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Selective oxidation of methane in CH_4–O_2–NO_2 over MoO_3

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Abstract

Selective oxidation of methane in CH_4–O_2–NO_2 was examined using MoO_3 catalyst at atmospheric pressure. The selective oxidation was enhanced with addition of NO_2 to the reaction system of CH_4 and O_2, in analogy with the gas-phase reaction. The initiation reaction was assured to take place between CH_4 and NO_2. The presence of MoO_3 catalyst increased CH_2O selectivity and decreased CH_3OH selectivity, compared with those for the gas-phase reaction in CH_4–O_2–NO_2. Based on variations in reaction of selectivities at several reaction conditions, it could be explained/concluded that formaldehyde was a main product on the MoO_3 catalyst and methanol was formed through gas-phase reactions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Selective oxidation; Methane; Methanol; Formaldehyde; NO_x; MoO_3

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1. Introduction

The direct selective oxidation of methane for producing valuable C_1-oxygenates such as methanol and formaldehyde has been a potentially important process. Many studies of direct selective oxidation in the presence or absence of catalysts have been carried out to get a higher selectivity of C_1-oxygenates in the products [1–4]. However, the yield of C_1-oxygenates for the direct selective oxidation of methane is still low, and CO and CO_2 are major products. The rate-determining step of this reaction is the abstraction of first hydrogen atom from methane. Hydrogen abstraction needed high reaction temperatures because its transition barrier is high, while high reaction temperature easily led over-oxidations of produced C_1-oxygenates to CO and CO_2. The transition barrier can be produced using nitrogen oxides [5–10,19]. Yamaguchi et al. [9] reported that the transition barrier of hydrogen abstraction from methane was lowered from 59.0 to 37.6 kcal/mol using NO_2 as an initiator. Otsuka et al. [5,19] obtained a comparatively high yield of formaldehyde in the gas-phase selective oxidation of CH_4–O_2–NO. Tabata et al. [10] also obtained ca. 7% yield of C_1-oxygenates in the gas-phase selective oxidation of CH_4–O_2–NO_2.

Irusta et al. [6] examined the selective oxidation of methane in CH_4–O_2–NO both in the presence and absence of catalysts (Mo/SiO_2 and V/SiO_2) at 1 bar. They reported that methane activation was hardly enhanced in the presence of their catalysts while the presence of these catalysts strongly decreased CH_2O selectivity. Such a reducible effect of solid catalysts on the yield of formaldehyde was suggested. Bañares et al. [7] reported that high yield of methanol was obtained in the direct selective oxidation of CH_4–O_2–NO on V_2O_5/SiO_2 at around 600°C. They examined the effect of NO concentration on methane activation and

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product selectivities, and suggested that formaldehyde formation was heterogeneously formed on the catalyst, while methanol was produced through gas-phase reactions. However, the reaction mechanism of formaldehyde formation on the catalyst was not described. They suggested that NO in the reactant gas alters the equilibria between gas-phase reactions and surface-catalyzed reactions.

Tabata et al. [10] reported plausible reaction mechanisms in the gas-phase selective oxidation of CH_4–O_2–NO_2 using the density functional calculation program package; the initiation reaction of methane activation took place between CH_4 and NO_2. There is a possibility that the reaction mechanism in the selective oxidation system of CH_4–O_2–NO_2 on solid catalysts is different from that in the gas-phase reaction. In this study, an attempt was therefore made to reveal an initial reaction and C_1-oxygenate selectivity in the direct selective oxidation of methane with a mixture of O_2 and NO_2 on MoO_3 catalyst.

2. Experimental

2.1. Mo catalysts

Three different MoO_3 catalysts were prepared: Sample A (Wako Pure Chemical Industries), Sample B (Japan New Metals), and Sample C was Sample B calcined at 630°C for 12 h in the air. Silica-supported Mo catalyst (9.0 wt.%) was prepared by impregnation of amorphous silica gel (1.0 g, Merck No. 10180: 70–230 mesh, pore of 40 Å, SA of 750 m^2/g, Aldrich) using the solution of ammonium molybdate (0.1915 g, $(NH_4)_6[Mo(Mo_6O_{24})]\cdot 4H_2O$, Aldrich) and distilled water (2.0 g). The precursor was dried overnight at 120°C, then calcined at 630°C, for 4 h in the air. Every sample was pre-oxidized at 500°C for 1 h in a stream of oxygen (O_2: 20%; He: 80%) at 240 ml min^{-1} before each characterization and reaction.

