The Partial Oxidation of Methane by Nitrous Oxide over Silica-Supported 12-Molybdophosphoric Acid

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실리카 담지 12-몰리브도인산 촉매상에서의 아산화질소에 의한 메탄의 부분산화반응

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Abstract: The partial oxidation of methane with nitrous oxide on silica-supported metal-oxygen cluster compounds, known as heteropoly acids, has been studied. The effects of several variables such as reaction temperature, partial pressure of reactants, residence time, loading of the catalysts, and pretreatment temperature, on the conversion and product distribution were observed. The kinetics also has been studied. The conversion and yield of formaldehyde show maximum values at a loading of 20 wt%. The apparent reaction order of methane conversion is ca. 1.0 with respect to CH_4 and ca. 0.4 with respect to N_2O. In addition, the apparent activation energy is 30.78 kcal/mole. The addition of small quantities of tetrachloromethane to the reactant stream enhanced the activity of the silica-supported HPMo in the oxidation of methane, whereas water introduced to the reactant decreased the activity of catalyst under present study.

요   약 : 실리카에 담지된 헤테로폴리산 촉매에서 아산화질소에 의한 메탄의 부분산화반응을 연구하였다. 여러 가지의 반응조건, 즉 반응온도, 반응물의 분압, 접촉시간, 촉매의 담지량 및 전처리온도 등이 전환율이나 생성물의 선택도 및 속도론에 미치는 영향이 연구되었다. 20wt%로 담지된 촉매가 전환율과 포름알데히드의 수율에 있어서 가장 높은 값을 보여 주었다. 메탄의 전환반응에서의 속도식을 구한 결과, 메탄에 대해서는 1차식을 보여 주었고, 아산화질소에 대한 반응차수는 약 0.4였다. 또한 전체반응의 겉보기 활성화에너지는 30.78 kcal/mole 이었다. 반응물 중에 첨가된 소량의 사염화탄소는 메탄의 산화반응에서 실리카 담지 HPMo 촉매의 활성을 증가시키는 반면에, 반응물에 첨가된 물은 오히려 활성을 감소시키는 것을 볼 수 있었다.

1. Introduction

Natural gas, the predominant component of which is methane, is found in plentiful supply in many areas of the world[1]. Methane has excellent combustion properties and thus readily reacts to form carbon monoxide and carbon dioxide and it can also react to form ethylene, ethane, methanol

and formaldehyde. However its application as either a precursor to gasoline or industrial chemicals has been limited. Thus the important thing is a shift in selectivity from carbon oxides to useful products.

Ever since Blair and Wheeler[2] first demonstrated that methane can be oxidized in the presence of catalysts, there have been a number of reports dealing with the partial oxidation of methane covering a variety of techniques and catalysts[3~10]. Lunsford and co-workers[11] have shown that methane can be partially oxidized on Mo/SiO_2 with N_2O. The O^- ions are capable of hydrogen atom abstraction from CH_4, the resulting methyl radicals rapidly react with the surface to form methoxide complexes. The methoxide may decompose to form HCHO or react with water to form CH_3OH. Somorjai and co-workers[12-13] have reported on the kinetics of the partial oxidation of methane with nitrous oxide over Mo/SiO_2 and V/SiO_2. At low temperatures CH_3OH and HCHO are formed from the same intermediate by parallel processes, whereas at high temperatures HCHO is formed from CH_3OH.

The heteropolyoxometalates possesses a Keggin structure and exists as an ionic solid under ambient conditions[3-7]. The anion is a packed high-molecular-weight cage with the tetrahedral PO_4 group at its center and twelve octahedral with molybdenum at their centers and oxygen at their vertices enveloping the central tetrahedron and sharing oxygen atoms with the latter and each other. The structure, surface and heterogeneous catalytic properties of heteropoly acid have been reported by many researchers[14-20].

A number of other workers[21] have shown that certain heteropolyoxometalates are effective in oxidation processes of organic compounds, although less work has been reported on the oxidation of methane.

