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Activity and Selectivity of Supported Rh Catalysts for Oxidative Carbonylation of Aniline[1]

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Oxidative carbonylation of aniline to ethyl phenyl carbamate (EPC) over supported Rh catalysts has been studied. The effect of catalyst preparation methods, supports, metal content, reusability, solvents, promoters, co-catalysts, and pretreatment on the activity and selectivity of the Rh/C catalyst has been investigated. Selectivity of EPC based on both aniline and CO has been discussed. Above 373 K, CO_2 formation was found to be significant, leading to lower selectivity based on CO. Below 393 K, the major product formed was *N,N'*-diphenylurea (DPU), but with increased temperature the selectivity of EPC based on aniline increased. The intrinsic kinetics of the reaction has been investigated at 443 K. The rate was found to be first order with respect to aniline, CO, and catalyst. With respect to oxygen, the rate showed linear dependence below 0.75 MPa, but was zero order at higher pressures. A rate equation has been proposed. Characterization of the Rh/C catalyst, before and after the reaction, was done by ESCA, XRD, and TEM. It was observed that the oxidation state of rhodium metal was 0 in both the fresh and the used catalysts. Redispersion of rhodium metal on the support was indicated in the used catalyst by XRD and TEM analysis.

INTRODUCTION

Catalytic oxidative carbonylation of amines is important in the synthesis of carbamates and urea derivatives (1). An important example of practical interest is the conversion of aniline to ethyl phenyl carbamate (EPC), which provides a nonphosgene route for methylene diphenyl diisocyante (MDI) (2). The stoichiometric reaction is

$$RNH_2 + CO + \tfrac{1}{2}O_2 \xrightarrow[R'OH]{\text{catalyst}} RNHCOOR' + H_2O. \quad [1]$$

A variety of catalysts, consisting of supported nobel metals along with alkali halide promoters, have been proposed for oxidative carbonylation of amines (3–5). Fukuoka and Chono (1) reported Pd/C–NaI catalyzed synthesis of EPC with 90% conversion of aniline and 95% selectivity. The roles of promoters, solvents, and catalyst pretreatment effects have been studied in detail by Gupte and Chaudhari (6) for the Pd/C–NaI catalyst system. They have shown that the catalytic oxidative carbonylation of aniline gives *N,N'*-diphenylurea (DPU) as a product, which in the presence of an alcohol is converted to the carbamate ester by a noncatalytic reaction. Other catalysts consisting of Rh, Ru, and Pt have also been reported (5); however, there have been no detailed investigations on the behavior of these catalysts, with respect to the role of promoters and reaction conditions in activity and selectivity. An important aspect overlooked in all the previous studies on oxidative carbonylation is selectivity with respect to CO consumed. This is important, since, with most of the catalysts proposed, oxidation of CO to CO_2 occurs in significant yields.

In this paper, we report a detailed investigation on oxidative carbonylation of aniline using a supported Rh catalyst with metal iodide promoters. The effect of supports, metal content, solvents, promoters, catalyst pretreatment, and reaction conditions on the activity and selectivity has been investigated. Catalyst samples before and after the reaction have also been characterized by ESCA, TEM, and XRD. For the Rh/C–LiI catalyst system, the intrinsic kinetics of the reaction has been studied at 443 K and a rate equation has been proposed.

EXPERIMENTAL

Aniline, ethanol, and the solvents (benzene, toluene, chlorobenzene, xylene, dimethyl formamide, methyl acetate, ethyl acetate, and acetonitrile) were freshly distilled before use. Rhodium chloride trihydrate was procured from Arrora Mathey, Calcutta. The gases such as oxygen, hydrogen (in catalyst preparation), and nitrogen were obtained from Indian Oxygen Limited, Bombay. Carbon monoxide used was >99.8% purity.

The supported Rh catalysts were prepared by a procedure described elsewhere (7). In a few cases, different

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types of reducing agents were used to study their effect on the catalytic activity.

The oxidative carbonylation experiments were carried out in a 300-ml stirred autoclave reactor made of SS316 (supplied by Parr Instrument Co.). This reactor was provided with automatic temperature control, a cooling coil, variable agitation speeds, and devices for sampling of gas and liquids.

In a typical experiment, 0.548 kmol/m^3 of aniline, 0.4 kg/m^3 of 5% Rh/C catalyst, 8.73 × 10^{-3} kg/m^3 of LiI, and solvent ethanol were mixed (made up to 1 × 10^{-4} m^3) and charged to the reactor. The contents were flushed with nitrogen and heated to 443 K. After the temperature was attained, a CO/O_2 mixture in a ratio of 14 : 1 was introduced into the reactor to a desired pressure (proper safety precautions were taken against explosion hazards in handling CO/O_2 mixtures). During an experiment, the pressure in the reactor was kept constant by supplying CO/O_2 in a stoichiometric ratio from a reservoir vessel. Most reactions were carried out for a period of 2 hr. At the end of the reaction, both gas and liquid samples were analyzed. In order to account for CO and O_2 consumed, the gas content in the reactor was transferred to a receiver at atmospheric pressure and the volume was recorded. This gas was analyzed for CO, O_2, and CO_2.

The liquid phase components aniline, ethanol, diphenylurea, and EPC were analyzed by GC and HPLC. In GC analysis, a 12% SE-30 column (6 ft length) with FID was used for liquid samples and an 5A molecular sieves column (6 ft length) and porapak-Q columns (6 ft length) were used with TCD for gas analysis. HPLC analysis was done on a ν-Bondopak column with mobile phase as 62%, methanol in 0.1 *M* aqueous sodium acetate solution.

For some cases, the catalyst samples before and after the reaction were examined by ESCA, XRD, and TEM. The ESCA spectrum of the catalysts were determined by using a VG Scientific ESCA 3 Mk spectrophotometer, using monochromated Al*Kα* radiation. The X-ray diffraction determinations of the catalyst were made using a Phillips PW-1730 X-ray diffractometer employing Cu*Kα* radiation. The catalysts were examined by a model 1200 JEOL Japan transmission electron microscope (TEM) with a 120 KeV electron source.

