

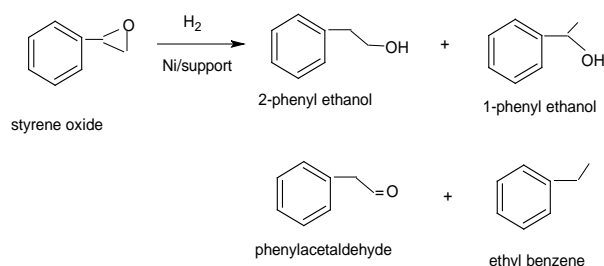
Hydrogenation of styrene oxide to 2-phenyl ethanol over supported Nanonickel catalyst.

Sunil K Kanojiya, Arvind Patel, Gaurav Shukla, Neerja Joshi, Prabhakar Sharma P L Gupta, M Batra, Rajendra Prasad*

Abstract. Hydrogenation of styrene oxide to 2-phenyl ethanol over Al₂O₃, Charcoal and MgO supported nanocrystalline Ni catalyst in methanol as solvent is reported. The reaction is carried out in the temperature range 50-100 oC and in the pressure range 100-300 psi. A maximum yield of % of 2-phenyl ethanol with selectivity of % to PEA is obtained. Present process can be used an alternative to the conventional method for production of PEA such as Grignard synthesis and Friedel-Craft alkylation for synthesis of 2-PEA. The process eliminates use of costly solvent diethyl ether, explosive ethylene oxide reagent and corrosive AlCl₃ as catalyst. The process is free from production of side products such as ethyl benzene responsible for destroying the aroma of 2-phenyl ethanol.

Introduction. 2-Phenyl ethanol (2-PEA), a colorless liquid, possesses a faint but lasting odor of rose petals. The material is used as base in formulations of perfumes, deodorants, soaps and detergents. Because of its bacteriostatic and antifungicidal properties it is also used in preparations of antiseptic creams. 2-PEA also finds application in preparations of hair shampoos and hair dyes to improve the texture and quality of hair. In chemical industries it is used for preparation of phenyl ethyl acetate, phenyl acetaldehyde. It can be sulphonated, nitrated or chlorinated to give substituted products.

2-PEA can be produced by hydrogenation of styrene oxide but the process is generally accompanied with the formation of side products such as phenyl acetaldehyde, benzaldehyde and ethyl benzene which can destroy the aroma of 2-PEA. Attempts therefore have been made to develop catalytic processes with increased selectivity towards 2-PEA.



2-PEA is conventionally prepared by Grignard process. In this process phenyl magnesium chloride prepared from chlorobenzene is reacted with ethylene oxide to produce phenylethoxy magnesium chloride which upon reaction with sulphuric acid produces 2-phenyl ethanol. Major side products such as biphenyl are difficult to remove even by vacuum distillation [1].

In another conventional process 2-phenyl ethanol is produced by reacting benzene with ethylene oxide and using anhydrous

AlCl₃ as a catalyst [2, 3, and 4]. The process has the disadvantages of using ethylene oxide, which is an explosive chemical and requires special care and license. AlCl₃ can be used only once and creates disposal problem. The process leads to the formation of side products such as biphenyl which results into poor selectivity of PEA [5]

Laboratory scale synthesis of styrene oxide to 2-phenyl ethanol is also possible using reducing agents such as LiAlH₄, B₂H₆, LiInH₄, NaBH₄, and LiBHET₃. Synthesis of 2-PEA by reduction of styrene oxide by LiInH₄ has been reported to give 33% yield [6].

Hydrogenation of styrene oxide to 2-PEA has been studied employing homogeneous catalysis as well as heterogeneous catalysis. Separation of catalysts is the major problem in homogeneous catalysis. Hydrogenation of SO in water in presence of emulsifier over Raney nickel, combination of Raney nickel with Co, Pt and Pd is reported [7, 17]. [U.S. Pat. No. 2,822, 403, U. S. Patent No. 3, 579, 593]. Problem of distillation of water, presence of emulsifier and formation of ethyl benzene which destroying the aroma of PEA is the major disadvantages. There are other patents describing almost similar process. James [18] Reported PEA selectivity as high as 97% by a two step hydrogenation of SO using acetic acid and triethyl amine as promoter system .

Platinum and palladium are commonly used as hydrogenation catalysts. Since these metals are expensive and rare, attempts have been made to replace them by other catalysts having comparable performance to them in the form of nanoparticles possessing increased surface area [19]. In the present manuscript we report the hydrogenation of styrene oxide by hydrogen in a pressure reactor over Nano crystalline Ni catalyst, prepared by glycol reduction method, and supported over Al₂O₃, Charcoal and MgO with the objectives of (1) finding the efficiency of the catalyst (2) comparing the suitability of the support and (3) to optimize the process conditions for maximum yield and selectivity towards 2-PEA.

