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Catalytic Hydrogenation of Benzoic Acid

Sunil B. Shinde and Raj M. Deshpande

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/Al$_2$O$_3$ is a chemoselective catalyst for hydrogenation of –COOH group of benzoic acid.

Keywords: hydrogenation, benzoic acid, catalysts, chemoselectivity, Ru/C, Ru-Sn/Al$_2$O$_3$

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/Al$_2$O$_3$ catalyst [3]. Cheath et al. prepared Ru-Sn/Al$_2$O$_3$ 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/CeO$_2$-Al$_2$O$_3$ 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/Al$_2$O$_3$, 5% Ru/TiO$_2$, 5% Re/Al$_2$O$_3$, 5% Co/C, 5% Ru-29%Sn/Al$_2$O$_3$, 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.

2.3. Analysis

The various hydrogenation products formed during the reaction were identified using GC-MS (Agilent GC 6890 with 5973 mass selective detector instrument).

For quantitative analysis, samples from the reaction mixture were filtered to remove the catalyst and analyzed by gas chromatography (Agilent Systems 6890 GC). For analysis, an HP INNOWax, polyethylene glycol capillary column (30 m × 320 μm × 0.25 μm) along with flame ionization detector was used on Agilent 6890 gas chromatograph controlled by HP ChemStation software, equipped with an autosampler unit.

3. Results and discussion

3.1. Catalyst screening study for hydrogenation of aromatic carboxylic acid

For catalyst screening study, hydrogenation of benzoic acid was carried out with different supported monometallic catalysts such as Pd, Ru, Re, and Co and bimetallic catalysts such as Ru-Re/C, Ru-Sn/Al$_2$O$_3$, and Pd-Re/C. For hydrogenation of benzoic acid, metal catalysts such as Co and Ru-Co were also used. The selectivity as well as activity for hydrogenation of benzoic acid was found to be dependent on the catalysts used. The results on catalyst screening study for hydrogenation of benzoic acid are discussed below.

3.1.1. Hydrogenation of benzoic acid with 5% Pd/C catalyst

It was observed that the aromatic ring was selectively hydrogenated to give cyclohexane carboxylic acid (CCA) as shown in **Scheme 1**. A 59.7% conversion of benzoic acid (BZA) with 100% selectivity to cyclohexane carboxylic acid was achieved.

3.1.2. Hydrogenation of benzoic acid with 5% Ru/C catalyst

5% Ru/C was an active catalyst as compared to 5% Pd/C. Conversion of benzoic acid at the end of 6 h was found to be 99%. The 5% Ru/C catalyst was found to hydrogenate the carboxylic group along with aromatic ring. The products formed in the reaction are as shown in **Scheme 2**. Under the reaction conditions, the selectivity to cyclohexane carboxylic acid was 70%, while that for cyclohexyl methanol, 30%.
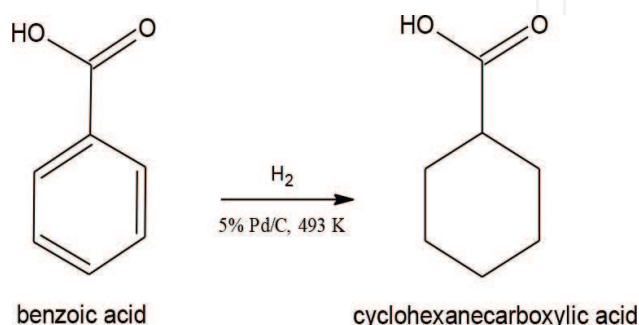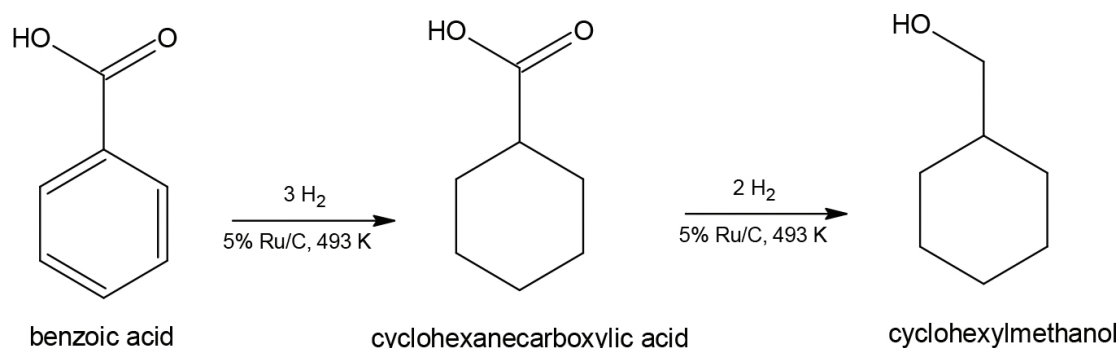

