



A Green Protocol for Selective Oxidation of Alcohols to Carbonyl Compounds Comparative Studies with Various Ni Heterogeneous Catalysts with O₂ and H₂O₂ as Oxidants.

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Abstract

The mini article highlights the versatility of Ni-Al hydrotalcite (HT) catalysts using molecular oxygen as oxidant compared to Ni/SiO₂, Ni and other catalysts reported for oxidation of alcohols to carbonyl compounds. Among the catalysts reported in literature to date, Ni-Al HT is the best catalysts suited for molecular oxygen initiated oxidation of alcohols to carbonyl compounds. Benzylic alcohols, substitute benzylic, allylic, α -ketols and substituted cinnamyl alcohols are oxidized to aldehydes and ketones. Ni in association with oxide of aluminium is the active precursor for the title reaction and Ni-Al HT catalysts was characterized by TPR, XRD, IR, and DSC. Ni/SiO₂ also exhibited some activity for oxidation of alcohols to carbonyl compounds with 30% H₂O₂ as oxidant, whereas, Ni/TiO₂ did not exhibit activity for the title reaction which is due to uneven distribution of Ni on TiO₂ surface. Hence, from these results, it is evident that Ni hydrotalcite catalysts with molecular oxygen is the active catalysts for alcohol oxidation to carbonyl compounds which have valuable applications in fine chemical industry and academia.

Keywords: Ni-Al hydrotalcite; heterogeneous catalysts; Ni/SiO₂; Ni/TiO₂; oxidation reactions.

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1. Introduction

The oxidation of allylic, benzylic and alicyclic alcohols to aldehydes or ketones functionality is the foundation in organic synthesis, from an industrial and academic point of view. Aldehydes and ketones have huge applications in fine chemical synthesis, whereas, from an environmental point of view, catalytic oxidation reactions with green oxidants like O₂, H₂O₂, CO and CO₂ as the green foundations, are good examples of highly atom efficient and greener developments. Many homogeneous catalyst reactions using stoichiometric oxidation of alcohols have been well documented in literature with the classical reagents. Cr, TsNBr₂, KMnO₄, SeO₂, MnO₂, author in reference [1, 4] has been an efficient combination for such oxidations [2, 8] performed under highly acidic conditions. Substrates having acid sensitive functionalities may not allow such acidity. The most popular reagent used is the Jones reagent for the oxidation of alcohols to carbonyl compounds. Using H₂O₂ as oxidant is desirable as its by-product is water. Oxidation of alcohols using homogeneous catalysts La, Ru, Co, Mo, Pd, Pt, Ru V, Mn, Co, Ru complex in reference [9, 12] well reported in literature many disadvantages use high temperature, pressure, additives, harsh reaction conditions preclude the wide use such reagents. The use of a single oxygen donor such as *m*-chloroperbenzoic acid [13, 15], persulfate (oxone) [13, 14], periodic acid (H₅IO₆) [15], and sodium hypochlorite [16] as the stoichiometric oxidant enables the use of catalytic amounts of TEMPO or derivatives thereof. Sheldon in reference [11] report supported metal ions and heterogeneous catalysts requires tedious procedure, higher temperature and pressure for oxidation of alcohols. The authors in [15, 17, 27] noted that Noyori and his colleagues sodium tungstate and 0.002 mol% of the phase transfer agent, methyltrioctylammonium bisulfate, [CH₃ (n-C₈H₁₇)₃N]+HSO₄ which rate yields. The authors in [27] noted that Muldoon and his colleagues showed the utilization higher pressure and high temperature for Pd (II) complexes of anionic N,O-chelating ligands, at 100 °C and 45 bar O₂/N₂ (8 : 92) for aerobic oxidation of 2-octanol to 2-octanone. The use of Cu complexes with external addition of K₂CO₃, KtBuO, BBCO, DIBAH have accelerated the reaction at elevated temperatures [28, 32]. The water-soluble dinuclear ruthenium(II) complex, Ru₂(fê-OAc)₃(fê-CO₃), catalyzes the aerobic oxidation of a variety of primary alcohols in water at 80 °C and ambient pressure, but it requires high catalyst loadings (10 mol% per Ru) [33]. The use of manganosilicate molecular sieves as heterogeneous catalysts for the oxidation of alcohols with peroxydisulfate as the terminal oxidant has been described [34]. The Montanari protocol, although widely applicable, has several environmental and/or economic drawbacks. It is not waste free because at least one equiv of sodium chloride is produced per molecule of alcohol oxidized, besides, the use of hypochlorite as oxidant can also lead to the formation of chlorinated by-products. Additional limitations are the use of 10 mol% bromide as a co-catalyst and dichloromethane as a solvent [35].

