

# Enhancement effects of methanol on the reactivity for methane partial oxidation in the gas phase reaction of CH<sub>4</sub>-O<sub>2</sub>-NO<sub>2</sub>

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The partial oxidation of methane in the gas phase reaction of CH<sub>4</sub>-O<sub>2</sub>-NO<sub>2</sub> was enhanced with the addition of a small amount of methanol; the selectivity of methanol at the same level of CH<sub>4</sub> conversion was enhanced in the presence of methanol which showed this effect exclusively in the presence of NO<sub>2</sub>.

Methanol is a desirable product in the partial oxidation of methane. Recently, we found high yield methanol formation at 808 K under atmospheric pressure in the gas phase reaction of CH<sub>4</sub>-O<sub>2</sub> upon the addition of a small amount of NO<sub>x</sub> (*x* = 1,2).<sup>1,2</sup> The transition barrier energy of hydrogen atom abstraction from CH<sub>4</sub> by NO<sub>2</sub> was lower than that by O<sub>2</sub>.<sup>3,4</sup> This brought about the enhancement effect of NO<sub>2</sub> on the reactivity of methane in CH<sub>4</sub>-O<sub>2</sub>-NO<sub>2</sub>. Since successive oxidation of the produced methanol has been reported at high temperatures for the CH<sub>4</sub>-O<sub>2</sub> gas phase reaction,<sup>5,6</sup> the successive oxidation of methanol could also occur in the CH<sub>4</sub>-O<sub>2</sub>-NO<sub>x</sub> gas phase reaction. The initial hydrogen atom abstraction is the first step of successive oxidation of methanol that probably initiates radical chain reactions to enhance methane partial oxidation, since Burch and co-workers<sup>5</sup> reported that the addition of C<sub>2</sub>H<sub>6</sub> lowered the reaction temperature by *ca.* 50 K at the same conversion of CH<sub>4</sub> for the gas phase reaction of CH<sub>4</sub>-O<sub>2</sub>. On the other hand, it was found in our previous study that the selectivity of the produced methanol was scarcely affected by a change of space velocity at a given temperature.<sup>1,2,4</sup> This indicates that methanol could be a fairly stabilized product in the gas phase. In addition, gaseous additives have been examined under high pressure so far,<sup>7-9</sup> but an enhancement effect of methanol was not found. Therefore it is important to clarify the behavior of methanol in the gas phase reaction of CH<sub>4</sub>-O<sub>2</sub>-NO<sub>2</sub>. In this study, a small amount of methanol was added to the CH<sub>4</sub>-O<sub>2</sub>-NO<sub>2</sub> system to investigate its effects on the partial oxidation of methane in the gas phase.

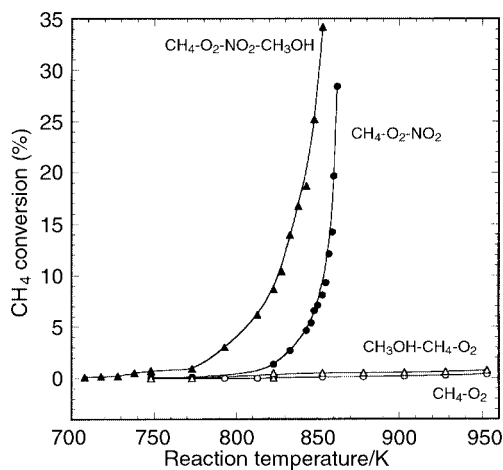
The reaction was carried out with using a test gas (CH<sub>4</sub>: 28%, O<sub>2</sub>: 14%, NO<sub>2</sub>: 0.5%, He: 57.3 or 57.5%, CH<sub>3</sub>OH: 0 or 0.16%). A quartz tube (7 mm i.d.) was used as a reactor and the length of heated reaction zone was 200 mm. The temperature was measured with a thermocouple attached on the outside of the reactor. Products were analyzed with two gas chromatographs. The carbon balance before and after the reaction exceeded 98%. Each reaction was performed for 30 min under each of the conditions and then the products were analyzed. All experimental data shown here were shown to be reproducible. Conversion and selectivities were calculated as follows (unit is mol): CH<sub>4</sub> conversion = (initial CH<sub>4</sub> - final CH<sub>4</sub>)/initial CH<sub>4</sub>; selectivity of a product = product/reacted CH<sub>4</sub>; selectivity of methanol = total methanol/reacted CH<sub>4</sub>.

