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Investigation of Parameters Influencing the Activity and Selectivity of Ru-Sn Catalyst for Chemoselective Hydrogenation of Benzoic Acid to Benzyl Alcohol

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This study assessed the Ru-Sn catalyst's performance in benzoic acid hydrogenation to benzyl alcohol, highlighting the optimal Sn/Ru ratio of 5 for peak activity in a Ru-Sn/Al_2O_3 system. TiO_2 support outperformed Al_2O_3 and SiO_2, achieving a 72% conversion rate and 83% selectivity towards benzyl alcohol. Increasing the reduction temperature enhanced catalyst activity and selectivity. While Ru remained stable, tin showed leaching; this decreased with reuse of catalyst and higher catalyst reduction temperatures. Notably, TiO_2 support minimized Sn leaching and benzoic acid's acidity did not induce Sn leaching. The findings provide key insights into optimizing the Ru-Sn catalyst for hydrogenation of benzoic acid.

Keywords: Hydrogenation, Chemo-selectivity, Bimetallic catalyst, Metal leaching, Benzoic acid, Benzyl alcohol.

INTRODUCTION

Supported Ru-Sn bimetallic catalysts have been reported to exhibit activity in the hydrogenation of carboxylic acids to alcohols [1]. These catalysts not only demonstrate the activity for the hydrogenation of carboxylic groups but also exhibit selectivity for the hydrogenation of carboxylic groups in the presence of other hydrogenable functional groups. For example, the Ru-Sn/Al_2O_3 catalyst has been utilized for the selective hydrogenation of oleic acid to 9-octadecen-1-ol [1]. Furthermore, a supported Ru-Pt-Sn/C catalyst has been found to suppress the hydrogenolysis reaction during the hydrogenation of 1,4-cyclohexane dicarboxylic acid to 1,4-cyclohexane dimethanol [2,3].

Tahara *et al*. [4] reported that the hydrogenation of rosin using a Ru-Sn/Al_2O_3 catalyst without calcination achieved a selectivity of 95% towards rosin alcohol. However, calcination of the catalyst at temperatures ranging from 573 K to 1173 K resulted in an increased selectivity from 95% to 100%. Additionally, the choice of metal precursors used in the preparation of the Ru-Sn/Al_2O_3 catalyst was observed to impact its activity and selectivity in the hydrogenation of carboxylic acids [4].

According to DFT calculations selective hydrogenation of benzoic acid to benzyl alcohol over Pt/SnO_2 catalyst occurred due to selective absorption of carboxylic group instead of aromatic ring of benzoic acid [5]. For hydrogenation of octanoic acid Ru-Sn supported on ZnO catalyst gives 99.4% conversion and 93.0% selective to octanol [6,7]. To date, no comprehensive study has been conducted on the influence of the Sn/Ru ratio in the Ru-Sn/Al_2O_3 catalyst on the hydrogenation of aromatic carboxylic acids, which could elucidate the role of Sn in inhibiting hydrogenolysis. Furthermore, the impact of the catalyst support and catalyst reduction temperature on the activity and selectivity in the hydrogenation of benzoic acid to benzyl alcohol has not been reported.

Regarding Ru-Sn catalysts, leaching of Sn into the reaction mixture has been observed during the hydrogenation of 1, 4-cyclohexane dicarboxylic acid with Ru-Pt-Sn trimetallic catalysts. The addition of Pt to the Ru-Sn catalyst has been shown to reduce the leaching of tin [2,3]. However, a comprehensive investigation into the parameters governing the leaching of Sn from the Ru-Sn catalyst is still lacking. In this study, the influence of the Sn/Ru ratio, the effect of catalyst support and the catalyst reduction temperature on the activity and selectivity of Ru-Sn catalysts in the hydrogenation of benzoic acid to benzyl alcohol were examined. Additionally, the leaching of Sn during the hydrogenation reaction in the reaction medium was also investigated.

