

Catalytic Hydrogenation Products of Aromatic and Aliphatic Dicarboxylic Acids

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Received: 7 January 2019;

Accepted: 27 January 2019;

Published online: 28 March 2019;

AJC-19344

Hydrogenation of aromatic dicarboxylic acids gave 100 % selectivity to respective cyclohexane dicarboxylic acid with 5 % Pd/C catalyst. 5 % Ru/C catalyst was observed to give over hydrogenation products at 493 K and at lower temperature (453 K) the selectivity for cyclohexane dicarboxylic acids was increased. Hydrogenation of phthalic acid with Ru-Sn/Al₂O₃ catalyst was observed to give phthalide instead of 1,2-benzene dimethanol or 2-hydroxy methyl benzoic acid. Ru-Sn/Al₂O₃ catalyst selectively hydrogenated the carboxylic group of cyclohexane dicarboxylic acids to give cyclohexane dimethanol. Use of proper catalysts and reaction conditions resulted in desired products.

Keywords: Hydrogenation, Dicarboxylic acids, Catalyst, Ru-Sn/Al₂O₃, Selectivity.

INTRODUCTION

Reduction of organic acids and esters is difficult than ketones and aldehydes [1]. Hydrogenation of carbonyl groups to give alcohol is important reaction for industry and hence hydrogenation technology is also significant [2]. Adding metals like Re, Ge or Sn to monometallic Ru, Rh or Pd catalyst produces bimetallic catalysts, which are better than the respective monometallic catalyst [3]. Ru-Sn/Al₂O₃ catalyst prepared by sol-gel method is reported for the hydrogenation of carboxylic acids and esters [4]. Ru-Sn bimetallic catalyst is also reported for chemo selective hydrogenation of different carboxylic acids [5].

Addition of Co to Ru catalyst was found to increase activity of Ru catalyst for hydrogenation of succinic acid. The amount of Co in bimetallic catalyst was also found to change the selectivity of hydrogenation [6]. Hydrogenation of succinic acid, adipic acid and glutaric acid using Re-Pd catalyst are found to yield diols [7]. Hydrogenation of 3-phenylpropionic acid over Re/TiO₂ is reported to give 3-phenylpropanol [8].

Also the products obtained by hydrogenation of aromatic dicarboxylic acids are extensively used in polymer industry, Therefore catalyst designing for hydrogenating aromatic

dicarboxylic acids to saturated dicarboxylic acids or diols is important. For instance ring hydrogenation of terephthalic acid gives 1,4-cyclohexane dicarboxylic acid, which is used for producing polymer Empol 1010 [9]. 1,4-Cyclohexane dicarboxylic acid is also used as a starting material for producing 1,4-cyclohexane dimethanol, which is also used in polyesters, paint, synthetic fibers and synthetic resins [10]. So our main aim was thus, to develop heterogeneous catalysts for reducing aromatic dicarboxylic acids and aliphatic dicarboxylic acids to get different hydrogenation products.

EXPERIMENTAL

Hydrogenation was carried in 0.25 L SS alloy Parr reactor. The qualitative analysis of hydrogenation products formed was done by GC-MS. The quantification of products and reactants was done by gas chromatography using HP INNOWax column. Calibration for the hydrogenation products was done using external standard method [11].

Quantitative analysis of carboxylic acids like terephthalic acid, isophthalic acid, phthalic acid, 1,2-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid and 1,4-cyclohexane dicarboxylic acid was not possible on GC as these acids

were retained on the HP INNOWax, capillary column due to their polarity and high boiling point. For quantitative analysis, such carboxylic acids were first esterified and then analyzed on GC. This analysis was found to be reproducible with experimental error of less than 3 %. The mass balance calculated for hydrogenation reaction and it was found to be 95 % or greater. Similarly gas balance for hydrogen consumed and products formed was found to be 95 % or greater.

