PdRuPVP catalyzed hydrogenation of quinoline under mild reaction conditions

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Abstract:

Polyvinylpyrrolidone(PVP)-stabilized mono metal (Pd and Ru) and different composition bimetallic nanoparticles ($Pd_{0.5}Ru_{0.5}$, $Pd_{0.7}Ru_{0.3}$ and $Pd_{0.3}Ru_{0.7}$) were prepared by wet chemical reduction method by using triethylene glycol as a reductant. The prepared catalysts were examined for the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline under mild conditions (25 ºC, 5 bar). Among the tested catalysts, $Pd_{0.5}Ru_{0.5}$PVP was an effective catalyst for the hydrogenation reaction. The optimized catalyst was recyclable and showed high to moderate yield for the hydrogenation of substituted quinoline to corresponding hydrogenated quinoline products.

Keywords: Heterogeneous catalyst, nanoparticles, Quinolines.

1. Introduction

1,2,3,4-tetrahyydroquinolines are important biological active molecules which are used for the synthesis of drugs, agrochemicals, dyes.[1] Catalytic hydrogenation of quinolines is a direct and efficient route to the synthesis of 1,2,3,4-tetrahyydroquinolines. Several catalytic methods have been reported by using heterogeneous (Pd, Rh, Ru, Au and Co) catalysts with high temperature (>80 °C) and pressure (>10 bar).[2-6] At room temperature, homogeneous (Ir) and heterogeneous (Pt) catalysts were studied for hydrogenation of quinolines using high pressure (>20 bar).[7,8] However, these catalytic methods require high temperature and/or high pressure.

Recently, our research group successfully synthesized uniform and homogeneous PVP-stabilized PdRu alloyed nanoparticles via chemical reduction of metal precursors by overcoming barriers of difference in redox potentials of Pd and Ru.[9] As part of continuing interest in applications of PVP stabilized PdRu nanoparticles, we herein report Pd-Ru nanoparticles catalyzed hydrogenation of quinoline under mild conditions.

2. Experimental

Synthesis of $Pd_{0.5}Ru_{0.5}$PVP nanoparticles

$Pd_{0.5}Ru_{0.5}$PVPcatalysts were synthesized via wet chemical reduction method.[11]The aqueous solution of $K_2[PdCl_4]$ (0.5 mmol)and $RuCl_3 \cdot nH_2O$ (0.5 mmol) were added slowly to a hot solution of PVP in triethylene glycol (100 mL) under constant stirring at 200 ºC in air. After completing the addition, the whole solution was cooled to RT under constant stirring and then the $Pd_{0.5}Ru_{0.5}$PVP nanoparticles were isolated by centrifuging followed by vacuum drying overnight.

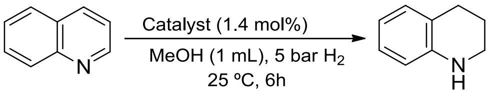
Typical procedures for quinolines hydrogenation

1 mmol of substrate, catalyst (1.4 mol %) and CH_3OH (1 mL) were placed to reactor and sealed. After being sealed, hydrogen was introduced to reactor and inside of the reactor was purged for multiple times. The reactor was pressurized at 5bar byhydrogen and stirred at 25°C. Conversion and yield of product were calculated by GC analysis using dodecane as an internal standard.

3. Results and discussion

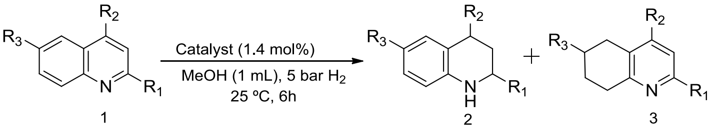
Our study began with hydrogenation of quinoline as a model reaction. **Table1.** shows the result of mono and different composition bimetallic catalysts screening for the reaction.Among tested catalysts, $Pd_{0.5}Ru_{0.5}$PVP showed the highest quinoline conversion (99%) and 1,2,3,4 tetrahydroquinoine yield (96%).

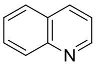
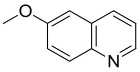
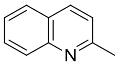
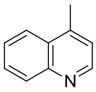
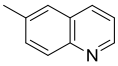
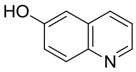
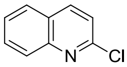
Table 1. hydrogenation of quinolines by mono and bimetallic catalysts



Sr. No	Catalyst (1.4 mol %)	Solvent	Conv. (%)	Yield (%)
1	$Pd_{0.5}Ru_{0.5}$PVP	MeOH	99	96
2	$Pd_{0.75}Ru_{0.25}$PVP	MeOH	56	45
3	$Pd_{0.25}Ru_{0.75}$PVP	MeOH	10	0
4	PdPVP	MeOH	22	0
5	RuPVP	MeOH	24	22
6	$Pd_{0.5}Ru_{0.5}$PVP	THF	67	60
7	$Pd_{0.5}Ru_{0.5}$PVP	Toulene	40	39
8	$Pd_{0.5}Ru_{0.5}$PVP	Dioxane	23	17

Table 2. hydrogenation of substituted quinolines over PdRuPVP catalyst



Sr. No	Substrate	Time (h)	Conv. (%)	Yield^2 (%)	Yield^3 (%)
1		6	99	96	0
2		24	99	90	0
3		24	99	76	17
4		24	99	57	38
5		24	99	80	0
6		24	64	60	0
7		24	99	84	12

After the screening of catalysts, the effect of solvent was studied for the hydrogenation of quinoline. Methanol solvent showed full quinoline conversion and yield of hydrogenated quinoline product. From these results, $Pd_{0.5}Ru_{0.5}$PVP with methanol as solvent was determined to be the optimal condition for the hydrogenation of quinolines. To study general applicability of $Pd_{0.5}Ru_{0.5}$PVP, we carried out hydrogenation of substituted quinolines under optimized conditions (**Table 2.**). Quinoline bearing electron-donating and electron-withdrawing group were hydrogenated to corresponding quinolines with high yield (entries 2-7). $Pd_{0.5}Ru_{0.5}$PVP catalyst was reused three times successfully (not shown).

4. Conclusions

In summary, we have developed an effective catalyst for hydrogenation of quinolines under mild conditions. Various substituted quinolines were hydrogenated to corresponding tetrahydroquinolines with high to moderate yield. The catalyst was recovered and reused three times without any loss in activity.

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