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Oxidative Carbonylation of Aniline over Pd/C Catalyst: Effect of Promoters, Solvents, and Reaction Conditions[1]

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Oxidative carbonylation of aniline to *N,N'*-diphenylurea over 5% Pd/C–NaI catalyst has been reported. The effects of promoters, solvents, reaction conditions, and pretreatment of catalyst with reactants have been investigated. Pretreatment of 5% Pd/C catalyst with O_2, CO, and aniline resulted initially in a decrease in the activity of the catalyst. Activity-versus-NaI concentration and activity-versus-O_2 pressure curves passed through maxima, indicating inhibition of rates at higher concentrations. CO pressure showed a linear dependence below 35 atm pressure, but zero-order behavior at higher pressures. The variation in activity was 1.6th order with respect to aniline concentration. Higher activity is obtained in polar solvents. Process parameters had a strong influence on the activity of the catalyst, but the selectivity for *N,N'*-diphenylurea was unaffected.

INTRODUCTION

Oxidative carbonylation of amines is important in the synthesis of carbamates, which have applications in insecticides and the polymer industry. This nonphosgene route has led to the development of a new process for methylene diphenyl diisocyanate (MDI) (*1, 2*). Oxidative carbonylation of aniline is an important step, which gives phenylurethane when the reaction is carried out in the presence of alcohol. The stoichiometric reaction is

$$R{-}NH_2 + CO + \tfrac{1}{2}O_2 \xrightarrow[R'OH]{\text{catalyst}} RNH\,COOR' + H_2O. \quad (1)$$

Oxidative carbonylation of aromatic amines is reported to be effectively carried out using a variety of supported noble metal catalysts (viz., Pd, Pt, Rh, Ir, Ru etc.) (*3, 4*) and in the presence of alkali metal or alkyl iodide promoters. However, metallic Pd or Pd/C with NaI promoter has been found to be highly active and selective for this reaction (*3*) and a phenylurethane yield of 90–95% from aniline has been reported. Most of the literature on this subject is patented (*5–8*), and recent papers (*3, 4*) describe mainly the activity of different catalyst systems. There is no report of a detailed investigation of the role of iodide promoters, the effect of reaction conditions, product distribution, and catalyst reusability. This prompted us to undertake the present work in which we study the effect of process conditions, solvents, and promoters on the activity and the selectivity of oxidative carbonylation of aniline with the Pd/C–NaI catalyst system. It is believed that the oxidative carbonylation of aniline proceeds through diphenylurea as an intermediate. Therefore, this step has been separately investigated in the absence of alcohol. Further, the effects of catalyst pretreatment and catalyst reusability have also been studied. Such a study seems most useful in view of the potential importance of this reaction in a new nonphosgene process for MDI.

EXPERIMENTAL

The catalyst, consisting of 5% Pd/C, was prepared according to the procedure described by Mozingo (*9*). The specifications

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0021-9517/88 $3.00

TABLE 1

Specification of Pd/C Catalyst

Catalyst particle size	10 μm
Particle density	2.0 g/cm^3
Pore volume	0.45 cm^3/g
Porosity	0.90
Surface area	7.7 × 10^2 m^2/g
Pd content	5.0 wt%

of the catalyst are given in Table 1. Palladium chloride was purchased from Arora Mathey Ltd; aniline, ethanol, and solvents were freshly distilled and used. Carbon monoxide gas generated and compressed in our own laboratory was used from the cylinder and was greater than 99.8% pure. Oxygen was used from a cylinder supplied by Indian Oxygen Ltd., Bombay.

Oxycarbonylation experiments were carried out in a 300-cm^3-capacity high-pressure stirred autoclave (Hastelloy C) supplied by Parr Instrument Company. This reactor was provided with automatic temperature control, agitation, a cooling coil, and devices for sampling gas- and liquid-phase components.

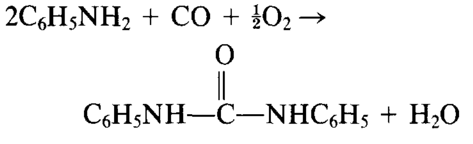
In a typical experiment, known quantities of aniline (53.8 mmol), catalyst, 5% Pd/C (5.0×10^{-3} g/cm^3), NaI (0.87 mmol) and solvent (DMF, 95 cm^3) were charged into the autoclave. The autoclave was pressurized with carbon monoxide and oxygen to a total pressure of 41 bar ($CO:O_2 = 5:1$). The contents were heated to 100°C and the reaction started by switching on the stirrer. The reaction was carried out at a constant pressure by supplying a $CO:O_2$ mixture (2 : 1 ratio) from a reservoir. After 2 hr, the contents were cooled and products analyzed by HPLC and GLC. The gas phase was also analyzed by GC.

RESULTS AND DISCUSSION

Several experiments were carried out on oxidative carbonylation of aniline using a 5% Pd/C–NaI catalyst system to investigate product distribution, role of promoters, solvents, reaction conditions, and catalyst reusability.

