Selective Reduction of 5-Nitro-2-Chloro-2',4'-Dimethylbenzene Sulfonanilide on Pd-Ru/γ-Al_2O_3 Catalysts in Ionic Liquids

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Abstract

The use of ionic liquids as reaction medium for hydrogenation of 5-nitro-2-chloro-n-(2',4'-dimethyl)benze-nesulonamid(NCD) to 5-amino-2-chloro-n-(2',4'-dimethyl) benzenesulfonamid (ACD) has enabled us to obtain high selectivity on Pd-Ru/γ-Al_2O_3 catalysts at 338 K under 0.35 MPa of hydrogen pressure. The selectivity for the hydrogenation of ACD in [EPy]Br or [BPy]Br was proved to be close to 100%. Additionally, the ionic liquids and molar ratio of Pd to Ru appeared to have a deepgoing influence on the selectivity of catalysts and at the highest-selectivity point, the molar ratio of Pd to Ru was 1:1 for hydrogenation of NCD in [XPy]Br.

Keywords: Chloronitrobenzene hydrogenation, Ionic liquids, Pd-Ru/γ-Al_2O_3

1. Introduction

ACD is one of the most important chemical intermediates in dyestuff, pharmaceuticals, fluorescent pigments, and synthetic pesticides etc(Xiong,Jun,2006,p.331-335). At present, a variety of methods are used for the synthesis of ACD through the reduction of NCD, in which iron powder, sulphur alkalies and hydration hydrazine are normally used as reduction agents(Xiong,Jun,2006,p.331-335). However, these methods have some drawbacks such as complex production route, many side products and poor product quality. Recently, there is a significant interest in performing the catalytic hydrogenation reaction of chloronitrobenzene in organic reaction medium, such as methanol, ethanol, DMF etc(Guo,Fang,2007,p.252-256). But ACD and NCD have lesser solubility in organic reaction medium, such as methanol, ethanol as the result that the solubility can't meet the demand of high-efficiency reaction. Besides, the characteristics of ionic liquids including high thermal stability, low vapour pressure and excellent solubility of organic compounds make them very attractive as reaction media for the synthesis of organic compound(Michal, Roth,2009, p.1861-1880). To the best of our knowledge, there have been no reports on the catalytic hydrogenation of NCD in ionic liquids which are regarded as environment benign solvents(P. J. Dyson,2002,p. 353-358). In this work, the catalytic hydrogenation of NCD was performed in [BPy]Br etc and the selectivity was nearly 100% at 338 K under 0.35 MPa with 100% conversion of NCD. Moreover, it was found that ACD can be effectively separated from the reaction mixture of ionic liquids by using H_2O extraction.

2. Experimental

2.1 Ioni Liquids Preparation

The pyridines ionic liquids have been synthesized in ultrasonic bath. Bromide n-butane pyridinium ([BPy]Br) was obtained by adding pyridine into 1-X-n-butane (1:1.4, mol/mol) in flask with the reflux device and the mixture was ultrasonically kept for 6 hours at 333K to obtain a crude product. The crude product was evaporated in a spinning evaporater at 358K and finally obtained white solid [BPy]Br. Then, $NaBF_4$ was added to the [BPy]Br/H_2O (1.2:1, mol/mol)mixture in flask with a reflux device and then was ultrasonically held for 4 hours at 333K. Lastly, it was cooled and filtered to remove the solid and obtain filtrate. The filtrate was evaporated in spinning evaporater at 358K to obtained yellow liquid [BPy]BF_4. The similar synthetic route was also applied for the synthesis of [EPy]BF_4, [BPy]$HSO_4$and [EPy]HSO_4.

2.2 Catalysts Preparation

The Pd-Ru /γ-Al_2O_3 catalysts were prepared by the deposition precipitation, in which the Al_2O_3 was mixed with an aqueous solution of 0.032 M palladium chloride ($PdCl_2 \cdot 4H_2O$) and ruthenium trichloride ($RuCl_3$)Chuang, Wang,2008,p.1749-1753). Then it was followed by drying at 110℃ for 12 h, calcined at 400℃ for 4 h and reduced in a flowing H_2 at 450℃ for 12h. The other Al_2O_3-supported metal catalysts in this paper were also prepared using the same procedure mentioned above (E.L.Margelefsky,2008,p.13442-13449).

