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Highly Efficient Vanadium-Catalyzed Transformation of CH_4 and CO to Acetic Acid

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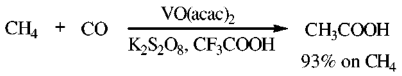
ABSTRACT



$$CH_4 + CO \xrightarrow[K_2S_2O_8,\ CF_3COOH]{VO(acac)_2} CH_3COOH$$

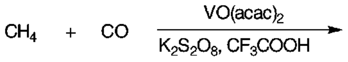
93% on CH_4

The $VO(acac)_2$ (acac = 2,4-pentanedionato) catalyst in the presence of $K_2S_2O_8$ and CF_3COOH has been found to efficiently transform methane and CO to acetic acid selectively. The reaction of methane (5 atm) with CO (20 atm) at 80 °C for 20 h gives acetic acid in 93% yield based on methane. Other vanadium compounds such as V_2O_3, V_2O_5, and $NaVO_3$ and various vanadium-containing heteropolyacids such as $H_5PV_2Mo_{10}O_{40}$, $H_4PVW_{11}O_{40}$, and $H_5SiVW_{11}O_{40}$ also work as catalysts.

Herein we report the highly efficient transformation of methane and CO to acetic acid by a vanadium catalyst in the presence of $K_2S_2O_8$ and CF_3COOH.

Activation and functionalization of C–H bonds of alkanes have attracted great attention recently in connection with resources for energy and chemicals production. Particularly, methane, a major component of natural gas, is the most abundant organic molecule, so its selective and high-yield conversion into useful chemicals is strongly desired in industry.[1] In 1992, we reported the first direct catalytic conversion of methane and CO to acetic acid by the $Pd(OAc)_2/Cu(OAc)_2/K_2S_2O_8/CF_3COOH$ and $Cu(OAc)_2/K_2S_2O_8/CF_3COOH$ catalyst systems.[2] Most recently, we found that the $Yb(OAc)_3/Mn(Ac)_2/NaClO/H_2O$ catalyst system causes methane carboxylation, giving acetic acid.[3] Acetic acid synthesis from methane and CO by Hogeveen et al.[4] and Olah et al.[5] has been reported using magic acids. Furthermore, $K_2S_2O_8$-assisted,[6] $RhCl_3$-catalyzed,[7] and V-catalyzed[8] carboxylations of methane with CO were reported by Sen and Lin and Shul'pin et al. However, the yields of acetic acid based on methane in these metal-catalyzed reactions are low. Therefore, there is a need to investigate new catalyst systems to increase the methane-based yield from the practical point of view.

In continuing studies on C–H bond activations,[2f,9] we have found that the $VO(acac)_2$ catalyst in the presence of $K_2S_2O_8$ and CF_3COOH affords acetic acid almost quantitatively from methane and CO.[10] We report this novel reaction of methane with CO in the presence of a catalytic amount of $VO(acac)_2$ to afford acetic acid almost quantitatively (eq 1).



$$CH_4 + CO \xrightarrow[K_2S_2O_8,\ CF_3COOH]{VO(acac)_2} CH_3COOH \qquad (1)$$

To improve the acetic acid yield, we first examined the catalytic activities of various vanadium compounds and

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heteropolyacids using $K_2S_2O_8$ (5.0 mmol) as an oxidant in CF_3COOH (5.0 mL) for the reaction of methane (40 atm) with CO (20 atm). The results are summarized in Table 1.

