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FULL PAPER

Selective catalytic oxidation of cyclohexene with molecular oxygen: radical vs. non-radical pathways

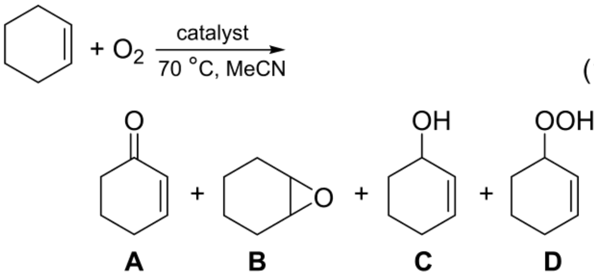
Ilse M. Denekamp[a], Martijn Antens[a], Thierry K. Slot[a] and Gadi Rothenberg[a]

Abstract: We study the allylic oxidation of cyclohexene with dioxygen under mild conditions in the presence of transition-metal catalysts. The catalysts are comprised of nanometric metal oxide particles supported on porous nitrogen-doped carbons (M/N:C, where M = V, Cr, Fe, Co, Ni, Cu, Nb, Mo, and W). Most of these metal oxides give only moderate conversions, whereof the majority of the products are over-oxidation products. Co/N:C and Cu/N:C, however, give 70–80% conversion and 40–50% selectivity to the ketone product, cyclohexene-2-one. Control experiments using free-radical scanvengers shows that the oxidation follows the expected free-radical pathway in almost all cases. Surprisingly, the catalytic cycle in the presence of Cu/N:C does not involve free-radical species in solution. Optimisation of this catalyst gives >85% conversion with >60% selectivity to the allylic ketone, at 70 °C and 10 bar oxygen pressure. Scanning electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction studies show that the active particles have a cupric oxide/cuprous oxide core/shell structure, with a correspondingly high TOF of ca. 1500 h^{-1}. We attribute the high performance of this Cu/N:C catalyst to a facile surface reaction between adsorbed cyclohexenyl hydroperoxide molecules and activated oxygen species.

Introduction

The allylic oxidation of alkenes is an important chemical reaction. It allows one to keep the double bond while creating a new alcohol or carbonyl function.[1,2] As such, it is useful across the board, from bulk chemicals and agrochemicals,[3,4] all the way to fine-chemicals and fragrances.[5–7] In theory, allylic oxidation is a straightforward exothermic reaction. It requires only molecular oxygen, a free, eco-friendly and widely available reagent. But there is a trade-off: Oxygen has a high activation barrier due to its resonance stabilisation.[8] Once this barrier is overcome, the active oxygen species often react with hydrocarbons via free-radical intermediates. These wreak havoc in solution, causing side reactions that all-too-often lead to unwanted over-oxidation products.[9–11]

Recently we showed that this problem can be solved for the specific case of oxidising activated alcohols to aldehydes and ketones, by using a bifunctional catalyst.[12] Yet this oxidation was "only" a dehydrogenation reaction. It involved the transfer of protons and electrons, without adding a new oxygen atom to the substrate. Allylic oxidation is trickier, because it is an oxygenation, involving the cleavage of at least one C–H bond and the creation of new C–O or C=O bonds. This requires a direct interaction between the substrate and an active oxygen species, which must then be stopped at the allylic alcohol/ketone stage before "burning" further to carboxylic acids, CO and CO_2.



(1)

Here we examine the catalytic oxidation of cyclohexene with molecular oxygen under mild conditions (eq 1). Cyclohexene is a good model compound for two reasons: First, it is a small and symmetric molecule, similar to many starting compounds in chemical synthesis. Second, it is itself industrially important, participating in the synthesis cycles of key C_6 chemicals such as adipic acid and caprolactone.[13,14] Building on our preliminary communication on alcohol oxidation,[12] we designed a set of metal oxide catalysts supported on nitrogen-doped carbons. We used no noble metals, focussing on abundant transition metal oxides as catalysts.

There are several reports on the allylic oxidation of cyclohexene catalysed by abundant transition metals. In general, using dioxygen as an oxidant requires additional activation, either by adding 5–10% of a free-radical initiator such as H_2O_2 or by using elevated temperatures. Tang *et al.*[15] reported a copper catalyst on expanded graphite which gave 99% conversion and 65% selectivity to 2-cyclohexene-1-one. Yin *et al*.[16] and Rossi *et al*.[17] used cobalt-based catalysts, obtaining 94% conversion and 44% selectivity and 90% conversion and 61% selectivity, respectively. Elsewhere, Peng *et al*.[18] used metal-free nitrogen-doped carbon nanotubes as catalysts. They tested 22 organic solvents and found that acetonitrile gave the best results, with 60% conversion and 39% selectivity to the 2-cyclohexene-1-one.

