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Effects of lowering reaction temperatures in the direct selective oxidation of CH_4–O_2–NO_2–CH_2O

Yonghong Teng [a], Kenji Tabata [a,b,*], Yoichi Yamaguchi [c],
Tetsuya Takemoto [a], Eiji Suzuki [a,b]

[a] Research Institute of Innovative Technology for the Earth, 9-2 Kizugawadai, Kizu-cho, Soraku-gun, Kyoto 619-0292, Japan
[b] Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma, Nara 630-0101, Japan
[c] Kansai Research Institute, Kyoto Research Park 17, Chudoji Minami-machi, Shimogyo-ku, Kyoto 600-8813, Japan

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Abstract

The lowering effects of reaction temperatures on both methane activation and C_1 oxygenates selectivity have been examined for the selective oxidation of methane in the gas-phase reaction of CH_4–O_2–NO_2 with CH_2O addition (CH_2O_{add}) in a feed gas. Formaldehyde addition in the feed gas was effective to enhance methane activation. Reaction temperature was decreased ca. 50 K at 5% level of CH_4 conversion by (CH_2O_{add}) to 1.1% level in the feed gas of CH_4–O_2–NO_2. This decrease was explained by the lowering effects of activation energy for hydrogen abstraction reaction from methane. Formaldehyde selectivity decreased at the same reaction temperature as the CH_2O_{add} concentration in the feed gas was increased. This decrease was explained by the increase of decomposition reaction between produced CH_2O and OH which was produced through CH_2O related reactions. The enhancement of CH_3OH selectivity by the addition of CH_2O in a lower temperature region was observed. It was explained by newly appeared CH_3OH formation route, which was derived from the CH_2O_{add} in the feed gas. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Selective oxidation of methane; Promotion effect of formaldehyde; NO_2; C_1 oxygenates

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1. Introduction

The direct selective oxidation of methane with oxygen to valuable C_1 oxygenates (methanol and formaldehyde) was a potentially important process for the effective use of natural gas resources. Many researchers have studied the direct selective oxidation of methane both in the presence and absence of catalysts. However, the products were mainly CO and CO_2. A trivial amount of CH_3OH and CH_2O was detected in the products [1–14]. The homogeneous gas-phase reaction in the selective oxidation of methane seems to be a superior process to the heterogeneous one to get a higher yield of C_1 oxygenates because the difficulty of desorption from a surface of catalysts is liberated. The rate-determining step of the reaction is the first hydrogen atom abstraction from methane, and this high transition barrier led over-oxidation of C_1 oxygenates in the reaction. Many kinds of initiators have been examined so as to reduce the activation energy of hydrogen abstraction from methane [14–16]. The promotion effects of added nitrogen oxides on the activation of methane in the reaction of CH_4–O_2 have been reported [13,14,17–23]. Otsuka et al. [20] examined the yield of C_1 oxygenates as a function of reaction temperature in the presence and absence

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[*] Corresponding author. Present address: Research Institute of Innovative Technology for the Earth, 9-2 Kizugawadai, Kizu-cho, Soraku-gun, Kyoto 619-0292, Japan. Tel.: +81-774-75-2305; fax: +81-774-75-2318.
E-mail address: kenjt@rite.or.jp (K. Tabata).

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of NO. The addition of NO in the feed gas enhanced clearly the yield of oxygenates. With regard to this enhancement of the yield, they suggested a new reaction path of C_1 oxygenate formation from CH_3ONO:

$$CH_3ONO \rightarrow HCHO + H^{\bullet} + NO \quad (1)$$

Tabata et al. [23] reported the enhancement of both CH_3OH and CH_2O selectivities in the presence of NO_2 in the feed gas. They also theoretically calculated both rate constants and activation energies of selected reaction routes. They calculated the transition barrier of new reaction route of CH_3O formation:

$$CH_3OO + NO \rightarrow CH_3O + NO_2, \quad E_A = -9.7\,\mathrm{kcal/mol} \quad (2)$$

was lower than that of the usual reaction without NO:

$$CH_3OOH \rightarrow CH_3O + OH, \quad E_A = 33.0\,\mathrm{kcal/mol} \quad (3)$$

