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RESEARCH ARTICLE

KINETICS AND MECHANISM OF DIRECT CONVERSION OF METHANE INTO METHANOL REACTION ON MOO₃ (010) CATALYST: A SIMULATION STUDY

^{1,2}Mehrnoosh Dashti

¹United Nations University, Institute for the Advance Study of Sustainability, Tokyo, Japan

²Department of Mechanical Engineering, Islamic Azad University, Central Tehran Branch, Tehran, Iran

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ABSTRACT

In this investigation, kinetics and mechanism of heterogeneous direct catalytic conversion of methane into methanol over MoO₃ (010) surface was studied using computer simulation. The rate of CH₃OH formation (TOF) was determined under different reaction conditions ($480\text{ }^{\circ}\text{C} < T < 590\text{ }^{\circ}\text{C}$, $P_{\text{CH}_4} = 40 - 80\text{ Torr}$, $P_{\text{O}_2} = 80 - 150\text{ Torr}$ and $P_{\text{H}_2\text{O}} = 100 - 200\text{ Torr}$). The presence of H₂O was found essential for selective CH₃OH production. According to this analysis, the TOF was increased with increasing $P_{\text{O}_2}/P_{\text{CH}_4}$ and reaches a maximum value at 9.2 ratios. The order of reaction with respect to P_{CH_4} , P_{O_2} and $P_{\text{H}_2\text{O}}$ at $T = 540\text{ }^{\circ}\text{C}$ were found $l = 0.7$, $m = 0.1$ and $n = 0.8$ respectively. The activation energy of the reaction was obtained $38 \pm 5\text{ kcal/mole}$. Selectivity toward CH₃OH formation was determined 77% in the above temperature range. However, the selectivity for HCHO and other products (C₂H₆ and CO₂) was obtained 22% and 1%, respectively, in this range.

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INTRODUCTION

In the past decades, fossil fuels have played a major role in production of energy for industry and transportation in the world. The energy consumption of these fuels resulted in increasing enormous amount of pollutants and green house gasses in our surrounding. To overcome this environmental pollutions and to adequate the shortage in the proved reserves of fossil fuels, it is necessary to use the new and cleaner energy resources as alternative ones. Conversion of methane into methanol as a transportable liquid fuel has attracted many attentions in both scientific and technological community. This challenge stems from both environmental and economical views. In this regard, Olah *et al.* (Olah *et al.*, 2006) have studied the economy of methanol as compare to oil and gas. From scientific viewpoints, the kinetics and mechanism of direct conversion of methane into methanol reaction is not clearly understood. Therefore, many research groups around the world attempt to elucidate detail understanding of this important process. Currently, methanol is produced from natural gas (mainly methane) through reforming reaction in two steps via syngas (CO+H₂) as an intermediate in industrial scale (Lunsford, 2000). Concerning the first step, Mariana and Schmal (Mariana and Schmal, 2003) have studied the support effects on syngas production through partial oxidation and CO₂ reforming reaction of methane using Pt catalyst.

Today, research is underway to oxidize methane directly into methanol in high yield by using a single exothermic reaction step. There are three different methods involving in the oxidation of methane into methanol: gas-phase non-catalytic homogeneous oxidation (Han *et al.*, 1995; Verma, 2002), liquid phase homogeneous catalytic oxidation of methane (Mylvaganam *et al.*, 2000) and heterogeneous catalytic oxidation (Raja and Ratnasamy, 1997). In these studies, the yield of methanol production for the direct selective oxidation of methane is low and formaldehyde is a major by-product of the reaction. A review on these three methods is reported in (Zhang *et al.*, 2003). Thus, direct heterogeneous catalytic conversion of methane into methanol is interesting and promising as compared to the other methods. In the present study, the direct catalytic conversion of methane into methanol reaction will be discussed under different conditions. Liu *et al.* (Liu *et al.*, 1984) have used N₂O oxidant in the conversion of methane into methanol reaction over MoO₃/SiO₂ catalyst. Their report indicates that during the reaction, the generated methyl radical reacts with the catalyst producing methoxide ions, and subsequently these ions could react with the H₂O to form methanol. Moreover, Khan and Somorjai (Khan and Somorjai, 1985) have studied the partial oxidation of methane with N₂O and H₂O on silica-supported molybdena who obtained the kinetics parameters of the reaction. Gesser *et al.* (Gesser *et al.*, 1985) have also investigated the effect of reaction parameters (temperature, pressure, O₂ concentration and residence time of reactants) on methanol yield in the direct

*Corresponding author: Mehrnoosh Dashti

Department of Mechanical Engineering, Islamic Azad University,
Central Tehran Branch, Tehran, Iran.

conversion of methane into methanol. A higher CH₃OH yield was reported in high pressures, high temperatures and low O₂ concentrations.

