

Direct formation of formaldehyde from methane and carbon dioxide over vanadium oxide catalysts

Takahiro Shimamura^a, Kimito Okumura^a, Kiyoharu Nakagawa^b,
Toshihiro Ando^c, Na-oki Ikenga^a, Toshimitsu Suzuki^{a,*}

^a Department of Chemical Engineering and High Technology Research Center, Kansai University, 3-3-35 Yamate, Suita, Osaka 5648680, Japan

^b Japan Science Technology Corporation (JST) and National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

^c National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received 28 July 2003; received in revised form 29 September 2003; accepted 29 September 2003

Abstract

The possibility of CO₂ as an alternative oxidant for the direct conversion of CH₄ to formaldehyde was investigated. The activity of the catalyst was measured at an atmospheric pressure and temperatures at which the homogeneous gas-phase reactions were negligible. Among various metal oxides loaded on SiO₂ catalysts, only vanadium oxide produced the desired product. V₂O₅/SiO₂ and V₂O₅/oxidized diamond catalysts, the most effective catalysts for formaldehyde synthesis, afforded about 500 μmol h⁻¹ g-cat⁻¹ and 300 μmol h⁻¹ g-cat⁻¹ of formaldehyde at 973 K, respectively. When the reaction of CH₄ was carried out in Ar atmosphere, both of the V₂O₅/SiO₂ and V₂O₅/oxidized diamond catalysts lost the catalytic activity as soon as the lattice oxygen of vanadium oxide was consumed. However, the activity recovered by switching the atmosphere from Ar to CO₂. These results strongly suggest that CO₂ acts as an oxidant for selective oxidation of CH₄ to formaldehyde via the lattice oxygen of vanadium oxide.

© 2003 Elsevier B.V. All rights reserved.

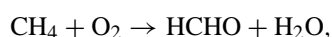
Keywords: Silica catalysts; Formaldehyde; Vanadium oxide; Oxidation with CO₂; Diamond catalysis

1. Introduction

The effective utilization of natural gas has attracted great interest in an effort to address the problem of increasing global consumption of fossil fuels. Formaldehyde, one of the important base chemicals in the petrochemical industry, is currently produced by a multi step process from CH₄; in addition, this process consumes a large amount of energy. From the perspective of simple green chemistry, direct conversion of alkane to oxygenates is of interest. In particular, direct conversion of CH₄ to methanol or formaldehyde is significant for an innovative utilization of natural gas and one of the most challenging issues in catalysis research.

Selective oxidation of light alkanes to oxygenates with oxygen has been carried out over various catalysts [1–16], such as the multi-component mixed oxides Mo–V–Al–Ti [1] or Mo–V–Nb–Pd [2], and supported transition metal oxides,

particularly molybdenum oxide [3–6], iron oxide [7,8], and vanadium oxide [6,9–11]. Zhao et al. recently reported a beneficial effect of addition of alkali metal to Fe/SiO₂ and V/SiO₂ catalysts on increasing acetaldehyde and acrolein formation from C₂H₆ [12–14]. However, selective oxidation of CH₄ requires a high reaction temperature to activate relatively inert CH₄ on catalysts, and deep oxidation to give CO_x occurs more easily than formation of oxygenate because the activation of the C–H bond in formaldehyde requires lower activation energy than the activation of CH₄ [15]. Therefore, in spite of great efforts, formaldehyde yields are still quite low. According to the literature survey by Otsuka and Wang [16] and Tabata et al. [17], the maximum formaldehyde yields of 4.2% with selectivity of 22.0% and the highest selectivity of 60% with the CH₄ conversion of 7% were reported. Such low yields or selectivities prevent a direct production from being applied in the chemical industry.

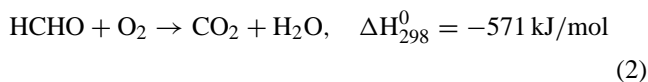


$$\Delta H_{298}^0 = -319 \text{ kJ/mol} \quad (1)$$

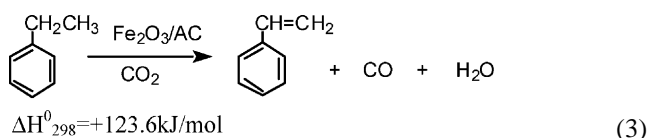
* Corresponding author. Tel.: +81-6-6368-0865;

fax: +81-6-6388-8869.

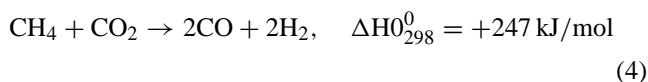
E-mail address: tsuzuki@ipcku.kansai-u.ac.jp (T. Suzuki).