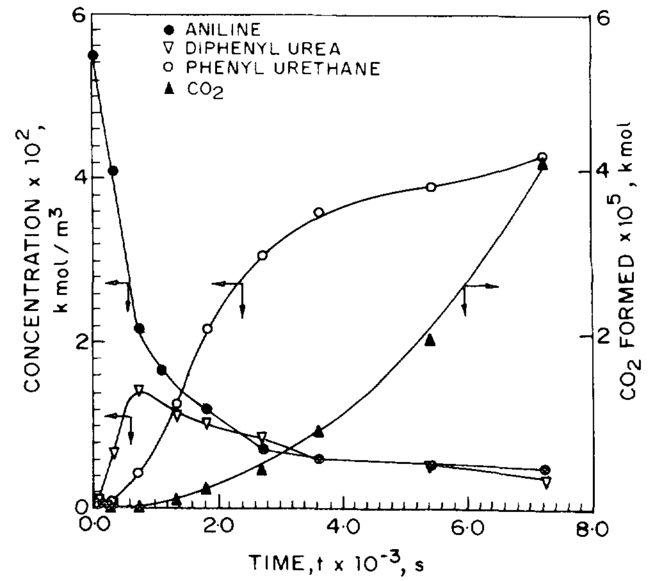


FIG. 1. Concentration–time profile for oxidative carbonylation of aniline using 5% Rh/C catalyst. Reaction conditions: aniline, 0.548 kmol/m^3; catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.69 MPa; temperature, 443 K; agitation speed, 600 rpm.

RESULTS AND DISCUSSIONS

A few initial experiments were carried out on oxidative carbonylation of aniline using an Rh/C–NaI catalyst system to investigate the product distribution. For this purpose, experiments were carried out to observe concentration–time data and the results are presented in Fig. 1. As also reported previously for Pd catalyzed oxidative carbonylation of aniline (Fukuoka and Chono (1) and Gupte and Chaudhari (6)), DPU and EPC were the major liquid phase products. The material balance of aniline consumed agreed with DPU and EPC formed to the extent of 95–98%. However, the selectivity based on CO consumed was found to be strongly affected by the formation of CO_2 via oxidation of CO. Separate experiments were carried out for different time durations to analyze the total CO_2 formation and evaluate the significance of CO oxidation. These results are also shown in Fig. 1. An interesting observation was that the CO oxidation rate increases as the concentration of aniline decreases. In the initial region of low conversion in a batch experiment, CO_2 formation was negligible except for conditions of high conversion (>98%) of aniline; the selectivity of DPU/EPC together, based on CO, was as low as 40%. Based on these preliminary results, the following reactions need to be considered:

$$2\,C_6H_5NH_2 + CO + \tfrac{1}{2}O_2 \rightarrow C_6H_5NHCONHC_6H_5 + H_2O \quad [2]$$

$$C_6H_5NHCONHC_6H_5 + C_2H_5OH \rightarrow C_6H_5NHCOOC_2H_5 + C_6H_5NH_2 \quad [3]$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2. \quad [4]$$

Several experiments were carried out to investigate the effects of catalyst and reaction parameters on the average activity and selectivity of Rh catalyzed oxidative carbon-

TABLE 1

Effect of Catalyst Precursors and Reducing Agents

Catalyst precursor/reducing agent	Average activity × 10^1, kmol/kg catalyst/hr	Selectivity				
		CO based			Aniline based	
		DPU %	EPC %	CO_2 %	DPU %	EPC %
$RhCl_3$ $3H_2O$/A	6.21	4.0	37.0	55.5	1.9	96.7
$RhCl_3$ $3H_2O$/B	5.47	4.7	36.5	55.4	2.3	94.9
$RhCl_3$ $3H_2O$/C	5.87	4.8	37.3	55.9	3.6	94.8
$RhCl_3$ $3H_2O$/D	5.76	5.6	33.6	56.3	5.7	93.2
$RhCl_3$ $3H_2O$/E	5.30	6.5	30.4	56.8	6.9	90.5
$Rh(CO)_2(acac)_2$/A	6.13	5.2	37.6	54.6	2.0	95.8
$Rh(CO)(PPh_3)_3$/A	6.03	4.9	38.3	54.8	2.3	94.8
$HRh(CO)(PPh_3)_2$/A	6.23	5.0	38.0	55.7	2.2	95.6

Note. A: sodium borohydride, B: methanol, C: hydrazine hydrate, D: formaldehyde and potassium hydroxide, and E: hydrogen. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C Catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{CO_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr.

ylation of aniline. The average activity of the catalyst is defined as

Average activity

$$= \left[\frac{\text{Amount of aniline reacted}}{\text{Weight of catalyst} \times \text{Time of reaction}}\right] \times \frac{\text{kmol}}{\text{kg catalyst, hr}}.$$

In particular, the significance of CO oxidation has been quantitatively studied in this work. The results are discussed below.

Catalyst Precursor/Reducing Agents

Rh/C catalysts containing 5% Rh (w/w) were prepared using different types of Rh salts/complexes as precursors (e.g., $RhCl_3 \cdot 3H_2O$, $Rh(CO)_2(acac)_2$, $RhCl(PPh_3)_3$, and $HRhCO(PPh_3)_3$) and reducing agents ($NaBH_4$, CH_3OH, hydrazine hydrate, formaldehyde–KOH, and hydrogen). These catalysts were tested under identical conditions using ethanol as a solvent and the results are presented in Table 1. It was observed that the activity of Rh/C catalysts, defined as amount of aniline reacted per unit wt of catalyst per hour, and the selectivity of EPC were independent of the type of precursors and the reducing agents used. The CO_2 formed was also independent of the reducing agent used. In all the further studies, $NaBH_4$ was used as a reducing agent.

Supports

The role of supports was studied using activated C, alumina, silica gel, titanium dioxide, calcium carbonate, ZSM-5, and molecular sieves (5A) in the preparation of 5% Rh/support catalysts. The effects on the performance of these catalysts are presented in Table 2. It was observed that Rh on activated carbon gave highest activity for oxidative carbonylation of aniline, while molecular sieves (5A) based catalyst showed the lowest activity. The selectivity based on aniline consumed was not affected by the type of support used, but the formation of CO_2 varied. Rh/molecular sieves catalyst gave the lowest EPC selectivity based on CO consumed. The selectivity of EPC based on CO consumed decreased in the order C > ZSM-5 > $CaCO_3$ > TiO_2 > Al_2O_3 > SiO_2 > molecular sieves. Thus, activated-C-supported Rh catalyst was found to be the optimal one.