2.2. Characterization of Mo catalysts

Specific surface areas of the pre-oxidized samples were measured at 77 K with the BET method (Quantachrome, AUTOSORB-1C). Each sample was outgassed at 200°C for 3 h before the measurement. Structure of the samples was examined with X-ray powder diffractometry (RIGAKU, RINT-2000) using monochromatic Cu Kα ($\lambda = 1.543$ Å, 40 kV, 40 mA). XRD patterns were measured in the range 10–70° with a scan speed of 1.7 min^{-1}. Crystallite size of the samples was calculated from the half width of diffraction peak of (0 4 0) plane with Scherrer's equation [11].

2.3. CH_4–O_2–NO_2 reaction

Highly purified methane (>99.9995%), oxygen (>99.9999%), helium (>99.9999%), and 3.0 mol% NO_2 (He balance) were used. The standard gas composition (CH_4: 55.5 mol%, O_2: 27.8 mol%, NO_2: 0.5 mol%, He: balance) was controlled with mass flow controllers. Every feed gas was mixed just before the inlet of the reactor. All the experiments were carried out using a conventional flow reaction system. A quartz-glass tubing reactor (7 mm i.d.) was heated with an electric furnace. The length of heating zone was 100 mm. The temperature of reaction was measured with a thermo-couple attached on the outside wall of the reactor tube at the center part of heating zone.

Furthermore, the feed gas was controlled at 240 ml min^{-1} (STP; SV = 3740 h^{-1}) in every test. The catalysts were fixed with quartz–glass wool at the center of the reactor. The feed gas was supplied from the top of the reactor. Methane conversion was measured as a function of reaction temperatures. Products were analyzed with two on-line gas chromatographs. For measurement of carbon monoxide, carbon dioxide, ethane, ethene, formaldehyde, methanol and nitromethane, Gaskuropack 54 column and FID were used. For methane and oxygen, activated carbon column and TCD were also used. Carbon balance was over 95%. All gas lines from the exit of the reactor to the gas chromatograph were heated at 120°C in order to avoid condensation of oxygenates and water. Data shown in this text were obtained at 30 min or more after beginning the reaction. All experiments were repeated at least three times.

2.4. CH_3OH–O_2 reaction

Highly purified oxygen (>99.9999%) and methanol (0.379%, He balance) were mixed with helium (>99.9999%). The standard gas composition (CH_3OH: 0.24 mol%, O_2: 20.0 mol%, He: balance) was controlled with mass flow controllers. All experiments were carried out with the same reaction system as that in the selective oxidation of CH_4. All reaction conditions and the analysis procedure of products were the same as those in the reactions of CH_4–O_2–NO_2.

3. Results and discussion

The MoO_3 catalysts promoted the methane oxidation using the O_2 and NO_2 mixture of $CH_4/O_2 = 2.0$ and $NO_2 = 0.5\%$ (Fig. 1). The differences in reactivities among the catalysts were small. The reaction temperature giving methane conversion of 10% was 606°C in the absence of catalyst while in the presence of catalysts decreased to 571–578°C. Each curve of methane conversion increased slowly with reaction temperature until it reached a critical point and then increased rapidly. Further increase of reaction temperature decreased the slope of conversion vs. temperature curve. Oxygen concentration at this region should be quite low.

Powder X-ray patterns of all samples agreed completely with that of orthorhombic MoO_3 [12]. No peak shift was observed between the supported and unsupported MoO_3. Table 1 shows surface areas and crystal sizes of the samples. The specific surface areas of unsupported catalysts were less than 5.0 m^2/g. The specific surface area of Mo/SiO_2 was larger than the MoO_3 catalysts, but the crystal size of the supported sample was of similar order as those of the MoO_3 samples.

Table 1
Surface areas and particle sizes for MoO_3 catalysts and silica-supported MoO_3 catalyst

Catalysts	Surface area (m^2/g)	Particle size (Å)
Sample A	2.5	311.2
Sample B	5	285.8
Sample C	0.7	311.2
Mo/SiO_2	81	285.8

Fig. 2 shows product compositions at methane conversion of 10% obtained for the catalysts. Methanol, formaldehyde, and CO were main products, and a little amount of CO_2 and nitromethane were detected. Ethane and ethene were in a trace amount, but both dimethyl ether and methyl formate were hardly observed. In the presence of MoO_3 catalysts, CH_2O selectivity in the C_1-oxygenates increased and CH_3OH selectivity decreased, but total selectivity of C_1-oxygenates in the presence of Sample A slightly exceeded that in the gas-phase reaction. Taylor et al. [13,14] examined methanol oxidation by O_2 on various metal oxide catalysts, and reported that MoO_3 showed a high selectivity to formaldehyde at 500°C.

