Effect of the Addition of Nitrogen Dioxide on the Gas-Phase Partial Oxidation of Methane with Oxygen under Normal Pressures

Li-Biao Han,* Susumu Tsubota, and Masatake Haruta*
Department of Energy and the Environment, Osaka National Research Institute, AIST, Midorigaoka 1-8-31, Ikeda 563

(Received July 4, 1995)

The addition of NO_2 to the gas-phase reaction of CH_4 with O_2 conducted under normal pressures at temperatures of 400~460 °C enhances the partial oxidation of methane with improved selectivities to organic products.

The selective partial oxidation of CH_4 with O_2 to organic oxygenates (MeOH and HCHO) is one of the most challenging topics in chemistry today.[1] Gas-phase radical reaction of CH_4 with O_2 under even normal pressures affords these products.[2] Unfortunately, however, good yields were hardly obtained from this reaction because selectivities of the products sharply decreased as methane conversions increased. Taking into consideration of the mechanisms both for the formation and decomposition of the organic oxygenates in these radical reactions,[1] we conceived that this problem might be solved by introducing a third compound, which serves as a radical scavenger, to the reaction system. It was expected that radicals attacking methanol and formaldehyde forming COx might be trapped by this compound yielding other organic products, as a result a good total selectivity of the organic products should be achieved even at a relatively high CH_4 conversion level.

Nitrogen dioxide was chosen as a candidate for this purpose because (a) it is a radical itself and is able to rapidly trap radicals such as Me•, MeO_2•, MeO•, HO_2•, which are involved in the gas-phase reactions of CH_4 with O_2,[3] and (b) products from NO_2 (RNO_2) can be possibly transformed to other organic oxygenates ($C_xH_yO_z$) with the regeneration of NO_2,[4] i.e. as a whole only a catalytic amount of NO_2 was required (Scheme 1). Our proposal has been proven to be true. Herein we communicate our results.

Scheme 1.

$$\text{(1)}\quad CH_4 + O_2 \longrightarrow MeOH + HCHO + CO_x + R\bullet$$

$$\text{(2)}\quad R\bullet + NO_2 \longrightarrow RNO_2 \dashrightarrow C_xH_yO_z + NO_2$$

R = radicals involved in (1)

For the convenience of conducting the experiment, nitric acid was chosen as the NO_2 source first.[5] The reaction was performed under normal pressures by bubbling a well mixed CH_4/O_2 gas through nitric acid in a glass container kept at a fixed temperature, and then introducing these gases to a quartz reactor which was heated by a computer-controlled electric furnace.[6]

The results are summarized in Table 1. While the major organic products in the gas-phase reaction of CH_4 with O_2 in the absence of NO_2 were MeOH and HCHO (run 1), a significant amount of $MeNO_2$ was additionally formed when HNO_3 was introduced.[7] It is clear that both CH_4 conversions and total organic product selectivities were improved by the addition of HNO_3. At 430 °C, CH_4 conversion and the total organic product selectivity in run 1 were 1.1 and 62%, respectively. The values increased to 1.3 and 67% when 60% HNO_3 was introduced at 20 °C (run 2), and further to 2.1 and 67%, respectively, when HNO_3 was introduced at 60 °C (run 3). Since at a fixed CH_4 conversion, little difference in selectivities to MeOH and HCHO was observed among runs 1, 2 and 3, the formation of $MeNO_2$ greatly contributed to the above improvements in oxygenates formation. Its fraction in the products increased as more HNO_3 was introduced (runs 2 and 3).

