

Convenient and Mild Epoxidation of Alkenes Using Heterogeneous Cobalt Oxide Catalysts**

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Abstract: A general epoxidation of aromatic and aliphatic olefins has been developed under mild conditions using heterogeneous $\text{Co}_x\text{O}_y\text{-N/C}$ ($x=1,3$; $y=1,4$) catalysts and *tert*-butyl hydroperoxide as the terminal oxidant. Various stilbenes and aliphatic alkenes, including renewable olefins, and vitamin and cholesterol derivatives, were successfully transformed into the corresponding epoxides with high selectivity and often good yields. The cobalt oxide catalyst can be recycled up to five times without significant loss of activity or change in structure. Characterization of the catalyst by XRD, TEM, XPS, and EPR analysis revealed the formation of cobalt oxide nanoparticles with varying size (Co_3O_4 with some CoO) and very few large particles with a metallic Co core and an oxidic shell. During the pyrolysis process the nitrogen ligand forms graphene-type layers, in which selected carbon atoms are substituted by nitrogen.

Epoxides constitute important intermediates for the production of fine and bulk chemicals, especially for industrial synthesis of polymers. Furthermore, they are valuable building blocks for the synthesis of a variety of bioactive molecules.^[1,2] The most efficient synthesis of oxiranes makes use of the in situ formation of two C–O bonds from an olefin and a respective oxidant. Regarding atom efficiency and waste generation, in general such oxidation reactions should be performed using molecular oxygen or hydrogen peroxide in combination with a suitable transition metal catalyst.^[3]

Although molecular oxygen is the most abundant oxidant, the vast majority of epoxidations with air still proceed with 50 % atom efficiency.^[4] For the synthesis of advanced building blocks, catalytic epoxidations with O_2 often require in situ activation by hydrides, H_2/Pt , ascorbic acid, or aldehydes.^[5] Hence, in recent years there exists an increasing interest in the utilization of hydrogen peroxide as oxidant, both on laboratory and industrial scales because of availability, price, and safety issues. In fact, reaction of propylene with hydrogen

peroxide in the presence of TS-1 is a state-of-the-art epoxidation process.^[6]

In addition to molecular oxygen and hydrogen peroxide, alkyl peroxides such as *tert*-BuOOH (TBHP) offer interesting possibilities for oxidation catalysis. For example, TBHP has been shown to significantly improve the performance of several transition-metal catalysts in their higher oxidation states in epoxidations. More specifically, transition metal–alkyl hydroperoxides of titanium(IV), vanadium(V), molybdenum(VI), and tungsten(VI) showed better activity and solubility compared to the corresponding transition metal–hydrogen peroxide complexes in nonpolar solvents. From a synthetic point of view, it is interesting that transition metal alkyl hydroperoxides allow for highly selective epoxidations towards allylic double bonds in comparison to other oxidants.^[7,8]

Apart from the well-known epoxidation catalysts based on Ti, Mo, and W, in the last decade several catalysts based on noble metals, for example, Pt, Pd, Ru, Ir, and Au were introduced for highly selective epoxidations of olefins.^[9] On the other hand, the use of novel cost-effective non-noble metal catalysts is less known.^[10] Therefore, we started some time ago a program to develop novel catalysts for the epoxidation of olefins and related reactions based on bio-relevant transition-metal complexes.^[10]

In 2013, we successfully designed a series of novel Co- and Fe-oxide supported catalysts for the selective reduction of functionalized nitroarenes and oxidative esterifications.^[11] Based on this work, we became interested in applying these materials in the epoxidation of olefins. Although cobalt-based heterogeneous catalysts are well-known to be active in various oxidation processes,^[12] only a few examples are known for selective epoxidation of alkenes.^[13] Herein, we report an efficient and general heterogeneous Co-catalyzed epoxidation of alkenes with *tert*-butyl hydroperoxide under mild conditions.