Our initial hypothesis was that the allylic oxidation reaction would follow a pathway similar to alcohol oxidation, with oxygen activation at the support surface followed by a reaction at the oxide particle. Based on the reports in the literature, we expected the reaction to involve free-radical intermediates.[10,17,19] Surprisingly, we found that at least in one case, namely when using copper oxide particles supported on nitrogen-doped carbon,

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Supporting information for this article is given via a link at the end of the document.

there are no free-radicals in the solution. In this paper, we try and resolve the different pathways leading to allylic oxidation, with the goal of gaining a better understanding of this important reaction.

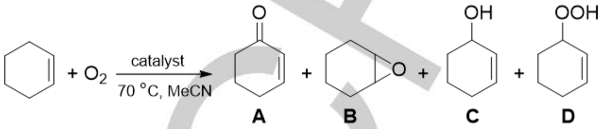
Results and Discussion

Catalyst synthesis and testing. We began by preparing and testing a set of nine *d*-block metal oxides supported on the same batch of hierarchically porous nitrogen-doped carbons[20] (1.2 mmolg^{-1} M/N:C, where M = V, Cr, Fe, Co, Ni, Cu, Nb, Mo, and W). The catalysts were prepared using vacuum-pore impregnation (see experimental section for details). To this set, we added two blanks: a clean N:C support and a carbon prepared from a citric acid precursor (denoted C_{cit}) having a similar surface area as the N:C (~1500 m^2/g).The latter has the same surface characteristics as the N:C sample but contains no nitrogen. All catalysts were then tested in cyclohexene oxidation in an autoclave under 10 bar O_2 and 55 bar Ar, keeping within safe explosion limits. In a typical reaction, each autoclave was charged with ca. 25 mmol of cyclohexene, 10 mg of catalyst (a nominal substrate:metal oxide ratio of 2000:1) and 15 mL of MeCN as solvent. Reactions were stirred for 16 h at 1000 rpm and analysed by gas chromatography (GC).

Cyclohexene is oxidised to four main products (Table 1): 2-cyclohexene-1-one **A**, cyclohexene oxide **B**, 2-cyclohexene-1-ol **C** and 2-cyclohexene-1-hydroperoxide **D** (herein the ketone, epoxide, alcohol and hydroperoxide, respectively). The rest of the products were over-oxidation products, mainly CO and CO_2. Products **A–C** were determined directly from the GC analysis. The hydroperoxide **D** could not be observed by GC, and was quantified by reacting each sample with PPh_3 (see experimental section for details). Control experiments confirmed that the internal standard, cyclohexane, showed no conversion at these reaction conditions. Further, in the absence of any catalyst the background reaction at 70 °C gives only 22% conversion, most of it to CO and CO_2 (Table 1, entries 1–3). Adding porous carbon doesn't change the conversion, but reduces the amount of over-oxidation slightly, possibly owing to radical-scavenging by carbon surface sites.[21] In the presence of pristine N:C, the conversion more than doubles, to ca. 50%. Moreover, the selectivity to the ketone **A** increases to 28%, at the expense of the hydroperoxide **D**. Indeed, we showed recently that these porous N:C materials are excellent oxygen reduction catalysts,[20] yet these results also point to a N:C-catalysed route from **D** to **A** *(vide infra)*.

Adding W, Ni, Mo, Fe, or Nb doesn't change the results significantly (Table 1, entries 4–8). For some of these catalysts, the selectivity to **A** is lower than that of the pristine N:C support, which may reflect the blocking of labile sites on the support by metal oxide particles. However, the catalysts containing V, Cr, Cu and Co showed a significant increase in conversion (entries 9–12). Vanadium oxide (V/N:C), which is known as a good epoxidation catalyst,[22,23] indeed gives a higher selectivity to the epoxide **B**. The remaining three catalysts are interesting: They are the only ones that give measureable yields of the alcohol **C**. All three give less hydroperoxide compared with the blanks, indicating a pathway from **D** to **C**. Cobalt oxide gives the highest conversion. But copper oxide gives the highest selectivity to the ketone product **A**, with a remarkably low amount of over-oxidation products. In fact, even at this unoptimised stage, the Cu/N:C catalyst gives a combined ketone+alcohol yield of nearly 45% with a minimum TON > 1400 and TOF > 88 h^{-1} (the actual TON and TOF per site are much higher, because most of the copper oxide is not accessible, see discussion below). We therefore focussed our investigation on these two catalysts.

