CHAPTER 3

THEORY

The oxidative coupling and combustion reactions vary on the catalysts, pressure, temperature, and mole ratio of CH_4/O_2 . These variables play important roles of conversion of methane to C_2 (ethane and ethylene) and CO_x (CO and CO_2).

3.1Catalyst

Before focusing on the characteristics of catalysts which effect on conversion and products from chemical reactions, it is necessary to consider mechanism of reaction of the OCM.

Amenomiya et al [1] presented the mechanism of reactions of OCM as following.

For alkali and alkaline earth metal oxides, they supported the study of Lunsford who proposed that the activation of methane takes place by abstracting hydrogen atoms on the $[Li^+O^-]$ centers. These centers are formed by oxygen vacant holes ([ ]) trappedd at O^{2-} ions adjacent to Li^+ ions as follows.

$$2Li^+O^{2-} + [\ ] + 1/2\ O_2 \longleftrightarrow 2Li^+O^- + O^{2-} \qquad (3)$$

$$Li^+O^- + CH_4 \longrightarrow Li^+OH^- + CH_3^{\cdot} \qquad (4)$$

The $[Li^+O^-]$ centers are regenerated by

$$2Li^+OH^- \longrightarrow Li^+O^{2-} + Li^+[\ ] + H_2O \qquad (5)$$

$$Li^+O^{2-} + Li^+[\ ] + 1/2\ O_2 \longrightarrow 2Li^+O^- \qquad (6)$$

or

$$2Li^+OH^- \longrightarrow Li^+O^- + Li^+[e^-] + H_2O \qquad (7)$$

$$Li^+[e^-] + 1/2\,O_2 \longrightarrow Li^+O^- \qquad (8)$$

Thus the surface O^- species are responsible for the activation of methane.

For lanthanides, the radicals $CH_3^\cdot$ were form in the gas phase with lanthanum oxides only when oxygen was present in the reactant stream. The O^- species were formed from O^{2-} during the reaction. Wang and Lunsford further suggested that the superoxide ions are in equilibrium with the surface peroxide ions and oxygen.

$$O_2 + O_2^{2-} \longleftrightarrow 2O_2^- \qquad (9)$$

When Ito and Lunsford first reported that lithium-doped magnesia was an efficient catalyst for methane coupling, they assumed that formation of $CH_3^\cdot$ radicals on the surface Li^+O^- centers and subsequent dimerization of the radicals in the gas phase.

$$2CH_3^\cdot \longrightarrow C_2H_6 \qquad (10)$$

The methyl radicals also produce CO_x through a series of chain reactions in the gas phase:

$$CH_3 + O_2 \longrightarrow CH_3O_2^\cdot \qquad (11)$$

$$CH_3O_2^\cdot + C_2H_6 \longrightarrow CH_3O_2H + C_2H_5^\cdot \qquad (12)$$

$$2CH_3O_2^\cdot \longrightarrow CH_2O + CH_3OH + O_2 \longrightarrow CO,CO_2 \qquad (13)$$

$$CH_3O_2H \longrightarrow CH_3O^\cdot + OH^\cdot \qquad (14)$$

$$CH_3O^\cdot + CH_4 \longrightarrow CH_3OH + CH_3^\cdot \qquad (15)$$

$$OH^\cdot + CH_4 \longrightarrow CH_3^\cdot + H_2O \qquad (16)$$

or on the surface:

$$CH_3^\cdot + O^{2-}\,(\text{surface}) \longrightarrow CH_3O^- + e^- \qquad (17)$$

$$CH_3O^{\cdot} \longrightarrow CH_3OH{\cdot}CH_2O \longrightarrow CO.CO_2 \qquad (18)$$

Ethane produced by the coupling reaction further reacts to form ethylene either on the surface:

$$C_2H_6 + [M^+O^-] \longrightarrow C_2H_5^{\cdot} + [M^+OH^-]_s \qquad (19)$$

$$C_2H_5^{\cdot} + O_2^{\cdot} \longrightarrow C_2H_5O^{\cdot} + e^- \qquad (20)$$

$$C_2H_5O^{\cdot} \longrightarrow C_2H_4 + OH^{\cdot} \qquad (21)$$

or in the gas phase through Eqs. (12), (22), (23), and (24):

$$CH_3^{\cdot} + C_2H_6 \longrightarrow CH_4 + C_2H_5^{\cdot} \qquad (22)$$

$$C_2H_5^{\cdot} \longrightarrow C_2H_4 + H^{\cdot} \qquad (23)$$

$$C_2H_5^{\cdot} + O_2 \longrightarrow C_2H_4 + HO_2^{\cdot} \qquad (24)$$

The foregoing mechanism has been sommarized by Lin et al. [1] in a scheme shown in Fig.3.1.