Hall *et al.* (Hall *et al.*, 1995) have presented an excellent review on history (since 1905) and catalysts performance in the partial oxidation of methane into methanol and formaldehyde reactions on the basis of the oxygen space-time yield (STY) values. Concerning the catalyst performance, Wang and Otsuka (Wang and Otsuka, 1996) have studied the effect of structure of active sites in the Fe-containing catalysts during the oxidation of methane into methanol reaction by using by H₂-O₂ gas mixture. A selectivity of 23% and 45% for methanol and formaldehyde was obtained over the FePO₄ model catalyst in the presence of H₂, respectively. In the other work, Beata (Beata, 2004) has studied the partial oxidation of methane to formaldehyde and methanol using molecular oxygen over Fe-ZSM-5 catalyst (Si/Fe = 45) with high selectivity of methanol ~74%.

Some research groups have also examined other catalysts. Aoki *et al.* (Aoki *et al.*, 1998) have investigated direct conversion of methane into methanol over MoO₃/SiO₂ catalyst at 873K in an excess amount of water vapor. They have measured a higher methanol yield due to depression of successive oxidation of methanol and formaldehyde into carbon oxides on the surface of the catalyst due to silicomolybdic acid (SMA) formation. In addition, the selective oxidation of methane in a gas mixture of CH₄-O₂-NO₂ over MoO₃ catalyst was studied by Takemoto *et al.* (Takemoto *et al.*, 2001) who found the enhancement of methane activation with O₂ and N₂O in the presence of the catalyst.

Since direct conversion of methane into methanol has an economic advantage as compared to indirect reaction, fundamental studies of the process are necessary to achieve this goal. According to analysis of different studies, it is observed that the MoO₃ surface is a selective catalyst for the direct conversion of methane into methanol reaction (Aoki *et al.*, 1998; Takemoto *et al.*, 2001; Moshfegh and Dashti, 2004). The kinetics and mechanism of this reaction over MoO₃(010) was studied from photocatalytic viewpoint by Moshfegh and Dashti (Moshfegh and Dashti, 2004). To investigation the reaction under thermal condition, this work has studied the kinetics and mechanism of direct catalytic conversion of methane into methanol over MoO₃ (010) surface in the presence of water vapor molecule using computer simulation method.

Reaction Model

MoO₃ (010) Catalyst

Molybdenum trioxide, MoO₃, has been known as a catalyst for many partial oxidation reactions. Catalytic activity of MoO₃ depends on chemical composition and special situation of oxygen atoms in its structure. The MoO₃ has an orthorhombic layer structure with the following lattice parameters: $a = 3.963 \text{ \AA}$, $b = 13.855 \text{ \AA}$ and $c = 3.696 \text{ \AA}$. Each layer consists of bi-layer planes of MoO₆ octahedral that are parallel to (010) crystal face.

This surface is the most exposed face of the catalyst that can participate in surface chemical reactions. Yin *et al.* (Yin *et al.*, 2001) reported that the three different types of surface oxygen centers exist at the (010) cleavage face. These are the terminal oxygen, O (1), the asymmetric bridging oxygen, O (2), and the symmetric bridging oxygen, O (3). The O (1) is coordinated to one molybdenum atom directly and O (2) and O(3) are located between two molybdenum atoms.

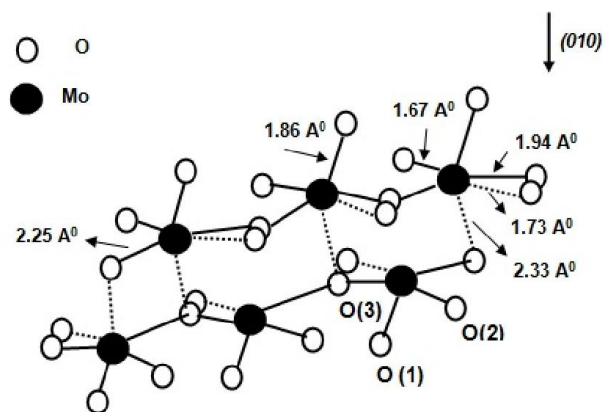


Figure 1. Crystal structure of orthorhombic MoO₃ with (010) direction, different surface oxygen and their corresponding bond length is also shown.

