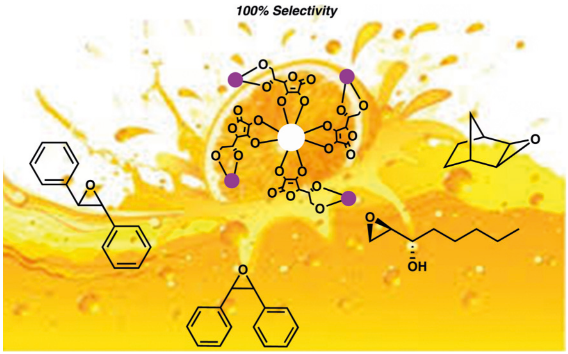
Aerobic Stereoselective Oxidation of Olefins on a Visible-Light-Irradiated Titanium Dioxide–Cobalt–Ascorbic Acid Nanohybrid

Maasoumeh Jafarpour*
Fahimeh Feizpour
Abdolreza Rezaeifard*

Catalysis Research Laboratory, Department of Chemistry,
Faculty of Science, University of Birjand, Birjand 97179-414,
Iran
mjafarpour@birjand.ac.ir
rrezaeifard@birjand.ac.ir



Received: 09.09.2016
Accepted after revision: 20.09.2016
Published online: 11.10.2016
DOI: 10.1055/s-0036-1588897; Art ID: st-2016-d0458-l

Abstract A visible-light-driven photocatalytically active nanocrystalline TiO_2 was prepared by surface modification with a cobalt–ascorbic acid complex. The photocatalyst exhibited high activity and excellent chemo-, diastereo-, and stereoselectivities in the aerobic epoxidation of olefins under visible-light irradiation in the absence of a reducing agent. The catalyst proved efficient and could be recycled at least five times.

Key words epoxidation, alkenes, titanium dioxide, nanoparticles, ascorbic acid, nanohybrids

Aerobic epoxidation of olefins is of extreme interest from an environmental as well as an economic viewpoint. The plethora of heterogeneous or homogeneous catalytic conditions available to accomplish this key reaction is testament to its value.[1] Nevertheless, developing an efficient heterogeneous catalyst for aerobic epoxidations in the absence of a sacrificial co-reductant is rather difficult.[2] Among the various transition metals used to catalyze olefin epoxidation, cobalt has been used extensively with various oxidants,[3] because it is much more abundant and cheaper than other metals such as ruthenium or iridium.

Despite considerable progress, significant metal contamination under homogeneous conditions has limited the number of industrial applications of most transition-metal catalysts. Development of heterogeneous cobalt catalysts for aerobic epoxidation facilitates separation processes and enhances the commercial viability of such catalysts.[1a–e,4] Nevertheless, the use of heterogeneous catalysts typically involves various problems, such as nontrivial preparation, low chemical stability, nonuniform structure, low efficiency, and the possibility of metal leaching during the transformation. In addition, the catalytic activity of most of these catalysts in oxidation reactions of olefins has been limited to a small range of substrates.[4a–g] Therefore, the design of a novel heterogeneous cobalt(II)-based catalyst for aerobic reactions that shows a high activity and ease of separation remains a challenging task.

Organic–inorganic hybrid materials have attracted considerable interest in the field of catalysis, especially in oxidative transformations of organic compounds. However, to the best of our knowledge, only a few reports have described the catalytic activity of transition-metal-coordinated organic–inorganic hybrid materials for the aerobic epoxidation of olefins.[4k,l]

In continuation of our research into the development of novel catalytic methods for aerobic oxidation of organic compounds,[5] we recently discovered that a TiO_2–ascorbic acid (AA)–Co nanohybrid is active in the selective aerobic benzylic C–H oxidation of alcohols or hydrocarbons in ethyl acetate.[5g] Here, we wish to describe the visible-light photocatalytic activity and selectivity of this combination for oxidation of olefins in ethyl acetate under heterogeneous conditions in the absence of a reducing agent (Scheme 1). Furthermore, spectroscopic analysis and leaching experiments demonstrated the preservation of the structural integrity of the solid catalyst after several reaction cycles.

