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Palladium Catalyzed Carboxylation of Cyclohexane with Carbon Monoxide

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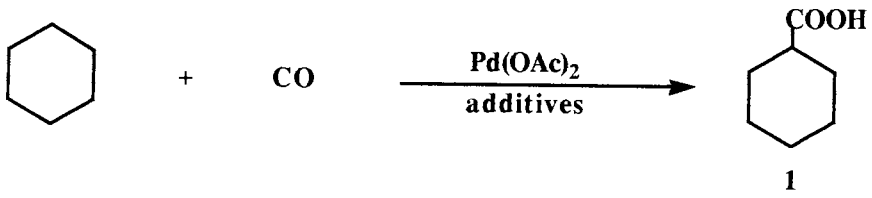
Very high turnover numbers of the catalyst in direct carboxylation of cyclohexane with CO have been obtained using palladium catalyst, to give 8.8% yield (turnover number 205) of cyclohexanecarboxylic acid based on the starting alkane.

In previous paper we reported carboxylation of alkanes with CO via direct thermal activation of an alkane C-H bond by a $Pd(OAc)_2/K_2S_2O_8/CF_3$-COOH catalyst system to give carboxylic acids.[1] This reaction proceeds under 30 atm of CO using a catalyst of $Pd(OAc)_2$ and $K_2S_2O_8$ in CF_3COOH and MeOH at 80 °C. However, the turnover number of the catalyst was only 1.95. We have found that the turnover number increases up to 200 when appropriate reaction conditions are employed.

We would like to report here the Pd-catalyzed synthesis of cyclohexanecarboxylic acid (**1**) from cyclohexane and CO via thermal C-H bond activation.[2]



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High turnover numbers of the catalyst were obtained by two methods: one by reducing the amount of $Pd(OAc)_2$ and the other by using Cu(OAc) as a cocatalyst.

Heating cyclohexane (5 cm^3) and $Pd(OAc)_2$ (0.005 mmol) in CF_3COOH (3.3 cm^3) with $K_2S_2O_8$ (9 mmol) under 20 atm of CO at 80 °C for 20 h resulted in the formation of cyclohexanecarboxylic acid (**1**) in 19616% yield based on

Pd (2.1% on cyclohexane). By this reaction high turnover number (ca. 200) was obtained, but the yield based on the starting cyclohexane was still low. Then in order to increase the yield, we investigated the effect of additives. We found that addition of $Cu(OAc)_2$ increases the yield based on the cyclohexane.

Table 1. Carboxylation of cyclohexane with CO to give cyclohexanecarboxylic acid (**1**)[a)]

Run	$Pd(OAc)_2$ (mmol)	$Cu(OAc)_2$ (mmol)	Yield of **1**/% Based on Pd	Based on cyclohexane
1	0.1	0.1	1634	3.5
2	0.1	0.2	1981	4.3
3	0.1	0.5	2024	4.3
4	0.02	0.2	9949	4.3
5	0.02	1.0	20504	8.8

a) Reactions were carried out using cyclohexane (5 cm^3), $K_2S_2O_8$ (9 mmol) and CF_3COOH (3.3 cm^3) under 20 atm of CO at 80 °C for 20 h.

Table 1 sumarizes the results of the reactions of cyclohexane with CO in the presence of $Cu(OAc)_2$. As can be seen from the table, the yield increases as increasing the amount of $Cu(OAc)_2$ (Run 1 to 3 and Run 4 to 5), and that the yield reaches to 8.8% (20504% based on Pd) when $Pd(OAc)_2/Cu(OAc)_2$=0.02 mmol/1.0 mmol. This remarkable increase of the yield would be due to acceleration of the reoxidation of Pd(0) to Pd(II) by $Cu(OAc)_2$.

Thus one can prepare cyclohexanecarboxylic acid (**1**) directly from cyclohexane and CO via thermal activation of an alkane C-H bond[3)] by Pd catalyst.

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References

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