Recently, conversion and utilization of CO_2 , a well-known global warming gas, and natural gas have received much attention. Although, chemical use of CO_2 would not significantly contribute to the reduction of CO_2 in air, we have first reported oxidation capability of carbon dioxide in the dehydrogenation of ethylbenzene to styrene using activated carbon supported iron oxides catalyst [18]. We further focused on the significant role of CO_2 in giving a high yield and high selectivity to styrene in the oxidative dehydrogenation of ethylbenzene with CO_2 , where a redox cycle between V_2O_5 and V_2O_4 was promoted by CO_2 [19]. In addition, dehydrogenation of C_2H_6 to C_2H_4 was promoted with CO_2 with Ga_2O_3 based catalysts [20].

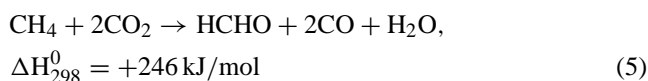


The most extensively developed reaction with CO_2 is the dry reforming reaction of CH_4 to give CO and H_2 from methane as shown below [21,22].



However, due to difficulty in transferring oxygen in CO_2 to organic compounds, no reports concerning the application of CO_2 to direct synthesis of oxygenates from alkanes have appeared although supercritical CO_2 fluid was used as a diluent and powerful solvent of reaction products in the direct O_2 oxidation of CH_4 [23].

As a new strategy, we aimed at extending the capability of CO_2 as an oxidant to selective oxidation of CH_4 to formaldehyde by use of a simple continuous plug flow reactor at an atmospheric pressure. The present paper deals with the feasibility of selective oxidation of CH_4 to formaldehyde using CO_2 (reaction (5)) over various metal oxide-loaded catalysts. We found that $\text{V}_2\text{O}_5/\text{SiO}_2$ and $\text{V}_2\text{O}_5/\text{oxidized diamond}$ catalysts were the most effective catalysts for formaldehyde formation.



2. Experimental

2.1. Catalyst preparation

All catalysts were prepared by the impregnation method. SiO_2 -supported metal oxide catalysts were prepared by

impregnating an oxalic acid solution of NH_4VO_3 onto SiO_2 , and aqueous solutions of NH_4MoO_4 , $\text{Fe}(\text{NO}_3)_3$, AgNO_3 , $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, and $\text{Cu}(\text{NO}_3)_2$ onto SiO_2 . Various supports were employed to prepare the V_2O_5 -loaded catalyst, including the commercially available SiO_2 (Fuji Silicia Chem. Co., S.A. = $110 \text{ m}^2/\text{g}$), diamond (General Electric Co., S.A. = $24 \text{ m}^2/\text{g}$), GeO_2 (Kishida Chemicals, S.A. < $1 \text{ m}^2/\text{g}$), SnO_2 (Wako Pure Chemical Industries, Ltd., S.A. = $3.6 \text{ m}^2/\text{g}$), TiO_2 (Japan Aerosil Co., S.A. = $52.8 \text{ m}^2/\text{g}$), Al_2O_3 (Sumitomo Chemical Ind., S.A. = $159 \text{ m}^2/\text{g}$), and MgO (Ube Materials Ind., S.A. = $144 \text{ m}^2/\text{g}$). The loading levels of metal oxides onto supports are expressed by weight percentages; wt.% = weight of metal oxide/(weight of metal oxide and support) \times 100. Into an aqueous solution of a metal salt, a certain amount of support was added and the suspension was stirred overnight. Excess water was removed under a vacuum, and the dried catalyst was calcined at 873 K for 5 h in the presence of air. $\text{V}_2\text{O}_5/\text{oxidized diamond}$ catalysts were calcined at 673 K for 3 h. Their surface areas were determined by the BET method (N_2 absorption at 77 K) with an automatic Micromeritics Gemini model 2375.

2.1.1. Preparation for oxidized diamond

Manmade industrial diamond, of fine particles of less than $0.5 \mu\text{m}$ in diameter, was oxidized at 723 K for 1.0 h under a stream of $\text{O}_2/\text{Ar} = 1/4$ mixture.

2.2. Activity measurement

A fixed-bed flow-type reactor (quartz, i.d. 10 mm) was used for the catalytic activity measurement, operating at an atmospheric pressure. Fifty or 100 mg of catalyst was placed in the center of the reactor tube with a quartz wool plug. A mixture of 10 ml/min CH_4 and 20 ml/min CO_2 was fed through the catalyst bed at an elevated temperature (773–973 K). Products were analyzed by an on-line high speed gas chromatograph using thermal conductivity detectors (CHROMPACK CP-2002, GL Sciences) with CP CIL 5CB and HYSEP A columns. Product yields were obtained after the run for 60 min.

