

A Non-phosgene Route Synthesis of Carbamate in Continuous Fixed Bed Reactor

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A non-phosgene route synthesis of carbamate was carried out in a continuous fixed-bed reactor through oxidative carbonylation of aniline using palladium catalysts and sodium iodide as promoter. The activity, selectivity and stability of both carbon and alumina-supported palladium catalysts were evaluated. It was found that the alumina-supported catalyst system exhibited a higher activity and selectivity than that of the carbon-supported system, and an average aniline conversion of 95.6% and carbamate selectivity of 74.6% were achieved for the Se-Pd/Al₂O₃ catalyst after 91 h on stream. Reclamation analysis of the spent Pd/C catalyst suggested that the deactivation was mainly due to the leaching and sintering of palladium metal and the accumulation of insoluble chemicals on catalyst support also aggravated the decline of catalyst activity. When small amounts of selenium were added to the Pd/Al₂O₃ catalyst, its activity, selectivity and stability were significantly improved which indicated that a promotional effect existed for carbamate formation on a Pd-Se catalyst system.

Keywords: Pd-Se bimetallic catalysts; Oxidative carbonylation; Continuous fixed bed reactor.

INTRODUCTION

Oxidative carbonylation of aromatic amines in the presence of noble metal catalysts have attracted considerable attention in developing a non-phosgene route of isocyanate for the past twenty years.¹ The major products of this reaction, carbamates, are widely used in the pharmaceutical and pesticide industries and can be readily converted to isocyanate for polyurethane synthesis via thermo decomposition.² A variety of catalyst systems have been investigated using oxygen as oxidizing agent for the carbonylation reactions. These include: Pd/C,³ Rh/C,⁴ Ru/C,⁵ Au/polymer,⁶ PdCl₂,⁷ PdCl₂-CuCl₂,⁸ PdCl₂-Fe,⁹ and PdCl₂-MnCl₂.¹⁰ Other base metals or main group catalyst systems such as ZnCl₂¹¹ and SeO₂¹² have also been proved satisfactory for carbamate formation under different conditions.

Reviewing previous studies, most carbonylation reactions have been carried out batchwise; little has been done for the continuous process, and reports regarding the recovery of catalysts as well as the deactivation phenomenon are also rather rare. Recently, Toochinda and Chuang¹³ have reported a gas-solid oxidative carbonylation reaction in a semibatch fixed-bed reactor wherein a two-step synthe-

sis via diphenyl urea was carried out using NaI-Pd/C catalyst. The semi-continuous carbamate synthesis proceeded for only two hours with 80.2% of aniline conversion and 74.8% carbamate yield. To the best of our knowledge, there are no reports in the literature describing the use of a continuous fixed-bed reactor for the carbonylation of aromatic amines. As the annual production of isocyanate has increased dramatically with an estimation of 4.4 millions metric tons and a growth rate of 5~7% worldwide today, the continuous fixed-bed reactor has advantages for its convenient operation as well as ease of catalyst separation in industrial production. Thus, the objectives of this study were to develop a modified palladium catalyst suitable for continuous preparation of carbamates and to investigate the catalyst deactivation phenomenon according to reclamation analysis of the spent catalyst.

EXPERIMENTAL SECTION

Materials and Catalyst Preparations

All the chemicals including palladium nitrate (Kojima Chemical Co. Ltd., Japan), sodium iodide, selenium stan-

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dard solution (Aldrich, USA), methanol, CO, O₂ (99.9% purity) were purchased from commercial companies and used as received. Reagent grade aniline was freshly distilled before use. Active carbon-supported palladium catalysts (Pd/C) were prepared by impregnating active carbon (coconut-based carbon, 1/8" extrudated in a 1 mm × 5 mm cylindrical, specific surface area 1000 m²/g) with Pd(NO₃)₂ in aqueous solutions for two hours. After filtration, the catalyst was dried in an air oven for 2 h at 353 K, reduced in flowing hydrogen at 323 K for 3 h and then cooled to room temperature under hydrogen flow before being used. The palladium loading was determined by dissolving a sample in aqua regia and then analyzing by atomic absorption spectroscopy.