In the present work the effects of a number of variables such as reaction temperature, contact time and reactant composition on the partial oxidation of methane on the silica-supported 12-molybdophosphoric acid are observed and the effect of water and tetrachloromethane(TCM) added to

reactant are also examined. The studies on the oxidation of methane are extended to study additional heteropolyoxometalates, in order to optimize the process for the production of formaldehyde and C_{2+} hydrocarbons.

2. Experimental

The catalysts, $HPMo/SiO_2$ and HPW/SiO_2, were prepared by impregnation of the support(Grace-Davison grade 400, 740 m^2g^{-1}) with an aqueous solution of 12-molybdophosphoric acid and 12-tungstophosphoric acid. Ten grams of support was impregnated with 20 ml of solution of the acid. The solutions were then evaporated to dryness at 80℃ and then calcined at 350℃ for 2 hours. The surface area of catalysts was measured by BET method. The gases used in this study, methane (99.0%), nitrous oxide(99.0%), and helium(99.9%) were used as received. The conversion of methane was studied with continuous flow reactor system that has a fixed bed in tubular catalytic reactor. The operating pressure was always near one atmosphere. The flow of reactants was regulated by needle valve and monitored by flowmeters. The additives, water and tetrachloromethane, was introduced to the system by flowing helium through a gas dispersion tube in a glass saturator containing the liquid. The reactor was made of quartz tube, 22.2 cm long and 0.9 cm in diameter, mounted horizontally in a tubular furnace. The catalysts were placed at the center of reactor and held in place by two pieces of quartz wool. The temperature was monitored by a thermocouple which was located at the catalyst bed. The reaction manifold was constructed with a 1/8" stainless steel tube and was heated to prevent liquid condensation. A 6-port gas sampling valve (VALCO) with a 5 ml sampling loop was connected to the reactor exit and to a reactor bypass. This allowed the analysis of both the reactor inlet and outlet flow. Prior to the reaction, the catalyst was calcined in situ in helium flow(30 ml/min) for 1 hour at reaction temperature, unless otherwise reported.
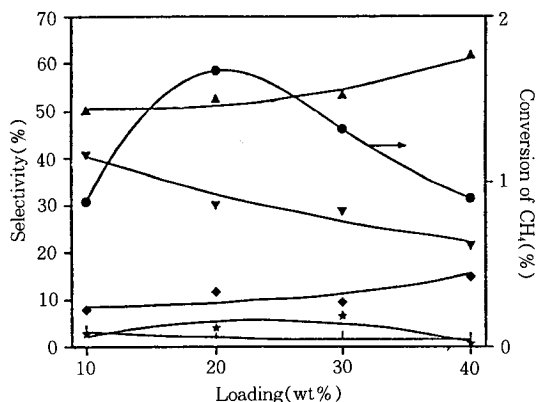
The reactants and products were analyzed with a

Fig. 1. Effect of loading of the HPMo on conversion of methane and selectivity over supported catalysts: $T_R=540℃$, $CH_4/N_2O=4/1$, $W/F=0.5g/25ml/min$, (●)conversion of CH_4, (▲) selectivity of CO, (▼)HCHO, (◆)CO_2, (★) CH_3OH, (|)C_2H_4.

Hewlett-Packard 5880A Gas Chromatograph equip -ped with a thermal conductivity detector(TCD). A Heysep Dip column(1/8 inch x 20 ft) enabled satis- factory separation of all reactants and products.

The reaction was monitored from the initial stage to the arrival of steady state with periodic analysis. The conversion of methane was calculated on a car- bon-account-for basis. The selectivity of products was calculated as the mole % of products.

Blank runs have been performed with the reactor full of quartz wool heated at 450℃~570℃ with conditions similar to those employed when catalyst was present. In helium, methane produced no de- composition or reaction products whereas N_2O yield- ed trace of N_2 and O_2.

