

Nanocrystalline Magnesium Oxide-Stabilized Molybdenum: An Efficient Heterogeneous Catalyst for the Aerobic Oxidation of Alcohols to Carbonyl Compounds

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Abstract: A nanocrystalline magnesium oxide-stabilized molybdenum(VI) complex catalyzed the oxidation of primary and secondary alcohols to carbonyl compounds in excellent yields using molecular oxygen as stoichiometric oxidant. The nanomaterials with their three-dimensional structure and defined size and shape act as suitable supports for metal

complexes. The catalyst can be reused for four runs without any significant loss of activity.

Keywords: alcohols; heterogeneous catalysis; molybdenum; nanocrystalline magnesium oxide; oxidation; oxygen

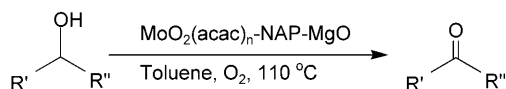
Introduction

Oxidation reactions increase the number of functional groups and are useful in the synthesis of complex organic molecules.^[1] The oxidation of alcohols to the corresponding aldehydes or ketones is an important process, and numerous oxidizing reagents such as dichromate, permanganate, manganese dioxide, selenium dioxide and molecular bromine have been traditionally employed to accomplish this transformation.^[2] However, the oxidizing reagents used in stoichiometric amounts in these reaction are sometimes toxic and may produce enormous amounts of metal salts as waste. From an economic and environmental perspective, catalytic aerobic alcohol oxidation represents a promising and green alternative. The use of molecular oxygen as the terminal oxidant has received great attention as it has such benefits as low cost, improved safety, abundance and produces water as the sole by-product. The oxidation of alcohols employing molecular oxygen require co-oxidants such as aldehydes, *N*-hydroxyphthalimide, diethyl azodicarboxylate, hydroquinone, or nitrosonium ions to accomplish the catalytic cycle, with catalysts based on Ru,^[3] Ru-Co,^[3c] Cu^[4] and Zr.^[5] Molecular oxygen as the sole oxidant is sufficient when catalysts based on Pt,^[6] Rh,^[7] Pd,^[8] Ru,^[9] Co,^[10] Mo,^[11] Os,^[12] Ni^[13] and V^[14] are used. Although these procedures for the oxidation of alcohols with molecular oxygen are efficient, most of them are

homogeneous systems. Despite the high activity and selectivity of homogeneous metal catalysts, obstacles in catalyst separation and recycling often make practical and industrial applications difficult. Minisci and co-workers reported highly selective aerobic oxidation of alcohols to carbonyl compounds catalyzed by the persistent tetramethylpiperidine *N*-oxyl (TEMPO) radical in combination with Mn(II) and Co(II) nitrates^[15a] and the non-persistent phthalimide *N*-oxyl (PINO) radical generated *in situ* from *N*-hydroxyphthalimide (NHPI), associated with a Co(II) salt^[15b] as catalysts. These catalytic systems appear to be convenient for industrial applications, because of the high selectivity, possibility of recovering and recycling the catalysts, the simple and mild reaction conditions and the cheap oxidant.^[15c] Heterogeneous catalysis provides the opportunity for easy separation and recycling of the catalyst, simple purification of products and possibly continuous or multiple processing of compounds. Recently, nanocrystalline metal oxides, such as nanocrystalline MgO and CaO, have been reported to be extremely effective for the destructive adsorption of numerous environmental toxins and several chemical warfare agents such as sarin and mustard gas.^[16–18] Nanocrystalline MgO is also used as an effective heterogeneous catalyst for various organic transformations.^[19] Recently, we have reported the use of nanocrystalline MgO as an inorganic solid sup-

port for the transition metal complex-catalyzed asymmetric epoxidation of unfunctionalized alkenes.^[20]

We herein report the efficient oxidation of primary and secondary alcohols to the corresponding carbonyl compounds in excellent yields using molybdenum acetylacetonate stabilized on nanocrystalline magnesium oxide (aerogel-prepared MgO, NAP-MgO) in the presence of molecular oxygen (Scheme 1).



