

Palladium(II) and/or copper(II)-catalyzed carboxylation of small alkanes such as methane and ethane with carbon monoxide

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Abstract

Small alkanes such as methane and ethane react with carbon monoxide in the presence of transition metal catalysts to give the corresponding carboxylic acids in high yields. For the reaction of ethane, the Pd(OAc)₂/Cu(OAc)₂ mixed catalyst is the best, whereas that of methane proceeds most efficiently by the Cu(OAc)₂ catalyst system.

Key words: Palladium; Carbon monoxide; Alkane activation; Copper; Methane; Ethane

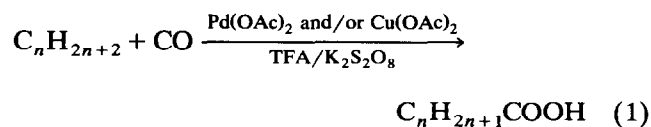
1. Introduction

Alkane activation/functionalization is a very challenging field, since it is difficult to cleave the C–H bond selectively under mild conditions while keeping the functionalized product less reactive than the starting material [1]. Alkanes, particularly methane, are the most abundant natural source of organic molecules. Thus the activation and functionalization of methane is important not only from an industrial but also from a synthetic point of view. The most popular way to activate the C–H bond of methane is by conversion into synthesis gases such as hydrogen and carbon monoxide (CO) by a solid catalyst under severe conditions. Within the last decade, many new methods for activation of the C–H bond other than by cracking have been proposed [2], but successful examples on the synthesis scale are limited to a few cases such as formylation by RhCl(CO)(PMe₃)₂ [3], ketonization by the Gif-system [4] and by an iron catalyst [5], and dehydrodimerization by the mercury-photosensitized reaction [6].

Alkane activation via electrophilic reaction, promoted by transition metals, has been seen as a potentially useful method; for example, H/D exchange by

K₂PtCl₄ [7], and chlorination by Rh(allyl)₃ [8], or Co(OAc)₃ [9]. Recently, the oxidation of methane to methanol, catalyzed by Pd^{II} or Hg^{II}, and the synthesis of propanal from methane and oxygen by metal oxides have been reported [10–12]. However, direct carboxylation of alkanes via C–C bond formation has never been achieved by transition metal catalysts.

In 1967, we reported the palladium-catalyzed reaction of olefins with aromatic compounds to give aromatic-substituted olefins via thermal activation of both aromatic and olefinic C–H bonds [13]. We have also demonstrated direct oxidation of benzene to phenol by the Pd(OAc)₂/1,10-phenanthroline/CO/O₂ system [14]. An important feature of these reactions is facile formation of an aryl-Pd σ-complex by electrophilic attack of Pd^{II} on an sp² C–H bond. We applied these palladium-catalyzed reactions to alkane C–H bond activation and found the carboxylation reaction with CO by the Pd(OAc)₂/Cu(OAc)₂/trifluoroacetic acid (TFA)/potassium peroxodisulfate (K₂S₂O₈) system [15–17] (eqn. (1)).



We have already reported [17,18] the direct carboxylation of alkanes such as cyclohexane and propane via

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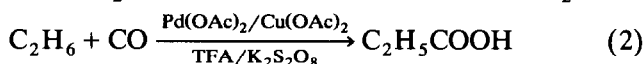
an electrophilic substitution reaction by the Pd(OAc)₂/Cu(OAc)₂/K₂S₂O₈/TFA system, and have elucidated the role of each metal complex in this reaction. In this system palladium(II) is an essential active species, because the yield of carboxylic acids is directly proportional to the concentration of palladium(II). The copper(II) complex plays the important role of strengthening the electrophilicity of palladium(II), especially when the ratio of Cu^{II}/Pd^{II} is more than unity, to give the corresponding carboxylic acids in high yields, and K₂S₂O₈ has been found to oxidize Pd⁰ to Pd^{II} [18,19]. We have also made it clear that the Cu(OAc)₂/K₂S₂O₈ system causes the radical reaction of alkanes with CO rather than ionic reactions [18].