The oxidation activity of the TiO_2–AA–Co nanohybrid, was initially examined in the epoxidation of norbornene (1 mmol) with O_2 (1 atm) in ethyl acetate (1 mL), as this reaction does not proceed in the absence of the catalyst under any conditions. The reaction conditions were optimized with respect to the nature and quantity of solvent, temperature, catalyst, quantity of *N*-hydroxyphthalimide (NHPI), and nature of the oxidant [for the experimental details, see the Supporting Information (Figure S5)].

An investigation of the effect of catalyst loading demonstrated that our catalyst has a high atom efficiency. Under visible-light irradiation, norbornene was converted com-

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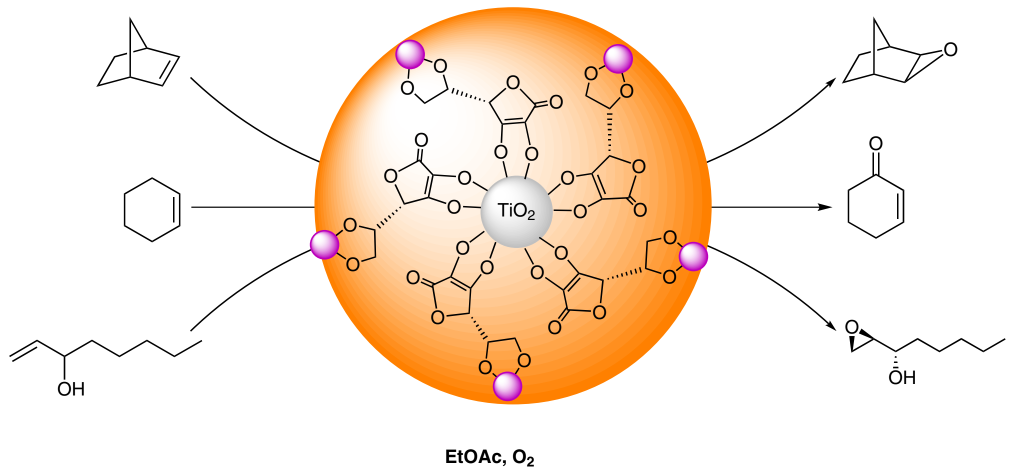


Scheme 1 Aerobic olefin oxygenation catalyzed by a TiO_2–ascorbic acid–Co nanohybrid

pletely within four hours by using a low loading of the catalyst (0.2 mol%) to give *exo*-norbornene oxide exclusively in 94% yield. No improvement in the reaction rate was observed (33% after 4 h) on adding 2-methylpropanal, a commonly used reducing agent, confirming the ineffectiveness of a reducing agent in this aerobic system. Inspection of the results in Figure S5(v) (Supporting Information) revealed that the efficiency of oxidation was dependent on the amount of NHPI, in that the reaction did not proceed in the absence of NHPI under any conditions. NHPI has been reported to act as a free-radical oxidation catalyst.[2,6] Therefore, a radical mechanism may be suggested for the title oxidation system using O_2; this is similar to previous reports on reactions conducted in the presence of cobalt complexes (Figure S6 in the Supporting Information).[2,7] Such a mechanism was further supported by the retardation of the oxidation of norbornene in the presence of radical scavengers such as 2,6-di-*tert*-butyl-4-methylphenol under the same conditions. Under the optimized conditions (0.2 mol% TiO_2–AA–Co and 15 mol% NHPI at 60 °C), with a continuous stream of O_2 in ethyl acetate, TiO_2–AA–Co exhibited a high efficiency and noteworthy selectivity toward aerobic oxidation of a wide range of olefins (Table 1).

