CHAPTER II
LITERATURE REVIEWS

In this section, special attention of related papers devoted directly to the non-oxidative conversion of methane over metal catalysts. However, the other points which related to this reaction are also mentioned so that all information can contribute and lead to some interesting subjects concerned in this thesis.

Koerts *et al.* (1992) reported that the direct conversion of methane to higher hydrocarbons without using oxygen over transition metals which were supported on silica (SiO_2) by wetness impregnation method. It required two steps under different conditions. The first reaction step was methane decomposition. It took place at 427 °C. In a second reaction step a particular surface carbonaceous intermediate produced hydrocarbons upon hydrogenation at 100°C. They observed that ruthenium (Ru) and cobalt (Co) catalysts were more selective toward higher hydrocarbon formation than rhodium (Rh), iridium (Ir), platinum (Pt) and nickel (Ni).

Koranne *et al.* (1992) studied about the effect of methane decomposition temperature, carbon coverage, methane partial pressure and multiple reaction cycles on a direct conversion of methane to higher hydrocarbons via an oxygen free (low-temperature route), two-step route. 3% silica-supported Ru catalyst at temperatures of methane decomposition between 127-527°C was used to produce surface carbonaceous species followed by dehydrogenation of these species to higher hydrocarbons between 77-107°C. For the effect of methane decomposition temperature, it is found that ethane yield and ethane selectivity (defined as moles of ethane/site) increased initially with an increase in the temperature of methane decomposition from 277 to 452°C. A further increase in the reaction temperature led to a decrease in the ethane yield. In the part of methane conversion, it increased monotonically with temperature. They also found that methane conversion, ethane selectivity and ethane yield were a function of surface carbon coverage. At a methane decomposition temperature of 452°C, the ethane selectivity and the ethane yield

initially increased with an increase in the carbon coverage with a maximum at around 40% coverage. After that increase in the carbon coverage led to a drop in the ethane selectivity and the ethane yield. The methane conversion decreased with an increase in the carbon coverage. When increase the partial pressure of methane partial pressure the methane conversion decreased. Furthermore they investigated effect of multiple reaction cycle. It was found that at 427°C, after approximately three cycles without intermediate hydrogenation, the ethane yield and the methane conversion decreased.

Solymosi et al. (1992) observed a comparative study on the activation and reactions of CH_4 on supported metals. They used silica support with Pt, Pd, Rh, Ir and Ru as catalysts. These catalysts were prepared by a wetness impregnation method. They reported that dissociation of methane was readily measurable at 200-400°C. Rate of initial decomposition at 250°C was the highest on Rh/SiO_2, but it dropped to a low value within a short contact time. On Pd/SiO_2 ethylene also appeared among the reaction products. The largest initial amount of ethane was formed on Pt/SiO_2. Moreover, methane flow rate had a much greater effect. The amount of ethane and ethylene was increased at higher flow rate. All these catalysts were exposed to CH_4 at 250°C for only a short time (1-2 min), C_2-C_5 hydrocarbons were also produced in addition to CH_4. When the exposure time was extended to 10 min, the absolute and relation amounts of CH_4 were greatly increased and higher hydrocarbons were detected. They concluded that the most active catalyst, as regarded the production of C_2 hydrocarbons, was Pt followed by Ru, Rh, Ir and Pd. In the case of methane decomposition the activity sequence is Ru, Rh, Ir, Pd and Pt.

Belgude et al. (1992) concluded that Pt, Ru and Co were all able to chemisorb CH_4 at low temperature. They explained that under flowing methane the desorbed hydrogen was continuously removed and the metallic surfaces became increasingly covered with CH_x species. After methane flow followed by hydrogen flush caused CH_4 to release as well as higher hydrocarbons ranging from C_2 to C_7. The largest amounts of products were obtained at about 250, 160 and 275°C for Pt, Ru and Co respectively. Factors which strongly influenced the conversion of the adsorbed CH_4 and the distribution of products were flow rates of CH_4 and H_2.

The direct conversion of methane to higher alkanes by platinum loaded zeolites was investigated by Mielczarski *et al.* (1993). 5 wt% Pt/HY and 5wt% Pt/HX were prepared by incipient wetness impregnation method. Temperature of two steps methane adsorption and hydrogenation reaction was the range from 200 to 350°C. It is found that for the Pt/HX total production of C_{2+} alkanes resulting from a reaction increases with temperature. In the case of Pt/HY the total amount of converted methane increased up to 275°C and decreased slightly beyond that temperature. Furthermore they observed that the total production of C_{2+} and the yields of the different products were influenced by the duration of the exposure to methane. At 250°C of the temperature reaction on the Pt/HX when exposure duration time was increased higher amount of methane could adsorp and resulted in higher production of alkanes. Nevertheless when the duration of the exposure was longer than 90 s, the amount of homologous methane became almost constant. In the case of Pt/HY, a similar behaviour was shown except that the amount of converted methane reached a constant value at a shorter exposure time (60 s instead of 90 s in the case of Pt/HX). For an application of successive cycles after 14 successive cycles at 250°C Pt/HX lest 6.5 % of its initial efficiency. The deactivation was much more severe at higher temperatures since the scheme number of cycles resulted in a decrease of the production by about 50% at 300°C.

