

Oxidation of Benzyl Alcohol in Liquid Phase Catalyzed by Oxides of Nickel

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Summary: The oxidation of benzyl alcohol in liquid phase catalyzed by nano sized nickel hydroxide and nickel oxide using water and toluene as solvent was studied. Benzaldehyde and benzoic acid were identified as the reaction products in alkaline aqueous medium, but with the toluene as a solvent benzaldehyde was the only product. Influence of different reaction parameters (speed of agitation, reaction period, flow of molecular oxygen and temperature) on the reaction performance was studied. Temkin adsorption model was found to be the best fit to experimental data. The reaction was found to be heterogeneous in nature in which catalyst can easily be separated from the reaction mixture by centrifugation.

Introduction

Nickel based oxides have been investigated for several years because they are important materials for many electrochemical systems especially alkaline systems like batteries, electrolyzers, fuel cells and their appreciable catalytic activities, good stabilities and low price. Due to the non-stoichiometric nature, oxide of nickel are oxygen rich, where nickel can be found in higher oxidation state in addition to its normal and stable oxidation state of +2 [1-7]. Different types of oxide are found to exist like NiO, NiO₂, Ni₂O₃, NiOOH, Ni(OH)₂, which can be used as catalyst for oxidation of organic compounds

Nakagawa, *et al.* [8] reported the use of nickel oxides as useful oxidizing agent for oxidation of alcohol, amines, phenols, hydrazones, sulfur compounds and nitriles. Konaka *et al.* [9] used nickel peroxide (NiO₂), prepared from nickel sulfate (NiSO₄) with sodium hypochlorite (NaOCl) in alkaline solution as catalyst for oxidation of benzhydrol and diphenylacetoneitrile, from which it can be concluded that one equivalent atom of available oxygen in nickel peroxide (NiO₂) correspond to two radical species. Christoskova *et al.* [10, 11] used nickel oxide as catalysts using the same preparation method as used by Nakagawa, *et al.* [8], for oxidation of phenol, formaldehyde and benzyl alcohol in alkaline aqueous medium [10, 11]. Ji and coworkers used nickel oxides prepared from Na₂CO₃ and Ni(NO₃)₂ in alkaline aqueous medium, and characterized them as Ni(OH)₂ [4] and NiO₂ [12] as catalyst for oxidation of alcohols, like benzyl alcohol,

cinnamyl alcohol, *para*-substituted derivatives of benzyl alcohol, secondary benzyl alcohol and hetero aromatic alcohols. However, in all these cases, the nickel catalyst used has been named differently based upon the supposed oxidation state of the nickel.

In the present work catalysts have been prepared by the same methods as used by Nakagawa, *et al.* [8] and Christoskova *et al.* [10, 11]. These catalysts have been characterized by using XRD, DRIFT, amount of excess and surface oxygen and their catalytic activity for benzyl alcohol oxidation in the liquid phase using molecular oxygen as oxidant.

Results and Discussion

Characterization of Catalyst

Fig. 1 shows the X-Ray diffractograms of catalysts. Using Scherer's equation, particle sizes were calculated as 6.2 nm, 6.1 nm and 12.4 nm for catalyst I, II and commercial NiO, respectively. Crystal structures were found to be hexagonal for catalyst I and cubic for catalyst II and commercial NiO. On comparison of XRD of these laboratory prepared catalysts with reported XRD, catalyst I is considered to be Ni(OH)₂ while catalyst II as NiO. Catalyst II and III have similar XRD patterns. The broadening of Peaks in Catalyst II could be due to the smaller particle size of catalyst II in comparison to catalyst III (commercial NiO).

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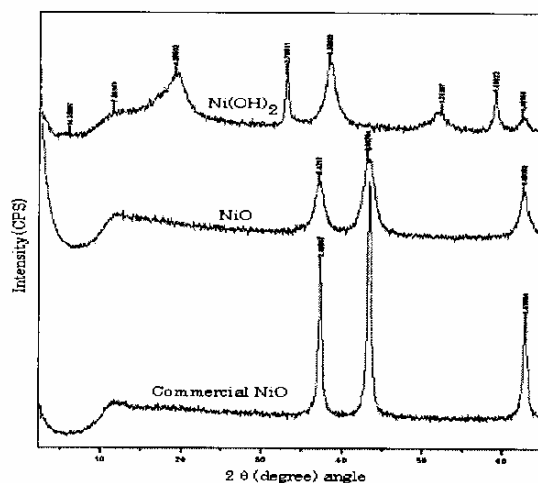


Fig. 1: XRD pattern of nickle oxide catalysts.