2. Experimental.

2.1. Preparation of catalyst and its characterization. In a three necked flask fitted with a thermometer and a water condenser a 2% solution of anhydrous nickel acetate in ethylene glycol was taken along with the support and refluxed till whole of the nickel acetate was converted to Ni indicated by change of color from green to brown. The anhydrous nickel acetate was prepared simply by drying laboratory grade nickel acetate in oven at 105 °C for few hours till a constant weight was achieved. Small amount of the product was taken out for characterization. The catalyst was always kept covered with ethylene glycol and taken out only when need for characterization or for application as a catalyst. XRD spectra of the sample were obtained Bruker D8 Advance diffractometer, with Cu-K_α radiation (λ = 0.154 nm). BET surface area of the alumina supported Ni catalyst was obtained from Smart Instruments & Services, Mumbai and was found to be 97.63 m²/g.

2.2. Catalyst evaluation. Catalytic performance of the prepared catalyst for reduction of styrene oxide was evaluated in a 2lt stainless steel pressure reactor supplied by Amar Engineering Mumbai. The reactor was fitted with a mechanical stirrer and pressure gauze. Heating was performed by circulating thermal fluid to the coil fitted internally to the reactor. In a typical run 50 g of styrene oxide in 500 ml of methanol and 2.5 g of catalyst was charged to the reactor and heated to 110°C. The reactor was pressurized through a hydrogen gas cylinder to the desired pressure (40-100 kg.cm⁻²). The gas pressure decreases slowly with time and finally becomes constant at completion of the reaction. After completion of the reaction the reactor is opened, catalyst filtered, solvent distilled and product mixture analyzed over a Chemito GLC machine using SE-30 column and FID detector.

3. Results and discussion.

The XRD pattern of the catalyst is shown in Fig.1. The pattern matches well with the reported pattern. The assignments are shown over respective peaks.

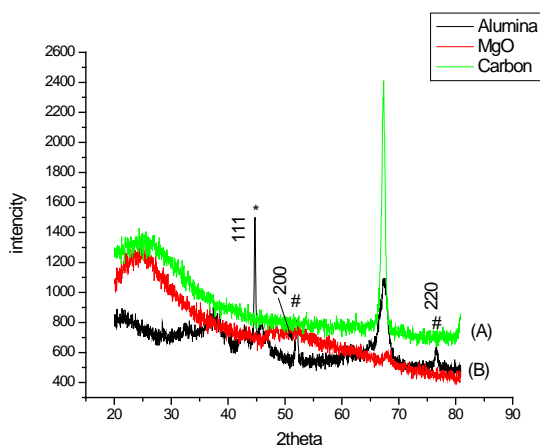


Fig. 1. XRD pattern of alumina supported Ni. (*) hcp

The comparative performance of various supported catalysts for hydrogenation of styrene oxide to 2-PEA is presented in Table 1. Similar performance of all the catalysts suggests passive role of supports except for providing more surface to the catalysts.

Table 1. Comparative performance of various supported catalysts in the hydrogenation of styrene oxide to 2-phenyl ethanol. Temperature = 105 °C, Pressure 50 Kg.cm⁻², catalyst loading =1 %, Time of run = 1hrs

Catalyst	Conversion (%)	Styrene oxide (%)	2-PEA (%)	Others (%)
Ni/Al ₂ O ₃	5.43	94.57	3.78	1.65
Ni/C	5.38	94.62	3.96	1.42
Ni/MgO	5.62	94.38	3.62	1.99

Effect of catalyst loading: The effect of catalyst loading on its performance was studied by varying the substrate/ catalyst weight ratio and analyzing for conversion of styrene oxide and yield of 2-PEA. The results are graphically presented in Figure 2(a), 2(b) and 2(c) respectively for Al₂O₃, charcoal and MgO supported catalysts respectively. Inspection of Figure 2 reveals that conversion and 2-PEA yield increase sharply with catalyst loading up to 1% and then becomes almost to constant. Further studies on other variables were therefore carried out at this loading. At all loadings conversion to by products was negligible.