Table 1. Reaction of Methane and CO Leading to Acetic Acid in the Presence of Various Metal Catalysts, $K_2S_2O_8$ and CF_3COOH[a]

	acetic acid		yield (%) based on		
catalyst	(mmol)	TON[b]	CH_4	CO	$K_2S_2O_8$
none	0		0	0	0
$H_3PMo_{12}O_{40}·30H_2O$	0.01	0.2	0.01	0.02	0.2
$H_4PVMo_{11}O_{40}·30H_2O$	1.11	22.2	0.56	1.12	22.2
$H_5PV_2Mo_{10}O_{40}·30H_2O$	1.23	24.5	0.64	1.28	24.5
$H_6PV_3Mo_9O_{40}·30H_2O$	1.21	24.2	0.63	1.26	24.2
$H_7PV_4Mo_8O_{40}·30H_2O$	1.46	29.2	0.76	1.52	29.2
$H_8PV_5Mo_7O_{40}·30H_2O$	1.21	24.2	0.63	1.26	24.2
$H_3PW_6Mo_6O_{40}·30H_2O$	0.02	0.4	0.01	0.02	0.4
$H_3PW_{12}O_{40}·30H_2O$	0.11	2.1	0.05	0.10	2.1
$H_4SiW_{12}O_{40}·30H_2O$	0.01	0.1	0	0	0.1
$H_5SiVW_{11}O_{40}·29H_2O$	1.56	31.1	0.81	1.62	31.1
$H_4SiW_4Mo_8O_{40}·29H_2O$	0.04	0.8	0.02	0.04	0.8
$H_4SiMo_{12}O_{40}·28H_2O$	0.03	0.6	0.02	0.04	0.6
$VO(acac)_2$	1.38	27.5	0.71	1.42	27.5
$VOSO_4·3H_2O$	2.00	39.9	1.03	2.06	39.9
V_2O_5	1.28	25.5	0.66	1.32	25.5
$NaVO_3$	1.41	28.2	0.73	1.46	28.2
Pr_6O_{11}	0.08	1.6	0.04	0.08	1.6
Gd_2O_3	0.19	3.8	0.10	0.20	3.8

[a] CH_4 (40 atm, 193 mmol), CO (20 atm, 97 mmol), catalyst (0.05 mmol), $K_2S_2O_8$ (5.0 mmol), CF_3COOH (5.0 mL), 80 °C, 20 h in a 120mL autoclave. [b] Turnover numbers (moles of acetic acid per mole of catalyst) determined by GLC based on the catalyst.

As can be seen from the table, no acetic acid was formed in the absence of catalyst. Addition of a catalytic amount (0.05 mmol) of vanadium compound increases the yield of acetic acid. Interestingly, the vanadium-containing heteropolyacids work as the catalyst, although the compounds are insoluble in CF_3COOH. Of the heteropolyacids tested, $H_7PV_4Mo_8O_{40}$ and $H_5SiVW_{11}O_{40}$ gave high turnover numbers (TON), 29.2 and 31.1, respectively. Furthermore, simple vanadium compounds such as $VO(acac)_2$, $VOSO_4·3H_2O$, and $NaVO_3$ were found to have high catalytic activity (TON: 27.5, 39.9, and 28.2, respectively, giving 0.71, 1.03, and 0.73% yields of acetic acid based on methane, respectively). We selected $VO(acac)_2$ as a catalyst for the reaction of methane and CO to convert to acetic acid because of its stability, solubility in CF_3COOH, and simplicity of the catalyst.

$K_2S_2O_8$ was found to be the best oxidant (TON 27.5) for the $VO(acac)_2$ catalyst in CF_3COOH. Other oxidants such as *tert*-BuOOH and NaOCl also work, while the TONs are low (TON: 6−9).[11] The reaction depends on the solvent. CF_3COOH is the best solvent for the carboxylation of methane. Water can also serve as a solvent, although the turnover number is low (TON: 5.9). Figure 1 shows the plot of CH_4 pressure vs TON of the catalyst of the reaction of methane with CO to give acetic acid. From the figure, one can see that the TON increases with increasing methane pressure until 20 atm. The TON became constant (ca. 30) at pressures of methane higher than 20 atm. On the basis of these results, a $VO(acac)_2/K_2S_2O_8/CF_3COOH$ catalyst system was found to be one of the best catalyst systems for efficient conversion of methane and CO to acetic acid.

