

## Research Article

# Hydrogenation of Styrene Oxide to 2-Phenylethanol over Nanocrystalline Ni Prepared by Ethylene Glycol Reduction Method

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Nanocrystalline nickel prepared by glycol reduction method and characterized by XRD and magnetic measurements has been used as a catalyst for hydrogenation of styrene oxide to 2-phenylethanol. Effect of process variables such as particle size of the catalyst, temperature, and pressure have been optimized to achieve a maximum conversion of 98% of styrene oxide with 99% selectivity towards 2-phenylethanol. The structure of the transition state has been computed employing density functional theory and using Gaussian 09 suite. The enthalpy of reaction ( $\Delta H$ ) and activation energy ( $E_a$ ) are calculated to be  $85.3 \text{ kcal}\cdot\text{mol}^{-1}$  and  $123.03 \text{ kcal}\cdot\text{mol}^{-1}$ , respectively. A tentative mechanism for the reaction is proposed according to which atomized hydrogen and styrene oxide react together over the catalyst surface to produce 2-phenylethanol.

## 1. Introduction

2-Phenylethanol (2-PEA) having smell of rose petals is a material of commerce and finds applications as fragrance chemical [1–4] antimicrobial and antifungicidal agent [5, 6]. Many perfumes, cosmetics, and deodorant formulations are based on this compound. Its esters such as phenyl ethyl acetate are equally important in perfumery industries. In conventional process 2-phenylethanol is produced by reacting benzene with ethylene oxide and using anhydrous  $\text{AlCl}_3$  as a catalyst [7–9]. The process has the disadvantages of using ethylene oxide, which is an explosive chemical and requires special care and license.  $\text{AlCl}_3$  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 towards 2-PEA.

Conventional catalyst used for many hydrogenation reactions is Raney nickel (particle size of about 25 nm) which is prepared by dissolving Ni-Al alloy in NaOH and removing

the sodium aluminate by repeated washing with water which is time consuming [10–13]. In the present work nanonickel is prepared by glycol reduction process which is simple and takes much less time compared to that required for Raney nickel preparation. Also particle size can be reduced to as low as 5 nm.

Liquid phase [14–20] as well as vapour phase [21, 22] processes have been used to convert styrene oxide (SO) into 2-PEA. Liquid phase reactions are performed under pressure using either pure metal (Ni, Pd, Pt) or supported metals on carriers like Cao,  $\text{SiO}_2$ , and MgO.

There are reports on the production of 2-phenylethanol by reduction of styrene oxide with hydrogen in slurry phase using Pd supported on carbon [4–6]. Recently, there have been few reports on the hydrogenation of styrene oxide employing alumina supported Pt catalyst [7]. In these processes costly metals like Pd and Pt are used as catalyst. There is a cursory report on reduction of styrene oxide to 2-PEA by hydrogen over transition metals supported over

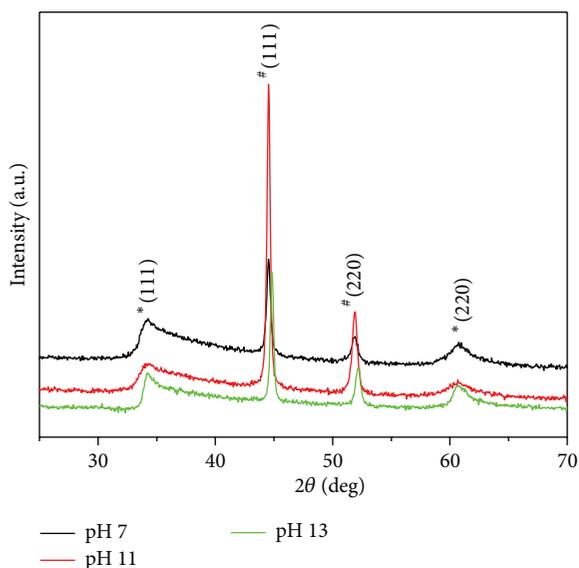


FIGURE 1: XRD pattern of nano Ni catalyst. \* = NiO, # = Ni.

