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CHAPTER II

LITERATURE SURVEY

2.1 Oxidative Reaction of Methane

Because of the limitation of oxidants which are able to react with methane, a few processes have been used to covert methane into others useful chemicals such as methanol. However, at the present, these processes have been done via a two-stage process of steam reforming to synthesis gas and catalytic conversion of methanol. This route suffers from the requirement of complicated engineering steps and also from the relative inefficiency of carrying out extensive oxidation of methane to carbon monoxide and then reduction of carbon monoxide to other compounds. In addition, the "synthesis gas" must be clean, free from catalyst poisons and seriously high pressure caused only available large-scale plant. Therefore, direct oxidation reaction of methane in one step have been considered extensively to investigate because it will be energywise more efficient. The pathways of direct oxidation of methane, those reports proceeded via three major routes,

1. Oxidative coupling
2. Partial oxidation

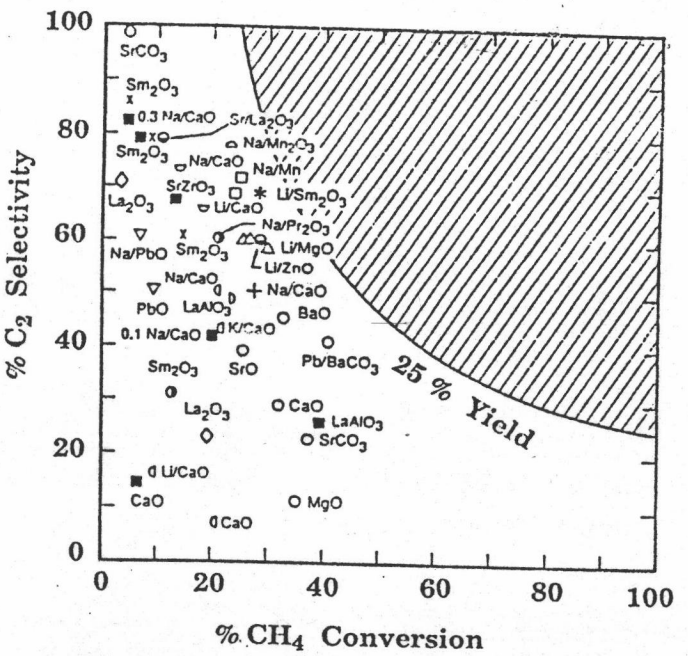
3. Oxyhydrochlorination

Oxidative coupling process use oxygen as an oxidant but the oxygen does not incorporate into the products. The resulting products oftenly are higher molecular weight olefins and paraffins which are mostly a mixture of ethylene and ethane. Partial oxidation process also use oxygen as the oxidant and the reaction products also have an oxygen part in their molecule such as methanol. As for the oxyhydrochlorination routes, chlorine is used as the oxidant and it incorporate into the products becoming a halo-hydrocarbon such as dichloroethylene.

However, the oxidative coupling process is the most attractive one, this is because ethylene is one of the most important chemical compounds used for petrochemical feedstock. Nevertheless, the process will considerably be economic for commercial use if the yield of C_2-hydrocarbons are at least about 25%. Although, many materials, mostly metal oxides, have been used for the investigation, however, until now it had not yet reached the economical region. The summary of C_2 selectivity and CH_4 conversion of various catalytic compounds are shown in Figure 2-1.

2.2 Oxidative Coupling Mechanism

In a series of related experiments, it is convenient to divide the oxidation of methane to ethane and ethylene via



McCarty et al. (SRI) 1990

Figure 2-1 The update attained of C_2 selectivity and CH_4 conversion of various catalytic compounds on oxidative coupling of methane

oxidative coupling reaction into two steps: firstly, generation of methyl radical ($CH_3\bullet$) and the second, formation of the stable products from $CH_3\bullet$ which normally are CO, CO_2, C_2H_4, C_2H_6, H_2 and H_2O. Methyl radicals are produced when methane and oxygen are passed over the metal oxide catalyst at high temperature. The methyl radicals are formed at the surface of catalysts and released into the gas phase which can be detected by trapping downstream in a solid argon matrix, where they be analyzed by EPR spectroscopy [1-4]. However, the mechanisms of catalytic path-ways to generate methyl radicals have been reported only for lithium doped on magnesium oxide while for the other catalysts only have the