Rh Content

The effect of Rh content was studied by preparing catalysts with 0.2%, 1%, and 5% Rh. The results are shown in Table 3. The activity of these catalysts decreased with decreasing Rh content, but the specific activity (defined as kmoles of aniline converted per unit wt of Rh metal per hour) was found to be highest for 0.2% Rh/C catalyst and decreased with increasing Rh content. Selectivity of EPC based on aniline was unaffected by a change in Rh content but the formation of CO_2 was found to increase with decrease in Rh content.

Reusability

In order to investigate the constancy of the catalytic activity and reusability, a few experiments were carried out in which the catalyst from the first batch was recycled. In each step the catalyst separated by filtration was

TABLE 2

Effect of Catalyst Supports

Support	Average activity × 10^1 kmol/kg catalyst/hr	Selectivity: CO based EPC %	CO based DPU %	CO based CO_2 %	Aniline based DPU %	Aniline based EPC %
Carbon	6.21	37.0	4.0	55.5	1.9	96.7
Silica	1.57	25.1	2.9	72.6	5.4	92.1
Alumina	2.20	26.0	3.8	70.4	5.1	95.4
ZSM-5	6.10	52.4	4.6	40.2	5.2	90.4
Calcium carbonate	5.57	30.5	2.6	60.5	3.6	97.3
Molecular sieves	1.20	8.3	1.1	85.5	4.5	94.2
Titania	4.50	23.0	4.8	58.3	3.2	94.7

Note. Reaction conditions: aniline, 0.548 kmol/m^3; catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr.

washed with acetone and then dried under vacuum before use in the next experiment. The results are presented in Table 4. It was observed that 5% Rh/C catalyst was reusable seven times without loss of significant activity and selectivity. The activity of the used catalyst after the first recycle was found to increase to about 20% of the original activity. This indicates that the catalyst structure has changed. The weight loss due to handling and transfer was less than 7–8% for the entire set of experiments.

Promoters/Co-catalysts

In order to understand the role of iodine compounds or metal iodide promoters, a few blank experiments were carried out without using any promoter. It was observed that Rh/C alone showed very low activity for oxidative carbonylation of aniline (Table 5), but in the presence of I_2 or metal halide promoter, the activity was significantly enhanced. Effects of different types of metal halides was studied and the results are shown in Table 5. It was observed that alkali metal iodide promoters are more effective compared to bromides and chlorides. However, among different metal iodides, LiI was most active, followed by NaI and KI, for equivalent amounts of iodine content. This indicates that the promoting effect is also dependent on the type of the metal ion. Other metal iodides such as SnI_2 and NiI_2 were also found to be effective promoters (Table 5). Thus, the observations indicate that Rh/C with LiI or SnI_2 gave the highest activity and selectivity for EPC. With SnI_2, a higher selectivity was observed even at lower conversion (≃70%), unlike the case of LiI promoter.

Concerning the effect of metal halide promoters on CO_2 formation, an interesting trend was observed. For metal iodides as promoters, CO_2 formation was less compared

TABLE 3

Effect of Rhodium Content in Catalyst

Metal content (%)	Average activity × 10^1 kmol/kg catalyst/hr	Specific activity[a] kmol/kg Rh/hr	Selectivity: CO based DPU %	CO based EPC %	CO based CO_2 %	Aniline based DPU %	Aniline based EPC %
5	6.20	1.65	4.0	37.0	55.5	1.9	96.7
1	4.63	4.63	0.5	19.8	68.1	4.2	87.2
0.2	1.82	9.11	0.8	15.8	83.5	7.9	80.8

Note. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr.

[a] Specific activity is the activity expressed per unit weight of Rh content.

TABLE 4

Catalyst Recycle Studies

		Selectivity	
		Aniline based	
Number of recycles	Average activity × 10^1 kmol/kg catalyst/hr	DPU %	EPC %
0	6.2	1.9	96.7
1	7.9	1.0	97.9
2	7.6	1.3	96.6
3	7.3	1.7	96.4
4	7.1	1.9	96.3
5	7.0	2.2	95.8
6	6.6	2.3	94.9
7	6.3	2.5	92.4

Note. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr.

TABLE 6

Effect of Anions on CO_2 Formation

Promoter	CO_2 %
Lithium iodide	5.7
Lithium bromide	35.2
Lithium chloride	42.7

Note. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; promoter concentration, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr; conversion level, 40%.

to chlorides and bromides for identical reaction times (Table 6). For example, with LiI and 100 min duration, CO_2 formation was lower compared to LiBr and LiCl. Even for the same conversion level (≃40%), CO_2 formation was much higher for LiBr and LiCl compared to that when LiI was used as a promoter.

Further experiments were carried out to investigate the combined influence of metal iodide promoters. For this purpose, the effects of LiI + $CoCl_2$, SnI_2 + $CoCl_2$, SnI_2 + $MnCl_2$, SnI_2 + $SnCl_2$ and SnI_2 + $NiCl_2$ combinations were studied and the results were compared with those in which only one of the components was used (Table 7). The effect of $CoCl_2$ on Rh/C–LiI catalyst led to a decrease in the activity and a marginal decrease in selectivity, however for Rh/C–SnI_2 system, the activity was found to increase, but the selectivity was nearly constant. The effect of the type of co-catalysts (e.g., $CoCl_2$, $NiCl_2$, $SnCl_2$, $MnCl_2$) on the activity and selectivity of Rh/C–SnI_2 system was also investigated (Table 7). Here, it was observed that $MnCl_2$ offered the highest activity, but the selectivity to EPC varied significantly in the following order.