Scheme 1. Reaction scheme for hydrogenation of benzoic acid with 5% Pd/C catalyst.

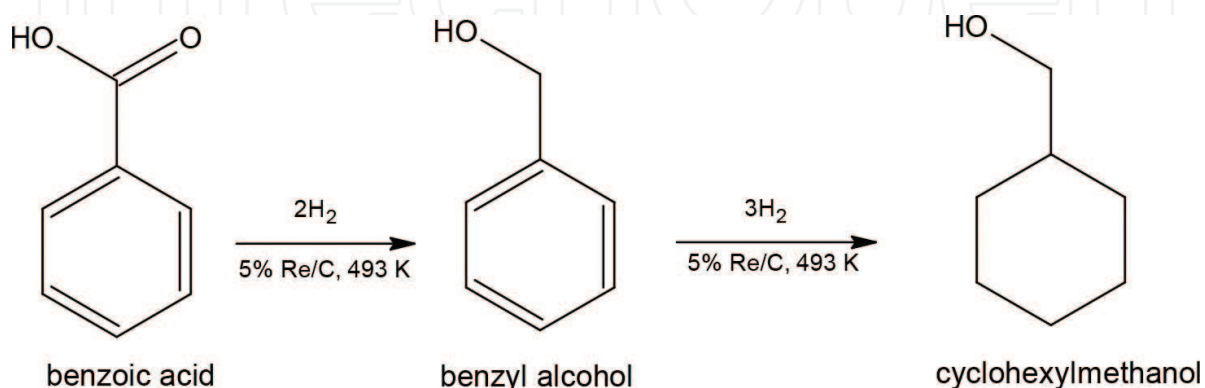### 3.1.3. Hydrogenation of benzoic acid with 5% Re/C catalyst

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 cata-lyst, 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/Al$_2$O$_3$ catalyst

Hydrogenation of benzoic acid with Ru catalyst on different supports such as carbon (C), alumina (Al$_2$O$_3$), titania (TiO$_2$), 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/Al$_2$O$_3$ catalyst, the selectivity of the 5%Ru/Al$_2$O$_3$ 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 cata-lysts. These catalysts were, however, found to be inactive for the hydrogenation of both aro-matic 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.
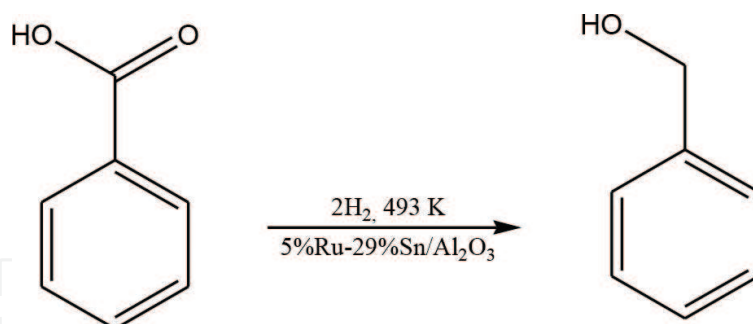
Scheme 4. Hydrogenation of benzoic acid with 5%Ru-29%Sn/Al$_2$O$_3$ catalyst.

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/Al$_2$O$_3$, 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).

Acknowledgements

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