Selective oxidation over CoAl-CrO₄ HT reported the oxidizing ability of Cr (VI) with tert-butyl hydroperoxide (TBHP) as oxidant for oxidation of adamantane [36]. Different oxidants like molecular oxygen, H₂O₂, TBHP as oxidants at higher temperatures were also reported [37, 39]. The authors in [40] noted that Su and his colleagues studied oxidation over different transition metal oxides and found that MnO₂ was effective and reusable under solvent free microwave conditions [40]. The authors in [41, 42] noted that Ji and his colleagues used MnFe_{1.8}Cu_{0.15}Ru_{0.05}O₄ as oxidation catalysts with molecular oxygen and found that Ru within the system was active for oxidation.

The authors in [43, 44] noted that Yang and his colleagues reported CuMn/Al₂O₃ for benzyl alcohol oxidation and achieved 90% with >99% selectivity towards benzaldehyde. Mn-Ni hydroxide as effective catalyst for these reactions. The authors in [44] noted that Kaneda and his colleagues reported Mn oxide generated from hydrotalcite as efficient catalyst for aerobic oxidation of alcohols [44]. Heteropolyoxometales, HCl-SiO₂ catalysts for oxidation of alcohols resulted in 52% table 1 [45].

In order to replace these catalayts and reagents heterogeneous catalysts have been the best catalysts used in fine chemical synthesis for decades. Nickel based catalysts have wide application in petrochemical industry and dates back to many years ago. Nickel-based catalysts meet these criteria in a whole range of chemical reactions and are therefore often the preferred choice. Amongst others, nickel-based catalysts find applications in petroleum refining including hydro-treating (e.g., hydro-denitrogenation to reduce NO_x and hydro-desulphurisation to reduce SO_x), hydrocracking and hydro-processing as well as steam reforming. In these processes, the active nickel is typically nickel metal that is finely dispersed over porous aluminium or a silica-based carrier resulting in a large catalytically active surface.

Recently few reports have appeared with Ni heterogeneous catalysts for oxidation of alcohols to carbonyl compounds. Diverse types of oxides are found to exist like Ni porphyrin, Ni Cr HT, NiO, NiO₂, Ni₂O₃, NiOOH, Ni(OH)₂, NiMnO, which are used as catalyst for oxidation of organic compounds [46-48]. The The authors in [52] noted that Nakagawa and his colleagues reported the use of nickel oxides as useful oxidizing agents for oxidation of alcohols, amines, phenols, hydrazones, sufur compounds and nitriles. The authors in [53] noted that Konaka and his colleagues reported the use of nickel peroxide NiO₂ prepared with nickel sulphate NiSO₄ with sodium hypochlorite NaOCl in alkaline solution as catalysts for oxidation of benzhydrol and diphenyl acetonitrile from which concluded that one equivalent atom of available oxygen in nickel peroxide NiO₂ correspond to two radical species. The authors in [54] noted that Christoskova and his colleagues reported the use of nickel oxide as catalysts using the same method the authors in [54] concluded that oxidation of phenol. The authors in [55] concluded the use of Nickel oxides prepared by NiNO₃ and Na₂CO₃ and characterized them as Ni(OH)₂ and NiO catalysts for oxidations of alcohols_i.e., benzyl alcohol, substituted benzyl alcohol and cinnamyl alcohols investigated the oxidation of alcohols and similarly used heterocyclic alcohols and named these Ni catalysts depending on their oxidation states. The authors in [46] noted the use of Ni AL HT cat. The authors in [47] concluded the use of Ni catalysts for oxidation of beanzlylic, allylic, and α ketols to carbonyl compounds employing transition metal heterogeneous catalysts Ni-Al HT with O₂, and Ni/SiO₂ with H₂O₂ as oxidant where quantitative yields were obtained and the characterization of catalysts were studied [46, 48].