3. Results and discussions

3.1. Effect of loaded metal oxides on the selective oxidation of CH_4 to formaldehyde with CO_2

Table 1 shows the distribution of products in the direct conversion of CH_4 with CO_2 over various metal oxide-loaded SiO_2 catalysts. SiO_2 was used as a standard support material in order to compare activities of various metal oxides, based on the fact that SiO_2 is a well-known effective support for the selective oxidation of CH_4 with O_2 [5–8,10–14,16]. Based on catalytic behavior in terms of product distribution, catalysts were divided into following

Table 1

Selective oxidation of CH₄ to formaldehyde with CO₂ over SiO₂ supported various metal oxide catalysts

Metal oxide	Yield/ $\mu\text{mol h}^{-1} \text{g-cat}^{-1}$	
	HCHO	CO
V ₂ O ₅	10.3	199.3
MoO ₃	0.0	0.0
Fe ₂ O ₃	0.0	131.7
Ag ₂ O	0.0	9.3
CuO	0.0	0
MnO ₂	0.0	0
ZnO	0.0	0
RuO ₂	0.0	0
NiO	0.0	424.8

Catalyst = 100 mg, support = SiO₂, loading level of metal oxide = 2.0 wt.%, reaction temperature = 873 K, gas flow = 30 ml/min, (CH₄/CO₂ = 1/5), SV = 18,000 ml h⁻¹ g-cat⁻¹.

three groups, those producing formaldehyde by selective oxidation, producing CO by CO₂ reforming, and showing no activities.

- Only the V₂O₅/SiO₂ catalyst produced formaldehyde, indicating that vanadium oxide exhibited a high activity for the selective oxidation of CH₄ in the presence of CO₂ as well as in O₂.
- The NiO/SiO₂ and Fe₂O₃/SiO₂ catalysts produced only CO. This means that CO₂ reforming of CH₄ to CO and H₂ might have occurred rather than the selective oxidation.
- The Metal oxides MoO₃, Ag₂O, CuO, MnO₂, ZnO, and RuO₂ loaded on SiO₂ catalysts did not exhibit any catalytic activities.

V₂O₅/SiO₂, MoO₃/SiO₂, and Fe₂O₃/SiO₂ are well-known catalysts that exhibited high catalytic activities for selective oxidation of CH₄ with O₂ [5–8,10,11,27]. However, upon substitution of CO₂ for O₂ as an oxidant, MoO₃/SiO₂ and Fe₂O₃/SiO₂ catalysts did not produce any oxygenates. Only vanadium oxide, in contrast to molybdenum oxide and iron oxide, showed the potential for high catalytic performance to formaldehyde formation with CO.

3.2. Effect of support on the selective oxidation of CH₄ to formaldehyde with CO₂

Fig. 1 shows the effect of the support on formaldehyde formation using CO₂ over V₂O₅-loaded catalysts at various temperatures. SiO₂ exhibited the highest activity among various supports, and oxidized diamond showed considerable activity. In particular, group 14 oxide materials promoted selective oxidation to formaldehyde. As previously shown, oxidized diamond surface is believed to be pseudo solid oxide phase of carbon [28,29]. The oxidized diamond is known to have oxygenated species like C–O–C and C=O on the surface of its sp³ hybrid orbital structure

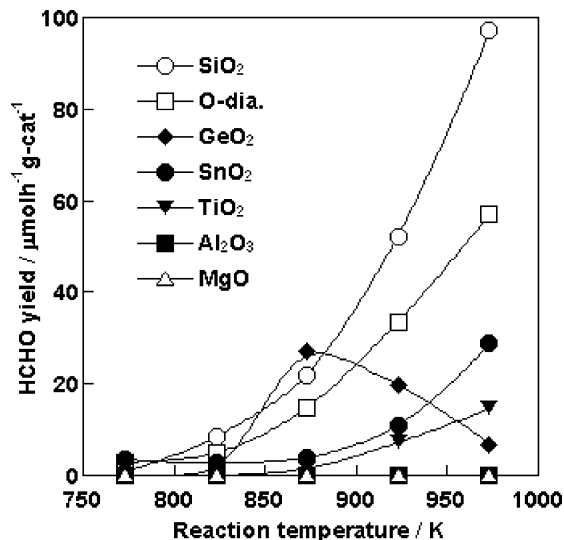


Fig. 1. Effect of various supports of vanadium oxide on the partial oxidation of methane to formaldehyde. Catalyst = 100 mg, V₂O₅ loading level = 2.0 wt.%, gas flow = 30 ml/min (CH₄/CO₂ = 1/2), S.V. = 18,000 ml h⁻¹ g-cat⁻¹.