The alumina-supported Pd catalyst (Pd/Al₂O₃) was prepared by incipient wetness impregnation technique using an acetone solution of Pd(NO₃)₂. γ -Alumina (BET: 203 m²/g, average pore size: 15.3 nm, pore volume: 0.59 mL/g) were immersed in a minimum amount of Pd(NO₃)₂/acetone solution for 2 h. After impregnation, the samples were dried at 383 K for 2 h and calcined at 873 K for 3 h, then cooled to room temperature and reduced at 573 K with a 10 °C/min linear raise in temperature under flowing hydrogen at 40 mL/min for 2 h. The nominal palladium loading was 5

wt.%.

The alumina-supported Pd-Se catalyst was prepared by sequential impregnation of the Al₂O₃ support with Pd first, using the general method described above, followed by selenium addition. Selenium was introduced to the catalysts system in a mole ratio of Pd:Se = 37:1 by incipient wetness impregnation of initially prepared 5% Pd/Al₂O₃ with the desired amount of selenium standard solution at ambient temperature for 2 h. Following impregnation, the resultant mixture was dried at 373 K and then calcined in air at 873 K for 3 h. After calcination, the catalysts were reduced for 3 h in flowing hydrogen at 573 K and then cooled to room temperature under hydrogen flow before being used.

Oxidative Carbonylation Reaction

The experimental setup for the fixed-bed reactor is shown in Fig. 1. The system consists of a reactor, one liquid feed pump, flow measurement for the liquid and gas, gas-liquid separator and back pressure regulator for accurate pressure control. The reactor was made of high-pressure stainless steel tube (length = 670 mm, i.d. = 18 mm), equipped with an axial (o.d. = 1.6 mm) thermowell to allow measurement of the temperature profile. Five grams of catalyst

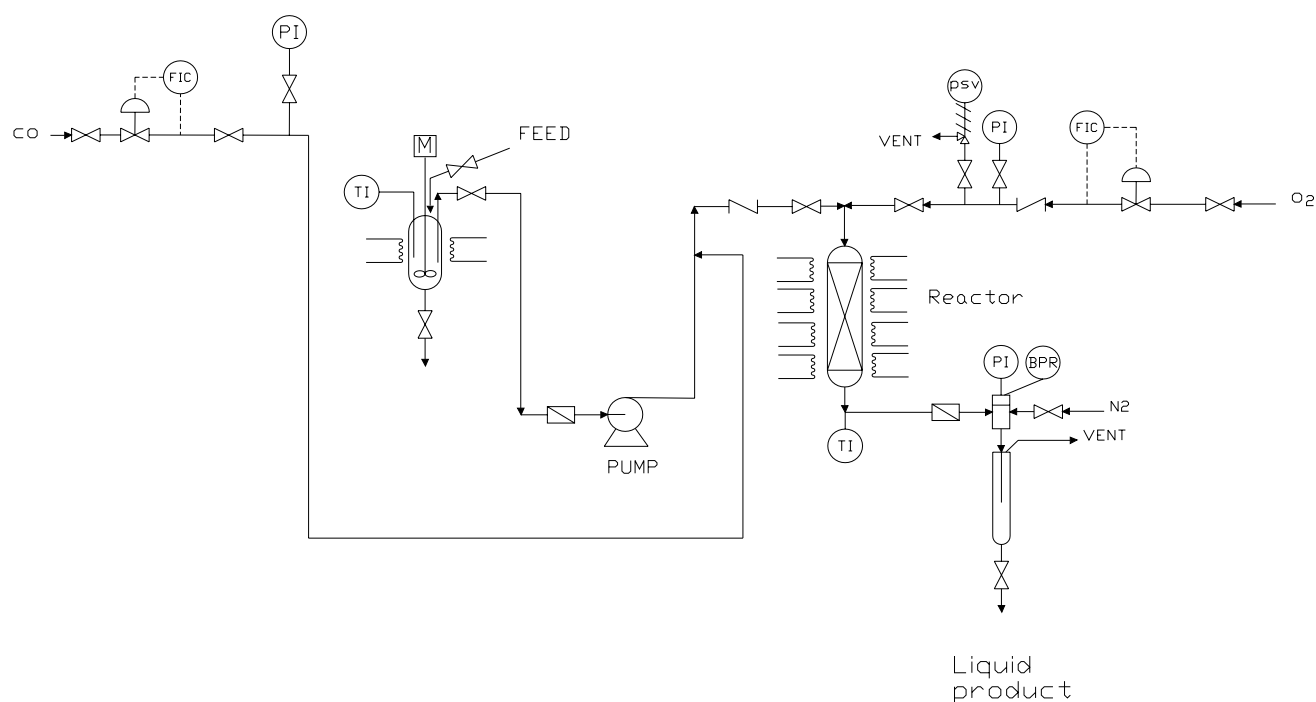


Fig. 1. Schematic diagram of continuous fixed-bed reactor set-up for carbamate synthesis.