EXPERIMENTAL

The chemicals used for the hydrogenation reaction, such as benzoic acid and 1,4-dioxane, were purchased from SD Fine Chemicals, India. Various supports including carbon, alumina, titania and silica, required for the preparation of different Ru-Sn catalysts, were procured from Aldrich Chemicals, USA. Hydrogenation products, namely cyclohexane carboxylic acid, cyclohexyl methanol, benzyl alcohol and benzyl benzoate, were obtained from Merck India Ltd. The hydrogen gas for the reaction and catalyst reduction was sourced from Indian Oxygen Ltd. Mumbai, India.

The Ru-Sn catalysts were prepared through calcination at 773 K, followed by thermal reduction at 573 K. Hydrogenation reactions were conducted in a stainless steel reactor manufactured by Parr Instruments Co. USA. The reaction conditions employed for the hydrogenation of benzoic acid using various Ru-Sn catalysts are presented in Table-1.

TABLE-1
REACTION PARAMETERS USED FOR PRELIMINARY STUDIES ON HYDROGENATION OF BENZOIC ACID WITH Ru-Sn/Al_2O_3 CATALYST

Reaction parameter	Range
Temperature	493 K
Catalyst concentration	10 kg m^{-3}
Substrate concentration	0.41 kmol m^{-3}
Pressure	6.89 Mpa
Stirring speed	1000 rpm
Total charge	1.0×10^{-4} m^3
Reaction time	6 h

RESULTS AND DISCUSSION

The effect of various parameters, such as the Sn/Ru ratio, catalyst support, catalyst reduction temperature and Sn leaching on the performance of the Ru-Sn catalyst was investigated.

Influence of tin percentage on the activity and selectivity of Ru-Sn/Al_2O_3 catalyst for the hydrogenation of benzoic acid to benzyl alcohol: The hydrogenation activity of the Ru-Sn/Al_2O_3 catalyst is known to be influenced by the surface concentration of Sn. The study investigated the effect of Sn/Ru ratio on the catalyst's activity for benzoic acid hydrogenation, and the results are presented in Fig. 1.

In the absence of Sn, the conversion of benzoic acid was 100%, but the selectivity towards benzyl alcohol was zero due to the hydrogenation of aromatic ring and hydrogenolysis of the formed benzyl alcohol. The presence of small amount of tin (Sn/Ru atomic ratio of 1 in Ru-Sn/Al_2O_3) in the catalyst completely inhibits the hydrogenation of aromatic ring and the hydrogenolysis of benzyl alcohol. Further increasing the tin content in the Ru-Sn/Al_2O_3 catalyst enhances the catalyst's activity for the hydrogenation of benzoic acid to benzyl alcohol, up to an Sn/Ru atomic ratio of 5 (5% Ru-29% Sn/Al_2O_3 w/w). Additional tin beyond this ratio has no effect on the catalyst's activity, as shown in Fig. 1. The energy-dispersive X-ray spectroscopy (EDX) analysis of the Ru-Sn/Al_2O_3 catalysts at different Sn/Ru atomic ratios is presented in Table-2. With an increase in Sn loading, the surface Sn/Ru ratio also increases, along with the catalyst's activity. The maximum activity is achieved at a Sn/Ru ratio of 5. An increase in activity for the hydrogenation of carboxylic group of benzoic acid to benzyl alcohol with an increasing Sn/Ru ratio is attributed to the creation of new sites for selective hydrogenation in the presence of tin, as described by Galvagno *et al*. [8]. Despite increasing the Sn content to a Sn/Ru ratio of 7.5, the surface Sn/Ru ratio does not show significant variation, as evidenced by the EDX analysis presented in Table-2. When benzoic acid was hydrogenated with Sn/Al_2O_3 catalyst, the conversion of benzoic acid was observed to be zero. Thus, Sn in the catalyst increases the selectivity of benzyl alcohol from 0% to 100% and also enhances the activity. Both Ru and Sn are therefore essential constituents of catalyst for the chemoselective hydrogenation of benzoic acid to benzyl alcohol. The importance of both Ru and Sn for the selective hydrogenation of benzoic acid is supported by a dual-site mechanism obtained from the kinetic study [8]. Hence, for all further studies, the catalyst composition employed was 5% Ru-29% Sn.

