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An efficient partial oxidation of methane in trifluoroacetic acid using vanadium-containing heteropolyacid catalysts☆

Dong-guo Piao, Kensuke Inoue, Hiroyasu Shibasaki, Yuki Taniguchi, Tsugio Kitamura, Yuzo Fujiwara *

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Fukuoka 812-8581, Japan

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Abstract

The new catalytic system has been examined for the partial oxidation of methane in liquid phase. It was found that the vanadium containing heteropolyacids/$K_2S_2O_8$/$(CF_3CO)_2O$/CF_3COOH catalyst system converts methane to methyl trifluoroacetate along with a trace amount of methyl acetate in a 95% yield based on methane. The activation energy of the reaction was estimated to be 27.9 kcal mol^{-1}. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Vanadium; Heteropolyacid; Methane; Partial oxidation; Methyl trifluoroacetate; Activation energy

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1. Introduction

The lower alkanes such as methane are the most abundant of the hydrocarbons but the least reactive. Thus, the partial oxidation of methane is of great practical interest which is appealing for the liquefaction of natural gas and the chemical conversion to more useful chemical products. Recently, various transition metal catalyst systems have been investigated for liquid-phase oxidation of methane to methanol derivatives [1–12]. In continuing studies on C–H bond activations [13], we have found that methane in trifluoroacetic acid (TFA) can be also converted to methyl trifluoroacetate (**1**) along with a small amount of methyl acetate (**2**) in the presence of a catalytic amount of $H_5PV_2Mo_{10}O_{40}$ and $K_2S_2O_8$ as an oxidizing agent, and $(CF_3CO)_2O$ (TFAA) under mild conditions Eq. (1):

$$CH_4 \xrightarrow[\substack{CF_3COOH \\ (CF_3CO)_2O}]{\text{V-cat, } K_2S_2O_8} \underset{\mathbf{1}}{CF_3COOCH_3} + \underset{\mathbf{2}}{CH_3COOCH_3} \qquad (1)$$

Herein we report an efficient partial oxidation of methane to its esters in TFA by V-containing heteropolyacid catalysts.

2. Results and discussion

First, we examined the activity of various catalyst systems for the partial oxidation of methane in TFA solution. Consequently, some vanadium-substituted Keggin type heteropolyacids such as $H_5PV_2Mo_{10}O_{40}$ gave good results as shown in Table 1. As is apparent from the table, the oxidation of methane with $K_2S_2O_8$ proceeds to afford small amounts of esters **1** and **2** even in the absence of the catalyst (entry 1). By the addition of the catalyst, especially vanadium containing heteropolyacids, the yields of the products (**1** and **2**) increased. Among them, $H_5PV_2W_{10}O_{40}$ gave the highest turnover number (TON) and the highest yields of esters (entry 21). On the selectivity of ester **1**, the $H_5PV_2Mo_{10}O_{40}$ catalyst gave higher selectivity than $H_5PV_2W_{10}O_{40}$ in similar TON and yield (entry 4). It is noteworthy that with the increasing numbers of vana-

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☆ This article is dedicated to the memory of the late Professor R. Okawara.

* Corresponding author. Tel.: +81-92-642-3548; fax: 81-92-642-3548; e-mail: yfujitcf@mbox.nc.kyushu-u.ac.jp.

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dium atom in the heteropoly anion the yield and the selectivity of the products decrease (entries 3–7 and 20–22) because of the over-oxidation of the products [14]. Vanadium(V) oxide and vanadyl acetylacetonate are also more effective than MoO_3 and Na_2WO_4 in this reaction (entries 23, 24, 30, and 31). One can see that the active site of the heteropoly anion as a catalyst is the oxo–vanadium moiety. Consequently, we selected $H_5PV_2Mo_{10}O_{40}$ as a catalyst on the basis of the yield and the selectivity of the product (entry 4).

This reaction requires strongly acidic conditions; TFA works best as a solvent. Furthermore, addition of TFAA accelerates the reaction rate. The effect of the amount of TFAA is summarized in Fig. 1. The yield of products **1** and **2** are dramatically increased by the addition of 10 mmol of TFAA. Excess use of TFAA of more than 10 mmol decreased the yield of **1**. The role of TFAA is not clear, but it seems that TFAA works as desiccant of the hydrate on the catalyst and activates the catalyst since heteropolyacid catalysts usually exist as 30 hydrates.