[24–26]. The surface property is expected to have a potential for novel catalytic reactions including selective oxidation of CH₄.

Formaldehyde yield increased with an increase in the reaction temperature over catalyst loaded on SiO₂, oxidized diamond, and SnO₂. On the other hand, the yield reached a maximum at 873 K over GeO₂-loaded catalyst. In addition to group 14 oxides, TiO₂ produced a small amount of formaldehyde. However, ZrO₂ gave no formaldehyde. V₂O₅ loaded on Al₂O₃ and MgO catalysts gave no formaldehyde, but produced a large amount of CO at 973 K. Al₂O₃ and MgO caused complete oxidation of CH₄.

When various SiO₂ having different surface area were used as supports, SiO₂ having higher surface areas (higher than 400 m²/g) afforded low formaldehyde yields. This particular SiO₂ (S.A. = 110 m²/g) exhibited the maximum formaldehyde yield.

3.3. Effect of V₂O₅ loading level on the selective oxidation of CH₄ to formaldehyde with CO₂

Fig. 2 shows product yields as a function of loading level of vanadium oxide on SiO₂. Formaldehyde yield increased with an increase in the vanadium loading level up to 2.0 wt.% and then leveled off. On the other hand, CO yield increased monotonously with V₂O₅ loading level. As seen in Fig. 3, similar tendency was observed over the V₂O₅/oxidized diamond catalyst. The formaldehyde yield reached a maximum at a loading level of 2.0 wt.%, while CO yield increased linearly with an increase in the loading level. V₂O₅/oxidized diamond catalyst produced approximately ten times as much CO as compared to V₂O₅/SiO₂. The possibility of the produced formaldehyde decomposing to H₂ and CO

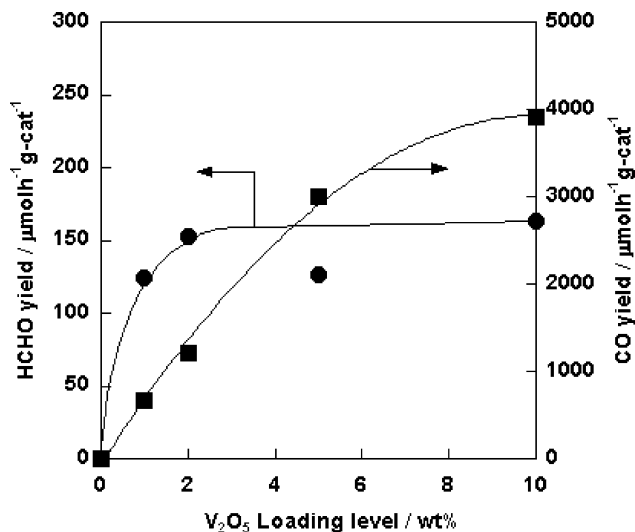


Fig. 2. Effect of V₂O₅ loading level on the conversion of CH₄ to formaldehyde and CO with CO₂ over V₂O₅/SiO₂. Catalyst = 50 mg, V₂O₅ loading level = 0–10 wt.%, reaction temperature = 973 K, gas flow = 30 ml/min (CH₄/CO₂ = 1/2), S.V. = 36,000 ml h⁻¹ g-cat⁻¹.

was considered. In a separate experiment, decomposition of acetaldehyde over V₂O₅/oxidized diamond catalyst occurred under similar reaction conditions to give formaldehyde, CO, and H₂. The amount of H₂ in the gas phase, however, is much smaller than that of CO in the oxidation of methane with CO₂. A large amount of H₂O was observed during oxidation suggesting that H₂ produced might have reacted with CO₂. Given that the amount of CO produced was much larger than the yield of formaldehyde, the following must be considered. At an elevated reaction temperature, a portion of surface carbon on the

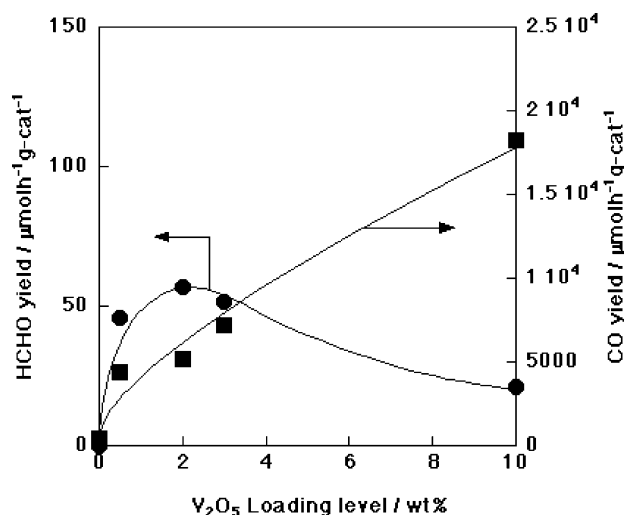
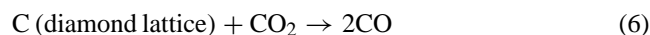


