

Catalytic Hydrogenation Of Benzoic Acid In Binary Solvent Mixture

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Abstract

Hydrogenation of benzoic acid was carried out using different ruthenium catalyst at 493 K and hydrogen pressure of 6.89 MPa. A binary solvent consisting of 1, 4-dioxane and water was used for the hydrogenation. The dioxane-water composition of 1:1 gave 100% conversion using 5% Ru/C catalyst and 86% selectivity to cyclohexane carboxylic acid for hydrogenation of benzoic acid. Binary solvent was also observed to increase selectivity of benzoic acid hydrogenation towards cyclohexane carboxylic acid with catalysts like 5% Ru/C, 1%Ru-6%Re/C, 5%Ru/Al₂O₃ and 5%Ru/TiO₂. The binary solvent has higher hydrogen solubility and also reduced the hydrogenolysis products like toluene and methyl cyclohexane.

Keywords: Hydrogenation, Binary Solvent, Benzoic Acid, Chemo-Selectivity, Henrys Constant

I. Introduction

The hydrogenation of aromatic carboxylic acids is a very versatile reaction as it contains aromatic ring and carboxylic group which can be hydrogenated. A supported ruthenium catalyst hydrogenates both aromatic ring and carboxylic group [1]. Hydrogenation of benzoic acid with Pd-Re/C catalyst using 1, 4-dioxane solvent gives hydrogenation products like cyclohexane carboxylic acid (CCA), cyclohexyl methanol (CHM), Benzyl alcohol (BZOH), toluene (TOL) and methyl cyclohexane (MCH) [2]. Similarly, hydrogenation of cinnamic acid using 5% Ru/C catalyst in 1, 4-dioxane solvent gives benzene propanoic acid, cyclohexane propanoic acid and cyclohexyl propanol [3].

There is always an effort to increase selectivity of hydrogenation reaction by designing a catalyst to give a desired reaction product for e.g., Mendes et al. have reported Ru-Sn/TiO₂ catalyst to be more selective to unsaturated alcohol as compared to Ru-Sn/Al₂O₃ catalyst [4]. Addition of Co to Ru catalyst is also reported to change selectivity in hydrogenation of succinic acid to GBL [5]. Similarly, hydrogenation of benzoic acid

with Rh nano particles at 150°C gives 96% yield of cyclohexane carboxylic acid with 99% conversion of benzoic acid [6].

Hydrogenation of benzoic acid to cyclohexane carboxylic acid using Pd nano particles supported on nitrogen doped carbon is also reported [7]. Other examples of chemoselective hydrogenation includes hydrogenation of benzoic acid using 5% Pd/C catalyst gives 100% selectivity to cyclohexane carboxylic acid and with 5%Ru-29%Sn/Al₂O₃ catalyst gives single product benzyl alcohol [2]. Pt/SnO₂ catalyst hydrogenates 98% of benzoic acid and selectivity for benzyl alcohol with this catalyst is 97% [8]. Palladium catalyst is found to be inactive for hydrogenation of carboxylic group present in succinic acid [9].

Other than catalyst solvent is also observed to affect activity and selectivity for homogeneous catalyst [10]. In literature it is also reported that reaction solvent can change the product distribution for competitive hydrogenation of two substrates because of interaction of substrates with the bulk solvent [11]. Addition of pyridine to tetrahydrofuran solvent for hydrogenation of cinnamaldehyde was found to increase selectivity towards formation of cinnamyl alcohol instead of hydrocinnamaldehyde [12].

The factors by which a solvent can affect the selectivity of hydrogenation are reactant solubility, polarity, chemisorption of product and solvent molecules on catalyst surface [13]. Electron donating groups on benzoic acid were found to reduce activity of Ni/C catalyst for hydrogenation of aromatic ring [14]. For hydrogenation of 2-butanone a pure solvent or its mixture is found to influence rate of reaction and its selectivity [15]. Addition of water to 1,4-dioxane solvent for hydrogenation of crotonaldehyde over Pt/TiO₂ catalyst was found to increase selectivity towards crotyl alcohol [16].

Selective hydrogenation of benzoic acid to cyclohexane carboxylic acid can be obtained by using Ni-Zr-B amorphous alloy catalyst with 90.6% selectivity and 64.9% conversion. The selectivity of Ni-Zr-B amorphous alloy catalyst for hydrogenation of benzoic acid to cyclohexane carboxylic acid was found to increase in polar solvent like water [17]. The activity of Ru catalyst for hydrogenation of benzoic acid is reduced as compared to Ir catalyst in water as reaction solvent due to competitive chemisorption of reactants and water on Ru catalyst [18].

