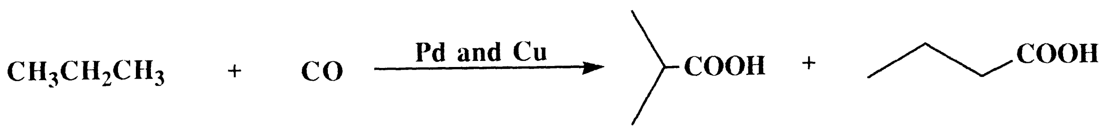
CHEMISTRY LETTERS, pp. 1005-1008, 1993.

Carboxylation of Propane with CO to Butyric Acids by Pd(II)/Cu(II) Based Catalysts

Tsutomu MIYATA, Kazuyuki NAKATA, Yoshinori YAMAOKA, Yuki TANIGUCHI, Ken TAKAKI, and Yuzo FUJIWARA
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724

Propane reacts with CO leading to isobutyric and butyric acids in good yields by the $Pd(OAc)_2/Cu(OAc)_2/K_2S_2O_8$ catalyst system via C-H bond activation. It is essential to use more than unity of the $Cu(OAc)_2/Pd(OAc)_2$ ratio to attain high yield.

Alkane activation/functionalization under mild conditions is one of the most challenging fields of modern chemistry since hydrocarbons, especially small molecules including methane, ethane, and propane are the most abundant natural source on the earth. In previous paper we reported that methane and propane react with CO in the presence of transition metal catalysts to give acetic acid and butyric acids, respectively.[1] However, the yield of butyric acids was as low as 300% based on the catalyst. In continuing studies on exploring synthetic reactions via thermal activation of C-H bonds, we investigated the reaction of propane with CO using the Pd/Cu based catalysts, and found that the $Pd(OAc)_2/Cu(OAc)_2/K_2S_2O_8$ system gives very high yields of isobutyric acid (**1**) and butyric acid (**2**). In this communication



1 **2**

we would like to report these results.

First, we have examined the reaction of propane (10 atm) with CO (20 atm) using several combinations of $Pd(OAc)_2$, $Cu(OAc)_2$, and $K_2S_2O_8$ as catalysts in trifluoroacetic acid with stirring for 20 h at 80°C in an autoclave. The results are summarized in Table 1. As is apparent from the table, the $Pd(OAc)_2/Cu(OAc)_2/K_2S_2O_8$ system gives the highest yields of butyric acids **1**

Table 1. Reaction of propane with CO by the $Pd(OAc)_2$ and/or $Cu(OAc)_2$ systems[a)]

Run	$Pd(OAc)_2$ (mmol)	$Cu(OAc)_2$ (mmol)	$K_2S_2O_8$ (mmol)	Product and yield/%[b)] **1**	**2**	Ratio of **1/2**
1	0.05	0.05	9	5500(6.7)	1600(2.3)	3.5
2	0.05	-	9	1400(1.7)	360(0.4)	4.0
3	-	0.05	9	1300(1.5)	600(0.7)	2.1
4	-	-	9	1.5(0.3)	0.9(0.2)	1.7
5	1.0	-	-	tr[c)]	tr[c)]	-
6	-	1.0	-	tr[c)]	tr[c)]	-

a) Propane 10 atm, CO 20 atm, CF_3COOH 5 ml, 80 °C, 20 h. b) GC yield based on the least amount of metal salts and the number in parenthesis is the yield on propane. c) Trace amount.

and **2** (run 1, Table 1), and the $Pd(OAc)/K_2S_2O_8$ (run 2, Table 1) and $Cu(OAc)_2/K_2S_2O_8$ (run 3, Table 1) systems give lower yields. In addition, $Pd(OAc)_2$ alone or $Cu(OAc)_2$ alone shows almost no activity (runs 5 and 6, Table 1). It is worthy of mention that the $Pd(OAc)_2/Cu(OAc)_2/K_2S_2O_8$ and $Pd(OAc)_2/K_2S_2O_8$ systems produce butyric acids in 3.5-4.0 **1/2** ratios (runs 1 and 2, Table 1) while the $Cu(OAc)_2/K_2S_2O_8$ system or $K_2S_2O_8$ alone produces the acids in lower ratio (runs 3 and 4, Table 1).

Since it became apparent that the combination of $Pd(OAc)_2$ and $Cu(OAc)_2$ gave the best result, we further investigated the reaction using various palladium and copper compounds as catalysts. Table 2 summarizes the results, and the data in the table also indicate that the combinations of

Table 2. Reaction of propane with CO by various palladium and copper catalysts[a)]

Run	Catalyst	Product and yield/%[b)] **1**	**2**
1	Pd black/$Cu(OAc)_2$	4200(5.1)	1100(1.3)
2	Pd black/$CuCl_2$	6100(7.5)	1500(1.9)
3	Pd black	360(0.4)	110(0.1)
4	$Pd(OAc)_2/Cu(OAc)_2$	5500(6.7)	1600(2.0)
5	$Pd(OAc)_2/CuCl_2$	6100(7.5)	1400(1.7)
6	$Pd(OAc)_2$/CuCl	5400(6.6)	1400(1.7)
7	$Pd(OAc)_2$/Cu powder	5600(6.9)	1400(1.7)

a) Propane 10 atm, CO 20 atm, catalyst 0.05 mmol each, $K_2S_2O_8$ 9 mmol, CF_3COOH 5 ml, 80 °C, 20 h. b) GC yield based on Pd, and the number in parenthesis is the yield based on propane.

both palladium and copper such as Pd(0)/Cu(II) (runs 1 and 2, Table 2), Pd(II)/Cu(0) (run 7, Table 2), and Pd(II)/Cu(I) (run 6, Table 2) are all effective as well as Pd(II)/Cu(II) (runs 4 and 5, Table 2) for the butyric acid synthesis. From these results we used the $Pd(OAc)_2/Cu(OAc)_2$ system together with $K_2S_2O_8$ for the reaction of propane with CO.