Using a combination of Pd^{II} and Cu^{II} complexes we have investigated the carboxylation reactions of smaller alkanes such as methane and ethane with CO and found that in the case of ethane, the Pd(OAc)₂/Cu(OAc)₂ catalyst is the best and in the case of methane, Cu(OAc)₂ is the best catalyst. In this paper we now report these results together with mechanistic considerations.

2. Results and discussion

2.1. The reaction of ethane

First we investigated the reaction of ethane with CO using Pd(OAc)₂, Cu(OAc)₂, and K₂S₂O₈ (eqn. (2)). The reaction was carried out in a 150 ml autoclave charged with transition metal catalysts, K₂S₂O₈, and TFA at 80°C for 20 h. The results are listed in Table 1; clearly the Pd(OAc)₂/Cu(OAc)₂ catalyst is the best for carboxylation of ethane, giving propionic acid in 7600% yield based on palladium (entry 1, Table 1), and Pd(OAc)₂ alone (entry 2, Table 1) or Cu(OAc)₂ alone



(entry 3, Table 1) give lower yields. K₂S₂O₈ alone without metal catalysts (entry 4, Table 1) gives propionic acid in only 1.9% yield, based on K₂S₂O₈. These

TABLE 1. Reaction of ethane with carbon monoxide ^a

Entry	Pd(OAc) ₂ (mmol)	Cu(OAc) ₂ (mmol)	Yield, % ^b
1	0.05	0.10	7600 (2.06)
2	0.05	–	440 (0.18)
3	–	0.05	700 (0.29)
4	–	–	1.9 (0.14)

^a Reaction conditions: ethane 30 atm, carbon monoxide 20 atm, catalyst, K₂S₂O₈ 9 mmol, TFA 5 ml, at 80°C, 20 h. ^b GC yield based on the limiting metal salt (based on ethane).

TABLE 2. Effect of reaction temperature ^a

Entry	Reaction temperature (°C)	Yield, % ^b
1	40	400 (0.10)
2	60	1700 (0.47)
3	80	7600 (2.06)
4	100	6500 (1.76)
5	120	6200 (1.69)

^a Reaction conditions: ethane 30 atm, carbon monoxide 20 atm, Pd(OAc)₂ 0.05 mmol, Cu(OAc)₂ 0.1 mmol, K₂S₂O₈ 9 mmol, TFA 5 ml, 20 h. ^b GC yield based on Pd (based on ethane).

results are quite similar to those obtained in the reactions of propane and cyclohexane with CO and show that the reaction proceeds via electrophilic attack of Pd^{II} on a C–H bond [17,18].

Since it became apparent that the combination of palladium and copper complexes gave the best yield of propionic acid, we investigated the effects of reaction temperature and of pressures of CO and ethane on the yield. Table 2 summarizes the results of reactions carried out at various reaction temperatures. At low temperature, the yield is low (entry 1, Table 2) but the yield increases with increasing reaction temperature, and reaches 7600% based on palladium at 80°C (entry 3, Table 2). But at higher reaction temperatures (entries 4 and 5, Table 2), the yield decreases a little. This is probably for two reasons: thermal self-decomposition of K₂S₂O₈ is accelerated at high temperature, slowing reoxidation of Pd⁰ to Pd^{II}, and the solubility of gaseous educts such as ethane and CO decreases at high temperature. On this basis, the following reactions were performed at 80°C.

In this carboxylation reaction, the educts, ethane and CO are gaseous starting materials, so the solubility of these gases in the liquid phase is very important for high reaction yields. In addition, CO acts not only as a carbonyl source but also as a reducing agent [14]. We therefore investigated the effects of pressures of CO and ethane on this reaction.

First we investigated the effect of the pressure of CO on this reaction (Table 3). As is apparent, this

TABLE 3. Effect of the pressure of carbon monoxide ^a

Entry	Pressure of CO (atm)	Yield, %
1	10	3700 (0.99)
2	20	7600 (2.06)
3	30	8200 (2.22)
4	40	3600 (0.99)

^a Reaction conditions: ethane 30 atm, carbon monoxide, Pd(OAc)₂ 0.05 mmol, Cu(OAc)₂ 0.1 mmol, K₂S₂O₈ 9 mmol, TFA 5 ml, at 80°C, 20 h. ^b GC yield based on Pd (based on ethane).