Fig. 3. Effect of V₂O₅ loading level on the conversion of CH₄ to formaldehyde and CO with CO₂ over V₂O₅/oxidized diamond. Catalyst = 100 mg, V₂O₅ loading level = 0–10 wt.%, reaction temperature = 973 K, gas flow = 30 ml/min (CH₄/CO₂ = 1/2), S.V. = 18,000 ml h⁻¹ g-cat⁻¹.

diamond lattice might have reacted with CO₂ to give CO. This reaction is remarkable at above 1100 K, as revealed by a temperature-programmed reaction of V₂O₅/oxidized diamond catalyst with CO₂.



At a lower V₂O₅ loading, the oxygenate selectivity increased in the oxidation of CH₄ with CO₂. The maximum formaldehyde yield of 0.06% was obtained with a low selectivity of 10%. We would like to stress two points; one is that oxidant is CO₂ not O₂, the other point is that the by-product is CO which is also a useful chemical feedstock as compared to CO₂.

It has been reported that high dispersion of vanadium oxide species over the support is favorable to selective oxidation of C₂H₆ with O₂ [13]. The present result is consistent with those previously reported [13]. Feraldos et al. [27] reported that turnover frequency in the O₂ oxidation of CH₄ with V₂O₅/SiO₂ and MoO₃/SiO₂ is quite sensitive to metal oxides dispersion. They claimed that maximum turnover frequency was observed below 1 vanadium per 1 nm². However, CH₄ conversion was as low as 0.7% with selectivity of 80% [29].

3.4. Effect of the partial pressure of CO₂ on the selective oxidation of CH₄ to formaldehyde

Fig. 4 shows formaldehyde yield as a function of the partial pressure of CO₂ for the selective oxidation of CH₄ to formaldehyde over the V₂O₅(2.0 wt.)/SiO₂ catalyst. The partial pressure of CH₄ and the space velocity (SV) were kept constant, while the partial pressure of CO₂ was changed by diluting CO₂ with Ar. Formaldehyde yield gradually increased with an increase in the partial pressure of CO₂. Higher partial pressure of CO₂ is favorable for the direct con-

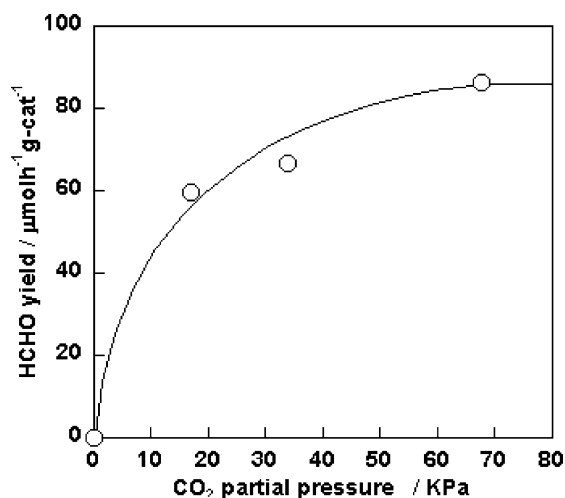


Fig. 4. Effect of partial pressure of CO₂ on the selective oxidation of CH₄ over V₂O₅/SiO₂. Catalyst = 100 mg, V₂O₅ loading level = 2.0 wt.%, reaction temperature = 973 K, gas flow = 30 ml/min (CH₄/(CO₂ + Ar) = 1/2), S.V. = 18,000 ml h⁻¹ g-cat⁻¹.

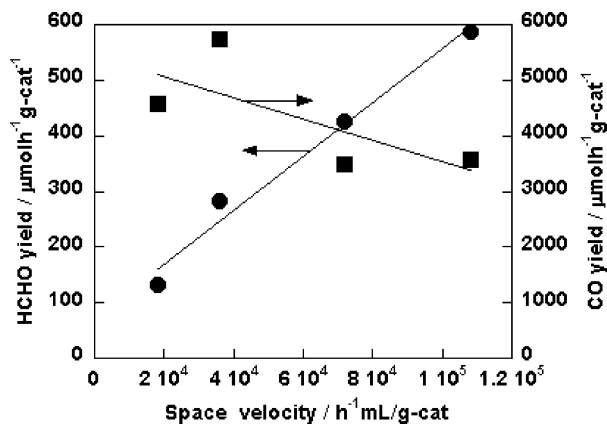


Fig. 5. Effect of space velocity on the selective oxidation of CH₄ to formaldehyde with CO₂ over V₂O₅/SiO₂. Catalyst = 50 mg, V₂O₅ loading level = 2.0 wt.%, reaction temperature = 973 K, gas flow = 15–90 ml/min (CH₄/CO₂ = 1/2).

version of CH₄ to formaldehyde. In contrast with O₂, CO₂ could not directly oxidize CH₄; higher CO₂ partial pressure did not promote complete oxidation.