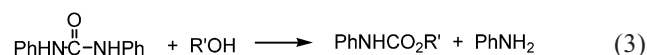
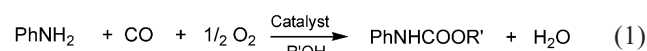
were placed in the middle portion of the reactor, whereas the top and bottom portions were filled with ceramic beads for material distribution and heat exchange. Typical reaction conditions were as follows: 7 wt.% aniline and 0.07 wt.% NaI were dissolved in absolute ethanol and were pumped by a high pressure metering pump with a flow rate of 20 mL/h. Pure CO and O₂ gas provided by gas cylinders was passed co-currently from the top of the reactor at 150 mL/min and 30 mL/min, respectively, to maintain a total pressure of 6.6 MPa to maintain the reactor at constant pressure during a carbonylation experiment. The temperature of the reactor was controlled by PID-controller and was maintained at 443 K during the course of reaction. The pressure in the reactor system was maintained through a backpressure regulator connected with a gas-liquid separator. Reactants and the product stream were analyzed by HPLC (Waters 600) using a UV detector (Waters Model 486, wavelength: 254 nm) furnished with a Inertsil column ODS 4.6 × 250 mm (Vercopak, USA), mobile phase (v/v) H₂O/Acetonitrile = 43/57, flow rate = 1 mL/min. BET surface areas of the catalysts were measured by using a Micromeritics Flowsorb II 2300 unit at -196 °C. X-ray diffraction of the catalyst was carried out with a Scintag ID-3000 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) for 2 θ of 10-70°.

RESULTS AND DISCUSSIONS

Evaluation and Characterization for Pd/C Catalysts

Numerous examples of homogeneous and heterogeneous catalysts have been shown to exhibit high selectivities toward carbamates in oxidative carbonylation of aniline or aliphatic amines.³⁻¹⁴ The reaction of oxidative car-

bonylation of aniline to the desired carbamate can be written as follows:



It was also demonstrated that N,N'-diphenylurea (DPU), found as intermediate in the reaction (eq 2), would undergo solvolysis reaction and yielded carbamates (eq 3). Regardless of the type of catalysts used, all the batch processes encountered catalyst separation and reusability problems which were difficult for process development in terms of operation simplicity and large scale production. Hence, we intended to explore the feasibility of the continuous process and investigate the performance of the catalysts in a continuous fixed-bed reactor. Three types of Pd/C catalysts denoted as catalyst A, B, C with Pd loading of 3.0%, 2.34% and 2.88%, respectively, were prepared in a similar manner described in the experimental section except that catalyst A was reduced at 573 K with flowing hydrogen, catalyst B was reduced at 323 K with flowing hydrogen and catalyst C was reduced at 318 K with 0.1N HCOONa. The reduction methods of catalyst precursors highly influenced the particle size and the dispersion of the precious metal as shown in Table 1. The reduction with sodium formate resulting in a lower dispersion than those prepared by hydrogen reduction suggested that hydrogen appeared to be a more potent reducing agent than sodium formate in obtaining a smaller palladium particle size and a higher dispersion on active carbon support. This result is in good agreement with the observations made by Pattabiraman¹⁵ and Farkas,¹⁶ wherein

Table 1. Physical characteristics of catalysts A, B, C

	Fresh Catalyst			Spent Catalyst		
	Pd loading ^a	Particle Size ^b	Dispersion ^c	Pd loading ^a	Particle Size ^b	Dispersion ^c
	%	nm	%	%	nm	%
Catalyst A	2.34	8.2	10.9	1.04	20	4.5
Catalyst B	3	11.2	8.1	0.81	49.2	1.8
Catalyst C	2.88	23.4	3.8	1.63	45.3	2

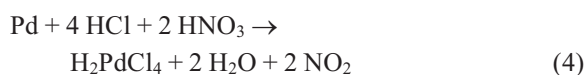
^a Analyzed by atomic absorption after digestion with aqua-regia.