effective role to produce C_2H_4 and C_2H_6 of overall reaction in terms of CH_4 conversion and C_2 selectivity was reported. These pathways showed the catalytic cycle of the formation and the regeneration of active oxygen sites on catalyst surface. The $[Li^+ O^-]$ centers which were formed in lithium oxide (Li_2O) is the active centers for the formation of methyl radicals because they have an activity of abstracting hydrogen atom from methane. The explanation will mention the mechanism for the $[Li^+ O^-]$ which are generated from Li_2CO_3 doped on MgO [1:62, 2:5066, 3:5886] and the formation of the stable products from these $CH_3\bullet$ [2 : 5067]. Li^+ ions are generated from Li_2CO_3 precipitates instead of Li_2O. For every two Li^+ ions leaving the carbonate phase, only one Mg^{2+} enters to form $MgCO_3$. This method is known as an arc-fusion technique [2: 5064]. From stoichiometric consideration, this excess of cations in the MgO matrix suggests the formation of oxygen vacancies which may exist on the surface. Gaseous oxygen molecules, however, immediately react with the vacancies at high temperature, resulting in O^{2-} ions and holes. The $[Li^+ O^-]$ centers are produced by these holes being trapped at O^{2-} ions which are adjacent to Li^+ ions. This process can be expressed as follows :

$$2\,Li^+ O^{2-} + \square + 1/2\,O_2 \rightleftharpoons 2Li^+ O^- + O^{2-} \qquad (2.1)$$

where $\square$ denotes an oxygen vacancy.

It is significant that the rate of radical formation and the

concentration of $[Li^+ O^-]$ centers behaved in a parallel manner with respect to Li loading which both can be analyzed by EPR spectrometer. Thus, it was concluded that CH_3 was produced by a reaction between CH_4 and O^- of $[Li^+ O^-]$ centers :

$$Li^+O^- + CH_4 \longrightarrow Li^+ OH^- + CH_3\cdot \qquad (2.2)$$

The regeneration of $[Li^+ O^-]$ center in equation (2.2) was proposed to occur by the following scheme.

$$2\ Li^+ OH^- \longrightarrow Li^+ O^{2-} + Li^+\square + H_2O \qquad (2.3)$$

$$Li^+ O^{2-} + Li^+\square + 1/2\ O_2 \longrightarrow 2\ Li^+ O^- \qquad (2.4)$$

The $[Li^+ O^-]$ centers produced in equation (2.4) again react with CH_4 by equation (2.2). Reaction in equation (2.3) is a typical dehydroxylation process which requires high temperature. However, reaction in equation (2.4) may also require high temperature because it includes the dissociation of the O-O bond, and perhaps the migration of Li^+ ions. Either reaction in equation(2.3) and (2.4) is the rate-determining step in the catalytic production of $CH_3\cdot$.

An alternate pathway may be possible for the regeneration process of reaction in equation (2.3) and (2.4). In the MgO matrix, Li^+ would be stabilized more by a nearby monovalent negative charge than by divalent or neutral one. In such a case the regeneration process is expressed as follows :

$$2\ Li^{+}\ OH^{-} \longrightarrow Li^{+}\ O^{-} + Li^{+}\boxdot + H_2O \quad (2.5)$$

$$Li^{+}\boxdot + 1/2\ O_2 \longrightarrow Li^{+}\ O^{-} \quad (2.6)$$

where $\boxdot$ denotes an electron trapped at an oxygen ion vacancy.

The formation of stable products have been supposed from methyl radicals. A coupling of two $CH_3\bullet$ radicals, probably in the gas phase but near the surface, produce C_2H_6,

$$2\ CH_3\bullet \longrightarrow C_2H_6 \quad (2.7)$$

which further reacts with surface O^- ions to produce ethylene [3:5067].

$$C_2H_6 + O^- \longrightarrow C_2H_5\bullet + HO^- \quad (2.8)$$

$$C_2H_5\bullet + O^{2-} \longrightarrow OC_2H_5^- + e^- \quad (2.9)$$

$$OC_2H_5^- \longrightarrow C_2H_4 + OH^- \quad (2.10)$$

According to reaction in equation (2.7) the formation of the C_2 compounds should be proportional to the square of the $CH_3\bullet$ concentration. There are three possible pathways to form CO and CO_2 from $CH_3\bullet$.