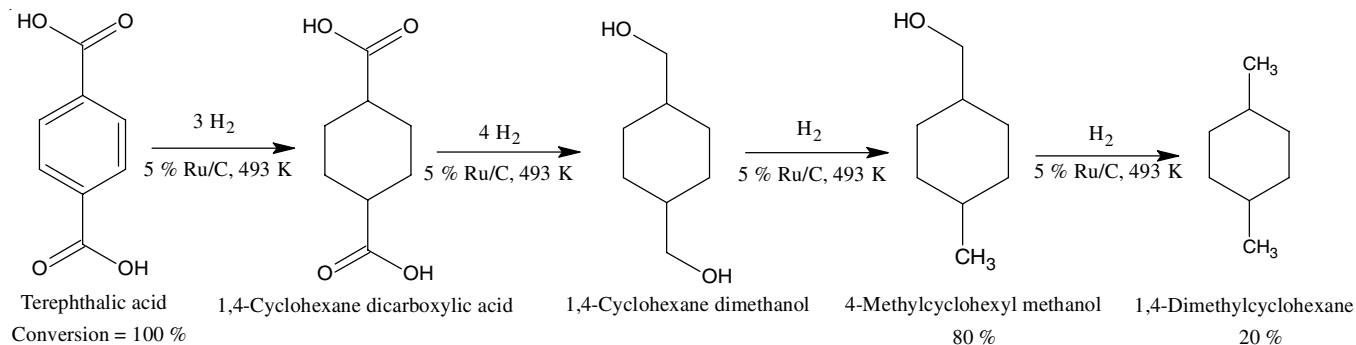
RESULTS AND DISCUSSION

Hydrogenation of terephthalic acid, isophthalic acid and phthalic acid with 5 % Ru/C, 5 % Pd/C and 5 % Ru-29 % Sn/Al₂O₃ (Sn/Ru atomic ratio is 5) as catalyst: The performance of 5 % Pd/C, 5 % Ru/C and Ru-Sn/Al₂O₃ catalyst for hydrogenation of terephthalic acid, isophthalic acid and phthalic acid, was assessed. All the reactions were carried out under the reaction conditions given in Table-1.

TABLE-1 REACTION CONDITIONS FOR HYDROGENATION OF AROMATIC AND ALIPHATIC DICARBOXYLIC ACIDS	
Reaction parameter	Range
Temperature	493 K
Catalyst concentration	10 kg m ⁻³
Carboxylic acid concentration	0.82 kmol m ⁻³
Pressure	6.89 MPa
Solvent	1,4-dioxane
Stirring speed	1000 rpm
Total charge	2.5 × 10 ⁻⁵ m ³
Reaction time	12 h

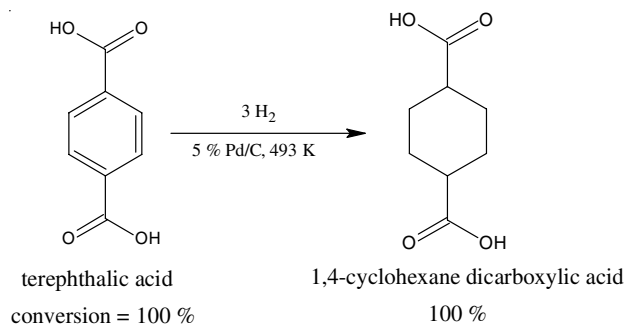
Hydrogenation of terephthalic acid (TPA): Hydrogenation of terephthalic acid with 5 % Ru/C catalyst under the conditions mentioned above gave products like 4-methyl cyclohexyl methanol and 1,4-dimethyl cyclohexane as shown in **Scheme-I**.

These products are obtained from hydrogenolysis of 1,4-cyclohexane dicarboxylic acid (1,4-CDCA) which is formed by hydrogenation of the aromatic ring of terephthalic acid [12]. Here the products like 1,4-cyclohexane dicarboxylic acid and 1,4-cyclohexane dimethanol (1,4-CHDM) are not observed due to hydrogenolysis of 1,4-CHDM. This is because of the high activity of Ru/C catalyst for hydrogenation and hydrogenolysis. With this catalyst, conversion of terephthalic acid was 100 % and selectivity to 4-methyl cyclohexyl methanol and 1,4-dimethyl cyclohexane was 80 and 20 %, respectively.



Scheme-I: Hydrogenation of terephthalic acid with 5 % Ru/C catalyst

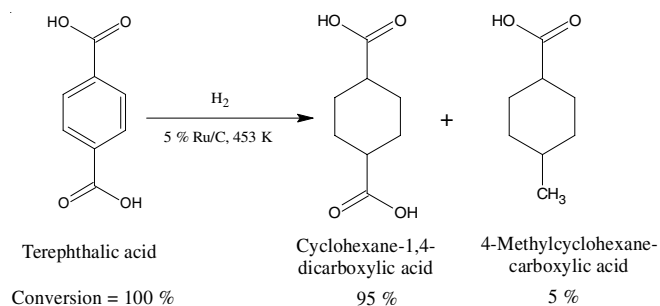
Hydrogenation of terephthalic acid with 5 % Pd/C catalyst at 493 K under the reaction conditions mentioned in Table-1, yielded only 1,4-cyclohexane dicarboxylic acid as the product with 100 % conversion of terephthalic acid as shown in **Scheme-II** (Pd catalyst are in active for -COOH group [13]).



