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Direct Carboxylation Reaction of Methane with CO by a $Yb(OAc)_3/Mn(OAc)_2/NaClO/H_2O$ Catalytic System under Very Mild Conditions

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A new method of synthesis of acetic acid in water has been developed from the carboxylation of methane with carbon monoxide using lanthanide catalysts. Ytterbium(III) acetate has been found to be the most active catalyst among the compounds of the lanthanide series in the carboxylation reaction of methane with carbon monoxide. Sodium hypochlorite or hydrogen peroxide was used as the oxidant in this reaction. Sodium hypochlorite exhibited more favorable activity than hydrogen peroxide in the reaction. The catalytic activity was improved by the addition of transition-metal salts such as manganese(II) acetate. The best result has been found at a ratio of manganese(II) acetate to ytterbium(III) acetate of 1:10. The optimum reaction conditions (reaction temperature, 40 °C; time, 20 h; methane, 20 atm; carbon monoxide, 5 atm) have been obtained. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

The direct conversion of methane as a building block for functionalization products and higher hydrocarbons is one of the most promising routes for future organic synthesis because of the enormous proven world reserves ($1.4 \times 10^{11}/m^3$ as CH_4) of it as the major ingredient of natural gas,[1] which is now used mainly as a relatively inexpensive and clean burning fuel. However, it is difficult to achieve such a goal because methane has the least reactivity of all hydrocarbons and control of the product selectivity is difficult because of the higher reactivity of the functionalized products (methanol, formaldehyde etc.) compared with that of methane, and because the thermodynamically more favorable complete combustion of methane to carbon oxides and water takes place. Therefore, finely tuned reaction conditions to achieve high conversion without total oxidation are required. At present, however, there is no commercially available process satisfying these requirements. The scientific challenges for developing the most sophisticated methods that would convert methane into more valuable solid or liquid chemicals and fuels such as methanol, formaldehyde, ethylene, acetylene, acetic acid etc. have greatly stimulated a large volume of research over the last two decades. This research includes gas-phase reactions (catalytic or noncatalytic and usually at high temperatures and pressures),[2–8] radiation chemistry and electrochemistry as well as catalytic reactions in solution or on solid surfaces via C–H bond activation.[9,10] Among methods for the direct conversion of methane as a building block for functionalization products and procedures, solution-phase homogeneous metal-catalyzed functionalization of methane has been recognized as one of the most efficient and useful approaches.

According to the mechanistic aspects, homogeneous metal-catalyzed reactions are divided into four categories: (1) oxidative addition;[11–15] (2) electrophilic substitution;[16–18] (3) σ-bond metathesis[19,20] and (4) biomimetic and metal-oxide

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reaction.[21–28] Electrophilic substitution of methane by palladium(II) and cobalt(III) catalysts to yield methyl trifluoroacetate in trifluoroacetic acid (TFA) has been reported.[29,30] A high-yield conversion of methane to methanol in sulfuric acid by a mercury(II) catalyst has also been reported[31]. Among the valuable products of methane conversion, acetic acid is the most important and useful target organic molecule; it is now produced through this process involving many steps under severe reaction conditions.

Acetic acid production from methane conversion on an industrial scale currently involves three separate steps: (1) high-temperature steam-reforming of methane over a nickel catalyst to synthesis gas; (2) high-temperature conversion of synthesis gas over copper catalyst to methanol; (3) carboxylation of methanol to acetic acid mainly through the Monsanto process.[32]

One disadvantage of this technology is the large energy requirement of the first, highly endothermic, step. The other problem is the number of reaction stages required. Hence, the direct conversion of methane would be a more efficient route for the production of acetic acid. In 1992, we reported the first direct catalytic conversion of methane to acetic acid using potassium peroxodisulfate ($K_2S_2O_8$) as oxidant in the presence of transition-metal catalysts in TFA.[33] It would be a great achievement if such a process were made feasible by using water as solvent and low-cost oxidant. The conversion of methane to acetic acid in water using oxygen as the oxidant in the presence of $RhCl_3$ catalyst has been also reported in the low yield and selectivity.[34,35]