TABLE 5

Effect of Promoters

		Selectivity				
		CO based			Aniline based	
Promoter	Average activity × 10^1 kmol/kg catalyst/hr	DPU %	EPC %	CO_2 %	DPU %	EPC %
—	0.58	0.9	3.2	93.2	20.0	67.3
Lithium iodide	6.20	4.0	37.0	55.5	1.9	96.7
Sodium iodide	5.03	5.3	36.2	56.4	3.7	94.6
Potassium iodide	4.96	5.7	33.3	56.6	57.4	42.1
Iodine	4.74	22.0	23.4	48.5	5.6	59.6
Tin iodide	4.80	4.4	33.5	53.0	2.5	90.2
Nickel iodide	2.26	3.8	16.7	62.4	29.8	68.8
Lithium bromide	3.94	5.4	22.9	60.2	45.4	53.9
Lithium chloride	3.13	6.7	18.5	69.6	48.7	50.6
Sodium chloride	1.38	7.3	6.9	80.0	64.3	32.4

Note. Reaction conditions: Aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; promoter concentration, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr.

TABLE 7

Effect of Co-catalysts

Catalyst system	Average activity × 10^1 kmol/kg catalyst/hr	Selectivity				
		CO based			Aniline based	
		CO_2 %	DPU %	EPC %	DPU %	EPC %
Rh/C LiI	6.20	55.5	4.0	37.0	1.9	96.7
Rh/C SnI_2	4.80	53.0	4.2	35.3	2.5	90.2
Rh/C $CoCl_2$	4.33	44.9	23.6	30.2	73.6	20.2
Rh/C SnI_2 $CoCl_2$	6.11	49.2	7.2	38.7	11.2	88.7
Rh/C LiI $CoCl_2$	5.40	45.6	5.6	46.5	7.4	85.3
Rh/C LiI $MnCl_2$	6.52	50.5	7.8	38.5	20.5	77.6
Rh/C LiI $SnCl_2$	5.14	51.2	4.6	36.4	8.7	91.2
Rh/C LiI $NiCl_2$	5.33	55.7	20.7	23.6	63.5	35.2
$CoCl_2SnI_2$	—	32.3	—	—	—	—

Note. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; promoter concentration, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K, time of reaction, 2 hr.

$$SnCl_2 > CoCl_2 > MnCl_2 > NiCl_2.$$

The results on the effect of temperature for Rh/C–SnI_2–$CoCl_2$ catalyst system are shown in Table 8, which indicate as expected an increase in activity with temperature. The concentration of SnI_2 for Rh/C–SnI_2–$CoCl_2$ system, showed no significant variations in both the activity and selectivity for EPC.

Solvents

The effect of solvents on rate, conversion, and selectivity was studied for Rh/C–NaI catalyst system. The results are presented in Table 9. The initial rates varied in the order xylene ≈ chlorobenzene ≈ ethyl acetate ≈ toluene > benzene > methyl acetate > DMF > ethanol > acetonitrile. A similar profile was observed with respect to conversion of aniline after 1 and 2 hr durations. The selectivity of EPC in highly polar solvents such as DMF and acetonitrile was significantly lower even for higher conversions compared to other solvents and most of the aniline was converted to DPU. In the presence of water the reaction was inhibited.

Pretreatment

The pretreatment of catalyst with reactant often has influence on the rate and selectivity in many reactions and such effects have already been reported in hydrogenation

TABLE 8

Effect of Temperature for Rh/C–SnI_2–$CoCl_2$ Catalyst

Temperature K	Average activity × 10^1 kmol/kg catalyst/hr	Selectivity				
		CO based			Aniline based	
		CO_2 %	DPU %	EPC %	DPU %	EPC %
373	2.43	20.5	63.7	9.8	82.5	16.5
408	4.96	35.2	20.4	42.2	32.00	64.1
443	6.11	49.2	7.5	38.6	11.2	88.7

Note. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr; promoter SnI_2 concentration, 8.7 × 10^{-3} kg/m^3.

TABLE 9

Effect of Solvents

Solvents	Time min	Average activity × 10^1 kmol/kg catalyst/hr	Selectivity Aniline based DPU %	 EPC %
Benzene	60		35.8	63.23
	120	6.57	19.2	72.8
p-Xylene	60		40.2	57.4
	120	6.85	17.5	74.8
Toluene	60		45.6	50.3
	120	6.65	26.2	72.8
Chlorobenzene	60		32.4	64.7
	120	6.85	17.5	73.0
Ethanol	60		23.4	75.3
	120	5.48	1.9	96.7
Methyl acetate	60		50.4	37.5
	120	5.96	34.5	49.8
Ethyl acetate	60		29.7	68.3
	120	6.85	10.2	81.0
Acetonitrile	60		87.3	7.3
	120	5.14	76.1	19.9
Dimethylformamide	60		85.3	10.2
	120	6.30	70.8	23.3
Water	60	—	—	—
	120	—	—	—

Note. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr, ethanol concentration in other solvents, 1.734 kmol/m^3.

TABLE 10

Effect of Catalyst Pretreatment

Pretreatment with	Initial rate × 10^{10}, kmol/m^3/s	Selectivity CO based DPU %	 EPC %	 CO_2 %	 Aniline based DPU %	 EPC %
Nitrogen	2.23	4.0	37.0	55.5	1.9	96.7
Carbon monoxide	3.51	4.2	36.9	54.3	1.8	96.1
Oxygen	2.82	4.5	37.2	55.3	1.9	96.4
Carbon dioxide	2.95	3.5	36.4	56.3	1.6	97.4
Hydrogen	4.13	2.4	37.7	57.3	1.3	96.8
Aniline	2.47	5.6	34.6	54.5	3.3	94.5

Note. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.69 MPa; agitation speed, 600 rpm; temperature, 443 K, time of reaction, 2 hr.

(Chaudhari *et al.* (8)) and carbonylation reactions (Gupte and Chaudhari (6)). For the Rh/C–NaI catalyst system, the effect of pretreatment with CO, O_2, CO_2, H_2, and aniline on the activity and selectivity in the oxidative carbonylation of aniline was investigated. The results are presented in Table 10. The pretreatment of Rh/C–NaI catalyst with aniline, O_2, CO, H_2, and CO_2 resulted in increase in the initial rate of the reaction. While the increase in the rate on pretreatment with aniline, oxygen, and CO_2 was marginal, a significant enhancement in the rate was observed on pretreatment with CO and H_2. This is in contrast to the observations of Gupte and Chaudhari (6) for Pd-catalyzed oxidative carbonylation of aniline. The selectivity of EPC was found to be unaffected by the pretreatment. The selectivity for CO_2 formation was also unaffected by the pretreatment of the catalyst.