Scheme-II: Hydrogenation of terephthalic acid with 5 % Pd/C catalyst

This also confirms that 5 % Pd/C catalyst is not active for hydrogenation and hydrogenolysis of carboxylic group of 1,4-CDCA.

Selective hydrogenation of terephthalic acid to 1,4-benzene dimethanol does not take place with Ru-Sn/Al₂O₃. When hydrogenation of terephthalic acid was carried out at a lower temperature of 453 K with 5 % Ru/C catalyst, the hydrogenolysis of 1,4-cyclohexane dicarboxylic acid was reduced from 100 to 5 %. The only hydrogenolysis product obtained was 4-methyl cyclohexane carboxylic acid. At 453 K the conversion of terephthalic acid was observed to be 100 % and selectivity to 1,4-CDCA was 95 %. Thus, reducing the temperature of reaction reduces the hydrogenolysis activity of 5 % Ru/C catalyst. The probable reaction for hydrogenation of terephthalic acid with 5 % Ru/C catalyst at lower temperature is shown in **Scheme-III**.

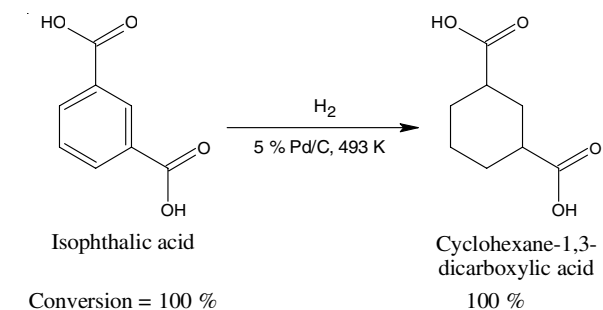


Scheme-III: Hydrogenation of terephthalic acid with 5 % Ru/C catalyst at 453 K

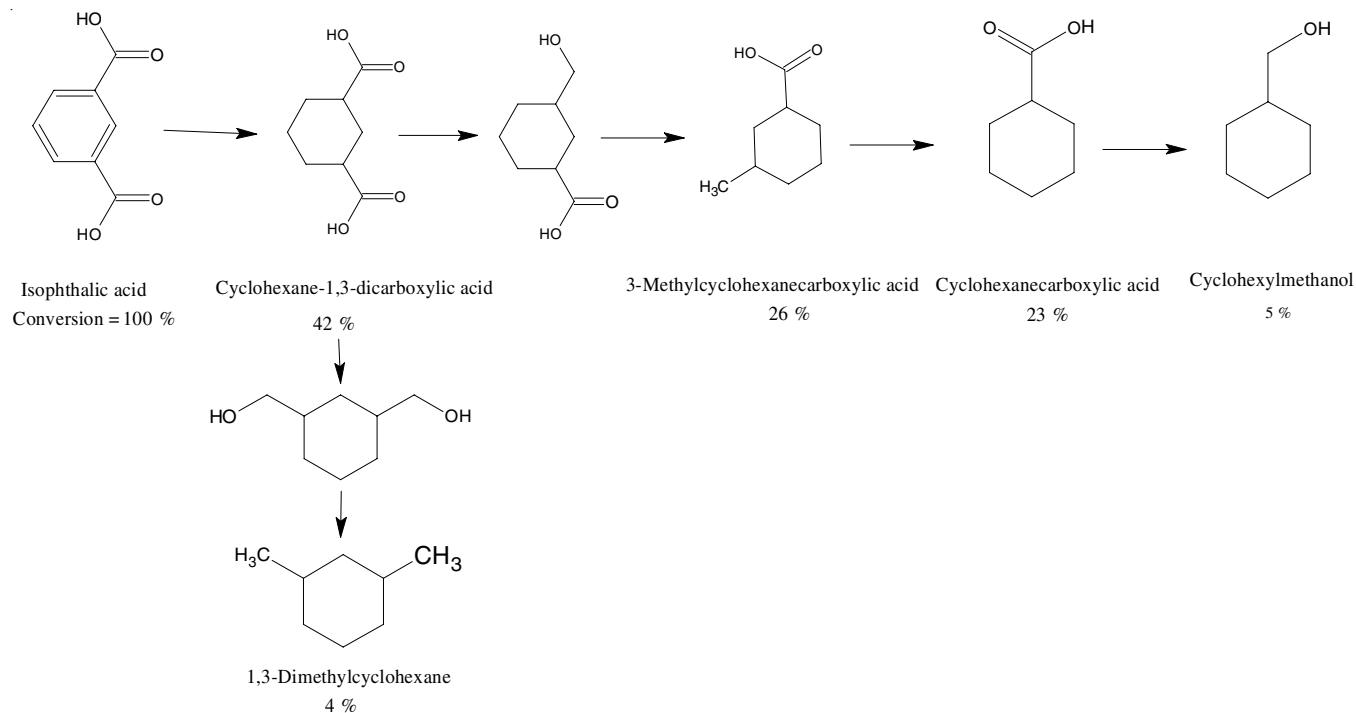
Hydrogenation of isophthalic acid: Hydrogenation of isophthalic acid was carried out with 5 % Ru/C, 5 % Pd/C and Ru-Sn/Al₂O₃ catalyst under the reaction conditions mentioned in Table-1, to give a variety of products.

