CHAPTER II
LITERATURE SURVEY

2.1   Acetylene Hydrogenation

Sulfided catalyst, e.g., nickel sulfide, or nickel tungsten sulfide were the first generation of selective acetylene hydrogenation catalysts. Because of their low activity, the operation temperature had to be high to achieve good conversion. But undesirable side reactions such as polymerization also occured, resulting in activity and selectivity losses due to catalyst bed plugging and very short cycle lengths. The second generation of catalysts is based on supported palladium which has been found to be the most active and selective metal. However, there are still some disadvantages, e.g., the fouling of catalyst caused by accumulation of the C_4^+ oligomers on the surface. To improve the deactivation characteristics of palladium, addition of a second metal component such as Ag, or Cu has proven to be beneficial. It has been proposed that the co-metal acts like a physical promoter preventing the link-up of two molecules of adsorbed acetylene to form the C_4^+ oligomer.

There are several different schools of thought trying to explain the high selectivity of palladium for hydrogenation of acetylene. The first explanation is based on the large difference in adsorption enthalpy of acetylene and ethylene on Pd leading to strong adsorption of acetylene while ethylene adsorption is weak (Bond et al., 1962). The ratio of surface coverage of acetylene and ethylene remains very high even if there is very low partial pressure of acetylene in the gas phase. As a result, in acetylene/ethylene

mixtures the hydrogenation of acetylene to ethylene is the main reaction. However, in absence of acetylene, ethylene hydrogenation readily takes place. This could also explain the influence of CO which is known to increase the selectivity. Similar to acetylene, CO absorbs more strongly than ethylene so at low acetylene partial pressures in the gas phase, the surface coverage of ethylene remains low. However, it becomes increasingly clear that this classical interpretation does not provide a complete explanation for all the phenomena observed.

McGown et al. (1978) proposed two types of active sites. One type of sites was mainly occupied by acetylene due to the higher adsorption enthalpy compared to that of ethylene. The second type of sites adsorbed and hydrogenated ethylene even at relatively high acetylene partial pressures in the gas phase. In this explanation, adding CO increases the selectivity toward ethylene by competing with ethylene for adsorption on the second type of sites and by decreasing the availability of adsorbed H_2.

Margitfalvi et al. (1981) studied the acetylene hydrogenation by ^{14}C labeling experiments. They found that acetylene is hydrogenated to ethane directly, acting parallel to the hydrogenation of acetylene to ethylene. This direct hydrogenation was thought to occur via the formation of strongly adsorbed surface species, e.g., ethyledyne. The influence of carbon monoxide in selectivity was proposed to be due to the decrease in the number of sites available for ethylidyne. Since ethylidyne requires an ensemble of three adjacent Pd sites, adsorbed CO may be very effective in blocking some of these ensembles. As a result, ethane formed via the direct hydrogenation decreases, and this, in turn, improves the selectivity.

Battiston et al. (1982) studied the selective hydrogenation of acetylene under industrial tail-end condition, evaluating the differences in activity, selectivity and activation energies among different Pd catalysts. They

concluded that the optimum operating conditions, e.g. CO level, H_2/C_2H_2 ratios and reaction temperature, depended on the type of catalyst, and that the activation energies were different for different catalysts.

LeViness et al. (1984) using support Pd-Cu catalyst, proposed that at high concentration of acetylene, the support material may be being covered by surface polymers. Hydrogen is proposed to spill over from Pd sites and migrate to the support material through the surface polymer where it can hydrogenate adsorbed ethylene. The influence of Cu is to decrease the surface polymer concentration by decreasing the dissociative adsorption of acetylene.

Sarkany et al. (1984) showed that only a small percentage of the total ethane formed comes from the direct hydrogenation pathway of acetylene and that most of the ethane formed stems from ethylene hydrogenation.

Contradictory to the work of Battiston et al., Gigola et al. (1986) reported an apparent activation energy in the order of 65 kJ/mole for a series of different Pd catalysts, assuming first order of H_2 and zero[th] order of hydrocarbon dependence.

Nakatsuji et al. (1987) proposed a mechanism involving a vinyl radical. Hydrogenation of acetylene leads to ethylene adsorbed in a coplanar configuration with the active surface sites. This species readily desorbs, thus favoring ethylene production over further hydrogenation to ethane, thus achieving high selectivity.