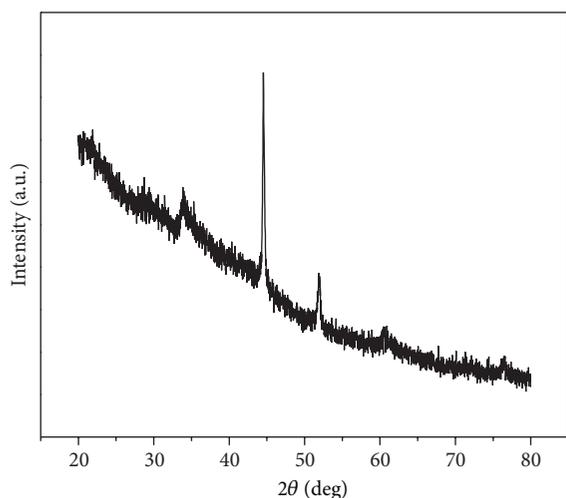


FIGURE 2: XRD pattern of spent catalyst.

carbon [8]. To the best of our knowledge, there seems to be no report on the hydrogenation of styrene oxide using nanonickel as catalyst prepared by glycol reduction process. In view of this the present problem of reduction of styrene oxide with hydrogen over nanonickel was undertaken with the objectives of (1) synthesizing the nanonickel by glycol reduction process (2) to characterize it by spectroscopic and surface area measurement process (3) to evaluate its performance as catalyst for hydrogenation of styrene oxide to 2-phenylethanol and (4) to predict a tentative mechanism of the process.

## 2. Experimental

**2.1. Preparation of Catalyst and Its Characterization.** In a three necked flask fitted with a thermometer and a water

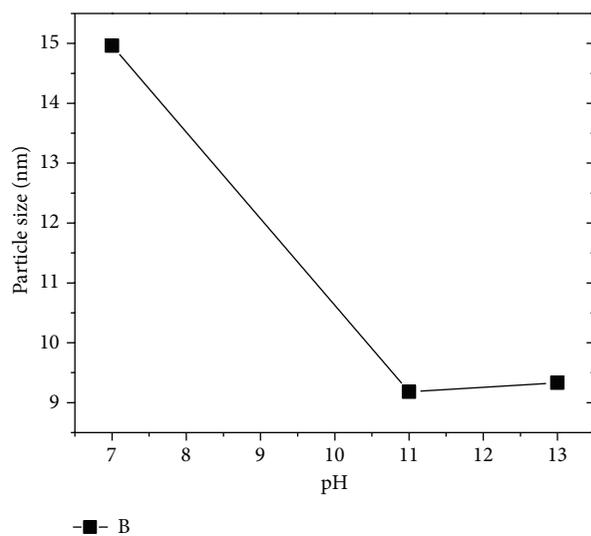


FIGURE 3: Effect of pH on particle size of catalyst.

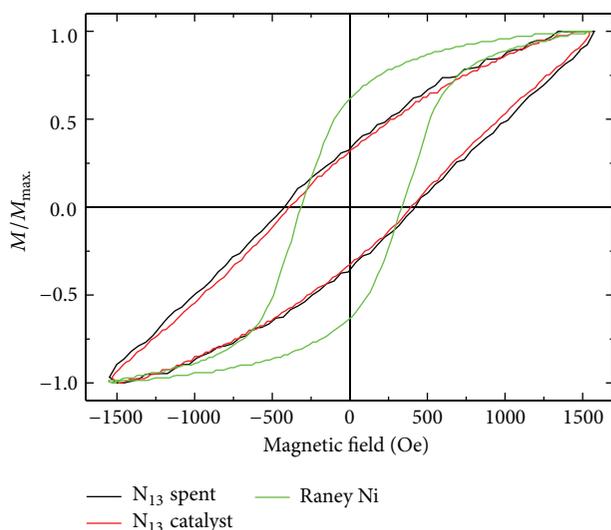


FIGURE 4: (a) Raney nickel (b),  $N_{13}$  catalyst, and (c)  $N_{13}$  spent catalyst.