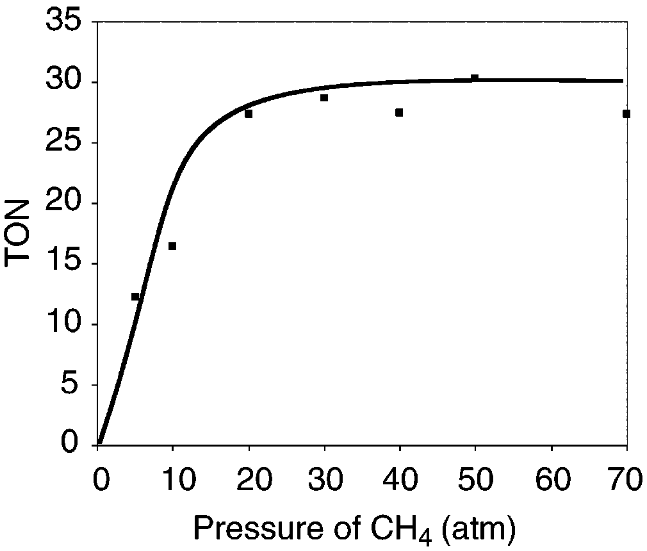

Figure 1. Plot of CH_4 pressure vs turnover number (TON) of the $VO(acac)_2$ catalyst (0.05 mmol). The reaction of CH_4 and CO (20 atm) in the presence of $K_2S_2O_8$ (5.0 mmol) and CF_3COOH (5 mL) was carried out under the conditions of 80 °C, 20 h in a 120 mL autoclave.

To increase the yield of acetic acid based on methane, we examined the carboxylation of methane (5 atm) under various CO pressures in the presence of $K_2S_2O_8$ (10 mmol), CF_3COOH (20 mL), and a catalytic amount of $VO(acac)_2$ using a 25 mL stainless steel autoclave. The reaction with 2 and 5 atm of CO gave acetic acid in 37 and 45% yields based on methane (the yields correspond to 92 and 45% based on CO), respectively.[12] The yield increased with increasing pressure of CO and reached 93% at 20 atm. In this case, the yields based on CO and $K_2S_2O_8$ are 23 and 8.7%, respectively.[13] This is the highest yield of acetic acid from methane

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(10) Presented at the Symposium on Oceanian-Japanese Organic Chemistry, Tokushima, Japan, December, 1996, and the International Forum on Environmental Catalysis '97, Tokyo, Japan, March, 1997.

(11) From a practical point of view, expensive $K_2S_2O_8$ would not be appropriate. The investigation to substitute $K_2S_2O_8$ with air (O_2) is now under way.

(12) In all cases, the oxidation of CO leading to CO_2 did not occur under these reaction conditions on the basis of gas analysis.

and CO so far reported.[14] Reactions at CO pressures higher than 20 atm resulted in lower yields of acetic acid.

From the ^{13}C NMR spectra of the control experiments using C-13 labeled CH_4 and CO and the comparison with authentic samples, it is confirmed that the methyl group and carboxyl group of the acetic acid formed come from CH_4 and CO, respectively. Figure 2 shows the ^{13}C NMR spectrum of the reaction mixture after the reaction of CH_4 and ^{13}CO. Except for two quartets due to CF_3COOH used as solvent, only a singlet at 182.3 ppm assigned to the carbonyl group of acetic acid was seen. In contrast to this, the spectrum of the reaction mixture of a similar reaction using $^{13}CH_4$ and CO showed the presence of only the methyl group (singlet at 19.4 ppm) of acetic acid and the absence of a carbonyl group (disappearance of the singlet at 182.3 ppm) (Figure 3).