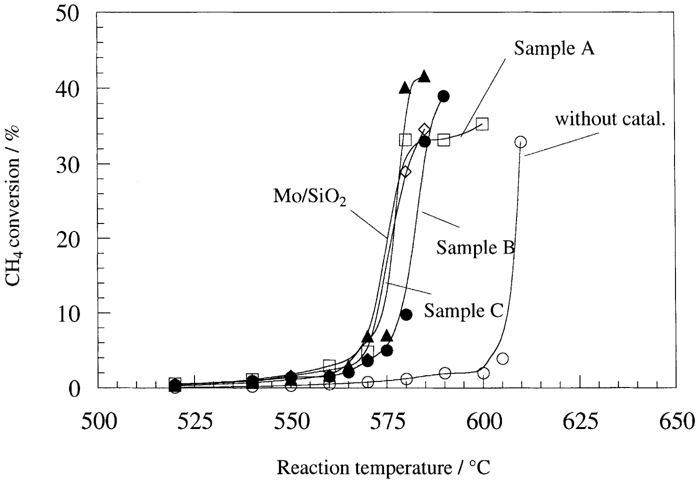

Fig. 1. Methane conversions as a function of reaction temperature. Catalysts: MoO_3 (Samples A, B and C) and silica-supported MoO_3 (Mo/SiO_2). Feed gas composition: CH_4 — 55.5%, O_2 — 27.8%, NO_2 — 0.5%, He — balance; Flow rate: 240 ml min^{-1} (STP); reaction pressure: 0.1 MPa; catalyst weight used: 0.05 g.

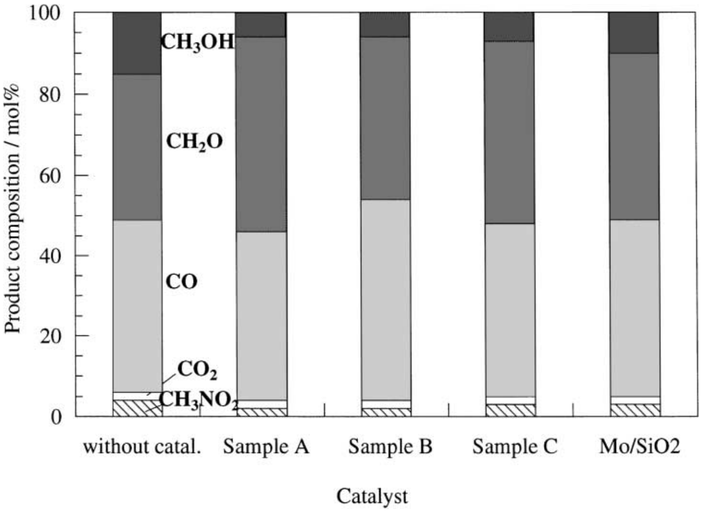

Fig. 2. Product compositions at methane conversion of 10%. Catalysts, feed gas composition, flow rate, reaction pressure and catalyst weight used were the same as those in Fig. 1.

Several reports demonstrated that formaldehyde in methanol oxidation over MoO_3 was formed through methoxide species [15–18].

Figs. 3 and 4 show the dependence of NO_2 concentration on methane activation and the selectivities to CH_3OH, CH_2O and CO for methane selective oxidation in the presence and absence of Sample A. The selectivity in Fig. 4 was determined at methane conversion of 10%. Methane activation was improved with increasing NO_2 concentration both in the presence and absence of MoO_3 (Sample A). Degree of the improvement at the same NO_2 concentration was larger in the reaction on MoO_3 catalyst. Yamaguchi et al. [9] suggested that the initial reaction in hydrogen abstraction