condenser a 2% solution of anhydrous nickel acetate in ethylene glycol was taken, pH adjusted with NaOH solution, and refluxed till whole of the nickel acetate was converted to Ni indicated by change of color from green to brown. Samples were prepared at pH 7, 11, and 13, and named as  $N_7$ ,  $N_{11}$ , and  $N_{13}$ . The anhydrous nickel acetate was prepared simply by drying laboratory grade nickel acetate in oven at  $105^\circ\text{C}$  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 needed for characterization or for application as a catalyst. X-ray diffraction "XRD" ( $\theta$ - $2\theta$ ) configuration patterns of the studied sample were obtained by Bruker D8 Advance diffractometer, with Cu- $K_\alpha$  radiation ( $\lambda = 0.154$  nm). Room temperature magnetic properties of the studied samples were measured using a digital hysteresis

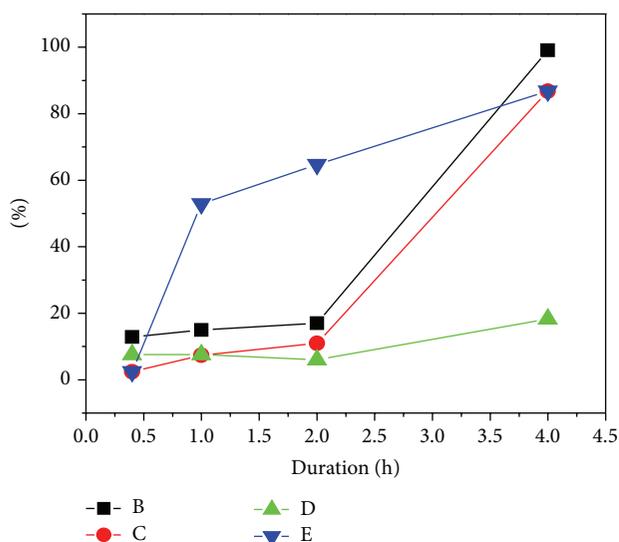


FIGURE 5: Effect of duration of reaction. B = conversion, C = 2-PEA yield, D = others, and E = 2-PEA selectivity.

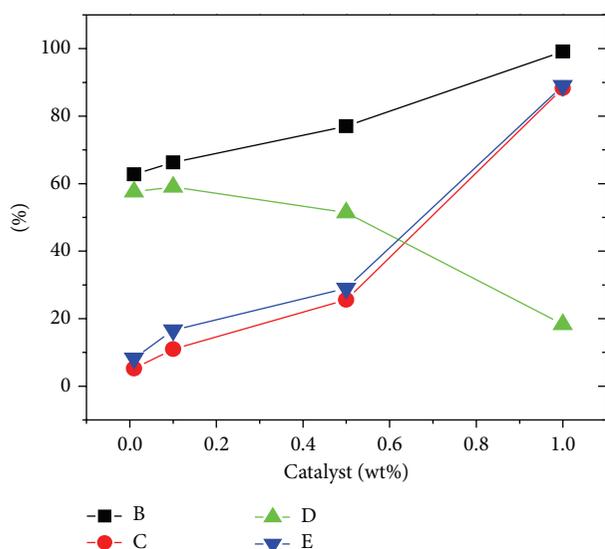


FIGURE 6: Effect of catalyst loading on the performance of the catalyst. B = conversion, C = 2-PEA yield, D = others, and E = 2-PEA selectivity.

loop tracer employing conventional induction technique with a maximum field of  $\pm 1600$  Oe.

