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Catalytic Hydrogenation of Benzoic Acid

Sunil B. Shinde and Raj M. Deshpande

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Abstract

Hydrogenation of benzoic acid using mono- and bimetallic catalyst of Ru, Pd, Co, and Re yielded different products. It was observed that 5% Ru/C was an active catalyst for hydrogenation of both aromatic ring and carboxylic group, while Pd/C catalyst hydrogenated only aromatic ring. Ru-Sn/Al₂O₃ is a chemoselective catalyst for hydrogenation of –COOH group of benzoic acid.

Keywords: hydrogenation, benzoic acid, catalysts, chemoselectivity, Ru/C, Ru-Sn/Al₂O₃

1. Introduction

The hydrogenation of carboxylic acids or their esters poses major challenges, as among the carbonyl compounds, the acid/ester carbonyl is less reactive than that of ketone and aldehyde [1]. The formation of alcohols by the hydrogenation of the carbonyl group is one of the important reactions, for academia as well as industry, particularly for fatty alcohols, which have been extensively manufactured from fatty acids using hydrogenation technology [2]. Hence, there is a need for new type of catalysts that make it possible to hydrogenate carboxylic acids to alcohols under mild reaction conditions. The combination of group VIII metals with metals like rhenium, germanium, and tin has resulted in better catalysts for this reaction. The first report on the hydrogenation using these catalysts was by Louessard et al., who studied the hydrogenation of ethyl acetate to ethanol over Ru-Sn/Al₂O₃ catalyst [3]. Cheath et al. prepared Ru-Sn/Al₂O₃ catalyst by sol-gel method for the hydrogenation of carboxylic acids and esters; this catalyst was found to exhibit high catalytic performance [4]. They have also reported this catalyst for selectively hydrogenating different carboxylic acids; however, for terephthalic and isophthalic acid, the selectivity to the corresponding alcohols was 19 and 9.2%, respectively, with considerable amount of over-hydrogenated products [5].

The bimetallic Ru-Co catalyst has been reported for hydrogenation of succinic acid. The doping of ruthenium in cobalt increases the overall hydrogenation activity and the Ru/Co ratio in the Ru-Co bimetallic catalyst was found to affect the selectivity of gamma butyrolactone and tetrahydrofuran [6]. Catalysts such as Mn-K/CeO₂-Al₂O₃ are also reported for hydrogenation of benzoic acid to benzaldehyde [7].

Anderson et al. have reported that product distribution for hydrogenation of aromatic acids over Pd/C and Pd supported on carbon nanofiber in aqueous and aprotic organic solvents was almost the same [8]. Chemoselective hydrogenation of benzoic acid to cyclohexane carboxylic acid was found to be efficient over Ni-B[Ni-Zr-B-PEG(800)] amorphous alloy catalyst than noble catalyst [9].

This chapter gives information related to hydrogenation of benzoic acid, which contains two groups, i.e., aromatic ring and carboxylic group, which is not reported in detail.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by impregnation method followed by thermal reduction. The following catalysts were prepared: Ru/C, 5% Pd/C, 5%Re/C, 5% Pd-2% Re/C, 1% Ru-6% Re/C, 5% Ru/Al₂O₃, 5% Ru/TiO₂, 5% Re/Al₂O₃, 5% Co/C, 5% Ru-29%Sn/Al₂O₃, and 5% Ru/MgO.

2.2. Reaction conditions

The reactions were carried out in a 250 ml capacity high-pressure high-temperature reactor supplied by Parr Instruments Co. USA. The reaction conditions for catalyst screening are given in **Table 1**.

Reaction parameter	Range
Benzoic acid quantity	0.82 kmol m ⁻³
Hydrogen partial pressure	6.89 MPa
Catalyst	5.00 kg m ⁻³
Solvent	1,4-Dioxane
Temperature	493 K
Agitation speed	1000 rpm
Total volume	1.0 × 10 ⁻⁴ m ³
Reaction time	6 h

Table 1. Reaction conditions for catalyst screening.