Table 1
Catalyst effect for the partial oxidation of methane[a]

Entry	Catalyst	TON	Yield (%)[b]	Ratio/**1**:**2**
1	None	–	0.4	79:21
2	$H_3PMo_{12}O_{40}$	5	0.1	76:24
3	$H_4PVMo_{11}O_{40}$	80	2.4	83:17
4	$H_5PV_2Mo_{10}O_{40}$	161	4.7	88:12
5	$H_6PV_3Mo_9O_{40}$	92	2.8	86:14
6	$H_7PV_4Mo_8O_{40}$	76	2.1	73:27
7	$H_8PV_5Mo_7O_{40}$	62	1.8	67:33
8	$H_3PW_2Mo_{10}O_{40}$	4	0.1	83:17
9	$H_3PW_4Mo_8O_{40}$	8	0.2	90:10
10	$H_3PW_6Mo_6O_{40}$	17	0.4	73:27
11	$H_3PW_8Mo_4O_{40}$	14	0.3	54:46
12	$H_3PW_{10}Mo_2O_{40}$	12	0.3	72:28
13	$H_3PW_{12}O_{40}$	22	0.5	76:24
14	$H_4SiW_{12}O_{40}$	15	0.4	72:28
15	$H_4SiW_4Mo_8O_{40}$	6	0.1	80:20
16	$H_4SiW_6Mo_6O_{40}$	32	0.8	56:44
17	$H_4SiW_9Mo_3O_{40}$	18	0.4	59:41
18	$H_5SiVW_{11}O_{40}$	161	3.5	73:27
19	$H_4SiMo_{12}O_{40}$	19	0.5	74:26
20	$H_4PVW_{11}O_{40}$	50	1.0	76:24
21	$H_5PV_2W_{10}O_{40}$	241	6.4	73:27
22	$H_6PV_3W_9O_{40}$	139	3.3	55:45
23	V_2O_5	57	4 0	83:17
24	$VO(acac)_2$	56	3.5	71:29
25	V_2O_3	37	3.1	76:24
26	$NaVO_3$	17	1.5	54:46
27	Ta_2O_5	9	0.7	88:12
28	Nb_2O_5	12	0.8	87:13
29	TiO_2	31	2.1	63:37
30	MoO_3	5	0.3	78:22
31	Na_2WO_4	16	1.0	96: 4
32	$Pd(OAc)_2$	14	0.9	91: 9
33	$Cu(OAc)_2$	11	0.7	93: 7
34	$Pd(OAc)_2/CU(OAc)_2$	31	2.0	91: 9

[a] Reaction conditions: CH_4 (20 atm), catalyst (50 mg for heteropolyacid, 0.05 mmol each for entries 23–34), $K_2S_2O_8$ (5.00 mmol), TFAA (10.0 mmol), TFA (5.0 ml), 80°C, 20 h.

[b] GLC yield of **1** and **2** based on CH_4.

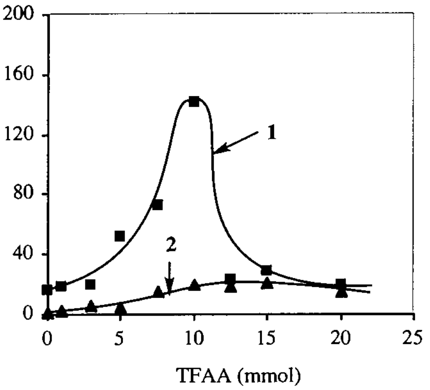

Fig. 1. Effect of the amount of TFAA. Conditions: CH_4 (20 atm), $H_5PV_2Mo_{10}O_{40}$ (0.022 mmol), $K_2S_2O_8$ (5.00 mmol), TFA (5 ml), 80°C, 20 h.

Fig. 2 shows the effect of the amount of an $H_5PV_2Mo_{10}O_{40}$ catalyst. The yield of products increased with an increasing amount of the catalyst. The highest yield of products (**1** and **2**) was obtained by using 0.013 mmol (TON = 490) of the catalyst. Excess use of the catalyst resulted in lower yields because the complex reaction took place.