**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<sup>-2</sup>).

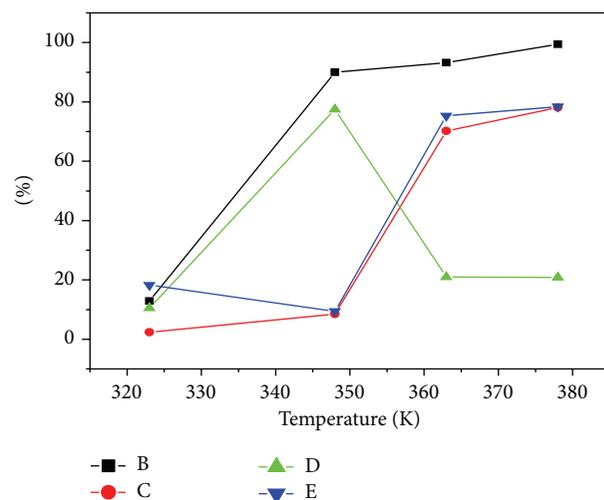


FIGURE 7: Effect of temperature on performance of catalyst. B = conversion, C = 2-PEA yield, D = others, and E = 2-PEA selectivity.

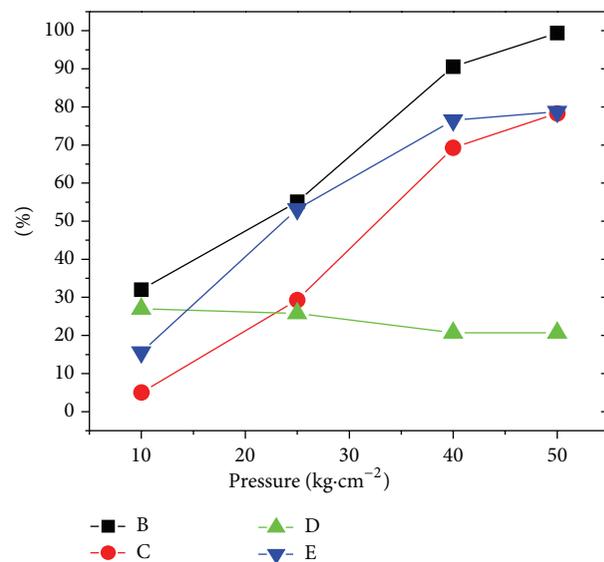


FIGURE 8: Effect of pressure on catalyst performance. Temp. = 378 K, catalyst loading = 1%, duration = 4 hrs. B = conversion, C = PEA yield, D = Others, and E = Selectivity.

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 is filtered, solvent is distilled, and product mixture is analyzed over a Chemito GLC machine using SE-30 column and FID detector.

### 3. Results and Discussion

**3.1. Catalyst Characterization.** The XRD patterns of the catalyst prepared at different pH are reproduced in Figure 1. The particle size was calculated from the 111 peak of the powder employing Scherer's formula [23]. Assignment of XRD peaks were made by comparing the reported pattern