As summarized in Table 1, olefins generally behaved as good substrates for this nanocatalyst. Besides norbornene, 1-methylcyclohexene, 1-phenylcyclohexene, and indene selectively gave the corresponding epoxides (Table 1, entries 1–4). The poor reactivities of cyclohex-1-en-1-ylbenzene and indene (entries 3 and 4) possibly point to a degree of steric hindrance around the active site of the catalyst. When cyclooctene was subjected to the oxidation procedure, cyclooctene oxide was formed as the major product (85%) along with 15% of the related α,β-unsaturated ketone formed through allylic oxidation (entry 5). As expected, cyclohexene, which is prone to allylic oxidation, gave cyclohex-2-en-1-one as the only product (entry 6). Likewise, oxidation of cyclohex-2-en-1-ol occurred easily to give cyclohex-2-en-1-one in high yield and with excellent selectivity (entry 7). Nevertheless, linear allylic alcohols (entries 8 and 9) were converted selectively into the corresponding epoxides in moderate yield (40–54%) and with no product resulting from oxidation of the hydroxy group. Oct-1-en-3-ol (entry 9) gave *threo*-1,2-epoxyoctan-3-ol exclusively in 40% yield, according to ^1H NMR analysis. In addition to norbornene, which exclusively gave the corresponding *exo*-epoxide (entry 2), epoxidation of *cis*- and *trans*-stilbene proceeded with total stereoselectivity (entries 10 and 11). Note that no activity was observed for oct-1-ene, a less reactive linear terminal olefin, or for electron-deficient *trans*-benzylideneacetophenone.[8]

Table 1 Aerobic Oxidation of Alkenes Catalyzed by the TiO_2–AA–Co Nanohybrid in EtOAc[a]

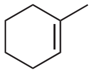
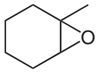
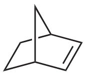
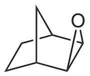
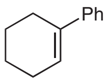
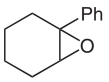
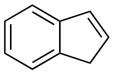
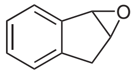
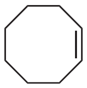
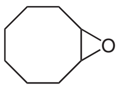
Entry	Alkene	Product[b]	Time (h)	Yield[c,d] (%)
1			5	100 (95)
2			4	100 (94)
3			10	28 (21)
4			6	50 (43)
5			6	100 (85)[e]

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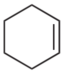
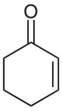
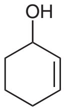
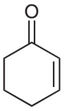
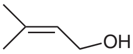
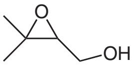
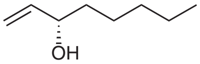
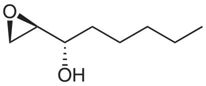
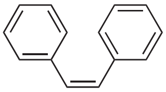
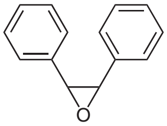
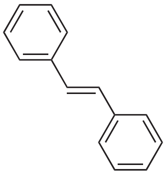
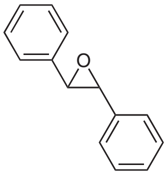
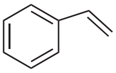
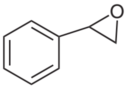
Table 1 (continued)

Entry	Alkene	Product[b]	Time (h)	Yield[c,d] (%)
6			5	100 (96)
7			4.3	100 (95)
8			7	54 (48)
9			5	40
10			5	68 (59)
11			5	56 (50)
12			6	30[f]

[a] The substrate/NHPI/catalyst molar ratio was 1000:150:2. Reactions were carried out under a continuous stream of O_2 (5–7 mL/min) in EtOAc (1 mL) at 60 °C.

[b] The products were identified by ^1H NMR or by comparison with the GC retention times of authentic samples.

[c] GC yield; isolated yields are given in parentheses.

[d] The selectivity toward the products was >99%, based on GC analysis.

[e] The remainder was the related α,β-unsaturated ketone.

[f] The remainder was benzaldehyde (70%).

Replacement of TiO_2–AA–Co nanoparticles by other nanoparticulate metal oxides such as MoO_3,[9] monoclinic ZrO_2,[10] γ-Fe_2O_3, or TiO_2 or their nanocomposites, such as TiO_2–AA, AA–Co, γ-Fe_2O_3–AA–Co and MoO_3–AA–Co, extended the time for oxidation of norbornene under the same conditions (Figure S7 in the Supporting Information). No oxidation product was observed in the presence of AA or AA/Co$(OAc)_2$.