TABLE 4. Effect of the pressure of ethane ^a

Entry	Pressure of ethane (atm)	Yield, % ^b
1	30	7600 (2.06)
2	20	5500 (2.23)
3	10	4400 (3.56)
4	5	4200 (6.88)
5	1	3300 (17.7)

^a Reaction conditions: ethane, carbon monoxide 20 atm, Pd(OAc)₂ 0.05 mmol, Cu(OAc)₂ 0.1 mmol, K₂S₂O₈ 9 mmol, TFA 5 ml, at 80°C, 20 h. ^b GC yield based on Pd (based on ethane).

carboxylation reaction proceeds most effectively under 20 or 30 atm of CO (entries 2 and 3, Table 3). But under low pressure such as 10 atm (entry 1, Table 3), the yield of propionic acid decreases to 3700% based on palladium. Under low CO pressure, the solubility of CO may be lower than that under moderate pressure. In addition, under a higher pressure such as 40 atm, the yield is also low (entry 4, Table 2), because CO acts as a reducing agent under these conditions, and will reduce Pd^{II} to Pd⁰. From these results, the reaction of ethane was carried out under 20 atm of CO.

We then investigated the effects of the pressure of ethane (Table 4); the yield of propionic acid increases as the pressure of ethane increases. Under 30 atm (entry 1, Table 4), the yield reaches 7600%, the maximum yield we obtained. However, interestingly enough, the yield based on ethane increases with decreasing ethane pressure. When ethane pressure is 1 atm (entry 5, Table 4), the yield based on ethane reaches 17.7% while the yield based on palladium is low. In the case of propane, the maximum yield (23% on propane) of the products, butyric and isobutyric acids, was also obtained when the pressure of educt was as low as 1 atm [20]. These results suggest that in this system the

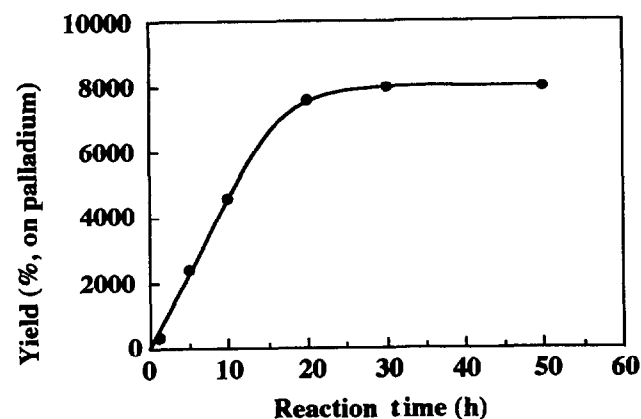
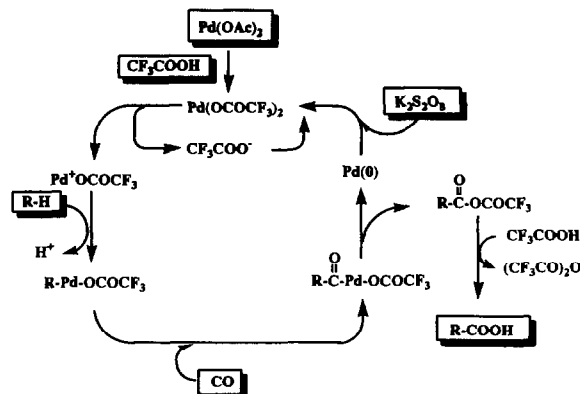


Fig. 1. Yield of propionic acid vs. time in the reaction of ethane (30 atm) with CO (20 atm) in the presence of Pd(OAc)₂ (0.05 mmol), Cu(OAc)₂ (0.10 mmol), K₂S₂O₈ (9 mmol) and TFA (5 ml) at 80°C.