Scheme 1. Oxidation of primary and secondary alcohols in the presence of molecular oxygen.

Results and Discussion

Preparation of MoO₂(acac)_n-NAP-MgO Catalyst

Various magnesium oxide crystals [commercial MgO, CM-MgO (SSA; 30 m² g⁻¹), conventionally prepared MgO, NA-MgO (SSA; 250 m² g⁻¹), aerogel-prepared MgO, NAP-MgO (SSA; 590 m² g⁻¹)] were treated with MoO₂(acac)₂ in dry THF under a nitrogen atmosphere to afford samples of MoO₂(acac)_n-MgO. The exchange capacity of MoO₂(acac)₂ on various MgO supports showed that the maximum amount of MoO₂(acac)₂ is loaded on NAP-MgO when compared to other MgO samples. This is attributed to the presence of large surface ionic charges on NAP-MgO (Scheme 2).

Characterization of MoO₂(acac)_n-NAP-MgO

The MoO₂(acac)_n-NAP-MgO catalyst was characterized using several techniques, including XRD, XPS, AAS, TGA-DTA and IR. The X-ray photoelectron spectroscopic (XPS) analysis of the MoO₂(acac)_n-

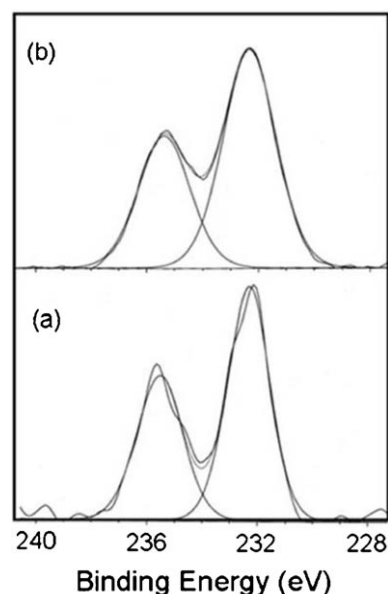
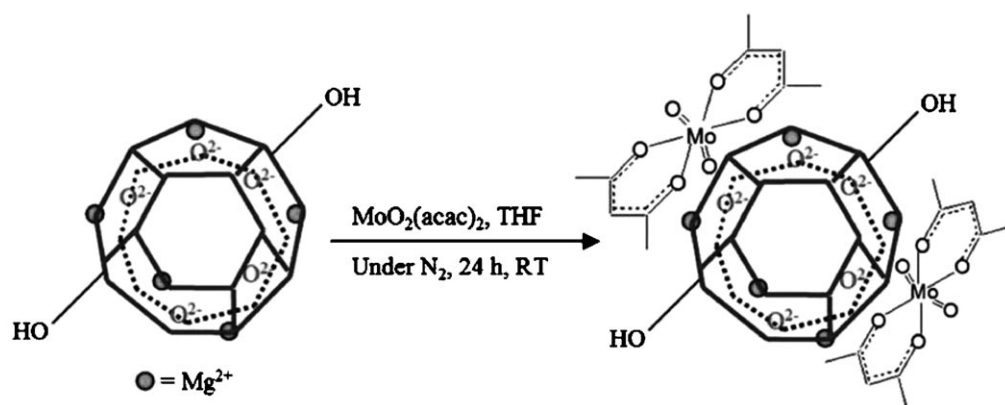


Figure 1. XPS trace of (a) fresh MoO₂(acac)_n-NAP-MgO and (b) used MoO₂(acac)_n-NAP-MgO.