The catalyst materials were prepared by wet impregnation of a combination of cobalt(II) acetate and different nitrogen-containing ligands on Vulcan XC72R.^[11] Subsequent pyrolysis at 800 °C led mainly to oxidic nanoparticles with varying size (2–10 nm, predominantly Co_3O_4 with some CoO) and agglomerates in a range of 20–80 nm, in addition to very few large particles with a metallic Co core and an oxidic shell. During the pyrolysis process the nitrogen ligand forms graphene-type layers, in which selected carbon atoms are substituted by nitrogen. X-ray photoelectron spectroscopy (XPS) revealed three distinct nitrogen species (pyridine-type nitrogen, pyrrole-type nitrogen, and a small amount of quaternary amine species). Deconvolution showed that

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Table 1: Co_xO_y-N/C (x = 1,3; y = 1,4)-catalyzed epoxidation of *trans*-stilbene with *tert*-butyl hydroperoxide.

$\text{Ph}-\text{CH}=\text{CH}-\text{Ph} \quad \text{1a} + \text{tBuOOH} \xrightarrow[\text{MeCN, 70 } ^\circ\text{C, 20 h}]{\text{Co}_x\text{O}_y\text{-N/C (x = 1,3; y = 1,4) catalyst}} \text{Ph}-\text{CH}(\text{O})-\text{CH}(\text{O})-\text{Ph} \quad \text{2a}$					
Entry	Support	Co cat. [mol %]	Ligand	Conv. [%] ^[h]	Yield [%] ^[i]
1 ^[a]	—	—	—	2	0
2 ^[a]	—	4	—	3	0
3 ^[a]	—	4	L1	10	0
4 ^[b]	Vulcan XC72R	4	—	5	0
5 ^[b]	Vulcan XC72R	4	L1	15	5 ^[j]
6 ^[c]	Vulcan XC72R	4	L1	> 99	97
7 ^[c]	Vulcan XC72R	4	L2	70	65
8 ^[c]	Vulcan XC72R	4	L3	63	60
9 ^[c]	BN	4	L1	75	70
10 ^[c]	TiO ₂	4	L1	65	61 ^[j]
11 ^[d]	Vulcan XC72R	4	L1	8	5
12 ^[e]	Vulcan XC72R	4	L1	4	0
13 ^[f]	Vulcan XC72R	4	L1	16	0
14 ^[g]	—	4	L1	10	7 ^[j]

[a] Reaction under homogeneous conditions: *trans*-stilbene (0.5 mmol), Co(OAc)₂·4H₂O (4 mol %), ligand (8 mol %), CH₃CN (6 mL), *tert*-BuOOH (5 equiv). [b] Reaction performed without pyrolysis. [c] Reaction under heterogeneous conditions: *trans*-stilbene (0.5 mmol), catalyst (40 mg; 4 mol % Co; 3 wt % Co), CH₃CN (6 mL), *tert*-BuOOH (5 equiv). [d] Reaction with H₂O₂ (30%). [e] Reaction with NaOCl. [f] Reaction without *tert*-BuOOH. [g] Reaction was performed with carbon-supported mixed Co-oxides. [h] Conversions were determined by GC-MS analysis of the crude reaction mixture. [i] Yield of isolated product. [j] In the case of lower yields, 5–10% of benzaldehyde was detected as a minor side product. **L1** = 1,10-phenanthroline, **L2** = terpyridine, **L3** = pyridine bis-(imidazoline).

around 64% of all N atoms are bound to the metal ions. In a similar manner, new cobalt oxides supported on boron nitride and on TiO₂ were also prepared.

For our initial catalytic tests, we choose *trans*-stilbene as our model substrate. As a commercially available oxidant, aqueous *tert*-butyl hydroperoxide (70%) was used (Table 1). Not surprisingly, epoxidation under homogeneous conditions using Co(OAc)₂·4H₂O did not form any of the desired *trans*-stilbene oxide **2a** (Table 1, entries 1–3). Similarly, the use of unpyrolyzed phenanthroline-Co^{II}-acetate supported on Vulcan XC72R showed only poor conversion into **2a** (Table 1, entries 4 and 5). Gratifyingly, the model reaction resulted in nearly quantitative yield of *trans*-stilbene oxide in the presence of the pyrolyzed carbon-supported phenanthroline-Co^{II}-acetate complex (Table 1, entry 6). Scale-up of this reaction by a factor five led to *trans*-stilbene oxide in 94% yield. Further reactions of different nanostructured cobalt oxides, for example, carbon-supported terpyridine or pyridinebisimidazoline Co-catalysts also gave significant yields (60–65%) of the desired product (Table 1, entries 7 and 8). Next, we investigated the effect of different support materials. To our delight, pyrolysis of Co^{II}-**L1** under standard conditions (800 °C) on boron nitride (BN) and TiO₂ also resulted in active materials (Table 1, entries 9 and 10). When performing the model reaction with hydrogen peroxide (30% aqueous solution) or NaOCl as oxidant, only poor or no conversion to the desired product was observed (Table 1, entries 11 and 12). The reaction with commercially available mixed Co^{II,III} oxide