Figure 1 illustrates these three different types of oxygen with their corresponding bond length. It is well established that the O(1) is an active site for CH₄ adsorption (Chen *et al.*, 2000). Following CH₄ adsorption on the catalyst surface, the first C-H bond is broken and the produced methyl radicals are adsorbed at the O(1) sites. As a result, a vacancy (defect) is generated on the surface according to the following steps (Haber and Lalik, 1997):



where V represents oxygen vacancy. Equilibrium between oxygen atoms in the lattice, surface and gas phase is a dynamic one. A continuous process of evaluation of oxygen from the surface and its re-adsorption by the surface must take place, as shown in Figure 2.

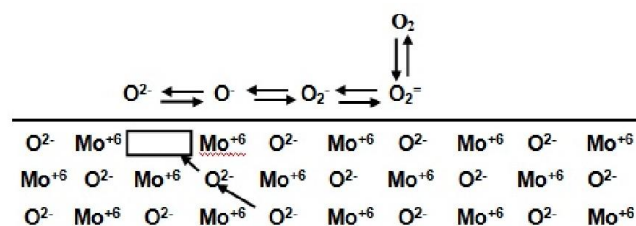
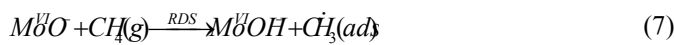
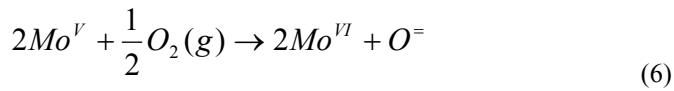
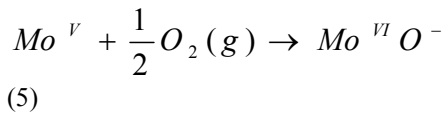
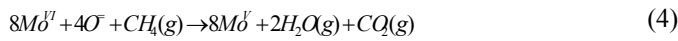


Figure 2. Equilibrium between lattice and surface oxygen and gas phase oxygen

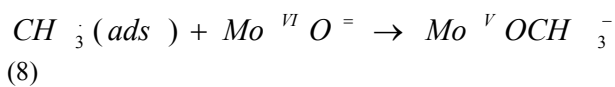
The surface always populated by transient oxygen species $O_2^{\cdot-}(\text{surf})$, $O_2^-(\text{surf})$ and $O_2^{\cdot-}(\text{surf})$, which are strongly electrophilic species and are responsible for the total oxidation of hydrocarbon molecules (Haber and Erwin Lalik, 1997).

Reaction Mechanism

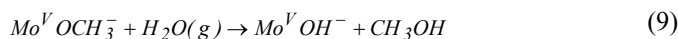
For the direct catalytic conversion of methane into methanol, this study proposed three elementary steps as follows: 1) hydrogen abstraction from methane resulting in formation of methyl radical ($\dot{C}H_3$) formation, 2) insertion of oxygen to form methoxide ion (CH_3O^-), and 3) hydrolysis of the methoxide into methanol (Aoki *et al.*, 1998). In general, O^- ion surface sites in early transition metal oxides such as TiO_2 , V_2O_5 , MoO_3 and WO_3 are able to abstract H from methane (Kaliaguine *et al.*, 1978). In this context, formation of surface active site and dehydrogenation of methane is proposed by the following reactions sequence:



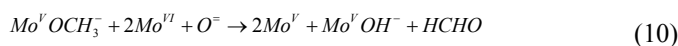
It is well documented (Chen, 2000; Ward *et al.*, 1987) the rate determining step (RDS) for conversion reaction of methane into methanol is the abstraction of first hydrogen atom from methane as specified in reaction (7) shown above. The methyl radical formed ($\dot{C}H_3$) on the surface is highly active and therefore it reacts with $Mo^{VI}O^-$ surface site of MoO_3 (010) catalyst. As a result, the intermediate methoxide ion will produce according to the following reaction:



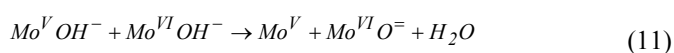
Then, the facile reaction of molybdenum methoxide ($Mo^VOCH_3^-$) with water vapor forms methanol (Liu *et al.*, 1984):



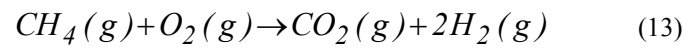
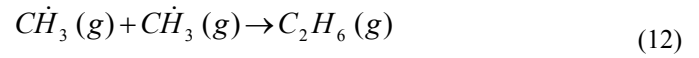
In a parallel reaction, the molybdenum methoxide ion may also react with surface sites to produce formaldehyde by the following mechanism:



To refresh the surface sites and complete the catalytic reaction cycle, the following reaction is also suggested:



In addition to formaldehyde, the formation of other by-products namely C_2H_6 and CO_2 are also considered in this model. These products can be produced through the following reactions:



Therefore, according to the above mechanism, the $Mo^{VI}O^-$ active surface site plays an important role in the direct conversion of methane into methanol reaction over $MoO_3(010)$ surface.