The effect of oxidants was studied using an $H_5PV_2Mo_{10}O_{40}$ catalyst in TFA. The peroxide $K_2S_2O_8$ works best as the oxidant for the partial oxidation of methane. The use of other oxidants such as $Na_2S_2O_8$, $(NH_4)_2S_2O_8$, MnO_2, $KMnO_4$, and H_2O_2 in lieu of $K_2S_2O_8$ gave inferior results. Fig. 3 shows the effect of the amount of $K_2S_2O_8$. The yield of products increased with an increasing amount of $K_2S_2O_8$. The best result was obtained by using 5 or 6 mmol of $K_2S_2O_8$. Excess use of the oxidant resulted in lower yields because of lower efficiency of stirring and the complex reaction.

The time course of the reaction at several temperatures under the same conditions is shown in Fig. 4. The initial reaction rate (within 10 h) increased as the

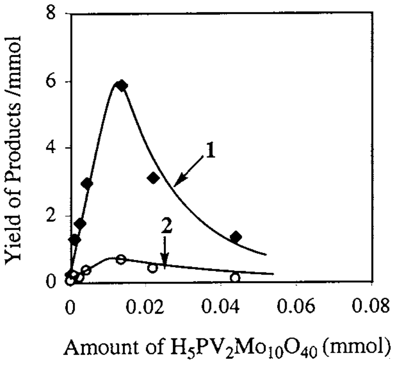

Fig. 2. Effect of the amount of catalyst. Conditions: CH_4 (20 atm), $K_2S_2O_8$ (5.00 mmol), TFA (5.0 ml), TFAA (10.0 mmol), 80°C, 20 h.

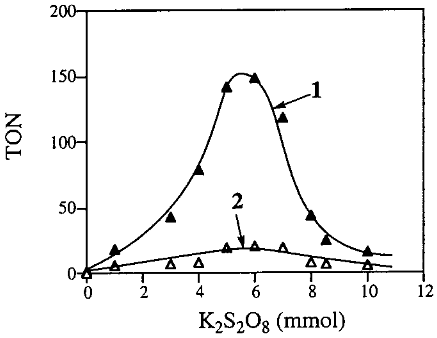

Fig. 3. Effect of the amount of $K_2S_2O_8$. Reaction conditions: CH_4 (20 atm), $H_5PV_2Mo_{10}O_{40}$ (0.022 mmol), TFA (5.0 ml), TFAA (10 mmol), 80°C, 20 h.

temperature increased. The yield of the reaction at 100°C increased up to 10 h and then decreased rapidly. The best yield of products was obtained in the reaction at 80°C for 20 h. The activation energy of this reaction was calculated by the Arrhenius plot of initial reaction rate within 5 h. From Fig. 5, the activation energy (ΔE) is estimated to be 27.9 kcal mol^{-1}. A lower value (15.3 kcal mol^{-1}) for the similar partial oxidation of methane with the $CuCl_2/K_2PdCl_4/H_2O/TFA/CO/O_2$ catalyst system was reported by Sen and co-workers [6].

Then, we investigated the effect of the CH_4 pressure. The representative results are summarized in Fig. 6. The TON of the catalyst increased with an increasing pressure of methane. The best result was obtained at 20 atm of CH_4. Under a higher pressure than 20 atm, the yield of the ester **1** decreased whereas the yield of ester **2** increased with the increasing pressure of CH_4.

In order to improve the yield based on methane, the reaction using a 25-ml autoclave was examined. The representative results are listed in Table 2. The yield based on methane increased with increasing amounts of the solvent (entries 1–3).

The reaction under the lower pressure of methane (6 atm) afforded the product in an 87.6% yield (entry 4). Furthermore, we succeeded the almost quantitative conversion (95%) of methane to methyl esters by pressurizing inert nitrogen (5 atm) (entry 5).

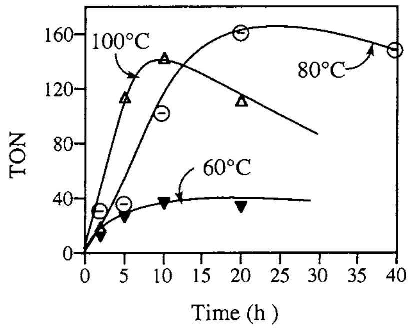

Fig. 4. Time course of the reaction. Conditions: CH_4 (20 atm), $H_5PV_2Mo_{10}O_{40}$ (0.022 mmol), $K_2S_2O_8$ (5.00mmol), TFA (5.0 ml), TFAA (10 mmol).