2. Results and discussion

We report here comparison of various Ni heterogeneous catalysts used for oxidation of alcohols by use of various oxidants reported so far which is represented in table 1 where with NiO oxidation of benzylalcohol resulted into benzoic acid S.No 2. In order to identify the best suitable catalysts the author has compared a series of nickel catalysts and from the results its is evident that the best evolved catalysts for oxidation of alcohols with Ni-Al HT using molecular oxygen as the sole oxidant the concluded in [46, 48].

The authors in reference [47] concluded the use of NiSiO₂ catalysts for oxidation of alcohols using H₂O₂ as oxidant the results were encouraging and their focus was on characterization of NiSiO₂ catalysts. In addition, the generation of Cr-based side products may be viewed which offers many advantages over classical reagents used as homogeneous catalysts [15].

The use of Ni-Al HT for oxidation of allylic & benzylic alcohols to carbonyl compounds stands its importance in oxidation reaction due to its activity. P-nitro benzaldehyde is obtained from p-nitrobenzyl alcohol at 100 % conversion with maximum selectivity and menthol gave only 50% conversion whereas with Ni SiO₂ catalysts [47] only 80% conversion was achieved when 30% H₂O₂ oxidant was utilized when compared to Ni-Al HT [46]. Extensive characterization studies with XRD, IR and SEM were carried out for NiSiO₂ catalysts at 2, 5 and 10%. The oxidation of substituted benzylic alcohols irrespective of the electron-donating or -withdrawing substituent at the aromatic nucleus, is faster than that of benzyl alcohol. It is crucial to evaluate the oxidation of 1-phenylethanol to acetophenone in the presence of air instead of oxygen occurred in 50% yield (12 h), which indicates that the presence of CO₂ present in air had not poisoned the reaction. This method was successful to synthesize α -dicarbonyl compounds, which are useful intermediates in the synthesis of heterocyclic compounds, by the oxidation of α -ketols. Cinnamyl alcohol and its substituted counterparts are selectively oxidized to their corresponding α,β -unsaturated aldehydes without affecting the double bond. In addition, the oxidation of the aliphatic primary allyl alcohol, geraniol, provides the corresponding α,β -unsaturated aldehyde selectively in a moderate yield of 46% in 8 h [46].

The best Ni catalyst was evaluated by testing various Ni Al HT catalysts for the activation of molecular oxygen, a study on various hydrotalcite catalysts of different Ni:Al ratios prepared [46-52] by different coprecipitation agents and Ni-Al₂O₃ in the oxidation of 4-nitrobenzyl alcohol with molecular oxygen was undertaken. Whereas series of hydrotalcites containing different ratios of Ni-Al, such as 2:1, 2.5:1, and 3:1, were screened and Cat. A Ni-Al 2:1 was found to be the most active. The calcined and rehydrated forms of the hydrotalcite cat. A were further evaluated in the oxidation reactions [46, 47]. Table 1 describes different catalysts studied so far in literature cited in comparison to these catalysts and conditions. Ni-Al HT is a better developed catalysts than other catalysts which selectively resulted into aldehyde compared to the catalysts reported in literature which is presented in table 2 S.No. 3, 5, 8-10,12, 15, 16, 18 which afforded acids in some most cases additives are utilized to increase the rate of a reaction, increase of temperature, pressure more time is required with catalysts to show the efficiency of the system. The author reports that Ni-Al HT catalysts showed excellent activity after 4 cycles where Ni-Al HT retained its activity. In table 1 S. No 18 benzyl alcohol on oxidation gave benzyl acetate where TBHP was used as oxidant with NiAlCr N catalysts. This shows that the catalyst was active for ester formation via aldehyde formation.

In table various catalysts that have been used far for oxidation of alcohols to carbonyl and acid compounds are illustrated. From this table its evident that the there is no selectivity for the formation carbonyl compounds.

