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Low-temperature oxidation of methane to form formaldehyde: role of Fe and Mo on Fe–Mo/SiO_2 catalysts, and their synergistic effects

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The partial oxidation of methane with molecular oxygen was performed on Fe–Mo/SiO_2 catalysts. Iron was loaded on the Mo/SiO_2 catalyst by chemical vapor deposition of $Fe_3(CO)_{12}$. The catalyst showed good low-temperature activities at 723–823 K. Formaldehyde was a major condensable liquid product on the prepared catalyst. There were synergistic effects between iron and molybdenum in Fe–Mo/SiO_2 catalysts for the production of formaldehyde from the methane partial oxidation. The activation energy of Mo/SiO_2 decreased with the addition of iron and approached that of the Fe/SiO_2. The concentration of isolated molybdenum species (the peak at 1148 K in TPR experiments) decreased as the ion concentration increased and had a linear relationship with the selectivity of methane to formaldehyde. The role of Fe and Mo in the Fe–Mo/SiO_2 catalyst was proposed: Fe is the center for the C–H activation to generate reaction intermediates, and Mo is the one for the transformation of intermediates into formaldehyde. Those phenomena were predominant below 775 K.

Keywords: C–H activation, methane oxidation, formaldehyde, chemical vapor deposition, Fe–Mo/SiO_2 catalyst

1. Introduction

The direct partial oxidation of methane to form oxygenated compounds such as methanol and formaldehyde has been an issue for the last two decades [1–3]. There have been various efforts to develop an active catalytic system for the methane oxidation with molecular oxygen [4–7]. The commercial catalyst for the formaldehyde synthesis from methanol partial oxidation, Mo/SiO_2, has been known to carry out the methane partial oxidation, too [8–16]. The partial oxidation of methane has generally been performed above 800 K due to the high C–H bond energy of 105 kcal. The selectivity was poor because partial oxidation products, such as formaldehyde and methanol, were unstable and easily oxidized to CO_2 at the reaction temperature [17].

Formaldehyde decomposed to carbon oxides above 823 K on Mo/SiO_2. Kinetic studies showed that the complete oxidation of methanol and formaldehyde occurred in the gas phase by a free radical mechanism as well as on the surface of a catalyst at the high reaction temperature [18]. Therefore, it is important to understand the role of active species in the oxidation catalyst to minimize the decomposition of reaction intermediates, while maximizing yields of methanol and formaldehdye. Herein, we report the characterization of Fe–Mo/SiO_2 catalysts for the partial oxidation of methane. The low-temperature activity increased with the addition of small amounts of iron on Mo/SiO_2 by the CVD (chemical vapor deposition) of $Fe_3(CO)_{12}$. The presence of iron and molybdenum showed synergistic effects to give formaldehyde as a major condensable liquid product. Their individual roles were discussed.

2. Experimental

2.1. Catalyst preparations

The silica-supported molybdenum catalyst (2% Mo/SiO_2) was prepared by an incipient wetness impregnation method. To the aqueous solution of $(NH_4)_4Mo_7O_{24}\cdot 4H_2O$ (Aldrich Co., 1 g in 20 ml H_2O) was added SiO_2 (Davis, Grade 645, 40 g). The resulting slurry was dried at 393 K for 4 h and calcined at 823 K for 3 h in air.

The Fe–Mo/SiO_2 catalyst was prepared by a typical CVD method. Triirondodecacarbonyl, $Fe_3(CO)_{12}$, was prepared as described in the literature [19]. Mo/SiO_2 was placed in a tubular reactor. The vaporized triirondodecacarbonyl was transferred to the tubular reactor under slight vacuum and decomposed on Mo/SiO_2 at 373 K. Metal ion contents (%) in catalysts were designated as Fe($x.xx$)Mo(x).