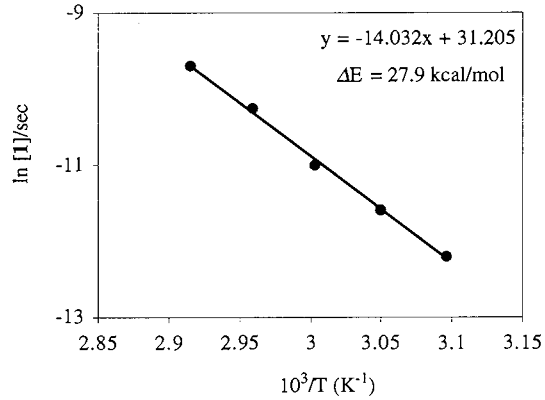

Fig. 5. Arrhenius plot of the V-catalyzed oxidation of methane. Conditions: CH_4 (10 atm), $H_5PV_2Mo_{10}O_{40}$ (5.0 μmol), $K_2S_2O_8$ (5.0 mmol), TFA (5.0 ml), TFAA (10 mmol), 5 h.

Although the details of the mechanism of the partial oxidation of methane by vanadium catalysts are not yet clear, a possible mechanism is shown in Fig. 7. A high oxidation state oxo-vanadium species V(V) = O would abstract $H^•$ from CH_4 to form a methyl radical ($CH_3^•$) which would be oxidized by V(V) = O to a methyl cation (CH_3^+). The CH_3^+ cation would then react with CF_3COO^- to give CF_3COOCH_3 (**1**). The by-product CH_3COOCH_3 (**2**) would be formed via ester exchange between **1** and acetic acid which would be formed from the reaction of CH_4 and CO, derived from the decomposition of TFA and/or TFAA [13,15].

3. Experimental

3.1. General

Analytical GLC evaluations of the products were performed on a Shimadzu GC-8A gas chromatography equipped with a flame ionization detector by using two 2.0 m × 3.0 mm i.d. stainless columns ([Unisole 10T +

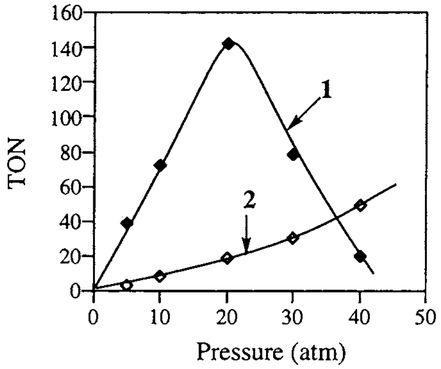

Fig. 6. Effect of CH_4 pressure. Conditions: $H_5PV_2Mo_{10}O_{40}$ (0.022 mmol), $K_2S_2O_8$ (5.0 mmol), TFA (5.0 ml), TFAA (10 mmol), 80°C, 20 h.

Table 2
Quantitative conversion of methane to methyl trifluoroacetate[a]

Entry	TFA (ml)	TON (**1**+**2**)	Product (**1**+**2**)/mmol	Yield (%)[b]
1	5	36	0.79	13.9 (93:7)
2	7.5	118	2.57	54.3 (93:7)
3	9	128	2.72	67.7 (89:11)
4	9[c]	98	2.11	87.6 (89:11)
5	9[d]	81	1.80	95.0 (82:18)

[a] Reaction conditions: 25-ml autoclave, $H_5PV_2Mo_{10}O_{40}$ (0.022 mmol), CH_4 (10 atm), $K_2S_2O_8$ (5.00 mmol), TFAA (10.0 mmol), 80°C, 20 h.

[b] GC yield based on CH_4. Numbers in parentheses are the ratio of **1** and **2**.

[c] CH_4 (6 atm).

[d] N_2 (5 atm) added to the reaction mixture, CH_4 (5 atm).

