

CHAPTER II

LITERATURE REVIEW

The selective hydrogenation of acetylene in the presence of excess ethylene has attracted much interest due to its industrial importance. A great deal of research has been undertaken in this area. McGown et al. [5] have studied the kinetics of the hydrogenation of mixtures containing 2% of C_2H_2 in C_2H_4 on an alumina supported palladium catalyst in a static system. Tracer studies using carbon-13 labelled acetylene, light ethylene and hydrogen have shown unambiguously that ethane produced from the hydrogenation of a mixture of acetylene in ethylene comes predominantly from the ethylene. It is postulated that two types of site exist on the surface, type X which hydrogenates both acetylene and ethylene and on which acetylene is adsorbed ~2200 times more strongly than ethylene at 293 K and type Y which is easily poisoned by carbon monoxide and can hydrogenate ethylene even in the presence of acetylene.

The adsorption of [^{14}C] ethylene and [^{14}C] acetylene on supported palladium, rhodium and iridium catalysts has been investigated by Al-Ammar et al. [6] and has been observed to occur irreversibly at 298 K in two distinct stages : a non-linear primary region, in which the species are predominantly dissociatively adsorbed, and a linear secondary region, in which hydrogenation catalysis is involved. It is concluded from [^{14}C] carbon monoxide adsorptions that the hydrocarbon primary region is associated with the metal, whilst the secondary region probably involves the formation of overlayers on the primary adsorbed species. The co-adsorption of ethylene and acetylene shows that, under acetylene hydrogenation conditions, both are adsorbed at separate sites and undergo hydrogenation independently of each other.

Al-Ammar et al. [7] have examined possible effects of the deactivation upon the kinetics, the selectivity for ethylene formation and the adsorption of [^{14}C] acetylene and [^{14}C] ethylene over supported palladium, rhodium and

iridium catalysts in the hydrogenation of acetylene. They report that the activity of the catalysts progressively decreases to a steady state constant activity. This deactivation is irreversible at 298 K and can only be effected by acetylene + hydrogen mixtures ; acetylene alone produces no significant deactivation. It is found that the deactivation is associated with the progressive build up of permanently retained acetylene species on the catalyst surface. Three types of adsorbed acetylene are recognised. The results are interpreted in terms of the hydrogenation reaction occurring by a hydrogen transfer mechanism between a dissociatively adsorbed C_2H_x species and associatively adsorbed acetylene, which forms an overlayer on the dissociatively adsorbed acetylene.

The hydrogenation of acetylene in the presence of various pressures of [^{14}C] ethylene has been studied over silica-supported palladium, rhodium and iridium catalyst by Al-Ammar et al. [8]. The results show that with each catalyst the yield of ethane from the hydrogenation of ethylene is small ; the major route to ethane formation is by direct hydrogenation of acetylene. Three distinct types of surface site are involved in the hydrogenation of acetylene and ethylene. It is shown by direct surface monitoring that ethylene does not adsorb on the acetylene hydrogenation sites. The increase in rate observed when all the acetylene has reacted is not due to an increase in ethylene surface coverage, but is an increase in hydrogen availability for ethylene hydrogenation. Addition of 0.1-1.0 Torr of carbon monoxide to the acetylene hydrogenation results in complete poisoning of the rhodium and iridium catalysts, but only partial reduction in the activity of the palladium catalyst. [^{14}C] tracer studies of the adsorption of carbon monoxide, acetylene and ethylene show that the poisoning is not due to a hydrocarbon site-blocking effect, but rather to a blocking of the hydrogen adsorption sites. Hydrogen effectively competes with carbon monoxide for these sites on palladium.

Berndt et al. [9] have reported the hydrogenation of acetylene, at low pressure, over a 25.4 % w/w Ni/SiO₂ at 293 K that the acetylene is hydrogenated to ethylene and ethane, with the selectivity for ethylene formation being 76%. It is shown that the predominant reaction pathway to ethane formation is a direct route acetylene, rather than via ethylene. The results are

interpreted in terms of four types of sites on the catalyst surface which are responsible for acetylene self-hydrogenation, conversion of acetylene to ethylene, ethane production from acetylene and the hydrogenation of ethylene to ethane. These sites also account for the selectivity of the catalyst in acetylene hydrogenation.