Therefore, there is an urgent need to investigate the new catalyst system in order to overcome all the problems. All of the catalytic conversion of methane to more useful chemical products involve the *d*-block transition-metal catalysts, although the long-neglected lanthanide elements (*f*-block transition metals) are also active in hydrocarbon conversion.[36,37] Recently, lanthanide elements have become of considerable importance in many areas of modern technology due to some special properties such as catalysis and superconductivity, and in advanced materials for optical, electronic, and excellent magnetic properties. Various organolanthanide complexes exhibit remarkable activity towards the C–H bonds of methane,[38–40] the polymerization of olefins[41–43] and chemical vapor deposition.[44–46]

Moreover, a different type of organolanthanide compounds can be used as efficient and selective catalysts and, therefore, they have become powerful tools in synthetic organic chemistry.[47] A pioneering example of methane conversion to methanol is reported using europium catalyst in TFA, where zinc dust and titanium(II) as reductant and promoter, respectively, have been used with Eu.[48] Recently, we found that lanthanide catalysts cause the direct conversion of methane to acetic acid in TFA with $K_2S_2O_8$ as oxidant.[49]

Here we describe the lanthanide-catalyzed carboxylation of methane to acetic acid with carbon monoxide (CO) *in water*, where sodium hypochlorite(NaClO) has been used as oxidant. Ytterbium(III) acetate [$Yb(OAc)_3$] exhibits the best catalytic activity among the lanthanide compounds tested in water in the presence of NaClO. The addition of transition-metal salts promoted the carboxylation reaction of methane. The catalytic activity of ytterbium was increased remarkably by the addition of a small amount of manganese(II) acetate [$Mn(OAc)_2$]. The reaction proceeds catalytically, as shown in Eqn [1].

$$CH_4 + CO \xrightarrow[\text{NaClO/H}_2\text{O, 40°C}]{\text{catalyst}} CH_3COOH \quad [1]$$

EXPERIMENTAL

Chemicals

All reagents were of analytical grade and were used without further purification. Methane and CO gases were purchased from Sumitomo Pure Chemical Co. Lanthanide(III) chloride, lanthanide(III) acetate, manganese(II) acetate, sodium hypochlorite solution and hydrogen peroxide (H_2O_2) solution were obtained commercially. The de-ionized water has been prepared in our laboratory.

Apparatus

The reactions were carried out in a 25-ml stainless steel autoclave. The product mixtures were analyzed by a Shimadzu GC-3BF gas chromatograph equipped with a flame ionization detector, by using a 2.1 m × 3.0 mm i.d. glass column packed with Unisole 10T + H_3PO_4 (5 + 0.5%) on 80/100-mesh Uniport HP with injection temperature 120 °C.

Table 1. Effect of oxidants on the lanthanoid-catalyzed carboxylation of methane in water[a]

Entry	Catalyst	Oxidant		Yield of AcOH		TON[d]
		NaClO (mmol)	H_2O_2 (mmol)	(μmol)[b]	(%)[c]	
1	None	10	—	Trace	Trace	0
2	None	—	10	0	0	—
3	$YbCl_3$	10	—	4.8	0.05	0.10
4	$EuCl_3$	10	—	4.3	0.04	0.09
5	$GdCl_3$	10	—	8.0	0.08	0.16
6	$NdCl_3$	10	—	25.0	0.26	0.50
7	$LuCl_3$	10	—	3.3	0.03	0.07
8	$Yb(OAc)_3$	10	—	75.0	0.80	1.50
9	$YbCl_3$	—	10	1.5	0.02	0.03
10	$EuCl_3$	—	10	0	0	0
11	$GdCl_3$	—	10	0	0	0
12	$NdCl_3$	—	10	0	0	0
13	$LuCl_3$	—	10	0	0	0

[a] Conditions: 25-ml autoclave, CH_4 (20 atm), CO (10 atm), catalyst (0.05 mmol), NaClO (9 ml 8.5% solution + 1 ml H_2O), H_2O_2 (1 ml 35% solution + 9 ml H_2O), 80 °C, 20 h.

[b] Determined by GC using Unisole 10T-H_3PO_4 (5 + 0.5%).