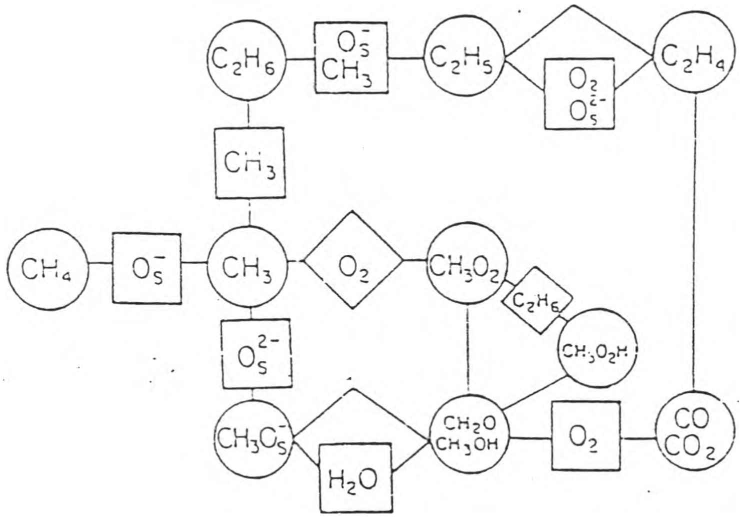


Fig. 3.1 Reaction scheme of the oxidative coupling of methane. Reproduced from Ref. 1 with permission of *Journal of Catalysis*.

The catalyst is the major concerned subject subject in the OCM. There are many important aspects of catalyst such the pores, surface area of catalyst and other chemical properties.

3.1.1 Pores and surface area

A catalytic reaction is related to the pores and surface area of catalysts. The overall process by which heterogeneous catalytic reactions proceed can be broken into the sequence of individual steps at catalyst. The steps are :

1. Mass transfer (diffusion) of the reactant (s) from the bulk fluid to the external surface of the catalyst pellet.
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface.
3. Adsorption of reactants onto the catalyst surface.
4. Reaction on the surface of the catalyst.
5. Desorption of the products from the surface.
6. Diffusion of the products from the interior of the pellet to the pore mouth of the external surface.
7. Mass transfer of products from the external pellet surface go to the bulk fluid.

Consider a general chemical reaction occurring isothermally inside a single porous catalyst pellet which posses a uniform catalytic activity profile. The pellet is assumed to possess sufficient symmetry so that the composition at any point in space can be described as a function of only one spatial variable. The mass balance equation for the first order reaction is

$$\frac{d^2C_A}{dx^2} - \frac{2k_sC_A}{Dr} = 0 \qquad (25)$$

or

$$\frac{d^2C_A}{dx^2} - \frac{kC_A}{D} = 0 \qquad (26)$$

For solving this equation gives the concentration gradient of the reactant within the pore is

$$\frac{C_A}{C_{AS}} = \frac{\cosh m(L-x)}{\cosh mL} \tag{27}$$

This progressive drop in concentration on moving into the pore is shown in the figure and this is seen to be dependent on the dimensionless quantity 'mL', called the Thiele modulus.

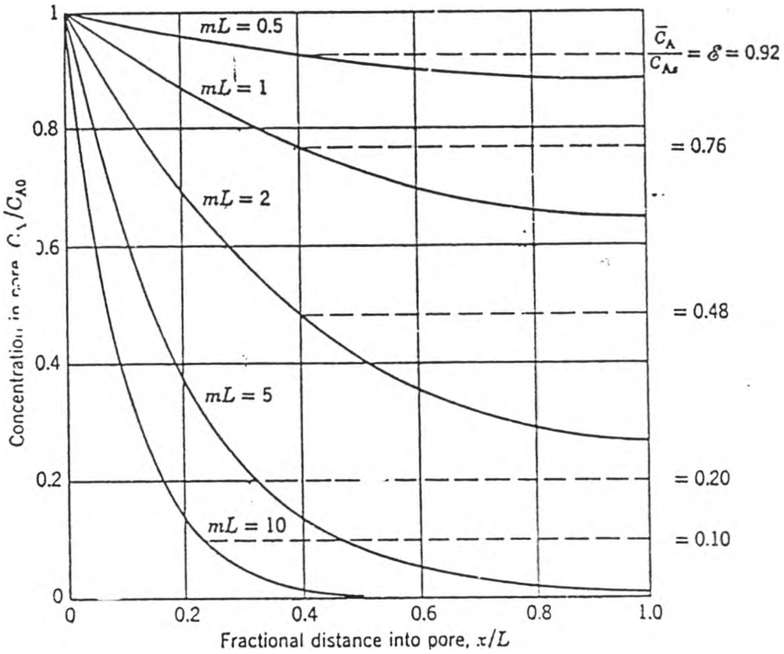


Fig 3.2 The progessive drop inconcentration on moving into the pore

To measure how much the reaction rate is lowered because of the resistance to pore diffusion the quantity ξ called the 'effectiveness factor' as follows

