

NOTE

SELECTIVE CONVERSION OF NITROBENZENE TO PHENYLCARBAMATES CATALYZED BY Pd(II) AND HETEROPOLYACIDS

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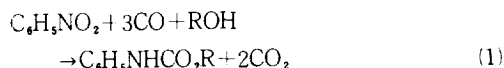
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Abstract—A homogeneous catalyst system of Pd(II) and a heteropolyacid (HPA) converts nitrobenzene to N-phenylcarbamate with a selectivity of 96.3% at 100% nitrobenzene conversion, which appears to be the best value known in the literature. However, the catalyst forms solid deposits during the reaction.

INTRODUCTION

Carbamates decompose thermally or catalytically to give organic isocyanates and alcohols in good yields [1]. Thus synthesis of N-phenylcarbamates by reductive carbonylation of nitrobenzene in the presence of an alcohol (Eq. 1) would also provide a phosgene-free route to methylene diphenyl isocyanate (MDI) which is an important raw material in the manufacture of polyurethanes.



Many catalyst systems have been reported to be efficient for the reaction. Recent examples include Ru or Rh carbonyls [2,3], Ru carbonyls promoted by a halide [4,5], and Pd complexes [6-9]. Among these, palladium halide-containing catalysts have received the greatest attention. The catalyst system comprises a Pd(II) salt and a Lewis acid which must contain metal components capable of undergoing redox reactions such as CuCl_2 , FeCl_3 , and FeOCl . The reaction appears to involve the Wacker-type redox reaction, because the catalysts have been present at several oxidation states, e.g., Pd^0 , Pd^{2+} , Fe^0 , Fe^{3+} , etc. in the reaction mixture during and after the reaction [10].

It has been shown that Pd(II)-heteropolyacid (HPA) system behaves similarly to the traditional Wacker system [11-13]. There is also a patent report that dichloro bis-pyridine-palladium in combination with $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ catalyzes the carbonylation of 2,4-dinitrotoluene to 2,4-toluene diisocyanate [14]. The purpose

of the present work is to apply Pd(II)-HPA system for the synthesis of N-phenylcabamate by reductive carbonylation of nitrobenzene. This catalyst system is expected to give a less corrosive reaction mixture compared to traditional Wacker system [11-13].

EXPERIMENTAL

A 50 cm³ high pressure stirred autoclave with Hastelloy-C wall was charged with 15 cm³ of solution containing 2.46 g (0.02 mol) of nitrobenzene (Fluka Chemie AG, 99.5%) and 0.886 g of t-butylbenzene (internal standard for gas chromatographic analysis) in methanol (Merck, 99.7%) and 1.52 mmol of a Pd salt and 0.137 mmol of HPA. Heteropolyacids were prepared according to the standard procedure and the structure of Keggin ions was confirmed by typical four infrared bands between 700 and 1200 cm⁻¹ [15]. All other chemicals were used as received. The gas phase in the vessel was replaced with carbon monoxide (Airco, 99.2%) and then pressurized to 100 bar at room temperature. The reactor contents were then heated to 160°C. After 6 h of the reaction, the reactor was cooled down and the liquid phase in the vessel was analyzed by a gas chromatography (HP-5890) equipped with a flame ionization detector and a 0.635 cm O.D. and 2 m long QF-1 column.

RESULTS AND DISCUSSION

Results for various catalyst systems are summarized in Table 1. In the most favorable case with PdCl_2

Table 1. Conversion of nitrobenzene by Pd(II)-HPA catalysts^a

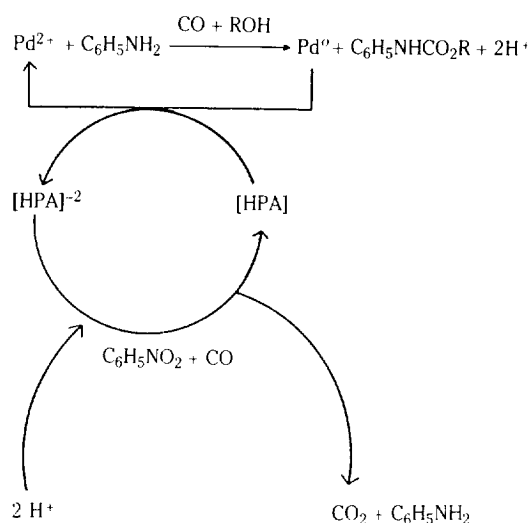
Entry	Pd salt	Co-catalyst	Nitrobenzene Conversion / %	Selectivity to N-phenylcarbamate / %
1a	PdCl ₂	H ₄ SiMo ₁₂ O ₄₀	100	96.3
1b	PdCl ₂	H ₄ SiW ₁₂ O ₄₀	15.1	36.3
1c	PdCl ₂	H ₃ PMo ₁₂ O ₄₀	88.3	90.3
1d	PdCl ₂	H ₃ PMo ₆ W ₆ O ₄₀	47.0	74.4
1e	PdCl ₂	H ₃ PW ₁₂ O ₄₀	12.2	20.9
2a	(CF ₃ COO) ₂ Pd	H ₄ SiMo ₁₂ O ₄₀	8.7	0.0
2b	(CH ₃ COO) ₂ Pd	H ₄ SiMo ₁₂ O ₄₀	4.3	0.0
2c	Pd(NO ₃) ₂	H ₄ SiMo ₁₂ O ₄₀	17.1	0.5
3a	PdCl ₂	FeCl ₃	99.9	77.1