3. Results

The effect of loading of supported HPMo on the catalytic activity and selectivity to products was in- vestigated at 540 ℃. Figure 1 shows that the con- version of methane has maximum at a loading of 20 wt% of support. Since the same mass of the sup- ported catalyst was used in all experiment, the in-
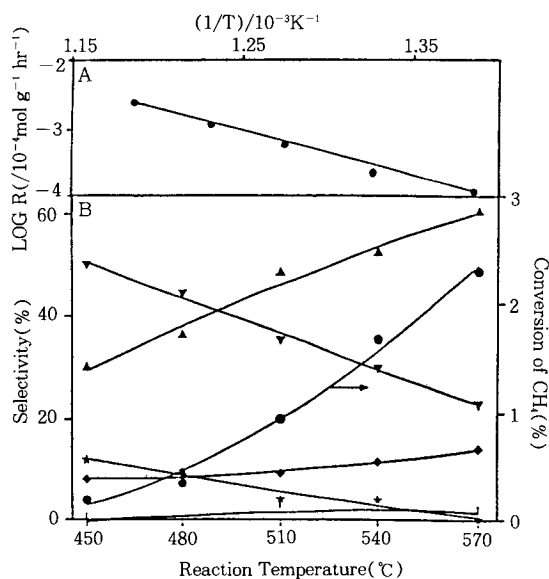

Fig. 2. Arrhenius plot(A) and effect of reaction temperature on conversion of methane and selectivity over 20 wt% HPMo/SiO₂(B): W/F=0.5g/25ml/min, $CH_4/N_2O=4/1$, same symbols as those in Figure 1.

trinsic activities of the catalysts(conversion of methane is divided by loading of the catalyst) are each 8.8, 8.4, 4.4 and 2.3. The selectivities to carbon dioxide and carbon monoxide slightly increase while the selectivity to formaldehyde decreases with in- creasing loading up to 40wt%.

In the remainder of this work, reactions were per- formed with 20 wt% loaded catalyst, since this cat- alyst showed the highest conversion and the lowest deactivation of the catalyst.

The effect of reaction temperature on conversion and selectivity was examined on 20 wt% HPMo/ SiO₂. As is shown in Figure 2, the selctivities to for- maldehyde and methanol decrease, whereas the se- lectivity to carbon monoxide increases with increas- ing temperature. The selectivity to carbon dioxide slightly increases with temperature in contrast to carbon monoxide. The overall selectivity to deep ox- idation products increases with temperature resulting in expensing of partial oxidation products, formaldehyde and methanol.
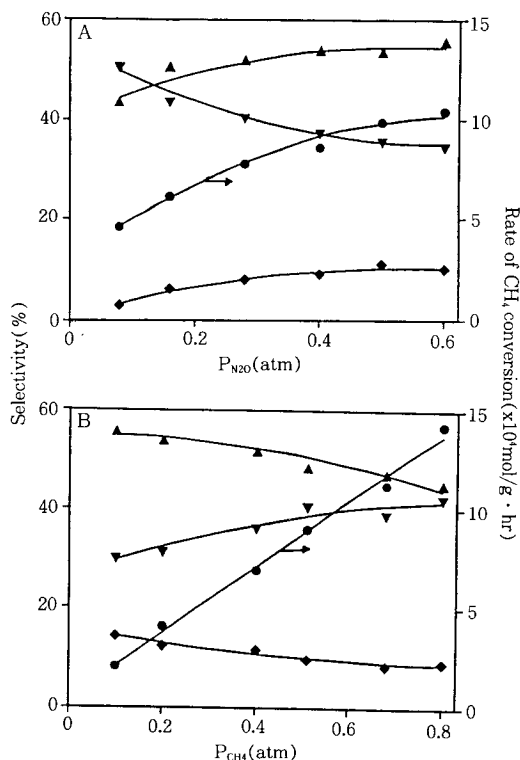
Fig. 3. Effect of partial pressure of CH_4 and N_2O on conversion of methane and selectivity over 20 wt% HPMo/SiO$_2$: T_R=540℃, W/F=0.5g /25ml/min, (A)P_{CH4} =0.4 atm, (B)P_{N2O}=0.2 atm, same symbols as those in Figure 1.

