CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Mechanism of Acetylene Hydrogenation

Figure 2.1 shows the proposed three pathways of acetylene hydrogenation [Bos, A.N.R., *et al.,* 1993]: Path a is the acetylene hydrogenation to ethylene followed by desorption and possible readsorption of ethylene which further hydrogenates to ethane. Path b is the reactive adsorption of acetylene to produce multiple bond intermediates, which are directly hydrogenated to ethane. The relative significance of the two paths and, therefore, the selectivity can be controlled by the catalyst and the reaction parameters. Oligomerization/polymerization of acetylene (path c) leads to the formation of hydrocarbons of even carbon numbers ranging from C_4 to C_{32}. This path results in green oil which can affect catalyst activity by masking active sites [33]. It has been reported that there are different sites involved in the reaction: one fraction of sites acetylene is selectively hydrogenated to ethylene whereas the other, non-selective sites promote ethylene hydrogenation even in the presence of acetylene [McGown, W.T., *et al.,* 1977]. ^{14}C labeling experiments have shown the existence of a direct route from acetylene to ethane [LeViness, S., *et al.,* 1984].

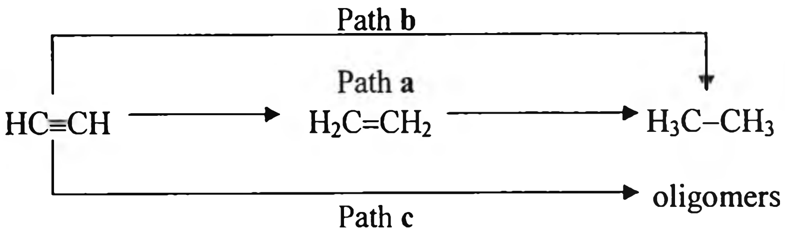

Figure 2.1 Acetylene hydrogenation pathways.

From surface science observations (FT-IR, EELS, SFG, HREELS, etc.) combined with kinetic studies, seven intermediate species participating in the above processes were proposed (Figure 2.2).

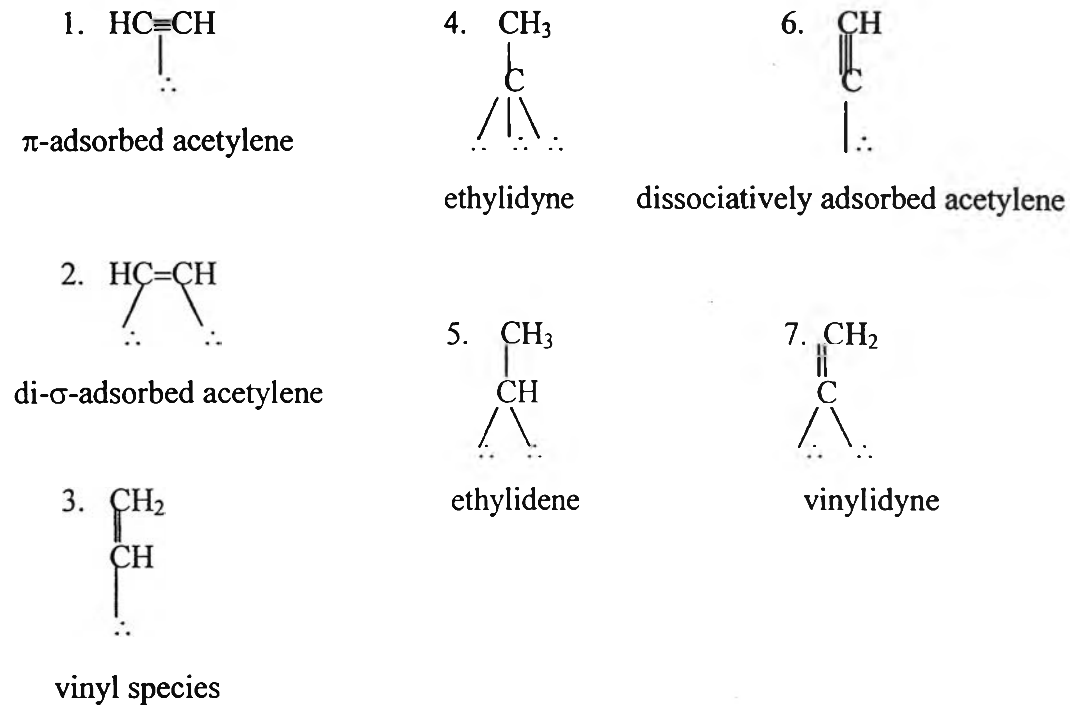

Figure 2.2 Proposed surface intermediates in hydrogenation of acetylene [Molnár, Á., *et al.*, 2001, Doring, T.A., *et al.*, 1968, Guo, X.C., *et al.*, 1995, Molero, H., *et al.*, 1999]

