

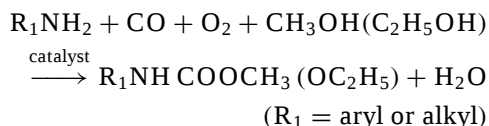
RESEARCH NOTE

A Novel $\text{PdCl}_2/\text{ZrO}_2\text{--SO}_4^{2-}$ Catalyst for Synthesis of Carbamates by Oxidative Carbonylation of AminesFeng Shi, Youquan Deng,¹ Tianlong SiMa, and Hongzhou Yang*State Key Laboratory for Oxo Synthesis and Selective Oxidation, Center for Ecological and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China*

Received September 7, 2000; revised June 11, 2001; accepted June 11, 2001

At 170°C and ca. 4.0 MPa, oxidative carbonylation of aromatic amines to synthesize corresponding carbamates over a novel $\text{PdCl}_2/\text{ZrO}_2\text{--SO}_4^{2-}$ catalyst could proceed with high conversion and selectivity. © 2001 Academic Press

Mono- and diisocyanates are very important intermediates in the manufacture of pesticides, polyurethane foam plastics, synthetic leather, adhesive, and coatings. They are currently manufactured by phosgenation of the corresponding amines, which has resulted in serious social and environmental problems. To avoid the use of poisonous phosgene, nonphosgene routes for producing isocyanates have attracted considerable interest in the last two decades (1, 2). In one of the approaches adopted, synthesis of carbamates occurs first, either by oxidative carbonylation of amines or by reductive carbonylation of nitro compounds in the presence of alcohol (3–11), and is followed by thermal decomposition of the carbamates to yield the corresponding isocyanates (12, 13). Although reductive carbonylation of nitro compounds should be a more attractive route for indirect production of isocyanates, catalyst deactivation due to the reduction of noble metal ions, e.g., Pd^{2+} to Pd^0 , under the strong reductive conditions may be difficult to overcome (14, 15). On the other hand, although amines have to be obtained through the hydrogenation of corresponding nitro compounds, such a problem can be avoided by oxidative carbonylation of the corresponding amines:



The catalysts employed for the above process reported previously were generally Co, Mn, Rh, Ru, and Pd, which

were coordinated with complicated N-containing or macrocyclic compounds, in the presence of a cocatalyst, such as iodide (9–11, 15). These catalyst systems are so complicated that they are hardly of practical use from an industrial viewpoint. In this work, a relatively simple catalyst system consisting of PdCl_2 and sulfated zirconia was developed for the synthesis of carbamates by oxidative carbonylation of amines. The experimental results indicate that this catalyst is particularly effective for the carbonylation of aromatic mono- and diamines to produce corresponding carbamates.

All chemical reagents used in this work were A.P. Under stirring, 25% $\text{NH}_3\text{--H}_2\text{O}$ solution was added dropwise into 12 ml 0.62 M zirconyl chloride solution until the pH reached 8–9. The resulting precipitate was filtered, washed several times with distilled water, dried at 120°C for 12 h, and then crushed and screened. The resulting zirconia oxide powder was further impregnated with 150 ml 1 M H_2SO_4 for 15 min, and then it was calcined in air at 500°C for 6 h. Solid PdCl_2 0.1 g and $\text{ZrO}_2\text{--SO}_4^{2-}$ 0.7 g were mixed together and ground with a small amount of water in an agate mortar. $\text{PdCl}_2/\text{ZrO}_2\text{--SO}_4^{2-}$ catalyst was obtained after the resulting slurry was dried in air at 120°C for 3 h. X-Ray photoelectron spectroscopy (XPS) analysis (VG ESC ALAB 210) showed that only S^{6+} was detected and the sulfate content on the catalyst surface was ca. 2 at. %. $\text{RuCl}_3/\text{ZrO}_2\text{--SO}_4^{2-}$ was also prepared with the same procedure used for $\text{PdCl}_2/\text{ZrO}_2\text{--SO}_4^{2-}$.

Oxidative carbonylation of aliphatic or aromatic amines was conducted in a stainless-steel autoclave with an 80-ml glass tube inside. For each reaction, 40 mg catalyst, 1 ml liquid substrate or 0.5 g solid substrate, and 20 ml methanol or ethanol as solvent were charged into the reactor. CO (99.99% purity, 3.0 MPa) and oxygen (99.99% purity, 1.0 MPa) were introduced into the reactor respectively at room temperature. Each reaction was typically allowed to proceed for 0.25–3 h at 170°C. At this temperature the initial total pressure of the reactor would approach ca. 6 MPa.

¹ To whom correspondence should be addressed.