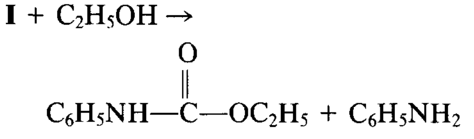
Preliminary Observations

A few initial experiments were carried out to identify the role of the Pd/C catalyst system in the synthesis of phenylurethane. Figure 1 shows a typical concentration profile in a batch reactor. This indicates that complete conversion of aniline is possible and *N,N'*-diphenylurea and phenylurethane are the products. Obviously, *N,N'*-diphenylurea is an intermediate product. The overall reaction (1) can therefore be described by the following steps.



$$2C_6H_5NH_2 + CO + \tfrac{1}{2}O_2 \rightarrow C_6H_5NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NHC_6H_5 + H_2O \qquad (2)$$

(I)



$$\mathbf{I} + C_2H_5OH \rightarrow C_6H_5NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5 + C_6H_5NH_2 \qquad (3)$$

(II)

Here, a question arises as to whether Pd/C catalyst is also required for reaction (3). Earlier workers (*3, 4*), proposed that *N,N'*-diphenylurea is converted to phenylurethane by catalytic oxidative carbonylation in the presence of alcohol. However, there is no evidence that the reaction is catalytic or noncatalytic. To investigate this aspect, oxidative carbonylation of aniline was carried out in the absence of ethyl alcohol using DMF as a solvent. This led to nearly 100% conversion of aniline to *N,N'*-diphenylurea. In another experiment, *N,N'*-diphenylurea was reacted with ethyl alcohol at 150°C in the absence of the Pd/C–NaI catalyst system. This resulted in quantitative conversion of *N,N'*-diphenylurea to phenylurethane and aniline. Thus, reaction (3) does not require a catalyst. In the presence of the Pd/C–NaI catalyst system under N_2 atmosphere, the rate

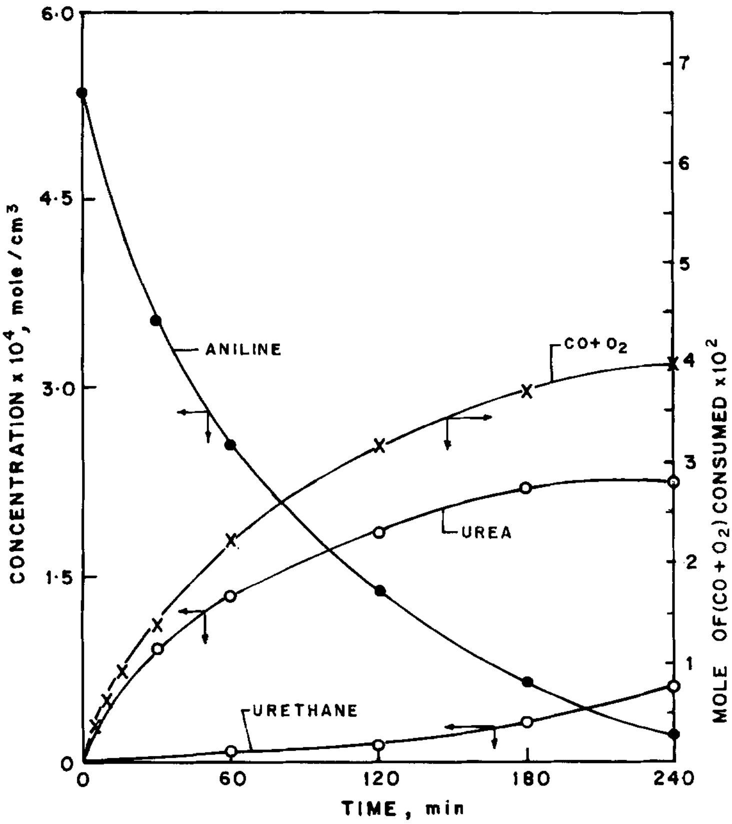


FIG. 1. A typical concentration–time plot for oxycarbonylation of aniline. Conditions: aniline, 53.8 mmol; 5% Pd/C, 0.5 g; NaI, 0.87 mmol; temperature, 100°C; solvent, ethanol; stirrer speed, 700 rpm; P_{CO}, 34 atm; P_{O_2}, 6.8 atm.

of reaction between *N*,*N*′-diphenylurea and ethyl alcohol was not found to be affected (see Table 2). These results indicate that mainly reaction (2) involves catalytic oxidative carbonylation and reaction (3) is indeed a noncatalytic reaction. However, if the reaction is carried out in a single step, it has the obvious advantage of *in situ* conver-

TABLE 2

Preliminary Experiments on Oxidative Carbonylation of Aniline[a]

Aniline (mmol)	Catalyst 5% Pd/C [g (Pd mmol)]	NaI (mmol)	Solvent, (cm^3)	P_{CO} (atm)	P_{O_2} (atm)	Temperature (°C)	Contact time (hr)	Conversion of aniline (%)	Product distribution (mmol)	
									Diphenylurea	Phenylurethane
53.8	0.5 (0.24)	0.87	Ethanol (95)	55	11	170	3.0	80	nil	42.8
53.8	nil	0.87	Ethanol (95)	55	11	170	3.0	nil	—	—
53.8	0.5 (0.24)	nil	Ethanol (95)	55	11	170	3.0	nil	—	—
53.8	0.5 (0.24)	0.87	Ethanol (95)	55	nil	170	3.0	nil	—	—
53.8	0.5 (0.24)	0.87	DMF (95)	55	11	170	3.0	100.0	26.7	—
20.5[b]	—	—	Ethanol[c] (95)	—	—	150	1.5	—	23.6[c]	20.3[b]
20.4[b]	0.5 (0.24)	0.87	Ethanol[c] (95)	—	—	150	1.5	—	23.6[c]	20.4[b]

[a] Conditions: volume of liquid, 100 cm^3; agitation speed, 700 rpm.

[b] Indicates mmol of aniline and phenylurethane produced.

[c] Noncatalytic reaction between urea and ethanol under N_2 atmosphere.

sion of *N*,*N*′-diphenylurea to phenylurethane. Also, aniline formed in reaction (3) is further converted to phenylurethane.