Furthermore, NO_x ($x = 1, 2$) related formation routes of CH_2O were suggested:

$$CH_3O + NO_2 \rightarrow CH_2O + H\text{–}NO_2, \quad E_A = 6.7\,\mathrm{kcal/mol} \quad (4)$$

$$CH_3O + NO \rightarrow CH_2O + H\text{–}NO, \quad E_A = 5.6\,\mathrm{kcal/mol} \quad (5)$$

They finally suggested that the increase of the selectivities of CH_3OH and CH_2O resulted from the decline of decomposition rate of these oxygenates with OH radicals because the CH_3O formation route was substituted from Eq. (3) for Eq. (2) in the presence of NO. However, the sole effects of lowered reaction temperatures in the presence of NO_x and the effects of newly appeared NO_x related reactions on the C_1 oxygenates selectivities could not explain separately in these studies.

Recently, Teng et al. [24] reported the enhanced effect of methane activation with a small amount of added methanol in the feed gas. CH_3OH selectivity in the products at 5% level of CH_4 conversion increased with added CH_3OH concentration in the feed gas. The difference in reaction temperatures among the different concentrations of methanol addition was not so large (794–812 K). With regard to the higher selectivity of methanol in the products, they suggested that the produced intermediate, HO_2 played an important role:

$$CH_3OH + NO_2 \rightarrow CH_2OH + HNO_2, \quad E_A = 28.4\,\mathrm{kcal/mol} \quad (6)$$

$$CH_2OH + O_2 \rightarrow CH_2O + HO_2, \quad E_A = 0.9\,\mathrm{kcal/mol} \quad (7)$$

$$HO_2 + OH \rightarrow H_2O + O_2, \quad E_A = -0.5\,\mathrm{kcal/mol} \quad (8)$$

The decrease of OH species through Eq. (8) in the reaction gas was assumed to depress the decomposition rate of methanol.

The sole effect of the temperatures on both CH_3OH selectivity and its yield in the gas-phase reaction of CH_4–O_2 was examined at relatively higher pressure conditions [25]. Both selectivity and yield increased with temperatures and passed through a maximum at relatively lower temperature. It was addressed that lower temperatures favored methanol production.

From these results, a lower reaction temperature could be favorable to get a higher yield of C_1 oxygenates. However, the sole effect of lowered reaction temperature in the reaction and the sole effect of the promoter at a lower temperature region on the yield of C_1 oxygenates were not clear. Their relationships were also unclear. We try to separately indicate the sole effect of lowered reaction temperatures and that of a small amount of the CH_2O_{add} as a promoter on CH_3OH and CH_2O selectivities in the products of methane selective oxidation of CH_4–O_2–NO_2. The newly considerable promoter related reaction pathways in the selective oxidation of methane are discussed using theoretical calculations.

2. Experimental

2.1. Activity test

All of the experiments were carried out using a single-pass flow reactor made of a quartz tube with an inside diameter of 7.0 mm at atmospheric pressure. A heated length with an electric furnace was

200 mm. The reaction temperature was controlled from the outside of the quartz tube with a thermocouple at the center position of the heated zone. The total flow rate was $120\,\mathrm{cm}^3\,\mathrm{min}^{-1}$ (STP) and the space velocity (SV) was $940\,\mathrm{h}^{-1}$. SV was calculated by dividing the gas flow volume per 1 h at 298 K and at 1 bar by the volume of vacant heated zone of the reactor. An activity test was carried out with a mixing gas of highly purified CH_4 (99.9995%, Air Liquide, Japan), O_2 (99.995%, Air Liquide, Japan), NO_2 (0.298%, He balance, Sumitomo Seika Chemicals), formaldehyde and He (99.9999%, Nippon Sanso). The 0.14% formaldehyde in the reaction gas was prepared by oxidizing higher concentration of methanol provided from a 0.38% methanol cylinder (He balance, Sumitomo Seika Chemicals). High concentrations for added formaldehyde (>0.14%) were produced by the oxidation of passing He gas through liquid methanol (99.7% Kanto Chemicals). The oxidation of methanol was carried out at 573 K with a synthesized MoO_3 (85%)–Fe_2O_3 (15%) catalyst by co-precipitation procedure [26]. Produced CH_2O from liquid methanol was purified through $CaCl_2$ (Extra pure grade, Wako Chemicals). We obtained 86% formaldehyde after this treatment. The standard gas composition was CH_4 (28.00%), O_2 (14.00%), NO_2 (0.50%), CH_2O (0.14%) and He (57.36%). All of the reaction lines from the exit of reactor up to the inlet of gas chromatographs were heated at 393 K to avoid the condensation of oxygenates and water. For checking the temperature increase before and after the addition of formaldehyde, a thermocouple covered by a quartz tube was set on the inside of the reactor. Products were analyzed with two on-line gas chromatographs serially connected. The carbon balance before and after the reaction exceeded 98%. Each measurement of product gas was conducted after the run for 30 min under each condition. Conversion and selectivity were calculated as follows (in mol):