Reaction Conditions

The effect of reaction conditions such as catalyst loading, aniline concentration, P_{CO}, P_{O_2}, and ethanol, and water concentrations was studied using Rh/C–LiI catalyst in the temperature range 373–443 K. The effects on initial rates are shown in Figs. 3 to 6. The effects on average activity and selectivity are presented in Tables 11–15. The important observations are summarized below.

- The initial rate (Fig. 3) as well as average activity (Table 11) increase with increase in catalyst loading for lower values of LiI (LiI/Rh ratio <1). For higher concentrations of LiI, catalyst loading has a mild effect on the rate and average activity. This is mainly because in oxidative carbonylation the Rh/C–LiI combination is an active catalyst and for higher LiI, the rate is inhibited significantly

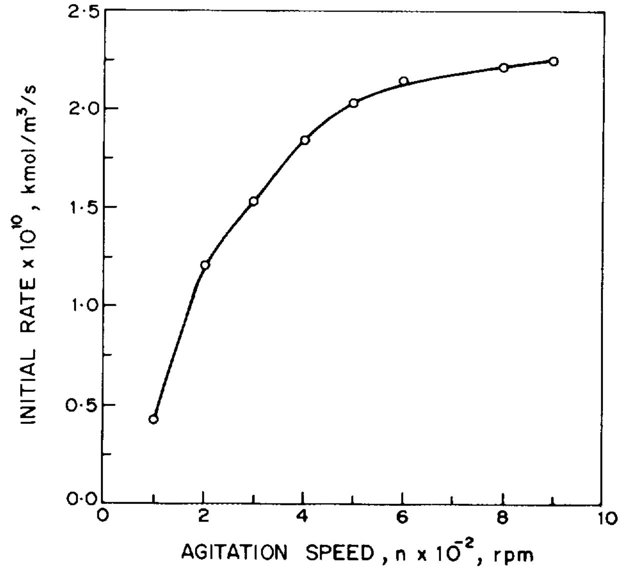


FIG. 2. A plot of initial rate of reaction vs agitation speed. Reaction conditions: aniline, 0.548 kmol/m^3, catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.69 MPa; temperature, 443 K.

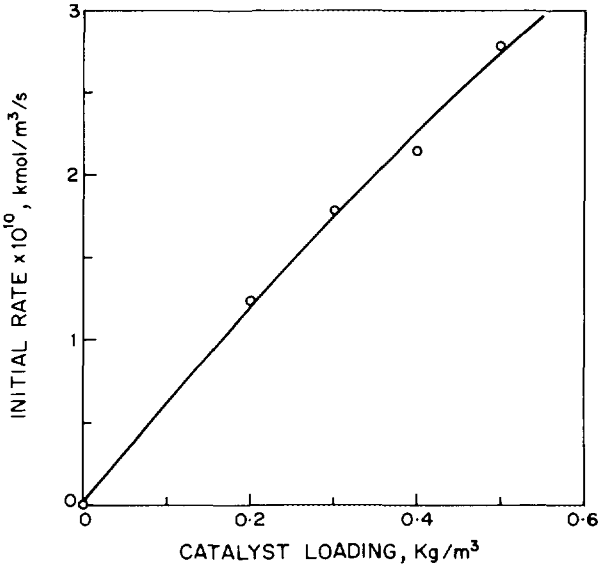


FIG. 3. A plot of initial rate of reaction vs catalyst loading. Reaction conditions: aniline, 0.548 kmol/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.69 MPa; agitation speed, 600 rpm.

due to the strong adsorption characteristics of LiI on the support. Therefore, in this region, an increase in Rh/C loading does not show a significant effect on the rate. The other possible mild catalyst loading effect is due to mass transfer limitations for dissolution of CO and or O_2. However, the effect of agitation (Fig. 2) showed no effect of rates beyond 500 rpm, which indicates that the data are mainly in the kinetic regime.

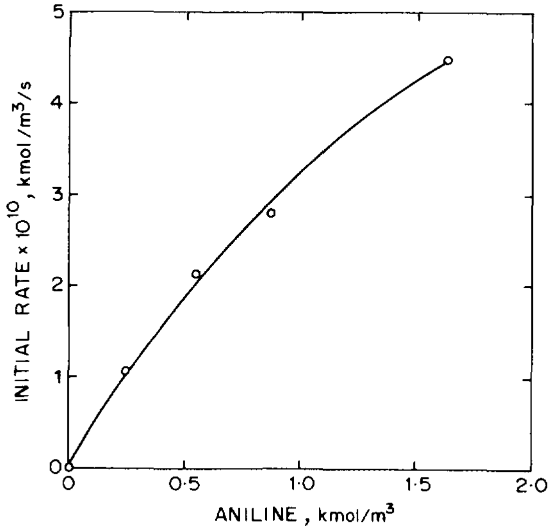


FIG. 5. A plot of initial rate of reaction vs concentration of aniline. Reaction conditions: catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.69 MPa; agitation speed, 600 rpm.

- The initial rates (Figs. 4, 6) and average activity (Tables 13, 14) were found to increase with increased P_{CO} and P_{O_2}; however, the selectivity was found to be unaffected.
- The initial rate was found to increase with increased aniline concentration (Fig. 5), however, the average activity was found to decrease (Table 12), and the selectivity to the formation of DPU to increase.
- The effect of ethanol concentration showed that the

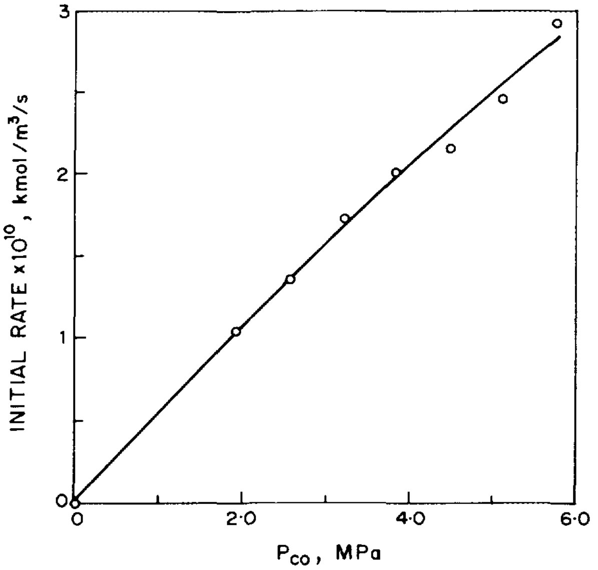


FIG. 4. A plot of initial rate of reaction vs partial pressure of CO. Reaction conditions: aniline, 0.548 kmol/m^3; catalyst, 0.4 kg/m; LiI, 8.7 × 10^{-3} kg/m^3; P_{O_2}, 0.69 MPa; agitation speed, 600 rpm.