2.2. Catalytic reactions

The methane oxidation reaction was carried out in a fixed-bed reactor (quartz, 8 mm O.D., 20 cm length) heated by an electrical furnace. Catalysts (400 mg) were loaded and used without further treatment. A mixed gas of $CH_4 : O_2 : N_2$ (9 : 1 : 1 volume ratio) was introduced into the reactor under atmospheric pressure. Gas flows were controlled by mass flow controllers (Matheson Co.). Reaction products were analyzed by an on-line gas chromatograph

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(Varian Vista 6000) with a thermal conductivity detector (Carbosphere, 3 m) for analyses of N_2, CO, CO_2, and CH_4, and with a flame-ionization detector (Porapak Q, 2 m with methanizer) for analyses of CO, CO_2, CH_4, C_2H_4, C_2H_6, HCHO, and CH_3OH. The lines between the reactor and the GC were heated to avoid the condensation of liquid products.

2.3. Temperature-programmed reduction (TPR) experiments

Temperature-programmed reduction experiments were performed with 300 mg of catalysts in a flow of 5% hydrogen/argon. Catalysts were heated to 1375 K at a heating rate of 20 K/min and maintained for 20 min. The hydrogen consumption was monitored by a TCD detector. The moisture thus formed was removed by a molecular sieve trap.

3. Results

3.1. Partial oxidation of methane and synergistic effects of iron and molybdenum

The methane conversion with different iron contents in Fe–Mo/SiO_2 catalysts were monitored at three different temperatures, 723, 773, and 823 K. The major condensable liquid product was formaldehdye with trace amounts of methanol. The Mo/SiO_2 showed no catalytic activity at 723 K, and the conversion became 0.1 and 0.3% at 773 and 823 K, respectively (figure 1(a)). As the iron contents