H_3PO_4 (5 and 0.5%) on 80/100 mesh Uniport HP] and Porapak QS) attached with a switch valve. ^{1}H- and ^{13}C-NMR spectra were obtained on a JEOL JNM-AL300 FT-NMR spectrometer in TFA solution, and chemical shifts (δ) were expressed in ppm downfield from 4,4-dimethyl-4-sila-pentanesulfonic acid sodium salts (DSS).

3.2. Materials

Methane (Sumitomo Pure Chemical Co. Ltd.) and nitrogen (BOC gases Co. Ltd.) gases were commercial grade. Trifluoroacetic acid (TFA), trifluoroacetic anhydride (TFAA), and potassium peroxodisulfate were purchased from Wako Pure Chemicals Co. Ltd. All heteropolyacids were gifted and were used without further purification.

3.3. Typical procedure for the partial oxidation of methane by heteropolyacid catalyst

In a 100 or 25-ml stainless steel autoclave fitted with a glass tube and a magnetic stirring bar, were added the catalyst, $K_2S_2O_8$, TFA and TFAA, successively. The autoclave was closed and then pressurized to 10 atm with CH_4. The mixture was heated with stirring at 80°C for 20 h. After cooling the autoclave was opened and the mixture in TFA was directly analyzed by GLC using ethanol as an internal standard. Methyl trifluoroacetate (**1**) was obtained along with a small amount of methyl acetate (**2**) as a by-product of this reaction. The formation of the esters **1** and **2** was confirmed by ^{1}H- and ^{13}C-NMR spectra of the reaction mixture. Methyl trifluoroacetate (**1**): ^{1}H-NMR (CF_3COOH) δ 4.04 (s, CF_3COOCH_3); ^{13}C-NMR (CF_3COOH) δ 54.8 (s, CH_3), 115.1 (q, CF_3, $J_{C-F} = 282$ Hz), 162.6 (q, C=O, $J_{C-F} = 43.5$ Hz). Methyl acetate (**2**): ^{1}H-NMR (CF_3COOH) δ 2.17 (s, CH_3CO, 3 H), 3.81 (s, CH_3O, 3 H); ^{13}C-NMR (CF_3COOH) δ 19.5 (s, CH_3), 53.2 (s, CH_3O), 178.8 (s, C=O).

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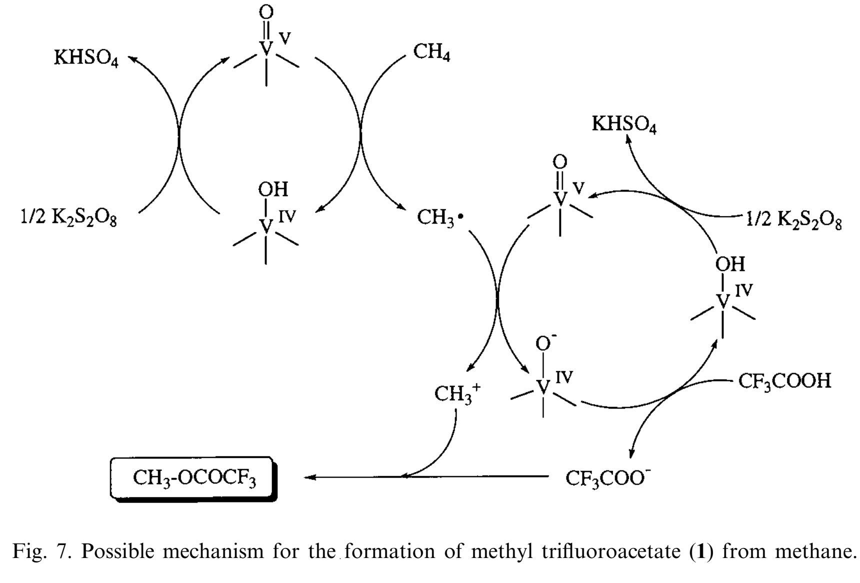

Fig. 7. Possible mechanism for the formation of methyl trifluoroacetate (**1**) from methane.

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[14] In these cases, a few uncharacterized products derived from **1** and **2** were observed by ^{1}H-NMR spectroscopy.

[15] Thus, the yield of **2** in Table 1 was calculated as 100% when 1 mol of **2** was formed from 2 mol of CH_4.