By studying the hydrogenation of acetylene - [^{14}C] ethylene mixture in the presence of deuterium, Guzzi et al. [10] have clearly demonstrated that at the initial stage of the reaction ethane is directly formed from acetylene. That is, under a given condition, formation of ethane cannot be influenced by lowering the ethylene hydrogenation activity of the palladium black catalyst. It is proposed that initially the surface is monopolized by acetylene and subsequently, after the acetylene partial pressure had decreased, ethylene could be competitively adsorbed in significant quantities.

The observed selectivity is always subject to the influence of experimental conditions. Thus, on aging, Weiss et al. [2] have found that the selectivity of acetylene deuteration to ethylene in the ethylene-acetylene mixture decreases as a function of time as the catalyst ages. Activity for acetylene conversion remains constant, but that for deuterium conversion increases to accommodate the additional ethane formed. The decrease in selectivity with aging observed might correlate with the slow build up of the β -Pd hydride phase, which has been suggested by Palczewska et al. [11] to be responsible for a decrease in selectivity of acetylene hydrogenation. The hydrogen in the hydride phase is provided by the dissociative adsorption of acetylene.

The effect of aging on the hydrogenation of a tail-end mixture (0.29 mol% C_2H_2 , 0.44 mol% H_2 balanced by C_2H_4) has been investigated on Pd-black and on various Pd/ Al_2O_3 catalysts by Sarkany et al. [12]. It has been reported that over supported catalysts the selectivity of ethylene formation decreases with time on stream in the first 40-60 hours of operation whereas the C_2H_2 conversion is not, or only slightly, influenced. With Pd-black the selectivity of ethylene formation changes in the opposite direction. [^{14}C] C_2H_2 experiments have revealed that the aging has only a minute effect on the intrinsic selectivity

of C_2H_2 hydrogenation. The surface polymer is observed for all catalysts and also increased with time. It is known that C_2H_4 hydrogenating sites are located mainly on the polymer-covered support rather than on the metal. This suggested that C_2H_4 be adsorbed on the support and hydrogenated there. Spill-over hydrogen may tentatively be identified as a source of hydrogen. Because of the parallelism between polymer formation and ethylene hydrogenation, it is proposed that the surface polymer serves as a hydrogen pool or facilitates the surface diffusion of hydrogen from Pd sites to the support.

Margitfalvi et al. [13-14] have studied the deuteration of trace amounts of acetylene in the presence and absence of ethylene on Pd black catalyst in a continuous flow reactor. At nonsteady state the Pd black catalysts show very low selectivities whereas higher selectivities are obtained at steady state. Using $[^{14}C]$ C_2H_2 , it is demonstrated that at low acetylene partial pressure the main route of acetylene hydrogenation is the formation of ethane, ethylene and C_4 hydrocarbons. It is suggested from the observed kinetic data that different surface species such as dissociatively and associatively adsorbed acetylene as well as ethynylidyne species are present on the palladium surface.

A study has been made by Bond et al. [4] of the degree of selectivity of C_2H_4 formation in the hydrogenation of C_2H_2 catalyzed by Rh, Pd, Pt and some palladium + silver mixtures supported on α - Al_2O_3 . Palladium is found to be the most active metal of the pure metals. Palladium + silver catalysts containing 10 to 30% silver show notably higher initial selectivities than pure palladium and are also highly active.

Borodzinski et al. [15] have investigated the simultaneous processes of acetylene hydrogenation and α - β -phase transformation in the Pd-H catalytic system. It is found that the β -Pd-H phase of the catalyst is the less selective, and the α -Pd-H phase resulting from the decomposition of the hydride phase is the more selective in acetylene hydrogenation. It is also shown that a palladium catalyst with a high degree of dispersion is unable to form the β -phase and exhibits a high selectivity. It is suggested that there are two mechanisms of

acetylene hydrogenation. One of them operates on Palladium hydride catalyst crystallites; the other on palladium crystallites.

