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Oxidative Carbonylation of Aniline Using Manganese-Based Catalysts

Isocyanates are key intermediates for the manufacture of polyurethanes. Commercially, isocyanates are produced by the phosgenation of primary amines. Because of the toxicity of phosgene, considerable interest has been devoted to find suitable methods of synthesizing isocyanates without the use of phosgene.

Carbamates have been proposed as precursors for the manufacture of isocyanates via nonphosgene process (*1*). One of the approaches to prepare carbamates is the catalytic oxidative carbonylation of aromatic amines. Following are the reactions for the carbonylation of aniline in ethanol solution to form ethyl *N*-phenylcarbamate (EPC) (*2*):

$$2C_6H_5NH_2 + CO + \tfrac{1}{2}O_2 \xrightarrow{\text{catalyst}} \underset{\text{(DPU)}}{C_6H_5NHCONHC_6H_5} + H_2O \quad (1)$$

$$C_6H_5NHCONHC_6H_5 + CO + \tfrac{1}{2}O_2 \xrightarrow{C_2H_5OH} \underset{\text{(EPC)}}{2C_6H_5NHCOOC_2H_5} + H_2O. \quad (2)$$

N,*N'*-diphenylurea (DPU) is an intermediate, which further reacts to form EPC.

In previous papers, noble metal catalysts (Pd, Pt, Rh, Ir, Ru, etc.) and promoters have been employed for the synthesis of carbamates by oxidative carbonylation of primary amines (*2–7*). Recently, we found that manganese compounds were also capable of catalyzing the reactions effectively. The purpose of this paper is to report the use of managanese-based catalysts to prepare carbamates by oxidative carbonylation of aniline in ethanol solution and to present the effects of several parameters on the performances of the catalyst system.

A 250-ml high-pressure autoclave (Ernst Haage) equipped with an impeller and a temperature control unit was employed for carrying out the catalytic oxidative carbonylation. The autoclave was heated by a thermoregulated oven and a thermocouple was used to monitor the reaction temperature. In a typical run, 25 mmol of aniline, 65 ml ethanol, and 5 mmol of catalyst were placed in the reactor. The reactor was pressurized with oxygen and then carbon monoxide to a total pressure of 70 kg/cm^2 ($CO : O_2$ = 16.5 : 1). The reactor was then heated to 150°C under stirring. The agitation speed was maintained at 1000 rpm. Under the conditions, the reaction rates were found to be chemically controlled because further increase of agitation speed to 1750 rpm had little effect on aniline conversion and EPC selectivity. After 3 h, agitation was stopped and the reaction mixture was cooled and then discharged from the reactor for quantative analysis. It was found that catalysts were soluble in the reaction mixture.

Product solution was diluted and its composition was determined by HPLC (Waters-60) using a 25 cm × 0.46-cm I.D. stainless-steel column, Inertsil 5 ODS (VERCOPAK). The mobil phase was a mixture of acetonitrile and deionized water in a ratio of 53 to 47. Flowrate of the mobile phase was equal to 0.8 ml/min. The UV detector (Waters Model 441) wavelength was set at 254 nm.

Aniline and $MnBr_2 \cdot 4H_2O$ were obtained

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TABLE 1

Catalyst Screening

Catalyst	Aniline conversion (%)	EPC selectivity (%)	DPU selectivity (%)
"Blank run"	15	6.3	0
$MnBr_2 \cdot 4H_2O$	97.3	88.6	0.3
$MnCl_2 \cdot 4H_2O$	96.7	92	0.4
Mn powder	26.2	53.5	6.6
$CoCl_2 \cdot 6H_2O$	80.0	72.5	9
$CuCl_2 \cdot 2H_2O$	97.5	27.7	0
$CuBr_2$	97.8	18.1	0

Note. Catalyst, 5 mmol; ethanol, 65 ml; benzene, 10 ml; P_{CO}, 66 atm; P_{O_2}; 4 atm; T, 150°C; and reaction time, 3 h.

TABLE 2

Influence of Temperature

Temperature (°C)	Aniline conversion (%)	EPC selectivity (%)	DPU selectivity (%)
90	73.2	8.8	84.7
120	92	49.1	49.2
150	97.3	88.6	0.3

Note. Catalyst, 5 mmol; ethanol, 65 ml; benzene, 10 ml; P_{CO}, 66 atm; P_{O_2}, 4 atm; and reaction time, 3 h.

from Janssen Chimica and had purities of 99.8 and 98%, respectively. They were used without further purification. Carbon monoxide was CP grade supplied by Air Product and was assayed 99.3% purity by the supplier. Ethanol was supplied by Seoul Chemical Industries Co. and had a purity greater than 99.5%.

The N_2 BET surface areas of the catalyst powders, as measured with a Flowsorb II 2300 surface area analyzer, were 0.3, 0.83, and 0.2 m^2/g for $MnBr_2 \cdot 4H_2O$, $CuCl_2 \cdot 4H_2O$, and $CuBr_2$, respectively.

A "blank run" was made with no catalyst presented in the reacting solution. For the "blank run," the yield of EPC detected in the final solution was less than 1%, as shown in Table 1. Table 1 also shows the activity and the product selectivity obtained from the oxidative carbonylation of aniline in ethanol solution using six different catalysts. All six catalysts tested improve aniline conversion and EPC selectivity. The best catalysts among them are $MnBr_2 \cdot 4H_2O$ and $MnCl_2 \cdot 4H_2O$. Manganese powder gives poor yield of EPC. The copper halides show high activity but poor selectivity. Cobalt chloride performs worse than manganese chloride, but better than copper chloride. In order to investigate the effects of process parameters on the performance of manganese catalysts, $MnBr_2 \cdot 4H_2O$ was used as the oxidative carbonylation catalyst in the following sections.

