CHAPTER II

LITERATURE REVIEWS

In 1964, zeolite Y was first synthesized by Breck. Since then, the investigation of its properties was undertaken in many laboratories. Some of the more prominent studies and the modified zeolite for methane coupling reaction were summarized below.

2.1 Reviewed Papers

In this section, special attention of related papers devoted directly to the non-oxidative methane coupling 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. The non-oxidative methane coupling consists of two-step reactions. The first reaction was methane decomposition and the other was hydrogenation. The investigation of non-oxidative methane coupling can separate into two periods which depends on the temperature of two-step reactions.

In the first period the researchers found that at a temperature between 177-527 ^{o}C methane was decomposed but the hydrogenation can occur at 27-127°C

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 ^{o}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. They used 3% silica-supported Ru catalyst at temperatures of methane decomposition between 127-527°C 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 they 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.

In the second period the researcher found a temperature which both steps can take place. The details of this period are describe below.

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 $250^{\circ}C$ 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 hydro-carbons, 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 on 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. On this research they found that the largest amounts of products were obtained at about 250, 160 and $275^{\circ}C$ 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). They used 5 wt% Pt/HY and 5wt% Pt/HX as catalyst in their work. The platinum was loaded onto the zeolite by the incipient wetness impregnation method. Temperature of two steps methane adsorption and hydrogenation reaction was the range from 200 to $350^{\circ}C$. They 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 $275^{\circ}C$ 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 $250^{\circ}C$ of the temperature reaction on the Pt/HX when they increased the exposure duration time higher amount of methane could adsorp and resulted in higher production of alkanes. Nevertheless when the duration of the exposure was longer than 90 sec, the amount of

homologous methane became almost constant. In the case of Pt/HY, it showed a similar behaviour but the only difference was that the amount of converted methane which reached a constant value after a shorter exposure (60 sec instead of 90 sec in the case of Pt/HX). For an application of successive cycles after 14 successive cycles at $250^{\circ}C$ 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 $300^{\circ}C$.

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 ($700^{\circ}C$). 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 were 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.

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°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 therefore 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.

Chen *et al.* (1996) studied the influence of modification of Mo/HZSM-5 catalyst by Pt on methane non-oxidative transformation to ethylene and aromatics under the conditions of 700°C, 1 atm and GHSV of methane of 1400 ml/(g cat h). They found that the addition of Pt to Mo/HZSM-5 which was prepared by the impregnation method enhanced the catalyst stability and reduced the carbon deposition on the catalyst. They suggested that the coke on the Pt-Mo/HZSM-5 catalyst could easily be oxidized (at a much lower temperature) as compared to that on the unmodified Mo/HZSM-5 catalyst. They found that the addition of Pt to Mo/HZSM-5 did not improved the selectivity of ethane and benzene.

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.

Xie *et al.* (1997) investigated the aromatization of methane over Mo/HZSM-5 zeolites without using oxidants. All of Catalysts were prepared by impregnating. They observed that the methane conversion showed a maximum at about 2-3% Mo loading. It increased with increasing pressure under lower reaction pressures (<200 kPa). Furthermore, the selectivity and the conversion of methane to aromatics over 2% Mo/HZSM-5 decreased with increasing space velocity of methane and calcination temperature. On the Pt/HZSM-5, Ni/HZSM-5 and Mo/NaZSM-5 catalysts the selectivity to ethylene was much more than the selectivity to aromatics. In contrast, on the Mo/HZSM-5 catalyst aromatics was main product.

2.2 Some comments on the previous work

From all of the above reviews, the transition metal catalysts for non-oxidative methane coupling are Pt, Co, Ru, Ni, Rh, Re, Mo, Zn and Ir. They are supported on ZSM-5, SiO_2, Al_2O_3 and zeolite Y. The non-oxidative methane coupling has two steps reaction, the first step is methane chemisorption and the other step is hydrogenation, both steps were carried out at temperatures between 200 and 500 °C. Those reactions were operated at atmospheric pressure and gas hourly space velocity (GHSV) in the region of 4960-6200 h^{-1}. There are very few papers related to this reaction over metal/NaY support catalyst.

Accordingly, this thesis interests in other point beyond the above reviews which are investigation of non-oxidative methane coupling over Pt, Co, Ru supported Y type zeolite. The non-oxidative methane coupling reaction was executed under the following conditions; atmospheric pressure, temperature 200-400 °C, gas hourly space velocity (GHSV) 4960-6200 h^{-1}. This thesis study the effects of Y type zeolite form, NaY form and HY form. Furthermore, the preparation method of metal catalysts wet impregnation and ion exchange, were investigated.