Wang *et al.* (1993) reported the methane conversion over HZSM-5, Mo/HZSM-5, Zn/HZSM-5 and Mo/NaZSM-5 that were prepared by impregnation method, under non-oxidizing conditions. The results showed that benzene was the only hydrocarbon product at high temperature (700°C). The catalytic activity of ZSM-5 was greatly improved by incorporating a metal cation (Mo or Zn). The Mo/HZSM-5 catalyst exhibited the best activity because it was stable for this reaction and the methane conversion was highest (7.2%).

Guczi *et al.* (1994) observed mechanism of the decomposition process of Pt-Co bimetallic particles in supercage of NaY zeolites. The process was summarized by the following three steps. Step one, during reduction of the exchanged samples after calcination, bimetallic particles were formed that consist of Pt° and Co°. Pt atoms

segregated to the surface of the particles and were stabilized by protons that produced during the reduction. Step two, after the second oxidation, the Co^{2+} ions formed and then segregated to the outermost surface of the metal particles. Subsequently, they detached from the surface and migrated to the sodality and hexagonal cages. Step three ; Co^{2+} ions which located in the hexagonal or sodality cages, they cannot be fully reduced. So they concluded that during the decomposition of the Pt-Co bimetallic particles located in the supercage of NaY zeolite the less reducible component (Co^{2+}) migrates in the sodality and/or hexagonal cages thereby preventing the Pt migration to the external surface.

Pareja *et al.* (1994) investigated the increasing of the yield in methane homologation through an isothermal two-reaction sequence at 250 °C on 6.3 wt% Pt/SiO_2. Their experiment was performed in a stirred batch reactor at atmospheric pressure. From this research they found that C_5-C_8 alkanes represented more than 59% of the converted methane. As the duration of methane exposure increased from 1 to 5 and 16 min respectively, they reported that at the 5 min exposure as well as the 1 min one, only traces of C_7 and C_8 were observable, C_{4+} were lower than in the case of the 16 min exposure and C_2-C_4 were the most abundant alkanes.

Solymosi *et al.* (1995) investigated the dehydrogenation of methane on MoO_3 supported on various oxides under non-oxidizing conditions in a fixed bed, continuous flow reactor. The following supports were used: Al_2O_3, TiO_2, SiO_2, MgO and NH_4ZSM-5. The reaction of methane was observed above 650°C after a significant time lag, when a partial reduction of Mo^{6+} occurred. H_2, CO and several higher hydrocarbon, C_2H_4, C_2H_6, C_3H_8, C_6H_6, C_7H_8 were identified among the products. They found that the maximum value for the selectivity for benzene formation on MoO_3/SiO_2 was 56% at the methane conversion of 3.2%.

In addition, Solymosi and Szoke (1996) studied the reaction of methane with K_2MoO_4/ZSM-5 under non-oxidizing condition. The reaction was observed above 650°C. At the very beginning of the reaction partial reduction of the catalyst predominated, as indicated by the formation of CO, CO_2 and H_2O. After an initial

reduction of the catalyst the formation of several hydrocarbons was observed. The main products were benzene, ethylene, and ethane. The selectivity to benzene was in the range of 60-70% at 1.2-6.3% methane conversion. The catalyst was found to be active in the dehydrogenation of ethane and in the aromatization of ethylene. Moreover, it was suggested that CH_4 treatment transforms a significant amount of MoO_3 into MoC_2.

Guczi *et al.* (1996) studied the methane activation and coupling of the CH_x species formed from methane into higher hydrocarbons over NaY, Pt/NaY, Co/NaY, Co-Pt/NaY and Co-Pt/Al_2O_3 catalysts. These catalysts were prepared by ion exchange of zeolite Y. They reported that the Co-Pt/NaY and Co-Pt/Al_2O_3 showed exceptionally high yields, the adsorbed CH_x species and high selectivity in the formation of C_{2+} hydrocarbons (83.6 and 92.6% , respectively), than the others. The reaction was taken in two steps, the first step was chemisorption at $250^{\circ}C$ and the other was hydrogenation at the same temperature. The best catalyst appears to be when cobalt and platinum were combined inside the zeolite cage since cobalt alone was an excellent Fischer-Tropsch catalyst to form higher hydrocarbons and methane was easily activated on platinum. The amount of CH_x on Co-Pt/NaY was higher than Co-Pt/Al_2O_3.