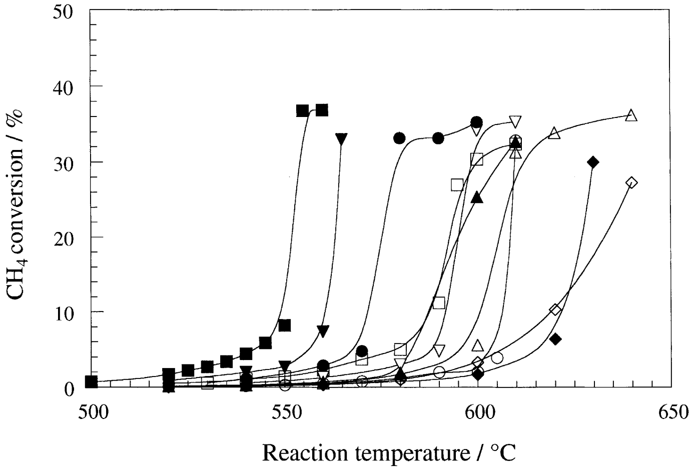

Fig. 3. Methane conversions as a function of reaction temperature in the presence (solid marks) and absence (open marks) of MoO_3 catalyst (Sample A). NO_2 concentration: 0.1% (◆, ◇); 0.2% (▲, △); 0.5% (●, ○); 0.7% (▼, ▽); 1.0% (■ , □). Other reaction conditions were the same as those in Fig. 1.

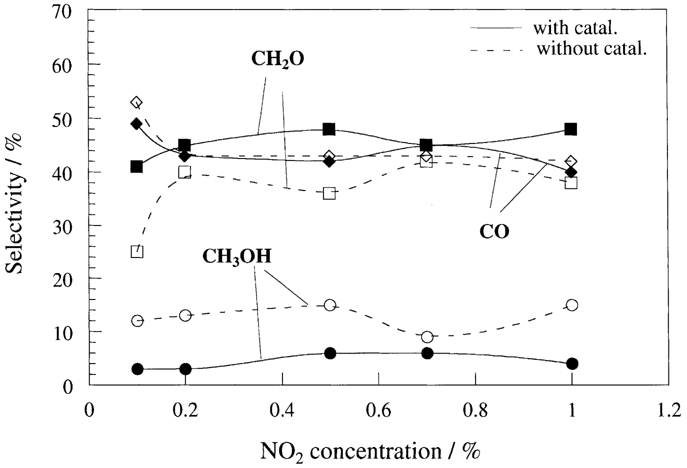

Fig. 4. CH_3OH, CH_2O and CO selectivities as a function of NO_2 concentration in the presence and absence of MoO_3 catalyst (Sample A). The selectivity was determined at methane conversion of 10%. Other reaction conditions were the same as those in Fig. 1.

from methane took place between CH_4 and NO_2. So, it is speculated that the hydrogen abstraction from methane with NO_2 occurs on MoO_3 and the transition barrier of this reaction is reduced largely in comparison to that in the gas-phase reaction.

Since the reaction temperature giving methane conversion of 10% in the presence of MoO_3 was lower than that in the gas-phase reaction, we examined the reaction temperature dependence of conversion and selectivity. CH_3OH selectivity was lowered, but CH_2O selectivity raised in the methane oxidation on MoO_3. CO selectivity was almost unchanged in the presence and absence of MoO_3.

The possibility might be considered that the produced methanol was sequentially oxidized to formaldehyde on MoO_3. However, it could also be possible to assume that formaldehyde formation was enhanced, but methanol formation was retarded in the presence of MoO_3. Further oxidation from formaldehyde to CO was not affected by the presence of MoO_3. Reaction temperature giving methane conversion of 10% with 1.0% NO_2 was 548°C, and this value was lower by 75°C than that with 0.1% NO_2 in the presence of MoO_3 catalyst. CH_2O selectivity at 1.0% NO_2 was slightly higher than that at 0.1% NO_2, but CH_3OH selectivity was almost the same at these two different NO_2 concentrations. C_1-oxygenate selectivity was not affected solely by the difference of reaction temperature.

Concerning the relation between catalyst weight and product composition, both methanol and formaldehyde were oxidized not to CO_2, but to CO with increase of the catalyst weight. The formation of CO_2 hardly changed through the experiments.

Variations in the selectivities to CH_3OH, CH_2O and CO with CH_4/O_2 ratio and the space velocity (SV) are shown in Figs. 5 and 6. The selectivity in Figs. 5 and 6 was determined at methane conversion of 10%. CO selectivity increased and CH_2O selectivity decreased at a high ratio of CH_4/O_2 in the presence of the Sample A. However, CH_3OH selectivity hardly changed with variation in the CH_4/O_2 even in the presence of Sample A, although in a gas-phase reaction the selectivity slightly increased.