The results in Fig. 1 indicate almost 99.5% material balance of liquid-phase components and greater than 95% material balance of CO and O_2 consumed. This suggests that almost no side reactions occur under the conditions used in this work. Since reaction (2) is a catalytic step, all the experiments aimed at investigating the role of promoters, solvents, reaction conditions, and catalyst reusability were carried out in the absence of ethyl alcohol.

Initially, some blank experiments were carried out in which oxidative carbonylation of aniline was studied using Pd/C catalyst with and without NaI. The results are presented in Table 2. It was observed that in the absence of NaI, no conversion of aniline occurs, while with NaI, almost 80% conversion of aniline is observed. Another experiment carried out using only NaI in the absence of Pd/C catalyst indicated no conversion of aniline. These results suggest that neither Pd/C nor NaI catalyzes the oxidative carbonylation, but the combination of Pd/C and NaI acts as a catalyst for oxidative carbonylation of aniline.

Pretreatment

Catalyst pretreatment can play an important role in the activity and selectivity of catalytic reactions. Although such effects are well known in catalytic hydrogenation reactions, there is practically no information on pretreatment effects in oxidative carbonylation catalysis. Therefore, some experiments were conducted to learn the effect of pretreatment of Pd/C catalyst with CO, O_2, and aniline. In these experiments, the catalyst system with solvent was pretreated with CO, O_2, or aniline individually and then oxidative carbonylation was carried out. The results are presented in Table 3 along with the conditions of pretreatment. It was observed that treatment of Pd/C catalyst with all the reactants resulted in a decrease in the initial activity compared to that without any pretreatment. Pretreatment with O_2 resulted in a significant decrease in the activity of the catalyst. The selectivity of formation of *N*,*N*′-diphenylurea was, however, not found to be affected. The pretreatment is likely to modify the nature of active sites, thus resulting in a decrease in the activity. It is important to note that such changes in the nature of ac-

TABLE 3

Effect of CO, O_2, and Aniline Pretreatment on Activity of 5% Pd/C–NaI Catalyst[a]

Pretreatment	Pretreatment conditions			Contact time (min)	Conversion of aniline (%)	Selectivity of diphenyl (%)
	Duration (min)	Temperature (°C)	Pressure (atm)			
Fresh catalyst	—	—	—	30	35.6	100
				120	73.6	99.8
CO pretreatment	60	100	20	30	30.7	99.0
				120	73.2	99.2
O_2 pretreatment	60	100	20	30	14.4	99.0
				120	73.5	98.8
Aniline pretreatment (under N_2)	60	100	20	30	25.3	98.9
				120	74.1	98.6

[a] Catalyst testing conditions: 5% Pd/C, 0.5 g; NaI, 0.87 mmol; P_{CO}, 34 atm; P_{O_2}, 6.8 atm; aniline, 53.8 mmol; temperature, 100°C; solvent (DMF), 95 ml.

tive sites appear to be reversible, as indicated by the observation that the difference in the average activity at higher conversions (see Table 3) is less than the difference in initial activity. A drastic effect of O_2 pretreatment could be due to formation of PdO_x-type sites and there is a possibility that there exist two types of sites, Pd(O) and PdO_x, only one of which [Pd(O)] may be active. Such observations are recorded for oxidation of CO with Pt catalyst (*10*). Though a detailed mechanism for pretreatment effects has not been studied here, the reported data would be useful in explaining some of the interesting trends in operating conditions (as discussed later). As there was no advantage to catalyst pretreatment with reactants, all further experiments were carried out without any pretreatment.

Reusability of Catalyst

To obtain reliable data on the effect of various process conditions on the conversion of aniline and selectivity of *N,N'*-diphenylurea, it is necessary to ensure that the catalyst activity remains constant throughout a run. For this purpose, 5% Pd/C catalyst was reused several times. These data indicate that even after the catalyst was used five times, more than 90% of the catalyst activity was retained.

Stirrer Speed

To ensure that the catalytic activity observed is under conditions of negligible gas–liquid mass transfer resistance, a few experiments were carried out to see the effect of agitation speed. It was observed that above 500 rpm, agitation speed has no effect on the activity of the catalyst and hence mass transfer effect is unimportant beyond 500 rpm. All experiments were therefore carried out at a stirrer speed of 700 rpm.

Promoters

As already observed in the preliminary experiments, promoters containing iodide are absolutely necessary in the oxidative carbonylation catalyst system. Therefore, the effects on the activity of Pd/C catalyst of a variety of iodide-containing promoters, particularly NaI, I_2, C_2H_5I, KI, CH_3I, and KIO_3, were studied and the results are presented in Table 4. The activity was found to decrease in the order $I_2 > NaI \simeq C_2H_5I > CH_3I \gg KI0_3 \simeq KI$. The observed activity levels with I_2 and NaI were comparable and

TABLE 4

Oxidative Carbonylation of Aniline to *N,N'*-Diphenylurea: Effect of Iodide Promoter[a]

Promoter (mmol)	Conversion of aniline (%)		Yield of urea (mmol)		Selectivity (%) 2 hr
	1 hr	2 hr	1 hr	2 hr	
I_2 (0.95)	71	96	19	25.8	98.5
NaI (0.95)	65	97	17.3	26.2	97.8
C_2H_5I (0.95)	61	76	16.2	20.4	97.9
CH_3I (0.95)	44	68	11.7	18.3	98.3
KIO_3 (0.95)	17	18	4.6	4.8	99.3
KI (0.95)	11	17	3.0	4.6	98.9

[a] Reaction conditions: Pd black, 0.95 mmol; aniline, 53.8 mmol; temperature, 100°C; solvent (DMF), 95 ml; P_{CO}, 34 bar; P_{O_2}, 6.8 bar.

the highest; KIO_3 and KI had the lowest activity. The selectivity of *N*,*N*′-diphenylurea was, however, very high (>98%) with respect to the promoters studied.