Table 1. Cyclohexene oxidation in the presence of different catalysts.[a]



Entry	Catalyst	Conversion (%)	Selectivity (%)				
			A	B	C	D	other
1	None	22	8	2	0	10	80
2	C_{cit}	23	14	2	0	17	67
3	N:C	49	28	3	0	5	64
4	W@N:C	43	17	4	0	12	67
5	Ni@N:C	44	17	3	0	17	63
6	Mo@N:C	45	17	5	0	11	69
7	Fe@N:C	53	23	3	0	3	74
8	Nb@N:C	58	25	6	0	8	61
9	V@N:C	64	20	15	0	2	63
10	Cr@N:C	66	32	7	1	4	56
11	Cu@N:C	71	47	9	16	4	24
12	Co@N:C	80	38	6	6	6	44

[a] Reaction conditions: 10 bar O_2; 2,5 mL (24,7 mmol) cyclohexene; 0,5 mL (1,85 mmol) cyclohexane (IS); 10 mg catalyst; 15 mL MeCN; stirred in an autoclave (1000 rpm); 70°C; 16 h.

Control reactions using equivalent amounts of cobalt oxide supported on γ-alumina showed lower conversions and more side-products, confirming the importance of the N:C support (Table 2, entry 2). The copper oxide supported on γ-alumina does show a good conversion, but lower selectivity and more side-products, therefore making the γ-alumina-supported catalyst less favourable (entry 6). Note that the difference in surface area between the carbon and the γ-alumina was corrected for by increasing the catalyst amount accordingly. To boost the number of free-radicals at the start of the reaction, we added hydrogen peroxide (entry 3, 13 mol% relative to substrate).[5,7] Hydrogen peroxide can decompose into water and oxygen under these reaction conditions. The water molecules themselves do not change the conversion and selectivity (the H_2O_2 solution is already 90% water), but the decomposition of H_2O_2 affects the reaction by releasing free-radicals into the solution. Adding hydrogen peroxide increased the conversion, but didn't change the selectivity significantly. A similar increase was observed when the reaction was run at 80 °C. With copper oxide, however, adding H_2O_2 or increasing the reaction temperature affected both the conversion and the selectivity (entries 7 and 8). The conversion increased to 85%, and the combined selectivity to **A**+**C** increased to 70%. Importantly, this increase in selectivity came at the expense of the over-oxidation products (unlike with cobalt, where there were still a lot of over-oxidation products). To our mind, this was counter-intuitive: one would assume that adding an initiator such as H_2O_2 or increasing the temperature would lead to more CO and CO_2. These results led us to think that perhaps the copper-oxide catalysed reaction is not a simple free-radical process. Previous reports comparing the oxidation kinetics of cyclohexene and cyclohexene-*d₁₀* show a clear primary isotope effect (k_H:k_D = 8.2), indicating that the rate-determining step involves C–H bond scission.[10] Moreover, adding a radical scavenger quenched the reaction.[10,15] To check if this also applies our system, we ran additional control experiments in the presence of 6 mol% of 2,6-di-t-butyl-4-methylphenol (BHT, see details in the experimental section). Adding BHT to the reaction mixture containing the N:C support or the Co/N:C catalyst stopped the reaction completely (Table 3, entries 2 and 4, *cf*. with entries 1 and 3). But when we added BHT to the Cu/N:C-catalysed reaction, there was only a slight drop in conversion and selectivity (from 85% to 76% and from 53% to 46%, respectively, see entries 5 and 6). This shows that while the reactions catalysed by metal-free N:C and by Co/N:C are definitely free-radical processes, the Cu/N:C-catalysed reaction is not affected by free-radical scavengers (these experiments were repeated multiple times by different people to ensure their repeatability and reproducibility). Therefore, we conclude that in the copper-catalysed system, there are no free-radicals in solution.

Table 2. Oxidation of cyclohexene with various copper oxide and cobalt oxide catalysts.[a]

Entry	Catalyst	Temp (°C)	Conversion (%)	Selectivity (%)				
				A	B	C	D	other
1	Co@N:C	70	80	38	6	6	6	44
2	Co@Alu	70	56	20	3	0	3	74
3[b]	Co@N:C	70	87	43	6	11	nd[c]	40
4	Co@N:C	80	87	41	12	5	nd[c]	42
5	Cu@N:C	70	71	47	9	16	4	24
6	Cu@Alu	70	77	31	7	2	0	60
7[b]	Cu@N:C	70	86	61	15	8	nd[c]	16
8	Cu@N:C	80	85	53	10	17	nd[c]	20

[a] Reaction conditions: 10 bar O_2; 2,5 mL (24,7 mmol) cyclohexene; 0,5 mL (1,85 mmol) cyclohexane (IS); 10 mg carbon catalyst, 73 mg alumina catalyst; 15 mL MeCN; stirred in an autoclave (1000 rpm); 16 h. [b] Added 1,0 mL H_2O_2 (10 wt%, 3.3 mmol, 13 mol% based on cyclohexene). [c] Not determined.