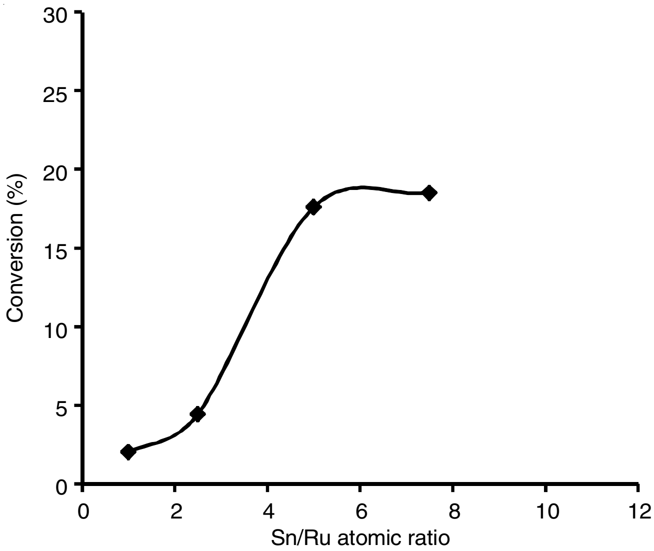

Fig. 1. Impact of Sn percentage on the activity of Ru-Sn/Al_2O_3 catalyst (**Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kg m^{-3}, Benzoic acid = 0.41 kmol m^{-3}, Solvent = 1,4-dioxane, Time = 6 h, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3)

Based on the EDX analysis shown in Table-2, it appears that a minimum surface Sn/Ru ratio of 3-4 is required in the

TABLE-2
SURFACE Sn/Ru RATIO OF THE Ru-Sn/Al_2O_3 CATALYSTS

Bulk Sn/Ru ratio	EDX analysis surface atomic (%)		Surface Sn/Ru ratio from EDX analysis
	Sn	Ru	
1.0	0.0900	0.10900	0.82
2.5	0.1004	0.05644	1.77
5.0	0.1430	0.03832	3.73
7.5	0.1833	0.04515	4.06

catalyst to achieve maximum activity and selectivity for the hydrogenation.

Screening of catalyst supports for Ru-Sn catalyst in the hydrogenation of benzoic acid: To investigate the influence of catalyst support on the activity and selectivity of the Ru-Sn catalyst, various supports such as alumina, titania and silica were utilized in the preparation of the Ru-Sn catalysts. The catalysts employed a consistent Sn percentage of 5% and a Ru percentage of 29% on all support materials. The atomic ratio of Sn/Ru in the Ru-Sn catalysts using different supports was maintained at 5. The outcomes of benzoic acid hydrogenation utilizing the Ru-Sn catalyst on different supports are presented in Fig. 2.