Structure and catalytic activity of Co-based bimetallic systems in zeolite Y at low temperature methane activation was studied by Guczi *et al.* (1997). They investigated non-oxidative methane coupling reaction over Co/NaY, Co-Pt/NaY, Ru/NaY and Co-Ru/NaY catalysts. These catalysts were prepared by ion exchange method. On their research they found that the yield and the selectivity of C_{2+} increased by addition of Pt to Co in NaY. Since the sample was reduced, the bimetallic particles leaving Pt particles in the supercage whereas Co^{2+} ions migrated into the hexagonal and sodality cages that could not been reduced. For Co-Ru systems, Ru/NaY and Co-Ru/NaY when samples were calcined in oxygen instead of treating them in He, Ru particles migrated to the external surface and form large particles. Hence, when the sample was decomposed in helium the yield was low but

C_{2+} selectivity on both catalysts were over 85 %. On the contrary, when the samples were treated with oxygen the yield was higher but the selectivity in C_{2+} was lower.

In addition, Guczi *et al.* (1997) investigated the dissociative chemisorption of methane over ruthenium, cobalt, and ruthenium-cobalt bimetallic catalysts supported by alumina, silica, and NaY under a wide range of temperatures. The extent of hydrogen loss from methane was monitored by deuterium uptake of the surface carbonaceous species (CH_x) formed from methane and/or by the amount of hydrogen evolved during the course of methane chemisorption. The presence of a high average number of deuteriums in the desorbing methane suggested a wide spread dissociation of methane. The initial distribution of the deuterated products generally decreased in the sequence $CD_4 > CHD_3 > CH_2D_2$. The amount of chemisorbed methane and the evolution of hydrogen during methane chemisorption increase with temperature and follow the sequence of reducibility of the supported metals and the particle size which, in turn, depends on the support and the alloy formed. CH species prevailed on alumina-and silica-supported catalysts, while on NaY-supported metals, CH_2 species were dominant when small metal particles were stabilized inside the supercage.

Joseph *et al.* (1998) studied the structure and density of active Zn species in Zn/HZSM-5 catalysts for propane aromatization. Propane conversion turnover rates were greater on Zn/HZSM-5 than on HZSM-5. When Zn cations were introduced into HZSM-5 channels, dehydrogenated products were produced with higher selectivity and the rate of formation of aromatics increased markedly. The selectivity to C_{6+} aromatics at similar conversions (7.6-8.3%) increased from 2.4% to 35.4% when Zn (1.30 wt%) is ion-exchanged into HZSM-5. Aromatic site time yields increased monotonically with increasing Zn content (0-1.30 wt%).

Guczi *et al.* (1998) investigated the methane conversion to higher hydrocarbons in a "one-step" process under non-oxidative conditions at low temperature over Co-Pd/SiO_2 catalysts at 250°C as a function of hydrogen concentration in helium and of catalyst composition. A maximum in the production of C_{2+} hydrocarbons including aromatics (benzene and toluene) was observed at

1.3 vol% H_2/He mixture in which one pulse of methane was introduced. Additional hydrogenation with the same H_2/He mixture at 400°C was efficient to remove the larger hydrocarbon fragments already existing on the surface. On pure Pd/SiO_2 the one-step process is not so efficient as on cobalt-rich samples, but in the latter case the hydrocarbon removal is the most efficient during high-temperature hydrogenation. It was found that methane conversion in the one-step process is at least 2.5 times greater than that measured in the "two-step" process and, in some cases, 80% of the methane introduced is converted to larger hydrocarbons.

Vereshchagin *et al.* (1998) studied conversions of methane, ethane, propane, benzene and hydrogen on HZSM-5 at 418°C using binary mixtures R_1:R_2:N_2O:He (where R_1, R_2 were substances under study). Relative reactivities were determined, and it was shown that the rates of conversion of hydrocarbons were determined by the strengths of C-H bonds (H-H for hydrogen).

Wang *et al.* (1998) studied the effect of carbon dioxide on the conversion of methane to C_2 hydrocarbons over praseodymium oxide in the absence of gaseous oxygen at 500-650°C. The oxygen vacancies in praseodymium oxide were suggested to play crucial roles in the low-temperature reaction conversion of methane to C_2 hydrocarbons by CO_2. It was plausible that CO_2 adsorbs on the oxygen vacancy to form surface oxygen species, which then activate CH_4.