Hydrogenation of isophthalic acid with 5 % Ru/C catalyst at 493 K was also a fast reaction. Here, hydrogenolysis of 1,3-cyclohexane dicarboxylic acid takes place which gives a range of products like 1,3-dimethyl cyclohexane, cyclohexane carboxylic acid, cyclohexyl methanol and 3-methyl cyclohexane carboxylic acid. Since under the same reaction conditions, hydrogenation of terephthalic acid with 5 % Ru/C catalyst gave only hydrogenolysis product, it is understood that hydrogenolysis of 1,3-cyclohexane dicarboxylic acid is difficult as compared to 1,4-cyclohexane dicarboxylic acid. The proposed reaction along with the selectivity achieved for different products in the hydrogenation of isophthalic acid with 5 % Ru/C catalyst is shown in **Scheme-IV**.

Hydrogenation of isophthalic acid under the reaction conditions mentioned above with 5 % Pd/C catalyst is a selective reaction yielding a single product 1,3-cyclohexane dicarboxylic acid with 100 % conversion of isophthalic acid. The reaction for hydrogenation of isophthalic acid is shown in **Scheme-V**.

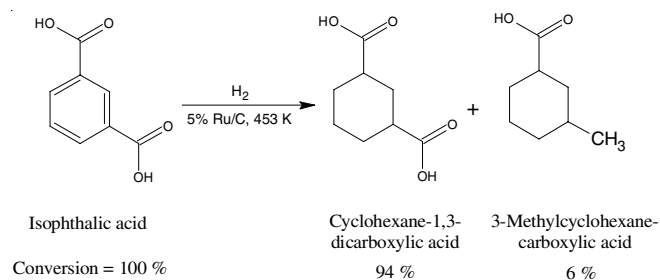


Scheme-V: Hydrogenation of isophthalic acid with 5 % Pd/C catalyst



Scheme-IV: Hydrogenation of isophthalic acid with 5 % Ru/C catalyst

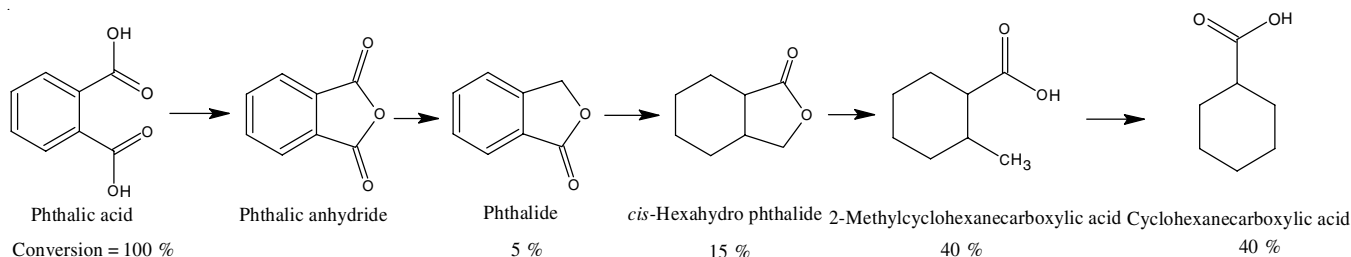
Hydrogenation of isophthalic acid with 5 % Ru/C catalyst at 453 K, under the same reaction conditions shows a reduction in hydrogenolysis products. A 94 % selectivity to 1,3-cyclohexane dicarboxylic acid and 6 % selectivity to 3-methyl cyclohexane carboxylic acid were achieved. Conversion of isophthalic acid at a reaction temperature of 453 K was 100 %. The reaction representing the hydrogenation of isophthalic acid with 5 % Ru/C catalyst along with product selectivity at 453 K is shown in **Scheme-VI**.