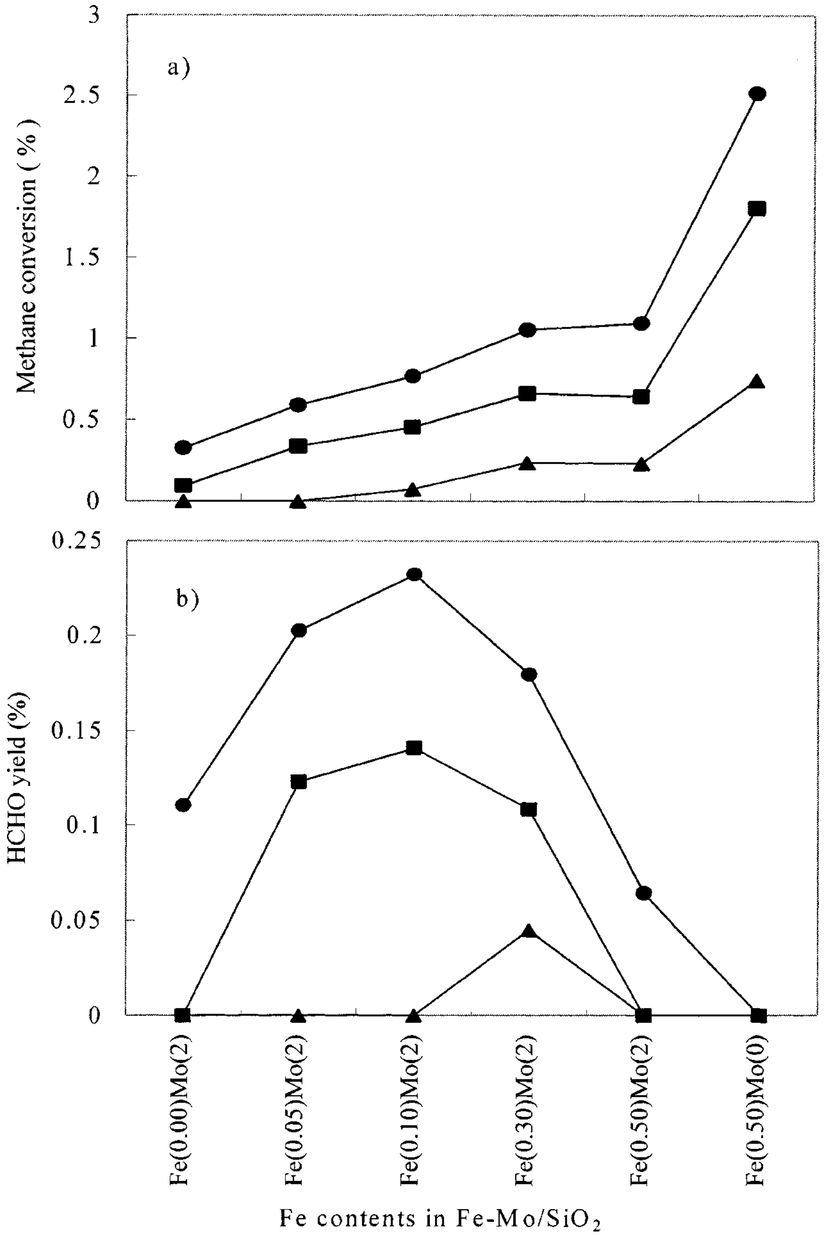

Figure 1. Temperature dependency with the addition of iron to Mo/SiO_2: (a) conversion of methane and (b) yield of methane to formaldehyde; (●) 723 K, (■) 773 K, (▲) 798 K; $CH_4:O_2:N_2 = 9:1:1$ (volume ratio), GHSV = 3000 ml/g_{cat} h.

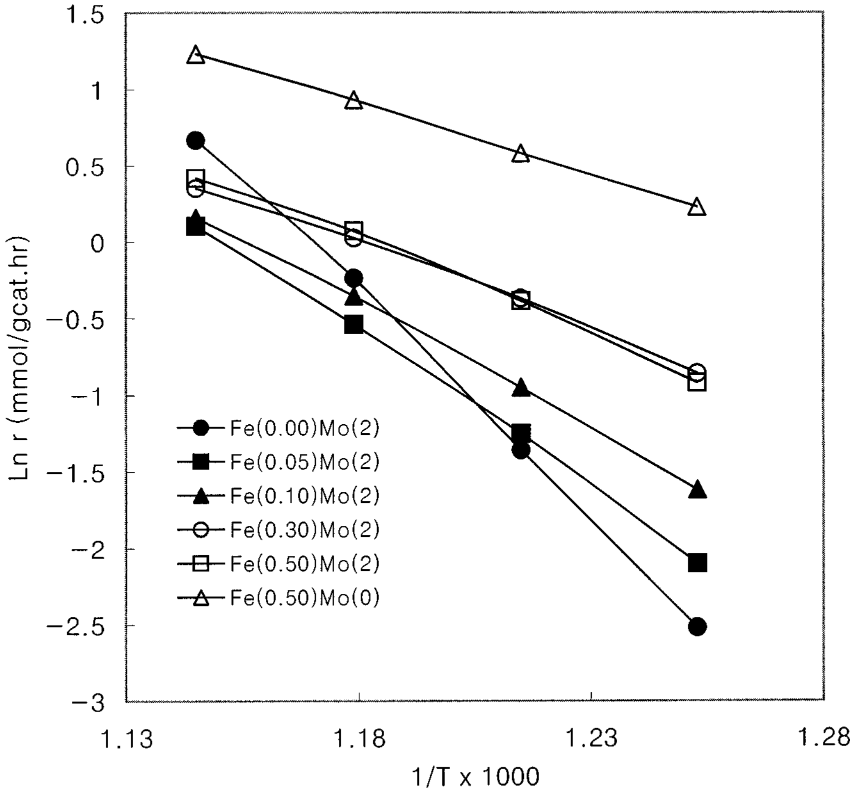

Figure 2. Arrhenius plots of methane conversion on different Fe–Mo/SiO_2 catalysts.

increased to 0.5%, the methane conversion increased up to 0.3% at 723 K and 1% at 823 K. In the presence of 0.5% of iron on SiO_2 without molybdenum, the methane conversion was 2.5% at 823 K, the highest among the tested catalysts. The conversion increments at the three different temperatures were almost linear with the addition of iron, indicating the active participation of the iron component in the C–H activation of methane.