$$\xi = \frac{\text{(actual reaction rate within pore)}}{\text{(rate is not slowed by pore diffusion)}}$$

$$= r_A \text{ with diffusion}/r_A \text{ without diffrsion}$$

For first-order reaction ξ = Ca/Cas because the rate is proportional to the concentration. Evaluating the average rate in the pore from eq. gives the relationship.

$$\xi = \frac{C_A}{C_{AS}} = \frac{\tanh mL}{mL} \tag{28}$$

For small mL, or mL < 0.5, $\xi \approx 1$, the concentration of reactant does not drop apprcibly within the pore, thus pore diffusion offers neglegible resistance to reaction. This can also be verified by nothing that a small value for means either the short pore, slow reaction or rapid diffusion, all three factors tending to lower the resistance to diffusion.

For large mL or mL > 5 it is found that $\xi = 1/mL$ the reactant concentration drops rapidly to zero on moving into the pore, hence diffusion strongly influences the rate of reaction. These condition is called strong pore resistance. It is well known that when mL (Thiele modulus) is large, the reaction takes pace almost entirely near the surface of the catralyst.

3.1.2 Chemical properties

A belief that chemisorption of one or more of the reactants is involved, as an intermediate step, in essentially all solid catalyzed reactions leads to the hope that an understanding of chemisorption phenomena on catalysts would illuminate and clarify the mechanisms of catalytic reaction. Several aspects of chemisorption are of particular interest in catalysis.

a. The rate of chemical adsorption of reactants or desorption of products, studied individually, may indicate the slow and therefore rate limiting step in the catalytic reaction. They are also help characterize surface heterogeneity.

b. The heat chemisorption is a measure of the strength of bonds formed between adsorbent and adsobate. The variation of heat of adsorption with surface coverage is a measure of surface heterogeneity.

c. The nature of the actual chemisorbed species as revealed, for example, by infrared adsorption gives direct evidence of possible chemical intermediate in the reaction.

Thus chemisorption affects the rate of chemical reaction. Here, the adsorbed atoms or molecules are held to the surface by valence forces of the same type as those that occur between bonded atoms in molecules. Like physical adsorption, chemisorption is an exothermic process, but the heats of adsorption are generally as the same magnitude as the heat of a chemical reaction. If a catalytic reaction involves chemisorption, it must be carried out within the temperature range where chemisorption of the reactants is appreciable.

Within groups of hydrocarbon, the strength of adsorption typically is in the order :

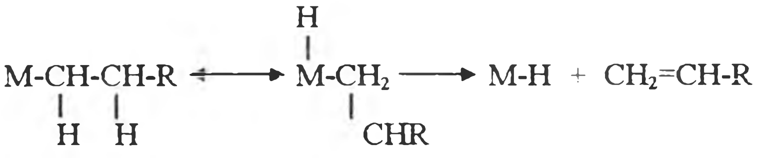
Acethylene > diolefins > olefins > paraffins

Polar substances are generally more strongly adsorbed than nonpolar substances, with the consequence that in hydrogenetion reactions the product is usually less strongly adsorbed than the reactants. The opposite is frequently the case in partial oxidation reactions. It was found that in general the strength of adsorption for some gases and vapors falls in the sequence :

$$O_2 > C_2H_2 > C_2H_4 > CO > H_2 > CO_2 > N_2$$

Oxygen is so strongly adsorbed that it frequently leads to reaction in which oxygen no longer confined to a chemisorbed surface layer. In that event the catalyst structure become altered or even perhaps destroyed. Similarly, metal carbides may be formed from a metal, as occurs with iron or nickel. For example of Cailin's study, the roles of oxygen on OCM, in the reaction zone the oxygen concentration decreases rapidly from the feed concentration of 11 % to zero. The reaction rate dropped suddenly at a bed height of 11.5 mm, just at the point where oxygen was completely consumed. It is significant to note that oxygen reaches zero concentration at the end of the reaction zone, the rate of methane oxidation is still maintained at a high level.