Table-1 shows the results of surface area analysis. It has been shown that catalyst II has larger surface area ($169 \text{ m}^2\text{g}^{-1}$) than catalyst I ($87.4 \text{ m}^2\text{g}^{-1}$) and III ($84.7 \text{ m}^2\text{g}^{-1}$). This could be due to the higher micro pore volume of catalyst II in comparison to catalyst I and III.

Table-1: Surface area and pore size analysis of the catalyst.

Catalyst	Surface Area (m^2g^{-1})	Porosity by BJH method	
		Pore volume (cc g^{-1})	Pore diameter (\AA)
$\text{Ni}(\text{OH})_2$	87.50	0.04	24.10
NiO (Lab)	169.10	0.08	23.90
NiO (comm.)	84.70	0.05	24.00

Fig. 2 shows SEM images of these catalysts. These images show that the particle sizes of these catalysts are in the range of micron size [4, 12-14]. Apparently, there is a contradiction between SEM and XRD results. However, XRD shows the size of the crystallites while a particle could be formed of several crystallite grains [13].

FTIR spectra of Catalyst I, II and commercial NiO are shown in Fig. 3. Bands in range $480\text{-}680$, $1500\text{-}1600 \text{ cm}^{-1}$ are assigned to Ni-O bond and physisorbed water molecules, respectively. A strong band at 3640 cm^{-1} in spectrum of catalyst I is assigned to OH ion. Considering the low penetration power of IR, it is obvious that it can only show the surface layers. All these three catalysts have different types of surface groups. These include various types

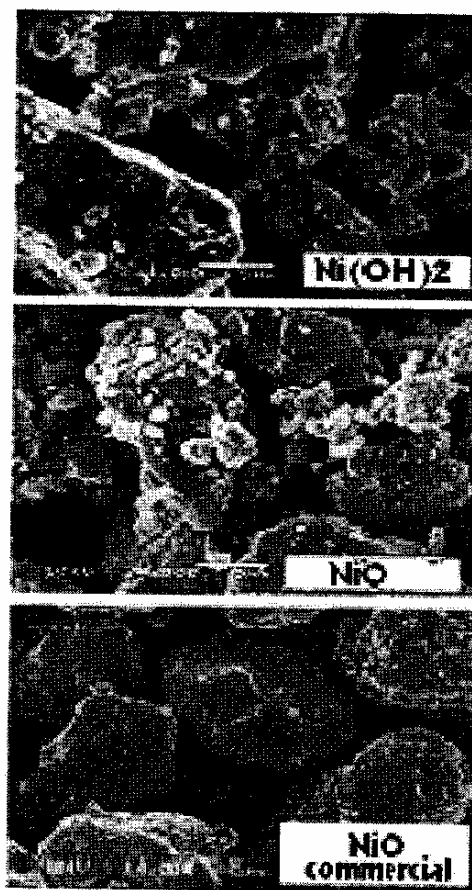


Fig. 2: SEM images of catalysts.

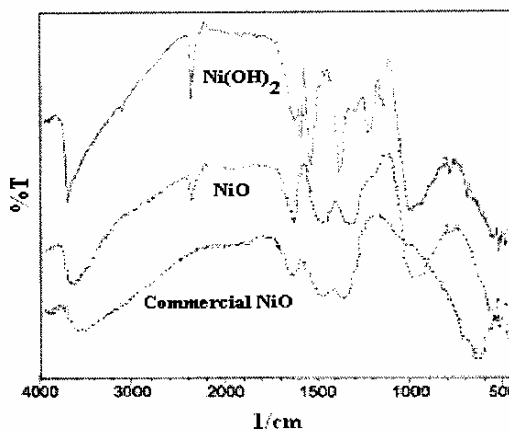


Fig. 3: Diffuse reflectance FTIR (DRIFT) spectra of catalysts.

of surface Ni-O bonds and surface OH groups. Based on comparison of these spectra with the reported FTIR spectra it is concluded that catalyst I is $\text{Ni}(\text{OH})_2$, confirming the XRD results. However, considering the FTIR spectra of catalyst II and III, it is concluded that these catalysts are having different oxygen groups at the surface [14-20]. This difference could be only limited to the surface layers and bulk of these catalysts could have the same crystalline structure as shown by XRD (Fig. 1).