It is interesting to note the bell shape pattern of the formaldehyde yield with the increment of iron contents on the Mo/SiO_2 (figure 1(b)). The yield of formaldehyde increased as iron contents increased, and gave the maximum yield of 0.23% at 0.1% Fe–Mo/SiO_2. The Mo/SiO_2 catalyst without iron did not produce formaldehyde at 723 and 773 K at all. Fe/SiO_2 without molybdenum also could not produce any formaldehyde at the reaction temperature investigated because of the poor selectivity. The synergistic effects were maximized at 773 K. The addition of 0.1% of iron to the Mo/SiO_2 gave the maximum yield of formaldehyde, showing the synergistic effects of iron and molybdenum to produce formaldehyde from the methane partial oxidation.

3.2. *Measurement of activation energy depending on iron contents*

The Arrhenius plots were obtained with different iron contents (figure 2). The apparent activation energies were obtained from the slope of straight lines (table 1). The activation energy of Mo/SiO_2 without iron was 247 kJ/mol, which was the highest value among the tested catalysts. As shown in figure 1, the conversion of the Mo/SiO_2 catalyst was the lowest, which is consistent with the highest apparent activation energy based on the assumption that the frequency factor of the Arrhenius equation was not much changed with the addition of $Fe_3(CO)_{12}$ by CVD. The apparent activation energy reduced from 247 kJ/mol with the addition of iron to Mo/SiO_2, ranging from 169 to 93 kJ/mol as the iron contents increased (table 1). Compared to 78 kJ/mol of Fe/SiO_2 and 247 kJ/mol of Mo/SiO_2, the activation energy of Fe–Mo/SiO_2 shifted toward that of Fe/SiO_2 as the iron contents increased. The addition of iron to the Mo/SiO_2 increased the methane conversion with the decrease in the apparent activation energy. The reduction of the activation energy with the addition of iron was an important indication that iron plays a role of activating a C–H bond at the initial stage of the methane oxidation.

Table 1
Apparent activation energies of methane conversion on Fe–Mo/SiO_2 catalysts.

Catalyst	E_a (kJ/mol)
Fe(0.00)Mo(2)	247
Fe(0.05)Mo(2)	169
Fe(0.10)Mo(2)	137
Fe(0.30)Mo(2)	93
Fe(0.50)Mo(2)	103
Fe(0.50)Mo(0)	78