Scanning electron microscopy (SEM, Figure 1) of the Cu/N:C catalyst showed copper oxide spherical particles, ca. 200–250 nm in diameter, distributed evenly across the surface. Unlike the support, the particles are non-porous. This means that most of the copper oxide is “inside” the particle and unavailable for catalysis. If we consider that the active outer shell is about five atomic layers (roughly 2 nm in thickness), the actual active catalyst comprises only 0.1 wt%. Accordingly, the actual TON of this catalyst would be > 24000, with a corresponding TOF > 1500 h^{-1}.

Table 3. Effects of adding free-radical scavengers.[a]

Entry	Catalyst	Addition	Conversion (%)	Selectivity (%)			
				A	B	C	other
1[b]	N:C	-	49	28	3	0	69
2[b,c]	N:C	BHT	0	0	0	0	0
3	Co@N:C	-	87	41	12	5	42
4[c]	Co@N:C	BHT	0	0	0	0	0
5	Cu@N:C	-	85	53	10	17	20
6[c]	Cu@N:C	BHT	76	46	10	20	24

[a] Reaction conditions: 10 bar O_2; 2,5 mL (24,7 mmol) cyclohexene; 0,5 mL (1,85 mmol) cyclohexane (IS); 10 mg carbon catalyst; 15 mL MeCN; stirred in an autoclave (1000 rpm); 80 °C 16 h. [b] Reaction temperature 70°C. [c] Added 354 mg BHT (7mol% based on cyclohexene).

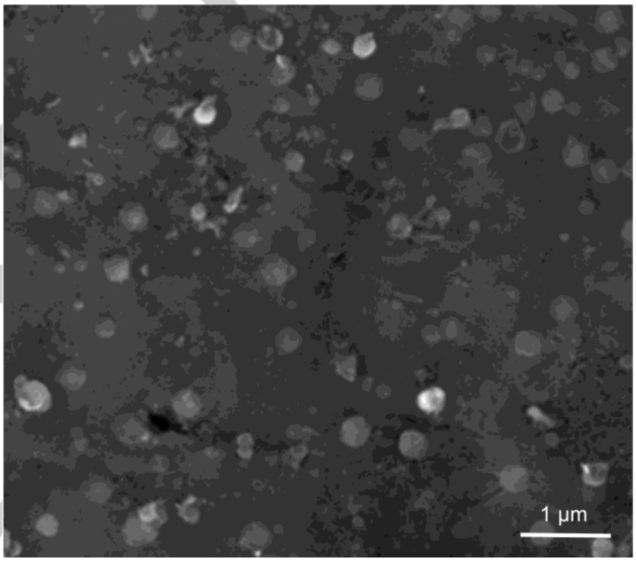


Figure 1. Scanning electron micrograph of Cu/N:C at ×15.000 magnification (an image with particle measurements is included in the Supporting Information).

X-ray photoelectron spectroscopy (XPS, Figure 2) showed that impregnating the N:C surface with copper oxide doesn’t affect the nitrogen binding energy. This suggests that the copper oxide is not coordinated to surface nitrogen atoms. The impregnation does increase the intensity of the O 1s peak, indicating a higher oxygen content in the sample. For copper, the XPS shows the typical Cu 2p 1/2 and 2p 3/2 peaks, which can pertain to both Cu^+ and Cu^{2+}. Yet the characteristic CuO peak at 945 is absent, supporting the presence of Cu_2O,[24] (metallic copper is unlikely at such low treatment temperatures[25] and considering the increase in the oxygen signal). The carbon peak is not affected by impregnation with copper. However, powder X-ray powder diffraction (XRD) measurements of the catalyst show CuO as the major component in the particles (see details in the supporting information). These results are consistent with a CuO-CuO_2 core-shell structure, as XRD measures the entire particle while XPS penetrates only a few atomic layers.[26] We therefore suggest that during the thermal treatment following the impregnation step, the adsorbed $Cu(NO_3)_2$ precursor is first converted to CuO and NO_2(g). As the temperature approaches the final temperature of 300 °C, the Cu_2O shell starts forming. Indeed, temperature programed reduction measurements indicate the presence of multiple copper oxides (details in Supporting Information). Similarly, thermogravimetric analysis of the pristine N:C and the Cu/N:C samples shows that the latter decomposes at a lower temperature (400 °C vs 500 °C, respectively. This supports the hypothesis that copper partially oxidises the surface, creating more labile sites (see details in the supporting information).