nanopowder gave only 7% yield of *trans*-stilbene oxide (Table 1, entry 14). It is worth noting that in cases with lower product yield, 5–10% of benzaldehyde was observed as a side-product in GC-MS analysis of the crude reaction mixture. The catalytic epoxidation also took place in *iso*-propyl alcohol and *tert*-amyl alcohol, albeit with lower activity.

For the development of advanced, cost-effective, and benign industrial processes, catalyst stability and recycling are important. In metal-containing heterogeneous catalysts, the leaching of the active metal from the supported materials is often a problem. Such leaching processes result in diminished reactivity and selectivity in catalytic processes. When studying the recycling of our catalyst system, we did not observe any leaching of the metal by atomic absorption spectroscopy (AAS), even after several recycling experiments (Figure 1; see also the Supporting Information). Similarly, a hot filtration test revealed no significant leaching.

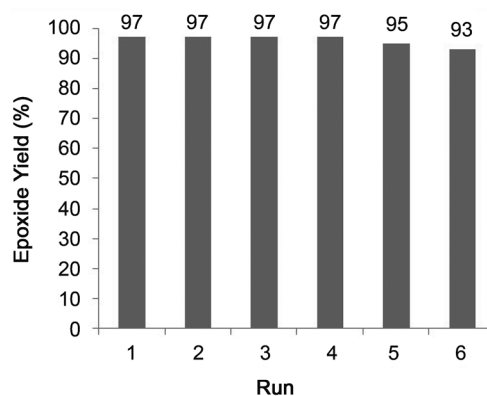
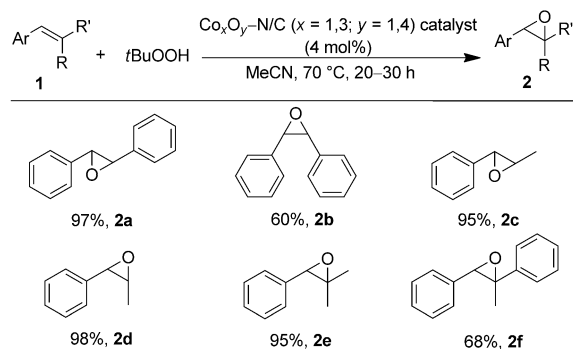


Figure 1. Recycling of the active Co_xO_y-N/C (x = 1,3; y = 1,4) catalyst for the epoxidation of *trans*-stilbene, according to the reaction conditions of the model reaction (Scheme 1). Run 1 is with fresh catalyst.

To understand the influence of the oxidant as well as reaction conditions on the structure of the active material, transmission electron microscopy (TEM) analyses of both the freshly pyrolyzed and the recycled catalyst after the first and the fifth run were performed. These investigations indicated no significant structural change during the oxidation procedure, although a carbon support is used. In the active catalyst, oxidic particles of different size coexist with larger ones containing a metallic Co core and an oxidic shell. After the first oxidation reaction, these core-shell particles are more abundant. In addition to TEM measurements (Supporting Information, Figure S1), XRD powder patterns show narrow peaks of metallic cobalt, which point to a rather large crystallite size. The presence of ferromagnetic Co metal particles is suggested by temperature-dependent EPR measurements (Figure S3). Furthermore, XRD analysis shows very weak and broad reflections of CoO, suggesting that divalent Co^{II} is more predominant after recycling (Figure S2). This is also confirmed by XPS data, which indicate the exclusive presence of oxidized Co (mainly Co²⁺; Figure S4). Thus, it is very probable that at least the larger particles consist of

a metallic Co core covered by a CoO shell. This is also supported, by TEM-EDX elemental mapping, which shows the enrichment of oxygen on the large Co-containing particles (Figure S1b). In agreement with our previous studies,^[11] XP spectra in the N1s region indicate the presence of three different N species: a) N bound to Co ions at 399.0 eV (comprising 65–70% of the N content of the sample), b) pyrrolic nitrogen at 400.8 eV, and c) NH_4^+ or R-NH_3^+ species at 403.2 eV. Interestingly, almost no change in the structural properties were observed after repeated use of the catalysts, apart from slightly more pronounced agglomeration of particles after the 5th run (Figure S1). A more detailed description of all characterization data can be found in the Supporting Information.