$$CH_4\ \text{conversion} = \frac{\text{initial}\ CH_4 - \text{final}\ CH_4}{\text{initial}\ CH_4}$$

$$\text{Selectivity of product} = \frac{\text{product}}{\text{reacted}\ CH_4}$$

$$\text{Selectivity of}\ CH_2O = \frac{\text{total}\ CH_2O}{\text{reacted}\ CH_4}$$

2.2. Method of calculations

Calculations were carried out with the GAUSSIAN 94 ab initio program package [27]. The geometrical optimization for all the molecules present was performed with the MP2 (frozen core) level of theory and a 6-311++G(2d, p) basis set. On the basis of the optimized geometries, single point calculations of the energies were carried out at the CCSD(T)/6-311++G(2d, p) level with the zero-point energy (ZPE) corrections of the MP2 level. All the optimized geometries corresponding to a local minimum point have real frequencies, except for a transition state with one imaginary frequency. Thermal rate constants for all the present elementary reactions at 800 K and 1 atm were also estimated using the calculated results of MP2 and CCSD(T) levels of theory. Thermal rate constants for all the present elementary reactions at 800 K and 1 atm were also estimated using the calculated results of MP2 and CCSD(T) levels of theory. A Silicon Graphics Origin 2000 R10000 workstation was used for the calculations in this study.

3. Results

Methane activation was enhanced with the addition of CH_2O_{add} in a feed gas (Fig. 1). However, the reactivity did not always increase with the percentage of CH_2O_{add} in a feed gas. Methane conversion with 0.83% CH_2O_{add} was lower in comparison to that with 0.57% CH_2O_{add} in a feed gas. The reactivity at 773 K for the reaction gas with 1.1% CH_2O_{add} and that of 823 K for the reaction gas with 0.14% CH_2O_{add} in the feed gas were almost the same.

We examined the conversion of sole CH_2O_{add} as a function of reaction temperature in the mixed feed gas of CH_2O, O_2 and NO_2 so as to consider the effects of the mixing of CH_2O_{add} in the feed gas on the products (Fig. 2). CH_2O_{add} in the range of 0.14–1.74% in a feed gas was completely oxidized over 800 K with a small amount of NO_2 (0.5%) in O_2 (14.0%). Therefore, CH_2O measured in the region over 800 K should be the produced one during the reaction. The large difference between CH_2O_{add} conversions in the presence and absence of a small amount of NO_2 suggested that CH_2O_{add} oxidation could be initiated by the reaction between CH_2O_{add} and NO_2. The difference of reaction

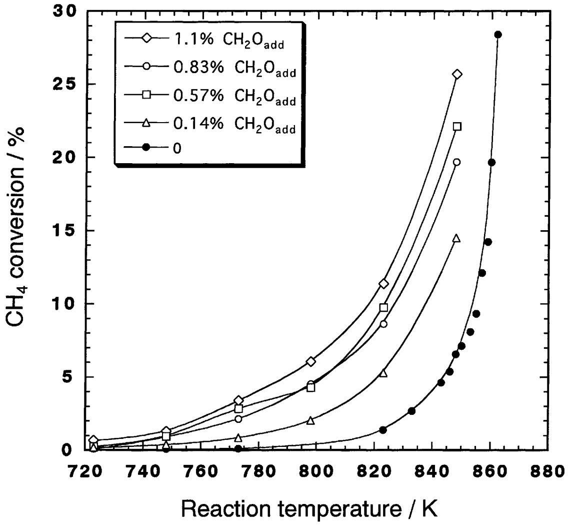

Fig. 1. The effects of formaldehyde concentration on methane conversion as a function of reaction temperature. Values shown in the figure represent the formaldehyde concentration in the reaction gas. The standard reaction gas consisted of CH_4 (28%)–O_2 (14%)–NO_2 (0.5%) with different concentrations of formaldehyde (He balance).