^b Analyzed by X-ray line broadening analysis (XLBA) according to Scherrer equation at 2 $\theta = 47^\circ$.

^c Calculated according to semi-empirical formula $d = 0.9/D$, d is particle size (nm); D is dispersion.

Pd/C catalyst obtained by the hydrogen reduction method gave higher dispersion than the sodium formate method.

Catalytic conversion and product selectivity on catalysts A, B, and C are plotted in Fig. 2. For all catalysts, deactivation appeared during the reaction time on stream and catalyst A exhibited the highest aniline conversion and ethyl phenyl urethane (EPU, or carbamate) selectivity after 20 h. In catalyst A, the selectivity of DPU gradually increased from 7 to 30% (Fig. 2c), whereas the selectivity of EPU dropped from 63 to 46% (Fig. 2b) after 91 h which represented the typical decline feature of catalytic activity. Catalyst B exhibited similar deactivation behavior to Catalyst A except that the conversion and product selectivity was lower than that on Catalyst A. We presumed that the poor catalytic performance of catalyst B was related to the lower reduction temperature which led to the incomplete reduction of palladium metals and resulted in more severe leaching and sintering of palladium metals thereafter. The higher activity was in agreement with the higher metal dispersion prepared by different reduction methods. The catalytic reactions were run for approximately 91 and 96 h on stream for catalysts A and B and thereafter, the fixed-bed reactor was cooled to room temperature and spent catalyst samples were unloaded for characterizations. Despite the highest initial selectivity, catalyst C was tested for only 26 h due to the significant drop of carbamate selectivities and rapid increase in diphenyl urea selectivity after 20 h on stream. The reclamation analysis of spent catalysts of A, B and C was performed by atomic absorption spectroscopy and power X-ray diffraction. For palladium loading determination, the Pd metals and active carbon were digested with concentrated hydrochloric acid and nitric acid in the form of chlorocomplex $[H_2PdCl_4]$ (eq 4) and analyzed by atomic absorption spectroscopy.



The mean crystallite size of the crystalline palladium on spent catalyst was measured from X-ray line broadening analysis (XLBA) using the well-known Scherrer equation:¹⁷

$$d = \frac{0.89\lambda}{B(2\theta)\cos\theta}$$

where $B(2\theta)$ is the width of the XRD peak at half peak-

height in radians, λ is the wavelength of the X-ray radiation (Cu K = 0.154 nm), θ is the Bragg angle of the XRD peak in

