

OXIDATIVE ETHOXYCARBONYLATION OF ANILINE TO ETHYL PHENYLCARBAMATE CATALYZED BY SILICA-SUPPORTED POLY- γ -AMINOPROPYLSILOXANE-METAL COMPLEXES

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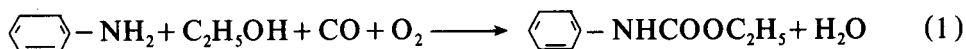
ABSTRACT

Several silica-supported poly- γ -aminopropylsiloxane-monometal and bimetal complexes ($\text{Si}-\text{NH}_2-\text{M}$, $\text{M} = \text{Cu}$ or Co ; $\text{Si}-\text{NH}_2-\text{Cu}-\text{M}'$, $\text{M}' = \text{Co}$, Sn , Mn , Ni or Fe) have been prepared. Their catalytic properties for oxidative ethoxycarbonylation of aniline to ethyl phenylcarbamate have been investigated. The catalytic reaction was carried out under relatively mild conditions. The catalyst $\text{Si}-\text{NH}_2-\text{Cu}-\text{Co}$ had high activity and selectivity, and the turn-over number (molar of aniline converted/molar of metal in $\text{Si}-\text{NH}_2-\text{Cu}-\text{Co}$ -added) could amount to 450 under the conditions: 150°C , 4 MPa ($\text{CO}/\text{O}_2 = 3$) and 40 hours.

The results of XPS and IR indicated that the coordination bonds were formed between nitrogen and metals in $\text{Si}-\text{NH}_2-\text{Cu}$, $\text{Si}-\text{NH}_2-\text{Co}$ and $\text{Si}-\text{NH}_2-\text{Cu}-\text{Co}$, and the coordination pattern was not single. In the oxidative ethoxycarbonylation of aniline to ethyl phenylcarbamate, the catalytic property of $\text{Si}-\text{NH}_2-\text{Cu}-\text{Co}$ bimetallic complex was better than $\text{Si}-\text{NH}_2-\text{Cu}$ or $\text{Si}-\text{NH}_2-\text{Co}$ monometallic complex. This indicated that there was synergistic action between different metals in the bimetallic complex.

INTRODUCTION

Ethyl phenylcarbamate is an important compound not only as agricultural chemicals or pesticides but also as precursor of phenyl isocyanate, because it can be thermally decomposed to give phenyl isocyanate^[1]. Ethyl phenylcarbamate can directly be prepared from aniline, ethanol, carbon monoxide and oxygen:

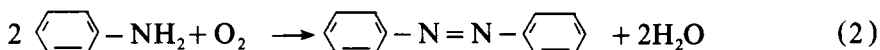


The reaction is usually catalyzed by the catalysts containing noble metal such as palladium or platinum. Some of the catalysts contain hydrochloric acid or Lewis acid^[2,3,4].

In the previous papers, silica-supported poly- γ -aminopropylsiloxane-platinum or palladium complex could catalyze the hydrogenation of aldehyde or ketone effectively^[5], and iron or cobalt complex had very high activity for the carbonylation reaction of propylene oxide and carbon dioxide to propylene carbonate^[6].

Recently, we found that some silica-supported poly- γ -aminopropylsiloxane-metal complexes could catalyze the oxidative ethoxycarbonylation of aniline to ethyl phenylcarbamate. In the complexes, the copper-cobalt bimetallic complex