High bond polarity promotes attack by reagents because it has a source of separated poles of electropositive and electronegative where supplies the reaction. The very electropositive elements of Group I and II form alkyls with extremely polar M-C bonds. A very significant reaction of alkyls containing beta-hydrogen(β-H) reacts to give olefin, this reaction is called β-elimination.



$$\underset{}{\text{M-}}\underset{\text{H}}{\text{CH}}\text{-}\underset{\text{H}}{\text{CH}}\text{-R} \longleftrightarrow \overset{\text{H}}{\text{M}}\text{-}\underset{\text{CHR}}{\text{CH}_2} \longrightarrow \text{M-H} + \text{CH}_2\text{=CH-R} \qquad (29)$$

Olefins is eliminated and H remains bonded to the metal. This reaction affords a facile decomposition path for M = Li, Na, Mg, Be, B and Al, all of which have a vacant metal orbital to interest with the C-H bond, and ultimately, to bond the eliminated H-. A common way of increasing the stability of organometals is to tie up vacant metal orbitals by complexation. Organometallic compounds of the smallest and the most electropositive main-group metals (Li, Be, Mg, Al, etc.) have a structural chemistry and reactivity strongly influenced by their having too few electrons and too many valence orbitals to obey the octet rule.

Another chemical property is basicity of metal oxides. All oxides of alkali metals are strong base. This property is important for the OCM reaction. For example of Li_2O is the strong base, thus it is an electron-pair donner by the definition to Lewis. It donate electron to oxygen, then it becomes as following :

$$Li_2O + 1/2\,O_2 \longrightarrow 2Li^+O^- + O^{-2} \qquad (30)$$

$$Li^+O^- + CH_4 \longrightarrow .CH_3 + LiOH \qquad (31)$$

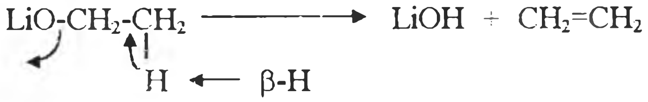
$$^{\cdot}CH_3 + CH_4 \longrightarrow CH_3\text{-}CH_3 + H \qquad (32)$$

$$Li^+O^- + CH_3\text{-}CH_3 \longrightarrow {}^{\cdot}CH_2\text{-}CH_3 + LiOH \qquad (33)$$

or

$$\longrightarrow LiO\text{-}CH_2\text{-}CH_3 + H^- \qquad (34)$$

β-elimination



$$\underset{\substack{\uparrow\\ H\ \leftarrow\ \beta\text{-}H}}{LiO\text{-}CH_2\text{-}CH_2} \longrightarrow LiOH + CH_2{=}CH_2 \qquad (35)$$

3.2 Pressure

Even though the study is run at atmosphere, no pressure cocerned, but partial pressure and space velocity can be determined as pressure on the reactor. This concept comes from the conclusion of the kinetic-molecular of gases.

$$P = (1/3)\, nmu^2/V \qquad (36)$$

P is the pressure, n is the mumber of molecules, m is the mass, u is the velocity of gases and V is the volume of reactor.

$$u = \frac{\text{volumetric flowrate}}{\text{cross section area of reactor}}$$

$$= v_o/a \qquad (37)$$

$$v_o = (\text{space velocity}) \times (\text{volume of catalyst}) \qquad (38)$$

From these conclustion, it can be substituted the pressure by velocity.

In study of OCM in absence of catalyst shows the conversions of methane and oxygen as a function of the total pressure at two inlet methane to oxygen ratios. The residence time was kept constant at 0.5s in order to have a common basis for comparison. At atmospheric pressure, no reaction was observed under similar condition. The conversion increase sharply with increasing total pressure. The effect of pressure on conversions can also be seen by comparing the following figures.