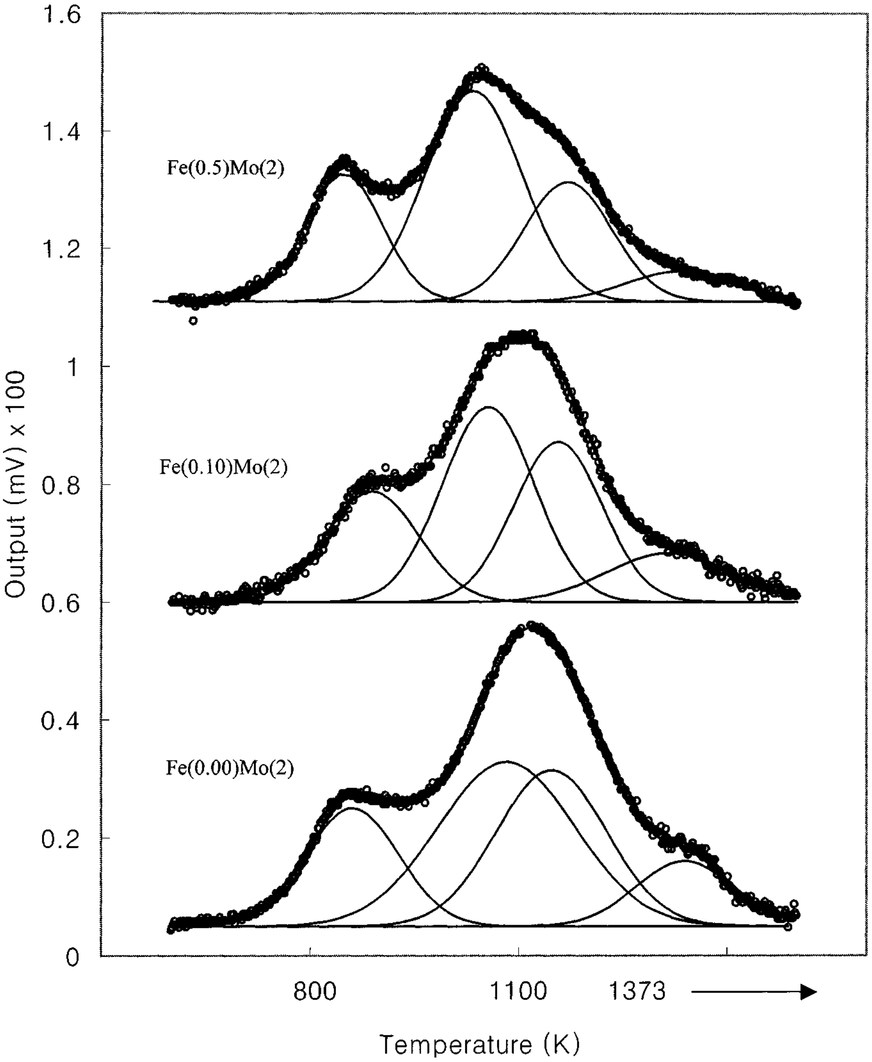

Figure 3. TPR spectra with Fe–Mo/SiO_2 catalysts: (○) measured value, (–) deconvoluted value.

3.3. Temperature-programmed reduction (TPR) experiments

Temperature-programmed reduction (TPR) experiments were carried out in a flow of 5% hydrogen/argon with programmed heating up to 1373 K at a rate of 20 K/min and maintained for 10 min (figure 3). Round symbols in figure 3 indicate experimental data from Mo/SiO_2, 0.1% Fe–Mo/SiO_2, and 0.5% Fe–Mo/SiO_2, and were deconvoluted (solid lines). The TPR spectrum of Mo/SiO_2 showed two maximum peaks at 864 and 1128 K, which were attributed to the reduction of molybdenum oxide species. The peak at 1350 K resulted from the maintenance of temperature at 1373 K. The TPR spectrum of 0.5% Fe–Mo/SiO_2 generated the maximum peak at 1042 K with the shoulder at 1176 K. The peak at 864 K was not much affected by the addition of iron. The deconvolutions of the TPR spectra were performed and summarized in table 2. From the deconvolution experiments, the peaks at 1083 and 1148 K were monitored. The ratio of hydrogen consumption at 861 and 1083 K (the ratio of A_2/A_1) was close to 2 in three samples. From the ratio of $A_2/A_1 = 2$, the two peaks were attributed to the reduction of MoO_3 to MoO_2 (2e reduction) and MoO_2 to Mo (4e reduction), respectively. According to Arena's assignments on molybdenum species in Mo/SiO_2 [20], the peaks at 861 and 1083 K could be assigned to the reductions of polymeric molybdenum oxides. The peak at 1148 K was assigned to the reduction of isolated molybdenum oxides. Reduction peaks of iron were not identified in TPR experiments. It is inferred that iron reduction peaks were hidden in molybdenum peaks, since the ratio of A_2/A_1 was slightly changed with the addition of iron.

Table 2
Temperature (T) and areas of deconvoluted peaks (A) of TPR spectra of Fe–Mo/SiO_2 catalysts.

