variant of it, may not be too dissimilar to the pathway adopted by nature in the biosynthesis of this natural product. Studies to further elucidate the mechanism of the postulated oxidative dimerization process and the application of the developed chemistry to the construction and biological evaluation of hybocarpone libraries are in progress.

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The First Example of Activation of Molecular Oxygen by Nickel in Ni-Al Hydrotalcite: A Novel Protocol for the Selective Oxidation of Alcohols**

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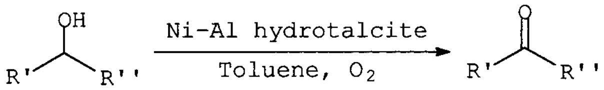
The oxidation of α-ketols as well as allylic and benzylic alcohols to a carbonyl functionality is the foundation of many important current industrial and fine-chemical processes. Several methods are available to effect this conversion and continuous attention is drawn to newer and selective methods of oxidation.[1] Catalytic oxidation with molecular oxygen is particularly attractive from an economical and environmental point of view.[2] The oxidation of alcohols employing molecular oxygen requires co-oxidants such as aldehydes, *N*-hydroxyphthalimide, diethyl azodicarboxylate, hydroquinone, or nitrosonium ions to accomplish the catalytic cycle with catalysts based on Ru and Co,[3] Cu,[4] and Zr,[5] while molecular oxygen as the sole oxidant is sufficent when catalysts based on Pt,[6] Rh,[7] Pd,[8] Ru,[9] Co,[10] V,[1e] and Os[1f] are used. To the best of our knowledge no report is available in the literature in regard to the activation of molecular oxygen by a nickel catalyst.

The use of heterogeneous catalysts in the liquid phase offers several advantages over homogeneous ones, such as ease of recovery and recycling, atom utility, and enhanced stability in the oxidation of alcohols. Layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTLCs) have recently received much attention as basic catalysts.[11] We report herein the first direct activation of molecular oxygen by nickel in Ni-Al hydrotalcite as demonstrated by the selective oxidation of various kinds of α-ketols as well as benzylic and allylic alcohols (Scheme 1) at atmospheric pressure. Incidentally, this is also the first report of the selective oxidation of α-ketols by a solid oxidant catalyst.



Scheme 1. Oxidation of allylic and benzylic alcohols in the presence of molecular oxygen.

In order to identify and develop the best Ni catalyst for the activation of molecular oxygen, a study on various hydrotalcite catalysts of different Ni:Al ratios (prepared[12] by different coprecipitation agents) and Ni:γ-Al_2O_3 in the oxidation of 4-nitrobenzyl alcohol with molecular oxygen was undertaken (Table 1). A 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. The activity of the calcined catalyst was considerably reduced, whereas the activity was slightly lowered on rehydration. Hydrotalcite cat. **B** (Ni:Al 2:1) was prepared by an ammonia

Table 1. Oxidation of 4-nitrobenzyl alcohol by different nickel catalysts using molecular oxygen.[a]

Entry	Catalyst	Time [h]	Yield [%][b]	Specific activity $[\mathrm{mmol\,g^{-1}\,h^{-1}}]$[c]
1	Ni-Al HTLC (2:1, cat. **A**)	6	98	0.65
2	Ni-Al HTLC (2:1, rehydrated)	6	80	0.53
3	Ni-Al HTLC (2.5:1)	6	78	0.51
4	Ni-Al HTLC (3:1)	6	37	0.24
5	Ni-Al HTLC (2:1, calcined)	21	58	0.11
6	Ni-Al (cat. **B**)	20	47	0.09
7	Ni:γ-Al_2O_3 (2%)	20	no reaction	–
8	Ni:γ-Al_2O_3 (5%)	20	no reaction	–
9	Ni:γ-Al_2O_3 (10%)	20	no reaction	–

[a] All reactions were performed with 2 mmol of substrate in 10 mL of toluene using 0.5 g of catalyst under oxygen at 90°C in the specified time. [b] Yields after column chromatography. [c] Specific activity: mmol of product obtained per gram of catalyst per hour.