Oxygen Content of the Catalysts

The available oxygen content and surface oxygen content in each catalyst is shown in Table-2. It also shows that the reactivity of the catalyst was found to be proportional to active oxygen, as shown in Table-2. The order of active oxygen and reactivity for oxidation of benzyl alcohol was found as $\text{Ni}(\text{OH})_2 > \text{NiO} > \text{Commercial NiO}$.

No Leaching of the Catalyst

The heterogeneous nature of the catalyst was confirmed by performing an experiment with catalyst and solvent for a pre-determined time and temperature. Catalyst was removed and reactant, benzyl alcohol, was added to filtrate and run the experiment. Absence of products confirmed the absence of leaching of catalyst to solvent. This was further confirmed by adding alkaline dimethyl glyoxime and bromine water to the filtrate, (which gives wine red coloration with nickel ion). The absence of coloration assured the heterogeneous nature of the catalyst [21].

Solvent Effect

Comparison of the activity of catalyst I and II for oxidation of benzyl alcohol was made in two solvents, i.e., water and toluene. Analysis of the reaction mixture showed that with catalyst I benzaldehyde was the only product when toluene was used as the solvent while benzaldehyde and benzoic

acid when water was used as solvent. In case of catalyst II, only benzaldehyde was the product in toluene as solvent. This catalyst was found inactive in aqueous medium.

Effect of Agitation

The process is typical slurry reaction having one liquid reactant. The effect of mass transfer on the rate of reaction was determined by studying the change in conversion at various agitation speeds from 50 to 900 rpm. The increase in agitation speed over 750 rpm has no effect on conversion indicating minimum effect of mass transfer resistance (Fig. 4).

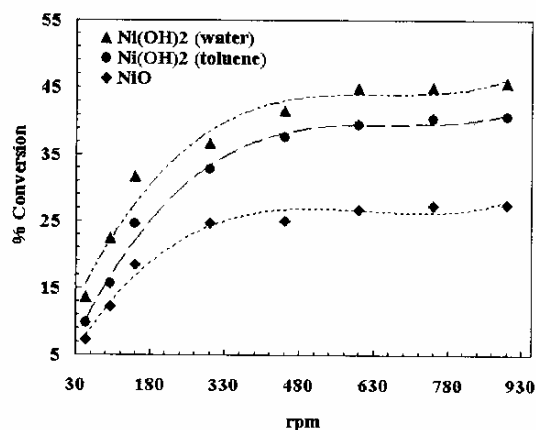


Fig. 4: Effect of stirring on the oxidation of benzyl alcohol.

Reaction conditions: benzyl alcohol 1mmol/5 mL solvent, time 60 min, catalyst 0.3 g.

Temperature Study

Temperature profile study was carried out at different temperatures (303-363 K) for one hour. It was found that conversion increase with increase with temperature. In water as solvent, conversion increases with increase in temperature up to 353 K

Table-2: Reactivity of the catalysts.

Catalyst	Active Oxygen (g-atom oxygen g ⁻¹ of catalyst)	Surface active oxygen (g-atom oxygen g ⁻¹ of catalyst)	Solvent	Conversion* (m.mole)
[Ni(OH) ₂]	3.50 x 10 ⁻⁴	2.90 x 10 ⁻⁴	Toluene	0.41
			Water	0.46
[NiO]	9.60 x 10 ⁻⁵	7.10 x 10 ⁻⁵	Toluene	0.28
			Water	No Reaction
[NiO (Commercial)]	5.40 x 10 ⁻⁵	4.40 x 10 ⁻⁵	Toluene	0.11
			Water	0.07

*m.mol of BzOH converted in the first 60 minutes.

and then decreases, while in case of toluene as solvent, it increases linearly with temperature. Arrhenius equation was applied to conversion obtained after one hour. The apparent activation energy, for nickel hydroxide as catalyst, was found to be 31.5 kJmol^{-1} and 39.8 kJmol^{-1} using water and toluene as solvents respectively. When nickel oxide was used as catalyst and toluene as solvent, activation energy was calculated as 54.5 kJmol^{-1} (Fig. 5). These activation energies show that these reactions are free from mass transfer limitation.