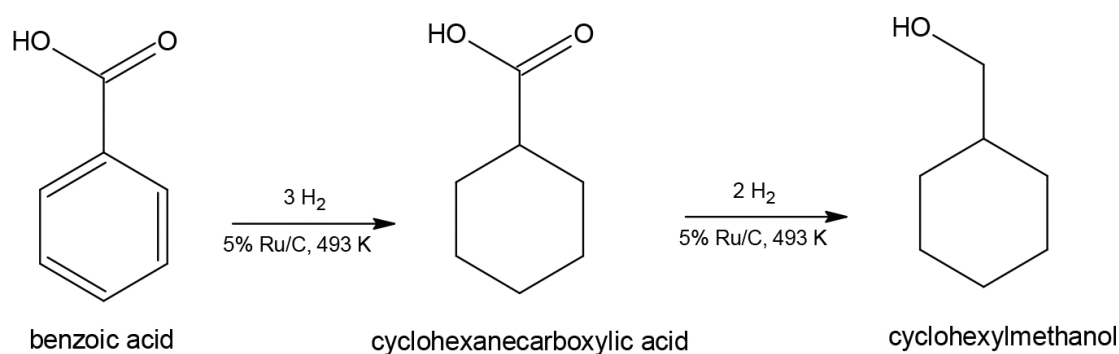
Scheme 1. Reaction scheme for hydrogenation of benzoic acid with 5% Pd/C catalyst.

3.1.3. Hydrogenation of benzoic acid with 5% Re/C catalyst

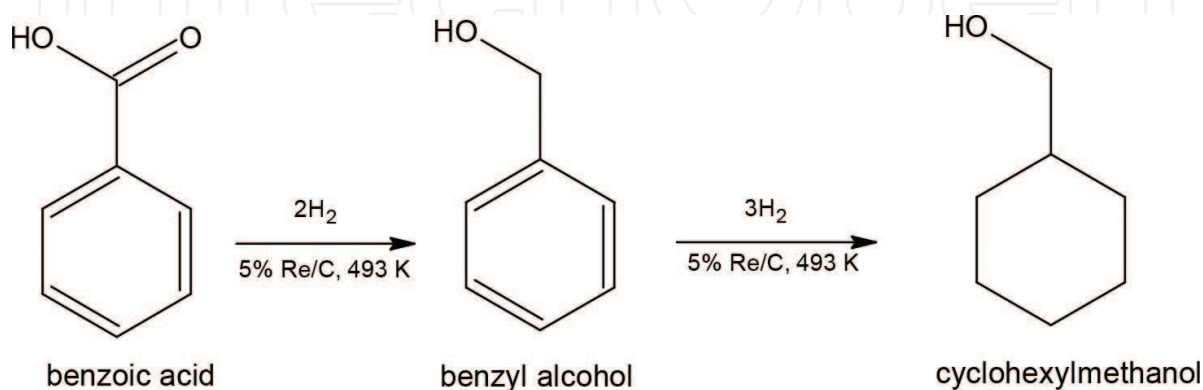
Hydrogenation of benzoic acid over 5% Re/C is very slow as compared to 5% Ru/C and 5% Pd/C catalysts. The reaction pathway for hydrogenation of benzoic acid over 5% Re/C is also different from that for the other two catalysts as shown in **Scheme 3**. In the literature, ReO_3 is reported to be active for selective hydrogenation of terephthalic acid to p-hydroxymethyl benzoic acid [10]. Conversion of benzoic acid was 6.1%, and selectivity to benzyl alcohol and cyclohexyl methanol was 50% each.

3.1.4. Hydrogenation of benzoic acid with 5%Pd-2%Re/C bimetallic catalyst

The activity of bimetallic 5%Pd-2%Re/C catalyst was higher than that for monometallic 5% Pd/C and 5% Re/C catalysts in terms of benzoic acid conversion (98.5%). But the selectivity to benzyl alcohol, cyclohexane carboxylic acid, or cyclohexyl methanol was low as compared to the other catalysts such as 5% Re/C and 5% Pd/C. This is because hydrogenation of benzoic acid with 5%Pd-2%Re/C catalyst gives benzyl alcohol which undergoes hydrogenolysis. The reaction is thus both consecutive and parallel, which gives a series of products such as CCA, cyclohexyl methanol (CHM), toluene (TOL), and methyl cyclohexane (MCH).



Scheme 2. Reaction scheme for hydrogenation of benzoic acid using 5%Ru/C catalyst.



Scheme 3. Reaction scheme for hydrogenation of benzoic acid with 5% Re/C catalyst.

The selectivity for hydrogenation of BZA with 5%Pd-2%Re/C to CCA, CHM, TOL, and MCH is 19, 47, 3.3, and 30.6%, respectively (at 6 h). Such a difference in activity and selectivity for mono-metallic and bimetallic catalyst only confirms that Pd and Re form a synergistic combination [11].