Scheme-VI: Hydrogenation of isophthalic acid with 5 % Ru/C catalyst at 453 K

Hydrogenation of phthalic acid: Hydrogenation of phthalic acid is more complex as compared to hydrogenation of terephthalic acid and isophthalic acid. This is due to the proximity of two -COOH groups of phthalic acid, which can undergo dehydration to give phthalic anhydride at higher temperature [14]. Formation of phthalic anhydride from phthalic acid is a thermal process and not catalytic. Thus, a low selectivity for hydrogenation products of phthalic acid due to formation phthalic anhydride is expected.

Hydrogenation of phthalic acid with 5 % Ru/C catalyst was carried out under the reaction conditions mentioned in Table-1. Phthalic acid like the other isomers also undergoes hydrogenolysis with 5 % Ru/C catalyst at 493 K. The probable

**Scheme-VII:** Hydrogenation of phthalic acid with 5 % Ru/C catalyst at 493 K

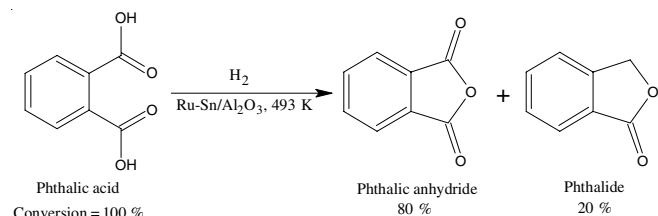
reaction for hydrogenation of phthalic acid is shown in **Scheme-VII** along with the product selectivity.

The major products obtained were 2-methyl cyclohexane carboxylic acid (40 % selectivity) and cyclohexane carboxylic acid (40 % selectivity); other products which were obtained were *cis*-hexahydro phthalide (15 %) and phthalide (5 %). Phthalide and *cis*-hexahydro phthalide are the hydrogenation products of phthalic anhydride.

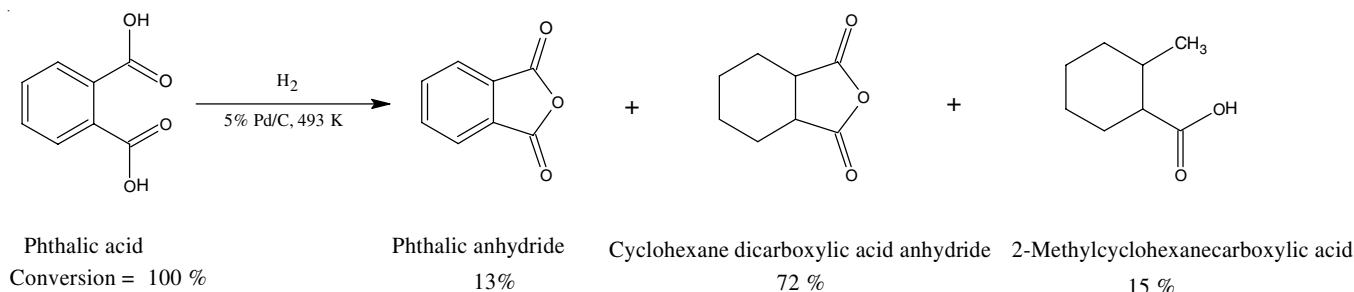
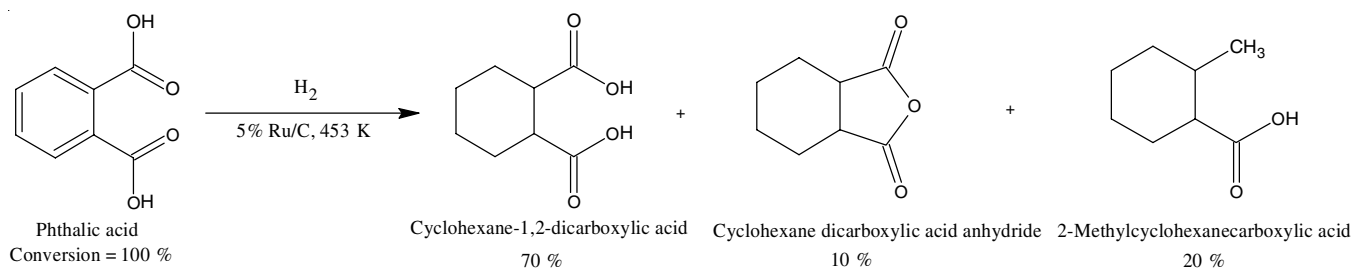
Hydrogenation of phthalic acid with 5 % Pd/C catalyst under the reaction conditions mentioned in Table-1 gave cyclohexane dicarboxylic acid anhydride as a major product (72 % selectivity); the other product, 2-methyl cyclohexane carboxylic acid, (15 %) was obtained by hydrogenolysis. Hydrogenation of phthalic acid with 5 % Pd/C catalyst did not produce 1,2-cyclohexane dicarboxylic acid; this is due to formation of phthalic anhydride. In this reaction some unreacted phthalic anhydride (13 %) was also observed at the end of 12 h. The reaction for hydrogenation of phthalic acid with 5 % Pd/C catalyst is shown in **Scheme-VIII** along with the selectivity observed.

