

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

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(Received December 19, 1994)

The Pd(OAc)₂/Cu(OAc)₂/O₂/CF₃COOH system has been found to catalyze the direct conversion of methane to acetic acid in the presence of CO. The reaction of methane with CO₂ 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 K₂S₂O₈ and CF₃COOH (TFA).¹ In particular, methane has been found to be converted to acetic acid catalytically by the Pd(OAc)₂/Cu(OAc)₂/K₂S₂O₈/TFA or Cu(OAc)₂/K₂S₂O₈/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 K₂S₂O₈, an oxidant can be substituted with O₂ and that more interestingly, CO can be also substituted with CO₂.

In this communication, we would like to report our preliminary results on the acetic acid synthesis from methane and CO or CO₂ 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 O₂ 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

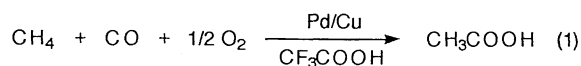


Table 1. Acetic Acid Synthesis from Methane and CO^a

Run	K ₂ S ₂ O ₈ /mmol	Time/h	AcOH Yield/% ^b
1	-	20	240
2	-	40	410
3	-	20 ^c	0
4	9 ^d	20	120

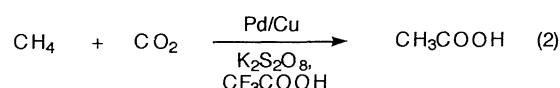
^aCH₄ (20 atm), CO (15 atm), O₂ (15 atm), Pd(OAc)₂ (0.05 mmol), Cu(OAc)₂ (0.05 mmol), TFA (5 mL), 80 °C. ^bGC yield based on Pd. ^cNo metal catalyst used. ^dNo O₂ used.

results are summarized in Table 1. The data in the table show that K₂S₂O₈ can be substituted with cheap O₂. The reaction without the catalyst gives no acetic acid (run 3) which shows

that O₂ initiated radical reactions are not involved in the reaction. Thus, one can synthesize acetic acid from methane and CO using O₂, 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 O₂ 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 CO₂ in our catalyst systems. Thus, the reaction of methane (40 atm) and CO₂ (20 atm) in the presence of Pd(OAc)₂, Cu(OAc)₂ (0.05 mmol each) and K₂S₂O₈ (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}



The possibility that acetic acid is formed from the oxidation of ethane³ derived from coupling of methane can be eliminated by the fact that only a trace amount of ethane is formed in the absence of CO₂ 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 CO₂ is under current investigation.

This work was supported in part by a Grant-in-Aid for Scientific Research No. 04241222 in Priority Area of "Activation of Inactive Small Molecules" from the Ministry of Education, Science and Culture. We are also grateful to the Japan Gas Association for grants.

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