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A New Catalytic System Consisting of Mo for Acetic Acid Synthesis from Methane and CO

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In trifluoroacetic acid (TFA), methane and CO can be converted to acetic acid by a new catalytic system, Mo/$CaCl_2/K_2S_2O_8$/TFA. The best result (89.4% of acetic acid) was obtained in a reaction of methane (20 atm) and CO (50 atm) using the catalytic system at 85 °C for 20 h.

Methane, a major component of natural gas, is the most abundant hydrocarbon and a promising compound as carbon resources in the near future. To date, methane has been mostly consumed as an energy source, like fuel. One reason for the difficulties incurred in the use of methane is its low chemical reactivity.[1] However, the development of new processes for converting methane to useful substances, such as acetic acid or methanol, is a challenging theme to contribute to the prosperity of society.

We have already reported some catalytic systems for acetic acid synthesis from methane and CO,[2–6] namely, $Pd(OAc)_2/Cu(OAc)_2/K_2S_2O_8$/trifluoroacetic acid (TFA), $Cu(OAc)_2/K_2S_2O_8$/TFA, and $[VO(acac)_2]/K_2S_2O_8$/TFA. Hogeveen,[7] Olah,[8] Sen,[9,10] and Shul'pin[11] also reported on an acetic acid synthesis from methane and CO.

In our search for an effective catalytic system for producing acetic acid from methane and CO, we screened metals and metal salts. Consequently, we found that molybdenum is an active element as a new catalyst that is effective for acetic acid synthesis. Here, we report on our new result concerning acetic acid synthesis by a molybdenum-catalyzed reaction of methane with CO.

$$CH_4 + CO \xrightarrow[\text{TFA}]{\text{Mo cat.}/K_2S_2O_8} CH_3CO_2H \quad (1)$$

Some molybdenum compounds were investigated as a catalyst for acetic acid synthesis from methane and CO. The results are summarized in Table 1. In TFA, methane was converted to acetic acid by molybdenum catalysts with $K_2S_2O_8$ as the oxidant, as shown in Eq 1.

Table 1. Effect of Molybdenum Compounds on Synthesis of Acetic Acid[a)]

Run	Molybdenum compound	Yield of acetic acid[b)] mmol	%
1	None	trace	trace
2	Mo[c)]	0.03	0.4
3	Mo[c,d)]	1.29	17.7
4	MoO_2	0.04	0.5
5	MoO_2[d)]	trace	trace
6	$MoCl_5$	0.04	0.5
7	$[Mo(CO)_6]$	trace	trace
8	$[MoO_2(acac)_2]$	0.11	1.5
9	$[MoO_2(acac)_2]$[e)]	0.11	1.5

a) Reaction conditions: methane (20 atm), CO (20 atm), a Mo compound (0.2 mmol), $K_2S_2O_8$ (5 mmol), and TFA (5 mL) in 25-mL autoclave equipped with a glass tube at 85 °C for 20 h. b) GC yield based on methane. c) Molybdenum powder. d) In the presence of $CaCl_2$ (0.5 mmol). e) In the absence of methane.

Table 2. Effect of the Amount of Molybdenum Powder[a)]

Run	Mo powder mmol	Yield of acetic acid[b)] mmol	%
1	0	0.18	2.5
2	0.01	0.32	4.4
3	0.1	0.68	9.3
4	0.2	1.29	17.7
5	0.25	1.35	18.5
6	0.4	1.34	18.4

a) Reaction conditions: methane (20 atm), CO (20 atm), Mo powder, $CaCl_2$ (0.5 mmol), $K_2S_2O_8$ (5 mmol), and TFA (5 mL) in 25-mL autoclave equipped with a glass tube at 85 °C for 20 h. b) GC yield based on methane.

The combined catalyst of molybdenum powder and $CaCl_2$[12] was the most effective (Table 1, run 3). Thus, acetic acid synthesis was studied in detail with the Mo/$CaCl_2/K_2S_2O_8$/TFA catalytic system. The effect of the amount of molybdenum powder on acetic acid formation was examined under the reaction conditions given in Table 2. When the reaction was carried out in the absence of Mo, the yield of acetic acid was only 2.5%. The yield of acetic acid increased constantly with increasing amount of Mo up to 0.25 mmol, and reached 18.5%.

