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## Mild and Efficient Oxidation of Primary and Secondary Alcohols Using NiO<sub>2</sub>/Silica Gel System (Solvent Free)

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**Abstract:** Oxidation of alcohols by nickel peroxide and silica gel system using grinding method has been studied. In the oxidation process, NiO<sub>2</sub> is converted to NiO, which is recoverable.

**Keywords:** Synthesis, Oxidation, Alcohols, Nickel peroxide, Solvent free.

### Introduction

The powerful common oxidants are mostly derived from metals located around the middle of the first transition series. In contrast, the metals at the end of the first transition series are not capable of forming high-valent oxides and thus remain less studied. However, among these metals, nickel can readily form peroxide (NiO<sub>2</sub>) which was used for oxidation of several substrates<sup>1</sup>. It was proved that a variety of alcohols could be converted to the corresponding carbonyl compound by treatment with nickel peroxide in organic solvents<sup>2</sup>. In 1974, George and Balachandran published an excellent review covering most of the research which was carried out using nickel peroxide as oxidant<sup>3</sup>. Since then, only sporadic reports have appeared in the literature dealing with oxidation of various organic substrates by nickel peroxide<sup>4-7</sup>.

Solvent free reactions have become important due to increasing demand for clean and efficient protocols<sup>8</sup>. The elimination of volatile organic solvents in organic syntheses is a most important goal in 'green' chemistry. Solvent-free organic reactions make syntheses simpler, save energy and prevent solvent wastes, hazards and toxicity<sup>9</sup>. The oxidation of alcohol to carbonyl compounds is an important transformation in organic synthesis and because of its significant role, the development of newer oxidative protocols continues to receive attention in spite of the availability of several methods to accomplish this objective. The use of supported reagent has gained popularity because of the improved selectivity, reactivity and associated ease of manipulation<sup>10-11</sup>.

## Experimental

Chlorine gas that is generated from 20 g of  $\text{KMnO}_4$  and 120 mL of concentrated  $\text{HCl}$  (37%) was slowly bubbled through a solution of  $\text{KOH}$  (36 g) in 100 mL of water for one hour period, with stirring. Simultaneously, this system is chilled in an ice bath. To the resulting yellow solution of  $\text{KClO}$ , was added 11.63 g (0.04 mol) of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  portion-wise in 20 min while stirred in an ice bath. A fine black precipitate formed which was filtered and washed with deionized water and dried by means of a vacuum desiccator under calcium chloride. The yield is 95% (3.42 g of  $\text{NiO}_2$ ).

### *Oxidation of alcohols*

To a homogeneous mixture of 2 mmol of nickel peroxide and 0.5 g of silica gel (grinding for about 2 min), 1 mmol of an alcohol was added. The mixture is ground very well and the reaction is monitored by TLC. When the reaction completed, the product was washed with  $\text{CH}_2\text{Cl}_2$ . Then, the  $\text{CH}_2\text{Cl}_2$  was evaporated in a rotary system. After removing of the solvent the product was isolated and characterized by comparing its spectroscopic data with an authentic sample.

### *Recovery of nickel peroxide*

The spent nickel peroxide was first washed with acetone and then with water to remove the adhered organic compounds and often impurities. The solid was then stirred with  $\text{KClO}$  solution (about ten times the quantity of  $\text{NiO}_2$ ) for 30 min. The recovered  $\text{NiO}_2$  was filtered, washed with water and kept dried for new oxidation process.

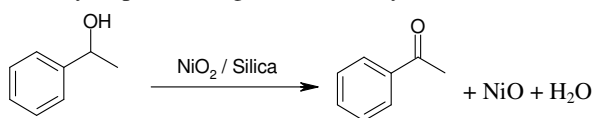
## Results and Discussion

Nickel peroxide is prepared by Nakagawa *et al.*<sup>1</sup> method, with some modification<sup>12</sup>. We examined various mineral supports such as alumina, wet alumina and silica gel 60 and found that silica gel 60 provided the best result in terms of grinding and the reaction time. All of the alcohol oxidation reactions herein were carried out in silica supported nickel peroxide and the grinding time is less than 10 min (Table 1).