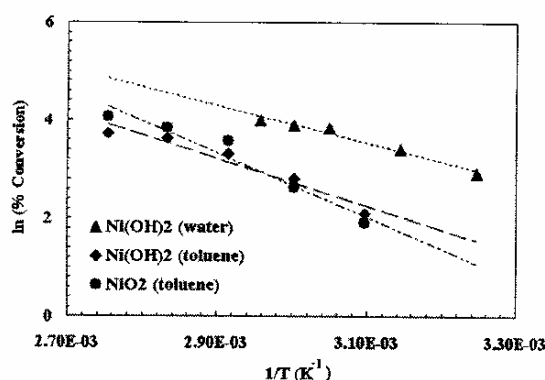


Fig. 5: Arrhenius plots for benzyl alcohol oxidation. Reaction conditions: benzyl alcohol 1mmol/5 mL solvent, time 60 min, catalyst 0.3 g

Time Profile

The time course study for oxidation of benzyl alcohol was monitored periodically. This investigation was carried out at 328 K and 363 K, using water and toluene as solvents, respectively, for 360 minutes. With increase in reaction time, conversion of benzyl alcohol increases linearly reaching a maximum value and becomes constant or slower as shown in Fig. 6. Conversions for the first 60 minutes are shown in Table-2.

Effect of Flow Rate

Effect of flow rate of oxygen was determined by studying the conversion of benzyl alcohol in toluene at different flow rate of molecular oxygen. Fig. 7 shows that conversion increases with flow rate up to 60 mL/min and then decreases, because at high flow rate the contact time of oxygen with benzyl alcohol decreases.

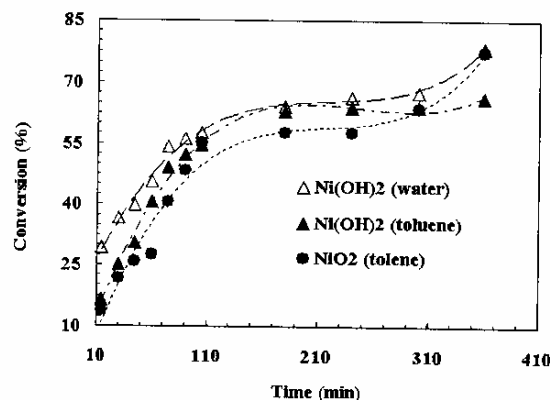


Fig. 6: Time profile for the oxidation of benzyl alcohol.

Reaction conditions: benzyl alcohol 1mmol/5 mL solvent, catalyst 0.3 g. Temp. 328K (water), 363 K (toluene), rpm 900.

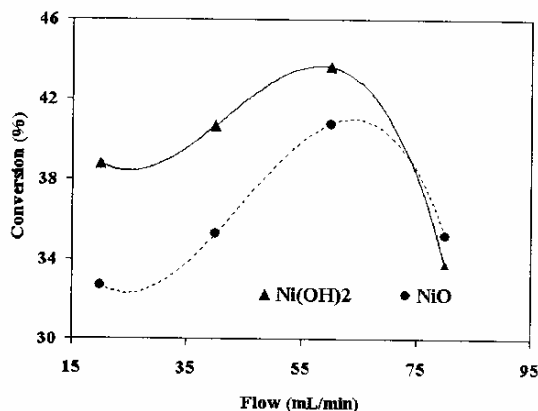


Fig. 7: Effect of flow rate of oxygen.

Reaction conditions: benzyl alcohol 1mmol/5 mL toluene, time 60 min, catalyst 0.3 g. Temp. 363 K, rpm 900.

Re-use of Catalyst

It was found that catalyst I, Ni(OH)_2 has the same activity after use when it was treated with NaOCl , however, catalyst II, NiO and catalyst III, commercial NiO lose their activity when these catalysts were reused with out further treatment (Fig. 9).

Table-3: Kinetics parameters.

Catalyst	Apparent rate coefficient ($k_r K_1$)	K_2
Ni(OH) ₂ (Water)	1.20×10^{-3}	15.62
Ni(OH) ₂ (Toluene)	1.40×10^{-3}	16.21
NiO (Toluene)	1.90×10^{-3}	13.18

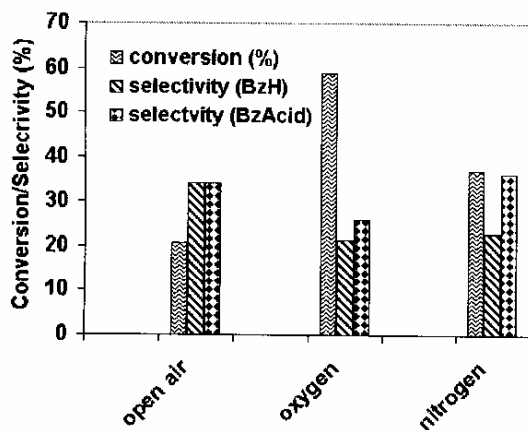


Fig. 8: Effect of atmosphere on conversion and selectivity of the products.