In this study we are using highly active Ru/C catalyst over Pd/C catalyst for selective hydrogenation of benzoic acid to cyclohexane carboxylic acid. Here we are trying to increase the selectivity of Ru/C with the help of binary solvent system of water. Water and 1,4-dioxane binary solvent system is considered for above study as benzoic acid is soluble in 1,4-dioxane and water is a universal solvent and less toxic. Novelty of the work is to increase selectivity of highly active Ru/C catalyst and to obtain sustainable binary solvent system.

II. Experimental

2.1. Chemicals:

Required chemicals like reaction solvent, reactants and reaction products required for experimentation were obtained from S. D. Fine chemicals, India. Catalysts with carbon as support were prepared by impregnation method followed by reduction. On the other hand, catalyst with Al_2O_3 and TiO_2 as support were prepared by impregnation method followed by calcination and reduction in H_2 atmosphere. The quantification of reactants and reaction products was carried out using GC analysis [20]. All the experiments are high pressure hydrogenation reactions so carried out in SS alloy Parr reactor. The reaction parameters for benzoic acid hydrogenation were monitored constantly and maintained as given in Table 1.

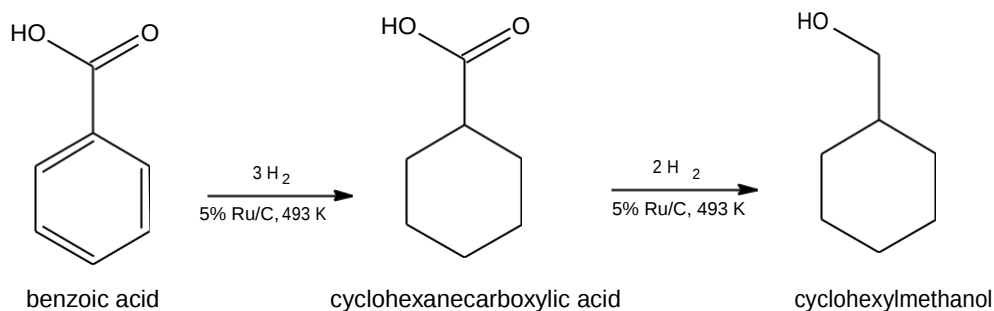
Table 1. Reaction parameters for hydrogenation of benzoic acid.

Reaction parameter	Magnitude
Benzoic acid	0.82 kmol m^{-3}
Hydrogen pressure	6.89 MPa
Catalyst	5 kg m^{-3}
Temperature	493 K
Time	6 hrs
Total volume	$1.0 \times 10^{-4} \text{ m}^3$
Agitation speed	1000 rpm

III. Results and Discussion

Hydrogenation of Benzoic acid using 5% Ru/C catalyst using 1,4-dioxane solvent gives cyclohexane carboxylic acid and cyclohexyl methanol [2] as shown in Figure 1. To understand the effect of binary solvent mixture on selectivity and conversion of hydrogenation of benzoic acid the study was conducted in three parts I) Effect of composition of binary solvent mixture on hydrogenation of benzoic acid, II) Hydrogenation of benzoic acid using different supported Ru catalyst in dioxane solvent and III) Hydrogenation of benzoic acid using different supported Ru catalyst in binary solvent mixture.

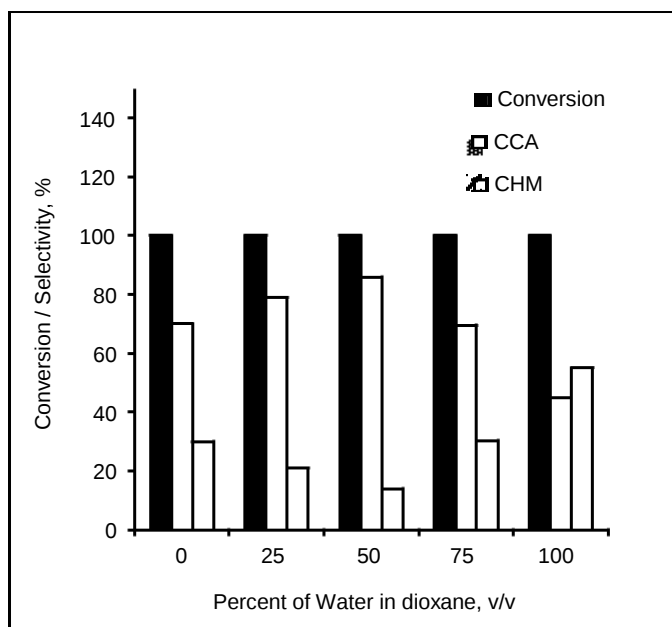
Figure 1. Hydrogenation of Benzoic acid over 5% Ru/C catalyst