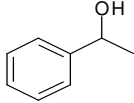
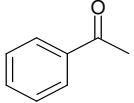
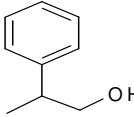
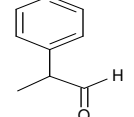
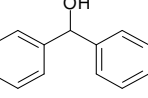
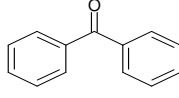
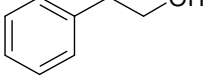
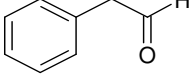
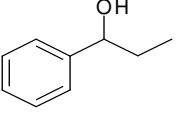
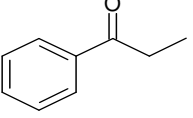
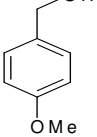
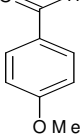

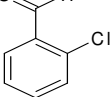
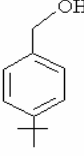
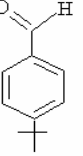
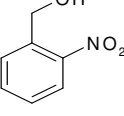
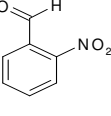
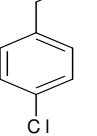
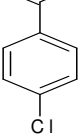
1-Phenyl ethanol is selected as a probe substrate and after examination, the magnitude of silica gel 60 is determined. Thus, 1-phenyl ethanol (1mmol), nickel peroxide (2 mmol) and various magnitude of silica gel 60 (0.25, 0.5, 1, 1.5 and 2 g) is mixed. The mixture is grinding and the reaction was monitored by TLC. The products were then isolated and characterized by comparison of their spectroscopic data with those reported in the literature. The stoichiometric oxidation is expressed as follows:

All of the alcohols (Table 1) are converted to carbonyl derivative when treated with nickel peroxide in the presence of silica gel. When the reaction occurred in a solution, 1-7 hours is needed to complete it. Also the yield of the product is fairly good<sup>1-3,12</sup>. But in solvent free method, the reaction time is very short (5-10 min) and the yield is high (71-93%).

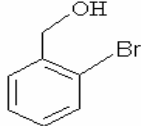
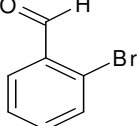
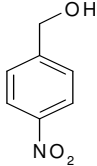
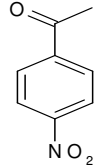
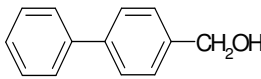
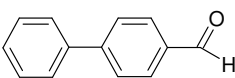
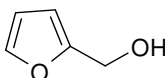
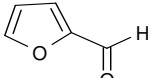
After oxidation process, the nickel peroxide is converted to nickel oxide that can be easily recoverable by washing in acetone. Thus, after oxidation no material remains in the environment and this case is very important to green chemistry.



**Table 1.** Oxidation of alcohols by means of nickel peroxide/silica gel system

Entry	Substrates	Products	Time, Min	Yield, %
1			5	84
2			5	75
3			7	80
4			5	85
5			5	75
6			5	93
7			7	82
8			7	79
9			9	71
10			7	85

*Cont...*

11			7	80
12			7	83
13			7	77
14			7	80

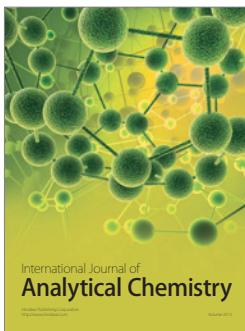
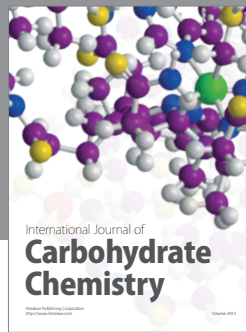
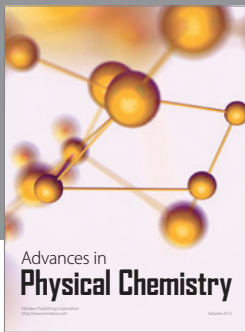
In conclusion, nickel peroxide and silica gel system is a rapid and selective oxidative protocol for alcohol when compared with the conventional solution phase reaction.

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