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Heterogeneous Catalysis

Cooperative Catalysis for Selective Alcohol Oxidation with Molecular Oxygen

Thierry K. Slot, David Eisenberg,* Dylan van Noordenne, Peter Jungbacker, and Gadi Rothenberg*[a]

Abstract: The activation of dioxygen for selective oxidation of organic molecules is a major catalytic challenge. Inspired by the activity of nitrogen-doped carbons in electrocatalytic oxygen reduction, we combined such a carbon with metal-oxide catalysts to yield cooperative catalysts. These simple materials boost the catalytic oxidation of several alcohols, using molecular oxygen at atmospheric pressure and low temperature (80 °C). Cobalt and copper oxide demonstrate the highest activities. The high activity and selectivity of these catalysts arises from the cooperative action of their components, as proven by various control experiments and spectroscopic techniques. We propose that the reaction should not be viewed as occurring at an 'active site', but rather at an 'active doughnut'—the volume surrounding the base of a carbon-supported metal-oxide particle.

Selective oxidation of organic molecules is the catch-22 of sustainable chemistry.^[1] On one hand, the best and most sustainable oxidant, dioxygen, is abundant and freely available. On the other hand, the high kinetic barrier for activating oxygen prevents any spontaneous oxidation. Whereas most people would say this is a good thing (fewer fires on a daily basis) the downside of this high barrier is that once dioxygen is activated, reactivity is high and selectivity is low. Due to its free-radical pathways, air oxidation all too often leads to large quantities of unwanted CO and CO₂.^[2]

There are three ways around this problem. The first is simply working at low conversions, keeping the selectivity high. This engineering solution is practical, yet incurs large recycling streams and low per-pass yields. The second is using an intermediate oxidant, such as hydrogen peroxide, peracetic acid or *tert*-butyl hydroperoxide.^[3–6] In this way, some of the activity of the oxygen is transferred to a chemical carrier, and the barrier

for oxygen activation is reduced. Still, chemical solution carries a hefty price tag: we have produced an extra reagent that is only necessary because of our inability to control the reactivity of the oxygen in the air. The third way is using a noble metal such as Pt or Ir that can activate molecular oxygen, but these are often too expensive and scarce for large-scale applications.^[7]

However, there are alternatives to platinum-group metals: Nitrogen-doped carbons are known to activate dioxygen electrochemically, catalysing the oxygen reduction reaction (ORR) in fuel cells.^[8–10] Recently, we reported the synthesis and application of such a carbon that has a similar electrochemical activity to platinum.^[11] Indeed, nitrogen-doped carbons can enhance the conversion of oxidations with air, either on their own or as supports for metal-oxide catalysts, reported by the groups of Beller, Arai, He, Ma and Wang.^[6,12–19] But how does this happen? Inspired by this work, we reasoned that the O–O bond in the dioxygen molecule is activated (i.e., lengthened) in the interaction with the nitrogen-carbon surface, becoming more "peroxide-like".^[20] Thus, in theory, placing an adjacent active site for catalysing this "peroxide"-mediated oxidation would result in cooperative catalysis, giving both high conversion and high selectivity.^[21]

We now report that combining nitrogen-doped carbon with various transition-metal oxides creates such a cooperative catalyst. These simple materials catalyse the oxidation of cinnamyl alcohol to cinnamaldehyde using molecular oxygen, with good conversion and high selectivity. The composite catalyst is prepared by impregnating mesoporous, nitrogen-doped carbon with metal salts. Importantly, we decouple the metal-doping step from the carbon growth step. Due to this decoupling, and by using undoped carbon controls, we can study the metal-nitrogen interactions (or lack thereof) and reveal the true nature of the active sites.

