Palladium-Catalyzed Acetic Acid Synthesis from Methane and Carbon Monoxide or Dioxide

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The $Pd(OAc)_2/Cu(OAc)_2/O_2/CF_3COOH$ system has been found to catalyze the direct conversion of methane to acetic acid in the presence of CO. The reaction of methane with CO_2 also gave acetic acid in high yields.

In previous papers we described carboxylation of alkanes such as methane, ethane, propane and n- and cyclo-hexanes with CO *via* C-H bond activation by palladium and copper based catalysts in the presence of $K_2S_2O_8$ and CF_3COOH (TFA).[1] In particular, methane has been found to be converted to acetic acid catalytically by the $Pd(OAc)_2/Cu(OAc)_2/K_2S_2O_8$/TFA or $Cu(OAc)_2/K_2S_2O_8$/TFA catalyst systems. In continuing studies on exploring synthetic reactions *via* thermal activation of alkane C-H bonds, we have investigated the reaction conditions for acetic acid synthesis and found that $K_2S_2O_8$, an oxidant can be substituted with O_2 and that more interestingly, CO can be also substituted with CO_2.

In this communication, we would like to report our preliminary results on the acetic acid synthesis from methane and CO or CO_2 by transition metal catalysts.

Heating methane (20 atm), $Pd(OAc)_2$, $Cu(OAc)_2$ (0.05 mmol each) in TFA (5 mL) under 15 atm CO and O_2 each at 80 °C for 20 h in a glass tube placed in an autoclave resulted in the sole formation of acetic acid in 240% yield based on Pd. And prolonged reaction time (40 h) increased the yield to 410%. The

$$CH_4 + CO + 1/2\,O_2 \xrightarrow[CF_3COOH]{Pd/Cu} CH_3COOH \quad (1)$$

Table 1. Acetic Acid Synthesis from Methane and CO[a]

Run	$K_2S_2O_8$/mmol	Time/h	AcOH Yield/%[b]
1	-	20	240
2	-	40	410
3	-	20[c]	0
4	9[d]	20	120

[a]CH_4 (20 atm), CO (15 atm), O_2 (15 atm), $Pd(OAc)_2$ (0.05 mmol), $Cu(OAc)_2$ (0.05 mmol), TFA (5 mL), 80 °C. [b]GC yield based on Pd. [c]No metal catalyst used. [d]No O_2 used.

results are summarized in Table 1. The data in the table show that $K_2S_2O_8$ can be substituted with cheap O2. The reaction without the catalyst gives no acetic acid (run 3) which shows that O_2 initiated radical reactions are not involved in the reaction. Thus, one can synthesize acetic acid from methane and CO using O_2, which gives the present reaction the potential to be developed into a large scale process.

The similar method of direct conversions of methane to acetic acid was reported by Lin and Sen using O_2 as an oxidant in the presence of CO and Rh based catalysts.[2] The catalyst efficiencies of the both catalyst systems are almost same.

Furthermore, very surprisingly, it was found that CO could be replaced with CO_2 in our catalyst systems. Thus, the reaction of methane (40 atm) and CO_2 (20 atm) in the presence of $Pd(OAc)_2$, $Cu(OAc)_2$ (0.05 mmol each) and $K_2S_2O_8$ (9 mmol) in TFA (5 mL) at 80 °C for ca. 20 h gave acetic acid in high yields (1650%) similar to that obtained in the reaction with CO.[1d,f,g]

$$CH_4 + CO_2 \xrightarrow[K_2S_2O_8,\ CF_3COOH]{Pd/Cu} CH_3COOH \quad (2)$$

The possibility that acetic acid is formed from the oxidation of ethane[3] derived from coupling of methane can be eliminated by the fact that only a trace amount of ethane is formed in the absence of CO_2 under the present conditions. Methane is the least reactive alkane, but one of the most abundant, and so selective conversion to useful chemical products is very valuable.

The optimization of the reaction with CO_2 is under current investigation.

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