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coprecipitation method and showed moderate activity. There was practically no reaction when the Ni:γ-Al$_2$O$_3$ catalyst with different compositions was used. Therefore, it is concluded that Ni-Al hydrotalcite cat. **A** was the best catalyst for an effective oxidation of 4-nitrobenzyl alcohol.

The effect of the organic solvents on the oxidation was examined by choosing 4-nitrobenzyl alcohol as the model substrate. Very little oxidation product was obtained with polar solvents such as acetonitrile and methanol (29 and 5% yields, respectively), while nonpolar solvents such as benzene, hexane, cyclohexane, and toluene led to 4-nitrobenzaldehyde in yields of 66, 86, 66, and 98%, respectively, in 6 h. The optimum temperature for the oxidation reaction was 90 °C, and further increase of temperature had no positive effect on the rate of the reaction.

Catalyst **A**, proved to be the best catalyst in our studies, and was further evaluated for the oxidation of various kinds of α-ketols, as well as benzylic and allylic alcohols (Table 2) to their corresponding carbonyl compounds using molecular oxygen as the sole oxidant. Although the oxidation of benzyl alcohol (Table 2, entry 1) with cat. **A** is low yielding, the oxidation of other substituted benzyl alcohols (Table 2, entries 2–12) proceeds in excellent yields. It is notable that the benzyl alcohols (Table 2, entries 1–12) are oxidized selectively to their corresponding aldehydes under the reaction conditions used. Secondary benzylic alcohols (Table 2, entries 13–21) are oxidized quantitatively in the present catalytic system at a faster rate than primary ones. This observation is in contrast to the study reported by Kaneda et al., using Ru hydrotalcites,[9] wherein primary benzylic alcohols were oxidized at a faster rate. The rate of oxidation of substituted benzyl alcohols, irrespective of the electron-donating or -withdrawing substitutent at the aromatic nucleus, is faster than that of benzyl alcohol. It is significant to note that 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 CO$_2$ present in air had not poisoned the reaction. By using our method it is possible to synthesize α-dicarbonyl compounds, which are useful intermediates in the synthesis of heterocyclic compounds, by the oxidation of α-ketols (Table 2, entries 18, 21). This result is quite impressive, since all the methodologies described earlier for the oxidation of α-ketols generate toxic wastes. Although the recently reported VOCl$_3$-mediated[1e] catalytic oxidation of α-ketols produces no toxic wastes, recovery of the catalyst from the reaction medium is difficult. It is significant that the oxidation of α-furoin to α-furil is a quite useful method for the synthesis of α-dicarbonyl compounds in high yields (Table 2, entry 21). The another unique advantage of this method is the one-pot oxidation of vicinal diols to α-dicarbonyl compounds in quantitative yields (Table 2, entry 19). Cinnamyl alcohol and its substituted counterparts (Table 2, entries 22–25) 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. However, the oxidation of aliphatic primary and secondary alcohols such as 1-decanol and 2-octanol affords the corresponding carbonyl derivatives in low yields (19 and 20%, respectively) in 10 h under these conditions. Furthermore, cat. **A** can be reused for several cycles without loss of its activity and selectivity. No reaction occurred when the reaction was conducted with the filtrate obtained after removal of the solid catalyst after the reaction, which indicates that the active ingredient was not leached out of the solid catalyst. The reused catalyst exhibited a similar hydrotalcite powder X-ray diffraction (XRD) pattern, even after the sixth cycle.

Table 2. The oxidation of various alcohols by Ni-Al hydrotalcite (Ni:Al 2:1, cat. **A**) using molecular oxygen.

Entry	R′	R″	Time [h]	Yield [%][a]
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 (94)[b]
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

[a] Yields of isolated products. [b] Yield after the 6th cycle.