The results presented in the Supporting Information (Figure S7) suggest that the catalytic performance of the TiO_2–AA–Co nanohybrid can be explained in terms of the oxidation activity of the Co(II) centers[2,7] in combination with the photocatalytic activity of the TiO_2 core, which also acts as a heterogeneous support.

To provide evidence for the photocatalytic properties of the TiO_2 core, we examined the oxidation of norbornene in darkness or under UV or visible-light irradiation in the presence of NHPI (15 mol%) and a continuous stream of O_2 at 60 °C. The accelerated rates observed under irradiation, particularly with UV irradiation, confirmed that the TiO_2 core has a photocatalytic effect on the oxidation efficiency of the TiO_2–AA–Co nanohybrid (Table 2, entry 3). The smaller bandgap of the TiO_2–AA–Co nanohybrid (2.8 eV), compared with that of TiO_2 nanoparticles (3.2 eV),[5g] might account for this activity (Figure S8 in the Supporting Information).

Table 2 Screening of the Photocatalytic Activity of TiO_2–AA–Co[a]

Entry	Catalyst	Conditions	Time (h)	Yield[b] (%)
1	TiO_2	UV	4	26
2	TiO_2–AA	UV	4	71
3	TiO_2–AA–Co	UV	2	quant
4	TiO_2	visible light	4	–
5	TiO_2–AA	visible light	4	42
6	TiO_2–AA–Co	visible light	4	94
7	TiO_2	darkness	4	–
8	TiO_2–AA	darkness	4	18
9	TiO_2–AA–Co	darkness	4	37

[a] The substrate/NHPI/catalyst molar ratio was 1000:150:2. The reactions were carried out under a continuous stream of O_2 (5–7 mL/min) in EtOAc (1 mL) at 60 °C.

[b] Yield by GC analysis.

The heterogeneous nature of the catalyst was confirmed by a filtration experiment. For this purpose, the catalyst was recovered by centrifugation and decantation of the reaction mixture. No catalytic activity was observed in the filtrate solution, and neither Co nor Ti was detected in the filtrate solution by ICP-AES analysis. Aerobic epoxidation of norbornene proceeded well in the presence of the recovered catalyst after it had been washed with ethyl acetate and dried under vacuum.

The ease of recovery, combined with the intrinsic stability of the TiO_2–AA–Co nanocomposite, permitted the catalyst to be used at least five times in aerobic epoxidation under the standard conditions for this study[11] (Figure S9 in the Supporting Information). A comparison of the FTIR and UV-vis spectra of used TiO_2–AA–Co nanocatalyst with those of the fresh catalyst showed that the structure of the catalyst remained almost intact after five recovery cycles (Figure S10 in the Supporting Information).

In conclusion, we have improved the visible-light photocatalytic properties of TiO_2 for aerobic oxidation of various olefins by incorporating Co$(OAc)_2$ on ascorbic acid coated TiO_2 nanoparticles. Oxidations with this catalyst showed remarkable chemo-, diastereo- and stereoselectivities. Our

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results demonstrate a synergistic effect of the cobalt–ascorbic acid complex and the TiO_2 nanoparticles on the visible-light photocatalytic activity of the combination. The use of oxygen as the simplest oxidant, the lack of a need for a co-reductant, the use of visible light as an energy source, and the reusability and recyclability of the photocatalyst are salient features of the present method from an environmental point of view, and render the catalyst amenable to use in industrial applications.

Acknowledgment

Support for this work by Research Council of University of Birjand is highly appreciated.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588897.

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(11) **Typical Procedure and Reusability of Catalyst:** To a mixture of norbornene (1 mmol) and TiO_2/AA/Co nanohybrid (0.2 mol%) in EtOAc (1 mL) was added NHPI (15 mol%, 0.024 g) and the reaction mixture was stirred under 1 atm O_2 (5–7 mL/min) and visible light at 60 °C for 4 h. After completion of the reaction, TiO_2/AA/Co nanohybrid was separated by centrifugation followed by decantation (3 × 5 mL EtOAc). The isolated solid-phase TiO_2/AA/Co nanohybrid was washed with EtOH then dried under reduced pressure and reused for the next run.

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