$$2\ CH_3\bullet \longrightarrow C_2H_6 \longrightarrow C_2H_4 \longrightarrow CO\ ,\ CO_2 \quad (2.11)$$

$$CH_3\bullet + O^{2-} \longrightarrow OCH_3^- \longrightarrow CO\ ,\ CO_2 \quad (2.12)$$

$$CH_3\cdot + O_2 \longrightarrow CH_3O_2\cdot \longrightarrow CO\ ,\ CO_2 \qquad (2.13)$$

In pathway as in equation (2.11), CO and CO_2 are produced from C_2 compounds, however, this is not a major route to produce CO and CO_2. For pathway in equation (2.12) $CH_3\cdot$ reacted with surface O^{2-} ions to produce methoxy ions, which subsequently decompose to CO and CO_2. The formation of CO and CO_2 via this route should be related to the surface area of catalyst. If the reaction temperature is sufficiently high the surface OCH_3^- ions can decompose according to the equation (2.14).

$$OCH_3^- \longrightarrow CO + 3/2\ H_2 + e^- \qquad (2.14)$$

The decrease in CO and CO_2 production as a function of time on stream may occur from a decreasing in surface area due to sintering of the catalyst [2:5067].

The last one is the pathway as shown in equation (2.13) which is a gas-phase reaction between $CH_3\cdot$ and O_2 to produce $CH_3O_2\cdot$ radicals. This reaction also must be included as one of the main route for complete oxidation. These methyperoxy radicals can be detected together with the methyl radicals by EPR spectroscopy, for example, a ratio of $[CH_3O_2\cdot\ ]\ /\ [CH_3\cdot\ ] = 0.056$ at 620°C in Li/MgO catalyst [2:5067].

2.3 The Active Catalyst

From the series of reaction sequence which had been demonstrated in oxidative coupling mechanism we see that the catalytic character must be active in both generation of methyl radicals and partial oxidation of C_2H_6 to C_2H_4. These will effectuate when it must be able to forming O^- and have to forming O^{2-} because C_2H_6 can be formed to C_2H_4 by, well-known, thermal-cracking at high temperature. Figure 2.2 shows the elements capable of forming these ions which alkali metals (1A, 2A) elements can be formed both peroxide and superoxide while some elements in transition metals have no capability of neither ones. According to this performance, we may suppose that alkali metals have the ability to convert methane to ethane and ethylene via oxidative coupling reaction. Furthermore, Table 2-1 shows the ability in chemisorption of various adsorbing species on various kinds of metal groups [5:22].

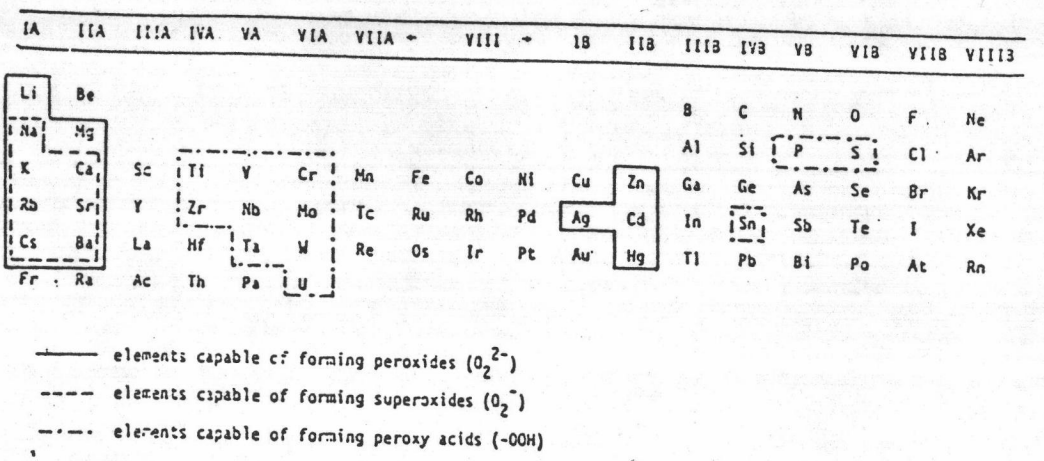


Figure 2-2 Different forms of adsorbed oxygen.

Table 2-1 A classification of metals according to their abilities in chemisorption [5:22].