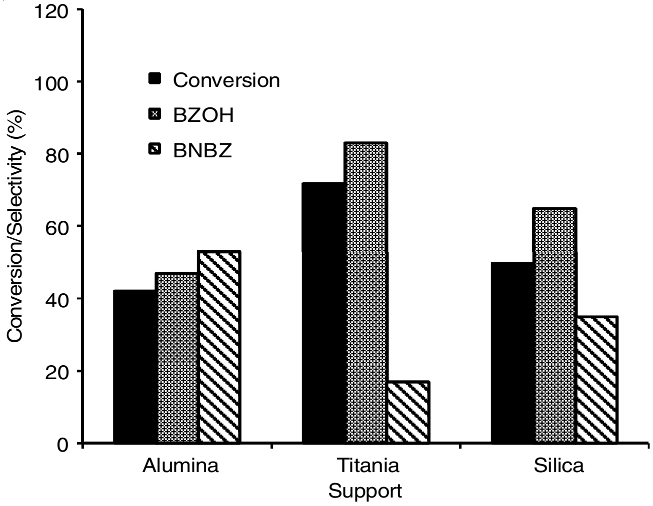

Fig. 2. Impact of catalyst support on the Ru-Sn catalyst for the hydrogenation of benzoic acid (**Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kg m^{-3}, Benzoic acid = 0.41 kmol m^{-3}, Solvent = 1,4-dioxane, Time = 6 h, Agitation speed = 1000 rpm, Total volume = 1.0 × 10^{-4} m^{3})

Based on the observations in Fig. 2, it can be concluded that TiO_2 serves as the most effective support for the Ru-Sn catalyst. It exhibits the highest activity and selectivity for the hydrogenation process. This enhanced performance can be attributed to the activation of the carboxylic group by TiO_2 species, specifically Ti^{3+}, present on the catalyst surface [9]. The Ru-Sn/TiO_2 catalyst achieved a conversion of 72% for benzoic acid with a selectivity of 83% towards benzyl alcohol and 17% towards benzyl benzoate.

Effect of catalyst reduction temperature on activity and selectivity of Ru-Sn/Al_2O_3 catalysts: To investigate the impact of catalyst reduction temperature on the activity and selectivity of the Ru-Sn/Al_2O_3 catalyst, alumina was impregnated with $RuCl_3·3H_2O$ and $SnCl_2·2H_2O$. The resulting catalyst precursors were then calcined at 773 K for 12 h. Subsequently, these calcined catalysts were subjected to thermal reduction under a hydrogen atmosphere for 12 h at different temperatures of 573 K, 723 K and 873 K, respectively, yielding three distinct catalysts. The Sn/Ru atomic ratio in all of these Ru-Sn/Al_2O_3 catalysts was maintained at 5. The reduced catalysts were employed in the hydrogenation of benzoic acid to benzyl alcohol, and the corresponding results are presented in Fig. 3.

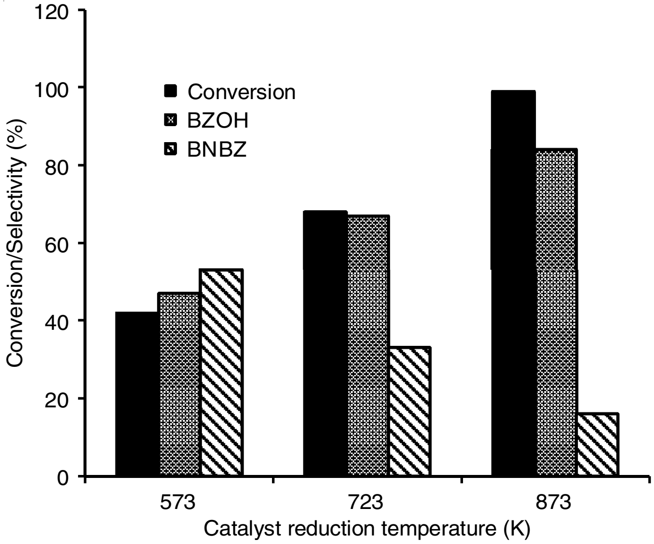

Fig. 3. Influence of thermal reduction temperature on the Ru-Sn catalyst for the hydrogenation of benzoic acid (**Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kg m^{-3}, Benzoic acid = 0.41 kmol m^{-3}, Solvent = 1,4-dioxane, Time = 6 h, Agitation speed = 1000 rpm, Total volume = 1.0 × 10^{-4} m^{3})