R = Ethyl, Propyl, Cyclohexyl etc.

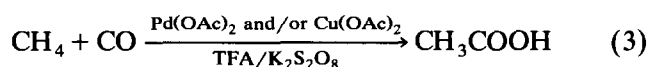
Scheme 1. Mechanism of electrophilic carboxylation reaction.

yields based on palladium and ethane can be controlled by the pressure of ethane. Since gaseous educts can be recycled, the efficiency of catalysts is more important than that of educts. We therefore performed the reaction under 30 atm of ethane.

Furthermore we have investigated the time-course of the reaction of ethane. The results are shown in Fig. 1. The yield of propionic acid increases steadily, and after 20 h becomes almost constant. This time-yield profile is quite similar to those of the reactions of cyclohexane and propane with CO which proceed via an electrophilic attack of Pd^{II} on C–H bonds as shown in Scheme 1 [17,18]. These results suggest that the reaction of ethane with CO by the Pd(OAc)₂/Cu(OAc)₂ catalyst also proceeds electrophilically.

2.2. The reaction of methane

We investigated the carboxylation of methane under similar reaction



conditions using a combination of Pd(OAc)₂ and/or Cu(OAc)₂ in the presence of K₂S₂O₈ as shown in eqn. (3). The results are summarized in Table 5. The reaction was carried out as described in the reaction of

TABLE 5. Reaction of methane with carbon monoxide ^a

Entry	Pd(OAc) ₂ (mmol)	Cu(OAc) ₂ (mmol)	Yield, % ^b
1	0.05	0.05	1300 (0.40)
2	0.05	–	100 (0.03)
3	–	0.05	2960 (0.91)
4	–	–	0.5 (0.03)

^a Reaction conditions: methane 40 atm, carbon monoxide 20 atm, catalyst, K₂S₂O₈ 9 mmol, TFA 5 ml, at 80°C, 20 h. ^b GC yield based on the least amount metal salt (based on methane).

ethane. Table 5 shows that the Pd(OAc)₂/Cu(OAc)₂ mixed catalyst gives rise to acetic acid in 1300% yield based on palladium (entry 1, Table 5), and that the yield is much higher than that by the Pd(OAc)₂ catalyst alone (entry 1 *vs.* 2, Table 5). This phenomenon is consistent with that of the reactions of other hydrocarbons such as ethane, propane, and cyclohexane, suggesting that the reaction by Pd(OAc)₂/Cu(OAc)₂ and Pd(OAc)₂ alone proceeds via electrophilic attack of Pd^{II} to C–H bonds [15–18]. However, interestingly enough, Cu(OAc)₂ alone gives the best yield of acetic acid (2960% on copper) (entry 3, Table 5). This reaction of methane with CO by the Cu(OAc)₂/K₂S₂O₈ catalyst would proceed via a radical process since the catalyst system has been found to cause a radical reaction rather than an ionic reaction [18]. Thus the reaction of methane with CO can also proceed via electrophilic substitution reaction by the Pd(OAc)₂/Cu(OAc)₂ or Pd(OAc)₂ catalyst, but the Cu(OAc)₂ catalyst gives the best yield of acetic acid via a radical reaction.

Since it became apparent that the reaction of methane was different from those of other hydrocarbons in that Cu(OAc)₂ gives a higher yield than does Pd(OAc)₂, we investigated the catalytic reactivity of metal acetates other than Cu(OAc)₂. The results using various metal acetates are summarized in Table 6. Cu(OAc)₂ is evidently the best catalyst and AgOAc gives only a moderate yield (entry 3, Table 6), whereas other metal acetates give inferior yields. In addition, the effect was examined of oxidation state of the metals on reactivity. The reaction was performed using metal powders and chlorides of copper and iron. As shown in Table 7, copper powder results in moderate yield (entry 2, Table 7). However, most metal chlorides are inactive in this reaction (entries 3, 4, 9, and 10, Table 7). In addition, the combination of Cu(OAc)₂ with Cu powder gives a moderate yield (entry 5, Table 7), but both Cu(OAc)₂ with CuCl and with CuCl and Cu powder give very low yields (entries 6 and 7, Table 7). Thus it was made clear that Cu(OAc)₂/K₂S₂O₈ is