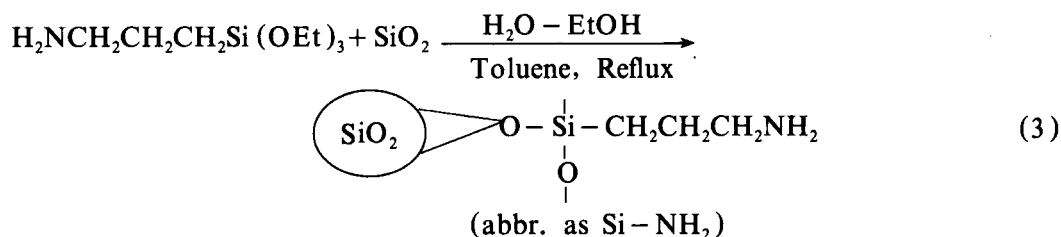
(Si-NH₂-Cu-Co) had the best catalytic property, and the conversion of aniline could amount to over 90% with 80% selectivity and 450 turnover number under relatively mild conditions. This is a new catalyst system, and the catalytic mechanism is unknown. In this series of reactions, azobenzene and other by-products were also formed in spite of the main product ethyl phenyl carbamate, because side reactions such as oxidation of aniline to azobenzene occurred:



EXPERIMENTAL

Preparation of silica supported poly-γ-aminopropylsiloxane (Si-NH₂)

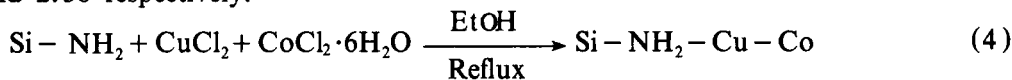
The preparation method of silica-supported poly-γ-aminopropylsiloxane was similar to that reported in the previous paper [5].



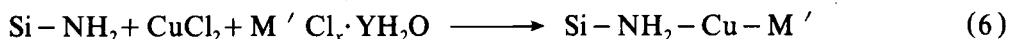
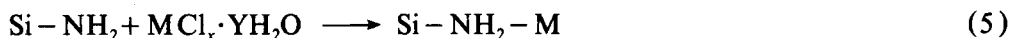
The nitrogen content of the product was 3.29–3.37wt% (determined by elemental analysis).

Preparation of silica supported poly-γ-aminopropylsiloxane monometal and bimetal complexes

A typical example was given as the preparation of Si-NH₂-Cu-Co: CuCl₂ (0.5mmol) and CoCl₂·6H₂O (0.5mmol) were dissolved in ethanol (15ml) in a 25-ml flask, and then silica-supported poly-γ-aminopropylsiloxane (1.0g) was added. The mixture was refluxed for about 4 hours until the solution became transparent and colorless and the color of solid particles became bluish green. The reaction mixture was filtered and solid particles were dried. The bluish green Si-NH₂-Cu-Co was thus obtained with molar ratio of Cu/Co and N/metal, 1 and 2.38 respectively.



Si-NH₂-M (M = Cu or Co) and Si-NH₂-Cu-M' (M' = Sn, Mn, Ni or Fe) were prepared by the similar method.



Note: MCl_x·YH₂O = CuCl₂ or CoCl₂·6H₂O

M'Cl_x·YH₂O = SnCl₂·2H₂O, MnCl₂·2H₂O, NiCl₂·6H₂O or FeCl₃·6H₂O

Preparation of ethyl phenylcarbamate

Aniline, silica-supported poly- γ aminopropylsiloxane-metal complex catalyst and ethanol were added to a 50-ml stainless autoclave. The autoclave was pressurized with carbon monoxide and oxygen, and then placed in a thermostat, heated and magnetically stirred for several hours. The autoclave was cooled to room temperature (25 °C) and the gas was vented slowly. After filtering off the catalyst, the dark red liquid was analyzed by GC-MS. By-products such as azobenzene were formed besides the main product ethyl phenylcarbamate. The products were quantitatively analyzed using gas chromatography.

The efficiency of the catalyst Si-NH₂-Cu-Co was investigated by the procedure similar to the preparation of ethyl phenylcarbamate, except increased amount of aniline and solvent was added. The reaction was stopped at an interval of 5 hours, and a small amount of the reaction mixture was drawn from autoclave for GC analysis, and then repressurized with CO and O₂ and then continued the reaction.