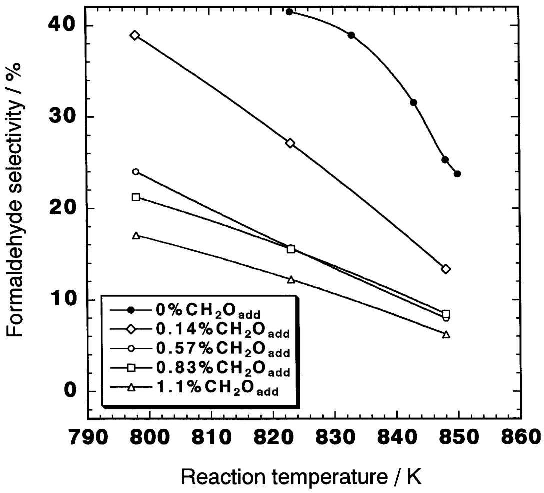

Fig. 3. Formaldehyde selectivity as a function of reaction temperature. Values shown in the figure represent the formaldehyde concentration in the reaction gas. The standard reaction gas consisted of CH_4 (28%)–O_2 (14%)–NO_2 (0.5%) with different concentrations of formaldehyde (He balance).

temperature with and without the addition of formaldehyde during the experiment was measured with the thermocouple set inside the reactor. The thermocouple was covered with a quartz tube, and it was set at the center part of the inside of the reactor. Temperature at the center part of the inside of reactor was raised lower than 2 K through the addition of 1.1% CH_2O_{add} in comparison to that without CH_2O_{add}. Therefore, the enhancement of CH_4 conversion in Fig. 1 cannot be explained solely by the temperature rise.

The variation of formaldehyde selectivity as a function of reaction temperature was examined for a variety of CH_2O_{add} concentrations in the feed gas (Fig. 3). The selectivity of CH_2O increased as the reaction

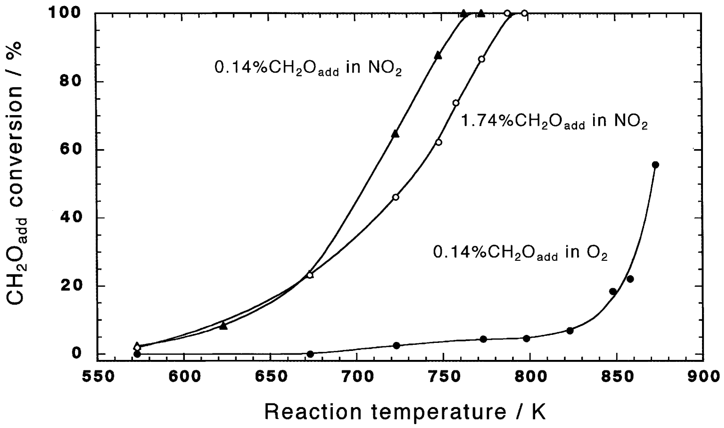

Fig. 2. Formaldehyde conversion obtained in the presence and absence of NO_2. The standard reaction gas consisted of CH_2O (0.14 or 1.74%)–O_2 (14%)–NO_2 (0.5%)–He (balance).

temperature decreased at every CH_2O_{add} concentration. This indicates that lower temperatures were favorable condition to enhance the selectivity of CH_2O. In the case of the reaction without CH_2O_{add}, the lower region than 820 K was not able to indicate the selectivity because the value of CH_4 conversion was too small (see Fig. 1). Observed formaldehyde selectivity for the reaction in the absence of CH_2O_{add} had the highest value is the lower region than 820 K. Slope of formaldehyde selectivity decreased as the concentration of CH_2O_{add} increased. All detected CH_2O in the products above 800 K was assumed to be produced one through the reaction because all the CH_2O_{add} was completely oxidized up to 800 K as shown in Fig. 2. Each concentration of produced CH_2O through the reaction (CH_2O_{add}: 1.1%) was 1.0% at 798 K (CH_4 conversion: 6.0%), 1.4% at 823 K (CH_4 conversion: 11.4%), and 1.6% at 848 K (CH_4 conversion: 26.0%), respectively.