NaI Concentration

Effect of NaI concentration on the activity of oxidative carbonylation reaction was studied at 100°C using Pd metal and Pd/C catalysts and the results are presented in Figs. 2 and 3 as conversion of aniline versus NaI/Pd ratio (mole/mole) and NaI concentration, respectively. It was observed that the conversion of aniline first increases with an increase in NaI/Pd ratio and then decreases with further increases in the NaI/Pd ratio. The selectivity for *N*,*N*′-diphenylurea was found to be greater than 95% for all concentrations. Thus, there exists an optimum concentration of NaI for a given set of conditions. Interestingly, this optimum NaI concentration was observed for a molar ratio of NaI/Pd as unity for Pd metal catalyst. For 5% Pd/C catalyst, the optimum NaI/Pd ratio (molar) observed was 3.6. This difference in NaI/Pd ratio for the Pd/C catalyst can be due to significant adsorption of NaI on the carbon support. At higher NaI concentration, it is likely that most of the active sites are occupied by NaI, thus leaving a smaller number of active sites vacant for adsorption of CO, O_2, and aniline. This appears to be a case of inhibition due to the strong adsorption properties of NaI.

Solvents

The effects of different solvents on the activity and selectivity of 5% Pd/C catalyst were investigated at 100°C with NaI as a promoter. The results are presented in Table 5. Under these conditions, even with alcohols as solvents, the selectivity of *N*,*N*′-diphenylurea was quite high (>95%).

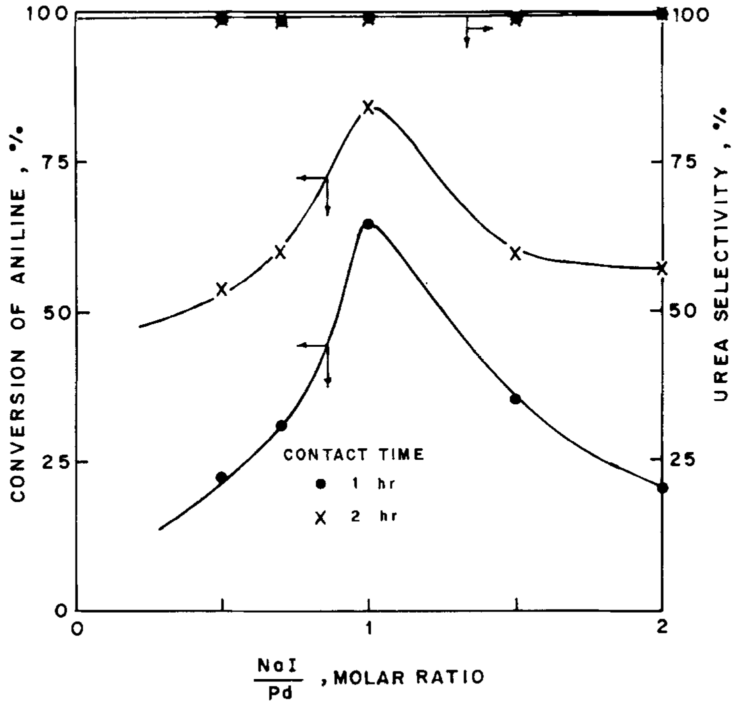


FIG. 2. Effect of NaI/Pd ratio on conversion of aniline to *N*,*N*′-diphenylurea. Conditions: aniline, 53.8 mmol; Pd metal, 0.94 mmol; NaI, 0.87 mmol; temperature, 100°C; DMF, 95 cm^3; contact time, 2 hr; stirrer speed, 700 rpm; P_{CO}, 34 atm; P_{O_2}, 5.8 atm.

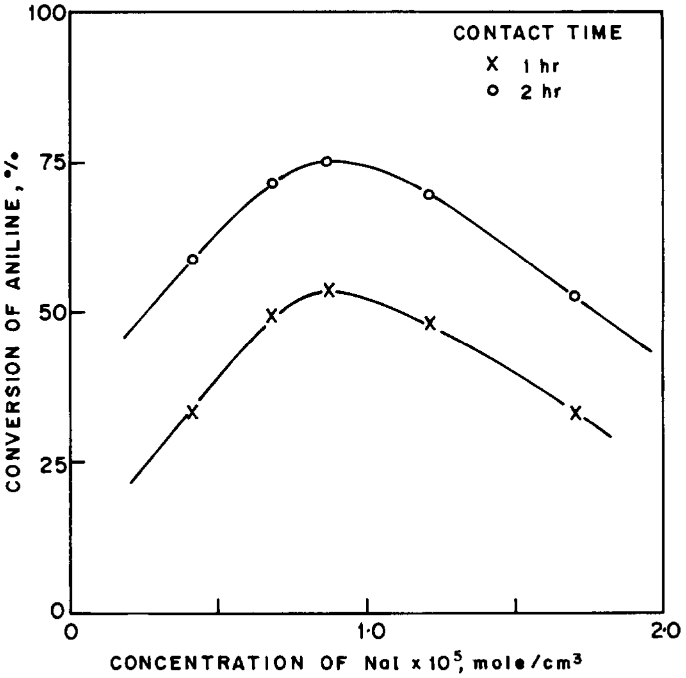


FIG. 3. Effect of NaI concentration on conversion of aniline. Conditions: 5% Pd/C, 0.5 g; aniline, 53.8 mmol; DMF, 95 cm^3; stirrer speed, 700 rpm; temperature, 100°C; P_{CO}, 34 atm; P_{O_2}, 6.8 atm.

