Catalytic Hydrogenation of Olefins on Metals: a New Interpretation

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Summary A general mechanism for hydrogenation is proposed which unifies various features of the reaction; it is suggested that hydrogenation on metals should be interpreted as hydrogen transfer between an adsorbed hydrocarbon and the adsorbed olefin and should not be regarded as addition of hydrogen direct to the latter.

OLEFIN hydrogenation on metal catalysts is the subject of a vast literature, yet it lacks a basic unifying theory. There is controversy over mechanism and kinetics and the underlying properties of metals which account for their behaviour as catalysts. Studies in catalysis have tended to be limited to single aspects of the subject. We summarise here, with typical references, the diverse features of olefin hyogenation and unify these with a single proposal.

(a) Kinetics have made only a partial contribution to the understanding of hydrogenation. Tamaru[1] and Boudart[2] point out that simplified kinetics applied to different mechanisms lead to identical rate expressions and detailed models[3,4] do not yield unequivocal results.

(b) Within kinetics there are innumerable statements on pretreatments and changes in catalytic activity: *e.g.*, the second run gave a slower reaction,[5] the catalyst was aged in hydrogen plus olefin[6] or with olefin alone,[4] and the smallest variation in activity was achieved by leaving new catalyst films in contact with olefin.[7] Acceleration after the start of a reaction has been observed.[8]

(c) Ethylene hydrogenation belongs[9] to a class of reaction where activation energies vary within narrow limits (*ca.* 8—10 kcal mol^{-1}) with change in metal. Activity changes are ascribed to the frequency factor. The opposite is true for reactions not involving a hydrocarbon, *e.g.* NH_3–D_2 exchange.[10]

(d) The nature of the metal surface has little effect on catalytic activity in ethylene hydrogenation. Films and dispersed catalysts, compared on an atom for atom basis, give equal rates.[5]

(e) In comparison with isomerisation and cracking,[11] hydrogenation is not a structure sensitive reaction. Over metal dispersions of 0·73 to 0·000039 for Pt the activity was the same for cyclopropane hydrogenation.[12] This has been generalised for hex-1-ene, cyclohexene, benzene, and allyl alcohol over Pt–SiO_2.[13]

(f) Self-hydrogenation of olefins occurs on catalytically active metals. It results in the formation of surface carbidic species of low hydrogen content.[14,15]

(g) Retention occurs when [^{14}C]-olefins interact with metal surfaces.[16] Thus [^{14}C]-ethylene-covered surfaces lose only a fraction of the adsorbed species upon evacuation or during hydrogenation or molecular exchange. Persistence of hydrocarbon species and formation of C_4 species from ethylene have been observed spectroscopically.[15]

(h) No satisfactory correlation exists between electronic, magnetic, or geometrical features of metals and catalytic activity. Correlations of activities with work function, holes in the *d*-band, heats of adsorption, density of electron states, *etc.* have had limited success. The only successful correlation between catalysis and activity involves rates with areas.

(i) There has been an attempt in a scholarly review[17] to distinguish between two views of metal alloy catalysts, the collective electron model and the localised individual atomic site model.[18,19] In *para*-hydrogen conversion,[20] formic acid decomposition,[21] carbon monoxide oxidation,[22] and nitrous oxide decomposition,[23] the activation energies change significantly at particular alloy compositions. In contrast, in hydrogenation reactions of ethylene on Cu–Ni,[24] benzene on Cu–Ni,[18] and but-2-yne on Pd–Au[8] any variation of rate over a wide range of alloy composition is smooth.

We propose, as a general mechanism for hydrogenation, a model which unifies all these features of the reaction and which gives an insight into each. We suggest that hydrogenation should be interpreted as hydrogen transfer between an adsorbed hydrocarbon species, M–C_2H_x, and the adsorbed olefin. It should not be regarded as hydrogen addition direct to the adsorbed olefin.

This suggestion makes the metal only of secondary importance and hydrogenation becomes an extension of self-hydrogenation: this latter reaction is self-poisoning but the process is continuous in the presence of added hydrogen. For C_2 hydrocarbons we have chosen as the active centre M–C_2H_x, for ^{13}C n.m.r. spectroscopy[25] and thermal desorption[26] studies show that C_2 species from ethylene retain their identity on Pt.

Observations (a) to (i) now fall into a coherent picture for hydrogenation:

(a) Kinetics could be accommodated.

(b) Catalyst pre-treatment with olefin represents the formation and stabilisation of active sites giving steady state concentration of M–C_xH_y. Site creation explains the acceleration for but-2-yne hydrogenation.

(c) Removal of direct dependence on the nature of the metal accounts for similarities in the energy barrier to hydrogenation when different metals are used; rates depend on hydrogen transfer from M–C_xH_y not from M–H. Variations in frequency factors would arise from different site densities of M–C_xH_y.

(d) The form of the metal ceases to be of direct significance if the active centre is M–C_xH_y.

(e) Facile and demanding reactions appear in a new light. Where a reaction depends on the formation of M–C_xH_y, crystallite size and dispersion will not affect the reaction provided equivalent numbers of active sites are formed. Catalytic cracking will remain as a sensitive reaction in that fission of C–C bonds appears to occur through the formation of M–C bonds with the reacting olefin.

(f) Self-hydrogenation is accommodated within the general framework of hydrogenation.

(g) Retention of hydrocarbons falls into place; M–C_xH_y is retained permanently with hydrogenation occurring on the same surface. When pulses of [^{14}C]-ethylene and hydrogen pass across a fresh catalyst, there is simultaneous hydrogenation and deposition of retained species.[27]

(h) If M–C_xH_y is the active centre in hydrogenation it is not surprising that the correlation sought so assiduously over many years should not exist. Correlation with area should exist[28] in that increased area will mean increased numbers of active sites. Correlation with physical properties should exist only in so far as they will influence formation and stability of M–C_xH_y centres. Some very low site densities have been estimated for metallic catalysts.[29]

(i) The emergence in alloy studies of the single site concept is explained if the active centres for any alloy composition are M–C_xH_y. Whereas direct molecular interaction with alloys occurs for H_2, CO, NH_3, and HCO_2H, the influence of the alloy is diminished if reaction occurs, not with the metal, but with M–C_xH_y.

It is possible to extend these ideas to a re-interpretation of other published work. For example, olefin disproportionation may depend on single site reactions[17] *via* M–C_xH_y. In the Pd–Au system, Dessing *et al.*[19] used carbiding of a surface in an attempt to produce single metal atom sites which we, on the other hand, would identify as M–C_xH_y and not isolated Pt atoms.

In all the fragmentary pieces of information on hydrogenation which we have examined, this model has been successful.

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