In table 2 the authors [46] concluded reported the oxidation of benzylic, allylic, α -ketals to corresponding aldehydes and ketones. In this Table substituted benzylic alcohols are converted to aldehydes and yield ranges from 31% to 98% in 2 to 15 hrs.

The substituent attached to the benzylic positions, methoxy, nitro, ethyl, phenoxy, chloro, and substituted cinnamyl alcohols are oxidized to cinnamaldehydes without affecting the double bonds also α -ketols are oxidized to ketones. All these have no effect during the reaction, they are not disturbed this is due to the activity of the catalysts, NiO which is insitu formed i.e. formation of nickel oxide in association with oxide of aluminium is the active precursor for selective oxidation of alcohols to carbonyl compounds [47].

Table 1: various catalysts used for oxidation of alcohols to aldehydes and ketones.

S.No	Substrate	Catalysts/Conditions Oxidant	Product	Conversion	Reference
1.	Benzyl alcohol	H ₂ O ₂ Polyoxometalate 90C, 5h	Aldehyde/Acid	52%	44
2.	Benzyl alcohol	NiO, O ₂ , 60 mins	Acid formed	100%	52-55
3.	Benzyl alcohol	H ₂ O ₂ -Ni Porphyrin, 353 K, 4h.	Aldehyde	30%	51
4.	Benzyl alcohol	Ru Complex, DMA, 80 C, 20 h, O ₂ .	Aldehyde	95%	33-34
5.	Benzyl alcohol	CuCl, Ligand, Ionic liquid, DBADH, O ₂ , solvent, 80 C	Aldehyde	90-97% Additives are many	28
6.	Phenethanol	TSNBr ₂ 30 min RT,	Aldehyde	99%	3
7.	Benzyl alcohol	Mn(by) ₂ complex TBHP, RT	Aldehyde	99% additives many added.	16
8.	Benzyl alcohol	Co, Mn, Salen catalysts H ₂ O ₂ , ACN solvent 343K.	Aldehyde	36% some acid	17
9.	Benzyl alcohol	KMnO ₄ Cat Cu complex, TBHP, CAN, H ₂ O, 3h	Ald	72-90%	1-2
10.	Benzyl alcohol	HCl/SiO ₂ , 4h, H ₂ O ₂	Ald	70-80%	45
11.	Benzyl alcohol	La ₂ O ₃ -TBHP, CH ₃ CN, 10-48 h, 85-95%.	Acid is formed	100%	12
12.	Benzyl alcohol	NiCrO ₄ , 65C, 6h, TBHP	Acid formed	29%	49
13.	S-Benzyl alcohol	O ₂ , 10 bar, CuSO ₄ , 80°C, diamine ligand, base water.	Ald	38%	29
14.	Benzyl alcohol	Cu diamine, alkaline, water, Tempo, K ^t BuO.	Ald	85	30
15.	Benzhydrol	Cu complex, Cu-DABCO, TEMPO, 100C.	Aldehyde	100%	29-32
16.	Benzyl alcohol to B.Acetate	TBHP-95 C, O ₂ , 130°C, CoAl ₂ -N-CrO ₄ , NiAl ₂ -N-CrO ₄	Ald, Acid	71% Ald, Acid 29%	49
17.	Benzyl alcohol	Cu TEMPO, 17h, 100°C, O ₂ .	Phenethanol	2%, 100% our	31

Table 2: Oxidation of various alcohols by Ni-Al hydrotalcite (Ni-Al 2:1 Cat.A) using molecular oxygen [46].