RESULTS AND DISCUSSION

The catalytic properties of several silica supported poly- γ aminopropylsiloxane metal complexes for the oxidative ethoxycarbonylation of aniline

Several silica-supported poly- γ aminopropylsiloxane-metal complexes were used to catalyze the oxidative ethoxycarbonylation of aniline and the results were shown in Table 1. It could be seen that Si-NH₂-Cu-Co had higher catalytic activity and the best selectivity.

Table 1 The catalytic properties of several silica-supported poly- γ aminopropylsiloxane-metal complexes for the oxidative ethoxycarbonylation of aniline

Catalyst	Conversion of aniline (mol%)	Selectivity (%)
Si-NH ₂ -Cu	42.3	63.4
Si-NH ₂ -Cu-Sn	70.0	36.6
Si-NH ₂ -Cu-Mn	40.0	20.5
Si-NH ₂ -Cu-Co	70.0	74.2
Si-NH ₂ -Cu-Ni	90.0	31.1
Si-NH ₂ -Cu-Fe	15.0	24.0
Si-NH ₂ -Co	35.0	67.0

Catalyst, 0.34g (N/Metal molar ratio=2.38, Cu/M molar ratio=2, M=Sn, Mn, Co, Ni or Fe); aniline, 0.4ml; ethanol, 10.0ml; total pressure, 4.5 MPa (CO/O₂=8, at room temperature); 150 °C; 5.0h.

The influence of several factors on oxidative ethoxycarbonylation of aniline catalyzed by Si-NH₂-Cu-Co

Table 2 showed the influence of Co/Cu molar ratio in Si-NH₂-Cu-Co on the catalytic property. It could be seen that the catalytic property was affected obviously by the Co/Cu molar ratio in the complex and the highest activity or selectivity was obtained at an optimum ratio. If Co/Cu molar ratio was ∞ or 0, namely, the catalyst was monometallic complex Si-NH₂-Co or Si-NH₂-Cu, the catalytic activity and selectivity were obviously lower than those of Si-NH₂-Cu-Co at an optimum Co/Cu molar ratio. This result indicated that synergistic action between copper and cobalt in the Si-NH₂-Cu-Co

complex occurred in the catalytic reaction.

Table 2 The influence of Co/Cu molar ratio in Si-NH₂-Cu-Co on the catalytic property

Co/Cu molar ratio	Conversion of aniline (mol%)	Selectivity (%)
∞	13.1	67.9
14 : 1	29.4	81.6
8 : 1	28.9	82.0
4 : 1	46.0	80.2
2 : 1	42.7	80.6
1 : 1	51.0	77.5
1 : 2	54.1	71.0
1 : 4	51.7	66.9
1 : 8	62.8	64.0
1 : 14	50.3	58.6
0	21.4	64.5

Si-NH₂-Cu-Co, 0.20g (N/Metal molar ratio=4.76); aniline, 0.5ml; ethanol, 5.0ml; total pressure, 4.2 MPa (CO/O₂=5, at room temperature); 150 °C; 6.0h.

We also found that the temperature greatly influenced the conversion of aniline, product distribution and the selectivity of Si-NH₂-Cu-Co. The results were given in Table 3.

Table 3 The influence of reaction temperature on the conversion of aniline, product distribution and the selectivity of Si-NH₂-Cu-Co

Temperature (°C)	100	120	140	160	180	200
Conversion of aniline (mol%)	4.3	25.9	24.0	38.5	69.3	14.7
Yield of ethyl phenyl carbamate (mol%)	0.8	19.4	18.9	26.8	34.9	2.3
Yield of azobenzene (mol%)	3.5	6.5	3.9	4.5	7.4	0.0
Yield of other by-products (%)	0.0	0.0	1.2	7.2	27.0	12.4
Selectivity (%)	18.6	74.9	78.8	69.6	50.4	15.6

Si-NH₂-Cu-Co, 0.20g (N/Metal molar ratio=4.76, Cu/Co molar ratio=1); aniline, 0.5ml; ethanol, 5.0ml; total pressure, 4.2 MPa (CO/O₂=5, at room temperature); 6.0h.