The effect of the amount of $CaCl_2$ was then investigated using Mo powder (0.2 mmol) under the conditions indicated in Table 2. In the absence of $CaCl_2$, the yield of acetic acid was only 0.4%. Similarly, the yield of acetic acid increased with increasing amount of $CaCl_2$ up to 0.4 mmol.

The above results indicate that the best molar ratio of Mo and $CaCl_2$ is 1:2.

To improve the yield of acetic acid, we further examined the pressure of CO, the amount of oxidant ($K_2S_2O_8$), and the amount of TFA. The yield of acetic acid increased almost linearly with increasing pressure of CO in the range of 0–50 atm CO pressure. When a reaction of methane (20 atm) with CO (50 atm) in the presence of Mo (0.2 mmol), $CaCl_2$ (0.4 mmol),

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Table 3. Effect of the Amount of TFA[a)]

Run	TFA	Yield of acetic acid[b)]		TON[c)]
	mL	mmol	%	
1	3	1.45	16.1	7
2	5	2.42	33.2	12
3	8	3.33	68.0	17
4	10	2.95	89.4	15

a) Reaction conditions: methane (20 atm), CO (50 atm), Mo powder (0.2 mmol), $CaCl_2$ (0.4 mmol), $K_2S_2O_8$ (5 mmol), and TFA in 25-mL autoclave equipped with a glass tube at 85 °C for 20 h. b) GC yield based on methane. c) Turnover number based on Mo.

and $K_2S_2O_8$ (5 mmol) in TFA (5 mL) was carried out at 85 °C for 20 h, the highest yield of acetic acid (33.2%) was obtained. Under the above conditions, the yield of acetic acid gradually increased until the amount of $K_2S_2O_8$ reached 5 mmol, and then became constant at over 5 mmol of $K_2S_2O_8$.

Finally, we examined the amount of TFA. With increasing amount of TFA the yield of acetic acid increased and led to 89.4% based on methane in a reaction using 10 mL of TFA, as shown in Table 3. When a large amount of TFA was used, the amount of methane introduced decreased and the yield based on methane increased. However, the amount of acetic acid was 2.95 mmol and the reaction in 8 mL of TFA gave a larger amount of acetic acid (3.33 mmol).

Although the mechanistic aspects of the reaction still remain unclear, the quenching reaction with radical scavengers strongly supports the intervention of radicals, such as a methyl radical. For example, the presence of 2,2,6,6-tetramethylpiperidin-1-oxyl completely prevented the formation of acetic acid.

In summary, we have found a new catalytic system, Mo/$CaCl_2$/$K_2S_2O_8$/TFA, for acetic acid synthesis. The new catalytic system provided a high yield of acetic acid from methane and CO. Therefore, we believe that this process has wide applicability in the synthesis of various carboxylic acids from alkanes.

Experimental

General. All of reactions in this work were carried out in a 25-mL stainless autoclave. The product mixture was analyzed by a Shimadzu GC-18A gas chromatograph equipped with a flame ionization detector by using a 30 m × 0.53 mm ϕ capillary column (H20M-PW30-300, liquid phase HR-20M) under the conditions of injection/detection temperature (250 °C) and column temperature (130 °C) for acetic acid.

Carboxylation Reaction of Methane. A catalyst and $K_2S_2O_8$ were placed in a 25-mL stainless-steel autoclave equipped with a Teflon-coated magnetic stirring bar, and TFA was introduced. The autoclave was closed and flushed with methane three times for replacing the inside air of the autoclave, and then pressurized with the desired pressures of methane and carbon monoxide. The autoclave was heated with stirring at a fixed temperature for the desired time. After the reaction, the autoclave was cooled on an ice bath and then opened. A small amount of valeric acid was added to the reaction mixture as an internal standard and acetic acid was analyzed by GC.

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12 Although we reported that $CaCl_2$ was a good reagent for acetic acid synthesis from methane and CO,[13] we also found that $CaCl_2$ showed a wall effect on this reaction. The interesting effect of $CaCl_2$ encouraged us to use a combination of a metal and $CaCl_2$.

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