As depicted in Fig. 3, the activity of Ru-Sn/Al_2O_3 catalyst for the hydrogenation of benzoic acid exhibited an increase with respect to reduction temperature. The conversion of benzoic acid using the Ru-Sn/Al_2O_3 catalyst reduced at 573 K reached 40%, whereas the catalyst reduced at 873 K achieved a conversion of 99%. Additionally, the selectivity for benzyl alcohol also experienced an enhancement when the catalyst was reduced at 873 K. Specifically, when the catalyst was reduced at 573 K, the selectivity to benzyl alcohol was 47%, with 53% of benzyl alcohol present as benzyl benzoate. Conversely, when the same catalyst was reduced at 873 K, the selectivity to benzyl alcohol increased from 47% to 84%. This augmentation in selectivity can be primarily attributed to the heightened activity of the Ru-Sn/Al_2O_3 catalyst, which leads to a more rapid consumption of benzoic acid. Consequently, there is a limited amount of benzoic acid available for esterification with benzyl alcohol, resulting in the production of benzyl benzoate.

To examine the oxidation states of Ru, Sn and Al, X-ray photoelectron spectroscopy (XPS) was employed to characterize the catalysts. Fig. 4 presents the obtained results for the oxidation state of Ru, Sn, and Al, respectively. The corrected binding energies and oxidation states for these metals are listed in Table-3. Given that there were no alterations observed in the oxidation states of Ru, Sn or Al, the increase in catalyst activity with respect to reduction temperature can be attributed to factors other than changes in the oxidation state of these elements. A plausible explanation for the enhanced activity of Ru-Sn/Al_2O_3 catalyst is the removal of entrapped Cl through a hydrodechlorination reaction, which has been reported to hinder the hydrogenation of the -C=O group [10]. This removal process leads to a more efficient and active catalyst.

Impact of various parameters on Sn leaching from Ru-Sn/Al_2O_3 catalyst into the reaction crude: In the literature, it has been reported that Sn leaches into the reaction crude from

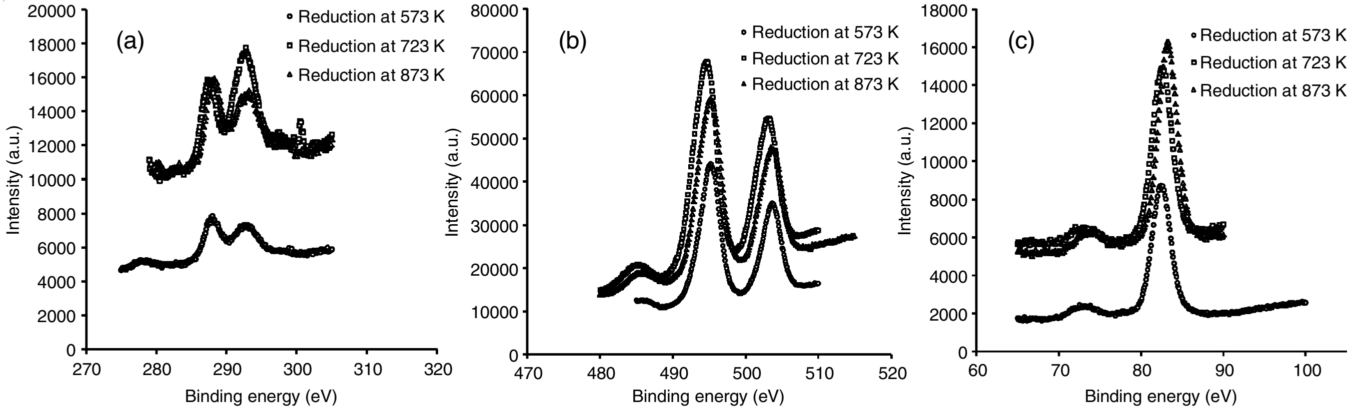

Fig. 4. XPS characterization of (a) ruthenium, (b) tin, (c) aluminium in Ru-Sn/Al_2O_3 catalyst reduced at 573, 723 and 873 K