Fig. 4. Effect of contact time on conversion of methane and selectivity over 20wt% HPMo/SiO$_2$: T_R=540℃, CH_4/N_2O=4/1, same symbols as those in Figure 1.

Arrhenius plots of the logarithm of the rate of methane conversion versus the reciprocal of the absolute temperature revealed that apparent activation energy is 30.78 kcal/mole(Figure 2A).

The rate of conversion and selectivities as a function of partial pressure of methane and nitrous oxide are shown in Figure 3. These experiments were carried out at constant reaction temperature and space velocity. The partial pressure of CH_4 and N_2O were varied, while holding the partial pressure of the remaining reactants at constant values. The flow of helium was adjusted to obtain the required space velocity. In order to establish the rate equation for the conversion of CH_4, the kinetic orders with respect to CH_4 and N_2O have been calculated from the logarithm of the rate of CH_4 consumption
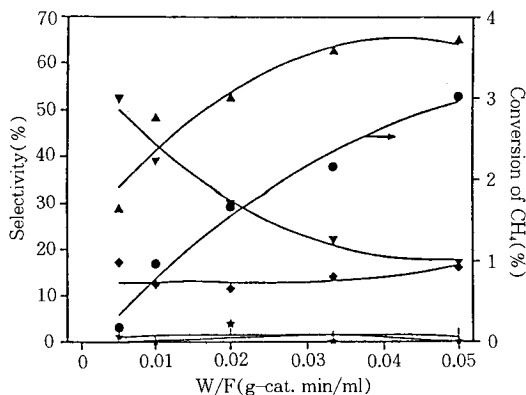
versus the logarithm of the partial pressure of CH_4 and of N_2O. The overall rate of CH_4 conversion may be described by:

$$-d[CH_4]/dt=k[CH_4][N_2O]^{0.4}$$

over the range of partial pressure P_{CH4}=0.1~0.8 atm, and P_{N2O}=0.1~0.6atm.

High value of the molar ratio N_2O/CH_4 favours the production of carbon monoxide and carbon dioxide, while the selectivity to formaldehyde shows reverse trend.

The effect of contact time on the conversion of methane and selectivity to products was investigated on 20 wt% HPMo/SiO$_2$ at 540 ℃ and the ratio of CH_4/N_2O=4. The variation in contact time was obtained by changing mass of catalyst at constant total flow rate. The result is shown in Figure 4. The conversion appears to increase with increasing contact time and the selectivities to carbon dioxide, ethylene and methanol are nearly constant at all contact time, whereas selectivities to carbon monoxide and formaldehyde show a strong dependence on contact time, with carbon monoxide selectivity increasing and formaldehyde selectivity decreasing with contact time. This result suggests that formaldehyde converts to carbon monoxide at high contact

Table 1. Conversion and Selectivity of Various Supported Heteropolyoxometalates

Catalyst Configuration	Conversion(%)		Selectivity(%)				
	CH₄	N₂O	CO	CO₂	C₂H₄	HCHO	CH₃OH
HPMo/SiO₂	1.67	12.85	52.4	11.7	1.7	30.2	4.0
HPMo/SiO₂+HPW/SiO₂ᵃ	1.10	8.69	48.5	7.6	4.4	39.2	0.3
HPMo/SiO₂+HPW/SiO₂ᵇ	0.87	7.45	53.5	9.1	4.2	33.0	0.3
HPMo/SiO₂+HPW/SiO₂ᶜ	0.83	6.70	50.9	10.1	5.6	32.8	0.6
HPW/SiO₂+HPMo/SiO₂ᶜ	0.81	7.06	46.4	11.0	2.9	36.3	3.4
HPMo/SiO₂+HPWᵈ	0.79	6.21	50.0	9.3	0.0	33.0	7.7