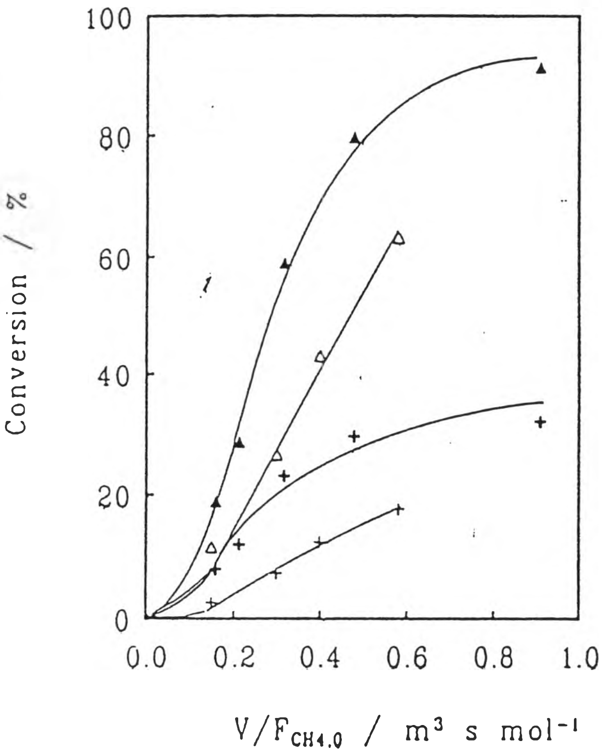


Fig 3.3 Conversion of methane and oxygen vs. space time at 100 kPa

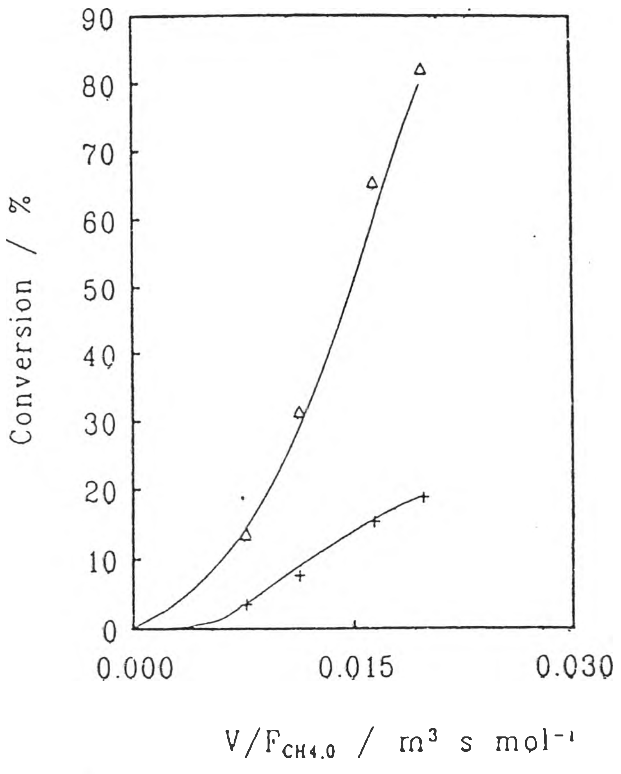


Fig 3.4 Conversion of methane and oxygen vs. space time at 400 kPa

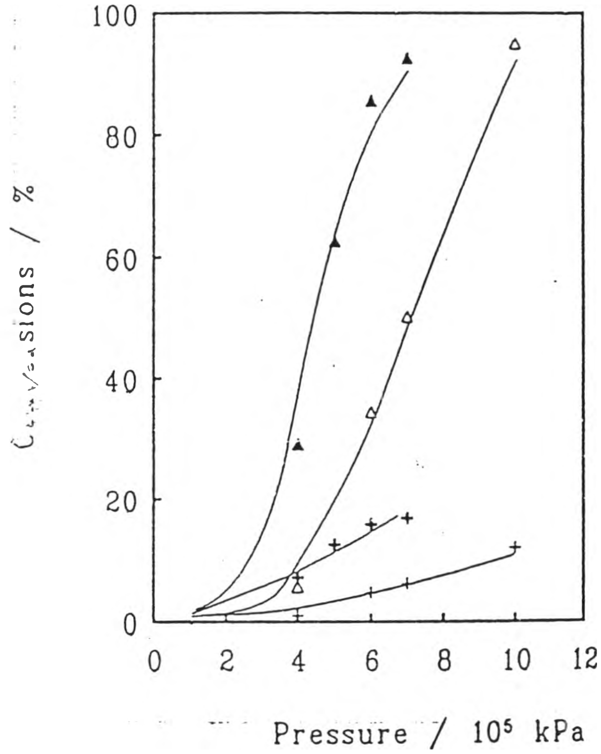


Fig 3.5 Effect of total pressure on the conversion of methane and oxygen

Mechanism of reactions for OCM in the absence of catalyst are depended on Arrhenius parameters were given in following model :