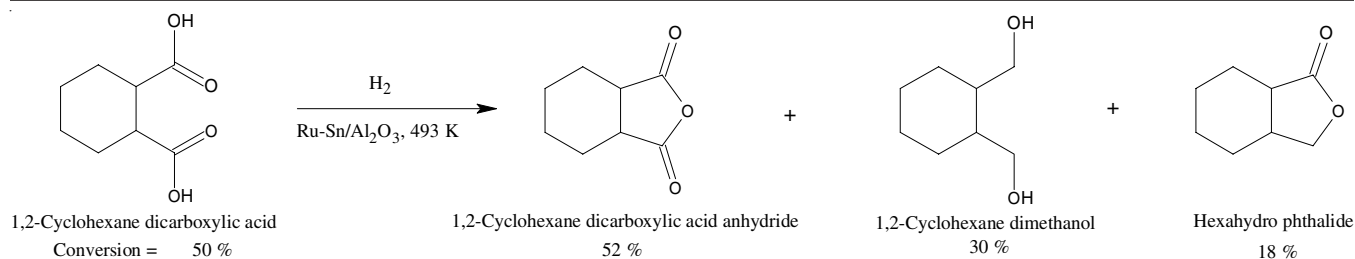
Hydrogenation of phthalic acid with Ru-Sn/Al₂O₃ catalyst under the reaction conditions mentioned in Table-1 gave benzofuranone (phthalide). Unlike terephthalic acid and isophthalic acid, phthalic acid undergoes hydrogenation with Ru-Sn/Al₂O₃ catalyst since phthalic anhydride formed by dehydration of phthalic acid is soluble in 1,4-dioxane. During reaction the phthalic acid was completely converted to phthalic anhydride.

Hydrogenation of C=O group of phthalic anhydride with Ru-Sn/Al₂O₃ catalyst gives phthalide. Conversion of phthalic anhydride is observed to be 20 % with 100 % selectivity to phthalide. The reaction for hydrogenation of phthalic acid with Ru-Sn/Al₂O₃ catalyst along with product distribution is shown in **Scheme-IX**.

**Scheme-IX:** Hydrogenation of phthalic acid with Ru-Sn/Al₂O₃ catalyst

Hydrogenation of phthalic acid with 5 % Ru/C catalyst was also conducted at 453 K under reaction conditions mentioned in Table-1. With lowering of reaction temperature, the formation of phthalic anhydride was drastically reduced and the percentage of hydrogenolysis products obtained was also reduced. Selectivity to 1,2-CDCA was 70 %; 2-methyl cyclohexane carboxylic acid was 20 % and 10 % cyclohexane dicarboxylic acid anhydride was also obtained during reaction. 100 % conversion of phthalic acid was observed. The reaction for hydrogenation of phthalic acid with 5 % Ru/C catalyst at 453 K is shown in **Scheme-X** along with product selectivity.