π-adsorbed acetylene (1) is transformed to associatively adsorbed (di-σ-adsorbed acetylene) flat-lying acetylene (2), then to vinyl species (3) which are the precursors for the formation of the ethylene (Figure 2.2). Multiple bound surface intermediates such as ethylidyne (4) ethylidene (5) are hydrogenated to ethane. Dissociatively adsorbed acetylene (6) and vinylidene (7) were suggested to participate in forming oligomers and benzene [Molero, H., *et al.*, 1999]. Recently, species (7) was also assumed to be the reactive intermediate in ethylene formation [Tysoe, W.T., *et al.*, 1983, Kesmodel, L.L., *et al.*, 1984, Beebe, T.P., *et al.*, 1986, Hoffman, H., *et al.*, 1992]. However, some of those proposed species were identified under UHV conditions, which might not be formed under atmospheric conditions. FT-IR and deuterium labeling (location of the D position) are of crucial importance in interpreting the formation of reactive and spectator species. These techniques verified the presence of species 2, 4 and 6.

Formation of C_4 from vinylidene or flat lying acetylene has been investigated. Benzene is also observed as a side product in the formation of oligomers during atmospheric hydrogenation since, after C_6 ring closure, further insertion of the C_2 unit is terminated [Molero, H., *et al.*,1999, Omerod, R.M., *et al.*, 1990, Goetz, J., *et al.*, 1995]. Reaction paths leading to all possible products and the corresponding surface intermediates are summarized in Figure 2.3. It is noted that only π- and di-σ-adsorbed acetylene species are involved in ethylene formation.

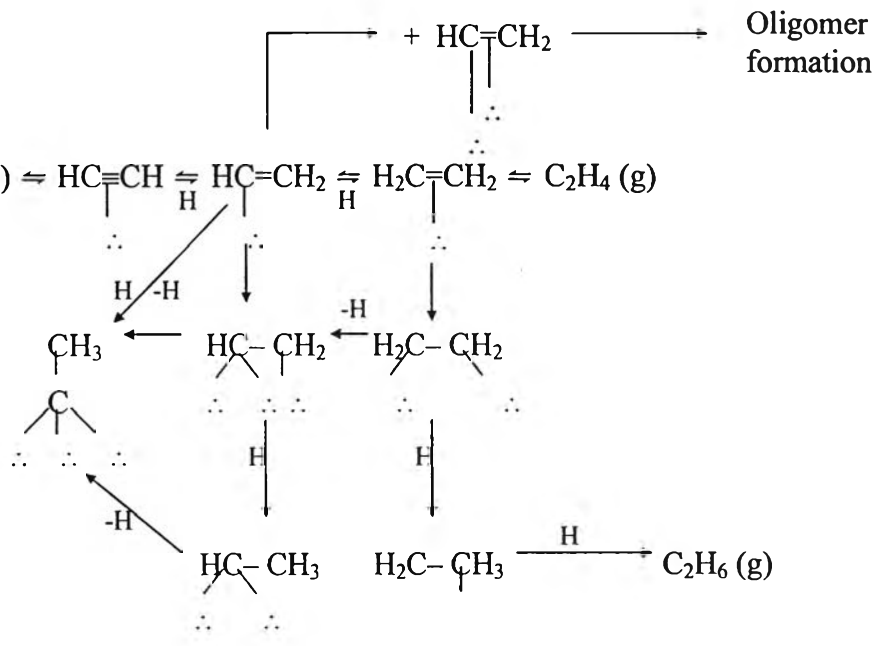

Figure 2.3 Reactionpaths for acetylene hydrogenation proceeding over surface intermediates [Bortók, M., *et al.*, 1985]