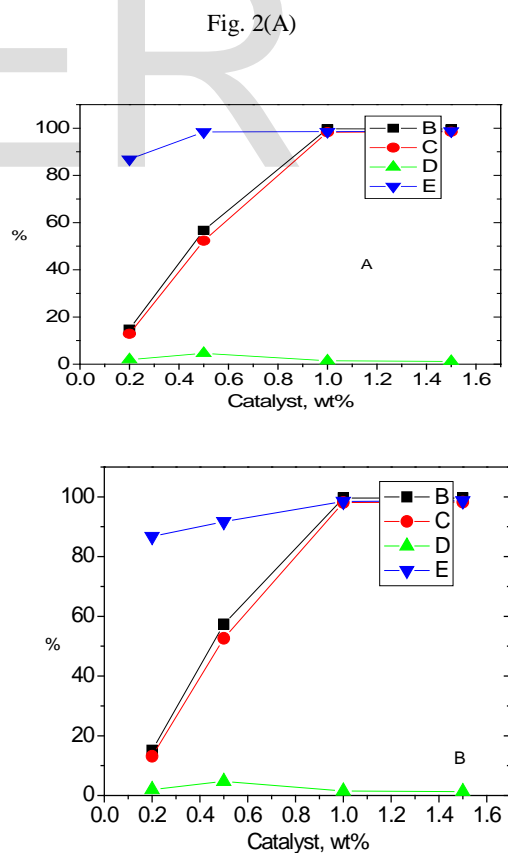


Fig. 2(B)

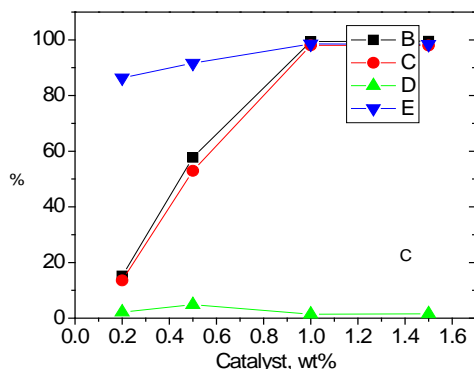


Fig. 2 (C)

Fig. 2. Effect of catalyst loading on the performance of (A) Al_2O_3 (B) charcoal and (D) MgO supported Ni catalyst. B= conversion, C= 2-PEA yield, D= others, E= 2-PEA selectivity. Temp. = 378.15 K, Pressure = 50 Kg. cm^{-2} , Time of run = 4hr.

Effect of temperature: Effect of temperature on the performance of alumina supported, Charcoal supported and MgO supported Ni catalyst was studied in the temperature range 320-400 K at constant catalyst loading, pressure and duration of experiments and is graphically represented in Figure 3(A), 3(b) and 3(C) respectively. For all the three catalysts although at lower temperature conversion of styrene oxide was above 80 %, conversion to by products was also high which led to low yield of 2-PEA. With rise in temperature yield and selectivity for 2-PEA increased and conversion to by products decreased considerable. At a temperature of 400 k a maximum yield of 98.22 % and selectivity of 98.98 % for 2-PEA could be achieved.

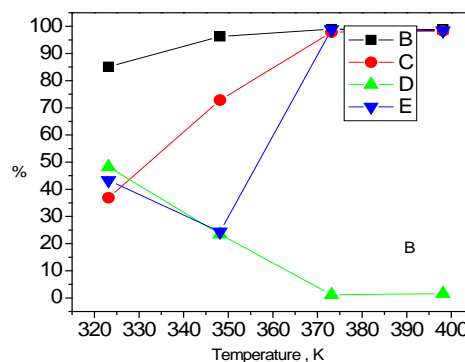


Fig. 3(B)

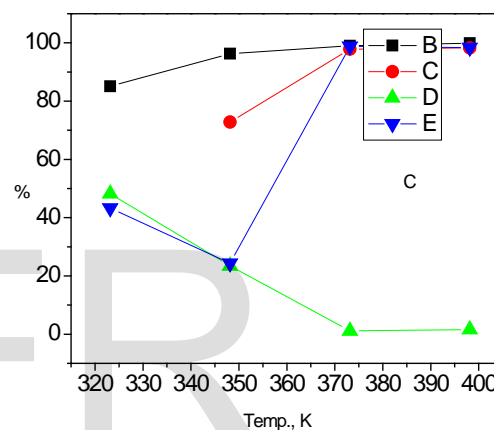


Fig. 3 (C)

Fig.3. Effect of temperature on the performance of (A) Al_2O_3 (B) charcoal and (C) MgO supported Nano Ni catalyst. B= conversion, C= 2-PEA yield, D= others, E= 2-PEA selectivity. Catalyst loading 1 %, Pressure = 50 Kg. cm^{-2} , Time of run = 4hr.

