

The Selective Reduction of 4-Propylthio-2-nitroaniline with CO Using $\text{Ru}_3(\text{CO})_{12}$ /PEDPA Complex as Catalyst

Jing Yang JIANG, Qiang MIAO, Yan Hua WANG, Zi Lin JIN*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012

Abstract: The $\text{Ru}_3(\text{CO})_{12}$ /PEDPA complex was firstly applied in the CO selective reduction of 4-propylthio-2-nitroaniline. The effects of reaction temperature, the pressure of CO and concentration of catalyst on the reduction were investigated. Under the optimum conditions of $T=140^\circ\text{C}$, $P_{\text{CO}}=5.0\text{MPa}$ and substrate/catalyst = 300 (molar ratio), the conversion and selectivity were 70% and 98%, respectively. After simple phase separation, the catalyst could be recycled.

Keywords: CO selective reduction, 4-propylthio-2-nitroaniline, $\text{Ru}_3(\text{CO})_{12}$, phosphine.

4-Propylthiobenzene-1,2-diamine, the reduction product of 4-propylthio-2-nitroaniline (abbreviated as PTNA) is an important intermediate of albendazole, a widely used efficient anthelmintic. Using the normal catalytic hydrogenation to reduce nitro group always makes the propylthio group destroyed. Especially, when Ni catalyst was employed, the propylthio group can make the catalyst poisoned^{1,2}. In the past ten years, Helya *et al*³ proposed to use hydrated hydrazine reduction to produce 4-propyl thiobenzene-1,2-diamine with FeCl_3 supported on active carbon as catalyst. Later on, Josie *et al*⁴ provided a biochemical reduction approach. However, the industrial application possibility of the two methods mentioned above was limited due to the easy combustion and explosion of hydrazine and the lower efficiency of biochemical reduction. Therefore, at present the industrial production of 4-propylthiobenzene -1,2-diamine had to be proceeded using more environmentally pollutant sodium sulfide as reducing agent.

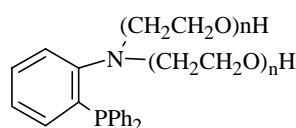
With transition metal complex as catalyst, the CO selective reduction of aryl nitro compounds to yield aryl amine dated back to the late of 1970s⁵. High selectivity has been observed. Moreover, CO can only reduce the nitro group to amino group and has no effect on carbonyl, double bond, CN group and halide substituent, which are sensitive to hydrogenation. Nomura reported that CO selective reduction of aryl nitro compounds have shown better catalytic activity and selectivity when $\text{Ru}_3(\text{CO})_{12}$ and $\text{HN}(i\text{-Pr})_2$ or HNET_2 complex was employed as catalyst in water/ethanol⁶.

The aqueous/organic biphasic reduction of nitrobenzene under the thermoregulated phase transfer catalytic system has been reported by Zilin Jin^{7,8}. In

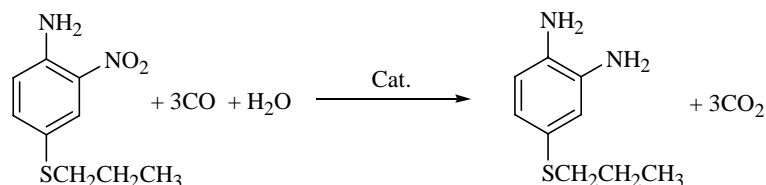
* E-mail: jingyan@mail.dlptt.ln.cn; jyjiang@chem.dlut.edu.cn

this paper, the complex formed from $\text{Ru}_3(\text{CO})_{12}$ and P, N-containing bidentate phosphine ligand PEDPA was firstly applied in the CO reduction of PTNA. The catalytic activity, selectivity and recycling efficiency of catalyst were also investigated.

Structure of PEDPA



The CO selective reduction of 4-propylthio-2-nitroaniline proceeded as follows:



The effects of temperature, pressure of CO and concentration of catalyst on the reduction were listed in **Table 1**. The conversion of the substrate increased with the increase of reaction temperature. With the increase of the CO pressure applied, the reaction conversion also increased. The reaction selectivity was not affected by reaction temperature and CO pressure. The optimum reaction conditions are selected as follows: $t=140^\circ\text{C}$, substrate/catalyst=300:1 (molar ratio), $P_{\text{CO}}=5.0$ MPa, solvent: toluene/water, $t=12$ h. Under the above-mentioned conditions, the conversion and selectivity are 70% and 98%, respectively.

Table 1 Effects of temperature, pressure of CO and concentration of catalyst on the CO reduction

Run	Temperature ($^\circ\text{C}$)	Pressure of CO (MPa)	Substrate/Catalyst (molar ratio)	Conversion (%)	Selectivity (%)
1	160	5.0	300	77	98
2	140	5.0	300	70	98
3	120	5.0	300	39	97
4	100	5.0	300	17	98
5	140	6.0	300	73	98
6	140	4.0	300	45	97
7	140	3.0	300	21	97
8	140	5.0	1500	10	98
9	140	5.0	900	28	97
10	140	5.0	600	53	97
11	140	5.0	100	75	97

Reaction conditions: PTNA: 0.048 mol, solvent: toluene/water = 20/20 (mL), ligand/catalyst: 5, $t=12$ h. The other conditions are indicated in **Table 1**.

In addition, the recycling efficiency of catalyst was presented in **Table 2**. The results showed that the catalyst could be recycled without any decreasing in selectivity,

but the reaction conversion decreased from 70% to 60% after three runs of reaction. The reason for this is probably due to loss of the catalyst in the organic phase. Because the polar product would cause the increase of the catalyst solubility in organic phase, which was separated off after reaction, the actual amount of catalyst in the reaction system decreased on recycling.

Table 2 The recycling efficiency of catalyst

Using times	Conversion (%)	Selectivity (%)
1	70	98
2	65	99
3	60	98

Reaction conditions: PTNA: 0.048 mol, T=140°C, P_{CO}=5.0 MPa, substrate/catalyst=300(molar ratio), t=12 h., solvent: toluene/water = 20/20 (mL), ligand/catalyst=5

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