The higher activity and selectivity of the catalyst were obtained in the range of 120 — 160 °C. At relatively lower temperature (100 °C), the main byproduct was azobenzene. But at relatively higher temperature (180–200 °C), the activity and selectivity of the catalyst decreased, and the main by-products were the other substances. The decrease of the activity and selectivity of the catalyst at higher temperature may be caused by structure change or decomposition of the catalyst.

Fig. 1 showed the relationship between the conversion of aniline and the reaction time. It could be seen that the conversion of aniline increased linearly with reaction time before 5 hours, namely, the reaction rate was not influenced by reaction time. But after 5 hours, the conversion amounted to over 90% and remained slight change with the reaction time.

The efficiency of the catalyst was studied and the results were shown in Fig.3. The turnover number increased with time, and up to 450 at 40 hours, after that then the reaction rate decreased to nearly one quarter of the initial reaction rate.

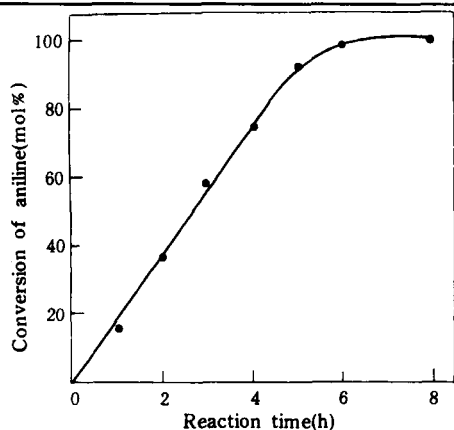


Fig. 1 Relationship between the conversion of aniline and the reaction time at 150 °C; aniline, 0.4ml; total pressure 6.0MPa ($\text{CO}/\text{O}_2=3$, at room temperature); for the others, the same as that of Table 3. selectivity is about 80%

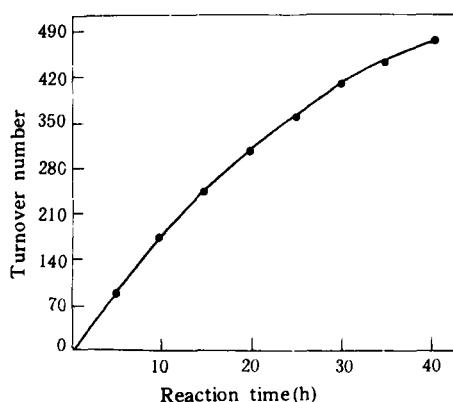


Fig. 2 Relationship between the turnover number and the reaction time
Aniline, 5.0ml; ethanol, 20.0ml; total pressure, 4.0MPa ($\text{CO}/\text{O}_2=3$, at room temperature); For the others, the same as that of Fig.1. Turnover number=Molar of aniline converted/Molar of metal in $\text{Si}-\text{NH}_2-\text{Cu}-\text{Co}$ used in the reaction system

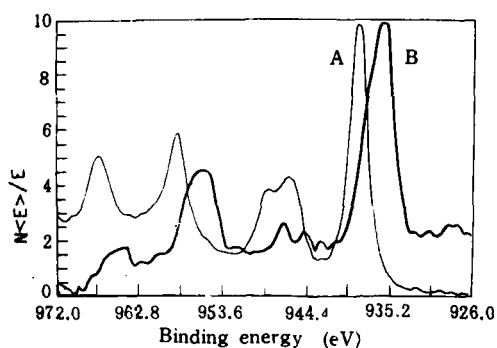


Fig. 3 XPS spectra of Cu_{2p} in CuCl_2 and $\text{Si}-\text{NH}_2-\text{Cu}$.
(A) Cu_{2p} in CuCl_2 ;
(B) Cu_{2p} in $\text{Si}-\text{NH}_2-\text{Cu}$;
 $\Delta C = C_{1s} - 284.6 = 4.1\text{eV}$