Fig. 1 shows CH<sub>4</sub> conversion in each different reaction gas mixture as a function of reaction temperature. The temperature at the level of 10% CH<sub>4</sub> conversion is lowered by *ca.* 30 K (827 K) with addition of methanol (0.16%) to CH<sub>4</sub>-O<sub>2</sub>-NO<sub>2</sub>. CH<sub>4</sub> conversion was scarcely observed at 827 K for both CH<sub>4</sub>-O<sub>2</sub> and CH<sub>4</sub>-O<sub>2</sub>-CH<sub>3</sub>OH systems. These differences indicate that

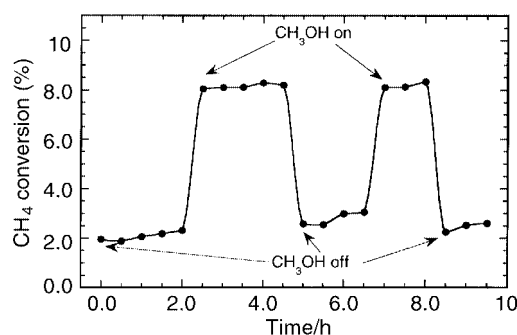
the decrease of reaction temperature is derived from the presence of both CH<sub>3</sub>OH and NO<sub>2</sub> in the reaction mixture. The enhancement effects of CH<sub>3</sub>OH are clearly seen on an ON-OFF experiment for the supply of methanol (Fig. 2). An increase of reaction temperature after the addition of methanol was observed but amounted to < 3 K in the center of the reactor.

On varying the methanol concentration, it was found that 0.016% CH<sub>3</sub>OH was the lower limit for which CH<sub>4</sub> conversion was enhanced.

The selectivity of CH<sub>3</sub>OH for the reaction in the presence of methanol is higher than that without methanol in the lower conversion region (Table 1). The selectivity of CH<sub>2</sub>O in the system CH<sub>4</sub>-O<sub>2</sub>-NO<sub>2</sub>-CH<sub>3</sub>OH had somewhat smaller values in the same region. The selectivity of CH<sub>3</sub>OH in the presence of methanol exceeded that in the absence of CH<sub>3</sub>OH for the regions of CH<sub>4</sub> conversion shown in Table 1.



**Fig. 1** CH<sub>4</sub> conversion vs. reaction temperature. Reaction gas: CH<sub>4</sub>(28%)–O<sub>2</sub>(14%)–NO<sub>2</sub>(0.5%)–He(57.3%)–CH<sub>3</sub>OH(0.16%) (▲), CH<sub>4</sub>(28%)–O<sub>2</sub>(14%)–NO<sub>2</sub>(0.5%)–He(57.5%) (●), CH<sub>4</sub>(28%)–O<sub>2</sub>(14%)–He(57.8%)–CH<sub>3</sub>OH(0.16%) (△), CH<sub>4</sub>(28%)–O<sub>2</sub>(14%)–He(58%) (○).



**Fig. 2** The enhancement effect of CH<sub>3</sub>OH on CH<sub>4</sub> conversion in CH<sub>4</sub>-O<sub>2</sub>-NO<sub>2</sub>. 0.16% CH<sub>3</sub>OH was fed into the reaction gas consisting of CH<sub>4</sub>(28%)–O<sub>2</sub>(14%)–NO<sub>2</sub>(0.5%)–He(57.5%).