After having the optimized reaction conditions for the model reaction in hand, we studied the selective epoxidation of a series of aromatic alkenes, including stilbene derivatives, 1-aryl-2-alkyl, and trisubstituted olefins (Scheme 1). The resulting epoxides are commonly used as intermediates for



Scheme 1. Catalytic epoxidation. Reaction conditions: stilbene (0.5 mmol), catalyst (40 mg; 4 mol% Co), CH_3CN (6 mL), *tert*-BuOOH (5 equiv). Yields shown are of isolated products.

the synthesis of various biologically active natural products and drug molecules, for example, the corresponding amino alcohols.^[14] To our delight, epoxidation of *cis*- and *trans*-stilbene, 1-phenylpropenes, and 1-phenyl-2-methylpropenes proceeded in moderate to excellent yields to the corresponding oxiranes **2b–2f** (Scheme 1). Notably, epoxidations of a variety of substituted stilbene derivatives also afforded **2g–2l** in 60–95% yield (Table 2, entries 1–6).

The high reactivity of the stilbene derivatives prompted us to check our optimized method for the selective epoxidation of more challenging cyclic and acyclic aliphatic alkenes (Table 2). The reaction of norbornene and 2-methyl-1-heptene resulted in selective formation of **2m** and **2n** in almost quantitative yields (Table 2, entries 7 and 8). Further, catalytic epoxidation of cyclooctene afforded **2o** in 85% yield (Table 2, entry 9). The reaction of 1-decene resulted in the selective formation of 1,2-epoxide; however, owing to the decreased reactivity of this linear terminal alkene, **2p** was obtained in only 30% yield (Table 2, entry 10). Gratifyingly, functionalized alkenes such as cinnamyl acetate also afforded almost quantitative yield of **2q** (Table 2, entry 11).

Table 2: $\text{Co}_x\text{O}_y\text{-N/C}$ ($x=1,3$; $y=1,4$)-catalyzed epoxidation of aromatic and aliphatic olefins.^[a]

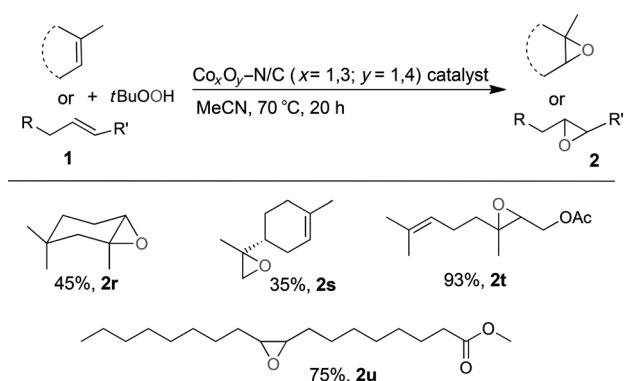
$\text{R}-\text{CH}=\text{CH}-\text{R}'$ 1		$\text{Co}_x\text{O}_y\text{-N/C}$ ($x=1,3$; $y=1,4$) catalyst (4 mol%) MeCN, 70 °C, 20–30 h	$\text{R}-\text{CH}(\text{O})-\text{CH}(\text{O})-\text{R}'$ 2	Yield [%] ^[b]
Entry	Olefin 1		Product 2	
1				90
2				95
3				95
4				70
5				95
6				60
7				98
8				96
9 ^[c]				85
10				30
11				95

[a] Reaction conditions: olefin (0.5 mmol), catalyst (40 mg; 4 mol% Co), CH_3CN (6 mL), *tert*-BuOOH (5 equiv). [b] Yield of isolated product.

[c] CH_3CN (2 mL), 85 °C.