Simulation procedure

Assumptions

The model is based on dynamic flow system that the reaction occurs at constant atmospheric pressure. The (010) face of the MoO_3 catalyst is considered as a two-dimensional 100×100 uniform $Mo^{VI}O^-$ surface sites with periodic boundary condition. In this reaction, the model has considered CH_4 , O_2 and H_2O as reactants and CH_3OH , $HCHO$, C_2H_6 , CO_2 and CH_3OH as products. The reaction temperature is varied from $480^\circ C$ to $590^\circ C$ K at constant total pressure of $P=760$ Torr. Liu *et al.* (Liu *et al.*, 1984) reported that the water vapor plays an important role in selective formation of methanol by nitrous oxide over MoO_3-SiO_2 catalyst, so, water vapor is essential for the selective formation of methanol. Assumptions of the model are as following:

(a) The principle of conservation of sites is considered at the catalyst surface as defined below:

$$\theta_{CH_4} + \theta_{O_2} + \theta_{H_2O} + \theta_V = 1 \quad (14)$$

where θ_{CH_4} , θ_{O_2} and θ_{H_2O} represents the fraction of surface coverage of methane, oxygen and water molecules, respectively and θ_V is fraction of surface vacant sites.

- All reactions proceed in forward direction.
- The occurrence probability of all the reactions considered one except the RDS reaction.
- Surface reaction mechanism is obeyed by Eley-Rideal scheme.
- Refreshment of surface sites is implemented by considering reaction (11).
- To obtain the surface density of any adsorbed species, the model has used canonical continuous partition function for the both gas and adsorbed phases. By assuming the identical chemical potential of both phases ($\mu_g = \mu_a$), the surface density of adsorbed CH_4 , O_2 or H_2O molecule ($\text{molecules}/\text{cm}^2$) is computed using the following expression:

$$n = \frac{P}{kT} \frac{h}{(2\pi mkT)^{1/2}} \exp[(E_b - E_a)/RT] \quad (15)$$

where P is partial pressure of incident gas in Torr, E_b is bonding energy of any adsorbed molecule on surface atom in unit of kcal/mole, E_a is adsorption activation energy for CH_4 , O_2 or H_2O molecules in unit of kcal/mole, T is absolute temperature in Kelvin and h, m, k, and R are usual definition.

g) It's convenient to generate a normalized adsorption probability that is defined between zero and one. This quantity is the ratio of surface density of CH_4 , O_2 or H_2O or generally n_i (where i represents any of the reactants) to sum

of all reactant surface species $\left(\frac{n_i}{\sum_j n_j}\right)$ is considered as

probability adsorption for any incident molecule in initial stage of the reaction.

h) The resident time of all products is negligible. In addition, the desorbed product molecules are not reabsorbed on the surface of the catalyst. In the other word, the deactivation of the catalyst surface is ignored.

Considering ensemble at microscopic reactions in this system, Metropolis Monte Carlo method (Metropolis *et al.*, 1953) was utilized to monitor the movement of species at the catalyst surface until obtaining equilibrium condition. At each surface site, there is a different probability for reaction to occur but for simplicity the model has considered equal probability for all reactions except RDS reaction.

Algorithm

As mentioned above, the MoO_3 surface catalyst is considered as a two-dimensional 100×100 uniform surface sites. Therefore, in every simulated time step, the number of incident reactant molecules (CH_4 , O_2 , H_2O) is 10000. So, on average there is one incident molecule per site. In addition, it has allowed that the system to reach stationary state in every time step. To simulate the reaction, first, a site and one incident specie are selected randomly. Then, by considering adsorption probability of the reactant molecules (discussed in Assumptions section), surface specie is identified.