NAP-MgO catalyst shows Mo 3d lines at 232.35 eV (3d_{5/2}) and 235.52 eV (3d_{3/2}) (Figure 1 a), characteristic of molybdenum metal in the +6 oxidation state. An XPS high resolution scan of the Mo 3d level of the used catalyst (Figure 1 b) shows lines at 232.30 eV (3d_{5/2}) and 235.38 eV (3d_{3/2}), which reconfirms the presence of molybdenum in the +6 oxidation state. As the take-off angle was decreased, the penetration level of the radiation decreased. The concentration of Mo⁶⁺ detected decreased as the penetration depth increased, indicating that the Mo⁶⁺ resides on the surface of the MgO.^[21]

The FT-IR spectrum (Figure 2) of MoO₂(acac)_n-NAP-MgO catalyst showed bands around 1610 cm⁻¹, corresponding to vibration of the C=O group of acac, confirming the adsorption of MoO₂(acac)₂ on NAP-MgO.



Scheme 2. Preparation of the MoO₂(acac)_n-NAP-MgO catalyst.

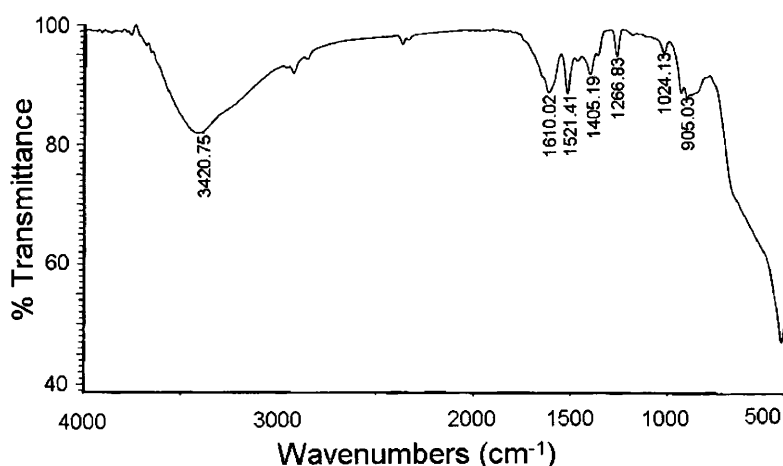


Figure 2. IR spectrum of fresh $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$.

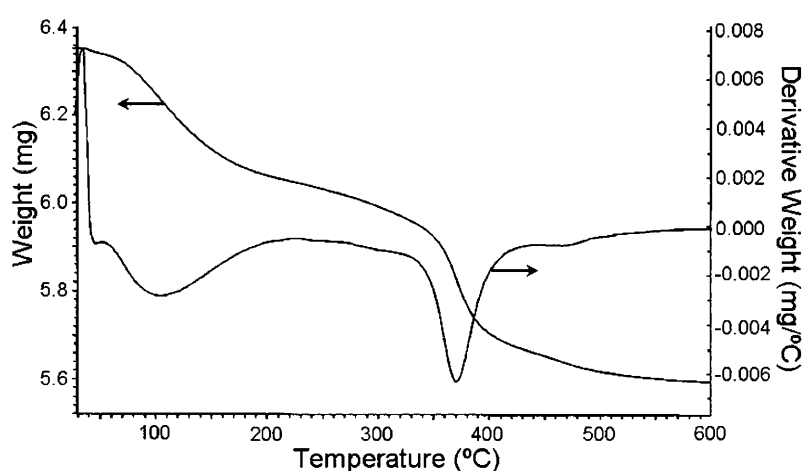


Figure 3. TGA-DTA profiles for $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$.

The thermogravimetric profiles and the relative derivative curves (TGA and DTA) for the $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$ catalysts show a weight loss of about 29% in the temperature range of 20–500 °C which is associated with the decomposition of the acac moiety from the $\text{MoO}_2(\text{acac})_n$ in the catalyst (Figure 3). The Mo content of the $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$ catalyst was found to be $0.715 \text{ mmol g}^{-1}$ by AAS (atomic absorption spectroscopy).