Table 3.1 Mechanism of reactions for OCM in the absence of catalyst

Step No.	Reaction	A	E_a	A/RT^*	r^*
(1)	$CH_4 + O_2 \rightleftharpoons CH_3 + HO_2$	$0.983 \times 10^{+07}$	193.86	− 1.4	$0.694 \times 10^{+00}$
(2)	$CH_4 + H \rightleftharpoons CH_3 + H_2$	$0.234 \times 10^{+09}$	51.17	0.7	$0.314 \times 10^{+02}$
(3)	$CH_4 + O \rightleftharpoons CH_3 + OH$	$0.127 \times 10^{+10}$	33.83	8.4	$0.732 \times 10^{+00}$
(4)	$CH_4 + OH \rightleftharpoons CH_3 + H_2O$	$0.743 \times 10^{+09}$	41.43	3.2	$0.570 \times 10^{+02}$
(5)	$CH_4 + HO_2 \rightleftharpoons CH_3 + H_2O_2$	$0.401 \times 10^{+08}$	99.61	2.4	$0.141 \times 10^{+02}$
(6)	$CH_3 + O_2 \rightleftharpoons CH_3O + O$	$0.308 \times 10^{+09}$	141.00	20.9	$0.111 \times 10^{+00}$
(7)	$CH_3 + O_2 \rightleftharpoons CH_2O + OH$	$0.459 \times 10^{+08}$	103.66	38.4	$0.107 \times 10^{+01}$
(8)	$CH_3 + HO_2 \rightleftharpoons CH_3O + OH$	$0.900 \times 10^{+08}$	0.00	30.7	$0.300 \times 10^{+02}$
(9)	$CH_3 + CH_3 + M \rightleftharpoons C_2H_6 + M$	$0.650 \times 10^{+08}$	0.00	4.8	$0.124 \times 10^{+02}$
(10)	$CH_3O + M \rightleftharpoons CH_2O + H + M$	$0.258 \times 10^{+15}$	115.00	3.3	$0.314 \times 10^{+02}$
(11)	$CH_2O + OH \rightleftharpoons CHO + H_2O$	$0.580 \times 10^{+09}$	5.00	9.1	$0.132 \times 10^{+01}$
(12)	$CH_2O + HO_2 \rightleftharpoons CHO + H_2O_2$	$0.417 \times 10^{+07}$	40.12	8.3	$0.572 \times 10^{+00}$
(13)	$CH_2O + CH_3 \rightleftharpoons CHO + CH_4$	$0.700 \times 10^{+08}$	25.03	5.9	$0.308 \times 10^{+02}$
(14)	$CHO + M \rightleftharpoons CO + H + M$	$0.280 \times 10^{+10}$	64.36	4.8	$0.332 \times 10^{+02}$
(15)	$CHO + O_2 \rightleftharpoons CO + HO_2$	$0.171 \times 10^{+06}$	0.00	9.1	$0.332 \times 10^{+00}$
(16)	$CO + HO_2 \rightleftharpoons CO_2 + OH$	$0.308 \times 10^{+09}$	107.34	36.3	$0.260 \times 10^{+01}$
(17)	$C_2H_6 + H \rightleftharpoons C_2H_5 + H_2$	$0.910 \times 10^{+09}$	51.70	2.3	$0.158 \times 10^{+01}$
(18)	$C_2H_6 + OH \rightleftharpoons C_2H_5 + H_2O$	$0.455 \times 10^{+07}$	17.12	4.8	$0.722 \times 10^{+01}$
(19)	$C_2H_6 + CH_3 \rightleftharpoons C_2H_5 + CH_4$	$0.225 \times 10^{+08}$	64.57	1.6	$0.322 \times 10^{+01}$
(20)	$C_2H_5 + HO_2 \rightleftharpoons CH_3 + CH_2O + OH$	$0.240 \times 10^{+08}$	0.00	33.4	$0.629 \times 10^{+00}$
(21)	$C_2H_5 + M \rightleftharpoons C_2H_4 + H + M$	$0.596 \times 10^{+14}$	167.66	0.6	$0.134 \times 10^{+02}$
(22)	$C_2H_5 + O_2 \rightleftharpoons C_2H_4 + HO_2$	$0.635 \times 10^{+07}$	53.20	4.9	$0.326 \times 10^{+01}$
(23)	$C_2H_4 + O_2 \rightleftharpoons C_2H_3 + HO_2$	$0.281 \times 10^{+07}$	144.55	2.1	$0.569 \times 10^{+00}$
(24)	$C_2H_4 + H \rightleftharpoons C_2H_3 + H_2$	$0.150 \times 10^{+09}$	42.70	4.2	$0.606 \times 10^{+00}$
(25)	$C_2H_4 + OH \rightleftharpoons C_2H_3 + H_2O$	$0.612 \times 10^{+08}$	24.70	6.7	$0.354 \times 10^{+00}$
(26)	$C_2H_4 + CH_3 \rightleftharpoons C_2H_3 + CH_4$	$0.199 \times 10^{+06}$	51.46	3.5	$0.104 \times 10^{+00}$
(27)	$C_2H_4 + OH \rightleftharpoons CH_3 + CH_2O$	$0.688 \times 10^{+07}$	0.00	3.6	$0.628 \times 10^{+00}$
(28)	$C_2H_3 + M \rightleftharpoons C_2H_2 + H + M$	$0.121 \times 10^{+16}$	176.44	− 2.1	$0.121 \times 10^{+00}$
(29)	$C_2H_3 + O_2 \rightleftharpoons C_2H_2 + HO_2$	$0.500 \times 10^{+07}$	0.00	2.2	$0.106 \times 10^{+01}$
(30)	$C_2H_3 + O_2 \rightleftharpoons CH_2O + CHO$	$0.500 \times 10^{+07}$	0.00	44.4	$0.106 \times 10^{+01}$
(31)	$C_2H_5 + CH_3 \rightleftharpoons C_3H_8$	$0.800 \times 10^{+07}$	0.00	5.2	$0.124 \times 10^{+00}$
(32)	$C_3H_8 + H \rightleftharpoons C_3H_7 + H_2$	$0.900 \times 10^{+09}$	32.00	2.0	0.844×10^{-01}
(33)	$C_2H_4 + CH_3 \rightleftharpoons C_3H_7$	$0.300 \times 10^{+06}$	29.00	0.2	$0.194 \times 10^{+01}$
(34)	$C_3H_7 + \rightleftharpoons C_3H_6 + H$	$0.150 \times 10^{+16}$	156.00	0.1	$0.135 \times 10^{+01}$
(35)	$O_2 + H \rightleftharpoons OH + O$	$0.220 \times 10^{+09}$	70.30	19.4	$0.616 \times 10^{+00}$
(36)	$O_2 + H + M \rightleftharpoons HO_2 + M$	$0.140 \times 10^{+06}$	0.00	4.3	$0.452 \times 10^{+02}$
(37)	$HO_2 + HO_2 \rightleftharpoons O_2 + OH + OH$	$0.200 \times 10^{+07}$	0.00	24.9	$0.112 \times 10^{+01}$
(38)	$H_2O_2 + M \rightleftharpoons OH + OH + M$	$0.127 \times 10^{+12}$	199.36	21.2	$0.131 \times 10^{+02}$