[c] Based on methane.

[d] Turnover number (TON) calculated as product (mol)/catalyst (mol).

Procedure for carboxylation of methane

A 25-ml stainless steel autoclave was charged with various chemicals in the following different ways: (1) the lanthanide catalyst (0.05 mmol), NaClO (10 mmol, 9 mL 8.5% solution), and deionized water (1 ml) were introduced into the autoclave; (2) the autoclave was charged with lanthanide catalyst (0.05 mmol), H_2O_2 (10 mmol, 1 ml 35% solution) and 9 ml deionized water; (3) the autoclave was charged with lanthanide catalyst (0.05 mmol), transition 1-1 metal catalysts (0.05 mmol), NaClO solution (10 mmol, 9 ml, 8.5% solution), and water (1 ml); (4) various amounts of $Mn(OAc)_2$ and $Yb(OAc)_3$ (0.05 mmol atom), NaClO (10 mmol, 9 ml 8.5% solution) and 1 mL water were introduced into the autoclave; (5) various amounts of $Yb(OAc)_3$ and $Mn(OAc)_2$ (0.005 mmol), NaClO (10 mmol, 9 ml 8.5% solution) and 1 ml water were introduced into the autoclave. A magnetic stirring bar was put in the autoclave in all cases. The autoclave was closed and flushed with CO three times for replacing the air inside the autoclave then pressurizing it carbon monoxide (10 atm) and methane (20 atm). Then the autoclave was closed and heated with stirring at 80 °C for 20 h. For determining the optimum temperature, the reactions were carried out at different temperatures from room temperature to 120 °C. The experiment on the time course of the reaction was performed from 5 to 130 h. Optimum pressures of methane and CO were also determined by performing the experiments at various pressures. In all cases, after completing the reaction, the final mixture was cooled on an ice bath for 15 min, then the autoclave was opened and the acetic acid formed in the reaction mixture was analyzed by GC using butyric acid as an internal standard.

RESULTS AND DISCUSSION

In the course of our studies on the activation of methane, we found that methane reacts with CO in the presence of lanthanide salts in TFA to yield acetic acid.[49] The problem encountered at this stage was that the yield of acetic acid was as low as 0.05% based on methane. In order to increase the yield and to make the reaction catalytic, we investigated the reaction of methane with CO using the lanthanide salts together with additives, and found that the $Yb(OAc)_3/Mn(OAc)_2/NaClO/H_2O$ system gives high yield of acetic acid.

First we investigated the lanthanide-catalyzed carboxylation of methane in the presence of NaClO or H_2O_2 in water in a 25-ml autoclave. The results are summarized in Table 1. It can be seen from the table that the NaClO alone promotes the reaction very slightly (entry 1) and the H_2O_2 alone does not work (entry 2). The reaction was promoted in low yield by lanthanide(III) chloride in the presence of NaClO in water. In the presence of 10 mmol H_2O_2,

Table 2. Effect of transition-metal salts in the ytterbium(III)-catalyzed carboxylation of methane in water using NaClO as an oxidant[a]

Entry	Catalyst	TON[b]	Yield %[c]
1	None	—	Trace
2	$Yb(OAc)_3$[d]	—	Trace
3	$Mn(OAc)_2$[d]	—	Trace
4	$Yb(OAc)_3$	1.5	0.8
5	$Mn(OAc)_2$	0.4	0.2
6	$Fe(OAc)_2$	0.9	0.4
7	$Ni(OAc)_2$	0.6	0.3
8	$Yb(OAc)_3/Mn(OAc)_2$	5.0	2.5
9	$Yb(OAc)_3/Fe(OAc)_2$	3.0	1.3
10	$Yb(OAc)_3/Cu(OAc)_2$	2.6	1.0
11	$Yb(OAc)_3/Ni(OAc)_2$	2.5	1.0
12	$Yb(OAc)_3/PV_2Mo_{10}O_{40}$	2.6	1.1
13	$Yb(OAc)_3/Mn(OAc)_2$[e]	2.0	1.0
14	$Yb(OAc)_3/Mn(OAc)_2$[f]	1.9	1.0
15	$Yb(OAc)_3/Mn(OAc)_2$[g]	5.2	2.6

[a] Conditions: 25-ml autoclave, CH_4 (20 atm), CO (10 atm), $Yb(OAc)_3$ (0.05 mmol), transition-metal salt (0.05 mmol), NaClO (9 ml 8.5% solution + 1 ml H_2O), 80 °C, 20 h. Yield of acetic acid was determined by GLC (FID) using Unisole 10T-H_3PO_4 (5 + 0.5%).