2.3 Hydrogenation Experiments

The hydrogenation experiments were carried out in a 50mL stainless steel autoclave equipped with a magnetic stirrer. The NCD, ionic liquids solvent and catalyst were quantitatively added to the reactor (H. Li,2009,doi:10.1016/j.molcata.2009.03.015). Then after being sealed, the autoclave was purged for six times with 1 MPa N_2 and H_2 in sequence. After the reaction temperature was increased to the set point and the H_2 pressure was adjusted to desired value, the reaction was started (Haowen, Ma,2009, doi:10.1016/j.catcom.20

09.01.028).

2.4 Purification of ACD

It is very important to separate ACD from the final mixture in order to obtain the purified product. It was found that ACD with purity of 99% can be achieved experimentally by using the salting-out phenomenon and inducing phase separation.Then, the sediment was filtered, dried and characterized. By LC-MS, NMR as well as melting point tester, the selectivity of ACD and conversion of NCD were tested out. At the same time, the water was evaporated from filter liquor by rotary evaporator at 358K, and the ionic liquids were reclaimed for recycle use (H. Li,2008, p.3936-3943).

3. Results and Discussion

3.1 Comparison of Different Reaction Medium

Selective hydrogenation of NCD to ACD was carried out in a steel autoclave at 338K for 2h under 0.35MPa of hydrogen pressure and autoclave was loaded with 30 mL different reaction solution of 0.1 M NCD. The reaction route involved in hydrogenation of NCD is shown as Figure1.

With a variety of reaction mediums (e.g. CH_3OH, CH_3CH_2OH, DMF, THF and [BPy] Br), hydrogenation reaction of NCD to ACD were examined in a steel autoclave and summarized in Table 1.

As shown in Table 1, different fractional conversion and selectivity for hydrogenation of NCD to ACD were studied and the highest selectivity was realized in [Bpy]Br. It was essential that the ionic liquid needed to thoroughly take part in the hydrogenation reaction and the deepgoing research was still wanted for these reaction systems.

3.2 Comparison of different ionic liquids

Several ionic liquids were prepared in our laboratory and tested for the hydrogenation of NCD. Typical results were summarized in Table 2.

It was proved that [BPy]Br, [EPy]Br, [BPy]Cl, [BPy]BF_4,[EPy]Cl as well as [EPy]BF_4 can achieve 100% conversion of NCD and more than 90% selectivity of ACD as shown in table 2. Obviously, every ionic liquid in table 2 has shown that the ionic liquids are good reaction mediums and can bring considerably higher conversion and selectivity. Thus, we focus our attention on applying ionic liquids as reaction medium. Comparing the results in Table 2, it clearly shows the advantages of the hydrogenation reaction in [BPy]Br or [EPy]Br. The role of solvents in catalytic processes is still unclear. However, the polarity of the reaction medium in selective hydrogenations is thought to be influential. Comparing [BPy]Br with [BPy]Cl, [BPy]Br was polarized conveniently by chlorine atom of NCD so that the interaction like hydrogen bonding was produced between [BPy]Br and Cl of NCD. The dehalogenating reaction in hydrogenation was reduced or eliminated so that the selectivity of this hydrogenation was enhanced and actually the coordination bond of Pd···Cl was built to weaken of C-Cl in dechlorination.

3.3 Comparison of different catalysts

In Table 1, it was found that the conversion of NCD was desirable to use CH_3OH, CH_3CH_2OH, DMF and THF as reaction medium, while the selectivity was poor, in which NCD had been seriously dechlorinated in the process of catalytic hydrogenation. Up to date, it remains a challenge to overcome dechlorination problem. A number of factors have been shown to affect the selectivity of ACD in the hydrogenation of NCD, such as catalyst (active metal , second metal , metal particles size), support, additives (promoter, inhibitor and poison) and reaction condition (reaction medium, temperature and pressure). Although the selectivity can be improved by modifying these factors, the dechlorination can not be completely avoided in organic reaction medium. However the dechlorination was completely overcame in some ionic liquids, especially in [Bpy]Br. In Table 2, it shows that the ionic liquids is a better reaction medium than some other organic reaction mediums. Therefore screening catalysts was carried on in this paper.