The catalytic activity was, in general, very poor in nonpolar solvents like toluene and *p*-xylene. Activity was found to be significantly higher for polar solvents such as ethanol methanol, DMF, and DMSO than for 2-ethyl hexanol and 2-methoxy ethanol, which are of intermediate polarity. The dielectric constants for the solvents studied

TABLE 5

Oxidative Carbonylation of Aniline with 5% Pd/C Catalyst and Iodide Promoter: Effect of Solvent[a]

Solvent	Conversion of aniline (%)		Product yield (mmol)				Dielectric constant[b] (ε, 20°C)	Protic	Aprotic
			Urea		Urethane				
	1 hr	2 hr	1 hr	2 hr	1 hr	2 hr			
p-Xylene	2	15	0.5	4.0	—	—	2.3	—	✓
Toluene	2	13	0.4	3.5	—	—	2.4	—	✓
2-Ethyl hexanol	8	21	2.2	5.7	nil	nil	4.4	✓	—
2-Methoxy ethanol	21	32	5.7	8.6	nil	Trace	16.9	✓	—
DMF	47	74	12.5	19.8	—	—	36.7	—	✓
Ethanol	53	84	14.2	21.9	0.1	0.2	24.6	✓	—
Methanol	78	88	20.5	23.5	0.2	0.5	32.7	✓	—
DMSO	100	—	26.6	—	—	—	46.7	—	✓

[a] Reaction conditions: 5% Pd/C, 0.5 g; aniline, 53.8 mmol; NaI, 0.87 mmol; temperature; 100°C; solvent, 95 cm^3; P_{CO}, 34 bar; P_{O_2}, 6.8 bar.

[b] "Lange's Handbook of Chemistry" (J. A. Dean, Ed.), McGraw-Hill, New York, 1979.

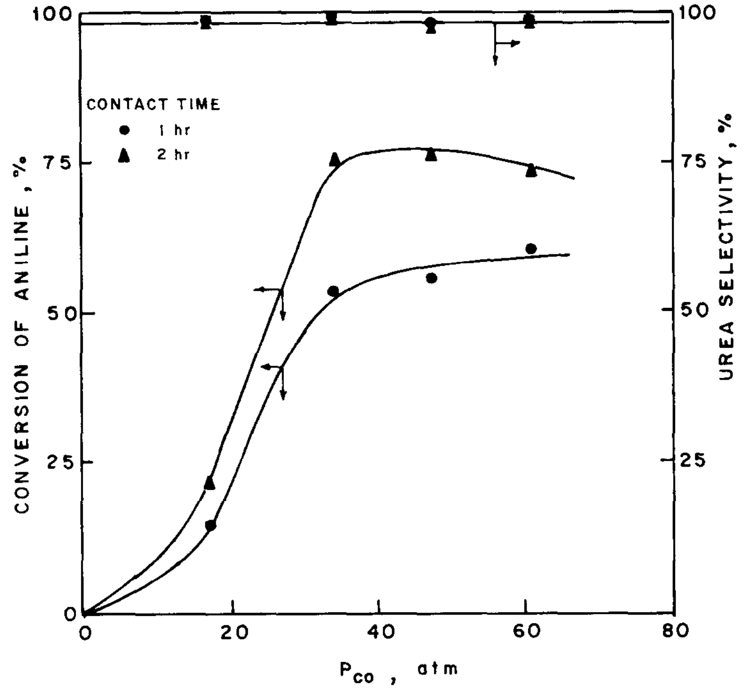


FIG. 4. Effect of carbon monoxide partial pressure of conversion of aniline to *N*,*N*′-diphenylurea. Conditions: 5% Pd/C, 0.5 g; aniline, 53.8 mmol; NaI, 0.87 mmol; temperature, 100°C; DMF, 95 cm^3; stirrer speed, 700 rpm; P_{O_2}, 6.8 atm.

are also listed in Table 5. The activity of the Pd/C–NaI catalyst system increases with an increase in the dielectric constant, but the protic/aprotic nature of the solvent alone is not enough to explain the observed change in activity of the catalyst.

CO Pressure

The effect of CO pressure on the activity of Pd/C–NaI catalyst was studied at 100°C and a constant O_2 pressure of 6.8 atm. Conversion of aniline is plotted versus CO pressure for different contact times in Fig. 4. An increase in total CO pressure from 10 to 35 atm causes an almost sixfold increase in the conversion of aniline, whereas an increase in CO pressure beyond 35 atm and up to 60 atm has no significant effect on the conversion of aniline. Thus, an optimum CO pressure of 35 atm was observed under the experimental conditions studied.