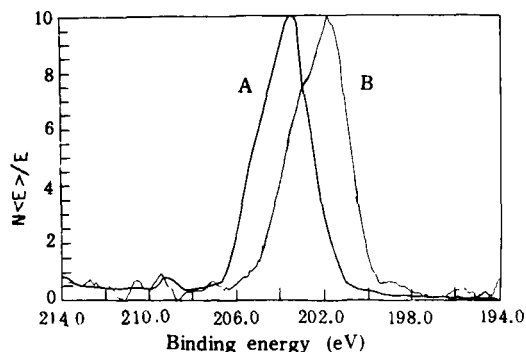


Fig. 4 XPS spectra of Cl_{2p} in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Si}-\text{NH}_2-\text{Co}$.
(A) Cl_{2p} in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$;
(B) Cl_{2p} in $\text{Si}-\text{NH}_2-\text{Co}$ $\Delta C = 4.6\text{eV}$

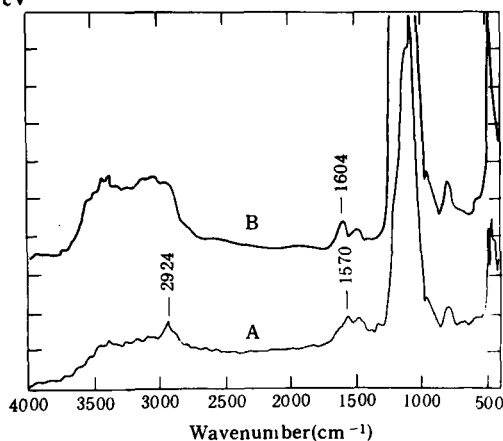


Fig. 5 IR spectra of $\text{Si}-\text{NH}_2$ and $\text{Si}-\text{NH}_2-\text{Co}$.
(A) $\text{Si}-\text{NH}_2$; (B) $\text{Si}-\text{NH}_2-\text{Co}$.

Study of structure of silica supported poly- γ -aminopropylsiloxane metal complexes

The structure of silica-supported poly- γ -aminopropylsiloxane metal complexes was investigated with XPS and IR. Table 4 showed the XPS data for Si-NH₂-Cu, Si-NH₂-Co and Si-NH₂-Cu-Co. It could be seen that the binding energy of nitrogen in the complexes was higher than that in Si-NH₂, and the binding energies of metals and chlorine on the complexes were lower than those in the corresponding metal chlorides.

Table 4 XPS data for Si-NH₂, Si-NH₂-Cu, Si-NH₂-Co, Si-NH₂-Cu-Co, CuCl₂ and CoCl₂·6H₂O

	Binding energy (eV)			
	N _{1s}	Cu _{2p3/2}	Co _{2p3/2}	Cl _{2p}
Si-NH ₂	399.0			
Si-NH ₂ -Cu	401.7	932.3		197.9
CuCl ₂		934.5		198.9
Si-NH ₂ -Cu-Co	401.5	932.1	780.6	198.0
CoCl ₂ ·6H ₂ O			781.6	198.8
Si-NH ₂ -Co	400.7		780.2	197.8

The XPS peaks of metals in the complexes became broader than those in the metal chlorides (Fig. 3), but the XPS peak of chlorine seemed to have no change (Fig. 4).

In IR (Fig. 5), the -NH₂ absorption bands at 1570cm⁻¹ in Si-NH₂ shifted to 1600-1620cm⁻¹ when the complexes formed.

All these results confirmed that coordination bonds were formed between metals and the nitrogen in the complexes, and the coordination pattern was not single.

Keywords:

Poly- γ -aminopropylsiloxane-Cu-Co complex catalyst; Aniline; Oxidative ethoxycarbonylation; Ethyl phenylcarbamate

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