The variation of methanol selectivity with reaction temperature in the absence and presence of CH_2O_{add} was shown in Fig. 4. In the absence of CH_2O_{add}, the variation of CH_3OH selectivity was quite different from that of formaldehyde selectivity. CH_3OH selectivity had a peak at around 845 K, then decreased in a higher region than this reaction temperature. In the presence of the CH_2O_{add}, this trend of decrease in methanol selectivity was similar at 0.14% CH_2O_{add}. CH_3OH selectivities at 798 K were raised as the concentration of CH_2O_{add} was increased over 0.14%. Therefore, the addition of formaldehyde in the feed gas was favorable to enhance methanol selectivity in the products at a lower temperature region.

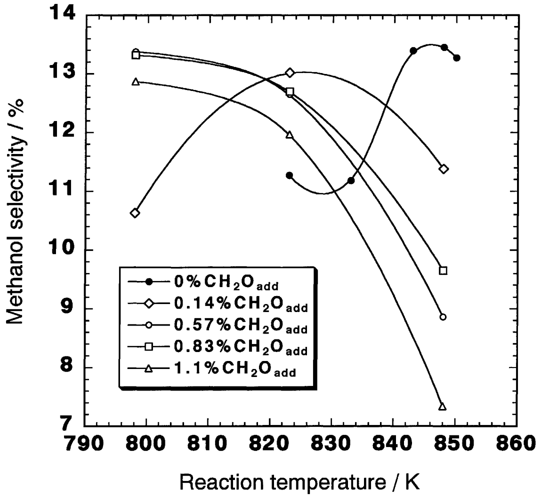

Fig. 4. Methanol selectivity as a function of reaction temperature. Values shown in the figure represent the formaldehyde concentration in the reaction gas. The standard reaction gas consisted of CH_4 (28%)–O_2 (14%)–NO_2 (0.5%) with different concentrations of formaldehyde (He balance).

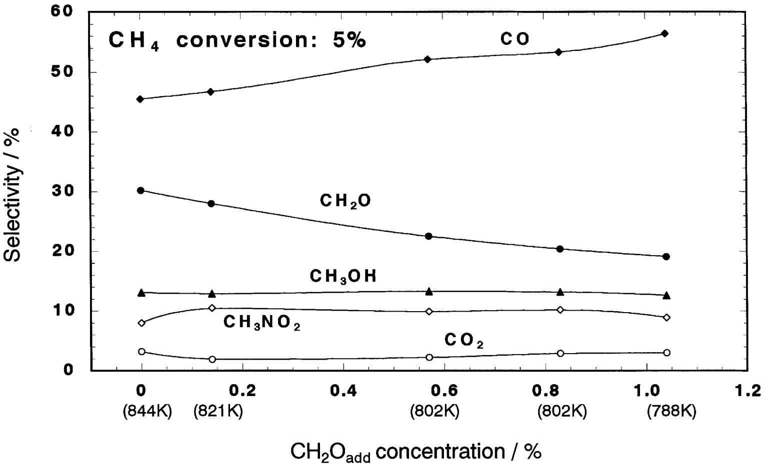

Fig. 5. The effects of formaldehyde concentration on selectivity of products at methane conversion of 5%. The standard reaction gas consisted of CH_4 (28%)–O_2 (14%)–NO_2 (0.5%) with different concentrations of formaldehyde (He balance). The reaction temperatures at each formaldehyde concentration are shown in parentheses.

The selectivity variations of all the products at 5% level of CH_4 conversion were shown as a function of CH_2O_{add} concentration in the feed gas so as to indicate the roles of the promoter in the reaction (Fig. 5). Each reaction temperature at every examined CH_2O_{add} concentration was listed in the figure. The selectivity of CO increased and that of CH_2O decreased with the CH_2O_{add} concentration in the feed gas. The selectivities of other products, i.e. CH_3OH, CH_3NO_2 and CO_2 were hardly affected by the concentration of CH_2O_{add}. It was assumed that produced CH_2O during the reaction was gradually oxidized to CO as CH_2O_{add} in the feed gas was increased. The total yield of C_1 oxygenates in the absence of CH_2O_{add} promoter in the feed gas had the highest value, although the measured temperature showed the highest value in the reaction without CH_2O_{add} promoter.