**Table 1** The effects of methanol addition on methane partial oxidation in the presence of NO<sub>2</sub><sup>a</sup>

	T/K	CH <sub>4</sub> conversion (%)	Selectivity (%)				
			HCHO	CH <sub>3</sub> OH	CH <sub>3</sub> NO <sub>2</sub>	CO	CO <sub>2</sub>
Without CH <sub>3</sub> OH	831	2.3	38.0	11.7	10.8	33.5	6.0
	846	5.6	27.3	13.1	8.2	48.2	3.2
	851	8.1	19.8	13.1	8.0	55.9	3.1
	857	12.1	11.3	11.9	6.2	66.7	3.9
With CH <sub>3</sub> OH	788	2.3 (0.3) <sup>b</sup>	29.1	18.8	11.7	35.1	5.3
	810	5.6 (0.7) <sup>b</sup>	25.0	17.1	11.9	42.3	3.7
	820	8.1 (2.3) <sup>b</sup>	19.6	15.7	11.1	50.4	3.2
	830	12.1 (5.6) <sup>b</sup>	14.0	14.0	7.4	60.7	3.9

<sup>a</sup> Reaction gas: CH<sub>4</sub>(28.0%)–O<sub>2</sub>(14.0%)–NO<sub>2</sub>(0.5%)–He(57.3 ~ 57.5%), with or without 0.16% CH<sub>3</sub>OH. <sup>b</sup> Values in parentheses are CH<sub>4</sub> conversion before CH<sub>3</sub>OH addition.

It is of note that >99% methanol was oxidized to CO and CO<sub>2</sub> in the CH<sub>3</sub>OH–O<sub>2</sub>–NO<sub>2</sub> system in the absence of methane below 750 K. Since all of the added methanol was completely oxidized up to 750 K, the obtained methanol in the CH<sub>4</sub>–O<sub>2</sub>–NO<sub>2</sub>–CH<sub>3</sub>OH system was assumed to be produced through the partial oxidation of methane. This indicates that the enhancement of reactivity of CH<sub>4</sub> in CH<sub>4</sub>–O<sub>2</sub>–NO<sub>2</sub>–CH<sub>3</sub>OH above 750 K was caused by reaction between NO<sub>2</sub> and CH<sub>3</sub>OH.

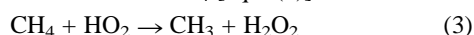
In previous papers, we suggested reaction pathways to form C<sub>1</sub>-oxygenates in the gas phase reaction of CH<sub>4</sub>–O<sub>2</sub>–NO<sub>2</sub>.<sup>1–4</sup> The rate-determining step is hydrogen abstraction from methane with an activation energy of 37.6 kcal mol<sup>–1</sup> at 800 K. The lowering of the initial reaction temperature upon CH<sub>3</sub>OH addition indicated the presence of other lower barrier reaction pathways for the dissociation of methane. Furthermore, the enhancement of CH<sub>4</sub> conversion indicated the presence of radical chain reactions. We considered the most probable reaction between CH<sub>3</sub>OH and NO<sub>2</sub> [eqn. (1)]:



Our theoretically obtained value for the activation energy of eqn. (1) was 28.4 kcal mol<sup>–1</sup> at 800 K calculated using the Gaussian94 *ab initio* program package and was close to that reported by Bromly *et al.*<sup>10</sup> The produced CH<sub>2</sub>OH was assumed to react easily with O<sub>2</sub> to produce formaldehyde [eqn. (2)]:



This HO<sub>2</sub> could then react with CH<sub>4</sub> [eqn. (3)]:



Since the reported<sup>10</sup> activation energy of eqn. (3) was 24.6 kcal mol<sup>–1</sup> and is lower than 37.6 kcal mol<sup>–1</sup> for the activation

energy of hydrogen abstraction from methane, we considered that this difference lowered the commencement temperature of CH<sub>4</sub> conversion.

The higher selectivity of produced methanol is explained by assuming that the subsequent oxidation of methanol is retarded under the reaction conditions.

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