3.1. Effect of composition of binary solvent mixture on hydrogenation of benzoic acid using Ru/C catalyst

Hydrogenation of benzoic acid (BZA) was carried using 5% Ru/C catalyst and different composition of water in 1, 4-dioxane solvent. The conversion and selectivity for hydrogenation using 5% Ru/C catalyst is as shown in Figure 2. From the figure it is clear that when the percentage of water is varied from 0-100%, the conversion of benzoic acid was 100%. The selectivity of 5% Ru/C catalyst for cyclohexane carboxylic acid (CCA) and cyclohexyl methanol (CHM) is observed to change with the amount of water in 1,4-dioxane. It is seen that selectivity for CCA increases for water composition from 0% to 50% and then it decreases on further increase of water content.

Figure 2. Effect of percentage water in 1, 4-dioxane on activity and selectivity of 5% Ru/C catalyst for hydrogenation of benzoic acid.



The reason is more orientation of aromatic ring in benzoic acid on catalyst surface as water is added in 1, 4-dioxane. A maximum of 86% selectivity for CCA was obtained with 50% (v/v) water in dioxane. Higher water content (>50%) is observed to give lower selectivity for CCA and selectivity to CHM is increased. Increase in

selectivity towards CHM can be attributed to lower solubility of reactant (BZA) and product (CCA) in water because of this CCA formed is not removed instantaneously from catalyst surface and thus undergoes further hydrogenation to give CHM.

From these results it is understood that selectivity for hydrogenation of benzoic acid to cyclohexane carboxylic acid can be tailored to 86% by using 1:1 1, 4-dioxane-water binary solvent system.

3.2. Hydrogenation of benzoic acid using different supported Ru catalyst in 1,4-dioxane solvent

Hydrogenation of benzoic acid was carried out using different supported ruthenium catalyst in 1, 4-dioxane solvent. The catalyst utilized for this study were 5% Ru/C, 1%Ru-6%Re/C, 5% Ru/Al₂O₃ and 5% Ru/TiO₂. The activity and selectivity for different ruthenium catalysts is given in Table 2.

Table 2. Activity and selectivity for benzoic acid hydrogenation with different Ru catalyst in 1, 4-dioxane.

No.	Catalyst	Conversion %	Selectivity				
			CCA	CHM	TOL	MCH	BZOH
			%	%	%	%	%
1	5 % Ru/C	100	70	30	-	-	-
2	1%Ru-6%Re/C	8.1	15	00	52	-	33
3	5% Ru/Al ₂ O ₃	96.1	56	10	6	28	-
4	5% Ru/TiO ₂	65	13	77	7.8	2.2	-

From the results shown in Table 2 it is clear that selectivity to CCA with different ruthenium catalyst using 1,4-dioxane solvent is less as compared to 1:1 1,4-dioxane-water as solvent. Selectivity to CCA using 1%Ru-6%Re/C, 5% Ru/Al₂O₃ and 5%Ru/TiO₂ catalyst is far less due to formation of hydrogenolysis products like toluene and methyl cyclohexane in 1, 4-dioxane solvent. This observation is as per reported trend where it is observed that hydrogenolysis is favored in 1, 4-dioxane solvent [21].

From Table 2 is also understood that the highest selectivity for CCA (70%) is given by 5% Ru/C catalyst and lowest selectivity for CCA (13%) is shown by 5% Ru/TiO₂ catalyst. In 1,4-dioxane solvent the selectivity of various supported ruthenium catalyst is reduced due to formation of byproducts like Cyclohexyl methanol (CHM), toluene (TOL), methyl cyclohexane (MCH) and Benzyl alcohol (BzOH).

3.3. Hydrogenation of benzoic acid using different supported Ru catalyst in 1:1 1,4-dioxane-water binary solvent

Here hydrogenation of benzoic acid was carried out in 1:1 binary solvent mixture of 1, 4-dioxane and water. The selectivity profile for different ruthenium catalyst was found to be modified when compared with hydrogenation of benzoic acid in 1, 4-dioxane as solvent. The modification was increased selectivity for cyclohexane carboxylic acid in binary solvent system.