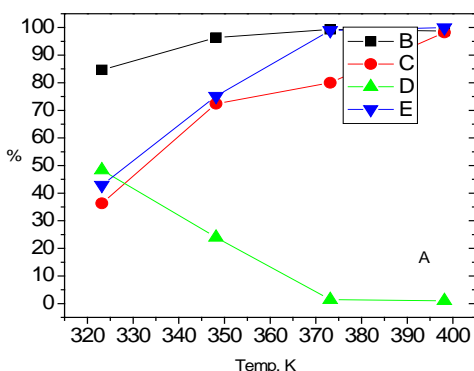


Fig. 3(A)

Effect of pressure: Effect of pressure on the performance of Al_2O_3 , charcoal and MgO supported Nano-nickel catalyst was studied in the pressure range 10- 100 Kg. cm^{-2} and results are shown in Figure 4(A), 4(B) and 4(C) respectively. Conversion of styrene oxide, yield to 2-PEA as well as its selectivity increased with increasing pressure. Conversion to by products was always low.

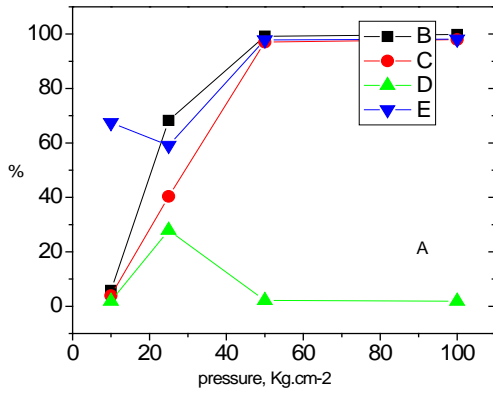


Fig. 4(A)

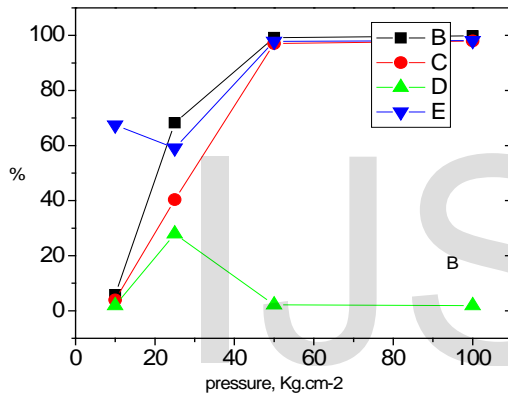


Fig.4 (B)

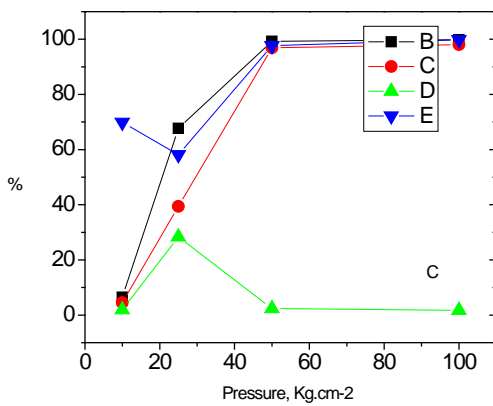


Fig. 4(C)

Fig.4. Effect of pressure on the performance of Al₂O₃, charcoal and MgO supported Nano Ni catalyst. B= conversion, C= 2-PEA yield, D= others, E= 2-PEA selectivity. Catalyst loading 1 %, Temperature 378.15 K, Time of run = 4hr.

Effect of time on stream: Effect of time on stream on the performance of Alumina supported, charcoal supported and MgO supported Nano Ni catalyst was studied at constant catalyst loading of 1 %, temperature of 378.15 K and pressure of 50 Kg.cm⁻². Data are graphically represented in Fig 4(A), 4(B) and 4(C) respectively. Conversion of styrene oxide, yield to 2-PEA and selectivity towards 2-PEA increased with increasing time on stream. Almost stoichiometric conversion could be achieved after 4 hours. Conversion to by products was always low.