TABLE 1
Synthesis of Carbamates by Oxidative Carbonylation of Amines

Entry	Subs.	Catalyst	<i>t</i> (h)	Solvent	Conversion		TOF ^a	Product	By-product (%)		
					(%)	(%)			Main	Other ^b	Other ^b
1	Aniline	PdCl ₂	1	EtOH	77	70	290			22	7
2	Aniline	PdCl ₂ /ZrO ₂ -SO ₄ ²⁻	1	MeOH	100	99	380			0.5	0.2
3	Aniline	PdCl ₂ /ZrO ₂ -SO ₄ ²⁻	1	EtOH	100	94	380			3	2
4	β -naphthylamine	PdCl ₂ /ZrO ₂ -SO ₄ ²⁻	0.25	EtOH	95.1	95	480			2	1
5	2,4-Diamine toluene	PdCl ₂ /ZrO ₂ -SO ₄ ²⁻	3	EtOH	100	85	50		—	11	(4)
6	<i>n</i> -Hexylamine	PdCl ₂	3	MeOH	100	3	93			74	13
7	<i>n</i> -Hexylamine	ZrO ₂ -SO ₄ ²⁻	3	MeOH	100	15.6	93		—	83	(1.4)
8	<i>n</i> -Butylamine	PdCl ₂ /ZrO ₂ -SO ₄ ²⁻	3	EtOH	100	80	115			15	3
9	<i>n</i> -Hexylamine	PdCl ₂ /ZrO ₂ -SO ₄ ²⁻	3	EtOH	100	81	93			1	8
10	<i>c</i> -Hexylamine	PdCl ₂ /ZrO ₂ -SO ₄ ²⁻	3	EtOH	95.1	65	98			24	9
11 ^c	<i>c</i> -Hexylamine	PdCl ₂ /ZrO ₂ -SO ₄ ²⁻	3	EtOH	90	32	88			25	21
12	1,6-Hexyl diamine	PdCl ₂ /ZrO ₂ -SO ₄ ²⁻	3	EtOH	100	<1	50		—	99	—
13 ^c	1,6-Hexyl diamine	PdCl ₂ /ZrO ₂ -SO ₄ ²⁻	5	EtOH	91.2	<1	45			44	40
14	Aniline	RuCl ₃ /ZrO ₂ -SO ₄ ²⁻	3	EtOH	85	83	320			8	5
15	<i>c</i> -Hexylamine	RuCl ₃ /ZrO ₂ -SO ₄ ²⁻	3	EtOH	95.1	35	98			40	20
16	1,6-hexylamine	RuCl ₃ /ZrO ₂ -SO ₄ ²⁻	3	EtOH	99	<1	50		—	99	—

^a mol substrate converted per mol Pd per h.
^b Unidentified species in brackets.
^c R = C₄H₉- or C₅H₁₁- or C₆H₁₃-.
^d R = C₃H₇- or C₄H₉-.
^e O₂/CO(Mpa) = 0.7/3.3.

When the reaction was complete, the reactor system was cooled to ambient temperature and the resulting liquid mixture was directly analyzed with a Hewlett–Packard 6890/5793 GC–MS instrument equipped with a HP-5MS column (30 m in length). The qualitative and quantitative data of the substrate and products were directly given by the system of GC/MS chemstation according to the area of each chromatographic peak.

The experimental results for the carbonylation of different aliphatic and aromatic amines are listed in Table 1. For aromatic amines, it can be seen that ZrO₂-SO₄²⁻ had a strong impact on both conversion and selectivity; e.g., 77% of aniline conversion and 70% of selectivity for the corresponding carbamate were obtained if PdCl₂ was used as catalyst only. The main by-products formed were 22% quinoline and 7% benzamide (entry 1, Table 1). The conversion and selectivity to the desired product could be much enhanced if PdCl₂/ZrO₂-SO₄²⁻ was used as catalyst (entries 2 and 3), and almost 100% conversion and 99% selectivity were achieved when methanol was used as solvent (entry 2). The corresponding turnover frequency (TOF) reached 380, which is much higher than that reported in previous literature (7). This may imply that there exists some kind of synergism between PdCl₂ and ZrO₂-SO₄²⁻ for the highly selective formation of corresponding carbamates. In comparison with ethanol, slightly higher selectivity for the desired product could be achieved when methanol was used as solvent; reaction results with better repeatability, however, were obtained with ethanol as solvent. When β -naphthylamine was oxidatively carbonylated, almost 100% conversion and 95% selectivity could be achieved as the reaction proceeded in only 15 min. It is noteworthy that reasonably high conversion and selectivity were achieved when the substrate used was 2,4-diaminetoluene, which is more difficult to carbonylate and is an important precursor for more useful toluene diisocyanate formation. The main by-product was monocarbamate (entry 5).