Hydrogenation of acetylene in an artificial acetylene-ethylene-deuterium mixture on three types of 0.04% Pd on alumina catalysts has been investigated by Moses et al. [16]. It is established that supported palladium behaves similarly to the previously studied palladium black [13-14] concerning the effect of carbonaceous deposits which affect the amount of surface hydrogen available for the formation of ethylidyne species. This form is responsible for the diminished selectivity.

Hartog et al. [17] has studied the effect of the particle size and carbonaceous deposits over supported Pt, Pd, and Ir catalysts in the hydrogenation of acetylene. The metals studied can be subdivided into two groups, Pd and Pt on the one hand and Ir and Rh on the other hand. The latter group shows effects that can most likely be explained by an influence of the particle size on the intermediate of direct hydrogenation to ethane, whereas in the case of Pd and Pt the effect of deposition of carbonaceous layers prevails.

Palczewska et al. [18] have investigated the surface mechanism of the influence of lead and carbon monoxide as additives modifying the selectivity of palladium catalysts in partial hydrogenation of acetylene. The results point out to the role of the additives as influencing the state of adsorbed acetylene, diminishing the surface concentration of ethylene and the availability of adsorbed hydrogen.

Reactions of acetylene /H₂ have been studied with Ir/Cu and Ir/Au catalysts by Hartog et al. [19]. Combining Ir with both Cu and Au has the (qualitatively) the same effect; the selectivity to ethylene increases by alloying. However; the effect is more pronounced with Cu than with Au and the Cu-metallics are more active. Selectivity changes with acetylene reactions indicate a suppression of dissociative adsorption forms by alloying.

Hydrogenation of C_2H_2 in the presence of a large excess of ethylene on 0.04wt% Pd/ Al_2O_3 catalyst containing 0:100, 30:70, and 80:20 atoms Cu: atoms Pd, and on 5 wt% Pd/ SiO_2 has been investigated by Leviness et al. [20]. Copper addition to palladium decreased the catalyst activity and increased its stability. This resulted in a significant decrease in the overall rate of C_2H_6 formation, as well as a marginal decrease in C_4+ selectivity.

Weiss et al. [21] have investigated the effect of added Cu to 0.04 wt% Pd/ Al_2O_3 catalysts for acetylene hydrogenation and found that dispersing Pd (to avoid formation of a Pd-H phase) almost eliminates the Pd catalysed formation of ethane from acetylene. The results suggest that hydrogenation of ethylene proceeds separately over the alumina support, presumably from H-atoms that "spill-over" from Pd sites to the support by way of carbonaceous deposit bridges. Added Cu reduces the rate of ethane formation on the support, apparently by providing desorption sites for spill-over hydrogen.

Schay et al. [22] have made an attempt to improve selectivity of 0.04 wt% Pd/ Al_2O_3 by alloying Pd with Cu in the selective hydrogenation of trace acetylene in ethylene. Large amounts of Cu improve C_2H_4 selectivity from acetylene when using 0.04 wt% Pd/ Al_2O_3 catalyst. Experiments with CO and [^{14}C] C_2H_2 show that C_2H_2 and C_2H_4 are hydrogenated simultaneously on the catalyst.

Park et al. [23] have reported an enhancement in the rate and selectivity to ethylene for the hydrogenation of traces of acetylene in ethylene by the addition of potassium to Pd/ Al_2O_3 catalysts. Further study from the same group has been made to understand the effects of the K promoter on the catalytic behavior of Pd/ Al_2O_3 [24]. It is found that K addition enhanced the partial hydrogenation of C_2H_2 to C_2H_4 but increased oligomer formation. An increase in the rate of C_2H_2 conversion is also observed upon the addition of K. Ethylene deuteration results show that the probability of ethylene desorption from the catalyst increases with increasing levels of K. A decrease in the rate of ethylene deuteration with K addition is observed, which contrasts with the enhanced rate of C_2H_2 hydrogenation.