3.5. Effect of space velocity on the selective oxidation of CH₄ to formaldehyde with CO₂

At an elevated temperature, formaldehyde is unstable and easily decomposes to CO and H₂. Because a high temperature above 773 K is required to produce oxygenate, this tendency is to be particularly considered in the selective oxidation of CH₄ with CO₂. Fig. 5 shows the effect of SV on the formation of formaldehyde and CO. Formaldehyde yield increased with an increase in SV. On the other hand, the yield of CO decreased with increasing SV. Such behavior is the opposite of that observed for common catalytic reactions under a moderate SV, in which a decrease in the SV increased yield of the product. A large SV seems to be favorable for formaldehyde synthesis with CO₂ in that it increases both the yield and the selectivity. These results suggest that a high SV decreases the residence time of the product formaldehyde in the catalyst zone to minimize decomposition of formaldehyde to CO and H₂. This indicates that rapid desorption of formaldehyde from the catalyst surface would be a key step for obtaining a higher yield of formaldehyde.

3.6. Capability of CO₂ as an oxidant for the selective oxidation of CH₄

Fig. 6 shows the results of long run oxidation of CH₄ with CO₂ over V₂O₅/SiO₂ and V₂O₅/oxidized diamond catalysts, respectively, at 973 K. The two catalysts exhibited similar catalytic behavior; formaldehyde yield gradually decreased in the initial 60 min. However, after the initial decrease in activity, the V₂O₅/SiO₂ catalyst sustained constant activity to produce formaldehyde for 5.0 h. The

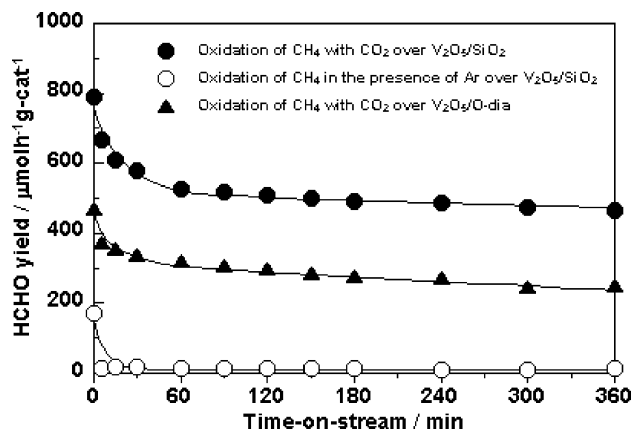


Fig. 6. Effect of time-on-stream on the selective oxidation of CH₄ to formaldehyde over V₂O₅/SiO₂ and V₂O₅/oxidized diamond. Catalyst: V₂O₅/SiO₂ = 50 mg, V₂O₅/oxidized diamond = 100 mg, V₂O₅ loading level = 2.0 wt.%, reaction temperature = 973 K, gas flow = 100 ml/min (CH₄/CO₂ = CH₄/Ar = 1/2). S.V.: V₂O₅/SiO₂ = 120,000, V₂O₅/oxidized diamond = 60,000 ml h⁻¹ g-cat⁻¹.

V₂O₅/oxidized diamond catalyst exhibited similar behavior with a smaller formaldehyde yield for 5.0 h. Initial rapid decreases in the target product in both catalysts seem to indicate that a certain portion of lattice oxygen of V₂O₅ was transferred to CH₄ with a reduction of V₂O₅ to lower the valence state of oxides. Oxidation of CH₄ in Ar on the V₂O₅ (2.0 wt.)/SiO₂ catalyst afforded a very small amount of formaldehyde at the initial reaction stage. However, no formaldehyde was obtained after 30 min in Ar atmosphere. This strongly supports that the lattice oxygen of vanadium oxide is transferred to CH₄ in the absence of CO₂. However, under a CO₂ stream, a certain amount of lattice oxygen seems to be supplied from CO₂ in gas phase to maintain catalytic activity. The average turnover frequency (TOF) in the oxidation of CH₄ with CO₂ in the long run-oxidation from 60 to 360 min was estimated as 4.6 mol HCHO h⁻¹/mol V₂O₅ on SiO₂ and 2.7 mol HCHO h⁻¹/mol V₂O₅ on oxidized diamond. Although the number of active centers in the oxide-based catalyst cannot be evaluated, it can be expected that the TOF per active center would be much higher.