The details of conversion and selectivity are given in Table 3. The increase in selectivity to cyclohexane carboxylic acid in presence of water as co-solvent is due to the orientation of aromatic ring towards catalyst surface. Due to interaction of the water molecules in the solvent with the polar carboxylic group, the aromatic ring is oriented towards the catalyst surface, while the carboxylic group faces the solvent [21].

Table 3. Hydrogenation of benzoic acid in 1:1 1, 4-dioxane-water solvent with different ruthenium catalyst

No.	Catalyst	Conversion	Selectivity				
			CCA	CHM	TOL	MCH	BZOH
		%	%	%	%	%	%
1	5 % Ru/C	100	86	14	-	-	-
2	1%Ru-6%Re/C	13.3	54.1	2.74	5.2	22	16
3	5% Ru/Al ₂ O ₃	85.3	93.7	6.3	-	-	-
4	5% Ru/TiO ₂	65.8	99	1	-	-	-

This results in selective hydrogenation of the ring to give cyclohexane carboxylic acid. There is no drastic change in conversion of benzoic acid in 1, 4-dioxane and 1:1 1, 4-dioxane-water binary solvent system.

3.4. Solubility of H₂ in 1,4-dioxane, water and 1:1 1,4-dioxane-water binary solvent

The solubility of H₂ in water, dioxane and 1, 4-dioxane-water (1:1) mixture was determined experimentally at 453, 473 and 493 K, using the method described by Purwanto et al [22]. The solubility measurements were conducted in the same reactor used for the reaction. The temperature of the liquid in the reactor was controlled within ± 1 K. A pressure transducer having a precision of ± 0.07 atm was used to measure the autoclave pressure.

In a typical experiment, a known volume of liquid mixture, which is same as the volume of reaction charge used for hydrogenation reaction was introduced into the autoclave. The autoclave was flushed with nitrogen and the contents heated to the desired temperature. After thermal equilibrium was attained, the void space in the reactor was pressurized with hydrogen to the pressure required. The contents were then stirred for about ten minutes to equilibrate the liquid phase with the solute gas phase.

The drop in the pressure in the autoclave was recorded and used for calculating solubility of hydrogen in the given solvent. In this way Henry's constant for hydrogen in water, 1,4-dioxane, and 1,4-dioxane-water (1:1) mixture were calculated. The results are shown in Table 4.

Table 4. Henry's constant for hydrogen in water, 1,4-dioxane and 1,4-dioxane-water (1:1) mixture.

No.	Henry's constant H_e , ($\text{kmol m}^{-3} \text{ atm}^{-1}$)			
	Temperature (K)	Water	1,4-dioxane	1,4-dioxane-water (1:1)
1	453	7.0×10^{-4}	8.7×10^{-4}	32.6×10^{-4}
2	473	11.0×10^{-4}	15.4×10^{-4}	39.2×10^{-4}
3	493	21.0×10^{-4}	24.8×10^{-4}	53.0×10^{-4}

It is understood from Table 4 that Henry's constant is high in 1:1 1, 4-dioxane-water mixture i.e. Hydrogen solubility is highest in 1:1 1,4-dioxane-water mixture as compared to water and 1,4-dioxane. The problem of reduction in reactivity due to less solubility of benzoic acid in water is removed by increase in solubility of H_2 in binary solvent [23]. This maintains the activity of catalyst in reaction medium 1, 4-dioxane and 1:1 1, 4-dioxane-water mixture.

IV. Conclusion

Addition of water in reaction medium (1, 4-dioxane) enhanced the selective hydrogenation of aromatic ring over carboxylic group in benzoic acid.

1:1 (v/v) 1, 4-dioxane-water binary solvent gives highest selectivity of 86% for CCA. The activity doesn't change much for supported ruthenium catalyst in binary solvent. The selectivity of all supported ruthenium catalyst increases for CCA in 1, 4-dioxane-water binary solvent system. The solvent system seems to orient aromatic ring of benzoic acid over catalytically active site and bring out chemo-selective hydrogenation of aromatic ring instead of carboxylic group. This shows that the chemoselective hydrogenation of aromatic ring over carboxylic group can be tailored by designing appropriate binary solvent system.

The binary solvent is also found to have higher H₂ solubility which makes it better reaction medium than water and 1, 4-dioxane.

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CONFLICTS OF INTEREST

The authors have no conflicts of interest to declare.

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