First, we prepared both the nitrogen-doped (N:C) and the control carbon (C_{undoped}) with similar microstructures.^[11] Briefly, magnesium nitriloacetate (MgNTA) was precipitated from a solution of magnesium carbonate and nitrilotriacetic acid. The MgNTA salt was pyrolysed under argon (900 °C/1 hr), washed with dilute citric acid to remove the MgO particles, which serve as *meso*-/*macropore* templates, and annealed under argon (1000 °C/1 hr) to yield the final carbon. The resulting nitrogen content was determined to be 7.6 at% (XPS, see below; detailed experimental procedures are included in the Supporting Information). We then used vacuum pore impregnation to distribute metal oxide sites on the N:C support, screening 10

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transition metals, which are known alcohol oxidation catalysts in the presence of peroxides (Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, W, Pb), as well as two alkaline-earth metals (Mg and Sr) for comparison. In each case, the loadings were about 1.3 mmol g^{-1} . This loading was chosen based on the known nitrogen content of the support (5.0 mmol g^{-1}), giving a nitrogen:metal equivalent ratio of 4:1. Thus, the nitrogens (which are responsible for oxygen activation^[8,9]) would outnumber the metal ions, and some would remain unoccupied.

For our test reaction, we chose the oxidative dehydrogenation of cinnamyl alcohol (**1**) to cinnamaldehyde (**2**, Table 1). This alcohol substrate can undergo several different oxidations (epoxidation, allylic alcohol oxidation, ring hydroxylation), as well as combustion to CO, CO₂ and water.^[17,22] Moreover, the aldehyde can react further on nitrogen-doped carbons, giving esters or acids.^[13,23,24] The variety of possible products makes this a good reaction for testing selective oxidation.

In a typical reaction, one equivalent of **1** was dissolved in ethanol and charged to an autoclave under 1 atm of oxygen (ca. 5 equiv oxygen per substrate) with 20 mg of catalyst (2.6 mol% of transition metal, based on **1**). The mixture was stirred at 80 °C for 16 h, and the products were analysed by gas chromatography (see the Supporting Information for full experimental details). Control experiments run at 25 °C gave

only 2% conversion. Table 1 shows the conversion, selectivity and yield for the different catalysts. Control experiments confirmed that <3% conversion was obtained without any catalyst, and <5% conversion was obtained in the presence of equivalent amounts of either C_{undoped} or a commercially available activated carbon (C_{comm}) with a similar surface area ($1500 \text{ m}^2 \text{ g}^{-1}$). Even when impregnated with Cu or Co, either of which could be expected to activate oxygen,^[25] these carbons gave much lower conversions compared with N:C.

The initial catalyst screening showed that Cu/N:C and Co/N:C were especially active. Therefore, we focused on these catalysts. First, we measured the intrinsic catalytic activity of equivalent amounts of copper oxide and cobalt oxide on C_{comm}, as well as on C_{undoped} (Table 1, entries 18–19 and 21–22). Cobalt oxide on carbon shows little or no activity, and although copper oxide shows some activity, it is nowhere near that of the Cu/N:C catalyst (see entries 21 and 5). Kinetic studies using the initial rates method showed that the reaction in the presence of the Co/N:C catalyst was three times faster than that in the presence of the plain N:C support (Figure S1). To rule out the possibility that carbon is simply not the ideal support for cobalt oxide, we synthesized an equivalent catalyst on $\gamma\text{-Al}_2\text{O}_3$.^[26] Here, one might expect a much better activity as the fit between the oxide support and the metal oxide crystals would enable the formation of smaller (and thus more active) particles.^[26–29] The fact that this material gave <5% conversion supports our hypothesis that the nitrogen-doped carbon is responsible for oxygen activation. We also studied the effect of metal-oxide loading on the catalytic activity. All metal oxides were prepared at two different loadings, 0.43 mmol g^{-1} and 1.3 mmol g^{-1} . The higher loadings (shown in Table 1) gave consistently higher yields by 20–30%. This suggests that the number of available metal-oxide sites is limiting the reaction in this loading range.

One key question for the performance of every heterogeneous catalyst is that of possible leaching. To test for leaching, we ran a simple filtration experiment (Figure 1) using the “cat-in-a-cup” concept.^[30] We ran the reaction for 5 h, then removed the catalyst and let the reaction run for another 20 h, and then re-introduced the catalyst. The stepped reaction profile in Figure 1 shows that the reaction stops when the catalyst is taken out. Moreover, the catalyst retains its activity after re-introduction, as shown by the similar reaction rates (0.47 and 0.51 mm h^{-1} , respectively).