TABLE 6. Effect of metal acetate ^a

Entry	Metal acetate	Yield, % ^b
1	none	tr
2	Cu(OAc) ₂	2960
3	AgOAc	930
4	Ni(OAc) ₂	20
5	Zn(OAc) ₂	20
6	Co(OAc) ₂	tr
7	Mn(OAc) ₂	tr

^a Reaction conditions: methane 40 atm, carbon monoxide 20 atm, catalyst 0.05 mmol, K₂S₂O₈ 9 mmol, TFA 5 ml, at 80°C, 20 h. ^b GC yield based on catalyst.

TABLE 7. Effect of metal salts ^a

Entry	metal salts	Yield, % ^b
1	none	tr
2	Cu powder	680
3	CuCl	tr
4	CuCl ₂	10
5	Cu(OAc) ₂ -Cu powder	1130
6	Cu(OAc) ₂ -CuCl	tr
7	Cu(OAc) ₂ -CuCl-Cu powder	20
8	Fe powder	tr
9	FeCl ₂	tr
10	FeCl ₃	tr

^a Reaction conditions: methane 40 atm, carbon monoxide 20 atm, catalyst 0.05 mmol (0.05 mmol each for entries 5–7), K₂S₂O₈ 9 mmol, TFA 5 ml, at 80°C, 20 h. ^b GC yield based on catalyst (based on copper acetate for entries 5–7).

the best catalyst for the carboxylation reaction of methane.

We then investigated the effect of methane pressure on the yield of acetic acid using the Cu(OAc)₂/K₂S₂O₈ catalyst (Table 8). The yield of acetic acid increases with increasing methane pressure, and when methane pressure is 50 atm, the yield reaches 3200% based on copper.

In order to clarify the difference of reactivity between the Cu(OAc)₂ system and the Pd(OAc)₂/Cu(OAc)₂ system, we investigated the time-course of the reaction of methane in each. The results are shown in Fig. 2. In the Pd^{II}/Cu^{II} system, the yield of acetic acid increases steadily becoming constant after 10 h. On the other hand, in the Cu(OAc)₂ system, the yield increases slowly with induction period and after 10 h it increases rapidly. After 25 h, the yield remains constant indicating that reaction is complete. At this point the yield of acetic acid is almost 4000% based on copper. The reactions evidently have different pathways: with Cu(OAc)₂ the reaction is radical and with Pd(OAc)₂/Cu(OAc)₂, electrophilic.

The yield of acetic acid against the amount of Cu(OAc)₂ in the reaction of methane (40 atm) with CO (20 atm) in the presence of K₂S₂O₈ (9 mmol) and TFA (5 ml) at 80°C for 20 h is depicted in Fig. 3. As

TABLE 8. Effect of the methane pressure ^a

Entry	Pressure of methane (atm)	Yield, % ^a
1	10	580 (0.71)
2	20	1190 (0.73)
3	30	1670 (0.68)
4	40	2960 (0.91)
5	50	3200 (0.78)

^a Reaction conditions: methane, carbon monoxide 20 atm, Cu(OAc)₂ 0.05 mmol, K₂S₂O₈ 9 mmol, TFA 5 ml, at 80°C, 20 h. ^b GC yield based on Cu (based on methane).