The loading of HPW and HPMo on silica is 20 wt%.
ᵃ HPW and HPMo are supported concomitantly(each 10 wt%).
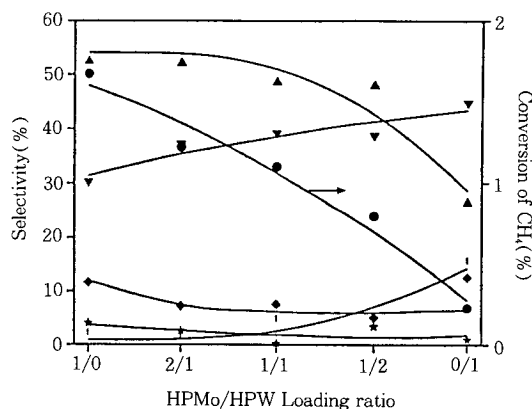ᵇ HPMo/SiO₂ and HPW/SiO₂ are mixed mechanically.
ᶜ Two catalyst bed are used.
ᵈ Non-supported HPW(parent acid).
Reaction conditions: T_R=540℃, CH₄/N₂O=4/1, W/F=0.5g/25ml/min.
All catalysts are pretreated by 30 ml/min He at 570 ℃ for 1 hr.

Fig. 5. Effect of HPMo/HPW loading ratio on conversion of methane and selectivity over supported catalysts: T_R=540℃, CH₄/N₂O=4/1, W/F=0.5g/25ml/min, same symbols as those in Figure 1.

time.

The trend which was found for the comparison of conversion and selectivities on various dual catalyst configurations with HPMo/SiO₂ catalyst are shown in Table 1. Several interesting results can be made from the comparison of various catalyst configurations with reaction of HPMo/SiO₂. The first thing is that all dual catalyst configurations result in a decrease on the conversion of methane and nitrous oxide, when compared to that of HPMo/SiO₂. In constrast, the selectivities to formaldehyde and ethylene increase. The second thing is that the catalyst configuration which HPMo and HPW are supported concomitantly shows an increment of selectivities to formaldehyde and ethylene, even if the selectivity to ethylene is not so high, whereas it shows a decrease of selectivities to methanol, carbon monoxide and carbon dioxide. The mechanical mixtures of HPMo/SiO₂ and HPW/SiO₂ also shows same tendency. The catalyst configuration which HPW/SiO₂ is mounted following to HPMo/SiO₂ shows an increase of selectivities to ethylene and formaldehyde, while the catalyst configuration which is used unsupported HPW does not show the formation of ethylene. It is thought that the Keggin structure of unsupported

HPW may be destroyed at this temperature.

These results are expected since HPMo/SiO₂ is responsible for converting methane to methanol and formaldehyde, whereas HPW/SiO₂ is responsible for converting methanol into ethylene and formaldehyde.

In addition, we changed the ratio of HPMo/HPW when they are concomitantly supported on silica gel and examined the conversion and selectivity to products at 540 ℃ and the ratio of CH₄/N₂O=4. As is shown in Figure 5, the conversion of methane gradually decreases and selectivities to CO, CO₂, and CH₃OH decrease with increasing HPW loading ratio, whereas selectivities to formaldehyde and ethylene gradually increase. Especially, the selectivity to ethylene increases to 15 % at HPW only supported catalyst. This result shows the same tendency as Table 1, that is, HPW is responsible for converting methanol to ethylene and formaldehyde.