Group	Metals	Gases						
		O_2	C_2H_2	C_2H_4	CO	H_2	CO_2	N_2
A	Ti,Zr,Hf,V, Nb,Ta,Cr,Mo, W,Fe,Ru,Os	+	+	+	+	+	+	+
B_1	Ni,Co	+	+	+	+	+	+	-
B_2	Rh,Pd,Pt,Ir	+	+	+	+	+	-	-
B_3	Mn,Cu	+	+	+	+	+-	-	-
C	Al,Au	+	+	+	+	-	-	-
D	Li,Na,K	+	+	-	-	-	-	-
E	Mg,Ag,Zn,Cd, In,Si,Ge,Sn, Pb,As,Sb,Bi	+	-	-	-	-	-	-

+ means that strong chemisorption occurs;

+- means that it is weak;

- means unobservable.

According to the Table 2-1, it shows that the metals of class A appearing in Group IV, V, VII and VIII_1 of the periodic classification (Group VIII_1 comprises Fe, Ru, Os; Group VIII_2 Co, Rh, Ir; Group VIII_3 Ni, Pd, Pt), those of class B_1 are the base metal of Group VIII_2 and VIII_3, while those of class B_2 are the noble metals of these Groups. Class B_3 contains two anomalous metals of the first long series (adsorption and catalysis are full of anomalies). The propensity which show strong chemisorption is therefore firmly associated with transition metals. These metals have a strong chemisorption of C_2H_4 and O_2, therefore C_2H_4 from oxidaive coupling of methane will be oxidized to be CO_x. We may be expected that catalyst in oxidative coupling of methane from transition metals will not be effective catalysts to produce C_2-hydrocarbons. Consider that all of the most weakly chemisorption metals (class C, D and E) come either before or after the transition series proper. These groups have an ability in chemisorption only of O_2 (C_2H_4 is not involved in oxidative coupling of methane), therefore, the active metal cation sites have to absorb the gaseous oxygen at their maximum capacity. Addition with, especially class D and E, their capability of forming peroxide and/or superoxide make them the active catalysts in oxidative coupling of methane to ethane and ethylene.

2.4 Literature Survey

Takeshi Moriyama and co-workers [13] have studied the role of the primary compounds or doped elements to the oxidative

coupling of methane. Many metal were doped over MgO to investigate the activity of catalysts. The reaction conditions were CH_4:air:He= 1.5:3.75:50 (CH_4:O_2=2) and atmospheric pressure. C_2 formation did not observed with the temperature below 873 K and the tendencies of the catalyts were observed with respect to the chemical periodicity of the doped element: 1) MgO doped with the transition metals (5A to 8 elements and Cu are active for CO_2 production, but less active for C_2 formation. 2) The 3B, 4B, 3A, 4A, and alkali earth elements are not appreciably effective either for CO_2 or C_2 production. 3) Alkali doped catalysts are less active in CO_2 formation and more active in the formation of C_2 compound than the undoped MgO. 4) Among alkali doped catalysts no chemical periodicity is observed, whereas Na and Rb give higher activities in C_2 formation.

Eiji Iwamatsu and co-workers [14] have studied the role of the catalyst in specific surface area by investigating various metal doped MgO which each combination gave the different specific surface area at the same 0.2 % metal doped concentration. Their results have shown that the catalysts with smaller surface area are more effective for C_2 formation and have presented the effects of doping by comparing samples having the same surface area that alkali metals are effective, but their effectiveness is not unusual while transition metals have a less significant effect on C_2 formation. This mean alkali metal addition is important in increasing catalyst activity but it also has an important

effect in decreasing the surface area.

H.S. Zhang and co-worker [4] have studied the effect of Li concentration which doped over ZnO, Temperature and the partial pressure of oxygen to the oxidative coupling of methane. The catalytic studied were carried out in a conventional fused-quartz flow reactor operated at atmospheric pressure. Typical reactant feeds consisted of a 2:1 methane:oxygen feed diluted with a helium and reaction temperature ranged from 600 to 770°C. Methane conversion continually increased with increasing temperature. The C_2 selectivity slowly increased to a maximum at a temperature of approxximately 675°C while a reverse temperature dependence was observed for the C_1 (CO and CO_2) selectivity. Addition of lithium resulted in a decreased of methane conversion but the C_2 selectivity rapidly increased and eventually leveled off at the doping level of approximately 1.0 wt% Li. Addition of lithium also decreased the surface area from 0.5 m^2/g over the pure oxide to a constant value of 0.1 m^2/g over all of Li-doped sample. As the oxygen partial pressure was increased, methane conversion continued to increase. At low oxygen partial pressure the formation of selective C_2 products was favoured whereas high oxygen partial pressures tended to promote the production of non-selective CO and CO_2.