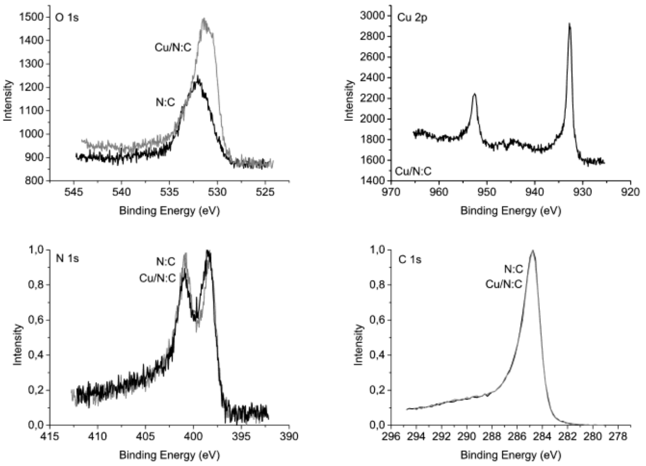


Figure 2. XP spectra of the Cu/N:C and pristine N:C samples showing the oxygen 1s, Cu 1/2p and 3/2p, nitrogen 1s and carbon 1s binding energies. Impregnation of copper oxide on the N:C increases the oxygen content but does not affect the nitrogen or carbon peaks. Note that the nitrogen and carbon graphs are normalised for clarity.

Mechanistic considerations. Based on the above results, we propose two alternatives for the catalytic allylic oxidation of cyclohexene with molecular oxygen. The first follows the traditional free-radical route, and pertains to the Co, Fe, Cr, Mo, V, Ni, Nb and W/N:C catalysts. Here, oxygen is either activated thermally or in a redox process on the N:C surface. Insertion of this activated oxygen into the allylic C–H bond gives the cyclohexenyl hydroperoxide **D**. This can then either rearrange to give the ketone **A** or undergo scission, giving oxo and peroxo radicals that propagate a chain oxidation reaction.[2,15] Accordingly, this pathway, which involves free-radicals in the solution bulk, is readily quenched when BHT is added.

Conversely, in the presence of Cu/N:C, there are no free-radicals in the solution bulk. Oxygen can still be activated at the N:C surface sites, but now there are two options: those small amounts of short-lived activated oxygen species (e.g. $O_2^{-\bullet}$radical anions) that do travel into solution will be quenched by BHT (Figure 3a, *cf.* also the difference in conversion between entries 5 and 6 in Table 3). The BHT molecules are too bulky to enter the micropores. Therefore, they will quench only the radicals in the solution. Conversely, the activated oxygen species that are close enough to diffuse to a supported copper oxide particle,[27] can react there with cyclohexene, forming an adsorbed hydroperoxide (Figure 3b). This adsorbed hydroperoxide can undergo two reactions. The first is rearrangement and dehydration, giving the ketone **A** and a molecule of water (Figure 3c).[9,28] The second is a disproportionation reaction with another cyclohexene molecule, giving two molecules of cyclohexene-1-ol **C** (Figure 3d). Compared with the other metal oxides, the scission of the RO–OH bond on the copper oxide surface is apparently much slower. This means that fewer free-radicals are released into the solution, giving enough time for the rearrangement and disproportionation reactions.

Interestingly, there is a marked difference between the oxidation of activated alcohols, which we reported earlier,[12] and that of cyclohexene. With an activated alcohol substrate such as cinnamyl alcohol, the N:C support is required for oxygen activation. There, no reaction was observed for copper oxide particles supported on C_{cit}, an analogous porous carbon with no nitrogen dopants. Cyclohexene oxidation, however, does proceed in the presence of Cu/C_{cit}, showing that the allylic oxidation in this case is easier. This is supported by the results of Gray and co-workers,[10] who showed that the allylic C–H bond scission is rate-determining, and by the fact that this bond is weaker than the alcohol C–H bond (83 $kcal mol^{-1}$ and 96 $kcal mol^{-1}$, respectively[29,30]).