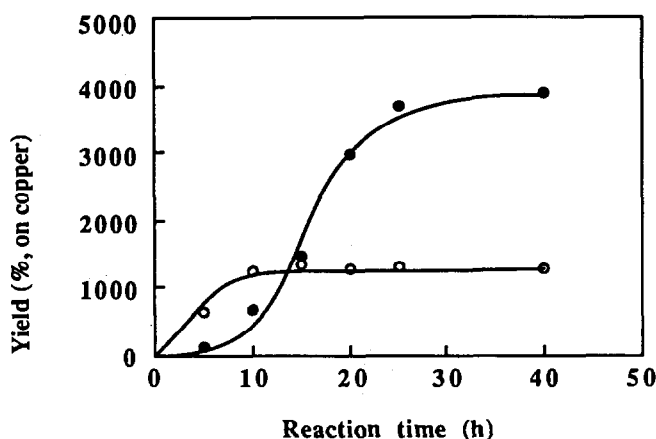


Fig. 2. Yield of acetic acid vs. time in the reaction of CH₄ (40 atm) with CO (20 atm) in the presence of K₂S₂O₈ (9 mmol), and TFA (5 ml) at 80°C. ●: with Cu(OAc)₂ (0.5 mmol); ○: with Pd(OAc)₂ and Cu(OAc)₂ (0.05 mmol each).

mentioned above, when 0.05 mmol of Cu(OAc)₂ is used, the yield is 2960% based on copper, and as the amount of Cu(OAc)₂ decreases the yield increases, reaching 11130% based on copper when 0.01 mmol of Cu(OAc)₂ is used. That the yield based on catalyst increases as the amount of catalyst decreases has often been observed in catalytic reactions [14], but interestingly enough, when a large amount of Cu(OAc)₂ is used, this reaction gives a very low yield. It is not clear why but there are two possible reasons: side reactions give ethane and carbon dioxide, as shown by GC analysis, and ligand exchange of Cu(OAc)₂ from CH₃COO⁻ to CF₃COO⁻ is difficult when there is a large amount of Cu(OAc)₂ present.

The mechanism of the Cu(OAc)₂ catalyzed carboxylation of methane with CO is not clear, but as men-

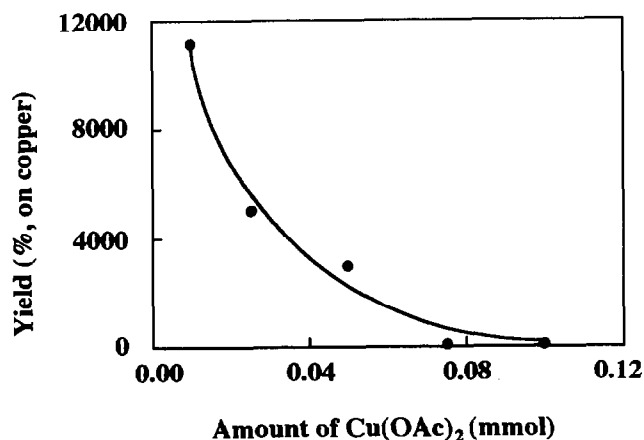


Fig. 3. Yield of acetic acid vs. the amount of Cu(OAc)₂ in the reaction of methane (40 atm) with CO (20 atm) in the presence of Cu(OAc)₂, K₂S₂O₈ (9 mmol), and TFA (5 ml) at 80°C for 20 h.

tioned above there may be a radical process; the source of the radical may be K₂S₂O₈ or CF₃· derived from the decomposition of Cu(OC(O)CF₃)₂ [21].

Recently, Sen and Lin reported the K₂S₂O₈-mediated carboxylation of methane and ethane with CO in water to give acetic acid and/or propionic acid [22]. However, in our reactions, K₂S₂O₈ gives only very low yields (entry 4, Tables 1 and 5). It is not possible to compare these results as a yield based on the starting methane or ethane is not given for the former reaction.

In the K₂S₂O₈-mediated reaction, SO₄^{•-} generated from S₂O₈²⁻ abstracts a hydrogen atom from methane and ethane to form the corresponding alkyl radicals which are trapped by CO and the resultant acyl radicals are converted into the carboxylic acid [22]. In the present reaction of methane by the Cu(OAc)₂/K₂S₂O₈ system, there are two possible radical sources, namely K₂S₂O₈ and CF₃·.

