

Synthesis of *p*-Anisidine by Hydrogenation with Raney-RuNiC as Catalyst

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Abstract: A new catalyst named Raney-RuNiC containing 20wt% ruthenium was used for liquid phase hydrogenation of *p*-nitroanisole to prepare *p*-anisidine. Effect of temperature, pressure and life time of the catalyst were studied. Reaction kinetics was also investigated. The catalyst was highly active under the conditions of 1.0Mpa and 100 . The catalyst was repeatedly used for 36 times in autoclave with constant activity, showing excellent stability and good potential for future commercial application.

Keywords: Raney-RuNiC; *p*-Anisidine; Hydrogenation; Ruthenium

1. Introduction

p-Anisidine is colorless crystal with melting point of 57.2 and boiling point of 243 . It is an important intermediate for synthesis of dye, medicine and perfume. Traditional preparation of *p*-Anisidine uses iron powder or sodium sulfide as reductant[1-3], which produces a large amount of waste and results in serious environment pollution problem[4]. Liquid phase catalytic hydrogenation is not only an environmentally benign technique but also of high yield. Thus, substituting the chemical reduction with catalytic hydrogenation has been attracting the worldwide interests.

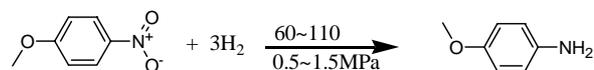
So far, there have been a few reports in literature on preparation of *p*-anisidine by liquid phase hydrogenation. ZHANG Wen-nan[5] synthesized the product at 140 under 4.0MPa with 35% H₂ in N₂ as reductant, but no catalyst information was mentioned in this paper. ZHANG Jian-hua[6] used Raney-Ni as catalyst for the reaction under the conditions of 115 ~ 130 and 1.0MPa ~ 1.2Mpa. The catalyst is low-cost, but the reactant was not completely converted, the reaction time was long(more than 7h), and life time of the catalyst was short.

Therefore, it is urgent to develop suitable catalyst for the reaction. Recently, we have patented a new hydrogenation catalyst, Raney-RuNiC containing 20wt% Ru[7], which was proved to be a good catalyst for the hydrogenation of *p*-nitroanisole to selectively produce *p*-anisidine.

2. Experimental

2.1 Reaction Principle

Raw material *p*-nitroanisole was hydrogenated in liquid phase with Raney-RuNiC as catalyst. The reaction equation is as follows.



2.2 Reagents and instruments

The reaction mixture was analyzed by Shimadzu GC-8A, FID, HP-5 capillary column(30 m ×0.25mm). A stainless steel autoclave(70mL) was used as reactor. Raw material *p*-Nitroanisole and solvent THF were analytically pure. The purity of H₂ was 99.99%.

2.3 Reaction procedure and analysis

All experiments were carried out in the autoclave stirring with magnetic bar, the solvent

was THF, and the temperature maintained at desired value with a derivation of ± 1 . Once the temperature reached at setting value, H_2 pressure inside the autoclave was manipulated to the desired value. The reaction started when agitation started. The reaction was quenched at suitable time by using cooling water bath. Then the reaction mixture was sampled and analyzed by GC after separation from catalyst.

3. Results and Discussion

3.1 Life time of the catalyst

During the first 2 hours, activity of the catalyst was very active, and then gradually changed to constant. According to our investigation, we have totally tested the activity for 62 hours and did not observed any loss of activity. That is to say, life time of the catalyst was more than 62 hours. To study activity change during the first 14 hours, we used 0.65g newly prepared catalyst. When the experiment was over, the catalyst was filtered off and used repeatedly. Fig.1 shows the activity change during the process. To study activity change during mature period, we used 0.65g catalyst in mature period. Its activity was stable during 36 times batch reactions.

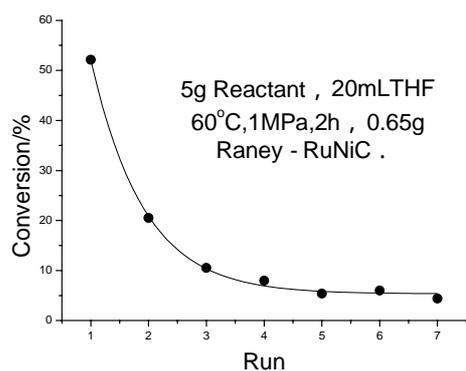


Fig.1 Activity change of the catalyst during the first 14 hours. Horizontal axis: Batch reaction times.

3.2 Effect of temperature on reaction

Table 1 shows effect of temperature on conversion and selectivity. It is obvious that the

reaction rate increased as the increasing of temperature, but the selectivity of desired product decreased a bit. The selectivity was above 98% at 110 and 100% at 70 or lower. The main byproduct of the reaction was (4-methoxycyclohexyl)amine as determined by GC-MS.