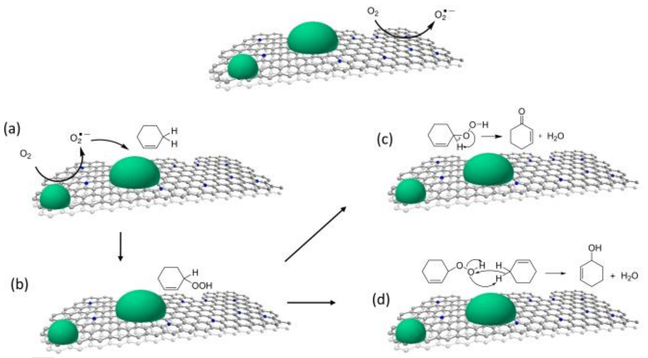


Figure 3. Proposed reaction pathways for the catalytic oxidation of cyclohexene with molecular oxygen in the presence of Cu/N:C. (a) Oxygen activation at the support surface followed by radical migration into solution. (b) Insertion of activated oxygen into the allylic C–H bond to give the adsorbed hydroperoxide **D** followed by either (c) rearrangement to the ketone **A** and water or (d) reaction with another cyclohexene molecule to give two molecules of the alcohol **C**.

In all cases, the epoxide **B** probably forms via another pathway.[4,31] Cyclohexene molecules can interact with M=O groups on the particles' surface, giving the epoxide and a labile surface site which is then re-oxidised by incoming oxygen.[24]

Conclusions

The catalytic oxidation of cyclohexene with molecular oxygen can follow different pathways depending on the type of catalyst. In the presence of transition-metal oxide nanoparticles supported on nitrogen-doped carbons, the key step is the insertion of the dioxygen molecule into the allylic C–H bond, giving the cyclohexenyl hydroperoxide. This reaction can be enhanced by

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oxygen activation at the nitrogen-doped carbon surface. In most cases, the allylic oxidation follows a free-radical pathway. However, in the presence of Cu/N:C the reaction does not release free-radicals into solution. This enables a more selective reaction at the copper oxide surface, which probably involves cuprous oxide sites.

Experimental Section

Materials and Instrumentation

Gas chromatography analyses were performed on a PerkinElmer Clarus 580 instrument. This system was equipped with a flame ionization detector and autosampler (G4513A). A 30 m x 32 mm I.D. Rxi-5ms fused silica, crossbond diphenyl dimethyl polysiloxane column with a film thickness of 0.25 µm was used. For the GC, the injector volume was 1 µl and the flow was 100 mL/min of He carrier gas. The temperature program was 40 °C, 20 °C/min, 160 °C for 2 min. SEM measurements were performed on a Verios-460 microscope (FEI) using an accelerating voltage of 5 kV, with a working distance of 2–5 mm. Powder XRD patterns were obtained with a MiniFlex II diffractometer using a Ni-filtered CuKα radiation. The X-ray tube was operated at 30 kV and 15 mA, with a 0.01° step and 1s dwell time. XPS measurements were performed with a PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany), using a monochromatic AlKα X-ray source with a power of 24.8 W and a beam size of 100 µm. The spherical capacitor analyser was set at 45° take-off angle with respect to the sample surface. The pass energy was 46.95 eV, yielding a full width at half maximum of 0.91 eV for the Ag $3d_{5/2}$ peak. Peaks were calibrated using the C-1s position. Curve fitting was performed using the XPSPeak 4.1 software package. All chemicals were obtained from commercial sources (>99% pure) and were used as received. Temperature programmed reduction (TPR) studies were done by placing 25 mg of sample sandwiched between two quartz wool plugs in a quartz tube reactor (4 mm i.d.). After purging with nitrogen, a flow of 5% hydrogen in nitrogen mixture was applied, and the system was allowed to equilibrate and then heated with at 5 °Cmin^{-1} to 800 °C (no hold time).

Procedure for preparing the nitrogen-doped carbon support

The N:C support samples were prepared following the procedure published by Eisenberg *et al*.[20] Briefly, nitrilotriacetic acid ($N(CH_2COOH)_3$, NTA) was mixed at a 1:1 ratio with magnesium carbonate ($(MgCO_3)_4Mg(OH)_2$). This was dissolved in de-ionized water, stirred for 10 min at 85 °C, and cooled down to room temperature. The solid was then precipitated by adding an excess of ethanol and chilling in an ice bath for 2 h. The white solid was scraped out and dried at 40 °C for 48 h and grinded to a fine white powder. This powder was then pyrolysed in argon at 900 °C. The MgO particles were washed out with 3 × 500 mL of 0,5 M citric acid. The resulting crude N:C sample was dried at 120 °C for 2 h and heat treated under argon at 1000 °C for 1 h.