O_2 Pressure

The influence of oxygen pressure on the conversion of aniline was investigated at 100°C and a constant CO pressure of 34 atm. These results are shown in Fig. 5 for two different contact times. An increase in O_2 pressure from 1 to 7 atm increases the conversion of aniline; with further increase in O_2 pressure to 14 atm, the conversion of aniline decreases. The selectivity of *N*,*N*′-diphenylurea was found to be independent of O_2 pressure. The observed substrate inhibition at higher O_2 pressure is consistent with the results of catalyst pretreatment effects: O_2-pretreated catalyst showed poor activity. At higher O_2 pressure, two situations leading to inhibition of catalyst activity are possible: (1) occupation of more active sites by O_2, thus reducing the sites available for adsorption of other reactants; (2) increased likelihood of a change in the

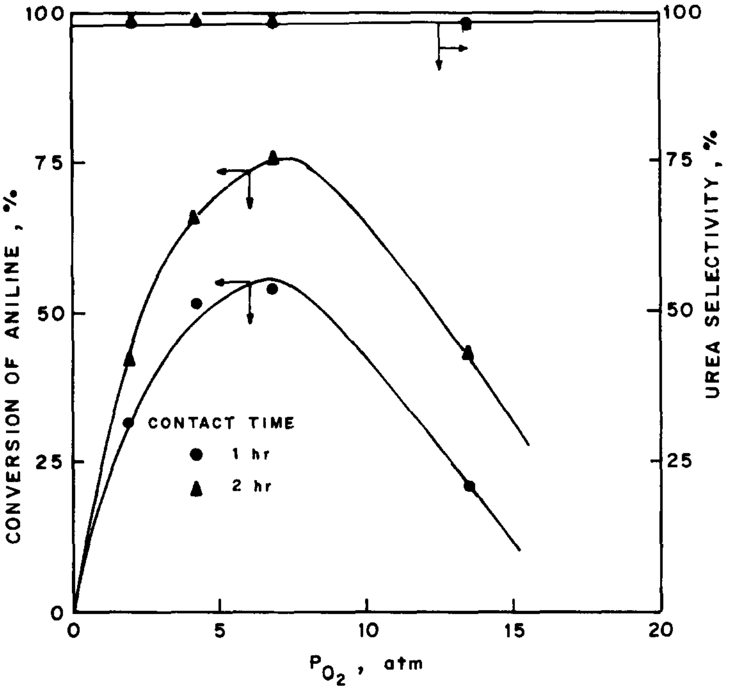


FIG. 5. Effect of oxygen partial pressure on conversion of aniline to *N,N'*-diphenylurea. Conditions: 5% Pd/C, 0.5 g; aniline, 53.8 mmol; NaI, 0.87 mmol; stirrer speed, 700 rpm; DMF, 95 cm^3; P_{CO}, 34 atm.

nature of active sites. The pretreatment results favor the latter mechanism.

The mechanism of oxidative carbonylation of amine is not well understood. Fukuoka *et al.* (*4*) have proposed a possible mechanism on the assumption that a Pd–carbamoyl complex (Pd–CONHAr) is formed as an intermediate species. However, this scheme does not explain the role of iodide promoter. In the absence of NaI, reaction does not take place, indicating that Pd/C catalyst modified in the presence of NaI is an active catalytic system for oxidative carbonylation of aniline. A modified scheme, based on Pd–I as an active species, is proposed in Fig. 6. Recently, Vasapollo *et al.* (*11*) have reported the reactions of palladium complexes with aniline and CO to produce cabamoyl-type complexes. These complexes, on further reaction with aniline and in the presence of a base under CO atmosphere, produce stoichiometric quantities of diphenylurea. This observation supports the proposed mechanism, based on a carbamoyl-type intermediate catalytic species. At higher O_2 pressure, the

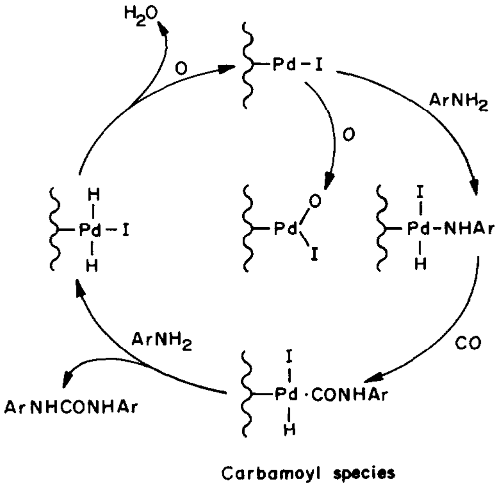


FIG. 6. Proposed mechanism for oxidative carbonylation of aniline to diphenylurea.

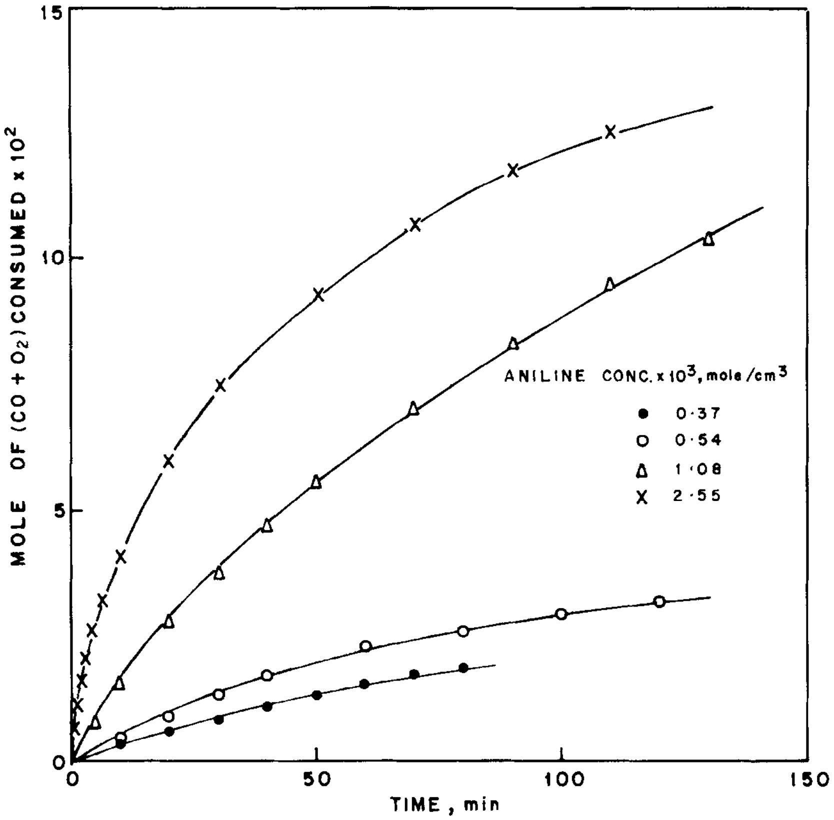
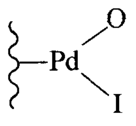