To understand how this Co/N:C catalyst works, we characterized its composition and structure. X-ray photoelectron spectroscopy (XPS) showed that Co/N:C contains 7.3 at% nitrogen and 1.4 at% cobalt (Table 1), both of which give an upper limit for surface concentrations of 4.06 and $0.88 \text{ } \mu\text{mol m}^{-2}$, respectively. Furthermore, XPS revealed that the binding energies of the nitrogen atoms (N 1s orbital) are unaffected by the cobalt impregnation (Figure 2, top). This suggests that there is no significant N–Co coordination, albeit without precluding the N...Co proximity required for cooperative catalysis. Moreover, the Co (3/2p) XPS signals are the same for the N:C and the C_{undoped} samples (Figure 2, bottom). Thus, the active sites are not simple metal–nitrogen sites. Earlier studies hypothesized

Table 1. Catalytic oxidation of cinnamyl alcohol with molecular oxygen.^[a]

Entry	Catalyst ^[b]	Conversion of 1 ^[c] [%]	Selectivity of 2 ^[c] [%]	Yield of 2 ^[d] [%]
1	none	2	49	1
2	C _{comm}	5	84	4
3	C _{undoped}	5	87	5
4	N:C	17	94	15
5 ^[e]	Cu/N:C	56	90	50
6 ^[e]	Co/N:C	48	96	46
7 ^[f]	Co/N:C	55	93	51
8 ^[g]	Co/N:C	80	79	63
9	Ni/N:C	31	94	29
10	Fe/N:C	27	97	26
11	Pb/N:C	22	91	20
12	Mn/N:C	23	94	22
13	Zn/N:C	20	95	19
14	Cr/N:C	19	91	17
15	Mo/N:C	14	92	13
16	W/N:C	13	93	12
17	Mg/N:C	16	90	14
18	Sr/N:C	11	90	10
19	Co/C _{undoped}	8	91	6
20	Co/C _{comm}	4	81	3
21	Co/ $\gamma\text{-Al}_2\text{O}_3$	4	89	4
22	Cu/C _{undoped}	10	92	9
22	Cu/C _{comm}	25	84	21

[a] Reaction conditions: 1 atm O₂, 1.0 mmol **1**, 20 mg catalyst, 5 mL ethanol; stirred in an autoclave, 80 °C, 16 h. [b] Catalyst notation: [Metal ion]/[dopant]:[support]. Example: Co/N:C designates a cobalt oxide on nitrogen-doped carbon; all metal loadings are $1.3 \pm 0.1 \text{ mmol g}^{-1}$. [c] Based on GC analysis (*n*-octane internal standard). [d] Conversion \times selectivity. [e] Results are the average of triplicate experiments. [f] 48 h reaction time. [g] 120 h reaction time.

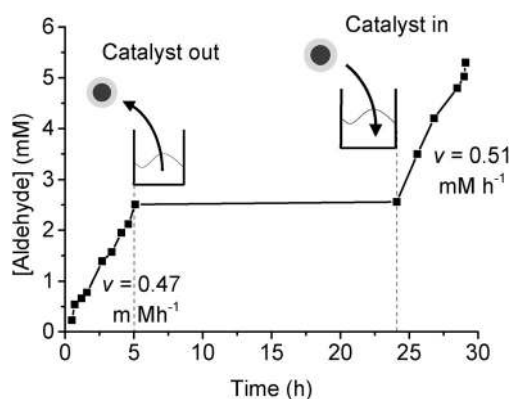


Figure 1. Filtration test reaction profile. Reaction conditions: 1 atm O₂, 2.0 mmol cinnamyl alcohol and 40 mg catalyst in 10 mL ethanol; stirred in a 20 mL tube, 80 °C.

the existence of Co–N bonds.^[14] However, the proposed Co–N binding peaks overlap with the abundant pyridinic nitrogen peaks, making such assignments difficult to confirm.^[14,31]