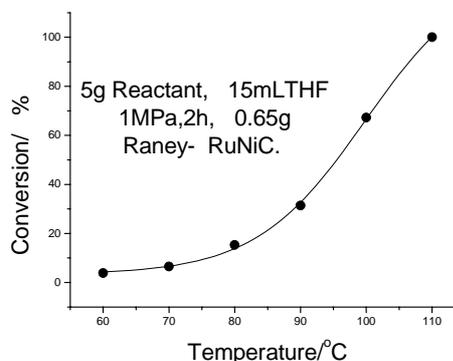


Fig.2 Effect of temperature on conversion

Fig.2 shows effect of temperature on reaction rate. The reaction rate increased sharply as the temperature increased. So the reaction was sensitive to temperature at below 110.

3.3 Effect of pressure on reaction

Fig.3 shows effect of pressure on reaction. The main effect of pressure was on reaction rate. The reaction rate increased obviously as the pressure increased under 1MPa. But when the pressure is above 1.3MPa, the effect of pressure on reaction rate is unobvious.

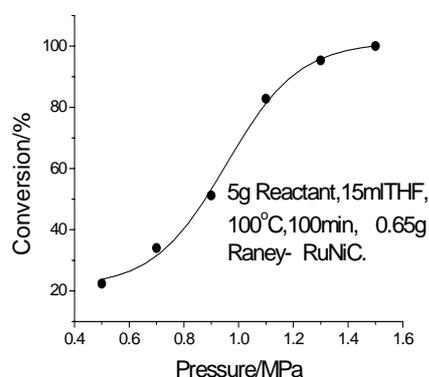


Fig.3 Effect of pressure on conversion

3.4 Order of the reaction

The order of the reaction was studied when temperature, solvent, catalyst and pressure were fixed. When the concentration of reactant was low (under 1.72mol/L), the relation between time and concentration of product was near linear (Fig.4), so the order of the reaction was near zero when the concentration of reactant was low.

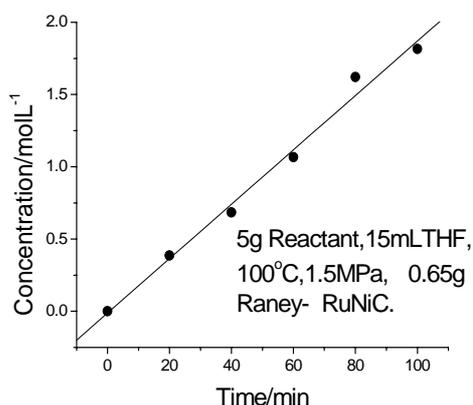


Fig.4 Effect of reaction time on concentration of product

3.5 Mass spectrum of product

Mass spectrum (Fig.5) of desired product was got by GC-MS. The product was assured by comparing Fig.5 with its standard mass spectrum.

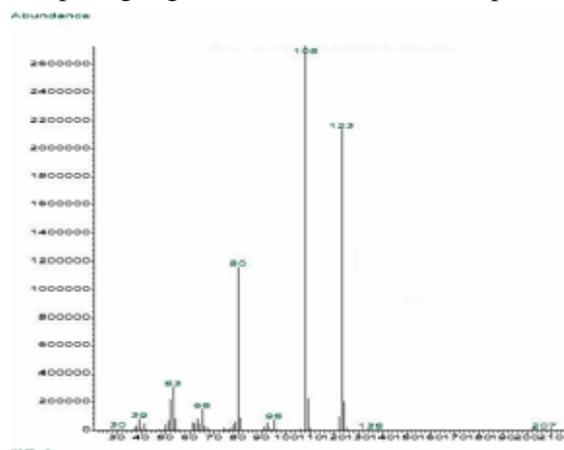


Fig. 5 Mass spectrum of *p*-anisidine

Table 1 Effect of temperature on selectivity

T/	60	70	80	90	100	110
Conv. %	3.8	6.5	15.3	31.4	67.2	100
Sel. %	100	100	99.5	99.2	99.1	98.1

Reaction conditions : 0.65g Raney-RuNiC , 5g *p*-Nitroanisole , 15mLTHF , 1MPa , 2h.

4 Conclusions

Raney-RuNiC was active and stable catalyst in the reduction of nitro of *p*-nitroanisole. The reaction was sensitive to temperature and pressure. The most suitable reaction conditions were 1.5MPa and 100 . The selectivity was above 99.0% under the conditions. So the reaction have bright prospect of industrialization.

References

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