**Scheme-VIII:** Hydrogenation of phthalic acid with 5 % Pd/C catalyst**Scheme-X:** Hydrogenation of phthalic acid with 5 % Ru/C catalyst at 453 K



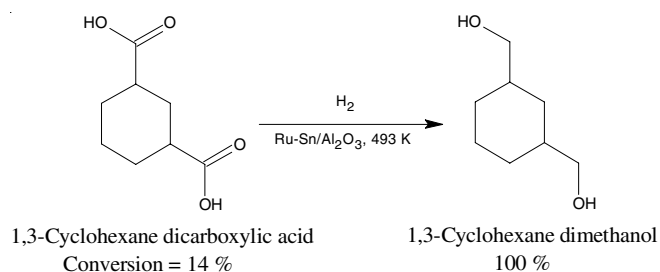
Scheme-XI: Hydrogenation of 1,2-CDCA with Ru-Sn/Al₂O₃ catalyst

Hydrogenation of cyclohexane dicarboxylic acids with 5 % Ru/C, 5 % Pd/C and 5 % Ru-29 % Sn/Al₂O₃ (Sn/Ru atomic ratio 5) catalyst: Cyclohexane dicarboxylic acids are hydrogenation products of terephthalic acid, isophthalic acid and phthalic acid [15-17]. Hence the activity of 5 % Ru/C, 5 % Pd/C and Ru-Sn/Al₂O₃ catalyst for hydrogenation of cyclohexane dicarboxylic acids was assessed. Hydrogenation reactions were carried out under reaction conditions mentioned in Table-1.

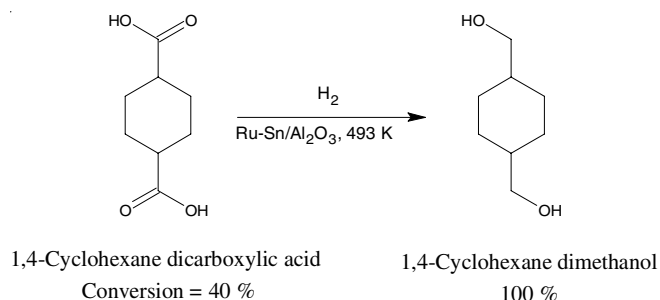
Hydrogenation of 1,4-CDCA, 1,3-CDCA and 1,2-CDCA with 5 % Ru/C catalyst yielded only over hydrogenation products.

5 % Pd/C catalyst was also found to be inactive for the hydrogenation of 1,4-CDCA, 1,3-CDCA and 1,2-CDCA under the reaction conditions mentioned in Table-1. This is because Pd/C is inactive for hydrogenation of carboxylic group.

The only catalyst which selectively hydrogenated 1,2-CDCA, 1,3-CDCA and 1,4-CDCA to corresponding 1,2-cyclohexane, 1,3-cyclohexane and 1,4-cyclohexane dimethanol respectively was Ru-Sn/Al₂O₃. The product distribution for hydrogenation with Ru-Sn/Al₂O₃ catalyst is shown in **Schemes XI-XIII** for 1,2; 1,3 and 1,4-cyclohexane dicarboxylic acid respectively.



Scheme-XII: Hydrogenation of 1,3-CDCA with Ru-Sn/Al₂O₃ catalyst



Scheme-XIII: Hydrogenation of 1,4-CDCA with Ru-Sn/Al₂O₃ catalyst

As seen in **Schemes II-XIII**, hydrogenation of 1,2-CDCA gives 18 % hexahydro phthalide, 52 % 1,2-cyclohexane dicarboxylic acid anhydride and 30 % 1,2-cyclohexane dimethanol, at a 1,2-CDCA conversion of 50 %.

Hydrogenation of 1,3-CDCA and 1,4-CDCA with Ru-Sn/Al₂O₃ gives 100 % 1,3 and 1,4-cyclohexane dimethanol

with 14 % and 40 % conversion of 1,3-CDCA and 1,4-CDCA respectively.