Then, adsorbed specie takes place in the reactions according to the proposed mechanism described in the Reaction Mechanism section. Finally, the numbers of product molecules formed are counted in each reaction step. The computed number is converted to rate of desired product formation in terms of Turn Over Frequency (TOF). The TOF value defines as number of CH_3OH molecule produced per surface site per second. For evaluating the effect of various parameters on reaction kinetics and the rate of methanol formation, TOF value for CH_3OH formation is computed under different conditions. In addition, it has also considered other reaction product molecules namely

C_2H_6 and CO_2 in the overall reaction.

It is to note that formation of these parallel reaction resulted in reduction of CH_3OH production.

RESULTS AND DISCUSSION

Effect of Pressure

In order to study the effect of reactants partial pressure on the rate of CH_3OH formation (TOF), it has investigated the influence of P_{O_2}/P_{CH_4} on the methanol production rate at constant temperature ($T = 540^\circ C$) and $P_{H_2O} = 200 Torr$. Figure 3 shows the variation of methanol formation rate in term of TOF as a function of O_2 to CH_4 partial pressure ratio.

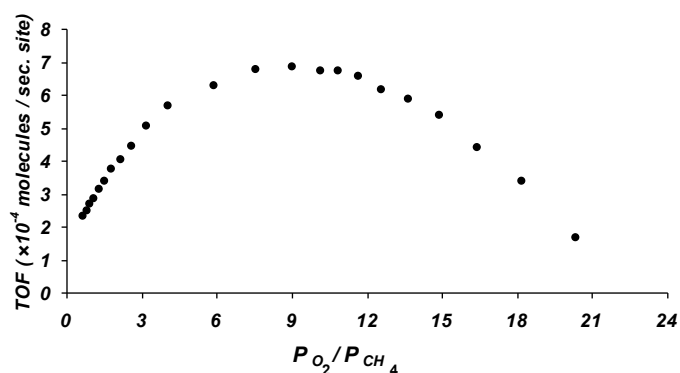


Figure 3. The variation of CH_3OH formation rate (TOF) with oxygen/methane partial pressure ratios ($P_{H_2O} = 200 Torr$, $T = 540^\circ C$).

It is obvious that the rate of methanol formation increased by increasing P_{O_2}/P_{CH_4} ratio. It is believed when the partial pressure of methane increases, the methyl radical ($\dot{C}H_3$) active species is produced extensively on the catalyst surface. This is consistent with the proposed model (reaction (7)).

The generated $\dot{C}H_3$ is reacted with surface oxygen resulting in $MoO^V CH_3^-$ formation (reaction (8)). Consequently, the rate of methanol formation is increased under these conditions. This behavior continues rising and reaches a maximum value of 6.9×10^{-4} (molecules/sec.site) at $P_{O_2}/P_{CH_4} = 9.2$. Then, the TOF is gradually declined with increasing the ratio. The reason for the reduction in the rate of methanol formation is believed due to HCHO formation via parallel reaction (10) since this reaction favors at higher O_2 partial pressures. Moreover, other carbonated products such as C_2H_6 and CO_2 may also produce as were specified in reactions (12) and (13).

Kinetics Order

In general, the rate of the reaction (r_r) is defined as following equation:

$$r_r = k_r P_{CH_4}^l P_{O_2}^m P_{H_2O}^n \quad (16)$$

k_r is reaction rate constant is defined by $k_r = A \exp(-E_a/RT)$ where A is the temperature independent pre-exponential factor, E_a is activation energy of overall reaction and l, m and n are reaction kinetic orders with respect to CH_4 , O_2 and H_2O partial pressure, respectively. In order to determine the orders of reaction, the model has utilized equation (16) by keeping reaction temperature constant ($T=540^\circ\text{C}$) by determining the rate of CH_3OH formation. To obtain reaction order with respect to CH_4 (l), the partial pressure of CH_4 was varied between 40 and 80 Torr at constant oxygen and water partial pressure ($P_{\text{O}_2} = 100\text{ Torr}$, $P_{\text{H}_2\text{O}} = 260\text{ Torr}$) (Liu *et al.*, 1984). Figure 4 shows the variation of TOF values versus methane partial pressure in log-log plot (equation (16)). In this plot, the slope represents the corresponding reaction order (l). According to this plot, it has found that the rate of CH_3OH formation with respect to CH_4 is $l=0.7$.