Table 1. Gas-phase reaction of CH_4 with O_2 in the presence of HNO_3

run	conditions[a]	temp (°C)	CH_4 conv.[b]	% product selectivity[b] MeOH	HCHO	$MeNO_2$	whole[c]
1	2.6% O_2	430	1.1	45	17		62
		440	1.3	44	12		56
		450	1.7	38	10		48
		460	1.9	30	8		38
2	2.6% O_2; 60% HNO_3 at 20 °C	430	1.3	43	13	11	67
		440	1.8	40	10	8	58
		450	2.0	36	8	5	49
		460	2.3	30	7	4	41
3	2.6% O_2; 60% HNO_3 at 60 °C	430	2.1	34	14	19	67
		440	2.3	35	11	15	61
		450	2.9	33	10	15	58
4	5.1% O_2; 60% HNO_3 at 50 °C	430	2.5	37	9	13	59
		440	3.4	34	7	9	50
		450	4.1	32	5	7	44
		460	4.7	26	5	7	38
5[d]	2.6% O_2; 90% HNO_3 at 1 °C	440	3.0	23	19	24	69
		445	3.4	22	19	21	66
		450	3.5	21	16	24	65
6[d]	5.1% O_2; 90% HNO_3 at 1 °C	400	2.1	18	29	23	74
		420	2.6	22	23	23	71
		430	3.1	29	9	19	64
		450	5.0	26	4	12	51

[a] Quartz reactor (ϕ = 10 mm), pressure = 3 atm, flow rate = 35 mL/min., residence time = 54s, bubbled through HNO_3 at the temperature shown in the table. [b] See ref. 6. [c] whole = MeOH + HCHO + $MeNO_2$ + $MeCO_2H$ + HCO_2H. [d] The concentration of HNO_3 in the reactant gas was estimated to be 0.26% from the vapor pressure of 90% HNO_3.

The effect of HNO_3 concentration (runs 3 and 5 at a CH_4 conversion near 3%) was noteworthy. Higher concentration (90%) led to improvements in both CH_4 conversion and total organic product selectivity with decreasing selectivity to MeOH and increasing selectivities to HCHO and $MeNO_2$. In addition, $MeCO_2H$ and HCO_2H were also obtained with a selectivity of about 3% when 90% HNO_3 was used. Further oxidation of the products, for example, the oxidation of MeOH to HCHO by the large amount of NO_2 may be responsible for this change.[8] An increase in O_2 concentration to 5.1% from 2.6% (runs 4 and 6) raised CH_4 conversion at a fixed reaction temperature. As shown by run 6, more than half of CH_4 could be converted to organic products even at a relatively high methane conversion of 5.0 %.

At a O_2 concentration of 5.1%, the use of more concentrated HNO_3 apparently facilitates the formation of the organic products.

The addition of HNO_3 improves not only CH_4 conversions but also the total selectivities to organic products in the gas-phase radical reaction of CH_4 with O_2, however, in the absence of O_2 only a trace amount of $MeNO_2$ could be formed from the reaction of HNO_3 with CH_4.[7] While the concentration of $MeNO_2$ in the reacted gases was about 0.3% at every experiment in run 4, $MeNO_2$ could hardly be detected in the absence of O_2.[9] A similar phenomenon was also observed when pure NO_2 was used as reactant. In comparison with a 0.15% concentration of $MeNO_2$ in the reacted gases when a $CH_4/O_2/NO_2$ mixed gas (flow rate = 39 mL/min., 5% O_2, 0.35% NO_2) was heated at 460 °C, the formation of $MeNO_2$ was only 0.03% without O_2.[10]

It is interesting to compare this with the results obtained from the radical nitration of higher alkanes by NO_2 forming nitroalkanes.[11] Nitration reactions were also reported to be accelerated by the addition of O_2,[11] however, O_2 and NO_2 played different roles. In the case of nitration reaction, NO_2 initiates the radical reaction. When O_2 is added, active form of NO_2 might be produced by the interaction of NO_2 with O_2, resulting in the acceleration of the reaction. In contrast, the effect of NO_2 as a radical initiator could hardly be observed in the partial oxidation of CH_4. In support of this, as shown in Table 1, all the reactions under 2.6% O_2 began to take place at almost the same temperature (around 410 °C). From these reactions, $MeNO_2$ can be assumed to be predominantly formed by the reaction of NO_2 with methyl radical generated via the reaction of CH_4 with O_2.