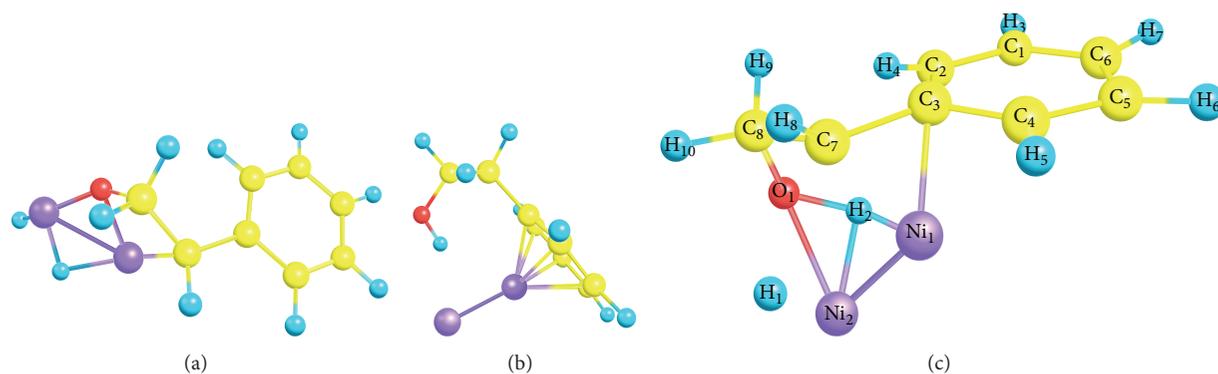


FIGURE 9: Structure of (a) reactant model, (b) product model, and (c) TS for hydrogenation of styrene oxide to 2-phenylethanol.

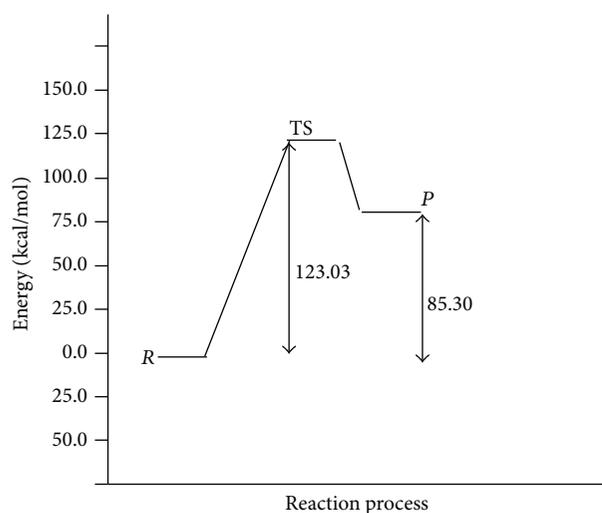


FIGURE 10: Potential energy diagram for hydrogenation of styrene oxide over Ni catalyst.

of Ni by Garcia-Cerda et al. [24] and are shown over the observed peaks. The sample is a mixture of Ni and NiO. The formation of NiO seems to be due to air exposure of the catalyst during XRD measurement.

The pattern matches well with the reported pattern. The XRD pattern of the spent catalyst is shown in Figure 2. The pattern matches well with the initial catalyst employing that there is no change in the crystal structure of the catalyst after use. The variation of particle size with pH for the fresh catalysts is shown in Figure 3. Increasing pH reduced the particle size. However, the crystal size of the spent  $Ni_{13}$  catalyst increased to 11.73 nm as compared to 9.33 nm for fresh  $Ni_{13}$  catalyst.

Magnetic measurements of Raney Ni as well as spent and fresh Ni nanoparticles prepared at pH 13 are depicted in Figure 4. Analysis of magnetic measurements shows that Raney Ni has coercivity of 330 Oe, whereas that of bulk Ni

is 0.7 Oe [25]. Observed change in the coercivity can be attributed to the different grain diameters in Raney Ni and in bulk Ni. Magnetic measurements done on spent and fresh Ni nanoparticles reveal that they are highly anisotropic (whereas Raney Ni is not that anisotropic), as can be seen in hysteresis measurements (Figure 4). As the applied magnetic field is less than saturating field for the case of prepared Ni nanoparticles the samples could not be saturated, so the coactivity could not be estimated. An inspection of the hysteresis loops for nano Ni suggests that its coercivity will be higher than that of Raney Ni. This further suggests smaller size of the prepared nanoparticles compared to bulk and Raney Ni.

**3.2. Effect of Duration of Reaction.** Effect of duration of reaction was studied to have an idea of completion of the reaction. Results are shown graphically in Figure 5. Increasing duration of reaction increased conversion of styrene oxide as well as yield and selectivity of 2-PEA. It was found that duration of 4 hrs was enough for the completion of the reaction. No hydrogen was consumed after 4 hrs. Duration of subsequent experiments was therefore kept at 4 hrs.