Similarly, Figure 5 depicts the variation of TOF as a function of P_{O_2} in logarithmic form. Variation of the partial pressure of O_2 over the range of 80 to 150 Torr at constant methane and water partial pressure ($P_{\text{O}_2} = 75\text{ Torr}$, $P_{\text{H}_2\text{O}} = 266\text{ Torr}$) results in $m=0.14$ for the order of reaction with respect to O_2 partial pressure. For determination of reaction order with respect to H_2O , the CH_4 and O_2 partial pressure were held in 75 and 280 Torr, respectively and $P_{\text{H}_2\text{O}}$ was varied between 100 and 200 Torr [9]. Figure 6 presents H_2O partial pressure versus TOF. It has obtained the order of reaction with respect to H_2O partial pressure (n) is 0.8.

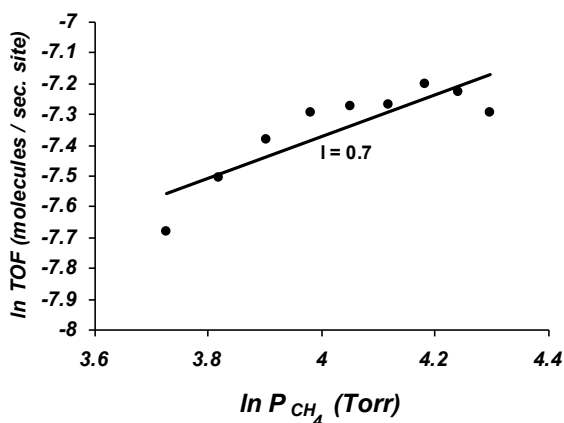


Figure 4, logarithmic plot of TOF as a function of CH_4 partial pressure ($T=540^\circ\text{C}$, $40 < P_{\text{CH}_4} < 80\text{ Torr}$, $P_{\text{O}_2} = 100\text{ Torr}$ and $P_{\text{H}_2\text{O}} = 260\text{ Torr}$)

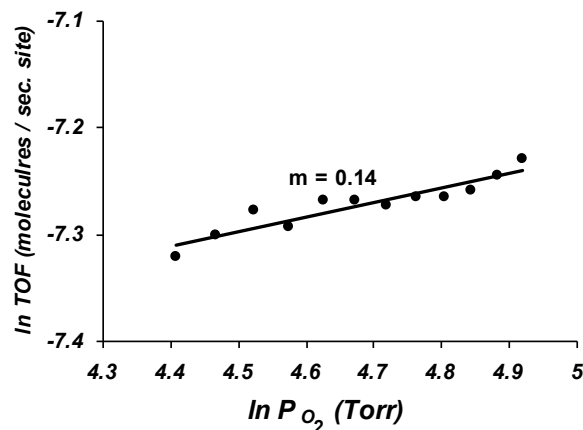


Figure 5. Logarithmic plot of TOF as a function of O_2 partial pressure ($T=540^\circ\text{C}$, $80 < P_{\text{O}_2} < 150\text{ Torr}$, $P_{\text{CH}_4} = 75\text{ Torr}$ and $P_{\text{H}_2\text{O}} = 266\text{ Torr}$)

Therefore, the rate of CH_3OH formation with respect to CH_4 , O_2 and H_2O partial pressure were approximately obtained first, zero and first order, respectively.

A similar result was also obtained by Khan and Somorjai (Khan and Somorjai, 1985) in the oxidation reaction of CH_4 with N_2O over $\text{MoO}_3\text{-SiO}_2$ catalyst in the presence of water vapor in the reactant gas. They have obtained $l=0.8$, $m=0.2$ and $n=1.1$ for reaction order of reactants. The positive values indicates that the increase of TOF resulting the rise in CH_4 and H_2O partial pressures and the zero order shows the independency of the rate on O_2 partial pressure.

It is worth noting that it has also investigated the order of the reaction under photo irradiation of MoO_3 (010) surface at atmospheric conditions. The following values were obtained $l=0.30$ and $m=1.03$ as reported (Moshfegh and Dashti, 2004).

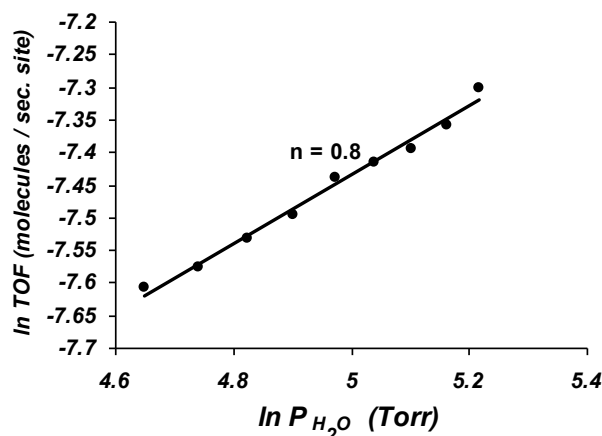


Figure 6. Logarithmic plot of TOF as a function of H_2O partial pressure ($T=540^\circ\text{C}$, $100 < P_{\text{H}_2\text{O}} < 200\text{ Torr}$, $P_{\text{CH}_4} = 75\text{ Torr}$ and $P_{\text{O}_2} = 280\text{ Torr}$)