Aerobic Oxidation of Alcohols to Aldehydes and Ketones

Various magnesium oxide crystals [CM-MgO, NA-MgO, NAP-MgO] were initially evaluated for the oxidation of alcohols in order to understand the relationship between structure and reactivity. These supports are not active as such for the oxidation of alcohols (Table 1, entry 3). To optimizing the alcohol oxidation reaction, we explored various MgO samples using molecular oxygen and *p*-nitrobenzyl alcohol as the model

substrate. Among the various MgO-supported $\text{MoO}_2(\text{acac})_2$ catalysts screened, the $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$ was found to be superior to CM-MgO and NA-

Table 1. Oxidation of *p*-nitrobenzyl alcohol using different catalysts and solvents.^[a]

Entry	Catalyst	Solvent	Yield [%] ^[b]
1	$\text{MoO}_2(\text{acac})_n\text{-CM-MgO}$	Toluene	0
2	$\text{MoO}_2(\text{acac})_n\text{-NA-MgO}$	Toluene	21
3	NAP-MgO	Toluene	0
4	$\text{MoO}_2(\text{acac})_2$	Toluene	53 ^[c]
5	$\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$	Toluene	64, ^[d] 88
6	$\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$	Acetonitrile	18, ^[d] 22
7	$\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$	Benzene	42, ^[d] 48
8	$\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$	Hexane	68
9	$\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$	Cyclohexane	46, ^[d] 54

^[a] Reaction conditions: *p*-nitrobenzyl alcohol (1 mmol), solvent (4 mL), catalyst (0.070 g), reflux temperature.

^[b] Isolated yields.

^[c] 10% of *p*-nitrobenzoic acid was obtained.

^[d] At 70 °C.

MgO in terms of yield (Table 1, entries 1, 2 and 5). The homogeneous process using $\text{MoO}_2(\text{acac})_2$ was less effective and gave a mixture of *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid in yields of 53% and 10%, respectively (Table 1, entry 4). The greater reactivity and selectivity of the $\text{MoO}_2(\text{acac})_n$ -NAP-MgO catalyst can be explained by the structural features of nanocrystalline magnesium oxide as support. The enhanced activity and selectivity of this catalyst over the different supported molybdenum catalysts screened as well as its homogeneous counterparts, results from the high basicity and surface area of the nanocrystalline magnesium oxide [aerogel-prepared MgO, NAP-MgO (SSA: $590 \text{ m}^2 \text{ g}^{-1}$)] support.^[14c,d] NAP-MgO has a three-dimensional polyhedral structure, showing the presence of high surface concentrations of edge/corner and various exposed crystal planes (such as 002, 001, 111), which lead to inherently high surface ionic charges per unit area. The presence of corner and edge sites on the surface of NAP-MgO could ap-

proach 20%, while on NA-MgO they amount to less than 0.5% and on CM-MgO are essentially 0%. The reactive sites on the surface of MgO are as follows: 1) Mg^{2+} site, which is of the Lewis acid type, 2) O^{2-} site which is of the Lewis base type, 3) lattice bound and 4) isolated hydroxy groups and anionic and cationic vacancies. An edge or even more so, a corner O^{2-} anion is coordinatively unsaturated and is seeking Lewis acids to help stabilize and delocalize its negative charge. Conversely, an Mg^{2+} ion on an edge or corner is seeking Lewis bases (acac) to stabilize and delocalize its positive charge (Scheme 2). Therefore, these coordinatively unsaturated O^{2-} and Mg^{2+} ions readily accept incoming reagents with Lewis acid or Lewis base character.