Conclusion

Hydrogenation of aromatic dicarboxylic acids like terephthalic acid and isophthalic acid gave 100 % selectivity to respective cyclohexane dicarboxylic acid with 5 % Pd/C catalyst. 5 % Ru/C catalyst was observed to be a very active catalyst for hydrogenation of dicarboxylic acids and gave overhydrogenation products at 493 K. At lower temperature (453 K) the selectivity for cyclohexane dicarboxylic acids was increased. Hydrogenation of phthalic acid with Ru-Sn/Al₂O₃ catalyst was observed to give phthalide instead of 1,2-benzene dimethanol or 2-hydroxy methyl benzoic acid. Hydrogenation of cyclohexane dicarboxylic acids like 1,4-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid and 1,2-cyclohexane dicarboxylic acid was studied using the catalysts Pd/C, Ru/C and Ru-Sn/Al₂O₃. Ru-Sn/Al₂O₃ catalyst selectively hydrogenated the carboxylic group of these cyclohexane dicarboxylic acids to give cyclohexane dimethanol. The selectivity of 1,2-cyclohexane dimethanol formed from hydrogenation of 1,2-cyclohexane dicarboxylic acid was low (30 %) due to dehydration of 1,2-cyclohexane dicarboxylic acid to give 1,2-cyclohexane dicarboxylic acid anhydride. The screening of the catalysts showed that with proper choice of catalysts it was possible to achieve selectivity towards desired products.

CONFLICT OF INTEREST

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

REFERENCES

- A.J. McAlees and R. McCrindle, *J. Chem. Soc. C*, 2425 (1969); <https://doi.org/10.1039/j39690002425>.
- T. Turek, D.L. Trimm and N.W. Cant, *Catal. Rev., Sci. Eng.*, **36**, 645 (1994); <https://doi.org/10.1080/01614949408013931>.
- P. Louessard, J.P. Candy, J.P. Bourneville and J.M. Basset, *Structure and Reactivity of Surface*, Elsevier: Amsterdam, p. 591 (1989).
- K.Y. Cheah, T.S. Tang, F. Mizukami, S. Niwa, M. Toba and Y.M. Choo, *J. Am. Oil Chem. Soc.*, **69**, 410 (1992); <https://doi.org/10.1007/BF02540940>.
- M. Toba, S. Tanaka, S. Niwa, F. Mizukami, Z. Koppány, L. Gucci, K.-Y. Cheah and T.-S. Tang, *J. Appl. Catal. A*, **189**, 243 (1999); [https://doi.org/10.1016/S0926-860X\(99\)00281-1](https://doi.org/10.1016/S0926-860X(99)00281-1).
- R.M. Deshpande, V.V. Buwa, C.V. Rode, R.V. Chaudhari and P.L. Mills, *Catal. Commun.*, **3**, 269 (2002); [https://doi.org/10.1016/S1566-7367\(02\)00119-X](https://doi.org/10.1016/S1566-7367(02)00119-X).
- Y. Takeda, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, *Catal. Sci. Technol.*, **6**, 5668 (2016); <https://doi.org/10.1039/C6CY00335D>.

8. T. Toyao, S.M.A.H. Siddiki, A.S. Touchy, W. Onodera, K. Kon, Y. Morita, T. Kamachi, K. Yoshizawa and K. Shimizu, *Eur. J. Chem.*, **23**, 1001 (2017); <https://doi.org/10.1002/chem.201604762>.
9. D.R. Fagerburg, Polyester auf basis von 1,4- Cyclohexandicarbonsaeure und 1,4-Cyclohexandimethanol, DE 2655434 (1977).
10. Z. Zhu, Z. Lu, B.G.S. Li and S. Guo, *Appl. Catal. A Gen.*, **302**, 208 (2006); <https://doi.org/10.1016/j.apcata.2006.01.005>.
11. A.I. Vogel, Text book of Quantitative Inorganic Analysis: Including Elementary Instrumental Analysis, Longman Group: UK Ltd., edn 3 (1961).
12. Y. Hara and K. Endou, *Appl. Catal. A Gen.*, **239**, 181 (2003); [https://doi.org/10.1016/S0926-860X\(02\)00388-5](https://doi.org/10.1016/S0926-860X(02)00388-5).
13. J.E. Carnahan, T.A. Ford, W.F. Gresham, W.E. Grigsby and G.F. Hager, *J. Am. Chem. Soc.*, **77**, 3766 (1955); <https://doi.org/10.1021/ja01619a025>.
14. P.Y. Bruice, Organic Chemistry, Prentice Hall, vol. 4, p. 717 (2003).
15. L.D. Lillwitz, Preparation of Cyclohexane Dicarboxylic Acids, US Patent 4754064 (1988).
16. T. Yoshiaki, S. Chihaya, T. Kotone, M. Mitsuo, O. Naoki and K. Kazuaki, EP 603825 (1994).
17. C.E. Sumner and B.L. Gustafson, Hydrogenation of Phthalic Acids, WO 2000078701 (2000).