Zeng *et al.* (1998) studied non-oxidative dehydro-aromatization of methane over strong acid-promoted W/HZSM-5-based catalysts. Over a W-Zn-H_2SO_4/HZSM-5 catalyst and under the reaction conditions of 850°C, 0.1 MPa, and GHSV=1500 mL/h gcat., methane conversion (X_{CH4}) reached 23%, with a selectivity to benzene at 97% and an amount of coking for 3 h operation at 0.02% of the weight of the catalyst used. During a stability test at 800°C for 3 h, X_{CH4}, had been maintaind at about 21.5% over the W-Zn-H_2SO_4/HZSM-5 catalyst, whereas dropped gradually to 13% from 19% in the initial stage over the Mo-Zn-H_2SO_4/HZSM-5, demonstrating that the former had a better heat-resisting peculiarity than the latter. The results of investigation of optimization of the catalyst composition showed that the optimal W-loading on the HZSM-5[n(Si)/n(Al)=38] zeolite support was about 2.5%, and that an optimal match-

ratio existed among the W and the promoters, Zn(or La or Nb) and H_2SO_4. The experimental results also indicated that the promoting effects of Zn and La were more pronounced than Nb.

Markpoon (1998) studied the non-oxidative methane coupling over metal-containing Y-type zeolite catalysts with Co, Ru and Pt. It is found that catalytic activity of the metal catalyst prepared by ion exchange method was better than the metal catalyst prepared by impregnation method. Comparison with 10%Co/HY, 10%NaY shows the very low activity for non-oxidative methane coupling. In addition, the percentage of metal loading, the appropriate percentages of cobalt, ruthenium and platinum were 10, 15 and 15% by weight, respectively. The products from this reaction are ethane and propane. Propane was produced on 10%Co/HY and 15%Ru/HY, while ethane was occurred on 15%Ru/HY and 15%Pt/HY. With the effect of space velocity of methane, the amount of propane was decreased when the space velocity of methane was increased from 4960 h^{-1} to 6200 h^{-1}. On the other hand the amount of ethane was increased. In hydrogenation step, it is found that the amount of propane produced on 10%Co/HY was much higher in argon stream than hydrogen stream.

Kai *et al.* (2000) studied the catalytic hydrodehalogenation of $CBrF_3$ with methane over NiZSM-5 and HZSM-5 in tubular reactor between 300 and 600°C and at ambient pressure. It was found that the incorporation of nickel into HZSM-5 significantly enhanced the activity of the zeolite. A variety of products were formed during reaction, including CH_3Br, CHF_3, CH_2Br_2, C_2F_6, C_2H_4, C_2H_2, $C_2H_2F_2$, $CHBrF_2$, CH_2BrF, and C_2H_3Br. XRD analysis showed that these two zeolite catalysts did not suffer any loss in their crystallinity during use. Deactivation of both NiZSM-5 and HZSM-5 may, in part, be due to poisoning of the zeolite by halogens. Coking is another cause of the deactivation of HZSM-5, but appears to play a minor role in NiZSM-5 deactivation. A series of methylated silicone oils was detected during reaction over NiZSM-5.

Eliasson *et al.* (2000) studied direct higher hydrocarbon formation from the greenhouse gases methane and carbon dioxide using a dielectric-barrier discharge

(DBD) with zeolite catalysts. This catalytic DBD can be operated at ambient conditions and leaded to direct hydrocarbon formation. The products include alkanes, alkenes, oxygenates, and syngas ($CO + H_2$). The product distribution depended on the pressure, the input power, the flow rate, the CH_4/CO_2 feed ratio, and the catalyst used. It was not sensitive to gas temperature in the range from room temperature to 150°C. From the experiments it can be concluded that a cogeneration of syngas and higher hydrocarbons can be achieved using the catalytic DBD. The optimum CH_4/CO_2 ratio in the feed for such cogeneration was in the range 2/1 to 3/1. The energy efficiency of CO_2 and CH_4 conversion increases substantially at higher discharge powers.

From all of the above reviews, the transition metal catalysts for non-oxidative conversion of methane are Pt, Co, Ru, Ni, Rh, Re, Mo, Zn, Ir and W supported on ZSM-5, SiO_2, Al_2O_3 and zeolite Y. The interesting catalyst is Mo-modified ZSM-5 catalysts because higher hydrocarbon such as benzene can be produced over this catalyst. It is necessary to understand in much greater detail the chemistry of the catalyst activation if progress is to be made in understanding the reaction mechanism and in developing improved versions of this potentially important catalytic process for upgrading natural gas. Thus this thesis interests in the catalytic performance of methane conversion over Mo/HZSM-5 catalyst. Besides Mo/HZSM-5 catalyst, Mo/HY and HZSM-5 catalysts are also studied. The reaction is executed under the following conditions; atmospheric pressure, temperature 600-700 °C with gas hourly space velocity (GHSV) 2000-6000 h^{-1}.