Reaction conditions: benzyl alcohol 1mmol/5 water, time 60 min, Temp 328 K catalyst 0.3 g (catalyst I, Ni(OH)₂), rpm 900

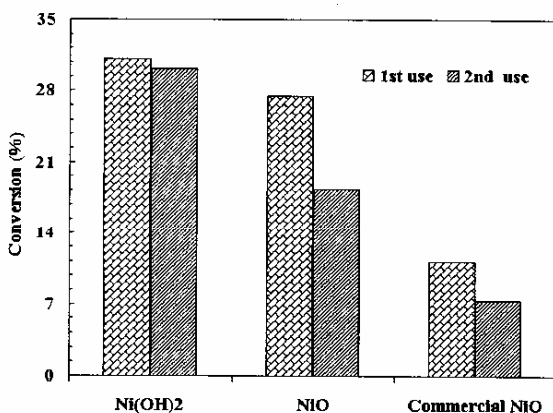


Fig. 9: Re-use of the catalysts.

Reaction conditions: benzyl alcohol 1mmol/5 mL toluene, time 60 min, catalyst 0.3 g Temp 363 K, rpm 900.

Kinetic Analysis

From the effect of stirring and apparent activation energy, it is concluded that the oxidation of

benzyl alcohol is most probably taking place in kinetically controlled regime. This is a typical slurry reaction having catalyst in solid state and reactants in liquid and gas phase.

As discussed earlier [22] the reaction kinetic analyses were performed by fitting the experimental data to one of the three possible mechanisms of heterogeneous catalytic oxidation:

- The Langmuir-Hinshelwood mechanism (L-H)
- The Mars-van Krevelen mechanism (M-K) or
- The Eley-Rideal mechanism (E-R)

The L-H mechanism involves adsorption of the reacting species on the active sites at the surface, followed by an irreversible, rate-determining surface reaction to give products.

The rate Law for Langmuir-Hinshelwood Model is:

$$\text{Rate} = k_r \theta \quad (1)$$

Where k_r is the rate coefficient and θ is the fraction of the surface covered. Using the Langmuir adsorption isotherm for replacing θ in equation (1) would give equation (2)

$$\text{Rate} = \frac{k_r K [\text{BzOH}]}{1 + K [\text{BzOH}]} \quad (2)$$

where K is the adsorption coefficient for benzyl alcohol (BzOH). Similarly replacing θ by Freundlich isotherm equation (1) would transform to equation (3):

$$\text{Rate} = k_r K [\text{BzOH}]^{1/n} \quad (3)$$

where K is the adsorption coefficient and n (>1) is a constant. The use of Temkin isotherm for θ in equation (1) would give equation (4):

$$\text{Rate} = k_r K_1 \ln K_2 [\text{BzOH}] \quad (4)$$

where K_1 and K_2 are constants related to the heat of adsorption, which decreases linearly with surface coverage.

The experimental results were fitted to equations (2), (3), (4) and to the rate equations derived according to M-K and E-R mechanisms, as described in our earlier paper [22, 23], using non-linear least square regression analysis. Among all these equations only equation (4) was applicable to the data as shown in Figs. 10-13.

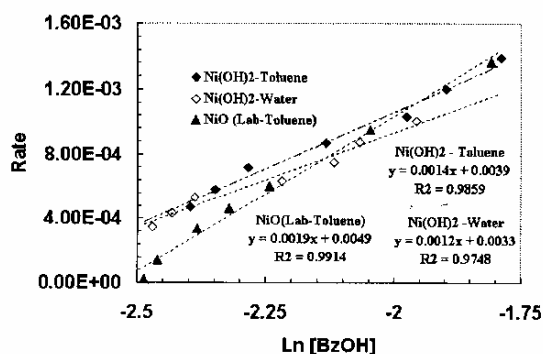


Fig. 10: Application of the Temkin adsorption isotherm (Equation 4) to the data obtained from benzyl alcohol oxidation.