FIG. 7. Effect of aniline concentration on activity of catalyst. Conditions: 5% Pd/C, 0.5 g; NaI, 0.87 mmol; temperature, 100°C; solvent, DMF; P_{CO}, 34 atm; P_{O_2}, 6.8 atm; stirrer speed, 700 rpm.

nature of the active sites is likely to be modified as



which may be inactive for the oxidative carbonylation reaction; hence an inhibition in the rate is observed.

Aniline Concentration

The effect of the initial aniline concentration on the activity of Pd/C–NaI catalyst was studied. In these experiments, the amount of CO + O_2 consumed was observed as a function of time. These experiments were carried out at a constant total reactor pressure and the progress of the reaction was followed by observing the pressure drop in the reservoir vessel containing CO + O_2 in the ratio 2 : 1. The results are shown in Figs. 7 and 8. At the end of each experiment, the material balance of CO, O_2, and aniline consumed was found to be consistent with the formation *N*,*N*′-diphenylurea as per reaction (2). The results in Fig. 8 indicate that the oxidative carbonylation rate increases with an increase in aniline concentration, indicating 1.6th-order dependence.

Product Concentration

To study the effect of product concentration, a few experiments were carried out in the same way as described above for aniline. The results are shown in Fig. 9 where plots of aniline conversion versus time as well as CO + O_2 consumed versus time are presented. It was observed that both products, H_2O and N,N'-diphenylurea, inhibit the rate of oxidative carbonylation. It is likely that at higher concentrations of these products, a significant number of active sites are blocked by the adsorbed products, leading to inhibition of the rate. These observations suggest that competitive adsorption of reactants and products would influence the activity of Pd/C–NaI catalyst for oxidative carbonylation of aniline.

CONCLUSIONS

Oxidative carbonylation of aniline using 5% Pd/C–NaI catalyst has been shown to give N,N'-diphenylurea as a product. In the presence of alcohol, N,N'-diphenylurea is converted to phenylurethane in a noncatalytic reaction at higher temperatures (>150°C). Pretreatment of catalyst with O_2, CO, and aniline retards the initial activity of oxidative carbonylation, with O_2 having a severe inhibitory effect.

The activity of the catalyst was found to increase with NaI concentration up to a certain point, after which it was found to decrease with increasing NaI concentration. In polar solvents, higher activity was observed for the catalyst. Similarly, the activity-versus-O_2 pressure curve passed

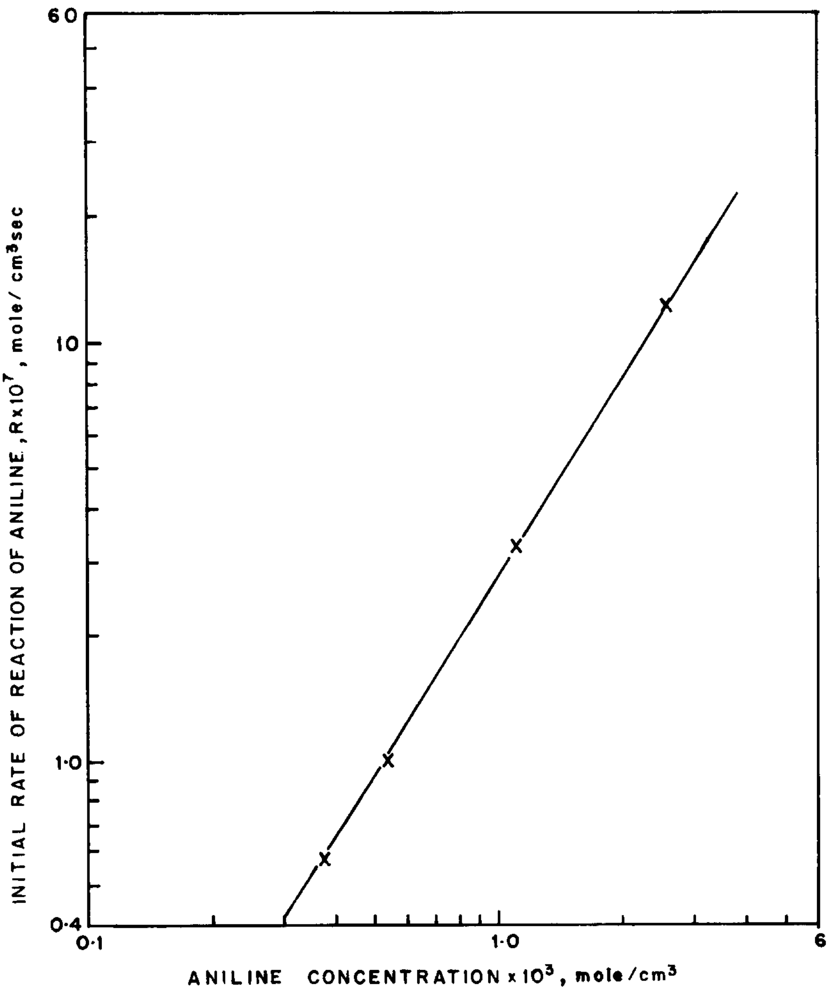


FIG. 8. Effect of aniline concentration on oxidative carbonylation reaction. Reaction conditions as in Fig. 7.