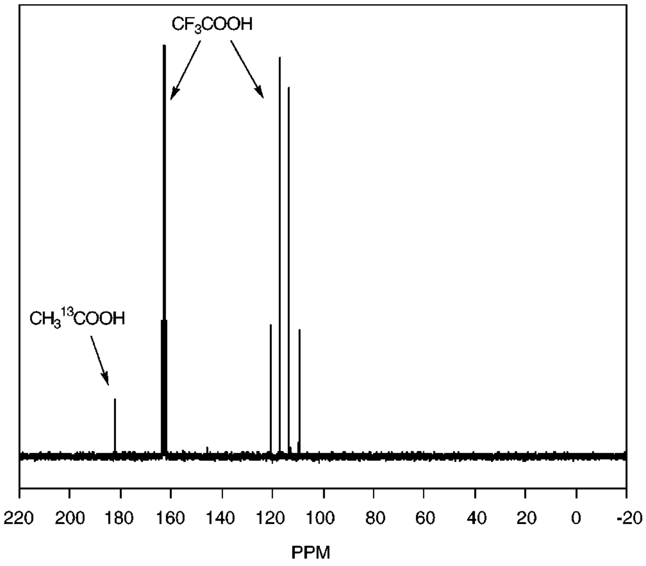

Figure 2. Carbon-13 NMR spectrum of the reaction mixture after the recation of CH4 with 13CO, showing that the sole product is CH313COOH.

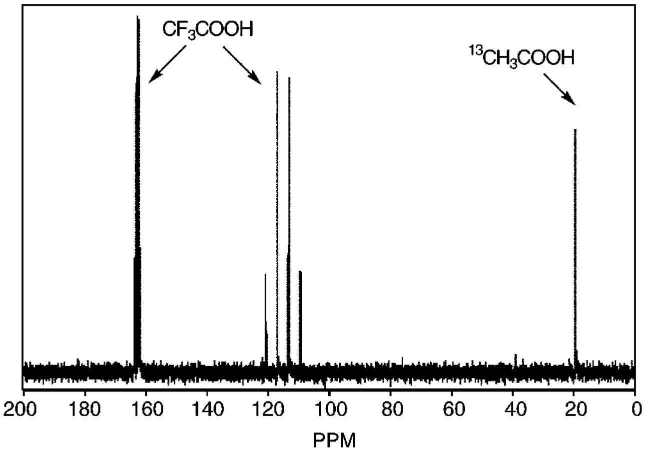

Figure 3. Carbon-13 NMR spectrum of the reaction mixture after the reaction of $^{13}CH_4$ with CO, showing that the sole product is $^{13}CH_3COOH$.

Although the mechanism of the reaction is not yet clear at this stage, a high oxidation state oxo-vanadium species V(V)═O could abstract H• from CH_4 to form a methyl radical (CH_3•), which could react with CO to give an acetyl radical (CH_3CO•). The CH_3CO• radical would give acetic acid via oxidation by V(V)═O to CH_3CO^+. The details of the mechanism are under investigation.[15]

In conclusion, we have found a new catalytic system that converts methane and CO to acetic acid almost quantitatively. The present reaction has the advantage that it employs cheap methane and thus would have a potential to be industrialized in the near future.

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(13) The volumetric productivity of the present reaction is 6.04×10^{-10} mol/(cm^3 s) lower than required for a practical process. The challenges in increasing volumetric productivity are also under way by optimizing the reaction conditions and the apparatus.

(14) Typical procedure: In a 25 mL stainless steel autoclave were placed $VO(acac)_2$ (0.05 mmol), $K_2S_2O_8$ (10 mmol), CF_3COOH (20 mL), and a Teflon-coated magnetic stirring bar. The autoclave was closed, flushed three times with CO, and pressurized to 20 atm with CO (3.80 mmol) and then 5 atm with CH_4 (0.94 mmol). The mixture was heated at 80 °C with stirring for 20 h. After cooling and venting of residual gases, the autoclave was opened and the mixture was analyzed directly by GLC (Unisole 10T + H_3PO_4) without aqueous workup using butyric acid as an internal standard to give acetic acid (0.87 mmol) in 93% yield based on CH_4.

(15) It is reported that radical initiators decompose CF_3COOH to give CF_3•, which abstracts H• from CH_4. However, the absence of $VO(acac)_2$ in our reaction gives a very low yield of acetic acid. (a) Sen, A. *Chem. Res.* **1998**, *31*, 550-557. (b) Reference 2d.