^aSee text for conditions.

as a Pd(II) salt and H₄SiMo₁₂O₄₀ as a heteropolyacid, the conversion of nitrobenzene was 100% and the selectivity to methyl N-phenylcarbamate was 96.3% (1a). To the best of our knowledge, this selectivity at 100% nitrobenzene conversion is the best value known in the literature. N,N-dimethylaniline and aniline were major by-products detected. Palladium salts other than PdCl₂ were much less effective (2a-c). Heteropolyacids with Mo as peripheral atoms were much more effective than with W (1a-e). A good trend is shown (1c-e) in both activity and selectivity; H₃PMo₁₂O₄₀ > H₃PMo₆P₆O₄₀ > H₃PW₁₂O₄₀. This may reflect the fact that the molybdates are much stronger oxidizing agents than the tungstates [16]. The effect of heteroatom was less pronounced (1a and 1c) although silicon HPA appears to show slightly better performance than its phosphorus analog. Results with FeCl₃ instead of HPA are also shown for comparison (3a).

In all the experiments listed in Table 1, solid deposits were observed after the reaction. The amount of deposits was greater for the batches with higher nitrobenzene conversions. In the case of 1a, the weight of deposits collected after reaction was close to the weight of the Pd salt and HPA initially charged into the reaction. Also, only traces of Pd and Mo were found in the filtrate of reaction mixture by an elemental analysis. Hence it appears that most of the catalyst initially forming homogeneous solution with reactants have resulted in solid deposits.

Considering the amount of solid deposits formed at the end of the reaction, there could be a question if the catalysts has turned over before forming solid deposits. From the feed composition, we can calculate, for the case of 1a, that Pd and HPA have turned over more than 13 and 146 times, respectively, on the average. Thus the reaction is certainly catalytic.

**Fig. 1. Proposed catalytic cycle of alkoxycarbonylation of nitrobenzene in the presence of Pd(II)-heteropolyacid catalyst.**[HPA]⁻² denotes a reduced form of heteropolyacid.

The solid deposits showed little catalytic activity when charged into the reactor with a new batch of reactants. To find if this is because Pd is in Pd⁰ oxidation state, 10% Pd/C (Alfa) and H₄SiMo₁₂O₄₀ were tested for the reaction. Little activity was found. Addition to the fresh reaction mixtures of 1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline or pyridine which are known to prevent the formation of Pd⁰ by strong ligation [8] did not improve the situation significantly.

A possible catalytic cycle involved in the present system is proposed in Figure 1. Aniline is assumed to be a stable reaction intermediate [1,2]. It is known that

palladium must be in the Pd^{2+} oxidation state to catalyze the production of carbamates from nitrobenzene. However, during the reaction Pd^{2+} is converted to the inactive Pd^0 oxidation state. Since the reoxidation of Pd^0 to Pd^{2+} is a slow process, Lewis acids or heteropolyacids in the present case should be used as promoters. During this reoxidation step, HPA itself is reduced and in order to complete the catalytic cycle, this reduced HPA, in turn, should be reoxidized by nitrobenzene. Unfortunately, it appears that this reoxidation by nitrobenzene is not fast enough to sustain the catalytic cycle very long. The breakage of the catalytic cycle would yield Pd^0 and reduced HPA, both of which are inactive for the reaction.

The high yield of the carbamate with Pd(II)-HPA catalyst system is interesting. However, a method has to be found to avoid solid deposits before practical applications of the catalyst system is considered. The key to the method should be the improvement in the reoxidation rate of reduced HPA and Pd^0 .

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