Catalyst	T_1	A_1	T_2	A_2	T_3	A_3	T_4	A_4
Fe(0.00)Mo(2)	861	0.33	1083	0.69	1148	0.53	1339	0.19
Fe(0.10)Mo(2)	888	0.32	1056	0.55	1156	0.43	1316	0.19
Fe(0.50)Mo(2)	848	0.30	1035	0.63	1152	0.33	1331	0.10

The concentration of isolated molybdenum, peaking at 1148 K, decreased with the addition of iron on the

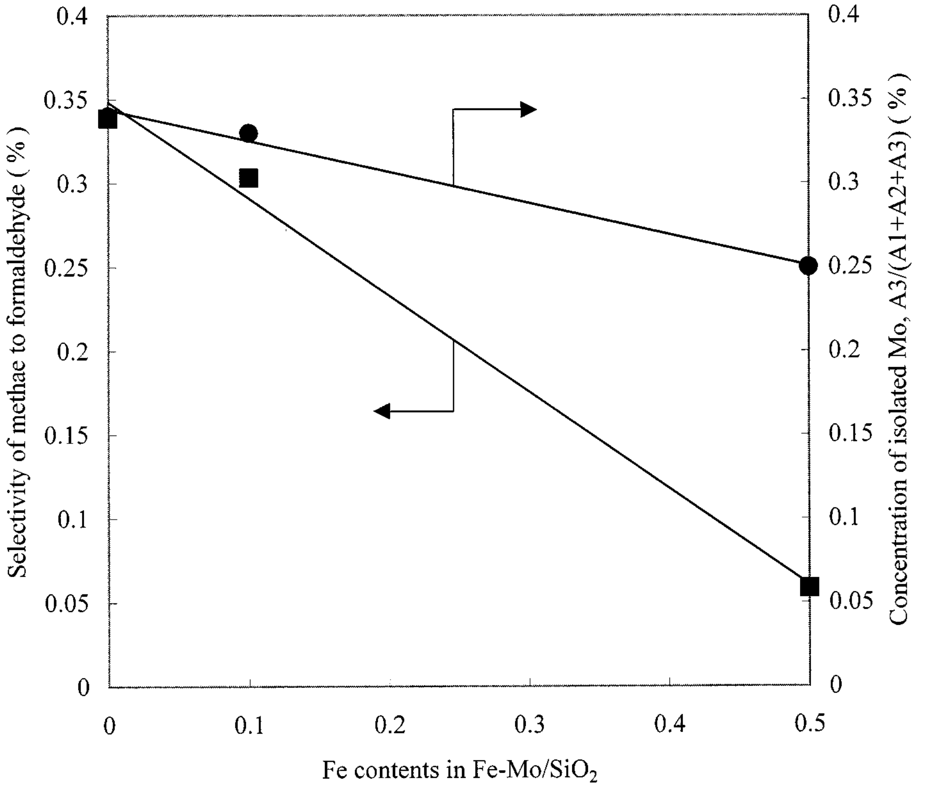

Figure 4. Relationship between selectivity of methane to formaldehyde (■) and concentration of isolated Mo center (•) with different Fe loading.

Mo/SiO_2 catalyst. The estimated concentrations of the isolated molybdenum ($A_3/(A_1 + A_2 + A_3)$) were 34.2% (Mo/SiO_2), 33.1% (0.1% Fe), 26.2% (0.5% Fe). The presence of small amounts of iron influenced the distribution of molybdenum species on the silica support. It is worthwhile to notice that the selectivity to formaldehyde from the methane partial oxidation was linearly correlated to the concentration of the isolated molybdenum (figure 4). As the iron content increased, the concentration of isolated molybdenum, which peaked at 1148 K, decreased with a linear relationship. At the same time, the selectivity decreased on a straight line, too. From the good linear relationships, it is suggested that the isolated molybdenum plays a role of controlling selectivity and produce formaldehyde as a final product.