TABLE-3
BINDING ENERGY AND OXIDATION STATE OF RUTHENIUM (Ru), TIN (Sn) AND ALUMINUM (Al) IN Ru-Sn/Al_2O_3 CATALYST REDUCED AT 573, 723 AND 873 K

Reduction temperature (K)	B.E. values (e.V)	Ru(0) $(3d_5)$	Sn(IV) $(3d_5)$	Al (III) $(2p_3)$	C (1s)
573	Observed	288.3	495.3	82.7	293.1
	Corrected	280.2	487.2	74.6	285.0
723	Observed	287.7	494.8	82.5	292.7
	Corrected	280.0	487.1	74.8	285.0
873	Observed	288.6	495.5	83.3	293.4
	Corrected	280.2	487.1	74.9	285.0
Literature [11] values		280.0	487.3	74.3	285.0

the Ru-Sn catalyst [12]. Therefore, the leaching of Sn into the reaction crude was investigated in the catalyst recycling experiments. In this study, at the conclusion of each recycling cycle, the reaction crude was separated from the catalyst and subjected to quantitative analysis of Ru and Sn using AAS/ICP techniques. No leaching of Ru into the reaction crude was observed throughout the recycling process. However, leaching of Sn into the reaction crude was confirmed. It was observed that the extent of Sn leaching decreased with each cycle of catalyst recycling, as shown in Fig. 5. The maximum leaching of Sn (3% of Sn content of catalyst) was observed during the first cycle, whereas by the end of fourth cycle, the leaching decreased to 0.5%. The retained activity and selectivity of Ru-Sn/Al_2O_3 catalyst after four recycling cycles suggest that the leaching of Sn into the reaction mixture is likely attributed to the excess superficial Sn, which does not participate in the hydrogenation of benzoic acid. Therefore, a study investigating the leaching of Ru and Sn in the reaction crude was conducted, considering different parameters related to the catalyst preparation and reaction conditions.

(i) Effect of catalyst support: Analysis of the reaction crudes for Ru-Sn catalysts supported on different materials reveals no leaching of Ru metal from catalyst into the reaction crude. However, the leaching of Sn into the reaction crude was confirmed for all the Ru-Sn catalysts supported on alumina, titania and silica. The highest Sn leaching was observed in the catalyst supported on alumina, while the lowest leaching was observed in the titania-supported catalyst (Table-4).

(ii) Influence of catalyst reduction temperature on the leaching of Ru and Sn in Ru-Sn/Al_2O_3 catalyst: GFAAS

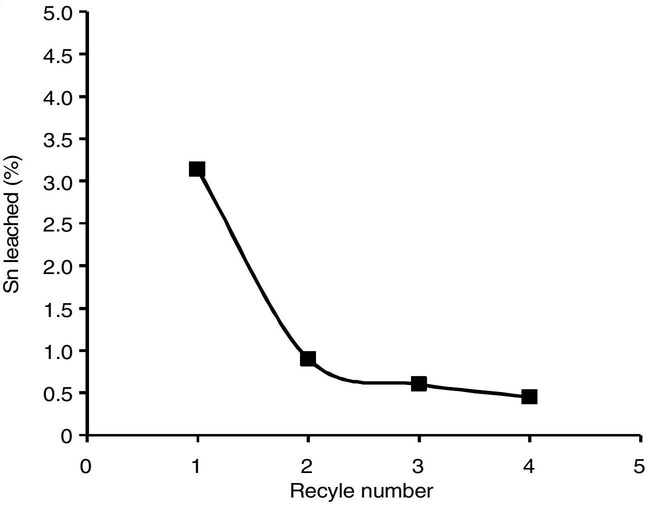

Fig. 5. Sn leaching study in the reaction crude (**Reaction conditions:** Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kg m^{-3}, Benzoic acid = 0.41 kmol m^{-3}, Solvent = 1,4-dioxane, Time = 6 h, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3)