E_a Determination

In order to study the effect of reaction temperature on the rate of methanol formation, this study has used the Arrhenius equation defined as:

$$r_r = C \exp(-E_a/RT) \quad (17)$$

where C is equal to $A P_{CH_4}^l P_{O_2}^m P_{H_2O}^n$. The coefficient C is considered a typical constant because the partial pressures are constant. Figure 7 illustrates the experimental and simulated Arrhenius plot for the reaction in different temperatures. The activation energy of the total reaction (activation energy of methanol formation) is obtained by variation of temperature over the range of 480 to 590 °C.

$$S_i (\%) = \frac{R_i}{\sum_j R_{Carbon\ products}} \times 100 \quad (18)$$

where R_i is the rate of formation of a certain product (i.e. CH_3OH) and \sum_j represents sum of all rates for all the reaction products containing carbon. The selectivity for both CH_3OH and $CHOH$ is computed under the reaction conditions. The highest selectivity toward CH_3OH formation was 76% at temperature of 843 K.

Methane conversion was also calculated in this reaction by using the following equation:

$$CH_4\text{ conversion (mol\%)} = \frac{\text{Total carbon of products}}{\text{Total carbon of products} + CH_4(\text{Unreacted})} \times 100 \quad (19)$$

Table 1. The rate of methanol and formaldehyde formation with their corresponding selectivity and CH_4 conversion in different reaction temperatures

| Temperature (°C) | TOF × 10 ⁻⁴ (molecules / sec. site) | | Selectivity (%) | | Conversion (%) |
|------------------|--|------|--------------------|-------|-----------------|
| | CH ₃ OH | CHOH | CH ₃ OH | CHOH | CH ₄ |
| 480 | 2.35 | 0.68 | 77.47 | 22.53 | 6.02 |
| 490 | 2.93 | 0.83 | 77.87 | 22.13 | 6.25 |
| 500 | 3.60 | 1.01 | 78.09 | 21.91 | 6.37 |
| 510 | 4.34 | 1.26 | 77.47 | 22.53 | 6.48 |
| 520 | 5.24 | 1.54 | 77.27 | 22.73 | 6.62 |
| 530 | 6.24 | 1.86 | 77.03 | 22.97 | 6.71 |
| 540 | 7.54 | 2.28 | 76.75 | 23.25 | 6.95 |
| 550 | 9.35 | 2.83 | 76.75 | 23.25 | 7.39 |
| 560 | 10.84 | 3.39 | 76.21 | 23.78 | 7.40 |
| 570 | 12.99 | 4.01 | 76.41 | 23.59 | 7.70 |
| 580 | 15.26 | 4.72 | 76.40 | 23.60 | 7.88 |
| 590 | 18.04 | 5.59 | 76.34 | 23.66 | 8.11 |

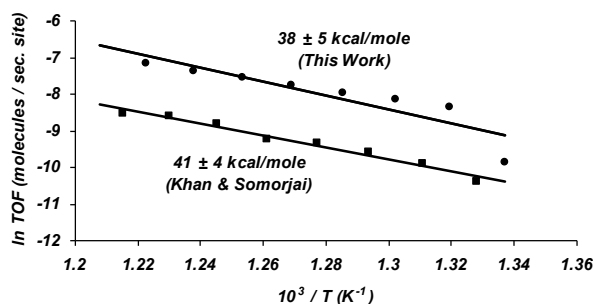


Figure 7. The Arrhenius plot for direct catalytic conversion of methane into methanol reaction
($P_{CH_4} = 56 \text{ Torr}, P_{O_2} = 504 \text{ Torr}, P_{H_2O} = 200 \text{ Torr}, 480 < T < 590^\circ C$)

According to the data analysis, activation energy of 38 ± 5 kcal/mole is obtained under the reaction conditions. This finding is consistent with the experimental result measured by Khan and Somorjai (Khan and Somorjai, 1985).

Selectivity and Methane Conversion

According to definition, the selectivity of a desired product in a catalyzed reaction defined by the following expression:

where products refer to CH_3OH , $CHOH$, C_2H_6 and CO_2 .