The effect of organic solvents on the oxidation of *p*-nitrobenzyl alcohol was also examined. The oxidation product was obtained in 18% yield with a polar solvent such as acetonitrile (Table 1, entry 6), while non-polar solvents such as benzene, hexane, cyclohex-

Table 2. Aerobic oxidation of primary and secondary alcohols to corresponding aldehydes and ketones using $\text{MoO}_2(\text{acac})_n$ -NAP-MgO.^[a]

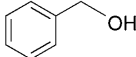
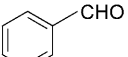
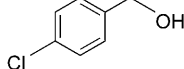
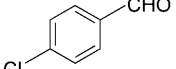
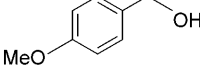
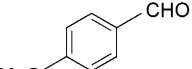
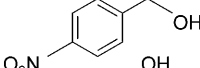
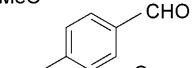
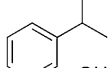
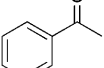
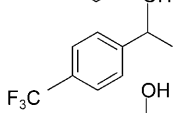
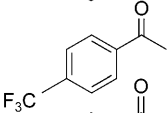
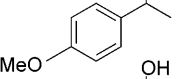
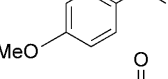
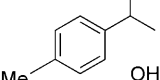
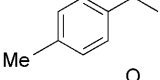
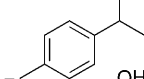
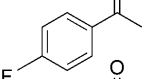
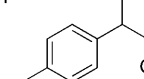
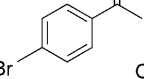
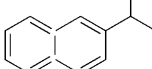
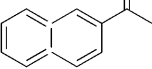
Entry	Substrate	Time [h]	Product	Yield [%] ^[b]
1		12		81
2		15		86
3		10		84
4		14		88
5		21		84
6		18		91
7		16		89
8		12		92
9		18		85
10		18		87
11		24		79

Table 2. (Continued)

Entry	Substrate	Time [h]	Product	Yield [%] ^[b]
12		28		81
13		15		93
14		22		89
15		17		49
16		23		68
17		18		51
18		16		64
19		26		82
20		16		85
21		18		82

^[a] Reaction conditions: alcohol (1 mmol), dry toluene (4 mL), catalyst (0.070 g), 110°C temperature.

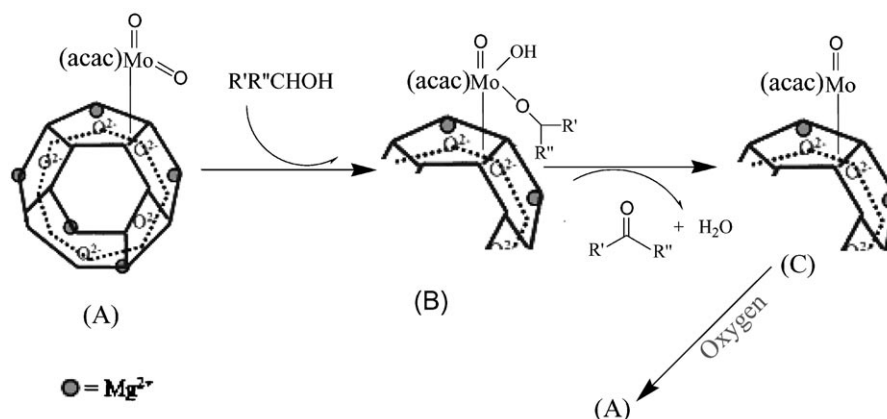
^[b] Isolated yields.

ane, and toluene afforded *p*-nitrobenzaldehyde in 42, 68, 46 and 64% yields, respectively, at 70°C. Although hexane and toluene show almost same activity, ultimately toluene was chosen due to its higher boiling point. To know whether the oxidation of toluene takes place under these reaction conditions, an experiment was done keeping all the reaction conditions same as in Table 1, entry 5, without *p*-nitrobenzyl alcohol. GC analysis of the reaction mixture after 14 h shows no benzoic acid formation. The reaction is selective towards the oxidation of alcohols to carbonyl compounds.