As was known to all, Ni, Pd, Ru metal etc have the capability of catalyzing hydrogenation because of the empty

orbit of transition metal with p-electron or π-electron pair of ligand favorable for the formation of coordinated metal complex. As a result, several hydrogenation catalysts were prepared in our laboratory and applied in the hydrogenation of NCD. Finally typical results were summarized in Table 3.

As shown in Table 3, the most outstanding catalysts were Pd/γ-Al_2O_3 and Pd-Ru/γ-Al_2O_3 for the hydrogenation. However, the cost of Pd/γ-Al_2O_3 catalyst was much more expensive than Pd-Ru/γ-Al_2O_3.

3.4 Recycle of [BPy]Br

In Table 3, the recycled times of [BPy]Br from 1 to 8 were investigated to test the reusability of ionic liquids. When the recycled times was increased to be as high as 7, the nature of [BPy]Br maybe has changed and consequently the conversion of NCD markedly decreased. Besides, other ionic liquids we had examined also have the same results. Thus, it can be concluded that ionic liquids were recyclable solvents in the hydrogenation of NCD.

3.5 Characterization

The products were quantitatively analyzed by melting point tester (X-6, Beijing Taike). The details were shown as mentioned below: mp 146-148℃. The molecular weights of products were characterized by LC-MS (1100LC/MSD Trap SL, Agilent Co.) as shown in Figure 2.

As shown in Figure 2, it was the spectrum of the molecular ion for m/z :309(M^+) in Figure 3 A,and droped a chlorine atom of fragment ion forin Figure 3 B.

The ^{1}H-NMR (AVANCE-300, Bruker Co.) of products were shown in Figure 4.

The structural characteristics of ^{1}H-NMR were illustrated as shown in Table 5.

4. Conclusion

The catalytic hydrogenation of NCD can be performed to produce ACD by using [BPy]Br. The selectivity of ACD was nearly 100% at 338 K under 0.35 MPa with 100% conversion of NCD. Ionic liquids with Br^- as the anion are effective solvent for the reaction which can successfully replace the organic solvent as reported in previous articles. ACD can be separated and purified by extraction with water. Above all, ionic liquids can be reused even more than 7 times and still have considerable reactivity.

Acknowledgement

This work was fancially supported by the Science & Technological Project of Zhe Jiang, China(Grant No.2009C33059) and the Science & Technological Project of Wen Zhou, Zhe Jiang, China(Grant No.G20090146 and G20090148)

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Table 1. Comparison of hydrogenation in different reaction mediums

Samples	*Catalysts*	*Reaction medium*	*Con/%*	*Sel/%*
1	Pd-Ru/γ-Al_2O_3	[Bpy]Br	100	100
2	Pd-Ru/γ-Al_2O_3	methanol	90.8	67.5
3	Pd-Ru/γ-Al_2O_3	ethanol	89.6	57.2
4	Pd-Ru/γ-Al_2O_3	DMF	89.1	50.3
5	Pd-Ru/γ-Al_2O_3	THF	85.7	60.2

Table 2. Comparison of different ionic liquids for hydrogenation

Samples	Reaction medium	T/K	P/MPa	Time/h	con[a]/%	Sel[b]/%
1	[BPy]Br	338	0.35	2.5	100	100
2	[BPy]Cl	338	0.35	2.5	100	94.2
3	[BPy]BF_4	338	0.35	2.5	100	93.9
4	[EPy]Br	338	0.35	2.5	100	100
5	[EPy]Cl	338	0.35	2.5	100	97.5
6	[EPy]BF_4	338	0.35	2.5	100	92.4
Reaction conditions: NCD 0.34g; Reaction medium 20ml; Catalyst(Pd-Ru/Al_2O_3) 0.5g. con[a]: Conversion of NCD; Sel[b]: Selectivity of ACD.						