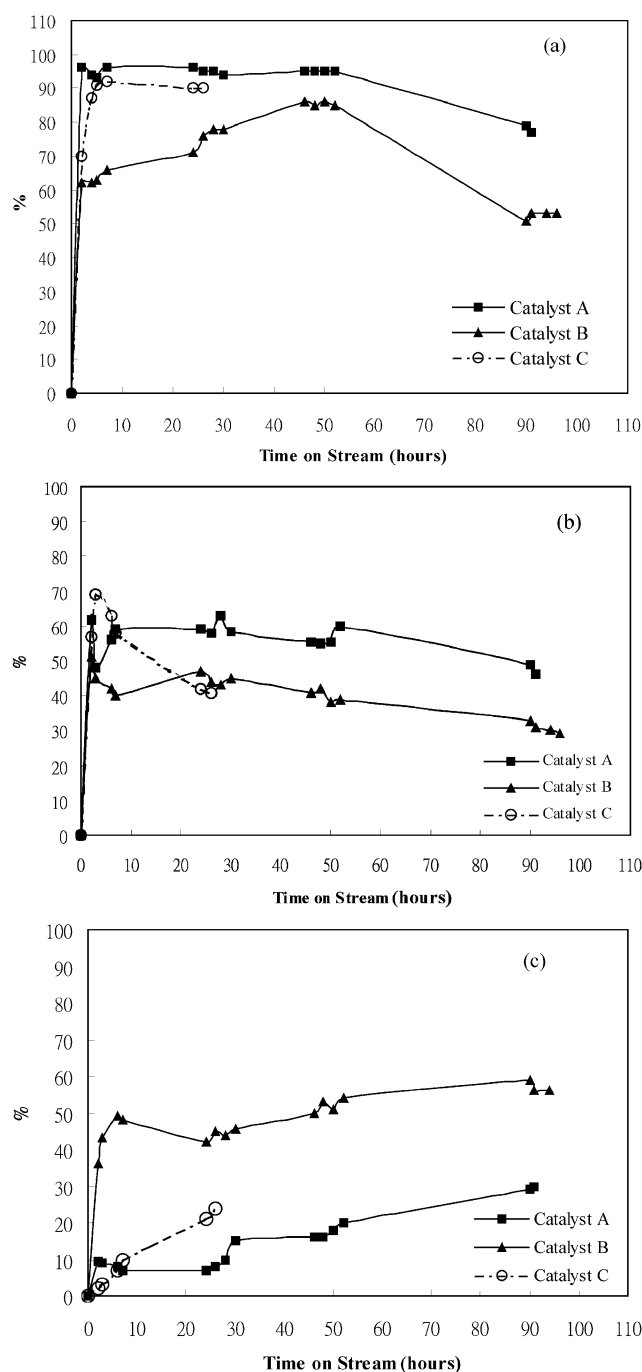


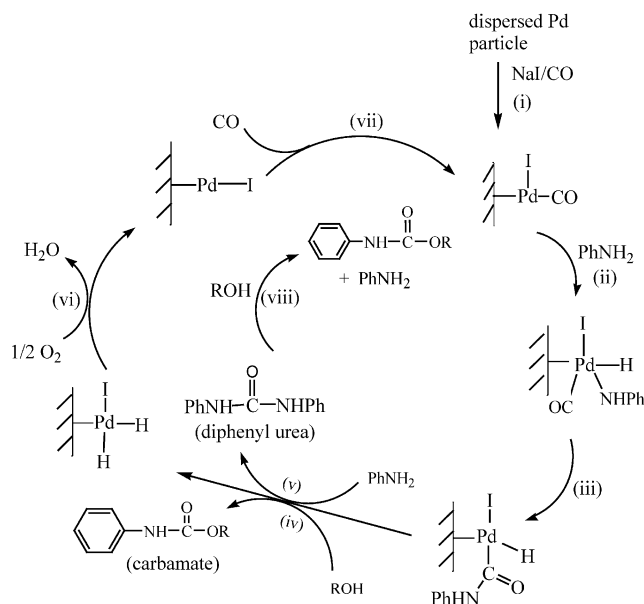
Fig. 2. Effect of Pd/C catalysts on conversion and product selectivity of continuous fixed-bed reactor (a) aniline conversion (b) carbamate selectivity (c) DPU selectivity. Reaction conditions: aniline, 7 wt.%; NaI, 0.07 wt.%; Solvent: Ethanol; P_{CO} , 5.5 MPa, P_{O_2} , 1.1 MPa; temperature, 170 °C; LHSV = 2 h⁻¹.

degrees, and d is the average crystallite size of the powder sample in nanometers. The dispersion is calculated according to the semi-empirical formula $d = 0.9/D$, where d is particle size (nm); D is dispersion.¹⁸ The calculated results are summarized in Table 1. They revealed that the reaction conditions had brought about drastic changes in the catalyst structure, especially the Pd particle size after the reaction. The decrease of activity is mainly caused by the sintering and leaching of palladium catalysts. For example, approximately 56, 73 and 43% of palladium are leached out from the catalyst matrix after catalytic reaction and the crystallite values measured by XRD were also much larger than that of fresh catalysts. Surface areas and pore volumes of the active carbon of Catalyst B were measured with nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$ on a Micromeritics Flowsorb II 2300 instrument.^{19,20} The textural properties of catalyst B showed that the surface area and pore volumes decreased by about 90% and 13%, respectively, compared to the fresh catalyst which also explained the gradual loss of activity during the reaction process. Residual analysis of spent catalyst by HPLC indicated that DPU was the major component that blocked the surface, probably due to its poor solubility in the ethanol solvent system.