Next we studied the scope and generality of this process in the oxidation of various alcohols using MoO₂(acac)₃-NAP-MgO as catalyst, at 110°C under an O₂ atmosphere. The results are listed in Table 2. It is notable that the benzyl alcohols having a wide range of functional groups, were quantitatively converted to the corresponding aldehydes and could be isolated in excellent yields under the reaction conditions used (Table 2, entries 1–4). Secondary alcohols

such as phenylethanol, substituted phenylethanol, 2-naphthylethanol, benzoin and diphenylmethanol required longer reaction times compared to the benzylic alcohols, to afford the corresponding ketones in 79 to 93% yields (Table 2, entry 5–14). However, the oxidation of aliphatic primary and secondary alcohols such as 1-octanol, cyclohexanol and 2-cyclohexylethanol afforded the corresponding carbonyl derivatives in moderate yields despite prolonged reaction times (Table 2, entry 16–18). Cinnamyl alcohol is oxidized to the corresponding α , β -unsaturated aldehyde without affecting the double bond (Table 2, entry 15). Heterocyclic alcohols such as 2-furanol, 2-thiophenemethanol and 2-pyridinemethanol were oxidized to the corresponding aldehydes in high yields (Table 2, entry 19–21).

A proposed reaction mechanism is given in Scheme 3. It is assumed that the first step of the reaction is the addition of the OH group of the alcohol across the Mo=O double bond resulting in the formation of the complex B.^[22] The complex B then under-



Scheme 3. Proposed mechanism for the $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$ -catalyzed alcohol oxidation.

goes elimination to afford the carbonyl compound and the intermediate C which then undergoes oxidation by molecular oxygen to complete the catalytic cycle.^[23]

Heterogeneity and Reusability of the Catalyst

The heterogeneity of the catalyst was also evaluated to determine whether the reaction which uses the solid Mo catalyst occurred on the solid surface or was catalyzed by Mo species leached into the liquid phase. To study the leaching of the metal, two separate experiments involving the oxidation of *p*-nitrobenzyl alcohol were undertaken. In the first experiment, the reaction was terminated after three hours. At this juncture, the catalyst was separated from the reaction mixture at the reaction temperature and the reaction was continued with the filtrate for an additional six hours. The conversion was found to remain almost identical. In the second experiment, the $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$ catalyst was stirred at 110 °C for ten hours and the filtrate was used for the oxidation of *p*-nitrobenzyl alcohol. No reaction was observed, indicating that leaching of the metal had not occurred. The molybdenum content of the used catalyst after the fourth cycle remained the same as confirmed by atomic absorption spectroscopy (AAS). Furthermore, a catalyst recycling experiment was carried out. As can be seen in Table 3, the $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$ catalyst can be reused for several cycles without a significant loss of activity.

The reused catalyst exhibited a similar powder X-ray diffraction (XRD) pattern, even after the fourth cycle, indicating that the structure and morphology of the catalyst remains the same after recycling (Figure 4).