CH_2O selectivity increased with increase in SV, but this variation was depressed in the presence of MoO_3 catalyst. Therefore, the formation rate of formaldehyde on MoO_3 catalyst was fast enough not to be affected by the variation in SV. Produced formaldehyde was oxidized to CO on MoO_3 catalyst at a lower SV up to ca. $1500\,h^{-1}$. The variation in CH_3OH selectivity as a function of SV in the presence of MoO_3 catalyst was not obvious.

Formaldehyde formation in the selective oxidation of methane mainly occurred on the catalyst, as suggested in the variations in CH_2O selectivity

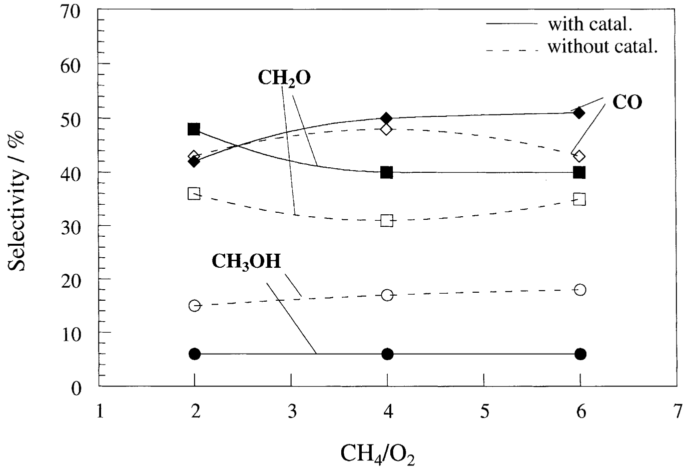

Fig. 5. Dependence of CH_3OH, CH_2O and CO selectivities on the CH_4/O_2 ratio in the presence and absence of MoO_3 catalyst (Sample A). The selectivity was determined at methane conversion of 10%. Other reaction conditions were the same as those in Fig. 1.

(Fig. 6). However, the formation route of methanol in the selective oxidation of methane on MoO_3 catalyst was not clear because the variations in CH_3OH selectivity in Figs. 4–6 were subtle. The decrease in CH_3OH selectivity with increase in the amount of MoO_3 catalyst was clear. This decrease could be derived from the further oxidation of methanol on MoO_3 catalyst. We carried out methanol oxidation on MoO_3 catalyst (Sample A) at the same reaction condition as that in the selective oxidation of methane except for the absence of NO_2. Methanol oxidation proceeded above around 280°C, and it was oxidized not to CO but to formaldehyde. Methanol was almost completely oxidized at the temperatures over 550°C. We concluded that the hydrogen abstraction from methane with NO_2 occurs on MoO_3 and methanol was mainly produced in the gas-phase reaction.

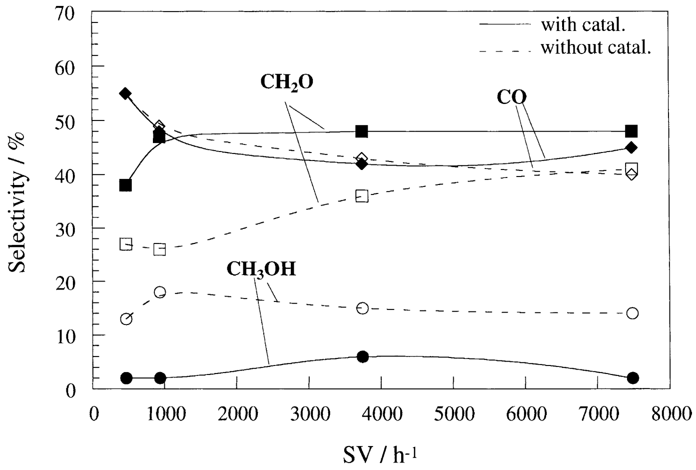

Fig. 6. Dependence of CH_3OH, CH_2O and CO selectivities on SV in the presence and absence of MoO_3 catalyst (Sample A). The selectivity was determined at methane conversion of 10%. Other reaction conditions were the same as those in Fig. 1.

4. Conclusions

Methane activation in the selective oxidation of methane with O_2 and NO_2 mixture was enhanced in the presence of the MoO_3 catalyst. It was clarified that the reaction between CH_4 and NO_2 was more enhanced on MoO_3, compared with that in a gas-phase reaction. In the presence of MoO_3 catalyst, CH_2O selectivity increased and CH_3OH selectivity decreased. From the results mentioned above, it is suggested that formaldehyde was produced on MoO_3 catalyst, and methanol was formed in the gas-phase reaction.

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