It should be noted that this effect of O_2 was very similar to that observed for the selective deNOx reactions by hydrocarbons where the presence of O_2 was essential for obtaining high catalyst efficiency.[12] Since the formation of nitrocompounds was supposed to be a key reaction in the deNOx reactions, the present results might be helpful in understanding their mechanisms.[12]

Another important feature of the reaction of CH_4 with O_2 and NO_2 is that N_2 was not detected under all the reaction conditions investigated, and under suitable conditions most of NO_2 added could be converted to $MeNO_2$. For example, the mixed gas of $CH_4/O_2/NO_2$ described above heated at 460 °C and 480 °C produced $MeNO_2$ in 0.17% and 0.32% yields, respectively, which corresponded to 43 and 83% NO_2 consumptions, respectively. This indicates the possibility to use NO_2 as catalyst for the partial oxidation of CH_4 with O_2 by converting $MeNO_2$ into other organic oxygenates and NO_2,[4] either *in situ* or by a separate process, and reuse NO_2 for another cycle of reaction. Studies on this possibility are now under way.

A financial support from the Science and Technology Agency, Japan, was acknowledged.

References and Notes

1 Reviews: O. V. Krylov, *Catal. Today*, **18**, 209 (1993); M. J. Brown and N. D. Parkyns, *Catal. Today*, **8**, 305 (1991); R. Pitchai and K. Klier, *Catal. Rev.-Sci. Eng.*, **28**, 13 (1986); H. D. Gesser and N. R. Hunter, *Chem. Rev.*, **85**, 235 (1985).

2 L.-B. Han, S. Tsubota, T. Kobayashi and M. Haruta, *J. Chem. Soc., Chem. Commun.*, **1995**, 93.

3 For kinetic studies on these reactions: M. J. Frost and I. W. M. Smith, *J. Chem. Soc., Faraday Trans.*, **89**, 4251 (1993); P. Biggs, C. E. Canosa-Mas, J. M. Fracheboud, A. D. Parr, D. E. Shallcross, R. P. Wayne and F. Caralp, *J. Chem. Soc., Faraday Trans.*, **89**, 4163 (1993); T. J. Wallington, M. M. Maricq, T. Ellermam and O. J. Nielsen, *J. Phys. Chem.*, **96**, 982 (1992); R. A. Cox, R. G. Derwent, P. M. Holt and J. A. Ker, *J. Chem. Soc., Faraday Trans. 1*, **72**, 2044 (1976).

4 For hydrolysis of aliphatic nitroalkanes, see N. Kornblum and R. A.Brown, *J. Am. Chem. Soc.*, **87**, 1742 (1965).

5 Nitric acid decomposes to NO_2 at an elevated temperature, Kagakudaijiten (Encyclopedic Dictionary of Chemistry), 1st ed, Tokyokagakudojin, Tokyo (1989), p 1118.

6 The methane conversion and product selectivity were calculated by using the following equations: CH_4 conversion (mol%) = 100 x (total carbon of products)/(total carbon of products + $CH_{4\ \mathrm{unreacted}}$); and product selectivity (mol%) = 100 x (carbon of the product)/(total carbon of all products), where products refer to CO, CO_2, MeOH, HCHO, HCO_2H, HCO_2Me, $MeNO_2$, C_2H_4, and C_2H_6. For more details of the experiment, see Ref. 2.

7 Nitration of alkanes by nitric acid affording nitroalkanes is known, see J. March, Advanced Organic Chemistry, 3th ed, John Wiley & Sons, New York (1985), p. 637-638. Formation of nitroalkanes by the reaction of NO_2 with alkanes in the presence of H_2O_2 was also known: D. L. Baulch, I. M. Campbell and J. M. Chappel, *J. Chem. Soc., Faraday Trans. 1*, **80**, 3609 (1984).

8 T. Nishiguchi and M. Bougauchi, *J. Org. Chem.*, **55**, 5606 (1990); S. A. Nyarady and R. E. Sievers, *J. Am. Chem. Soc.*, **107**, 3726 (1985).

9 The concentration of $MeNO_2$ in the reacted gases was 0.08% at 460 °C.

10 Reaction conditions were the same as shown in Table 1 except that the reaction was conducted at 1 atm using pure NO_2 gas.

11 A. I. Titov, *Tetrahedron*, **19**, 557 (1963).

12 K. Yogo, M. Ihara, I. Terasaki and E. Kikuchi, *Chem. Lett.*, **1993**, 229; M. Iwamoto and H. Hamada, *Catal. Today*, **10**, 57 (1991).