**3.3. Effect of Catalyst Loading.** Effect of catalyst loading was studied with the objective of finding optimum catalyst/styrene oxide ratio. The results are shown graphically in Figure 6. A 99% conversion was achieved at a catalyst loading of 1%. Yield as well as selectivity of PEA increased with increase in catalyst loading. It is interesting to note that with increased yield of 2-PEA, conversion to byproducts decreased.

**3.4. Effect of Temperature on Reaction.** Effect of temperature on the performance of the catalyst prepared at pH 13 was studied at pressure of  $50 \text{ kg}\cdot\text{cm}^{-2}$  and catalyst loading of 1%. The results are presented in Figure 7. The conversion rises sharply with increase in temperature. A maximum conversion of 99.42% with yield of 78% of 2-PEA was reached at a temperature of 378 K. At moderate temperature of 348 K the conversion to byproduct was high.

**3.5. Effect of Pressure.** Effect of pressure on the performance of the catalyst was studied in the range  $0\text{--}50 \text{ kg}\cdot\text{cm}^{-2}$  and

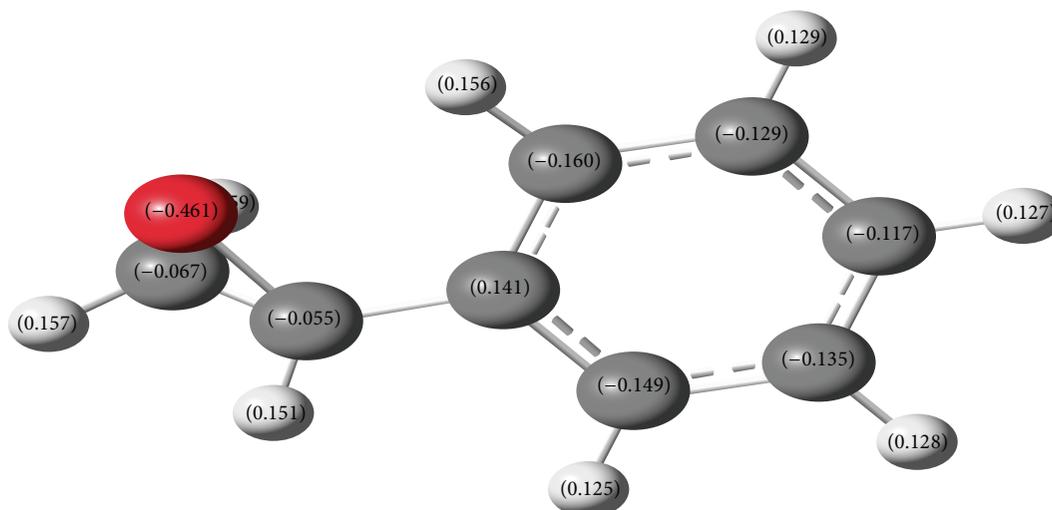


FIGURE 11: Geometry of styrene oxide showing atomic charges (Coulomb).

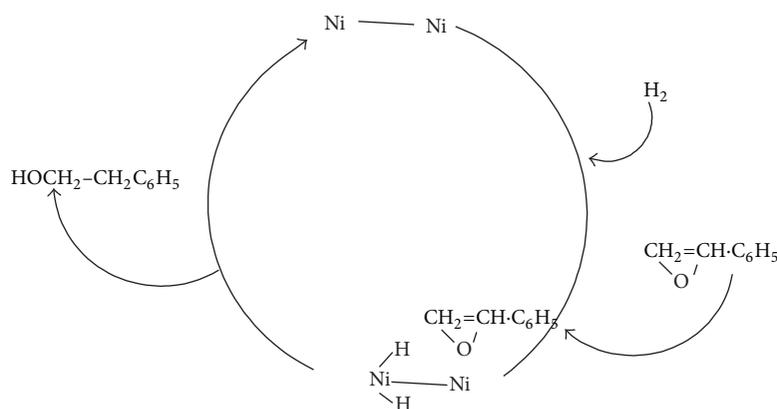


FIGURE 12: Model of the catalytic cycle for hydrogenation of styrene oxide over Ni catalyst.