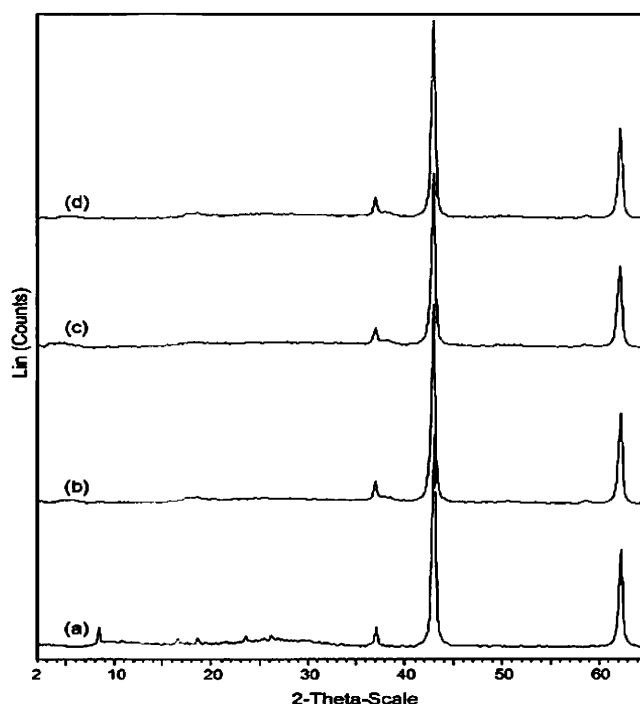


Figure 4. XRD pattern of $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$ (a) 1st cycle (b) 2nd cycle (c) 3rd cycle (d) 4th cycle.

Table 3. Recycling of the catalytic system for the oxidation of *p*-nitrobenzyl alcohol to *p*-nitrobenzaldehyde.^[a]

Run	Time [h]	Yield [%] ^[b]
1	14	88
2	14	83
3	14	80
4	14	79

^[a] Reaction conditions: *p*-nitrobenzyl alcohol (1 mmol), dry toluene (4 mL), catalyst (0.070 g), 110 °C.

^[b] Isolated yields.

Conclusions

In conclusion, $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$ has been used as a catalyst for the oxidation of primary and secondary alcohols to carbonyl compounds in excellent yields, in the presence of molecular oxygen. The nanomaterials with their three-dimensional structure and defined size and shape, act as suitable supports for metal complexes. The catalyst can be recycled four times without significant loss of activity.

Experimental Section

General Remarks

Nanocrystalline MgO samples were obtained from NanoScale Materials Inc., Manhattan, Kansas, USA. Commercial MgO was purchased from LOBA Chemie. $\text{MoO}_2(\text{acac})_2$ was synthesized as described in the literature.^[24] MoO_3 was purchased from S D Fine – Chem Limited, India. All other chemicals were purchased from Aldrich and used as received. All solvents were purchased as analytical grade and used as received from Merck India Pvt. Ltd. Dry toluene was used for all reactions. ACME silica gel (100–200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60-F254 plates. All alcohol oxidations were performed at 110°C in dry toluene under an oxygen atmosphere. The ^1H NMR spectra were recorded on a Varian Gemini 200 MHz and Bruker Avance 300 MHz spectrometers. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard in CDCl_3 . XPS data were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg $K\alpha$ anode. X-ray powder diffraction (XRD) data were collected on a Siemens/D-5000 diffractometer using Cu $K\alpha$ radiation. IR spectra were recorded on a Perkin–Elmer instrument.

Preparation of $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$

The MgO samples were heated under vacuum at 500°C before use. $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$ was prepared by treating vacuum-dried NAP-MgO (1.0 g) with $\text{MoO}_2(\text{acac})_2$ (0.400 g) in THF (20 mL) under a nitrogen atmosphere at room temperature with stirring for 24 h by a method similar to that reported by Klabunde and co-workers.^[18] The slurry was filtered, and the solid was washed with THF and vacuum dried to give $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$. The Mo content in $\text{MoO}_2(\text{acac})_n\text{-NAP-MgO}$ was found to be 0.715 mmol g^{-1} by AAS.

General Procedure for the Oxidation of Primary and Secondary Alcohols to Carbonyl Compounds using Molecular Oxygen

A dry 25-mL, two-neck, round-bottomed flask equipped with a reflux condenser connected with a balloon filled with oxygen was charged with catalyst (70 mg), alcohol (1 mmol) and dry toluene (4 mL) and was stirred at 110°C for the appropriate time (Table 2). After completion of the reaction,

as indicated by TLC, the reaction mixture was centrifuged to separate the catalyst which was reused after vacuum drying. The reaction mixture was concentrated under reduced pressure to afford the crude product which was purified by column chromatography on silica gel with ethyl acetate and *n*-hexane as eluent.

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