Then we investigated the role of two components, $Pd(OAc)_2$ and $Cu(OAc)_2$. As can be seen from Table 3, the yield of butyric acids (**1** and **2**) increases as the amount of $Pd(OAc)_2$ increases with constant amount of $Cu(OAc)_2$ (runs 2 to 5, Table 3). On the other hand, when the amount of $Cu(OAc)_2$ is raised

Table 3. Effect of the amount of $Pd(OAc)_2$[a)]

Run	$Pd(OAc)_2$ (mmol)	Molar ratio (Pd/Cu)	Product and yield/%[b)] **1**	**2**
1	0	0	tr[c)]	tr[c)]
2	0.025	0.05	1.9	0.3
3	0.05	0.1	2.2	0.3
4	0.25	0.5	2.5	0.4
5	0.5	1	4.2	0.7
6	1.0	2	1.8	0.3

a) Propane 10 atm, CO 20 atm, $Cu(OAc)_2$ 0.5 mmol, $K_2S_2O_8$ 9 mmol, CF_3COOH 5 ml, 80 °C, 5 h. b) GC yield based on propane. c) Trace amount.

with constant amount of $Pd(OAc)_2$, the yield increases until the Cu/Pd ratio reaches to unity, but after that, the yield becomes almost constant as shown in Fig. 1. These results suggest that the active species of the reaction

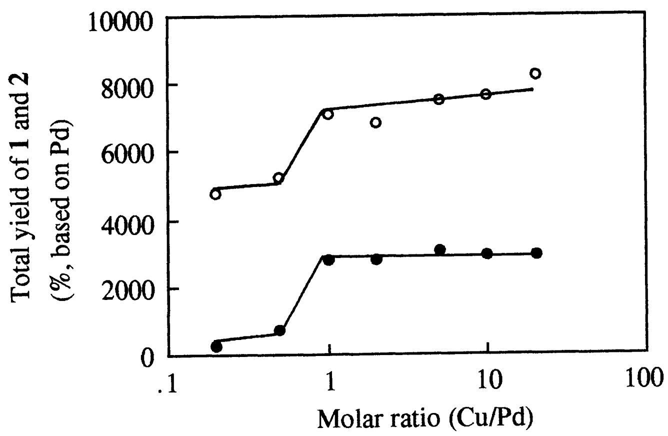


Fig. 1. The effect of the $Cu(OAc)_2/Pd(OAc)_2$ ratio on the total yield of butyric acids. Propane 10 atm, CO 20 atm, $Pd(OAc)_2$ 0.05 mmol, $K_2S_2O_8$ 9 mmol, CF_3COOH 5 ml, 80 °C. ● Reaction time 5 h. ○ Reaction time 20 h.

is Pd(II) rather than Cu(II), and that a Pd/Cu 1:1 complex is formed which plays an important role for the reaction.[2] The reaction of propane with the $Pd(OAc)_2/Cu(OAc)_2/K_2S_2O_8$ catalyst system would also proceed via electrophilic attack of Pd(II) to propane as is the case of other alkanes except methane which is activated best by the $Cu(OAc)_2/K_2S_2O_8$ system involving a radical process.[1,3]

The typical experimental procedure is as follows: In a 100-ml autoclave was placed a 50-ml centrifuge tube containing a magnetic stirring bar, $Pd(OAc)_2$, $Cu(OAc)_2$ (0.05 mmol each), $K_2S_2O_8$ (9 mmol), and CF_3COOH (5 ml). The autoclave was closed, flushed three times with propane, and pressured to 10 atm. The mixture was heated at 80 °C with stirring for 20 h. The reaction mixture was analyzed by gas chromatography using a PEG 6000 column and valeric acid as an internal standard to give isobutyric acid (**1**) and butyric acid (**2**) in 5500 and 1600% yields based on Pd, respectively. No by-products except a small amount of acetic acid derived from the catalysts, were detected.

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, Japan.

References

1) T. Nishiguchi, K. Nakata, K. Takaki, and Y. Fujiwara, *Chem. Lett.*, **1992**, 1141.
2) Since $Cu(OAc)_2$ without $K_2S_2O_8$ under the similar conditions cannot oxidize Pd black to Pd(II) as examined by ESCA,[4] it appears that the role of Cu(II) is not the oxidation of Pd(0) to Pd(II) but the formation of an active Pd/Cu 1:1 complex. However, because the $Cu(OAc)_2/K_2S_2O_8$ system oxidizes Pd black to Pd(II) and in this reaction Cu(II) is reduced to Cu(I) as examined by ESCA,[4] the role of Cu(II) as an oxidant cannot be eliminated completely.
3) Y. Fujiwara, T. Jintoku, and K. Takaki, *CHEMTECH* , **1990**, 636; K. Satoh, J. Watanabe, K. Takaki, and Y. Fujiwara, *Chem. Lett.*, **1991**, 1433; K. Nakata, K. Takaki, and Y. Fujiwara, *ibid.*, **1991**, 1437.
4) T. Miyata, K. Nakata, Y. Taniguchi, K. Takaki, and Y. Fujiwara, unpublished results.

(Received March 22, 1993)