

## CHAPTER II

### BACKGROUND

The first generation of selective acetylene hydrogenation catalysts were sulfided catalyst, e.g., nickel sulfide, or nickel tungsten sulfide. Since their activity was low, the operation temperature had to be high to achieve good conversion. This, in turn, favored undesirable side reactions such as polymerization, 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 among Group VIII elements. 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 (Boitiaux et al., 1985). 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.

The classic explanation of the high selectivity of palladium for hydrogenation of acetylene is based on a thermodynamic argument (Bond et al., 1962). There is a large difference in adsorption enthalpy of acetylene and ethylene on Pd leading to strong adsorption of acetylene while ethylene adsorption is weak. 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.

Nakatsuji et al. (1987) proposed a two-step mechanism involving a vinyl radical. According to their model, hydrogenation of acetylene produces 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.

McGraw et al. (1987) suggested two types of active sites. The X type sites are mainly occupied by acetylene due to the higher adsorption enthalpy compared to that of ethylene. The Y type sites, on the other hand, preferentially adsorb and hydrogenate ethylene even though the acetylene partial pressure in the gas phase may be relatively high. Adding CO increases the selectivity toward ethylene formation by competing with ethylene for adsorption on the Y type sites. Furthermore, CO decreases the oligomerisation (mainly the production of butenes from  $C_2H_2$ ) presumably by decreasing the availability of adsorbed  $H_2$ .

Margitfalvi et al. (1980) 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 is thought to occur via the formation of strongly adsorbed surface species, e.g., ethylidyne. The influence of carbon monoxide in selectivity is proposed to be due to the decrease in the number of sites available

for ethynylidyne. Since ethynylidyne 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.

LeViness et al. (1984) using support Pd-Cu catalyst, proposed that at high concentration of acetylene, the support material may get 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.

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

Contradictory to the work of Battiston et al. (1982), 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<sup>th</sup> order of hydrocarbon dependence.

Guczi et al. (1979) and Margitfalvi et al. (1980) proposed the mechanism of hydrogenation and oligomerisation pathways. These pathways consist of 1) the direct hydrogenation of acetylene to ethylene via a strongly adsorbed species e.g. ethynidyne, 2) the hydrogenation of acetylene to ethylene via associatively adsorbed acetylene and 3) oligomerisation via a dissociatively adsorbed acetylene.

Because of the rather complex mechanism, there have been only a few studies of the selective hydrogenation of acetylene/ethylene that present detailed kinetic expressions. Usually, the dependence of reaction on hydrogen and hydrocarbon were reported in terms of simple power rate laws. For hydrogen, the orders of reaction reported range from 1 to 0.5. For ethylene and acetylene, most authors report zero orders, but for acetylene, slightly negative orders were also reported (Beebe et al., 1986). Full rate expression with the corresponding parameter values have rarely been reported.

Men' shchikov et al. (1975), in contrast with the previous authors, reported that the rate of ethylene hydrogenation is not influenced by acetylene partial pressure. The explanation is that acetylene and ethylene might adsorb on different type of active sites.

Gva and Kho et al. (1988) conducted the experiments in a recycle reactor and in the absence of CO. The acetylene hydrogenation rate was found to be first order in  $H_2$ . They proposed a two-site mechanism, i.e., A-type sites on which acetylene is strongly adsorbed and B-type sites where the estimated free energy of adsorption of acetylene and ethylene differ by 4 kJ/mole, enabling competitive adsorption of acetylene and ethylene.

Bos et al. (1993) performed the kinetic experiment 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.

### Hydrogen adsorption on Pd

There are papers, stated here, providing the information of an interaction of hydrogen and palladium. Conrad et al. (1979) have studied the adsorption of hydrogen on clean Pd (110) and Pd (111) by means of LEED, thermal desorption spectroscopy and contact potential measurement in UHV system. There were 2 peaks observed. The first peak is from adsorbed hydrogen while the second peak caused by the desorption species that come from the bulk hydrogen. This statement is supported by the result obtained from LEED pattern.

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 and subsurface and bulk hydrogen as the higher temperature peak. In addition, it demonstrated that the experiments conducted at the same exposure values of 500 L ( $1 \text{ L} = 10^{-6} \text{ torr}\cdot\text{s}$ ) but at different exposure time and exposure pressures i.e., 500 s with  $10^{-6} \text{ torr}$  and 5000 s with  $10^{-7} \text{ torr}$ , contribute to a substantial difference in the area under the second peak (subsurface and bulk hydrogen) while the area of the

first peak does not have significant change. The TPD spectra obtained from the experiment performed at the same exposure time but different exposure pressures show the slightly different in the area of the first peak while the area of the second peak do not change significantly. These lead 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, provide the good agreement with the TPD spectra.

In contrast with the first two papers, the work of Cattania et al., (1983) provided a 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 demonstrates 4 hydrogen binding states. Two high temperature-states  $\beta_1$  and  $\beta_2$  are produced by chemisorbed hydrogen while the low-temperature states  $\alpha_1$  and  $\alpha_2$  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) have conducted the adsorption of CO, NO and H<sub>2</sub> on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (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 attributed to the subsurface absorbed hydrogen while the broad peak observed at higher temperature 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 contributed 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 absorbed hydrogen and the broad high-temperature peak attributed to the desorption of surface hydrogen.