* Calculated at the point in the reactor where the temperature is maximum. Conditions are T_{max} = 1,078 K, p_t = 400 kPa, inlet methane-to-oxygen ratio δ = 4.0 and $V/F_{CH_4,0}$ = 0.020 $m^3 \cdot s \cdot mol^{-1}$. The corresponding conversions at the point: X_{CH_4} = 12%, X_{O_2} = 41%. Units: A, s^{-1} or $m^3 \cdot mol^{-1} \cdot s^{-1}$ or $m^6 \cdot mol^{-2} \cdot s^{-1}$; E_a, $kJ \cdot mol^{-1}$; r, $mol \cdot m^{-3} \cdot s^{-1}$.

3.3 Partial pressure and velocity

The partial pressure and velocity of gas effict on adsorption of gas on catalyst and efect on collision of gas in the reactor. The Langmuir adsorption isotherm is of the greatest general application to catalysis because of its simplicity and because it serves as a point of departure for formulating many kinetic expressions for catalyzed reactions. A simplified version of the kinetic approach, which was originally used by Langmuir.

Consider a single pure vapor A at a pressure P_A that adsorbs without dissociation onto a surface. Let the occupied fraction of sites on which adsorption is possible be. The rate of adsorption dn_A/dt is proportional to the rate of molecular collisions with unoccupied sites :

$$dn_A/dt = k(1 - \theta_A)\, P_A \qquad (39)$$

The rate of desorption is proportional to the number of molecules adsorbed.

$$dn_A/dt = k'\theta_A \qquad (40)$$

At equilibrium, the rate of adsorption iquals the rate of desorption, so that

$$\begin{aligned} k(1 - \theta_A)\, P_A &= k'\theta_A \\ &= kP_A/(k'+kP_A) \\ &= K_AP_A/\,(1+K_AP_A) \qquad (41) \end{aligned}$$

Where the adsorption equilibrium constant $K_A = k/k'$ can be expressed in the form $K = A\exp(+\lambda/RT)$ where λ is the heat of adsorption. A large value of K implies strong bonding. The larger the value of K, the greater is the fractional surface coverage at a fixed temperature and a fixed value of P_A, or the higher is the temperature required for a specified fractional surface coverage at fixed P_A. At low value of P_A, the fraction of the sites covered is directly proportional to P_A, but a high value of P_A, the fraction approaches unity asymptotically and becomes independent of pressure.

For the hydrocarbon oxidation study, to develop a simple mathematical model, Mars and van Krevelen assumed that the rate of oxidation of the reactant is proportional to the fraction of active sites in the oxidized state and to the hydrocarbon partial pressure. The rate of reoxidation of the catalyst is taken to be proportional in the fraction of sites on the catalyst in the reduced (or empty) state of $P^n_{O_2}$ Then

$$r = kP_{HC}(1-\theta) = \frac{k^*}{\beta} P^n_{O_2}\theta \qquad (42)$$

where P_{HC} = partial pressure of hydrocarbon

k = reaction rate constant for oxidation of the hydrocarbon

k^* = reaction rate constant for surface reoxidation

β = moles O_2 consumed per mole of hydrocarbon reacted.