The observed order of the specific activity in the oxidation is: Ni-Al hydrotalcite (cat. **A** as synthesized) > rehydrated Ni-Al hydrotalcite > Ni-Al hydrotalcite (Ni:Al 2.5:1) > Ni-Al hydrotalcite (Ni:Al 3:1) > Ni-Al calcined hydrotalcite > Ni-Al (cat. **B**) $\gg$ Ni:γ-Al$_2$O$_3$. A temperature-programmed reduction (TPR) profile (Figure 1) of all the catalysts indicates that free NiO is reduced at low temperature (400 °C; T_{max}) and NiO in association with aluminum oxide is reduced at higher temperature (500 °C; T_{max}).[12c] The TPR of the samples of Ni:γ-Al$_2$O$_3$ indicate the presence of free NiO only, while the samples of Ni-Al hydrotalcite prepared by the coprecipitation agents, NaOH/Na$_2$CO$_3$, and ammonia display both free NiO and NiO in association with aluminum oxide. The inert nature of Ni:γ-Al$_2$O$_3$ in the oxidation of alcohols indicates that free NiO is the inactive species in the oxidation reactions. The activation of molecular oxygen by all the samples of Ni-Al hydrotalcites, as evident by the oxidation of alcohols, is attributed to the presence of Ni in association with aluminum oxide. The TPR profile of Ni-Al hydrotalcites prepared by NaOH/Na$_2$CO$_3$ precipitation displayed a shoulder at lower temperature which grows on increased free NiO content,

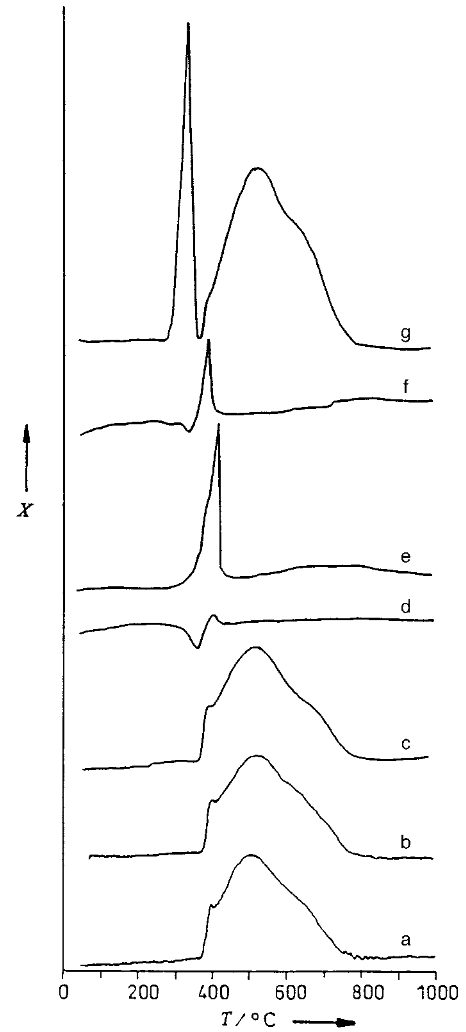


Figure 1. TPR profiles plotted as amount of hydrogen consumed (X in arbitrary units) versus temperature [°C] of a) Ni-Al hydrotalcite (cat. **A**), b) Ni-Al hydrotalcite (Ni:Al 2.5:1), c) Ni-Al hydrotalcite (Ni:Al 3:1), d) Ni:γ-Al_2O_3 (2%), e) Ni:γ-Al_2O_3 (5%), f) Ni:γ-Al_2O_3 (10%), g) Ni:Al (cat. **B**).