3. Conclusions

We have demonstrated the carboxylations of methane and ethane with CO using the Pd(OAc)₂/Cu(OAc)₂ or Cu(OAc)₂ catalyst systems. The reaction of ethane is catalyzed best by the former to give propionic acid in 7600% yield based on palladium, via electrophilic substitution reaction. The Pd(OAc)₂/Cu(OAc)₂ mixed catalyst has been found to bring about the carboxylation reaction of various alkanes via electrophilic substitution. In contrast, the reaction of methane is catalyzed best by the Cu(OAc)₂ catalyst, to give acetic acid in 11130% yield based on copper, probably via a radical process. The present Pd^{II} and/or Cu^{II} catalyzed carboxylations of alkane with CO via thermal C-H bond activation should be applicable not only in synthetic organic chemistry but also in industrial process. For instance, acetic acid is now commercially produced mainly by the Monsanto Process using methanol and CO with a rhodium catalyst. The present reaction can produce acetic acid using cheaper methane and a copper catalyst.

4. Experimental section

4.1. Materials and methods

Mass spectra were obtained on a Shimadzu GC-MS QP1000 spectrometer. GC analyses were performed on a Shimadzu GC-8A equipped with TCD or FID with a 1 m × 3.2 mm i.d. column of 10% polyethylene glycol 6000 on Chromosorb W for the analyses of liquid products, and 2 m × 3.2 mm i.d. columns of unibeads 1S and unibeads C for the analyses of gaseous products. Ethane, methane, CO (Sumitomo), K₂S₂O₈ and TFA (Waco) were used without purification. Pd(OAc)₂

was prepared by the literature procedure [23]. Cu(OAc)₂ and other metal salts were purchased (Waco) and dried by azeotropic distillation with benzene.

4.2. Identification of the products and determination of the yield

The products were identified by comparison of GC, GC-MS, and NMR spectra with those of the commercially available authentic samples. The yields of acetic and propionic acids were determined by GC using butyric acid as an internal standard. Gaseous products were analyzed by GLC by using a standard gas containing methane (0.986%), ethane (0.976%), propane (1.01%), n-butane (1.01%), iso-butane (1.02%), and CO (0.998%) in dinitrogen.

4.3. Reaction of ethane with CO

A 50 ml glass centrifuge tube equipped with a teflon-covered magnetic stirring bar was charged with Pd(OAc)₂ (11.2 mg, 0.05 mmol), Cu(OAc)₂ (18.3 mg, 0.10 mmol), and TFA (5 ml). The solution was stirred for 5 min. Then K₂S₂O₈ (2.43 g, 9 mmol) was added to the solution. A rubber septum with a glass needle was fitted to the tube, which was placed in a 150 ml stainless autoclave. The autoclave was closed, flushed with ethane, and pressurized to 30 atm with ethane and 20 atm with CO. The mixture was heated with stirring at 80°C for 20 h. After cooling and venting of the residual gas, the autoclave was opened and the mixture was analyzed directly by GLC without aqueous work-up using butyric acid as an internal standard to give propionic acid in 7600% yield based on palladium.

4.4. Time-course of the reaction of ethane

In a 150 ml stainless autoclave was placed a 50 ml glass centrifuge tube containing a magnetic stirring bar, with the same amounts of Pd(OAc)₂, Cu(OAc)₂, K₂S₂O₈ and TFA as above. The autoclave was closed, flushed with ethane, and pressurized to 30 atm with ethane and 20 atm with CO. The mixture was heated at 80°C with stirring for the required length of time (1, 5, 10, 20, 30 and 50 h). Results are shown in Fig. 1.

4.5. Reaction of methane with CO

In a 100 ml stainless autoclave was placed a 50 ml glass centrifuge tube containing a magnetic stirring bar, Cu(OAc)₂ (9.2 mg, 0.05 mmol), K₂S₂O₈ (2.43 g, 9 mmol), and TFA (5 ml). The autoclave was closed, flushed with methane, and pressurized to 40 atm with methane and then 20 atm with CO. After stirring for 1 h, the mixture was heated with stirring at 80°C for 20 h. After cooling, the residual gas was collected in the gas sampling bag (GL Science Co.), and then the autoclave was opened and the mixture poured into a

sample tube. The liquid layer was analyzed by GLC without aqueous work-up to give acetic acid in 2960% yield based on copper using butyric acid as an internal standard.

Acknowledgments

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