The selectivity of main reaction products (CH_3OH and $CHOH$) as well as methane conversion in temperature range from 763 to 873 K are listed in Table 1. It is important to note that the trace amount of C_2H_6 and CO_2 were also noticed under the assumed reaction conditions.

Conclusions

Kinetics and mechanism of heterogeneous direct catalytic conversion of methane into methanol over $MoO_3(010)$ surface was investigated in different reaction conditions ($480^\circ C < T < 580^\circ C, P_{tot} = 1 \text{ atm}$) using computer simulation method. Based on the proposed mechanism, $Mo^{VI}OH$ resulted from the RDS reaction step considered as an active site and the presence of H_2O vapor is essential in the CH_3OH formation.

The rate of CH_3OH formation in terms of TOF was increased with P_{O_2}/P_{CH_4} ratio and reaches a maximum ($6.9 \times 10^{-4} \text{ (molecules/sec.site)}$) at 9.2 ratios. According to the kinetics data analysis, the reaction order with respect to CH_4 , O_2 and H_2O at $T = 540^\circ C$ (813 K) were $l = 0.7, m = 0.1$ and $m = 0.8$, respectively.

The activation energy for the reaction from the Arrhenius plot was obtained $E_a = 38 \pm 5 \text{ kcal/mole}$. The selectivity toward CH_3OH and CHOH formation were obtained about 77% and 22% at temperature of 480°C (753K) and 590°C (863K), respectively.

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REFERENCES

- Aoki K., Ohmae M., Nanba T., Takeishi K., Azuma N., Ueno A., Ohfuné H., Hayashi H., and Udagawa Y. 1998. *Catalysis Today*, 45, 29.
- Beata M., 2004. *Applied Catalysis A: General*, 277, 147.
- Chen M., Friend C. M. and Kaxiras E. 2000. *Journal of Chemical Physics*, 112, 9617.
- Gesser H. D. and Hunter N. R. 1985. *Chemical Reviews*, 85, 235.
- Haber J. and Lalik E. 1997. *Catalysis Today*, 33, 119.
- Hall T. J., Hargreaves J. S. J. and Taylor G. J. 1995. *Fuel Processing Technology*, 42, 151.
- Han L.B. Tsubota S., Kobayashi T. and Uaruta M. 1995. *Journal of Chemical Society, Chemical Communication*, 93.
- Kaliaguine S. L., Shelimov B. N. and Kazansky V. B. 1978. *Journal of Catalysis*, 55, 384.
- Khan M. M. and Somorjai G. A. 1985. *Journal of Catalysis*, 91, 263.
- Liu H. F., Liu R. S., Liew K. Y., Johnson R. E. and Lunsford J. H. 1984. *Journal of American Chemical Society*, 106, 4117.
- Lunsford J. H. 2000. *Catalysis Today*, 63, 165.
- Mariana M. V. M. Souza and Schmal M., 2003. *Catalysis Letters* 91, 11.
- Metropolis N., Rosenbluth, A. W., Rosenbluth M. N., Teller, A. H. and Teller E. 1953. *Journal of Chemical Physics*, 21, 1087.
- Moshfegh A. Z. and Dashti M. 2004. *Surface Review and Letters*, 11, 33.
- Moshfegh A. Z. and Dashti M. 2004. Proceedings of the 13th International Congress on Catalysis, 11-16 July, Paris, France, P2-067.
- Mylvaganam K., Bacskay G. B. and Hush N. S. 2000. *Journal of American Chemical Society*, 122, 2041.
- Olah G.A., Goepfert A., Surya Prakash, G.K., Beyond Oil and Gas: The Methanol Economy, Wiley-VCH, Weinheim, 2006.
- Raja R. and Ratnasamy P. 1997. *Applied Catalysis A: General* 158, L7.
- Takemoto T., Tabata K., Teng Y., Dai L. X. and Suzuki E. 2001. *Catalysis Today* 71, 47.
- Verma S. S. 2002. *Energy Conversion and Management* 43 1999.
- Wang Y. and Otsuka K. 1996. *Journal of Molecular Catalysis A: Chemical*, 111, 341.
- Ward M. D., Brazdil J. F., Mehandru S. P. and Anderson A. B. 1987. *Journal of Physical Chemistry*, 91, 6515.
- Yin X., Han H. and Miyamoto A. 2001. *Journal of Molecular Modeling*, 7, 207.
- Zhang Q., He D. and Zhu Q. 2003. *Journal of Natural Gas Chemistry* 12, 81.