As shown in Fig. 7, transient response studies of CH₄ reaction were carried out by switching the atmosphere from CO₂ to Ar and from Ar to CO₂ in order to examine the capability of CO₂ as an oxidant. In the presence of CO₂, the V₂O₅/SiO₂ catalyst afforded about 500 μmol h⁻¹ g-cat⁻¹ of formaldehyde. When flowing gas was switched from CO₂ to Ar, the yield of formaldehyde suddenly decreased due to loss of the oxygen source and the consumption of active oxygen on the lattice. When Ar flow was changed to CO₂ flow, the same amount of formaldehyde as that in the first CO₂ atmosphere was obtained. The results shown in Figs. 6 and 7 suggest that CO₂ acts as an oxidant over V₂O₅/SiO₂ and V₂O₅/oxidized diamond catalysts for direct conversion of CH₄ to formaldehyde. Such oxygen transfer reaction from

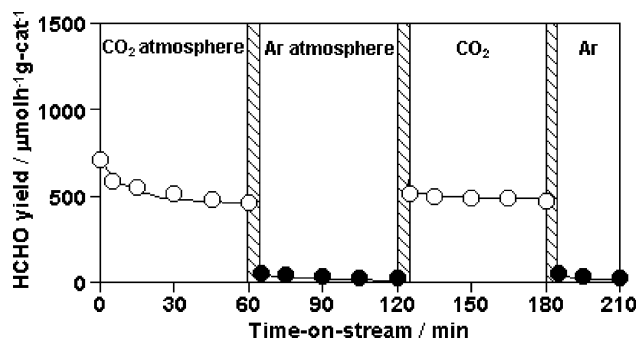


Fig. 7. Effect of switching atmospheres on the selective oxidation of CH_4 to formaldehyde over $\text{V}_2\text{O}_5/\text{SiO}_2$. Catalyst = 50 mg, V_2O_5 loading level = 2.0 wt.%, reaction temperature = 973 K, gas flow = 100 ml/min ($\text{CH}_4/\text{CO}_2 = \text{CH}_4/\text{Ar} = 1/2$), S.V. = 120, $000 \text{ ml h}^{-1} \text{ g-cat}^{-1}$. Atmosphere was changed from CO_2 to Ar at 60 min. Ar to CO_2 at 120 min, and then CO_2 to Ar. Hatched region indicates switching period of 5 min.

$\text{V}_2\text{O}_5/\text{SiO}_2$ to CH_4 and from gas phase O_2 to oxygen defect on surface V_2O_{5-x} was reported by Koranne et al. using O_2 as an oxidant [11]. In the present case, similar oxygen transfer occurred on the surface of vanadium oxide with gas phase CO_2 . Redox cycle between V_2O_{4+m} or V_2O_5 and V_2O_4 or V_2O_3 was confirmed in the dehydrogenation of ethylbenzene to styrene in the presence of CO_2 over V_2O_5 -loaded MgO catalyst, although thermodynamic is not favorable for oxidation (V^{4+} to V^{5+} , $\Delta G = 78 \text{ kJ/mol}$; and V^{3+} to V^{4+} , $\Delta G = 114 \text{ kJ/mol V}$ at 900 K) [19].

4. Conclusion

For the first time, the direct conversion of CH_4 to formaldehyde with CO_2 was achieved over vanadium oxide-loaded catalysts by use of a simple continuous plug flow reactor at atmospheric pressure. In this reaction, CO_2 acts as a mild oxidant and promotes formaldehyde formation.

Only vanadium oxide-loaded catalysts produced formaldehyde for the selective oxidation using CO_2 . Group 4 and 14 oxides, particularly SiO_2 and oxidized diamond proved to be superior supports for promoting formaldehyde formation.

Acknowledgements

This work was supported by a Grant in-Aid for Exploratory Research (146553019) from the Ministry of Education, Science, Culture, Sports, and Technology of Japan.