3.1.5. Hydrogenation of benzoic acid with 1%Ru-6%Re/C catalyst

As compared to 5%Pd-2%Re/C catalyst, 1%Ru-6%Re/C showed lower activity in terms of BZA conversion (8.1%). This may be attributed to the low percentage of Ru in the catalyst, which alone is a good hydrogenation catalyst for benzoic acid. With 1%Ru-6%Re/C as catalyst, it was observed that -COOH group was hydrogenated in preference to the aromatic ring. The advantage of 1%Ru-6%Re/C catalyst over 5%Pd-2%Re/C and 5%Ru/C is that the benzyl alcohol (33%) is obtained at the end of reaction.

3.1.6. Hydrogenation of benzoic acid with 5%Ru-29%Sn/Al₂O₃ catalyst

Hydrogenation of benzoic acid with Ru catalyst on different supports such as carbon (C), alumina (Al₂O₃), titania (TiO₂), and magnesia (MgO) was studied. The activity and selectivity of the catalyst varied with support as seen in **Table 2**.

5%Ru/MgO was the least active catalyst and hydrogenated only the aromatic ring, while Ru on carbon was very active for hydrogenation of aromatic ring but relatively less active for hydrogenation of carboxylic group. With Ru on carbon and magnesia, hydrogenation of BZA to BZOH was not observed. Ru on supports like alumina, silica, and titania was active for hydrogenation but not a selective as seen in **Table 2**.

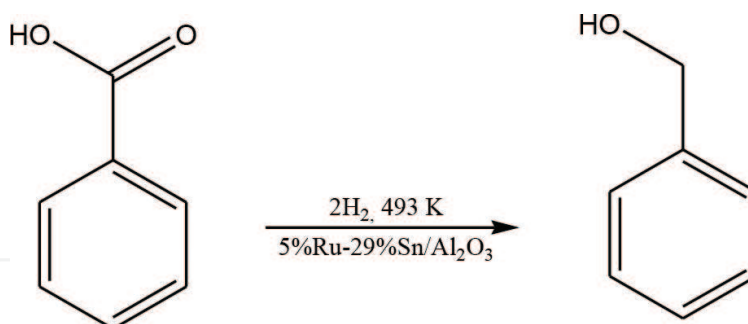
When Sn is doped in 5% Ru/Al₂O₃ catalyst, the selectivity of the 5%Ru/Al₂O₃ catalyst is changed completely. This catalyst is observed to hydrogenate only the carboxylic group of benzoic acid to give benzyl alcohol as shown in **Scheme 4**. The selectivity to benzyl alcohol is 100% with 24% conversion of benzoic acid.

3.1.7. Hydrogenation of benzoic acid with cobalt catalysts

Cobalt metal catalyst has been reported for the hydrogenation of carboxylic acid to alcohols [6]. Hydrogenation of benzoic acid was carried out with 5%Co/C, Co metal, and Ru-Co catalysts. These catalysts were, however, found to be inactive for the hydrogenation of both aromatic and carboxylic groups of BZA under the conditions mentioned in **Table 1**.

No.	Catalyst	Conv. %	TOF (s ⁻¹)	Selectivity				
				CCA%	CHM%	TOL%	MCH%	BZOH%
1	5% Ru/C	99	1.52×10^{-2}	70	30	–	–	–
2	5%Ru/Al ₂ O ₃	96.1	1.48×10^{-2}	56	10	6	28	–
3	5%Ru/TiO ₂	65	0.99×10^{-2}	13	77	7.8	2.2	–
4	5% Ru/MgO	29.2	0.45×10^{-2}	100	–	–	–	–

Table 2. Hydrogenation of benzoic acid with 5% Ru on different supports.



Scheme 4. Hydrogenation of benzoic acid with 5%Ru-29%Sn/Al₂O₃ catalyst.

4. Conclusion

Catalyst screening study for hydrogenation of benzoic acid suggests that 5% Ru/C catalyst was active for hydrogenation of both aromatic ring and carboxylic group, while Pd/C catalyst was observed to be active only for hydrogenation of aromatic ring. With bimetallic Ru-Sn/Al₂O₃ catalyst hydrogenation of aromatic ring was inhibited completely, and hydrogenation of carboxylic group was favored to give benzyl alcohol.

The screening of the catalysts showed that the product distribution for hydrogenation of benzoic acid with mono- and bimetallic catalyst of Ru, Pd, Co, and Re was versatile. The study also highlighted that products such as CCA, CHM, and BZOH can be selectively obtained from the same substrate (BZA).

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