In all reactions, we observed excellent chemoselectivity (>99%) for the respective epoxides, as shown by GC-MS analysis of the crude reaction mixtures. When we obtained a lower yield of epoxides, the corresponding olefins were recovered from the reaction mixtures.

Next, our optimized method was applied to the epoxidation of various renewables, including inexpensive terpenes, such as α -pinene, (*R*)-(+)-limonene, geraniol acetate, and methyl oleate (as an example of a fatty acid ester; Scheme 2). Functionalization and epoxidation of this latter substrate allowed access to industrially important intermediates for

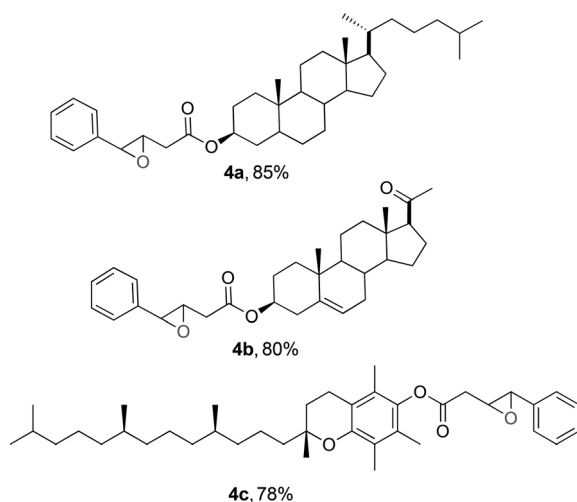


Scheme 2. Epoxidation of renewable olefins. Reaction conditions: alkene (0.5 mmol), catalyst (40 mg; 4 mol% Co), CH₃CN (6 mL), *tert*-BuOOH (5 equiv). Yields shown are of isolated products.

lubricants, basic chemicals, solvents, and biopolymers.^[15] Whereas epoxidation of α -pinene and (*R*)-(+)-limonene resulted in 35–45% yield of **2r** and **2s**, geraniol acetate and methyl oleate gave 75–93% yield of **2t** and **2u**.

Finally, we studied the epoxidation of biologically interesting cholesterol and vitamin derivatives **3a–c** (namely, 5 α -cholestan-3 β -ol and 5-pregnen-3 β -ol-20-one) of *trans*-styrylic acid (4-phenyl-3-butenic acid). To our delight, both reactions afforded 80–85% yields of the corresponding epoxides **4a** and **4b**, without affecting the parent cholesterol moiety. Similar reaction of ($\pm$)- α -tocopherol styrylicacetic ester resulted in 78% yield of **4c** (Scheme 3).

In summary, we have developed a convenient epoxidation method using heterogeneous cobalt catalysts. Key to the success of the reaction is the use of specific Co_xO_y-N/C ($x = 1,3$; $y = 1,4$) materials, which can be easily recycled. Various aromatic and aliphatic epoxides are cost-effectively prepared from the corresponding olefins with excellent selectivity and often high yields. Apart from the epoxidation of standard benchmark systems, this heterogeneous catalyst has proven to



Scheme 3. Epoxidation of cholesterol and tocopherol derivatives of 4-phenyl-3-butenic acid. Reaction conditions: ester (0.18 mmol), catalyst (20 mg; 4 mol% Co), CH₃CN (4 mL), *tert*-BuOOH (5 equiv), 70 °C, 30 h. Yields shown are of isolated products.

be useful for the oxidation of renewable olefins, as well as vitamin and cholesterol derivatives. Characterization studies using TEM, EPR, and XPS analysis did not show any significant difference in the structure of the recycled catalyst versus the fresh catalyst.

Experimental Section

The Co_xO_y-N/C ($x = 1,3$; $y = 1,4$) catalyst (Co-**L1**/C; 4 mol% Co, 40 mg) followed by an alkene (0.5 mmol) and acetonitrile (6 mL) were added to a 25 mL glass tube under air. Then, *tert*-butylhydroperoxide (5 equiv; 70% aqueous solution) was added to the reaction mixture and it stirred for 24 h in a preheated oil bath at 70 °C. The reaction mixture was cooled to room temperature and diluted with ethyl acetate. The catalyst was filtered off and concentrated under reduced pressure. The crude reaction mixture was subjected to silica gel column chromatography using an *n*-hexane/ethyl acetate mixture to afford the desired epoxides.

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