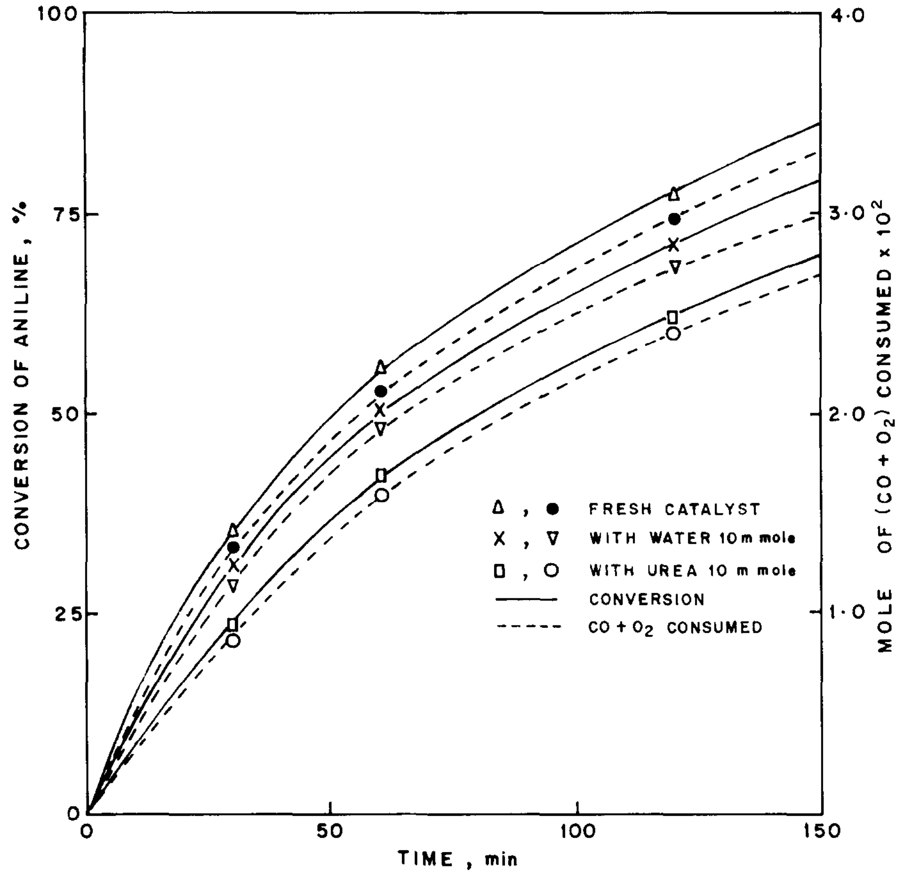


FIG. 9. Effect of product concentration on activity of catalyst. Conditions: 5% Pd/C, 0.5 g; NaI, 0.87 mmol; temperature, 100°C; solvent, DMF; P_{CO}, 34 atm; P_{O_2}, 6.8 atm; stirrer speed, 700 rpm; aniline 53.8 mmol.

through a maximum indicating substrate inhibition at higher O_2 pressures. Initially, activity increased with increasing CO pressure; however, the activity showed no dependence at higher CO pressures. The variation in activity was found to be 1.6th order with respect to aniline concentration, but the products *N*,*N*′-diphenylurea and water inhibited the catalyst activity. Competitive adsorption by several components is probably involved in the oxidative carbonylation catalysis. Selectivity was found to be unaffected by changes in the concentration of reactants and NaI. The Pd/C–NaI catalyst system could also be reused several times without a loss of activity. Finally, a reaction mechanism has been proposed for oxidative carbonylation of aniline to diphenylurea, based on a Pd–carbamoyl complex as an intermediate species.

REFERENCES

1. Fukuoka, S., Chono, M., and Kohno, M., *CHEMTECH,* Nov., 670 (1984).
2. Chono, M., Fukuoka, S., and Kohno, M., *J. Cell. Plastics,* Nov.–Dec., 385 (1983).
3. Fukuoka, S., and Chono, M., *J. Chem. Soc. Chem. Commun.,* 399 (1984).
4. Fukuoka, S., Chono, M., and Kohno, M., *J. Org. Chem.* **49,** 1460 (1984).
5. Becker, R., Groling, J., and Rasp, C., Ger. Offen. 290, 8251 (to Bayer A. G.) (1980).
6. Fukuoka, S., and Chono, M., Japanese Patents 5770855 (1982), 57171953 (1982), and 57171954 (1982) (to Asahi Chemical Industry Co., Ltd.).

7. Fukuoka, S., and Chono, M., European Patent 83096 (to Asahi Chemical Industry Co., Ltd). (1983).

8. Japanese Patents 58148844 (1983), 58157753 (1983), and 58164565 (1983) (to Asahi Chemical Industry Co., Ltd.).

9. Mozingo, R., in "Organic Synthesis" (E. C. Hornning, Ed.), Collective Vol. 3, p. 685. Wiley, London, 1955.

10. Carberry, J. J., *in* "Concepts and Design of Chemical Reactors" (S. Whitaker and E. A. Cassano, Eds.), p. 561, Gordon & Breach, New York, 1986.

11. Vasapollo, G., Nobile, C. F., and Sacco, A., *J. Organomet. Chem.* **296,** 435 (1985).