The effect of pretreatment temperature on the conversion of methane and selectivity on silica-supported HPMo was examined. Figure 6 shows that the conversion and selectivities in the oxidation of methane with nitrous oxide on silica-supported HPMo remains almost constant for pretreatment
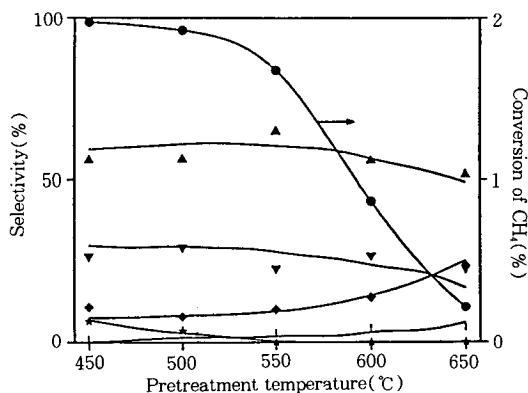
Fig. 6. Effect of pretreatment temperature on conversion of methane and selectivity over 20 wt% HPMo/SiO$_2$: T$_R$=540℃, CH$_4$/N$_2$O=4/1, W/F=0.5g/25ml/min, same symbols as those in Figure 1.

Fig. 7. Effect of the amount of water on conversion of methane and selectivity over 20 wt% HPMo/SiO$_2$: T$_R$=540℃, W/F=0.5g/25ml/min, CH$_4$(40%), N$_2$O(20%) He+H$_2$O(40%), same symbols as those in Figure 1.

temperature up to 500 ℃. For higher pretreatment temperature, the conversion and selectivities to methanol, carbon monoxide and formaldehyde decrease, while selectivities to carbon dioxide and ethylene gradually increase. The surface area of the 20 wt% HPMo/SiO$_2$ catalyst remains essentially constant for pretreatment temperature up to 550℃, but decreases for higher temperature (Table 2).

The effect of water added to the reactant on the partial oxidation of methane has been studied with other heterogeneous catalysts[11]. In this work with silica-supported HPMo catalyst, the introduction of water into the reactant results in a decrease on the conversion of methane. As is shown in Figure 7, the selectivities to methanol and formaldehyde slightly increase, while the selectivities to CO and CO$_2$ decrease very small. The water introduced into the reactant decreases the activity of catalyst in this work in contrast to other study [11].

The effect of organic halides added to the reactant on the oxidation of hydrocarbons has been studied[22,23]. In this work, the effect of the concentration of tetrachloromethane(TCM, CCl$_4$) in the reactant stream on the conversion of methane and selectivities to different products was examined.
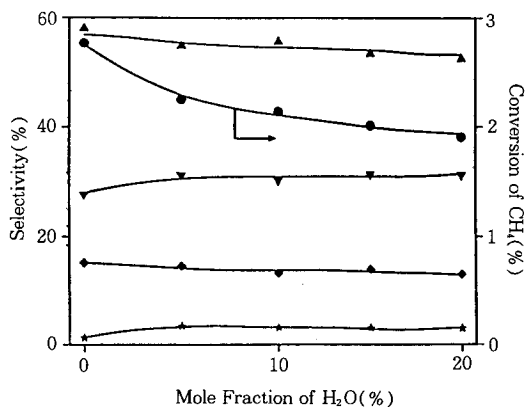

Fig. 8. Effect of the amount of TCM in the feed on conversion of methane and selectivity over 20 wt% HPMo/SiO$_2$: T$_R$=540℃, CH$_4$/N$_2$O= 4/1, W/F=0.5g/25ml /min, same symbols as those in Figure 1, (○)CH$_3$Cl.

Table 2. Surface Area of 20 wt% HPMo/SiO$_2$ at Various Pretreatment Temperature

Pretreatment Temperature(℃)	Surface Area (m^2/g)
450	806
500	762
550	791
600	720
650	513

As is shown in Figure 8, the presence of TCM enhances the activity of the silica-supported HPMo in the oxidation of methane, the effect of being more remarkable with small addition of TCM. With increasing concentration of TCM, the selectivity to formaldehyde decreases, to carbon monoxide almost remains constant, to carbon dioxide increases and to monochloromethane slightly increases.

4. Discussion

The present study convincingly demonstrates the activity and selectivity of silica-supported 12-molybdophosphoric acid and its dependence on contact time, reactant concentrations, reaction temperature, pretreatment temperature, loading ratio, catalyst configuration and the presence of water and tetrachloromethane. On silica-supported 12-molybdophosphoric acid, methane is converted to useful products, such as formaldehyde, methanol and ethylene.