[b] Based on $Yb(OAc)_3$.

[c] Based on methane.

[d] Experiment without NaClO.

[e] Concentrated HCl (10 mmol) added to the reaction mixture.

[f] 15 M aq. NH_3 solution (10 mmol) added to the reaction mixture.

[g] 2 M aq. NaOH solution (10 mmol) added to the reaction mixture.

only $YbCl_3$ is active for the reaction (entry 9). The best result was obtained with $Yb(OAc)_3$ and NaClO in water (entry 8). The strength of the oxidizing agent may be the cause of the reactivity of $Yb(OAc)_3$ in the presence of NaClO but not in the presence of H_2O_2 in water. The NaClO solution is strongly basic and H_2O_2 solution is almost neutral. In the basic NaClO solution, Yb^{3+} will be reduced to Yb^{2+} by CO due to the presence of OH^-, a strong electron-donor ligand. In fact, Yb^{3+} is reduced vigorously to Yb^{2+} by Zn in tetrahydrofuran (THF) (the electron-donor solvent), which causes the cyclodimerization of chalcone to give cyclopentanol derivatives.[50] These results suggest that the lower-valent Yb species such as Yb^{2+} cause the reaction.

It is also interesting to compare the results of entries 3 and 8; the yield of acetic acid is much higher with $Yb(OAc)_3$ (about 15-fold) than with $YbCl_3$ under the same reaction conditions. These results show that the presence of ligands with the ytterbium is significantly important in the carboxylation reaction of methane. It may be said that the chloride ligand, which is a comparatively strong electron-withdrawing ligand, prohibits the formation of a lower-valent active oxo radical of ytterbium. As a result the abstraction of hydrogen atoms from methane to form a methyl radical becomes difficult in the case of chloride ligand. The yield of acetic acid is thus very low in the case of $YbCl_3$. The highest yield (0.8% based on methane, turnover number (TON) = 1.5, entry 8) was obtained by the $Yb(OAc)_3/NaClO/H_2O$ catalyst system.

However, the yield of acetic acid is still low. Then, we attempted to improve the catalytic activity by adding the transition-metal salts as additives to reduce Yb^{3+} to Yb^{2+}. The results are summarized in Table 2. A trace amount of acetic acid was formed only by the use of $Yb(OAc)_3$ or $Mn(OAc)_2$, in each case in the absence of NaClO (entries 2 and 3, Table 2). The yield of acetic acid was increased slightly by the addition of NaClO (entries 4 and 5). The coexistence of three metal salts increased the yield remarkably, and the addition of $Mn(OAc)_2$ gave the best result (entry 8).

Although the exact role of $Mn(OAc)_2$ in the Yb^{3+}-catalyzed reaction is not clear, it could be thought that Mn^{2+} promotes the reduction of Yb^{3+} to Yb^{2+} in alkaline solution. In order to study this point, we performed separate experiments using concentrated hydrochloric acid (HCl, 0.85 ml, 10 mmol), ammonia solution (NH_3, 15 M, 0.7 ml, 10 mmol) or sodium hydroxide solution (NaOH, 2 M, 5 ml, 10 mmol), respectively, as an additive (entries 13, 14 and 15, Table 2). The addition of HCl (entry 13) gave a negative result because of the absence of OH^- ion. The addition of ammonia also gave a negative result (entry 14), but in this case the ammonia solution reacted vigorously with NaClO, probably to form NaOH and NH_4Cl. Furthermore, the addition of NaOH (entry 15) to the reaction mixture slightly increased the yield. From these results, OH^- ligand, a strongly electron-donating ligand, appears to facilitate the reduction of the Yb^{3+} to Yb^{2+} by Mn^{2+}. From the data in Table 2, one can see that $Yb(OAc)_3/Mn(OAc)_2/NaClO/H_2O$ is the best catalyst system for methane conversion to acetic acid.