results are presented in Figure 8. Conversion of styrene oxide, as well as yield and selectivity of 2-PEA, increased with pressure. At the same time yield of byproducts decreased with pressure. A maximum conversion of 99.42% of styrene and 78.3% yield of 2-PEA with selectivity of 78.8% could be achieved at a pressure of  $50 \text{ kg}\cdot\text{cm}^{-2}$ .

**3.6. Mechanism of the Reaction.** Most of mechanisms for hydrogenation of alkenes are based on the assumption that hydrogen is first atomized on the catalyst surface which is subsequently added to the double bond producing a saturated hydrocarbon. These descriptions are qualitative in general and there is no quantitative proof of the mechanism. In order to get a clue to the adsorption of hydrogen on the Ni surface and subsequent atomization we performed a density functional theory (DFT) calculation of the adsorption of hydrogen on Ni employing Gaussian 09 suite. We used Beck's three parameter hybrid method with the Lee, Yang, and Parr (B3LYP) exchange correlation functional to perform these

calculations. Geometries were optimized using standard 6-31 G\* basis set. Heat of adsorption was calculated using the following formula.

$E_{\text{ads}} = E_{(\text{adsorbate} - \text{substrate})} - (E_{\text{adsorbate}} + E_{\text{substrate}})$  and was calculated to be  $-77.59 \text{ kcal}\cdot\text{mol}^{-1}$ .

The optimized geometries of reactant model, product model, and transition state are shown in Figure 9 and the related potential energy surface is shown in Figure 10.

The atomic charges (coulomb) in the reactant models are, respectively,  $\text{Ni}_1 = 0.445$ ,  $\text{Ni}_2 = 0.332$ ,  $\text{O}_1 = -0.672$ ,  $\text{H}_1 = -0.082$ ,  $\text{H}_2 = -0.112$ ,  $\text{H}_3 = 0.126$ ,  $\text{H}_4 = 0.156$ ,  $\text{H}_5 = 0.122$ ,  $\text{H}_6 = 0.125$ ,  $\text{H}_7 = 0.124$ ,  $\text{H}_8 = 0.143$ ,  $\text{H}_9 = 0.154$ ,  $\text{H}_{10} = 0.164$ ,  $\text{C}_1 = -0.127$ ,  $\text{C}_2 = -0.164$ ,  $\text{C}_3 = 0.144$ ,  $\text{C}_4 = -0.167$ ,  $\text{C}_5 = -0.124$ ,  $\text{C}_6 = -0.125$ ,  $\text{C}_7 = -0.484$ , and  $\text{C}_8 = 0.021$ . Free nickel atom possesses no charge. Opposite charges on nickel atoms and negative charges on  $\text{O}_1$ ,  $\text{H}_1$ , and  $\text{H}_2$  suggest electrostatic nature of adsorption. All carbon atoms accept  $\text{C}_3$  and  $\text{C}_8$  bears negative charge. This can also be ascribed to adsorption of SO. It is worth noting that in the reactant model, the epoxide bond is broken and new bonds are formed

between O<sub>1</sub> and C<sub>7</sub> with Ni<sub>1</sub> and Ni<sub>2</sub>. The adsorbed reactant model is therefore something like an intermediate. The charge distribution in styrene oxide (SO) is shown in Figure 11. Higher atomic charge on oxygen in adsorbed SO compared to that in free SO suggests transfer of charge from Ni atoms to Oxygen atom. The enthalpy difference and activation energy are, respectively, found to be 85.30 and 123.03 kcal·mol<sup>-1</sup>. The catalytic cycle for the reaction is shown in Figure 12.

### Conflict of Interests

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

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