Entry	R'	R''	Time	Yield
1.	C ₆ H ₅	H	12	31
2.	.m-MeOC ₆ H ₅	H	2	88
3.	o-NO ₂ C ₆ H ₅	H	6	76
4.	p-NO ₂ C ₆ H ₅	H	6	98
5.	o-MeOC ₆ H ₅	H	1.5	86
6.	o-MeC ₆ H ₅	H	6	72
7.	m-ClC ₆ H ₅	H	15	63
8.	m-PhOC ₆ H ₅	H	10	71
9.	p-MeOC ₆ H ₅	H	10	88
10.	o-ClC ₆ H ₅	H	10	87
11.	p-ClC ₆ H ₅	H	10	73
12.	O,P-MeOC ₆ H ₅	H	12	88
13.	C ₆ H ₅	CH ₃	12	95
14.	p-MeOC ₆ H ₅	CH ₃	6	84
15.	p-MeC ₆ H ₅	CH ₃	2	96
16.	p-NO ₂ C ₆ H ₅	CH ₃	3	92
17.	C ₆ H ₅	C ₆ H ₅	1.5	95
18.	C ₆ H ₅ CO	C ₆ H ₅	2.5	93
19.	C ₆ H ₅	C ₆ H ₅ (OH)CH	1.5	93
20.	C ₆ H ₅	CH ₂ CH ₃	7	72
21.	C ₄ H ₃ OCO	C ₄ H ₃ O	3	96
22.	C ₆ H ₄ CH=CHCH ₂	H	6	88
23.	o-NO ₂ C ₆ H ₄ CH=CHCH ₂	H	10	84
24.	p-MeOC ₆ H ₄ CH=CHCH ₂	H	10	96
25.	p-BrC ₆ H ₄ CH=CHCH ₂	H	12	95

The oxidation of benzhydrol, cinnamyl alcohol, menthol to its respective products with 10% Ni/SiO₂ using 30% H₂O₂ as oxidant resulted into 20% conversion, with 100% selectivity Table 3 [47]. 2, 5, 10% Ni/SiO₂ catalysts were utilized, 10% Nickel silica was the most active catalyst this was due to Ni being well distributed which was confirmed by SEM studies. For 2%, 5%, 10% Ni/TiO₂ catalyst, which proved to be inactive, was due to uneven distribution of nickel on titania surface and authors in [47] concluded as characterized of these catalysts by XRD, IR, SEM.

From these results, it's evident that Ni-Al HT catalyst for oxidation of alcohols to carbonyl compounds which is more active catalysts which utilizes molecular oxygen as oxidant compared to Ni silica catalysts utilizes H₂O₂ as oxidant using Ni/SiO₂ catalysts which less active due to less formation of nickel oxide species during the reaction which decreased the progress of reaction which is characterized by XRD, and SEM instruemnts.

Table 3: Selective oxidations Aromatic alcohols to aromatic aldehydes or ketones in acetonitrile [47].

Starting material	Product	Conversion (%)	Selectivity (%)
Benzhydrol	Benzophenone	100	100
Cinnamyl alcohol	Cinnamaldehyde	20	100
Menthol	Menthone	20	100

The Ni-Al Hydrotalcite catalysts have been characterized by XRD, IR, TPR and from these characterization results its evident that nickel in association with oxide of aluminium is the active precursor for oxidation of alcohols to carbonyl functional group. To date this catalysts with molecular oxygen initiated oxidation of alcohols to carbonyl group stands to be the best active catalysts compared to the results in presented in table 2 [46].

3. Conclusions

These results above articulates the potential significance of Ni-Al hydrotalcite catalysts compared to Ni/SiO₂. Ni metal has many applications in petrochemical sector and other allied chemical industries. In this mini article comparative studies have been discussed for Ni-Al hydrotalcite, Ni/SiO₂ and other catalysts reported in literature to date on oxidation of alcohols to carbonyl compounds. Ni-Al HT is best catalysts suited for molecular oxygen initiated for oxidation of alcohols to carbonyl compounds and oxidation of benzylic alcohols, substitute benzylic, allylic, α -ketols and allylic alcohols are oxidized to aldehydes and ketones. Ni in association with oxide of aluminium is the active precursor for the title reaction and Ni Al HT catalyst was characterized by TPR, XRD, IR, and DSC. In comparison to Ni Al and other catalysts Ni/SiO₂ also exhibited some activity for oxidation of alcohols to carbonyl compounds with 30% H₂O₂. Ni/TiO₂ didn't execute any activity for the title reaction which is due to uneven distribution of Ni on TiO₂ surface. The authors conclude from these outcome that Ni-Al hydrotalcite catalysts stands to date is active catalysts for alcohol oxidation to carbonyl compounds.

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