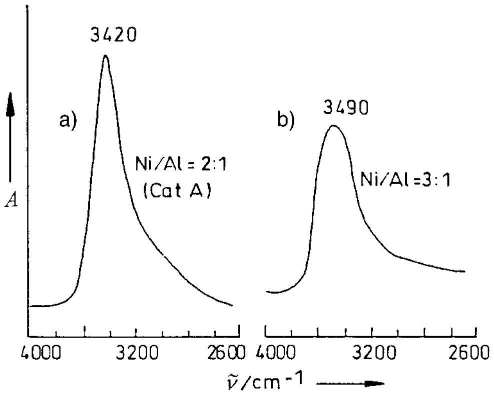
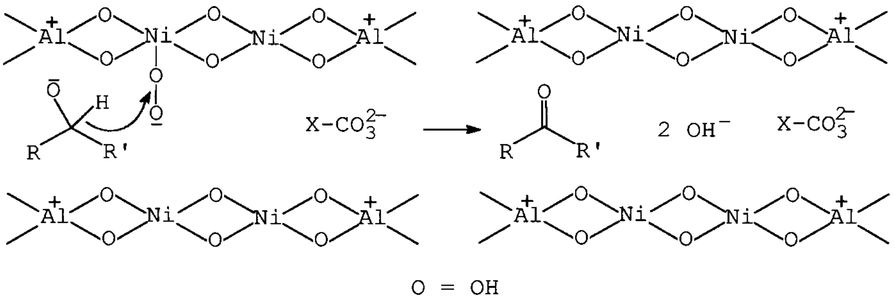


Figure 2. Hydroxy stretching vibrations of a) Ni-Al hydrotalcite, cat. **A** (Ni:Al 2:1) and b) Ni-Al hydrotalcite (Ni:Al 3:1).

namely from Ni:Al 2:1 to 3:1, although XRD analysis showed a crystalline hydrotalcite pattern. The rate of oxidation of alcohols, which is in the increasing order: 3:1 < 2.5:1 < 2:1 (Ni:Al), is in good agreement with the TPR data of hydrotalcites. The examination of IR spectra of various compositions of Ni-Al hydrotalcites shows that the vibrational stretching frequency of the hydrogen atom in a hydroxide group of the cat. **A** with a 2:1 Ni:Al ratio appears at lower wavenumber ($3420\,cm^{-1}$) and has a smaller half-width than the other compositions, which indicates there is a more-ordered cation distribution (Figure 2) in the former.[13] The higher specific activity ($0.65\,mmol\,g^{-1}h^{-1}$) of Ni-Al hydrotalcite (cat. **A**) as synthesized (Table 1, entry 1) is thus attributed to the presence of Brønsted basic hydroxyl groups and also an excellent layered structure that offers access of the reactants to the active sites of the catalysts. All these results identify Ni in association with aluminum oxide as the active species for the activation of molecular oxygen.

Further, the higher activity of hydrotalcite cat. **A** as synthesized is also a consequence of the presence of carbonate anion in the interlayers, which is in aggreement with the results obtained in the oxidation by Ru hydrotalcite.[9] The slightly lowered specific activity of $0.53\,mmol\,g^{-1}h^{-1}$ (Table 1, entry 2) obtained upon rehydration of the hydrotalcite cat. **A**, in which inclusion of carbonate anions is precluded, strengthens the assumption that the presence of carbonate anions enhance the activity in the synthesized cat. **A**. Upon calcination, the hydrotalcite cat. **A** displayed considerable reduction in activity as a consequence of the loss of both Brønsted hydroxyl groups and carbonate anions: a result that corroborates the above hypothesis.

A plausible reaction mechanism (Scheme 2), therefore, involves the formation of an alkoxide on interaction of the alcohol with the Brønsted OH group (basic site) of the brucite layer originally present in Ni-Al hydrotalcite. The hydrotalcite further reacts with molecular oxygen to form a peroxide. Hydride transfer then takes place from the alkoxide to the peroxide to generate the carbonyl product, with regeneration of an OH anion of the brucite layer. This in turn reacts with a fresh molecule of alcohol to give alkoxide and initiate another cycle. Aluminum is well documented both in Oppenauer oxidation and Meerwein–Ponndorf–Verley (MPV) reduction, as well as in the recently reported MPV reduction[11e] of ketones by Mg-Al hydrotalcite, to favor the formation of alkoxide, while the neighboring Ni atom



Scheme 2. Proposed mechanism for the oxidation.

facilitates the formation of a peroxide species with molecular oxygen. The hydride transfer from the aluminum alkoxide of hydrotalcite is effected by the neighboring peroxide on the nickel atom. Hydrotalcites are homogeneous mixtures of heterobimetallic composition having a periodic composition of M^{II} and M^{III} ions. The cationic order of cat. **A** as revealed by IR studies suggests that the presence of one aluminum atom for every two nickel atoms substituted alternately in the hydrotalcite provides the optimum use of nickel in cat. **A**, better than is possible with the other compositions, and is thus responsible for the display of higher activity.