Proposed Reaction Mechanism

Attempts to carry out the reaction in the absence of sodium iodide resulted in no reaction which indicated that Pd^0 was oxidized to form the active Pd-I species during the reaction. This phenomenon could cause a leaching of the metal into the reaction medium and explains the loss of Pd loading after a period of time. Although the mechanism of carbamate synthesis is still not clear, a postulated catalytic cycle of oxidative carbonylation of aniline over supported palladium is depicted in Scheme I. After impregnation, calcination and reduction, the dispersed Pd^0 particle was activated by NaI and CO (i) which underwent oxidative addition of aniline (ii) and carbonyl insertion (iii) to form the carbamoyl-palladium species subsequently. It seemed likely that the carbamoyl-palladium intermediate could undergo either alcoholysis (iv) or aminolysis (v) to afford the corresponding carbamate or DPU products. Thereafter, the resulting palladium hydride species could be dehydrogenated by oxygen (vi) to regenerate the catalyst and advance a new catalytic cycle by association with carbon monoxide (vii). Another pathway for EPU formation could proceed through the direct solvolysis of DPU with alcohol (viii) in a non-

Scheme I Proposed reaction mechanism for the formation of carbamate and diphenyl urea in a fixed-bed reactor



catalytic mode. The observation that DPU formation increased along with the decline of EPU with time on stream implied that aminolysis became more favorable when a catalyst was less active. Similar trends could also be found in the alumina-support catalyst system in this study.

Catalytic Studies for Pd/Al₂O₃

To improve efficiency of the fixed-bed process, we further investigated the alumina-supported catalysts system and evaluated catalytic performance of a bimetallic catalyst. Great interest has developed in recent decades in the palladium-based bimetallic catalysts.²¹⁻²³ The incorpo-

Table 2. Textural properties of catalyst B

	Support	Fresh cat.	Spent cat.
BET surface area ^a (m ² /g)	1090	1040	102
Pore volume ^b (mL/g)		0.56	0.49
Avg. pore diameter (nm)		4.4	5.0
Pore surface area (m ² /g)		166	40

^a Brunauer-Emmett-Teller (BET) surface area of the samples was measured using the adsorption-desorption isotherms of nitrogen.

^b Measured by Hg intrusion method.

ration of a second metal in catalysts has proven to often provide additional catalytic stability, selectivity and/or activity. Various Se-based catalysts have been reported in the carbonylation of nitrobenzene and aniline,²⁴⁻²⁸ however, disadvantages arose from the difficulty in catalyst separation and the malodorousness of toxic selenium species formed in the reaction mixture. Considering the role of selenium in carbonylation reactions, it was conceivable, but not yet demonstrated, to modify the catalyst structure by

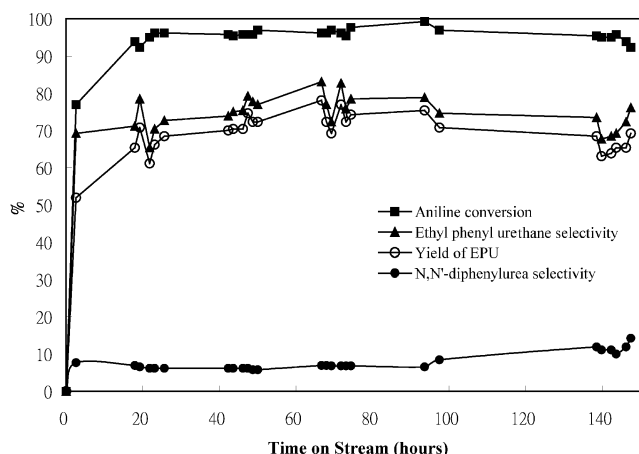


Fig. 3. Effect of Pd-Se/Al₂O₃ catalyst on conversion and product selectivity of a continuous fixed-bed reactor. Reaction conditions: aniline, 7 wt.%; NaI, 0.07 wt.%; solvent: absolute ethanol; P_{CO}, 5.5 MPa, P_{O₂}, 1.1 MPa; temperature, 170 °C; LHSV = 2 h⁻¹.

