pd) or no primary region (Figure B). The results obtained with palladium–alumina were similar to those observed with palladium–silica. No molecular exchange between $C_2H_2$ (adsorbed) and gas-phase acetylene or between $C_2H_4$ (adsorbed) and gas-phase ethylene is observed with any catalysts, either in the absence or presence of hydrogen, showing that the adsorption is essentially irreversible. This behaviour of ethylene is in contrast with that inferred previously from studies of the ethylene–deuterium reaction over alumina-supported rhodium and palladium.[6]

Admission of hydrogen to the [$^{14}C$]acetylene or the [$^{14}C$]-ethylene precovered surfaces, in the presence of gas-phase hydrocarbon adsorbate, results in the rapid removal of the species adsorbed on the secondary region, but only a slow, partial removal of the species from the primary region. Selective use of the $^{14}C$ tracer shows that the acetylene adsorbed on the primary region yields only ethane on hydrogenation. Admission of acetylene to [$^{14}C$]ethylene-precovered surfaces results in only a very small decrease in the surface count rate; this decrease is independent of the extent of ethylene adsorption on the secondary region and represents a removal of only 1·8% (Rh) or 0·8% (Pd or Ir) of the ethylene adsorbed at a pressure of 1 Torr of ethylene.

On palladium and iridium surfaces the extent of [$^{14}C$]-ethylene adsorption is independent of the presence or absence of acetylene in the gas phase. With rhodium the presence of acetylene in the gas phase results in a 30% decrease in the [$^{14}C$]ethylene adsorption capacity of the surface. The relative amounts of ethylene and acetylene [$n(C_2H_4) : n(C_2H_2)$] adsorbed under hydrogenation conditions at 298 K are 0·45 : 1 (Pd), 0·78 : 1 (Ir), and 1·17 : 1 (Rh), these values being constant up to hydrocarbon gas pressures in excess of 12 Torr. The selectivities for ethylene formation in acetylene hydrogenation at 298 K using a hydrogen–acetylene (3 : 1) mixture (50 Torr pressure) are 0·94 (Pd), 0·75 (Rh), and 0·16 (Ir), these values being similar to those reported previously.[7]

Addition of [$^{14}C$]ethylene to the acetylene hydrogenation mixture causes an increase in the ethane yield which, from the yield of [$^{14}C$]ethane, is directly proportional to the amount of added [$^{14}C$]ethylene. This behaviour is independent of whether the [$^{14}C$]ethylene is admitted to the catalyst immediately before or following the admission of the acetylene hydrogenation mixture.

From our results we conclude that at each catalyst surface at least two distinct types of site, which are independent of each other, exist during acetylene hydrogenation. At the first type of sites (Type A) the adsorption of acetylene and its hydrogenation to ethylene and ethane can occur; at the other type of site (Type B) the adsorption and hydrogenation of ethylene occurs independently of the hydrogenation of acetylene. The effects of added ethylene upon the selectivity for acetylene hydrogenation also suggest that at the Type A sites the predominant route to the formation of ethane is directly from acetylene, rather than by the subsequent hydrogenation of ethylene. Consequently, the observed selectivity depends upon the relative concentrations of the different types of surface site, rather than upon the different strengths of adsorption of acetylene and ethylene as suggested previously.[3] As such, the selectivity will be an inherent property of the catalyst surface under consideration, although such factors as the variation in availability of surface hydrogen with different hydrocarbon adsorbates must also be taken into account.

Our results also show that, under reaction conditions, the catalytic hydrogenation is associated with the secondary adsorption region, where the concentration of adsorbed hydrocarbon is directly proportional to the gas-phase pressure, rather than following Langmuir type behaviour. Comparisons of the amounts of acetylene or ethylene adsorbed with the metal area as determined from carbon monoxide adsorption indicates that the secondary adsorption arises either from spill-over of the hydrocarbon onto the support,[5] or more likely, involves the formation of overlayers on the metal surface.[8]

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