TABLE-4
Sn METAL LEACHING ON DIFFERENT SUPPORTS

Support	% Sn in reaction crude
Alumina	3.1
Titania	1.0
Silica	2.9

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kg m^{-3}, Benzoic acid = 0.41 kmol m^{-3}, Solvent = 1,4-dioxane, Time = 6 h, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

(Graphite Furnace Atomic Absorption Spectroscopy) analysis of the reaction crudes obtained from hydrogenation reactions using Ru-Sn/Al_2O_3 catalysts reduced at different temperatures revealed that the amount of Sn leaching into the reaction solution decreased as the reduction temperature of the catalysts increased. No detectable levels of Ru metal were found in the reaction crude for any of the reactions, indicating strong adhesion of ruthenium to the catalyst surface. The details of the leached Sn percentages from the catalysts reduced at 573 K, 723 K and 873 K are presented in Table-5. The reduced leaching of Sn can be attributed to the strong binding of Sn onto the catalyst surface at higher reduction temperatures.

TABLE-5
IMPACT OF CATALYST REDUCTION TEMPERATURE ON Sn METAL LEACHING

Reduction temperature (K)	% Sn in reaction crude
573	3.1
723	2.5
873	1.6

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kg m^{-3}, Benzoic acid = 0.41 kmol m^{-3}, Solvent = 1,4-dioxane, Time = 6 h, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

(iii) Influence of benzoic acid concentration on the leaching of Ru and Sn in Ru-Sn/Al_2O_3 catalyst: In literature, it has been reported that during the hydrogenation of benzoic acid using Ru-Sn catalysts, the carboxylic group is activated on Sn and activated hydrogen is transferred from ruthenium to this activated carboxylic group [13]. This mechanism involves the chemisorption of the carboxylic group on Sn, which may potentially lead to leaching due to interactions with the carboxylic group. To investigate this, the hydrogenation of benzoic acid was conducted at three different concentrations. At the end of reaction, the reaction crudes were analyzed for Ru and Sn. No leaching of Ru was observed in these reactions. The study also confirmed that benzoic acid did not contribute to the leaching of Sn, as the percentage of Sn leached into the reaction crude remained nearly constant (Table-6).

TABLE-6
IMPACT OF BENZOIC ACID CONCENTRATION ON Ru AND Sn METAL LEACHING

Benzoic acid (kmol/m^3)	% Sn in reaction crude
0.82	2.26
0.41	2.30
0.20	2.28

Reaction conditions: Temperature = 493 K, Hydrogen partial pressure = 6.89 MPa, Catalyst = 10 kg m^{-3}, Solvent = 1,4-dioxane, Time = 3 h, Agitation speed = 1000 rpm, Total volume = 1.0×10^{-4} m^3.

Thus, in this study, it was observed that Ru did not leach into the reaction crude under the aforementioned conditions. The leaching of Sn, however, was influenced by the catalyst reduction temperature and the support used for preparing the Ru-Sn catalyst. On the other hand, benzoic acid concentration in the reaction medium had no effect on the leaching of Sn.

Conclusion

The activity of Ru-Sn catalyst in the hydrogenation of benzoic acid to benzyl alcohol was examined. It was found that monometallic Ru/Al_2O_3 and Sn/Al_2O_3 were ineffective for hydrogenation of benzoic acid to benzyl alcohol. However, the Ru-Sn/Al_2O_3 catalyst showed 100% selectivity towards benzyl alcohol with an optimal Sn/Ru ratio of 5. Among various supports, TiO_2 outperformed alumina and silica. The elevated reduction temperatures boosted catalyst performance. The Ru-Sn/Al_2O_3 catalyst evidenced minimal Sn leaching, decreasing over four recycling cycles, ensuring its potential reusability, while Ru leaching was absent, Sn leaching depended on the catalyst's support and reduction temperature.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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