

CHAPTER II

BACKGROUND

Because of very large world reserves of natural gas, which consists mainly of methane, there are many ongoing research activities to develop commercially viable processes to convert methane into other valuable hydrocarbons, or petrochemical feedstocks.

Currently, the methane combustion for heat or power generation is the common way in using methane. Methane catalytic combustion is an alternative for preventing combustion related pollution.

Noble metals(Pt , Pd and Rh) are the metal catalysts used for oxidation reaction. Pd shows significant activity in methane combustion (Heck, 1995). Catalyst preparation is a very important step in determining the activity of the catalyst. T.R.Baldwin and R.Burch(1990 A.) studied the effect of various palladium precursors ; palladium nitrate (Pd(NO₃)) and palladium chloride (PdCl₄), on different supporting materials such as silica (SiO₂) and alumina (Al₂O₃), on the activity of catalyst. The results showed that catalytic activity increased dramatically after heating in reaction mixture, and the activation effects were different according to the precursor salt and support material used. The activities of silica sample occurred over a short period while that of alumina has a longer life.

T.R.Baldwin and R.Burch(1990 B.) also studied catalytic activity of palladium catalyst supported on α -alumina and δ -alumina. The results indicated that catalytic activity was not due to a direct support effect but may

reflect a difference in the morphology of palladium catalyst on different supports. Yuejin Li and John N. Armor (1994) compared the catalytic activity on different supports, i.e. alumina and zeolite (ZSM-5). The result showed that Pd on zeolite catalyst is more active than Pd on alumina due to the very high metal dispersion because zeolite has very high surface area, and the lower operating temperature at the same conversion. The higher activity relates to the lower energy of the Pd-O bond. Temperature programmed reduction experiments with carbon monoxide showed a lower reduction temperature for the Pd-ZSM-5 (430 K) than for PdO/Al₂O₃ (498 K). As zeolite has limitations in its thermal stability, it is only suitable for low temperature methane emission control.

Robert E. Ellis(1992) studied the methane oxidation in the temperature range 573-873 K. He used Pd/Al₂O₃ as the catalyst. The results indicated that the oxidation of methane in air is a first order reaction and the Pd/Al₂O₃ catalyst degrades with time at constant temperature.

Najat Mouaddib and co-workers(1992) studied the influence of oxygen-to-methane ratio for methane combustion in the temperature range 473-973 K. They studied the combustion at the oxygen-methane ratio of 4 and 2 for the oxygen excess operation and for methane excess the values are 1 and 0.665. They found that the selectivity of reaction depends on the oxygen-to-methane ratio and the operating temperature. At temperatures higher than 873 K. they found that CO selectivity is significant and at lower temperature, CO₂ is the main product. In the case of methane excess, palladium on alumina catalyst was found to be active for steam reforming and water-gas shift reaction because the presence of hydrogen as a product and the changes in amount of CO, CO₂ and methane in the gas mixture.

A.K. Bhattacharya and co-workers(1992) studied the selectivity of methane oxidation to carbon monoxide in the temperature range of 373-1023 K and $\text{CH}_4:\text{O}_2$ ratio of 4:1 and 8:1, which is methane-rich. The results obtained is similar to that of Najat Mouaddib et al.(1992) i.e. the selectivity of CO formation increased with increasing reaction temperature, decreasing specific velocity and increase in $\text{CH}_4:\text{O}_2$ ratio.

Edouard Garbowski et al.(1994) studied the properties of palladium before and after the catalytic combustion of methane by combining nanodiffraction, electron microscopy and Fourier-Transform IR (FT-IR) analyses. It was found that catalytic activity of palladium strongly increased after the $\text{O}_2\text{-CH}_4$ reaction at 873 K under reducing as well as under oxidizing conditions, at the same time the dispersion of metal decreased and the particle size increased. Patrick Briot and Michel Primet(1991) studied the properties of palladium with the aim to see the changes on the surface before and after use. They found that catalytic combustion of methane must be considered as a structure-sensitive reaction because the reactivity of adsorbed oxygen that affected the activity of catalyst increased with the metal particle size. The temperature-programmed oxidation measurement suggested that palladium was in the form of bulk palladium oxide for reaction temperatures above 673 K and depended on metal particle size. The instability of reaction was associated with the slow formation of bulk PdO.