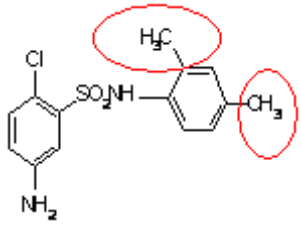
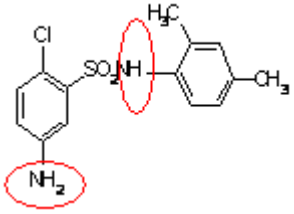
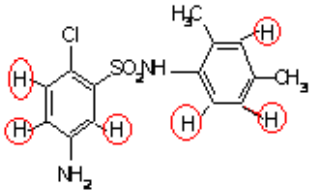
Table 3. Comparison of different catalysts

Samples	*Catalysts*	*Reation medium*	*Con[a](%)*	*Sel[b](%)*
1	Pd/γ-Al_2O_3	[Bpy]Br	100	100
2	Pd-Ru/γ-Al_2O_3[c]	[Bpy]Br	100	100
3	Pd-Ru/γ-Al_2O_3[d]	[Bpy]Br	94.6	100
4	Pd-Ru/γ-Al_2O_3[e]	[Bpy]Br	95.4	100
5	Ru/γ-Al_2O_3	[Bpy]Br	92.8	100
Reaction conditions: NCD 0.34g, solvent 20 mL, Cat. 0.5g; Temperature: 338K; Time: 2.5h; Con[a]: Conversion of NCD; Sel[b]: Selectivity of ACD; Pd-Ru/γ-Al_2O_3[c] : The molar ratio between Ru and Pd was1:1; Pd-Ru/γ-Al_2O_3[d] : The molar ratio between Ru and Pd was 1:1.2; Pd-Ru/γ-Al_2O_3[e]: The molar ratio between Ru and Pd was 1:0.5.				

Table 4. Recycle of [Bpy]Br

Samples	Catalysts	Reation medium	Con[a](%)	Sel[b](%)
1	Pd-Ru/Al_2O_3	[Bpy]Br	100	100
2	Pd-Ru/Al_2O_3	[Bpy]Br	100	100
3	Pd-Ru/Al_2O_3	[Bpy]Br	97.3	100
4	Pd-Ru/Al_2O_3	[Bpy]Br	96.7	100
5	Pd-Ru/Al_2O_3	[Bpy]Br	90.5	100
6	Pd-Ru/Al_2O_3	[Bpy]Br	87.4	100
7	Pd-Ru/Al_2O_3	[Bpy]Br	65.1	100
8	Pd-Ru/Al_2O_3	[Bpy]Br	48.2	100
Reaction conditions: NCD 0.34g; [Bpy]Br: 20 ml; Catalyst(the mole proportion of Ru and Pd was 1:0.5): 0.5g; Temperature: 338K; Time: 2.5h; Con[a]: Conversion of NCD; Sel[b]: Selectivity of ACD.				

Table 5. The data and structures for ^{1}H-NMR

δ_H/ppm	Number of hydrogen	Structured groups	Structure formula
2.25	6H	$2CH_3$	
3.25-4.25	3H	$-C_6H_3-$	
6.25-7.50	6H	$-C_6H_3-$ $-C_6H_3-$	