Cortright et al. (1991) used Pt catalyst to observed the deactivation. They found that the deactivated catalyst was regenerated successfully with hydrogen at 573 K for 1 hour. Accordingly, the carbonaceous species blocking the active sites are reactive with hydrogen at higher temperatures, as evident from the successful regenerations.

Bos et al. (1993) performed the kinetic experiments on a Pd commercial catalyst using a Berty reactor. Eight different sets of rate

expressions, proposed in the previous literature, were tested. They found that there was no particular expression that gave a perfect fit with the data and recommended to use a combination of rate expressions. It should be noted that these practical rate expressions are highly recommended to be used as an empirical correlation within the experimental range.

Borodzinski et al. (1997) identified three types of active sites (A_1, A_2 and E) of Pd/α-Al_2O_3 catalyst for hydrogenation of acetylene-ethylene mixtures. Their involvement in the process depends on the reaction conditions. It was suggested that these sites are created on the palladium surface by carbonaceous deposits formed during the stabilization process. A_1 and A_2 sites exhibit high activities for hydrogenation of acetylene to ethylene, while E sites exhibit a low activity for ethylene hydrogenation to ethane, which results in high selectivity of the catalyst.

2.2 Hydrogen Adsorption on Pd

There are numerous papers providing the information of an interaction of hydrogen and palladium. Mavrikakis et. al. (1994) developed the transient mean-field model accounted for both adsorption on the surface and diffusion of the hydrogen into the lattice of the palladium crystal (Pd [110] single crystal surface). The peaks obtained from TPD spectra show that there are 2 kinds of desorbed species, i.e., the surface hydrogen as the low temperature peak (375 K) and subsurface and bulk hydrogen as the higher temperature peak. (550-650 K). In addition, it demonstrated that the experiments conducted at the same exposure values of 500 L (1L = 10^{-6} torr·s) but at different exposure time and exposure pressure i.e., 500 s with 10^{-6} torr and 5000 s with 10^{-7} torr, contributed to a substantial difference in the area under the second peak

(subsurface and bulk hydrogen) while the area of the first peak did not have significant change. The TPD spectra obtained from the experiment performed at the same exposure time but different exposure pressures showed a slightly different area of the first peak while the area of the second peak did not change significantly. These led to the conclusion that the exposure time is the dominant variable. The model constructed with regard to three distinct palladium layers, i.e., surface, subsurface and bulk, provided a good agreement with the TPD spectra.

In contrast, with the aforementioned paper, the work of Cattania et al., (1983) provided different TPD spectra. The hydrogen adsorption of hydrogen on Pd [110] surface were conducted using Video-LEED, work function and thermal desorption mass spectroscopy (TDS) technique. The TDS result demonstrate 4 hydrogen binding states. Two high-temperature states (275-325 K), β_1 and β_2, are produced by chemisorbed hydrogen while the low-temperature states (160-225 K), α_1 and α_2, only occurred on the reconstructed surface and are attributed to hydrogen atoms that have moved to subsurface sites located below the topmost Pd atom layer. The reconstruction process occurred at exposure above 10 L, creates a new active surface, the atom of the second Pd layer that becomes accessible for adsorption of hydrogen and offers more channels for hydrogen atom to enter the Pd lattice and accumulate in the subsurface or surface near bulk regions of the crystal. The reconstruction is removed at the temperature around 180-200 K.

Codatos et al. (1995) conducted the adsorption of CO, NO and H_2 on a-Al_2O_3 [0001] supported Pd particle at 120 K with various particle sizes. For hydrogen adsorption experiments, TPD results obtained from Pd film, show 2 desorption regions. The low-temperature region, below 200 K, attributes to the subsurface absorbed hydrogen while the broad peak observed at higher temperatures is produced from the surface adsorbed hydrogen. For the smaller

particles, the low-temperature peak does not exist due to insubstantial amount of hydrogen absorbed in the Pd particle. Only the broad peak which is attributed to the surface hydrogen is observed. This is in agreement with the work of Cattania et al. (1983) in that the low temperature region produced from subsurface adsorbs hydrogen and the broad high-temperature peak attributes to the desorption of surface hydrogen.