In conclusion, Ni-Al hydrotalcite efficiently oxidizes a wide range of alcohols, such as allylic and benzylic, and α-ketols to the corresponding carbonyl compounds under mild reaction conditions by employing molecular oxygen as the stoichiometric oxidant. This process is not only economically viable but also applicable to large-scale reactions. Moreover, the high yields of oxidized products can be obtained in heterogeneous catalysis using hydrotalcites as catalysts.

Experimental Section

Various catalysts with varied composition of Ni-Al hydrotalcites (Ni:Al = 2:1 (cat. **A**), 2.5:1, 3:1) were prepared by coprecipitation employing NaOH/Na_2CO_3 as described in the literature.[12a] Catalyst **A** was rehydrated according to our previous report[11b] and calcined at 450 °C in a flow of air. Ni-Al hydrotalcite (Ni:Al 2:1, cat. **B**) was prepared by coprecipitation using ammonia solution.[12b] The samples of nickel impregnated on γ-alumina (2, 5, and 10 %) were prepared by adding the required amounts of $Ni(NO_3)_2 \cdot 6H_2O$ in water to γ-alumina and stirring occasionally while heating on a water bath till complete evaporation of water had occurred. The residue was dried in an oven at 110 °C for 16 h.

Typical oxidation procedure: Oxygen was bubbled at atmospheric pressure through a reaction mixture containing *p*-nitrobenzyl alcohol (2 mmol) and catalyst (0.5 g) in toluene (10 mL) at 90 °C under stirring. The reaction was monitored by thin-layer chromatography and purified by column chromatography (hexane:ethyl acetate, 95:5, v:v) to afford the *p*-nitrobenzaldehyde as a pale yellow solid: 0.296 g (98 %), m.p. 105 °C, ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.1$ (d, $^3J(H,H) = 8.3$ Hz, 2H, aryl-H), 8.4 (d, $^3J(H,H) = 8.3$ Hz, 2H, aryl-H), 10.2 (s, 1H, CHO); IR (KBr pellets) $\tilde{\nu} = 1700$ cm^{-1} (sh, C=O); MS (70 eV) m/z (%): 151 (64) $[M^+]$, 150 (61) $[M^+ - H]$, 105 (20) $[C_7H_5O^+]$, 77 (93) $[C_6H_5^+]$, 51 (100) $[C_4H_3^+]$.

TPR profiles were recorded on Micromeritics (Auto Chem 2910) using 0.05 g of the uncalcined sample. The sample was dried at 120 °C in an argon flow and then helium was replaced by a flow of a mixture of 5 % hydrogen in helium at room temperature.

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Highly Reactive Sm^{II} Macrocyclic Clusters: Precursors to N_2 Reduction[**]

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Divalent samarium complexes have been prepared with a wide variety of ligand systems,[1] but the extreme level of reactivity and the uniqueness of transformations displayed by the samarocene derivatives[2] was never reproduced. To date, the Sm^{II} polypyrrolide derivatives[3] are the only systems which share with decamethylsamarocene[4] the ability to react with an exceedingly inert molecule such as dinitrogen. Unlike samarocene, however, these species may perform *four-electron* reduction of dinitrogen, thus indicating that their reducing power is particularly strong. Particularly versatile with this respect are divalent samarium complexes of dipyrrolide dianions,[5] which are reminiscent of the ansa-metallocene ligand systems. So far these species have led to three novel dinitrogen complexes.[6, 7] However, attempts to isolate the presumably highly reactive divalent precursors

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