Since a combination system of $Yb(OAc)_3$ and $Mn(OAc)_2$ was found to be an active catalyst for the carboxylation reaction of methane, we investigated various factors that affected the efficiency of the reaction. First, the effect of the molar ratio of $Yb(OAc)_3$ and $Mn(OAc)_2$ was checked. To find out the optimum ratio of the metal salts, the experiments were carried out in two different ways: (1)

Table 3. Effect of the ratios of Yb/Mn on the carboxylation of methane[a]

Entry	$Yb(OAc)_3$ (μmol)	$Mn(OAc)_2$ (μmol)	Ratio Yb/Mn	TON[b]	Yield (%)[c]
1	50.0	—	—	1.5	0.8
2	—	50	—	0.4	0.2
3	50.0	5	10.0	5.5	2.8
4	50.0	27	2.0	5.1	2.6
5	50.0	50	1.0	3.1	1.7
6	50.0	253	0.2	2.4	1.2
7	50.0	500	0.1	0.0	0.0
8	50.0	1002	0.05	0.0	0.0
9	0.5	5	0.1	69.1	0.5
10	2.5	5	0.5	23.6	0.6
11	4.7	5	0.9	28.2	1.4
12	24.9	5	5.0	6.9	1.8
13	50.3	5	10.1	5.5	2.9
14	183.0	5	36.6	2.3	4.3

[a] Conditions: 25-ml autoclave, CH_4 (20 atm), CO (10 atm), NaClO (9 ml 8.5% solution + 1 ml H_2O), 80 °C, 20 h. Yield of acetic acid is determined by GC using Unisole 10T-H_3PO_4 (5 + 0.5%).
[b] Based on $Yb(OAc)_3$.
[c] Based on methane.

using the various ratios of $Mn(OAc)_2$ to $Yb(OAc)_3$ and (2) using the various ratios of $Yb(OAc)_3$ to $Mn(OAc)_2$; the results are listed in Table 3, from which it can be seen that methane was best carboxylated when the ratio of $Yb(OAc)_3$ to $Mn(OAc)_2$ was 10:1 (entry 3). The yields decreased steadily with an increasing proportion of $Mn(OAc)_2$ and finally it became zero (entries 3–8).

Using 0.005 mmol of $Mn(OAc)_2$, the yield of acetic acid increased sharply with an increase of $Yb(OAc)_3$ (entries 9–14). These strange phenomena raise the questions of why and how a very small amount (0.005 mmol) of $Mn(OAc)_2$ activates the $Yb(OAc)_3$ in the carboxylation of methane. The large amount of Mn^{2+} may act as a radical scavenger and the reaction becomes slower. Furthermore, the large amount of Mn^{2+} ion may cause the formation of manganese carbonyl complexes,[51] resulting in a lack of CO in the reaction system. It should be noted that a high TON (69.1) is obtained when the Yb/Mn ratio is 1:10 although the yield of acetic acid is low (0.5%) (entry 9).

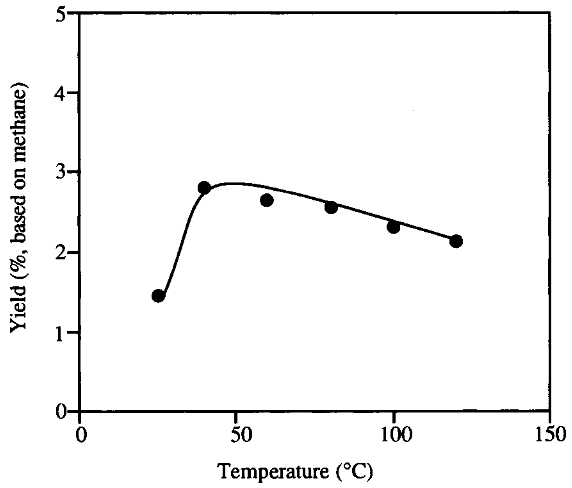


Figure 1 Effect of temperature on the yield of acetic acid. Conditions: 25-ml autoclave, CH_4 (20 atm), CO (10 atm), $Yb(OAc)_3$ (0.05 mmol), $Mn(OAc)_2$ (0.005 mmol), NaClO (9 ml, 8.5% solution + 1 ml H_2O), 20 h.