References

- [1] N.F. Chen, K. Oshihara, W. Ueda, *Catal. Today* 64 (2001) 121.
- [2] D. Linke, D. Wolf, M. Baerns, O. Timpe, R. Schogl, *J. Catal.* 205 (2002) 16.
- [3] A. de Lucas, J.L. Valverde, L. Rodriguez, P. Sanchez, M.T. Garcia, *Appl. Catal.* 203 (2000) 81.
- [4] L.-X. Dai, Y.-H. Teng, K. Tabata, E. Suzuki, T. Tatsumi, *Chem. Lett.* (2000) 794–795.
- [5] T. Suzuki, K. Wada, M. Shima, Y. Watanabe, *J. Chem. Soc., Commun.* (1990) 1159–1160.
- [6] A. Parmaliana, F. Arena, N. Giordano, *J. Catal.* 167 (1997) 57.
- [7] F. Arena, T. Torre, A. Venuto, F. Frusteri, A. Mezzapica, A. Parmaliana, *Catal. Lett.* 80 (2002) 69–72.
- [8] T. Kobayashi, K. Nakagawa, K. Tabata, M. Haruta, *J. Chem. Soc. Chem. Commun.* (1994) 1609–1610.
- [9] H. Berndt, A. Martin, A. Bruckner, E. Schreier, D. Muller, H. Kosslick, G.-U. Wolf, B. Lucke, *J. Catal.* 191 (2000) 384.
- [10] S. Tanaka, T. Kuriyama, T. Tanaka, T. Funabiki, S. Yoshida, *J. Catal.* 155 (1995) 196.
- [11] M.M. Koranne, J.G. Goodwin Jr, G. Marcelin, *J. Catal.* 148 (1994) 378.
- [12] K. Nakagawa, Y. Teng, Z. Zhao, Y. Yamada, A. Ueda, T. Suzuki, T. Kobayashi, *Chem. Lett.* 63 (1999) 79.
- [13] Z. Zhao, Y. Yamada, Y. Teng, A. Ueda, K. Nakagawa, T. Kobayashi, *J. Catal.* 190 (2000) 215.
- [14] Z. Zhao, Y. Yamada, A. Ueda, H. Sakurai, T. Kobayashi, *Appl. Catal. A.* 196 (2000) 37.
- [15] C. Batiot, B.K. Hodnett, *Appl. Catal. A.* 137 (1996) 179.
- [16] K. Otsuka, Y. Wang, *Appl. Catal. A.* 222 (2001) 145.
- [17] K. Tabata, Y. Teng, T. Takemoto, E. Suzuki, M.A. Banares, M.A. Pena, J.L.G. Fierro, *Catal. Rev.* 44 (2002) 1.
- [18] M. Sugino, H. Shimada, T. Turuda, H. Miura, N. Ikenaga, T. Suzuki, *Appl. Catal. A* 121 (1995) 125.
- [19] Y. Sakurai, T. Suzuki, K. Nakagawa, N. Ikenaga, H. Aota, T. Suzuki, *J. Catal.* 209 (2002) 16.
- [20] K. Nakagawa, C. Kajita, Y. Ide, M. Okamura, S. Kato, H. Kasuya, N. Ikenaga, T. Kobayashi, T. Suzuki, *Catal. Lett.* 64 (2000) 215.
- [21] M.C.J. Bradford, M.A. Vannice, *Catal. Rev.-Sci. Eng.* 41 (1999) 1.
- [22] K. Nakagawa, S. Hideshima, N. Akamatsu, N. Matsui, N. Ikenaga, T. Suzuki, *CO₂ conversion and utilization*, in: C. Song, A.F. Gaffney, K. Fujimoto (Eds.), ACS Symposium Series 809, vol. 205, 2002, and the references therein.
- [23] B. Kerler, A. Martin, A. Jans, M. Baerns, *Appl. Catal. A.* 220 (2001) 243.
- [24] T. Ando, K. Yamamoto, M. Ishii, M. Kamo, Y. Sato, *J. Chem. Soc. Faraday Trans.* 89 (1993) 3635.
- [25] M.P. D'Evelyn, Surface properties of diamond, in: M.A. Prelas, G. Popovici, L.K. Bigelow (Eds.), *Handbook of Industrial Diamonds and Diamond Film*, Marcel Dekker, New York, 1994, pp. 89–146 (Chapter 4).
- [26] T. Ando, S. Inoue, M. Ishii, M. Kamo, Y. Sato, O. Yamada, T. Nakano, *J. Chem. Soc. Faraday Trans.* 89 (1993) 749.
- [27] M. Faraldos, M.A. Banares, J.A. Andeson, I.E. Hangchun, J.G. Fierro, Hu, *J. Catal.* 160 (1996) 214.
- [28] K. Nakagawa, C. Kajita, N. Ikenaga, T. Kobayashi, M. Nishitani-Gamo, T. Ando, T. Suzuki, *Chem. Lett.* (2001) 1100–1101.
- [29] K. Nakagawa, H. Nishimoto, Y. Enoki, S. Egashira, N. Ikenaga, T. Kobayashi, M. Nishitani-Gamo, T. Ando, T. Suzuki, *Chem. Lett.* 460 (2001).