Procedure for preparing M/N:C catalysts

This is a modification of the procedure published by Slot *et al*.[12] The nitrogen-doped carbon support (100 mg) was placed in a small vial with a septum. The air was removed carefully using a needle and an aqueous solution of the desired metal precursor salt (0,2 mL, corresponding to a nominal loading of 1 mmol/m^2) was added to the vial under continuous stirring. The vial was shaken vigorously for 2–3 min, creating a uniform solid paste, which was then dried at 85 °C for 12 h. Each catalyst was then heat-treated at 300 °C under argon (except for Nb/N:C which was treated at 700 °C), and cooled down to room temperature. The different M/N:C catalysts were prepared from their respective precursors salts: $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, NH_4VO_3 (dissolved using 2 equiv of oxalic acid), $Cr(NO_3)_3 \cdot 9H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $C_{10}H_5NbO_{20} \cdot xH_2O$ and $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$. The Co/alumina catalyst sample was similarly prepared starting from (γ-Al_2O_3, Ketjen; ground and sieved to 200–400 nm) and using 0.8 mL of 0.55 M of $Co(NO_3)_2 \cdot 6H_2O$ stock solution.

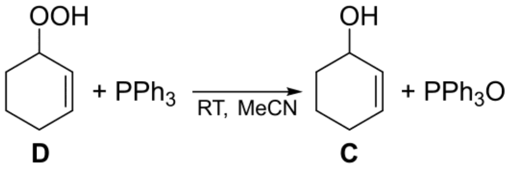
Procedure for catalytic oxidation of cyclohexene

This is a modification of the procedure published by Cao *et al*.[32] A 75 mL autoclave lined with a 50 mL Teflon insert was loaded with cyclohexene (2.5 mL, 24.7 mmol), cyclohexane (0.5 mL, internal standard), acetonitrile (solvent, 15 mL), catalyst (10 mg M/N:C carbon or 73 mg Co/alumina) and a stirring bar (30 mm). The autoclave was sealed, flushed with argon and oxygen twice before applying the final oxygen atmosphere (10 bar) and argon (55 bar). The autoclave was then heated to 70 °C for 16 h while stirring at 1000 rpm. After 16 h, the autoclave was cooled down to ambient temperature. Acetone (5 mL) was added with the sample and the reaction mixture was filtered using 0.45 µm PTFE syringe filters and analysed by GC.

Testing for the presence of free-radicals in solution was done by adding 2,6-di-t-butyl-4-methylphenol (BHT, 354 mg, 6 mol%) to the reaction at time zero and then following the above procedure. Reactions were performed in triplicate, and all GC samples were taken in duplicate.

Procedure for quantifying the cyclohexenyl hydroperoxide D.

The hydroperoxide **D** cannot be measured directly by gas chromatography due to its instability. Instead, we quantified it by comparing a control reaction sample to one where triphenylphosphine (PPh_3, 30 mg, 1mol%) was added. The sample was shaken for 1 min, generating heat in the process, as the PPh3 reacts with the hydroperoxide **D** to give PPh_3O and the alcohol **C** (eq 2). After this reaction, the sample was analysed by GC and compared to its untreated counterpart. Subtracting the initial amount of the alcohol formed in the control reaction from the amount of the alcohol after adding PPh_3 gives the amount of hydroperoxide **D** in the original sample.[6,33]



(2)

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Keywords: heterogeneous catalysis • autoxidation • sustainable chemistry • nanoparticles • nitrogen-doped carbons

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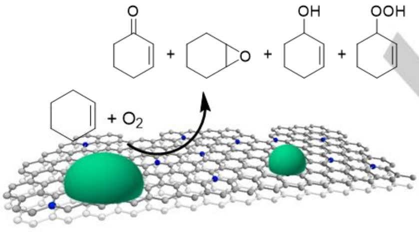

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Supporting Information for Selective catalytic oxidation of cyclohexene with molecular oxygen: radical vs. non-radical pathways.

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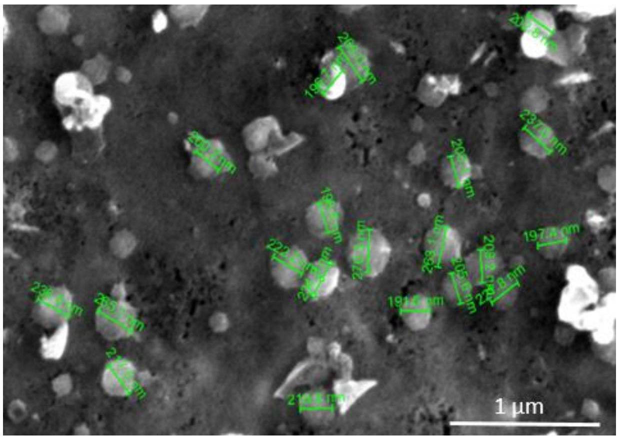

Figure S1. Scanning electron micrographs of Cu/N:C. The size of the copper oxide is ca. 200-250 nm Scanning electron microscopy (SEM) of Cu/N:C catalyst with particle measurements. The average size of the copper oxide spherical particles is ca. 200-250 nm. Furthermore, the clusters are evenly distributed onto the support surface.