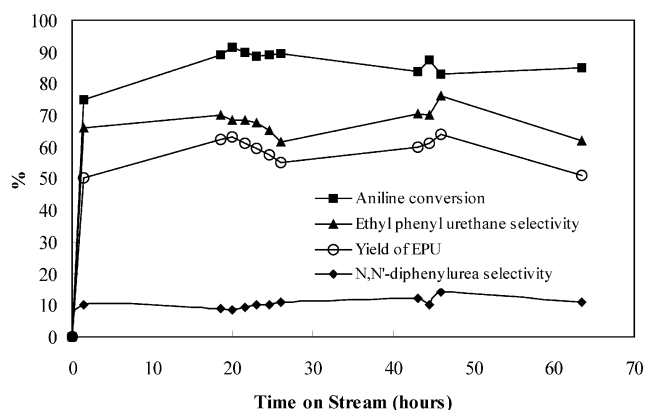


Fig. 4. Effect of Pd/Al₂O₃ catalyst on conversion and product selectivity of continuous fixed-bed reactor. Reaction conditions: aniline, 7 wt.%; NaI, 0.07 wt.%; solvent: absolute ethanol; P_{CO}, 5.5 MPa, P_{O₂}, 1.1 MPa; temperature, 170 °C; LHSV = 2 h⁻¹.

immobilizing a small amount of selenium on Pd/Al₂O₃ to solve the problems described above. The alumina-supported Pd catalyst (Pd/Al₂O₃) were prepared by the incipient wetness impregnation technique with nominal palladium loading of 5 wt.%. The alumina-supported Pd-Se catalysts were prepared by sequential addition of selenium solution to the initially prepared 5% Pd/Al₂O₃ catalysts system in a mole ratio of Pd:Se = 37:1 as described in the experimental section. Both catalysts were tested under similar reaction conditions, and the results are illustrated in Figs. 3 and 4. For Se-Pd catalyst, aniline conversion remained almost unchanged with an average of 95.6% during the 150 h running time, and the average selectivities of EPU and DPU were maintained at 74.6% and 7.8%, respectively, as shown in Fig. 3. These results were far more superior to carbon-supported catalysts and were also significantly better than the unmodified Pd/Al₂O₃ system. For the unmodified Pd/Al₂O₃ catalyst, as illustrated in Fig. 4, an average aniline conversion of 88.1 and average selectivity of 67.7% for EPU, 10.2% for DPU were obtained under similar conditions. Comparison of the average selectivities of EPU observed in Figs. 2, 3 and 4 showed that the type of support used could significantly affect activity and stability of catalyst. The higher catalytic activities of alumina supported catalysts could be in part ascribed to the nature of the support. The activated carbon support has more micropores and a narrower pore diameter (BET:1040 m²/g, pore volume: 0.56 mL/g, average pore size: 4.4 nm) than that of γ -alumina (BET:203 m²/g, pore volume: 0.59 mL/g, average pore size: 15.3 nm), which makes Pd particles in the inner cavities of active carbon inaccessible for catalytic reaction and increases the possibility of pore blockage as well. With the addition of a small amount of Se to the Pd/Al₂O₃ catalyst, significant activity enhancement was observed which indicated that a promotional effect existed for carbamate formation on Pd-Se catalyst system. The promoting effect of selenium is not well understood. It is probable that carbonyl selenide SeCO, formed under high CO pressure conditions, assisted the carbamate formation. In selenium-mediated carbonylation of amines, the carbonyl selenide reacted with amine to form carbamoselenoate (RNHCOSe) followed by nucleophilic attack (alcohol or amine) to yield corresponding carbamate or urea derivatives. Sonoda et al.^{24,28} isolated the carbamoselenoate intermediates as evidence for such a two-step process.

Table 3. Comparison of carbamate yields in oxidative carbonylation over 5 wt.% Pd/Al₂O₃ catalysts in autoclave reactor

Catalyst	Aniline Conv. %	Carbamate Selec %	Carbamate Yield %
5% Pd/Al ₂ O ₃ (This work)	100	88	88
5% Pd-Se/Al ₂ O ₃ (This work)	100	97	97

Reaction conditions: aniline, 54 mmol; Pd catalyst, 0.5 g; NaI, 0.87 mmol; Ethanol, 100 mL; P_{CO2}, 5.5 MPa P_{O2}, 1.1 MPa; temperature, 170 °C; reaction time, 3 h.

The catalytic performance of Pd-Se was also examined in an autoclave reactor, and it was found that selenium promoted bimetallic catalysts Pd-Se/Al₂O₃ showed much higher activity than that of the conventional monometallic palladium catalyst. The results are given in Table 3. Both conversion and selectivity observed in the batch reactor were higher than in the continuous process which could be attributed to the better mass transfer behavior due to external agitation force and a complete solid-liquid phase contact in the batch reactor.

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