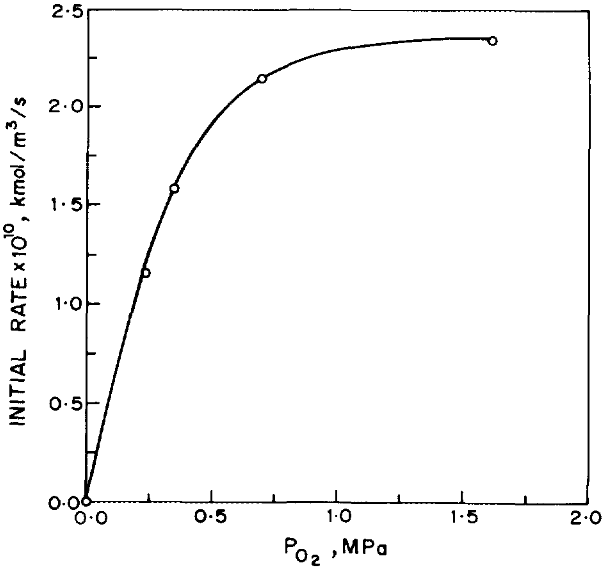


FIG. 6. A plot of initial rate of reaction vs partial pressure of oxygen. Reaction conditions: aniline, 0.548 kmol/m^3; catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; agitation speed; 600 rpm.

TABLE 11

Effect of Catalyst Loading

Catalyst loading kg/m^3	Average activity × 10^1 kmol/kg catalyst/hr	Selectivity Aniline based DPU %	 EPC %
0.2	3.10	45.5	53.7
0.3	4.41	32.5	66.8
0.4	6.21	1.9	96.7
0.5	6.35	0.8	97.6

Note. Reaction conditions: aniline, 0.548 kmol/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr.

average activity passed through a maximum with increase in ethanol. At higher ethanol concentrations, side products such as *N*-ethylaniline were observed but the selectivity of EPC was not affected.

- Increased H_2O concentration decreased both the average activity and the selectivity to EPC CO_2 formation was significantly enhanced with increased H_2O concentration. This is consistent with earlier work in which CO oxidation has been shown to be catalyzed in the presence of H_2O (9).
- Increased temperature (Table 15) resulted in increases in the rate as well as in the average activity. At temperatures up to 443 K, the selectivity of EPC increased. Beyond 443 K, the selectivity of EPC was found to decrease due to formation of side products, which is also consistent with earlier reports (10). Thus, the optimum temperature for EPC was found to be in the range 423–443 K.
- The formation of CO_2 (Table 15) was also enhanced significantly with temperature and hence the selectivity of EPC based on CO consumed decreased with temperature. Below 373 K, CO_2 formation was negligible and the major liquid product formed was DPU.

TABLE 12

Effect of Aniline Concentration

Aniline concentration kmol/m^3	Average activity × 10^1 kmol/kg catalyst/hr	Selectivity Aniline based DPU %	 EPC %
0.548	6.21	1.9	96.7
0.878	4.32	25.5	71.2
1.645	3.21	50.3	45.8

Note. Reaction conditions: Rh/C catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K, time of reaction, 2 hr.

TABLE 13

Effect of P_{CO}

		Selectivity				
		CO based			Aniline based	
P_{CO} MPa	Average activity × 10^1 kmol/kg catalyst/hr	DPU %	EPC %	CO_2 %	DPU %	EPC %
1.920	1.74	9.7	34.5	53.5	20.6	76.4
2.561	2.11	7.4	35.4	56.5	15.8	82.3
3.22	3.00	6.3	35.7	57.4	10.5	84.6
3.84	3.87	5.3	36.9	55.9	7.9	87.2
4.48	6.21	4.0	37.0	55.5	1.9	96.7
5.12	6.32	3.6	34.5	58.4	1.2	97.6
5.76	6.80	2.7	32.1	64.5	1.2	97.8

Note. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr.

Kinetic Study

The initial rate data obtained under different conditions were also used to study the intrinsic kinetics of oxidative carbonylation of aniline using Rh/C–LiI catalyst at 443 K. The results presented here are mainly representative for the kinetics of Reaction 2, involving the formation of DPU, since, in the region of initial rate evaluation, only DPU is formed as a major product (Fig. 1). Also, the formation of CO_2 is negligible at lower conversions (as discussed earlier), and hence oxidation of CO was not considered.

TABLE 14

Effect of P_{O_2}

		Selectivity				
		CO based			Aniline based	
P_{O_2} MPa	Average activity × 10^1 kmol/kg catalyst/hr	DPU %	EPC %	CO_2 %	DPU %	EPC %
0.23	3.15	5.3	38.7	53.5	6.1	86.5
0.32	4.58	4.9	37.3	54.9	6.5	87.2
0.69	6.21	4.0	37.0	55.5	1.9	96.7
1.61	6.85	6.31	32.3	63.8	1.2	97.5

Note. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; agitation speed, 600 rpm; temperature, 443 K; time of reaction, 2 hr.

TABLE 15

Effect of Temperature

Temperature K	Average activity × 10^1, kmol/kg catalyst/hr	Selectivity: CO based DPU %	CO based EPC %	CO based CO_2 %	Aniline based DPU %	Aniline based EPC %
373	1.53	21.9	6.1	47.9	80.1	11.2
408	4.37	18.9	31.1	38.2	54.4	44.8
443	6.20	4.0	37.0	55.5	1.9	96.7
473	3.97	—	17.4	68.8	—	67.3

Note. Reaction conditions: aniline, 0.548 kmol/m^3; Rh/C catalyst, 0.4 kg/m^3; LiI, 8.7 × 10^{-3} kg/m^3; P_{CO}, 4.48 MPa; P_{O_2}, 0.32 MPa; agitation speed, 600 rpm; time of reaction, 2 hr.