4. Discussion

Concerning the reason of enhancement of methane activation using CH_2O_{add} as a promoter, we considered that the activation energy of hydrogen abstraction from CH_4 was decreased. We assumed that the methane selective oxidation in the feed gas of CH_4–O_2–NO_2–CH_2O started from the reaction between formaldehyde and NO_2 as suggested from Fig. 2. Suggested reactions were as follows:

$$CH_2O + NO_2 \rightarrow CHO + HONO \qquad (9)$$

or

$$CH_2O + NO_2 \rightarrow CHO + H\text{–}NO_2 \qquad (10)$$

The experimentally obtained value of transition barrier of Eq. (9) was 16.1 kcal/mol [28]. We carried out theoretical calculations on the transition barriers of reaction (10) with ab initio procedures, because we could not find out that of Eq. (10) as far as we examined. Fig. 6 illustrates the optimized geometry of the transition state (TS 1) with the C_1 structure and the potential energy diagram for the reaction (10). The total energy of $CH_2O + NO_2$ was taken as a standard. In TS 1, the transition vector was located at a mode related to the abstracted hydrogen atom. The calculated transition barrier of reaction (10) was higher than that of reaction (9). The calculated rate constant at 800 K is summarized in Table 1. The data were calculated by using the conventional TS theory. The level of the theory maybe affected the predicted value. The difference of activation energies between Eqs. (9) and (10) may be too small to discriminate. Therefore, we assumed that both reactions progressed as the initial reaction in the feed gas of CH_4–O_2–NO_2–CH_2O.

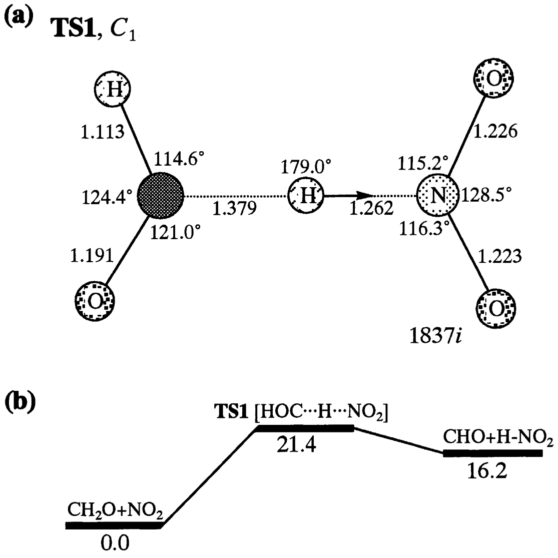

Fig. 6. Optimized geometries and potential energy diagram for the CH_2O+NO_2 reaction. The total energy for the separated reactants $CH_2O + NO_2$ is −318.9820 hartrees. Relative energies are given in kcal/mol.

The CHO produced was assumed to react subsequently with oxygen as shown below

$$CHO + O_2 \rightarrow CO + HO_2 \qquad (11)$$

The reported activation energy of the above reaction is 0 kcal/mol [4,14], so there was no transition barrier to cross. The HO_2 radical produced in reaction (11) was assumed to play a very important role in the activation

Table 1
Calculated rate constants, k and activation energies, E_A at 800 K[a]

Reaction	k	E_A
$CH_2O + NO_2 \rightarrow CHO + H\text{–}NO_2$	4.8×10^{-18}	25.7
$CH_4 + HO_2 \rightarrow CH_3 + H_2O_2$	1.0×10^{-18}	29.5
$CH_4 + NO_2 \rightarrow CH_3 + H\text{–}NO_2$[b]	5.4×10^{-20}	37.6

[a] Rate constants are given in $cm^3\,molecule^{-1}\,s^{-1}$, activation energies are given in kcal/mol.

[b] Data from Ref. [30].