θ = fraction of active sites in reduced state

$$= \frac{kP_{HC}}{kP_{HC} + (k^*/\beta)P^n_{O_2}} \qquad (43)$$

Substitution Eq. (42) into (43)

Then $$r = \frac{1}{(\beta/k^*P^n_{O_2}) + (1/kP_{HC})} \qquad (44)$$

For the hydrocarbon oxidation reaction, the data were best fitted by $n = 1$. Equation (44) leads to several conclusions. If the potential rate of oxidation of the hydrocarbon by the the catalyst exceeds that of reoxidation of the catalyst, then

$$kP_{HC} \gg k^*P^n_{O_2}/\beta$$

and Eq. (44) reduces to

$$\gamma = \frac{k^*}{\beta} P^n_{O_2} \qquad (45)$$

This conclusion of partial pressure effects on the reaction rate. Now consider the diffusion effcted by velocity. When the overall rate of reaction is subject to an appreciable influence of mass transfer of the gas phase to the external surface of catalysts, the mass transfer rate can be described by

$$r'_m = k_{gA}a_m(p_{Ab}-p_{As}) \tag{46}$$

Where r'_m is the mass transfer rate of component A under the steady state conditions in flow reactor, the reaction rate become equal to the rate of mass transfer.

$$-r'_A = r'_m \tag{47}$$

The k_{gA} is the function of velocity.

3.4 Temperature and velocity

It is related the velocity, temperature collision and rate of reaction. The collision depends on the velocity as

$$Z_{AB} = n_A n_B \pi \bar{u}_{AB} \sigma^2_{AB} \tag{48}$$

Where Z is the number of collisions, u is the velocity of molecule A and B. is the diameters of A and B.

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \tag{49}$$

$$u_{AB} = \sqrt{\frac{8kT\pi}{\mu_{AB}}} \tag{50}$$

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \tag{51}$$

It can be seen that the equation be shown velocity is a function of temperature. Then it can be written

$$Z_{AB} = (\sigma_{AB})^2 n_A n_B \frac{N^2}{10^6}\sqrt{\frac{8kT\pi}{\mu_{AB}}}.C_A C_B \tag{52}$$

From the Maxwell distribution law of molecular energies the fraction of all bimolecular collisions that involve energies in excess of E(activation energies) or E >> RT is given approximately by -E/RT. Since it can be related the rate of reaction with the collisions.

$$-r_A = -\frac{1}{V}\frac{dn_A}{dt} = kC_AC_B$$

$$= Z_{AB}\frac{10^3}{N}e^{-E/RT} \qquad (53)$$

A similar expression can be found for the bimolecular collision. The rate constant depends on the temperature.

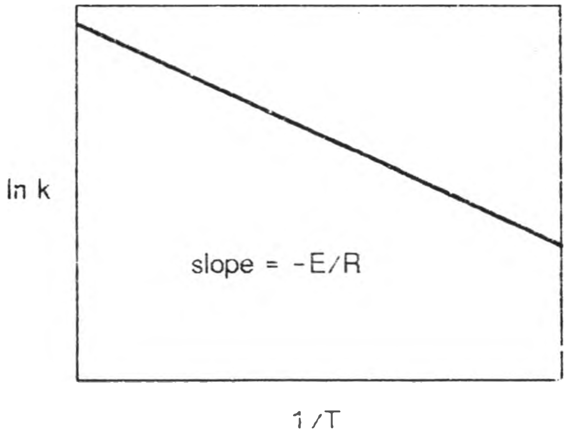
$$k \propto T^m e^{-E/RT} \quad , \quad k = Ae^{-E/RT} \qquad (54)$$

From Arrhenius equation, it was elaborated expressions for improving from various theories such as the collision theory and the transition state theory, then it is assumed the form

$$k = k_oT^m e^{-E/RT} \qquad (55)$$

The value of m range from 0 to 3 or 4. Arrhenius parameters E and A are evaluated from the measurements of rate constants at several different temperatures. There are two methods commonly used. One is to plot equation k = Ae $^{-E/RT}$and calculate the value of E from the slope of the straight line. This is based on the following equation.

$$\ln k = \ln A - E/RT \qquad (56)$$



The second method calculates E from adjacent pairs of k and T by simultaneouly solving two sets of the Arrhenius equation.

$$k_1 = Ae^{-E/RT_1} \qquad k_2 = Ae^{-E/RT_2} \tag{57}$$

From these equations,

$$E = \frac{R\ln(k_2/k_1)}{1/T_1 - 1/T_2} \tag{58}$$