The results are shown in Figs. 3 to 6. The following observations were made.

- The rate varies linearly with aniline concentration (Fig. 5), indicating approximately a first order dependence.
- The rate vs P_{CO} (Fig. 4) showed a first order dependence.
- The rate first increased with increased P_{O_2} (Fig. 6) and then was found to be independent of P_{O_2} beyond 0.75 MPa.
- The rate varied linearly with catalyst loading (Fig. 3) (keeping the Rh–LiI ratio constant at 1 : 1).

Based on these rate data, the following empirical rate equation was proposed:

$$R_A = \frac{wkABC}{1 + K_C C}. \qquad [5]$$

R_A is the rate of reaction of aniline, kmol/m^3/sec; A, B, and C, the liquid phase concentrations of aniline, CO, and O_2, respectively, kmol/m^3; k the rate constant, (m^3/kg) (m^3/kmol$)^2$/sec; k_C, the adsorption equilibrium constant, m^3/kmol; and w, the concentration of the catalyst, kg/m^3.

The rates predicted using Eq. [5] were found to agree with experimental data within 5–7% error.

Catalyst Characterization

In order to understand the nature of changes undergone during oxidative carbonylation, some catalyst samples (Rh/C) were characterized by ESCA, XRD, and TEM analysis. The ESCA results of the two catalysts are shown in Fig. 7, which indicates that Rh exists in a zero valent state both in the initial and in the as used sample. Obviously, Rh^0 undergoes changes in oxidation state during the reaction, but the transient species may not be stable enough and hence may reduce to zero valent state once the CO/O_2 atmosphere is removed.

The transmission electron micrographs of these samples are shown in Fig. 8, in which it is observed that Rh metal crystallite size decreased for the used catalyst. This can be interpreted as a result of redispersion of Rh metal, which was also observed earlier under a CO environment (11, 12). The X-ray powder diffraction (XRD) patterns of the two catalysts are shown in Fig. 9, which also shows a decreased Rh metal crystallite size in the used catalyst. These observations partly

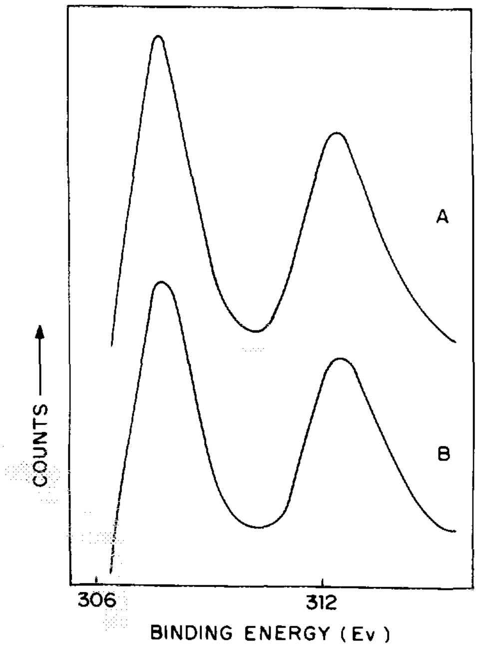


FIG. 7. ESCA spectrum of 5% Rh/C, catalyst, showing rhodium 3d electrons (A) before reaction and (B) after reaction.

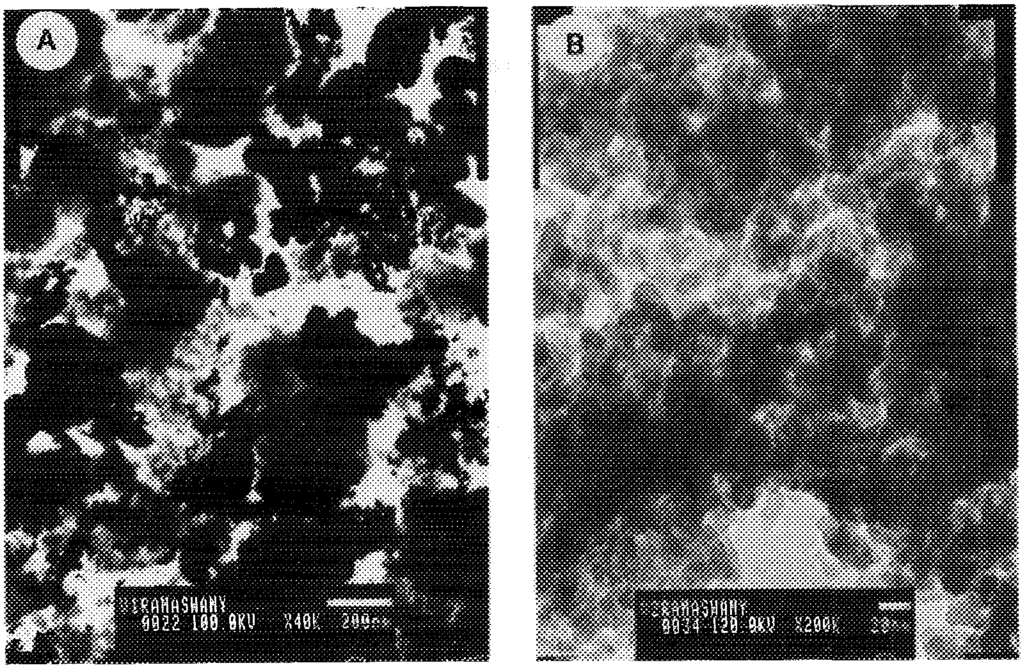
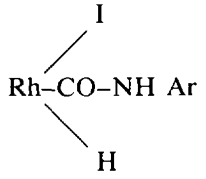


FIG. 8. Micrographs of 5% Rh/C catalyst (A) before reaction and (B) after reaction.

explain the increase in the initial rate of the reaction in the used catalysts (Table 4).