The effect of temperature on the carboxylation reaction of methane was investigated from room temperature to 120 °C. Careful examination of Fig. 1 reveals that the yield of acetic acid increases initially and reaches the maximum value at 40 °C and then slowly decreases with temperature. One explanation for this trend would be that the decomposition of acetic acid increases or a side-reaction may be increasingly promoted with the increasing temperature. At room temperature, the yield of acetic acid was low, and the color of the final reaction mixture was pink, whereas completely colorless solutions resulted when the reactions were performed above 40 °C.

The time course of the reaction of methane is shown in Fig. 2; it may be seen that the yield of acetic acid increases rapidly up to 20 h, and then increases slowly to attain the maximum value at 60 h.

The yield of acetic acid was also affected by the pressure of methane and CO. Figure 3 shows that

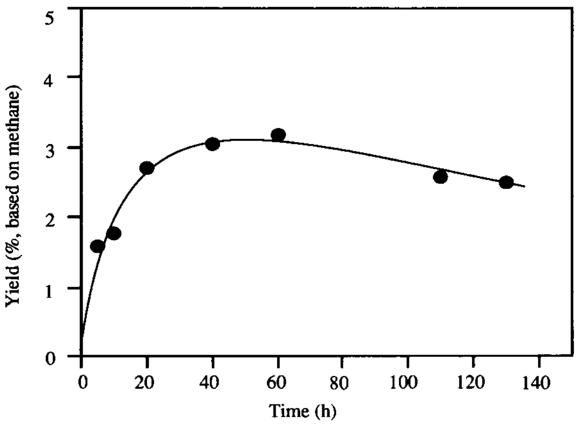


Figure 2 Effect of time on the yield of acetic acid. Conditions: 25-ml autoclave, CH_4 (20 atm), CO (10 atm), $Yb(OAc)_3$ (0.05 mmol), $Mn(OAc)_2$ (0.005 mmol), NaClO (9 ml, 8.5% solution + 1 ml H_2O), 40 °C.

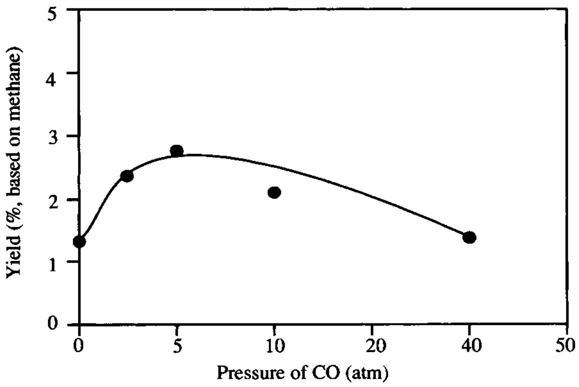


Figure 4 Effect of pressure of CO on the yield of acetic acid. Conditions: 25-ml autoclave, methane (20 atm), $Yb(OAc)_3$ (0.05 mmol), $Mn(OAc)_2$ (0.005 mmol), NaClO (9 ml, 8.5% solution + 1 ml H_2O), 40 °C, 20 h.

the yield of acetic acid increases rapidly up to 10 atm and then slowly increases until there is 20 atm of methane pressure. No further increase in acetic acid was observed above 20 atm methane pressure.

In Fig. 4 the effect of CO pressure is shown. The yield of acetic acid reaches the maximum value at 5 atm and decreases slowly with increasing CO pressure. This may be explained as follows. At high pressure, CO reacts with Mn^{2+} ion to form manganese carbonyl complexes.[51] As a result, the catalyst system loses the Mn^{2+} ion and hence catalytic activity decreases with increasing CO pressure.