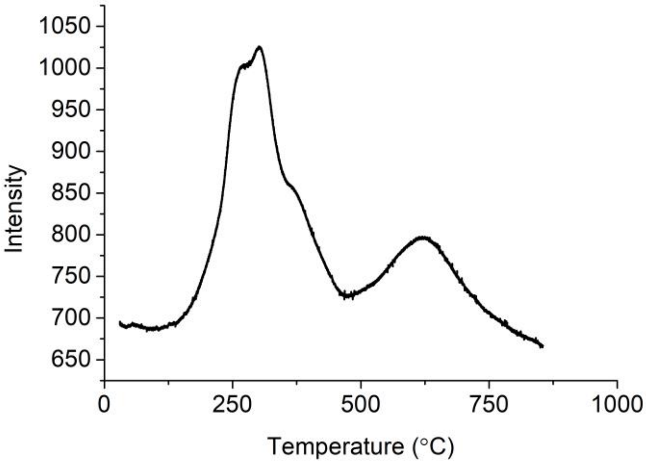

Figure S2. Temperature programmed reduction (TPR) spectrum for Cu/N:C.
The temperature programmed reduction (TPR) shows multiple copper oxide species presence inside the copper oxide catalyst. At 300 °C copper oxide is reduced, where multiple peaks indicate multiple copper oxide species. At 600 °C the support N:C is reduced. [1]

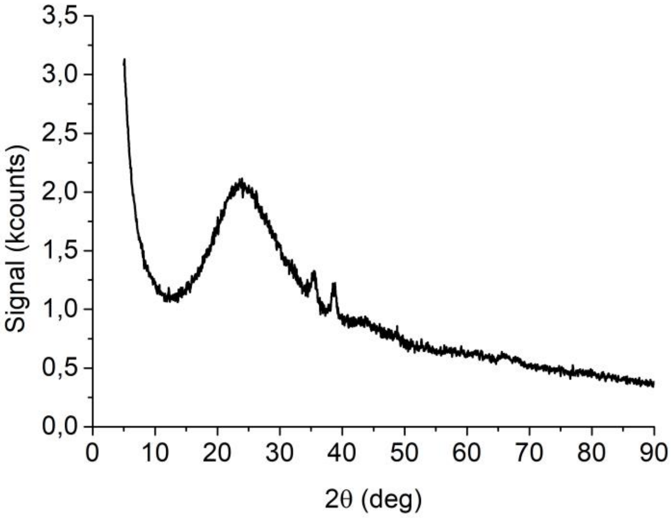

Figure S3. X-ray powder diffraction (XRD) spectrum for Cu/N:C.
X-ray diffraction showed a broad peak at 25° which is typical for carbon. The small peaks at 36.1° (-111) and at 39° (111) are typical for CuO.[2]

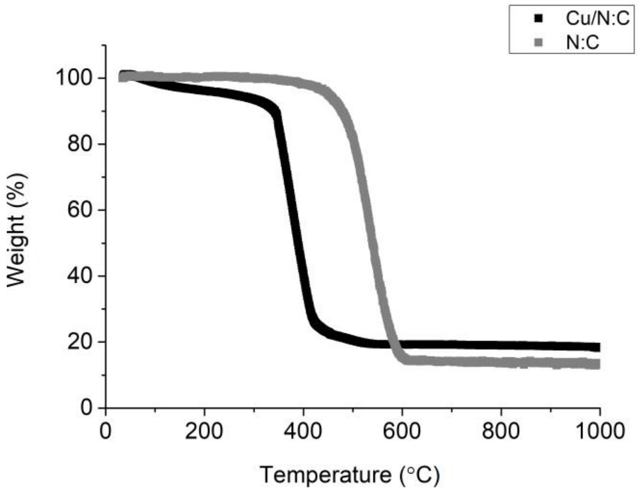

Figure S4. Thermal gravimetric analysis (TGA) curves of Cu/N:C and plain N:C.
TGA showed the mass loss of N:C at 500°C, whereas the Cu/N:C has a mass loss at a lower temperature. This difference indicates that the copper oxidises the nitrogen-doped surface during the treatment, thereby lowering the temperature of the mass loss. The difference in weight percentage at the end of the measurement around 600 °C is the copper oxide that is present in the Cu/N:C sample.

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