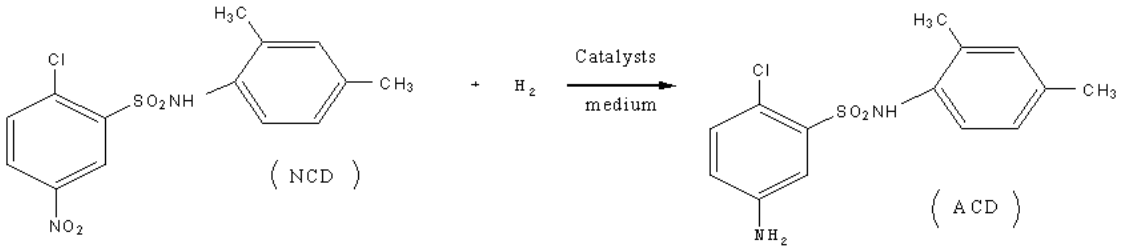


Figure 1. Hydrogenation Reaction Route from NCD to ACD

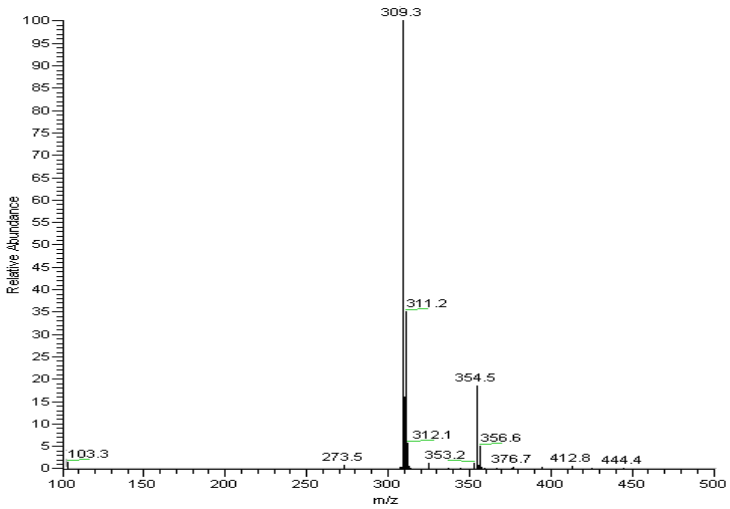
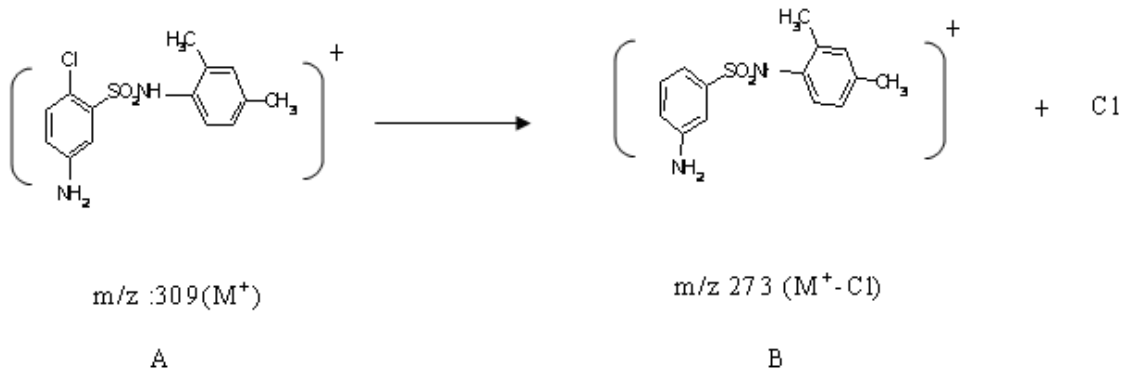


Figure 2. The MS spectrum by LC-MS spectrometry for products



m/z :309(M^+)

A

m/z 273 (M^+-Cl)

B

Figure 3. The structures of the major fragment ion in MS spectrum

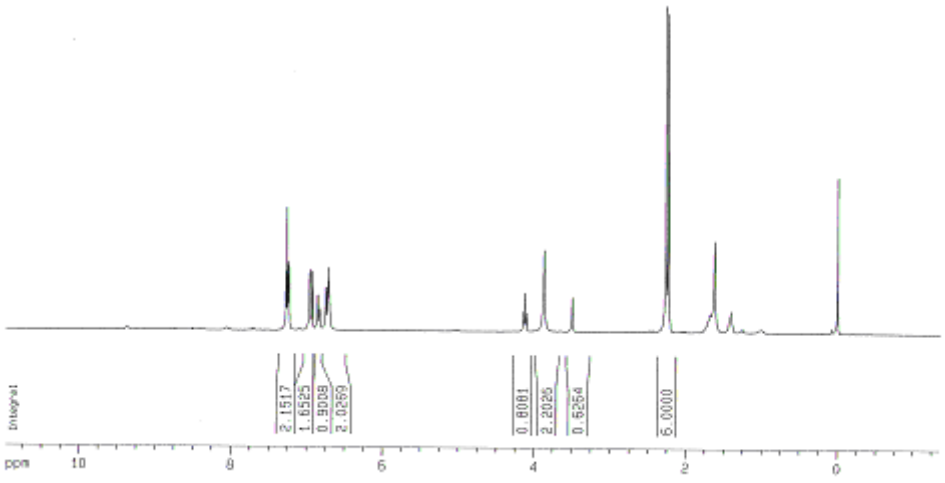


Figure 4. The 1H-NMS spectrum for products