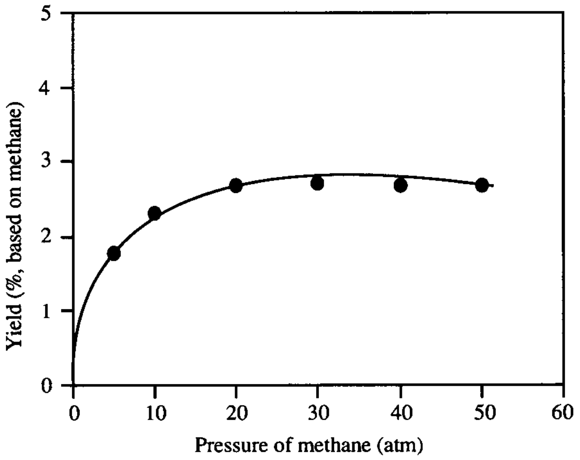
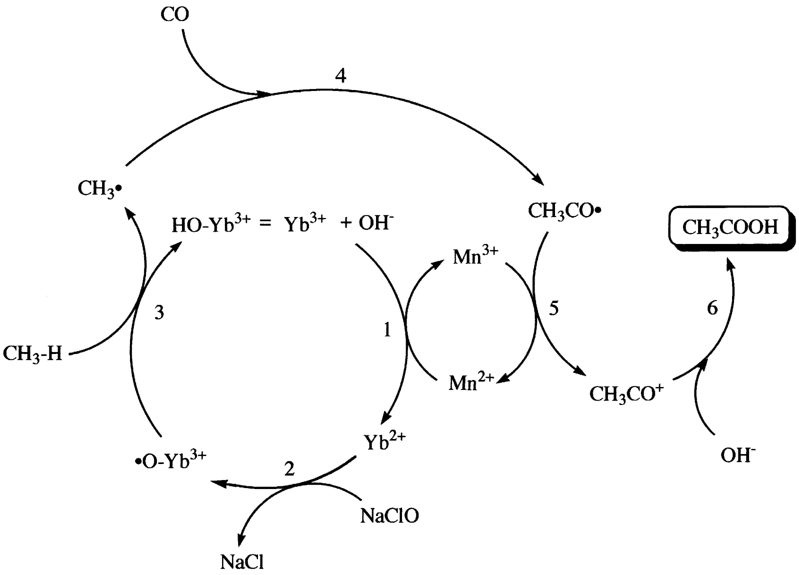


Figure 3 Effect of pressure of methane on the yield of acetic acid. Conditions: 25-ml autoclave, CO (10 atm), $Yb(OAc)_3$ (0.05 mmol), $Mn(OAc)_2$ (0.005 mmol), NaClO (9 ml, 8.5% solution + 1 ml H_2O), 40 °, 20 h.

The possible mechanism of this $Yb(OAc)_3$/$Mn(OAc)_2$/NaClO/H_2O-catalyzed carboxylation reaction of methane is shown in Scheme 1. First Yb^{3+} is reduced by Mn^{2+} to Yb^{2+} (step 1), which is oxidized by NaClO to form an oxo Yb radical (Yb^{3+}-O·) and NaCl (step 2). The oxo radical abstracts a hydrogen atom from methane to form a methyl radical which reacts with CO to yield an acetyl radical (steps 3 and 4). The acetyl radical is then converted to an acetyl cation by Mn^{3+} (step 5). The acetyl cation reacts with OH^- to give acetic acid (step 6). The formation of NaCl arising from step 2 was actually observed in this reaction.

CONCLUSION

The $Yb(OAc)_3$/$Mn(OAc)_2$/NaClO/H_2O catalytic system has been found to cause the carboxylation reaction of methane with CO under very mild conditions such as 40 °C for 20 h with 20 atm methane and 5 atm CO pressure. The roles of $Mn(OAc)_2$ and NaClO would be reduction and oxidation of Yb ion, respectively. A 2.8% yield of acetic acid based on methane (TON = 5.54) was attained by this method. Since the reaction employs cheap water as solvent and mild conditions, it has the potential to be industrialized in the future.



Scheme 1 Possible mechanism of the ytterbium-catalyzed carboxylation of methane to acetic acid.

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