2.2 Effect of Pd Dispersion and Catalyst Support

Supported palladium catalysts have been proven to be the best catalysts so far for selective hydrogenation of acetylene in excess ethylene. Various catalyst supports have been used to prepare supported palladium catalysts, including alumina [Park, Y.H., *et al.,* 1991, Cider, L., *et al.,* 1991, Zhang, Q., *et al.,* 2000, Duca, D., *et al.,* 1996, Borodzinski, A., 1999, Asplund, S.,1996, Boitiaux, J.P., *et al.,* 1983, Vincent, M.J., *et al.,* 2001], silica [Phillips, J., *et al.,* 1993, Jin, Y., *et al.,* 2001, Shin, E.W., *et al.,* 1998, Maetz, Ph., *et al.,* 1997, Albers, P., *et al.,* 1999, Albers, P., *et al.,* 2000], pumice [Maetz, Ph., *et al.,*1997, Larsson, M., *et al.,* 1998]. mesoporous and microporous materials [Choudary, B.M., *et al.,* 1999]. Most studies suggested that the reaction is structure sensitive when dispersion is high. However, some controversial behavior was also observed, e.g., increasing metal dispersion was found to bring about a decrease in specific activity especially over catalyst of small particle size [Hub, S., *et al.,* 1988, Boitiaux, J.P., *et al.,* 1983, Gigola, C.E., *et al.,* 1986, Ryndin, Y.A., *et al.,* 1988], while small particles of a medium dispersed Pd/Al_2O_3 catalyst exhibited slightly higher activity [Sárkány, Á., *et al.,* 1986]. Structure insensitivity was reported recently [Albers, P., *et al.,* 1999], activity drop with increasing dispersion was also found [Duca, D., *et al.,* 1996]. Direct comparisons of the result, however, are difficult since different substrates were studies under different reaction conditions. Nevertheless, strong complexion of the highly unsaturated alkyne to atoms of low co-ordination number on small metallic particles is usually invoked to explain the diminishing activity of small metal particles [Hub, S., *et al.,* 1988, Boitiaux, J.P., *et al.,* 1983, Ryndin, Y.A., *et al.,* 1988, Ponec, F., *et al.,*1995].

2.3 Effect of Silver Promoter

The bimetallic of the Pd-Ag catalysts has two beneficial effects [Jin, Y., *et al.,* 2001]. First, the production of oligomers is suppressed, leading to improved selectivity. Second, the nonselective hydrogenation of ethylene is also suppressed. Both of these beneficial effects could result from the altered surface arrangement of Ag atoms on the Pd surface. The oligomerization reaction requires multiple C_2H_2 molecules, which would not be present if the Pd sites are surrounded by Ag adatoms. Likewise, the Ag atoms might lower the concentration of H_2 in the vicinity of the catalyst sites, allowing the ethylene to desorb instead of becoming further hydrogenated.

A study by Roder *et al.* [Roder , H., *et al.,* 1993] suggested that in Ag/Pd and Ag/Pt bimetallic system, Ag atoms should stay at the surface in segregated form, rather than forming an alloy. The higher-temperature treatment in H_2 could enhance the mobility of surface Ag atoms, leading to surface structures where domains of Pd are separated by islands of Ag.

2.4 Effect of Carbonaceous Deposit and Oligomer Formation

Carbonaceous deposits have been found to strongly affect the selectivity to ethylene during acetylene hydrogenation. C^{14} acetylene and C^{14} ethylene adsorption studies suggest two-stage adsorption: in the first stage irreversible dissociative adsorption occurs, while in the second stage acetylene and ethylene adsorb and react upon the catalyst covered by the primary layer [Al-Ammar, A.S., *et al.,* 1978, Al-Ammar, A.s., *et al.,*1978, Al-Ammar, A.s., *et al.,* 1978]. A work reported later suggests that highly dehydrogenated C_xH_y species formed in the early stages of hydrogenation can be regarded as hydrogen sources which play a crucial role in the hydrogenation process [Webb, G., 1990].

The effect of carbonaceous deposits on the catalytic performance has also been investigated as a function of time on stream. Experimental results for the mixture of acetylene and ethylene have clearly revealed that ageing increased the selectivity of over-hydrogenation and the appearance of sites which hydrogenate ethylene to ethane even if there is sufficient amount of acetylene in the gas phase [Sárkány, Á., *et al.,* 1986].