The reaction temperature affects the product distribution dramatically, as can be seen from Table 2. Low reaction temperature favors the formation of *N*,*N*′-diphenylurea, and the EPC yield strongly increases with the increase of reaction temperature.

Since the *N*,*N*′-diphenylurea is the dominant product at low reaction temperature and it has been proposed as a more convenient intermediate in the phosgene-free synthesis of MDI (*6*, *8*), the following three-step procedure is suitable to synthesize EPC in order to avoid the catalyst recovery problem and to improve our process in the future: [1] preparation of DPU at low reaction temperature, [2] separation of DPU from the reaction solution by filtration or centrifugation, and [3] formation of EPC by reacting DPU with ethanol.

The effects of reaction time and catalyst

TABLE 3

Effect of Reaction Time

Reaction time (h)	Aniline conversion (%)	EPC selectivity (%)	DPU selectivity (%)
1.5	94.7	80.6	10
3	97.3	88.6	0.3

Note. Catalyst, 5 mmol; ethanol, 65 ml; benzene, 10 ml; P_{CO}, 66 atm; P_{O_2}, 4 atm; and T, 150°C.

TABLE 4

Effect of Catalyst Loading

Anilin/Mn molar ratio	Aniline conversion (%)	EPC selectivity (%)	DPU selectivity (%)
5	94.7	84.5	3.84
10	86.9	74.8	10.7

Note. Catalyst, 5 mmol; ethanol, 65 ml; P_{CO}, 66 atm; P_{O_2}, 4 atm; T, 150°C; and reaction time, 1.5 h.

loading on conversion and selectivities at 150°C are shown in Tables 3 and 4, respectively. The shorter the reaction time or the lower the catalyst loading, the higher the amount of *N,N'*-diphenylurea in the reaction mixture. The results in Table 3 were obtained in the presence of 10 ml benzene, while the results in Table 4 were obtained in the absence of benzene. Comparisons of Tables 3 and 4 show that the presence of benzene had no effect of aniline conversion, however, it decreased EPC selectivity slightly. We eliminated the use of benzene for the following experiments.

Table 5 shows the effect of O_2/CO molar ratio. As the partial pressure of oxygen is increased from 0 to 8 kg/cm^2, at constant P_{CO}, the conversion of aniline and the selectivity of EPC increase. At the same time, the selectivity of *N,N'*-diphenylurea decreases. The increase in aniline conversion arises from the fact that oxygen increase the rate of reaction (1). The decrease in DPU selectivity and the increase in EPC selectivity suggest that reaction (2) is more sensitive to oxygen pressure than reaction (1).

TABLE 6

Influence of Ligand

Benzoinoxim/Mn molar ratio	Aniline conversion (%)	EPC selectivity (%)	DPU selectivity (%)
0	86.9	74.8	10.67
1.17	96.54	94.3	0.97

Note. Catalyst, 2.5 mmol; ethanol, 65 ml; P_{CO}, 66 atm; P_{O_2}, 4 atm; T, 150°C; and reaction time, 1.5 h.

We have studied the effect of the addition of α-benzoinoxim on the performance of $MnBr_2$ catalyst. The amount of catalyst was reduced to 2.5 mmol in order to see the ligand effect clearly. As shown in Table 6, the addition of α-benzoinoxim increases both the aniline conversion and the EPC selectivity. That is, α-benzoinoxim is a promoter for the catalyst system.

The effect of water was studied by using anhydrous $MnBr_2$ instead of $MnBr_2 \cdot 4H_2O$ as catalyst. Table 7 compares the performance of the two catalysts. It seems that water has little effect on catalyst performance.

Manganese halides have high catalytic activity and high ethyl *N*-phenylcarbamate selectivity for the oxidative carbonylation of aniline, clearly superior to copper halides and cobalt halides. Reaction temperature was the most important factor affecting the selectivity of ethyl *N*-phenylcarbamate. De-

TABLE 5

Influence of O_2/CO Ratio

P_{CO} (kg/cm^2)	P_{O_2}	Aniline conversion (%)	EPC selectivity (%)	DPU selectivity (%)
66	0	10.9	31.3	24
66	4	94.7	80.6	10
66	8	96.8	92.1	0.6

Note. Catalyst, 5 mmol; ethanol, 65 ml; T, 150°C; and reaction time, 1.5 h.

TABLE 7

Influence of Water

Catalyst	Aniline conversion (%)	EPC selectivity (%)	DPU selectivity (%)
$MnBr_2 \cdot 4H_2O$	86.9	74.8	10.67
$MnBr_2$	84.4	73.7	5.63

Note. Catalyst, 2.5 mmol; ethanol, 65 ml; P_{CO}, 66 atm; P_{O_2}, 4 atm; T, 150°C; and reaction time, 1.5 h.

creasing the reaction temperature resulted in an dramatic increase in N,N'-diphenylurea selectivity. Increasing the O_2/CO molar ratio, the reaction time, or the catalyst loading resulted in an increase in both aniline conversion and ethyl N-phenylcarbamate selectivity. The addition of α-benzoinoxim improved the performance of the manganese-based catalyst.

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KUO-TSENG LI[1]
YUNG-JU PENG

China Technical Consultants, Inc.
Catalyst Research Center
P.O. Box 88, Toufen
Taiwan, Republic of China

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[1] To whom correspondence should be addressed at: Department of Chemical Engineering, Tunghai University, Taichung, Taiwan, Republic of China.