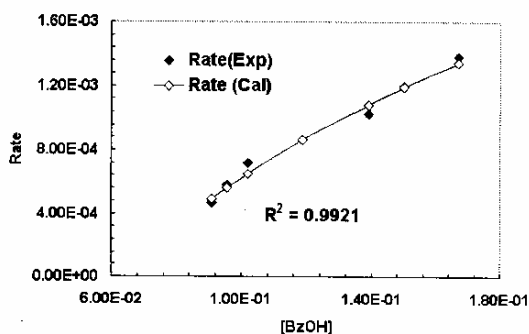


Fig. 11: Non-linear least square fit for Temkin model using $\text{Ni}(\text{OH})_2$ as catalyst and toluene as solvent.

Applicability of the Temkin adsorption isotherm to the data reveals that the surfaces of the oxides of nickel studied are heterogeneous in nature. However, the variation in the heat of adsorption with surface coverage is linear. This would argue that the difference in the nature of the active sites on the surface from each other is not very large. They may consist of various types of combination of Ni^{n+} , oxygen and hydrogen on the surface as shown by IR

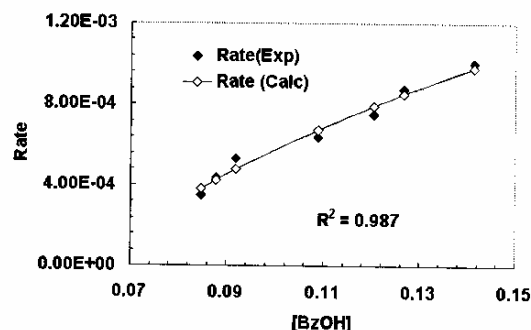


Fig. 12: Non-linear least square fit for Temkin model using $\text{Ni}(\text{OH})_2$ as catalyst and water as solvent.

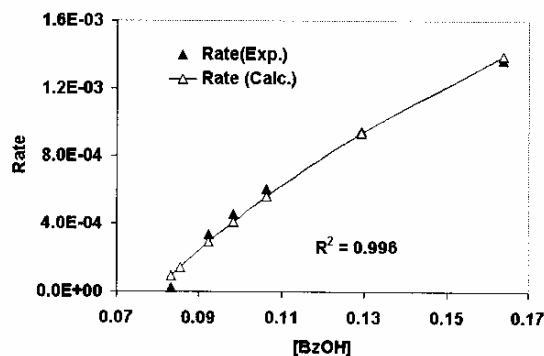


Fig. 13: Non-linear least square fit for Temkin model using NiO as catalyst and toluene as solvent.

peaks, which are in the region of OH, Ni^{n+} and oxygen bonds (Fig. 3). The inactivity of NiO for oxidation of benzyl alcohol in aqueous solution could be due to the effect of developed water clusters on hydrophilic sites that prevent or hinder the adsorption of benzyl alcohol on the surface.

Experimental

Materials

Sodium hypochlorite, sodium hydroxide, nickel sulfate hydrate, sodium thiosulfate, sodium carbonate, nickel nitrate, acetic acid, potassium iodide, potassium iodate, silver nitrate, benzyl alcohol, benzaldehyde, benzoic acid, nickel oxide and ethanol were supplied by Merck, BDH, Accros and Scharlau and were used without further purification. Nitrogen and oxygen gases were supplied by BOC, Pakistan Ltd. These gases were further purified by

passing through proper filters (C.R.S Inc. 202268). Traces of oxygen from nitrogen gas were removed by using specific oxygen traps (C.R.S Inc. 2002223).

Preparation of catalyst

Catalyst I (Nickel hydroxide, $Ni(OH)_2$)

Catalyst I (Nickel hydroxide) was prepared according to the literature [8] (by sodium hypochlorite (NaOCl 15%, Scharlau, SO 0436), sodium hydroxide (NaOH, Merck, 6462) and nickel sulfate hexa hydrate ($Ni(II)SO_4 \cdot 6H_2O$, Scharlau NI 0179). A mixture of sodium hypochlorite and sodium hydroxide was prepared by adding 42 g of sodium hydroxide in 300 mL of 6 % sodium hypochlorite. Another solution was prepared by taking 130 g of nickel sulfate hexa hydrate in 300 mL of distilled water. First solution was added drop wise to the second one in 30 minutes while stirring at 293 K. The mixture was stirred for 30 minutes more in order to ensure complete reaction. The resulted black nickel hydroxide was collected by filtration, and was washed by distilled water for several times to remove the active chlorine. Test for active chlorine was performed by adding silver nitrate to the filtrate. Absence of white precipitate on addition of silver nitrate to filtrate confirmed the absence of active chlorine.