The effect of oligomers/deposits acting as hydrogen reservoir was suggested for over-hydrogenation. Migration of polymeric material from the metal to the support may facilitate hydrogen surface transport (or hydrogen spillover) to certain fraction of sites that are not covered by acetylene, providing hydrogenation of intermediate ethylene [Weiss, A., *et al.,* 1984, Asplund, S. 1996, Sárkány, Á., *et al.,*1986]. This was assumed to be the reason for the increased ethane formation over a Pd/γ-Al_2O_3

catalyst compared with Pd/α-Al_2O_3 [Vincent, M.J., *et al.*, 2001]. However, the effect of carbonaceous deposits serving as hydrogen spillover agent is still obscure and requires a thorough study.

It was suggested that, over Pd/Al_2O_3 catalysts, carbonaceous deposits substantially decrease effective diffusivity by blocking the catalyst pores [Borodzinski, A., *et al.*, 1999, Duca, D., *et al.*, 1998]. Mass transfer limitations severely hinder intraparticle diffusion of acetylene and, thereby increase the rate of ethylene hydrogenation in the interior of catalyst grains.

2.5 Decoking

Carbonaceous deposits are one of the main contaminants of used hydrotreating catalyst. This so called coke may vary in structure and reactivity and may contain associated metals. If the catalyst is to be regenerated, removal of the coke is recommended, although it should be remembered that significant coke will be re-deposited almost as soon as the regenerated catalyst is brought back on line. However, removal of coke may remove particularly deleterious forms of coke and may remove appreciable quantities of metal contained in the coke.

Of the four classic modes of removing coke

$$C + O_2 \rightarrow CO_2 \qquad (1)$$
$$C + H_2O \rightarrow CO + H_2 \qquad (2)$$
$$C + 2H_2 \rightarrow CH_4 \qquad (3)$$
$$C + CO_2 \rightarrow 2CO \qquad (4)$$

Reactions with hydrogen and with carbon dioxide are generally too slow for regeneration, and attention has been focused on reactions (1) and (2). Prolonged treatment with stream may lead to enhanced sintering and irreversible deactivation; as a result, attention has mainly been focused on oxidative regeneration.

It must be recognized that generalized treatments of the kinetics of decoking is simply not possible. Although the decoking reaction is represented by reaction (1), this reaction in fact involves a variety of deposits, the nature of which depend on the reaction, the operating also vary by large amounts.

Combustion of coke liberates significant quantities of heat, and this heat may accelerate phase changes or sintering in catalysts. It is common practice to burn off coke initially in a gas stream containing small amounts of oxygen (2- 5%) and then slowly to increase the oxygen concentration in order to achieve final burn off in air.

Depending on the nature of the carbonaceous deposit, oxidation o f the most reactive components of coke may be observed at 250 - 350°C, although most of the coke is generally less reactive. The bulk of the coke is, in fact, removed by oxidation at temperatures between 400 and 500°C. Not all the coke is necessarily removed even by prolonged heating, and up to 5% of coke may remain on the burnt out catalyst.

Although the kinetics of the reaction is dependent on the nature of the deactivated catalyst, some general trends may be expected. Initial coke deposition on a fresh catalyst is high, with up to 25% of the weight of the catalyst pellet being deposited in the first few hours of operation. Subsequent coking and catalyst deactivation is relatively slow. On decoking, the initial reaction must involve diffusion through a porous coke matrix. Thus, it is not surprising that the early stages of decoking may be diffusion controlled.

2.6 Comment on the Previous Works

From the previous works, selectivity of Pd catalyst in selective hydrogenation of acetylene can be improved by adding of silver as second metal in catalyst. Acetylene conversion as well as ethylene gain can increase by pretreatment with N_2O. The carbonaceous species are deposited on the surface of catalysts which be used for long time. Coke deposited is block metal active site and consequent in drop of activity, and regeneration is required. An attempt to activated regenerated Pd-Ag catalysts via of pretreatment is not reported. Since the commercial catalysts must be used for several times, therefore pretreatment with N_2O on used catalyst is chosen for study in this research.