4. Discussion

Small amounts of iron were effectively deposited on the Mo/SiO_2 catalyst by chemical vapor deposition of $Fe_3(CO)_{12}$ to prepare $Fe–Mo/SiO_2$. The conventional impregnation method in an aqueous medium is difficult to evenly distribute the iron on the surface of supports in the molecular level. At the drying stage of the impregnation, iron salts will be recrystallized to form large clusters. It will form islands of iron oxides on the supports after the calcination and cannot be evenly spread on the surface. On the other hand, the CVD of $Fe_3(CO)_{12}$ spreads iron on the support in the molecular level. The surface-bound carbonyl clusters are easily decomposed to form oxides in the air, and the iron oxides would not be sintered under the catalyst preparation and reaction conditions. The CVD of $Fe_3(CO)_{12}$ enabled us to monitor the kinetic differences of the methane oxidation on Mo/SiO_2 catalysts in the presence of small amounts of iron.

The conversion increments at the three different temperatures were linear with the addition of iron on the Mo/SiO_2 catalyst (figure 1). Especially Fe/SiO_2 gave the highest conversion of methane among the tested catalysts. The conversion increment with the addition of iron indicated the role of iron in the methane conversion. The C–H bond breakage was known to be the highest activation barrier to the methane oxidation. The linear relationship between the methane conversion and the iron content implied the role of iron for the methane conversion. As shown in the apparent activation energy measurement, the presence of iron on the Mo/SiO_2 lowered the activation energy below half. The activation energies of $Fe–Mo/SiO_2$ catalysts (93–169 kJ/mol) were close to that of the Fe/SiO_2 (78 kJ/mol) rather than that of the Mo/SiO_2 (247 kJ/mol). The iron was believed to supply the active center for the C–H bond activation.

The bell shape shown in the production of formaldehyde suggested the role of molybdenum in terms of selectivity. From TPD experiments and their deconvolutions, the presence of iron not only supplied the C–H activation sites, but also controlled the composition of molybdenum species (figure 3). At the high reaction temperature of 823 K or higher, molybdenum showed high methane conversion capability. However, as the reaction temperature decreased to

773 K, the conversion activity decreased, and the selectivity to formaldehyde increased. The concentration of the isolated molybdenum (peak at 1148 K in figure 3) decreased from 34.2 to 26.2% (table 2) as the iron content increased. The concentration of the isolated molybdenum was well correlated to the formaldehyde selectivity (figure 4). The amounts of the isolated molybdenum species were proportional to the selectivity of formaldehyde. In figure 4, it was clear that the molybdenum supplied the active sites for controlling the selectivity to formaldehyde. Formaldehyde and methanol are thermodynamically metastable compounds before being converted to CO_2. The role of molybdenum in the methane oxidation reaction was believed to stabilize the reaction intermediates generated from the C–H activation and to transform the intermediates into formaldehyde at the low reaction temperature investigated.

It can be inferred that the formation of formaldehyde from the methane oxidation consists of two reaction steps: one is the C–H activation of methane generating reaction intermediates, and the other is the stabilization and transformation of the reaction intermediates into formaldehyde. Those results described above gave us understandings of the reasons for the synergistic effects of iron and molybdenum in the Fe–Mo/SiO_2 catalysts at the temperature investigated: the iron activated C–H bonds to form reaction intermediates and, the molybdenum transformed the intermediates into formaldehyde.

5. Conclusion

The addition of Fe to the Mo/SiO_2 catalyst enhanced the activities to form formaldehyde from the methane partial oxidation at relatively low temperature of 723–823 K. There were synergistic effects of iron and molybdenum for the production of formaldehyde. The activation energy of the methane oxidation decreased with the addition of iron and approached that of Fe/SiO_2. The concentration of the isolated molybdenum species (peak at 1148 K in TPR experiments) showed a linear relationship with the selectivity to formaldehyde. Based on the results described above, different roles of Fe and Mo of the Fe–Mo/SiO_2 catalyst at the low reaction temperature were proposed: Fe activated a C–H bond, generating oxidation intermediates, and Mo transformed the reaction intermediates into formaldehyde

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