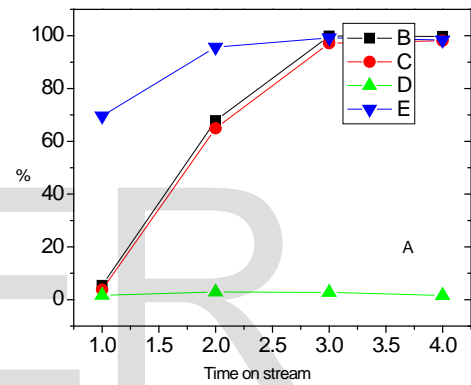


Fig. 5 (A)

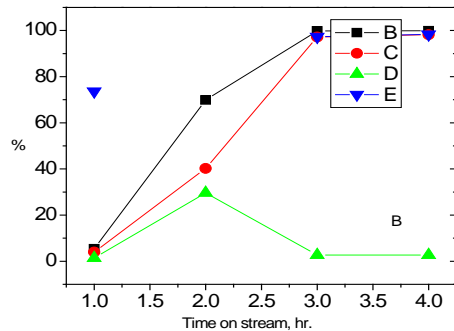


Fig. (5(B))

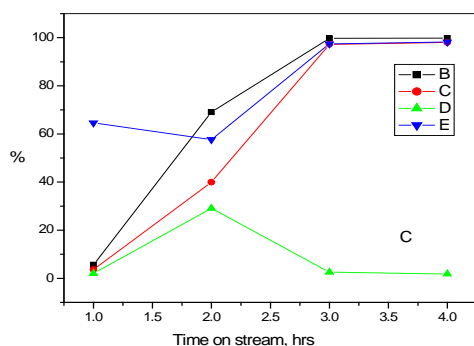


Fig. 5(C)

Fig.5. Effect of time on stream (hrs) on the performance of Al₂O₃, charcoal and MgO supported Ni catalyst. B= conversion, C= 2-PEA yield, D= others, E= 2-PEA selectivity. Catalyst loading 1 %, Temperature 378.15 K, Pressure 50 Kg. cm⁻².

References.

- [1] Ernst T. Theimer in Fragrance chemistry, page 271, Academic Press, New York (1982)].
- [2] K. Bauer, D. Garbe, H. Surburg, Common Fragrance and Flavor Materials, New York, 1990.
- [3] Harold S. Davis, Manufacture of Aromatic alcohol. U S patent 2125490A-1935
- [4] E. T. Theimer, N. J Newark, Synthetic production of alcohols, USP 2 047396 (1933)
- [5] Richard Wilson in Kirk other's Encyclopedia of Chemical technology, Vol4, page 116, John Wiley & Sons, New York, 1991
- [6] Koji Tanaka et al, Tetrahedron letters, 36, 18, 3169-3172 (1995)
- [7] Gibson, C. A., Theiling, L. F., Hydrogenation of styrene oxide to 2-henylethanol, USP 4064186 (1977)
- [8] Rode C. V., Telkar, M. M., Jaganathan, R., Chaudhari, R. V., Reaction kinetics of liquid phase hydrogenation of styrene oxide to β -phenethyl alcohol, J. Mol. Catal. A: Chemical 200 (2003) 279-290.
- [9] Bergada, O., Salagre, P., Cesteros, Y., Medina, F., Sueiras, J. E., High -Selective Ni-MgO catalyst for clean obtension of 2-phynylethanol, Applied catal. A: General, 272 (2004) 125-132
- [10] Smith, J. G., synthetically useful reactions of epoxides. Synthesis, 8 (1984) 629-656
- [11] Kirm, I., Medina, F., Sueiras, J. E., Salagre, P., Cesteros, Y., Hydrogenation of styrene oxide in the presence of supported P catalyst to produce 2-phenylethanol, J. Mole. Catal. A: Chemical 261 (2007) 98-103
- [12] Krishnamurthy, S., Schubert, R.M., Brown, H.C., Hydrogenation of styrene oxide forming 2- phenyl ethanol J. Am. Chem. Soc. 95 (1973) 8486-8487.
- [13] Dabhawala, A. A., Sudheeh, N., Bajaj, H.C., Palladium supported on chitosan as a recyclable and selective catalyst for the synthesis of 2- phenyl ethanol Dalton Trans, 2012, 41, 2910-2917.
- [14] Wood, T. F., Clifton, J., PROCESS FOR PREPARING BETA-PHENYL ethyl alcohol, USP 2,524,096 (1950)

[15] Kim, I., Edina, F., Rodriguez, X., Cesteros, Y., Salagre, P., and Sueiras, J. E., Preparation of 2-phenyl ethanol by catalytic selective hydrogenation of styrene oxide using palladium catalyst, J. Mole. Catal. A: Chemical 239 (2005) 215-221.

[16] U.S. Pat. No. 2,822, 403

[17] U. S. Patent No. 3, 579, 593.

[18] Brian Taylor, Jame, DE 3239611 A1

[19] Sunil K. Kanojiya, G. Shukla, A. Patel, R. Dwivedi , P.Sharma, R Prasad, M. Satalkar and S N Kane, Volume 2014 (2014), Article ID 406939, 6 pages