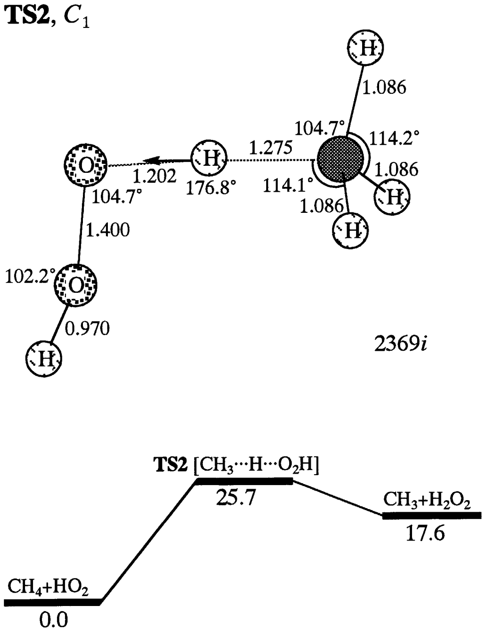

Fig. 7. Optimized geometries and potential energy diagram for the $CH_4 + HO_2$ reaction. The total energy for the separated reactants $CH_4 + HO_2$ is −191.0138 hartrees. Relative energies are given in kcal/mol.

of methane as shown below

$$CH_4 + HO_2 \rightarrow CH_3 + H_2O_2 \tag{12}$$

The reported activation energy of reaction (12) is 24.6 kcal/mol [2,4,14,29]. Since this value was quite important to consider the activation energy of CH_4, we carried out theoretical calculations on the transition energies of reaction (12) with the ab initio procedures. Fig. 7 illustrates the optimized geometry of the TS 2 with the C_1 structure and the potential energy diagram for the reaction (12). The total energy of $CH_4 + HO_2$ was taken as a standard. The predicted value of transition barrier was 25.7 kcal/mol and this value was very close to the reported one (24.6 kcal/mol). This value was lower than the calculated activation energy of hydrogen abstraction from methane with NO_2 (37.6 kcal/mol) [30]:

$$CH_4 + NO_2 \rightarrow CH_3 + H\text{–}NO_2 \tag{13}$$

The calculated rate constant of reaction (12) at 800 K is shown together with that of reaction (13) in Table 1. The rate constant for the reaction (12) was larger than that for the reaction (13). Therefore, the enhancement effects of the CH_2O_{add} on methane conversion were assured to be due to the lower barrier of hydrogen abstraction from methane by HO_2. Furthermore, this small barrier was also assumed to enable the starting temperature of methane activation to be lowered.

Concerning the variation of formaldehyde selectivity in CH_4–O_2–NO_2 without CH_2O_{add}, the selectivity was raised up in a lower temperature region (Fig. 3). We assumed that the rate of CH_2O oxidation by O_2 during the reaction

$$CH_2O + O_2 \rightarrow HO_2 + HCO, \quad E_A = 40\,\text{kcal/mol} \tag{14}$$

was lowered in a lower temperature region. Concerning the reason why formaldehyde selectivities in the products decreased at the same temperature as CH_2O_{add} promoter was increased in the feed gas, we considered as follows. The produced CHO in the reactions (9) and (10) was partly dissociated by the reaction with the third body such as the reactor wall as CHO increased in the reaction gas [28]:

$$CHO + M \rightarrow H + CO + M, \quad E_A = 17\,\text{kcal/mol} \tag{15}$$

The increase of CHO was derived from that of CH_2O_{add} concentration in the feed gas as shown in reactions (9) and (10). The H radical was assumed to react with HO_2, which was produced in reaction (11):

$$H + HO_2 \rightarrow 2OH, \quad E_A = 0.6\,\text{kcal/mol} \tag{16}$$

The increase of OH species in the reaction gas decreased CH_2O selectivity with reaction (17):

$$CH_2O+OH \rightarrow CHO+H_2O, \quad E_A = -0.4\,\text{kcal/mol} \tag{17}$$

The slope of CH_2O selectivities decreased as CH_2O_{add} concentration in the feed gas was raised up (Fig. 3). This variation of the slope could also be explained with the same increase of OH species through reactions (15) and (16), because the transition barrier of reaction (17) was −0.4 kcal/mol.