The mechanism of oxidative carbonylation of amines using supported Rh catalyst is not well understood. From the literature on activation of CO using supported Rh catalysts, formation of metal carbonyl species like Rh^1 $(CO)_2$ are likely to exist (13). In the presence of aromatic amines and metal iodide promoter, carbamoyl species of the type



are likely to be found, similarly to the results established earlier for Pd catalyzed reactions (14). However, further work would be necessary to characterize the nature of the active catalytic species.

It is also important to consider whether oxidative carbonylation occurred on the solid catalyst or in the homogeneous phase. Besides the results on catalyst recycling, which indicate that the catalyst could be used several times without loss of significant activity, the observations on the effect of Rh content on the average activity of the catalyst clearly indicate that the reaction occurs on the solid surface. It was observed that when the Rh content in the catalyst was reduced from 5% to 0.2% (w/w), the activity (expressed as kmol/kg Rh/hr) increased from 1.65 to 9.11 (5.5 times). If the reaction was to take place in the homogeneous phase by the leached Rh species, one would expect the concentration of Rh species to be much higher for 5% catalyst than the 0.2% catalyst; hence the activity trend expected would be exactly the reverse of what is actually observed. Therefore, the reaction is likely to occur on the surface of the solid catalyst and not in the homogeneous phase.

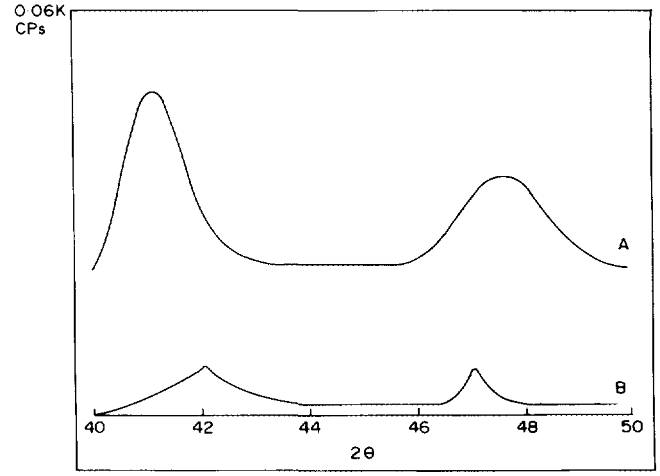


FIG. 9. XRD spectrum of 5% Rh/C, between 2θ values 40–50 for rhodium, (A) before reaction and (B) after reaction.

Also, the results of XRD and TEM analysis of fresh and used catalysts support the existence of Rh on the carbon surface.

CONCLUSIONS

Oxidative carbonylation of aniline over Rh/C catalyst has been investigated. The major products of the reaction are EPC and DPU. The effects of catalyst preparation methods, supports, metal content, reusability, promoters, co-catalysts, solvents, and pretreatment on the activity and selectivity of the Rh/C catalyst have been investigated. The selectivity based on aniline consumed to EPC was found to be independent of the catalyst preparation methods, supports, and metal content. CO_2 formation was found to be dependent on the support and the metal content. The selectivity for EPC was found to be dependent on the temperature up to 443 K, beyond which the selectivity decreased due to the thermal instability of EPC. CO_2 formation increased with increase in temperature beyond 373 K. Alkali metal iodides, as promoters, gave higher selectivity for EPC and lower selectivity for CO_2. Other metal iodides, such as NiI_2 and SnI_2, in combination with other co-catalysts, such as $CoCl_2$, $MnCl_2$, and $SnCl_2$, gave good selectivities for EPC. The selectivity to EPC was found to be higher in moderately polar and nonpolar solvents. In highly polar solvents such as DMF and acetonitrile, the major product was DPU. Pretreatment of the catalyst with CO, O_2, CO_2, H_2, and aniline gave higher initial rates. The average activity of the catalyst and the selectivities for EPC and CO_2 were found to be only marginally affected by the pretreatment of the catalyst.

ESCA, XRD, and TEM analysis of fresh and used catalyst indicated that (a) Rh exists in a zero valent state and (b) redispersion of Rh occurs during carbonylation leading to a lower Rh metal crystallite size.

The intrinsic kinetics of the reaction have been studied at 443 K. The rate of reaction was found to be linearly dependent on aniline, CO, and catalyst. The rate of the reaction was also found to be linearly dependent on the oxygen partial pressure up to 0.75 MPa, above which it was found to be independent of oxygen partial pressure. A rate model has been proposed.

REFERENCES

1. Fukuoka, S., and Chono, M., *J. Org. Chem.* **49,** 1460 (1984).
2. Fukuoka, S., Chono, M., and Kohno, M., *CHEMTECH* **14,** 687 (1984).
3. Becker, R., Groling, J., and Rasp, C., German Patent Documents 2,908,251 and 2,809,252 (1980).
4. Fukuoka, S., and Chono, M., European Patent 83,096 (1983).
5. Fukuoka, S., and Chono, M., *J. Chem. Soc. Chem. Commun.*, 399 (1984).
6. Gupte, S. P., and Chaudhari, R. V., *J. Catal.* **114,** 246 (1988).
7. Polyanszyky, E., Petro, J., and Sarkany, A., *Acta Chim. Acad. Sci. Hung.* **104,** 345 (1980).
8. Chaudhari, R. V., Jagananthan, R., Kolhe, D. S., Emig, G., and Hofmann, H., *Ind. Eng. Chem. Prod. Res. Dev.* **25,** 375 (1986).
9. Hadman, G., Thompson, H. W., and Hinshelwood, C. N., *Proc. R. Soc. London* **137,** 87 (1932).
10. Arnold, R. G., Nelson, J. A., and Verbanc, J. J., *Chem. Rev.* **57,** 47 (1957).
11. Bergeret, G., Gallezot, P., Gelin, P., Ben Taarit, Y., Lefebvre, F., Naccache, C., and Shannon, R. D., *J. Catal.* **104,** 279 (1987).
12. Buchanan, D. A., Hernandez, M. E., Solymosi, F., and White, J. M., *J. Catal.* **125,** 456 (1990).
13. Basu, P., Panayotov, D., and Yates, J. T., Jr., *J. Am. Chem. Soc.* **110,** 2074 (1988).
14. Vasapollo, G., Nobile, C. F., and Sacco, A. J., *J. Organomet. Chem.* **296,** 435 (1985).