With HPMo/SiO₂ the conversion reaches a maximum at a loading of approximately 20wt%. Similar loading effects were observed in partial oxidation of ethane on HPMo/SiO₂[24], in which the rates of conversion and product generation reached a maximum at a loading of HPMo on SiO₂ of approximately twenty percent. Kasztelan [25] has reported that the optimum loading of HPMo on SiO₂ corresponded to 20 wt% HPMo on SiO₂ and the heavier loading of HPMo on SiO₂ than 23 wt% gave rise to the formation of particles of HPMo which may exert to a blocking effect on those in direct contact with the support or the inability of the support to stabilize quantities of heteropoly compound greater than that at saturation. Consequently the formation of particles of HPMo on the surface of the support will render any Keggin unit contained within the bulk of the particle inaccesible to methane, nonpolar species, and hence inactive in the oxidation of methane. In addition, the lower loading of HPMo on SiO₂ than 10 wt% showed the fast deactivation.

The dependence of the conversion of methane and the selectivities to the various products on the pretreatment temperature provides further information on the properties of the catalyst. As the pretreatment temperature is increased from 450 to 500℃ the conversion and selectivities remain virtually unchanged. At a pretreatment temperature of 550℃ the conversion and selectivity to formaldehyde begin to decrease, while the selectivity to CO₂ begin to increase. These observation are similar to those obtained previously from the oxidation of ethane on the same catalyst[24].

Laser Raman spectra of 23 wt% HPMo/SiO₂ sample after calcination at temperature up to 700℃ show the presence of the Keggin anion, although at temperatures higher than 550℃ bands attributed to MoO₃ predominate and ³¹P NMR spectra of the sample at various loadings, calcination temperature and calcination times are also consitent with those expected for the Keggin anion[25]. The variation in the Mo_{3d}/Si_{2p} XPS intensity ratio with loading of HPMo shows that small aggregates the anion are dispersed over the surface up to approximately 10 wt%. For loading up to 23 wt% larger aggregates begin to appear while for loadings higher than aforementioned large aggregates are formed[26].

It is evident that the earlier work[24] and the present results strongly suggest that the Keggin anion of HPMo when supported on SiO₂ has an enhanced thermal stability, exists up to approximately 600℃ and is primarily responsible for the catalytic oxidation of ethane and methane and is largely intact up to temperatures between 500 and 600℃.

The activity and selectivities of products on dual catalyst configuration with HPMo/SiO₂ are different from each other and those change according to the loading ratio of HPMo/HPW on SiO₂. As is aforementioned, these two catalysts show different tendency in product distribution. Hong[27] reported that 12-tungstophosphoric acid is capable of converting methanol to hydrocarbons($>C_i$) apparently via a route in which the anionic terminal oxygen atoms are methylated. In contrast, with 12-molybdophosphoric acid, methanol is primarily con-

verted to oxidation products principally carbon monoxide. These are consistent with the results that the selectivity to ethylene increases with decreasing of the ratio of HPMo/HPW when they are concomitantly supported on silica gel. In addition, the catalyst configuration that HPW/SiO_2 is mounted following to HPMo/SiO_2 also shows an increase of selectivity to ethylene.

The beneficial effect of the presence of a halogenated species in the reactant stream is well-documented in the case of the oxidation of ethylene on silver catalyst[22] and in the case of oxidation of methane on palladium metal supported on Al_2O_3 [23]. In the case of oxidation of ethylene on Ag, the addition of a chlorinated compound reduces the conversion of ethylene, the drop in the conversion to deep oxidation products being more than the drop in the conversion to ethylene oxide, with the consequence that there is an apparent increase in the selectivity to the partial oxidation product. In the case of methane oxidation of on a supprted Pd catalyst, methane is converted entirely to CO_2 and H_2O in the absence of a chloromethane, while in the presence of chloromethane, formaldehyde is formed but at the expense of a substantial drop in the conversion of methane. In the present work of the oxidation of methane on silica-supported HPMo, the addition of tetrachloromethane, in constrast to observations of above studies, enhanced the conversion of methane. In addition, the selectivity to formaldehyde slightly decreases up to 0.4 mole% of additive. As a result, at similar reaction conditions, the yield of formaldehyde is higher in the presence of tetrachloromethane in the feed than in its absence. This indicates the beneficial effect of adding a small amount of a tetrachloromethane in the feed stream in the oxidation of methane.