Methanol selectivity for the reaction in the absence of CH_2O_{add} in the feed gas had a maximum point, and then decreased (Fig. 4). The main route of methanol

Table 2
Calculated rate constants, k and activation energies, E_A at 800 K[a]

No.	Reaction	k	E_A
Formation			
(4)	$CH_3O + NO_2 \rightarrow CH_2O + H–NO_2$	1.6×10^{-17}	6.7
(5)	$CH_3O + NO \rightarrow CH_2O + H–NO$	9.3×10^{-16}	5.6
(18)	$CH_3O + CH_4 \rightarrow CH_3OH + CH_3$[b]	1.0×10^{-15}	11.0
(20)	$CH_3O + H_2O_2 \rightarrow CH_3OH + HO_2$[b]	2.0×10^{-14}	4.0
Decomposition			
(9)	$CH_2O + NO_2 \rightarrow CHO + H–NO_2$	4.8×10^{-18}	25.7
(14)	$CH_2O + O_2 \rightarrow CHO + HO_2$[c]	2.1×10^{-21}	40.0
(17)	$CH_2O + OH \rightarrow CHO + H_2O$[c]	2.0×10^{-11}	−0.4
(15)	$CHO + M \rightarrow H + CO + M$[b]	9.4×10^{-15}	17.0
(19)	$CH_3OH + OH \rightarrow CH_2OH + H_2O$[b]	2.4×10^{-12}	1.4

[a] Rate constants are given in $cm^3 molecule^{-1} s^{-1}$, activation energies are given in kcal/mol.
[b] Data from Ref. [11].
[c] Data from Ref. [14].

production in the gas-phase reaction was suggested as the reaction between CH_3O and CH_4 [23]:

$$CH_3O + CH_4 \rightarrow CH_3OH + CH_3, \quad E_A = 11.0\,\text{kcal/mol} \tag{18}$$

The rate of this reaction could be decreased in a lower temperature region. Concerning the reason why methanol selectivities in the products decreased at the same temperature as CH_2O_{add} promoter was increased in the feed gas, we suggested the same reason for the case of CH_2O selectivity in Fig. 3. The increase of OH species in the reaction gas decreased CH_3OH selectivity with reaction (19):

$$CH_3OH + OH \rightarrow CH_2OH + H_2O, \quad E_A = 1.4\,\text{kcal/mol} \tag{19}$$

CH_3OH selectivity in a lower temperature region was enhanced with the addition of CH_2O_{add} in the feed gas. We considered that a new reaction route for methanol production was occurred by the addition of CH_2O_{add} in the feed gas because the variation of CH_3OH selectivity in this region was largely enhanced as CH_2O_{add} increased. We suggested the reaction between CH_3O and H_2O_2 [23]:

$$CH_3O + H_2O_2 \rightarrow CH_3OH + HO_2, \quad E_A = 4.0\,\text{kcal/mol} \tag{20}$$

H_2O_2 was produced in reaction (12). Since H_2O_2 concentration should be increased with CH_2O_{add} concentration in the feed gas, the slope of CH_3OH selectivity was increased with CH_2O_{add} concentration. Table 2 shows the rate constants of formation and decomposition reaction of C_1 oxygenates. In the start of the reaction in $CH_4–O_2–NO_2–CH_2O_{add}$, the decomposition of formaldehyde, Eq. (9), is the main reaction, and the formation of C_1 oxygenates and the decomposition of C_1 oxygenates with radical are the subsequent reactions.

5. Conclusions

Formaldehyde addition in the feed gas was effective to enhance methane activation for the selective oxidation of methane in $CH_4–O_2–NO_2$. Reaction temperature was decreased ca. 50 K at 5% level of CH_4 conversion by CH_2O_{add} addition at 1.1% level in the feed gas in comparison to that without CH_2O_{add} promoter. Formaldehyde selectivity decreased at the same reaction temperature as CH_2O_{add} concentration in the feed gas was increased. This decrease was explained by the increase in the reaction between produced CH_2O and OH which was produced through CH_2O related reactions. The enhancement of CH_3OH selectivity by the addition of CH_2O_{add} in a lower temperature region was explained by the new CH_3OH formation route, which was derived from CH_2O_{add} in the feed gas. A lower reaction temperature was favorable to get a higher yield of C_1 oxygenates, although newly appeared promoter related reactions affected the selectivity of C_1 oxygenates.

Acknowledgements

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