The oxidative carbonylation of aliphatic amines was also investigated under similar reaction conditions. They could be almost completely converted either in the presence of PdCl₂/ZrO₂-SO₄²⁻ catalyst or in the presence of PdCl₂ (entry 6) or ZrO₂-SO₄²⁻ (entry 7) as catalyst only. The selectivities for the desired products, however, were generally lower in comparison with the aromatic amines, and varied greatly with different aliphatic amines. For the aliphatic *n*-butyl-, *n*-hexyl-, and cyclohexylamine (entries 8, 9, and 10), the selectivities for the corresponding carbamates were 80, 81, and 65%, respectively. The main by-products during oxidative carbonylation were oxidized aliphatic amines, i.e., ethyl butyrate (15%), *N*-butylformamide (3%), *n*-butyric aldehyde (2%) for *n*-butyl amine; hexaldehyde (11%) and ethyl esters of C₄ to C₆ carboxylic acids (8%) for

n-hexylamine; and *N,N'*-dicyclohexylethane diamide (24%), cyclohexanone (9%), and ethyl esters of C₄ to C₆ carboxylic acids (2%) for cyclohexylamine. Under the same reaction conditions, the 1,6-hexyldiamine was almost completely oxidized to C₄ to C₆ aliphatic acid esters, probably because the aliphatic amines possess relatively strong reducibility and could be easily overoxidized. Therefore, oxidative carbonylation of cyclohexylamine (entry 11) and 1,6-hexyl diamine (entry 13) with lower oxygen concentration, i.e., the CO/O₂ pressure ratio = 3.3/0.7, was further conducted. The results showed that conversion decreased with decreasing oxygen concentration. The selectivity for the desired product was also decreased to 32% for cyclohexylamine, and the main products obtained were amide (monoamide 44%, diamide 40%) for 1,6-dihexylamine.

Under the same reaction conditions, RuCl₃/ZrO₂-SO₄²⁻ catalyst was investigated for the oxidative carbonylation of amines (entries 14–16). The experimental results indicate that the catalytic performance was less effective in comparison with PdCl₂/ZrO₂-SO₄²⁻ catalyst. The trend of conversion toward aromatic or aliphatic amines and the distribution of by-products obtained from RuCl₃/ZrO₂-SO₄²⁻ catalyst were also similar to those of the PdCl₂/ZrO₂-SO₄²⁻ catalyst system, suggesting that the mechanisms of oxidative carbonylation was similar on both catalysts.

From further analysis of the experimental results of entries 1, 2, and 6–8, it can be seen that ZrO₂-SO₄²⁻ possessed strong oxidizing capability and played an important role in further promoting the oxidation and esterification of carbonylated intermediates into corresponding carbamates during the reaction.

In summary, the synthesis of carbamates by oxidative carbonylation of amines over a PdCl₂(RuCl₃)/ZrO₂-SO₄²⁻ catalyst system can proceed with high conversion and selectivity, especially for aromatic amines. This catalyst system is relatively simple and can be further optimized. To our knowledge, it is the first time that such a catalyst system has been used for the oxidative carbonylation of amines. The role of ZrO₂-SO₄²⁻ and the synergism between homogeneous PdCl₂(RuCl₃) and heterogeneous ZrO₂-SO₄²⁻ is now under further investigation.

REFERENCES

1. Cenini, S., and Ragaini, F., "Catalytic Reductive Carbonylation of Organic Nitro Compounds," Kluwer Academic, Dordrecht, 1997.
2. Tafesh, A. M., and Weiguny, J., *Chem. Rev.* **96**, 2035 (1996).
3. Valli, V. L. K., and Alper, H., *J. Am. Chem. Soc.* **115**, 3778 (1993).
4. Mukherjee, D. K., Palit, B. K., and Saha, C. R., *J. Mol. Catal.* **91**, 19 (1994).
5. Wehman, P., Kamer, P. C. J., van Leeuwen, and Piet W. N. M., *J. Chem. Soc. Chem. Commun.* 217 (1996).

6. Islam, S. M., Mal, D., Palit, B. K., and Saha, C. R., *J. Mol. Catal.* **142**, 169 (1999).
7. Santi, R., Romano, A. M., Panella, F., Mestroni, G., Santi, A., and Sessanti O., *J. Mol. Catal.* **144**, 41 (1999).
8. Giannoccaro, P., Nobile, C. F., Mastrorilli, P., and Ravasio, N., *J. Organomet. Chem.* **419**, 251 (1991).
9. Kelkar, A. A., Kohle, D. S., Kanagasabhapathy, S., and Chaudhari, Raghunath V., *Eng. Chem. Res.* **31**, 172 (1992).
10. Leung, T. W., and Dombek, B. D., *J. Chem. Soc. Chem. Commun.* 205 (1992).
11. Valli, V. L. K., and Alper, H., *Organometallics*. **14**, 80 (1995).
12. Valli, V. L. K., and Alper, H., *J. Org. Chem.* **60**, 257 (1995).
13. Butler, D. C. D., and Alper, H., *Chem. Commun.* 2575 (1998).
14. Alessio, E., and Mestroni, G., *J. Mol. Catal.* **26**, 337 (1984).
15. Ugo, R., Psaro, R., Pizzotti, M., Nardi, P., Dossi, C., Andreetta, A., and Capparella, G., *J. Organomet. Chem.* **417**, 211 (1991).