Both the results shown in the present work for the conversion of methane and those found with the same catalyst in the conversion of ethane[21] show that the oxygen of the catalyst participates in the oxidation process. However it is not clear what proportion of the available catalytic oxygen partici-

pates in the process. However temperature-programmed desorption studies and more recent Raman spectral evidence[28,14] suggest that at least 1.5 oxygen atom, on average, of a total of 40 within each anion can be removed while retaining the structure of the anion.

Although the process by which methane is converted to oxygenated products is evidently dependent on the presence of HPMo/SiO_2, the mechanism by which the active sites are regenerated is less clear. Evidently N_2O may decompose in the gas phase to form O^- [29, 30] or may interact directly with the Keggin anion to regenerate the depleted oxygen. The participation of the Mo in the HPMo/SiO_2 may be similar to that proposed by Erdöhelyi et al.[30] for silica-supported alkali molybdate catalysts

$$Mo^{5+} + N_2O = Mo^{6+} - O^- + N_2$$
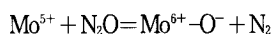
where, with HPMo/SiO_2, the Mo species occupy the peripheral metal positions in the Keggin anion.

There is considerable evidence available in the literature to support the contention that, in general, oxidation processes tend to proceed through radical mechanism[31]. Thus, with the Keggin anion

$$O^- + CH_4 \rightarrow CH_3 \cdot + OH^-$$
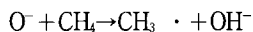
It should be noted that it is not clear, from this or any previous work, whether the oxygen species involved in the oxidation process occupy the terminal or bridging positions within the Keggin anion. The methyl radicals may, of course, remain on the surface of the anion presumably to methylate the Keggin anion

$$CH_3 \cdot + O^- \rightarrow CH_3 - O^-$$
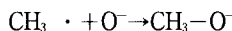
or alternatively enter the gas phase. Methyl radicals found in the gas phase are expected to be more likely to form deep oxidation products.

The formation of methanol could be result from the interaction between the protons present in the acid and the methoxy group formed from the methylation of the Keggin anion. In addition, this

methanol may rapidly decompose to HCHO, CO, and CO_2. In view of the present results the reaction is proceeded below scheme.

$$CH_4 \rightarrow CH_3OH \rightarrow HCHO$$
$$\downarrow \qquad \downarrow$$
$$CO,CO_2 \quad CO,CO_2$$
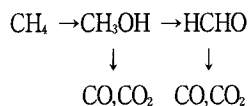
In addition, a considerable quantity of methyl chloride is formed in the presence of TCM. However this methyl chloride may be produced by methane directly.

5. Conclusions

The following conclusions are drawn from the present work.

1. 20 wt% loaded catalyst shows the highest activity and yield to formaldehyde.

2. The apparent reaction order of methane conversion is ca. 1.0 with respect to methane at the range of partial pressure $P_{CH4}=0.1\sim0.8$ atm and ca. 0.4 with respect to nitrous oxide at the range of partial pressure $P_{N2O}=0.1\sim0.6$ atm. In addition, the apparent acitivation energy is 30.78 kcal/mole.

3. The selectivity to ethylene increases in the catalyst configuration which HPW /SiO₂ is mounted following to HPMo/SiO₂ and with increasing HPW loading ratio of concomitantly supported HPW/ HPMo on silica.

4. The addition of small amount of tetrachloromethane to the reactant stream enhances the activity of silica-supported HPMo in the oxidation of methane, whereas water added to the feed decreases the activity of catalyst.

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