Catalyst II (Nickel Oxide (NiO))

Catalyst II (NiO_2) was prepared by a wet chemical method [12]. 16.8 g of Na_2CO_3 and 22.2 g of NaOH in 360 mL de-ionized water were taken in a conical flask. A second solution containing 54 g of $Ni(NO_3)_2 \cdot 6H_2O$ in 180 mL of de-ionized water was prepared and added drop wise to the first solution while stirring magnetically. The resultant green slurry was heated for 18 hours at 338 K. The dark slurry was filtered, washed with de-ionized water until neutral and dried at 338 K for 12 hours. The resultant stuff was calcined at 673 K for 3.5 hours.

Catalyst III, a commercial NiO (BDH) was used as received for comparison purposes.

Characterization of the Catalysts

XRD analyses were performed on a JEOL (JDX-3532) X-Ray Diffractometer using CuK_α radiation with a tube voltage of 40 KV and 20mA current

The BET surface area was determined by nitrogen adsorption at 77.4 K, using Quanta Chrome NOVA 2200e. Prior to adsorption measurement, the respective catalysts were degassed at 373 K for a period of 1 hour.

The morphologies of the catalysts were analyzed by scanning electron microscope (JEOL-JSM-5910, Japan). The elemental analysis (EDX) was performed by Energy Dispersive Spectrometer (EDS) Inca Oxford.

The FTIR spectra were recorded in KBr on IR Prestige 21, Shimadzu, Japan instrument in the range of $500-4000\text{ cm}^{-1}$.

The available oxygen content was determined by using chemical method as employed by Nakagawa *et al.* [8]. 2.5 g potassium iodide was dissolved in 20 mL of 36% acetic acid. About 0.2 g of the catalyst was added and allowed to stand for 15 minutes in the atmosphere of molecular nitrogen to liberate iodine. The solid catalyst was removed by filtration and the liberated iodine was titrated against 0.1 N sodium thiosulfate solution using starch as indicator. Available oxygen was calculated by relation

$$\text{Oxygen Content} = \frac{\text{Na}_2\text{S}_2\text{O}_3(\text{mL}) \times N(\text{Na}_2\text{S}_2\text{O}_3)}{1000 \times \text{Catalyst}(\text{g}) \times 2}$$

Surface oxygen was determined by using chemical method as employed by Christoskova *et al.* [24]. 0.2 g of the catalyst and about 2 g potassium iodide were added to 15 mL buffer solution of pH 7.1 and vigorously shaken in nitrogen atmosphere for 15 minutes. The reaction mixture was then filtered, acidified with 1 N HCl and the liberated iodine was titrated against 0.1 N sodium thiosulfate solution using starch as indicator.

Oxidation Procedure

All the experiments were carried out in a magnetically stirred round bottom Pyrex glass three-necked batch reactor, of 50 mL capacity, provided with reflux condenser and mercury thermometer, for measuring reaction temperature. Reaction temperature was maintained by using hot plate. A pre-determined quantity of benzyl alcohol (1 m.mol / 5 mL of solution in water or toluene) was taken in

reactor. After getting the required temperature, (328 K in aqueous and 363 K in toluene), the reactor was charged with 0.3 g catalyst (Nickel hydroxide / nickel oxide) (and/or 0.1 g NaOH in aqueous). Samples were withdrawn from the reaction mixture at predetermined time intervals. Catalyst was separated by centrifuge at 1500 rpm (Digi system Laboratory Instruments Inc.) for 5 minutes.

Analysis

Reactant and products were analyzed by using UV-Visible spectrophotometer. Concentration of benzyl alcohol was determined by fourth order derivative method, using pre-determined calibration curve [25].

Conclusion

The results of the present study concludes that $\text{Ni}(\text{OH})_2$ can be used as catalyst for conversion of benzyl alcohol to benzoic acid in both aqueous and organic. In comparison, NiO can be used as heterogeneous catalyst in organic solvents only. Temkin isotherm was found to be applicable to the data for both $\text{Ni}(\text{OH})_2$ and NiO . This shows that the conversion of benzyl alcohol to benzoic acid is taking place by similar mechanism on the surface of $\text{Ni}(\text{OH})_2$ and NiO . It also reveals the heterogeneous nature of the surface site responsible for this conversion.

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