Oxidative carbonylation of aniline over Pd-ZSM-5 catalyst ☆

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The oxidative carbonylation of aniline over Pd-ZSM-5 is reported. Pd-ZSM-5 catalyst is found to offer significant advantage with respect to CO_2 formation. The average activity of Pd-ZSM-5 catalyst was found to be about 80 times higher compared to soluble metal complex catalysts.

Keywords: carbonylation; oxidative carbonylation; catalysis; Pd-ZSM-5 catalyst; aniline

1. Introduction

Oxidative carbonylation of amines using homogeneous and heterogeneous catalysts has been studied extensively [1–6]. Recently Gupte et al. [6] reported a detailed investigation on the product distribution, selectivity and catalyst pretreatment effects in the oxidative carbonylation of aniline using supported Pd catalyst. At higher temperature ($>150°C$), a high selectivity of alkyl-N-phenyl carbamate is achieved based on aniline [6], but under these conditions the selectivity based on carbon monoxide consumed is significantly lower due to simultaneous formation of CO_2 by carbon monoxide oxidation. This important problem has not been addressed in any of the previous studies. In this note we wish to report a Pd-ZSM-5 catalyst which is highly active and selective based on both aniline and CO consumed.

2. Experimental

The support, ZSM-5 was prepared according to published procedures [7]. The chemical composition of fully crystalline ZSM-5 sample estimated by chemical

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analysis, atomic absorption and flame photometry was SiO_2/Al_2O_3 (oxide mole ratio) = 46.7 and Na_2O = 0.78 wt%. Pd-ZSM-5 was prepared by impregnating H-ZSM-5 with $PdCl_2$ solution and calcination in air at 773 K. The catalytic experiments were carried out in a 300 cm^3 capacity high pressure stirred autoclave (Hastelloy C) supplied by Parr Instrument Co USA. In a typical experiment, known quantities of aniline (32.25 mmol), catalyst (0.1 g of 1% Pd on ZSM-5), NaI (0.46 mmol) and methanol (97 cm^3) were charged into the autoclave. The autoclave was pressurized to 54 bar with CO : O_2 (16 : 1) at 443 K. The pressure was maintained by supplying CO : O_2 in a stoichiometric proportion (2 : 1). The products were analyzed by GC.

3. Results and discussion

The aim of this paper is to present results on the oxidative carbonylation of aniline using Pd and Ru catalysts with respect to the activity and selectivity behaviour. It is well known that oxidative carbonylation of amine to carbamate proceeds through urea derivative as an intermediate [6]. Similarly, oxidative carbonylation of aniline proceeds through the formation of N,N′-diphenyl urea (DPU) to produce N-phenyl methyl carbamate (PMC):

$$2C_6H_5NH_2 + CO + \tfrac{1}{2}O_2 \rightarrow \underset{\text{N, N′-diphenyl urea (DPU)}}{C_6H_5NHCONHC_6H_5} + H_2O\,, \qquad \text{(I)}$$

$$C_6H_5NHCONHC_6H_5 + MeOH \rightarrow \underset{\text{N-phenyl methyl carbamate (PMC)}}{C_6H_5NHCOOMe} + C_6H_5NH_2\,. \qquad \text{(II)}$$

The results showing a comparison of the performance of different catalysts are also presented in table 1. The activities of the catalysts were measured in terms of moles of aniline consumed per gram of metal per hour. For a given set of conditions, Pd-ZSM-5 catalyst was found to be the most active for oxidative carbonylation of aniline to PMC. For example, the average activity for Pd-ZSM-5 obtained is 16.1, for Pd/C 5.8 and for Pd metal it is 0.52 (table 1). The reaction did not take place in the absence of either the catalyst or the promoter.

The relative proportions of PMC and DPU are found to vary for different catalysts and these will depend on the kinetics of reactions (I) and (II). For PdI_2 as a catalyst the selectivity of PMC is higher than that for Pd metal catalyst even though the conversion in the former case is lower. In order to explain these results, detailed investigation on the effect of catalysts on reaction (II) will be necessary.

Another significant observation was that CO_2 formation with Pd-ZSM-5 catalyst was negligible with a selectivity for PMC about 98% based on CO consumed. In contrast, with Pd/C and Pd metal catalysts, as well as with homogeneous Ru metal catalysts, selectivities of PMC and DPU are very low based on CO consumed due to significant amount of CO_2 formation (table 1). To ensure the reusability of the Pd-ZSM-5 catalyst after the reaction, the catalyst was recovered by filtration and

Table 1
Results on oxidative carbonylation of aniline over different catalysts [a]

Run No.	Catalyst [b]	Temp. (K)	Conv. aniline (%)	Activity [c]	Selectivity (%)			
					based on aniline		based on CO	
					PMC	DPU	PMC & DPU	CO_2
1	1% Pd-ZSM-5	443	99.4	16.1	98.2	–	98.2	1.8
2	1% Pd-ZSM-5	423	35.9	5.8	72.5	27.2	98.3	1.6
3	1% Pd-ZSM-5	373	8.6	1.4	–	95.2	100.0	0.0
4	1% Pd/C	443	35.7	5.8	76.7	17.5	24.2	74.8
5	1% Pd/γ-Al_2O_3	443	57.8	9.3	74.3	17.5	23.6	75.3
6	PdI_2	443	58.3	0.38	97.2	1.3	25.7	74.1
7	Pd metal	443	80.0	0.52	76.7	22.6	26.5	72.8
8	$Pd(py)_2Cl_2$	443	22.1	0.14	41.8	56.9	33.4	65.8
9	$[Ru(CO)_3I_3]$ 18 crown 6 ether	443	49.6	0.34	76.8	19.8	22.2	77.5
10	$RuCl_2(PPh_3)_3$	443	31.8	0.21	58.7	38.7	36.6	63.2
11	$RuCl_2(py)_2(CO)_2$	443	42.9	0.29	61.4	38.5	28.4	70.4
12	cis-$Ru(CO)_2Cl_2(PPh_3)_3$	443	35.6	0.24	38.8	59.3	25.8	74.8

[a] Reaction condition: aniline (32.25 mmol), NaI (0.46 mmol), methanol (97 cm^3), $CO : O_2 = 16 : 1$, 54 bar, reaction time 2 h.

[b] Catalyst (9.4×10^{-6} mol of Pd equivalent for runs Nos. 1–5 and 2.36×10^{-4} mol Pd or Ru for runs Nos. 6–12).

[c] The activity defined as mol of aniline racted per gram of metal per hour.

reused after calcination at 800 K in air. There was no loss in the activity of the reused catalyst for five successive runs for Pd-ZSM-5 catalyst. As expected, at lower temperature (373 K), N,N-diphenyl urea is formed, whereas, at higher temperatures (443 K) N-phenyl methyl carbamate (>98%) is produced (table 1). The enhanced activity for the conversion of aniline to carbamate over Pd-ZSM-5 could be due to a better dispersion of Pd on the crystalline ZSM-5 support. The mechanism for the oxidative carbonylation of aniline over Pd-ZSM-5 is probably similar to that reported in the case of Pd supported on silica [4] or carbon [6].

4. Conclusions

The oxidative carbonylation of aniline over Pd-ZSM-5 catalysts is found to be significantly advantageous over soluble metal complex catalysts with respect to CO_2 formation and average activity.

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