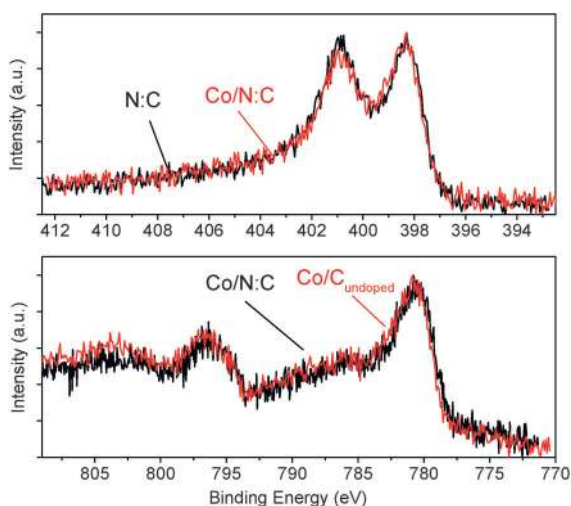


Figure 2. X-ray photoelectron spectra of N 1s orbital in Co/N:C and pristine N:C (top), and Co-3/2p orbital on Co/N:C and Co/C_{undoped} (bottom). The metal loadings for both Co/N:C and Co/C_{undoped} are 1.3 mmol g⁻¹.

In contrast, the cobalt impregnation does shift the O 1s XPS signals (Figure S2), reflecting the formation of cobalt oxide. Energy-dispersive X-ray spectroscopy (EDS) mapping confirms that the particles are composed of cobalt and oxygen (Figure 3c–f, see discussion below). Similarly, temperature-programmed reduction (Figure S3) showed a major reduction peak at 350 °C and a minor one at 450 °C, corresponding to Co₃O₄ with some CoO.^[32] Finally, X-ray diffraction showed only broad peaks near 24° and 44°, which are typical for carbon (Figure S4). No additional peaks were observed, indicating that the CoO_x particles are partially amorphous.

The type of nitrogen functionality (graphitic, pyridinic or other) may well affect the catalytic activity. However, the exact nature of oxygen-activating active sites in N-doped carbons is

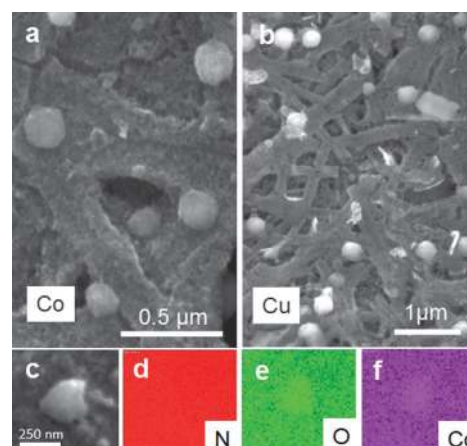


Figure 3. Scanning electron micrographs of (a) Co/N:C, (b) Cu/N:C, (c) a single CoO_x particle on N:C and (d–f) the corresponding EDS maps for elements N, O and Co, respectively.

a subject of open debate.^[8,34] Our carbon contains high proportions of the leading functionalities (38% pyridinic, 46% graphitic; Figure S2), which should support catalytic activity no matter the identity of the best functionality.

We then studied the morphology and distribution of the catalyst particles using scanning electron microscopy (SEM). As shown in Figure 3a–b, the Co/N:C catalyst has a hierarchical porous surface, on which spherical cobalt-oxide particles are dispersed. The size of these particles range from relatively large (100 nm) to 30 nm. Whereas the nitrogen atoms are evenly distributed (Figure 3d), cobalt oxide is available only at the surface of the particles. This emphasizes the importance of the immediate regions around the metal-oxide particles for combined oxygen reduction and oxidative dehydrogenation catalysis.^[35]

Based on these results, we can formulate a simplified picture of the catalytic reactions on the surface (Figure 4). First, oxygen is activated by the nitrogen-doped sites, lengthening the O–O bond and creating a “peroxide-like” species. This can react with the labile allylic hydrogen of the cinnamyl alcohol. The fact that no other oxidation occurs, nor is there any dehydrogenation of the ethanol solvent, shows that this reaction requires an activated substrate.^[36] Oxygen activation may occur through an electron transfer from the support. This step is not spatially limited, because the support is conductive and nitrogen sites are omnipresent (see EDS mapping in Figure 3d). However, the oxidative dehydrogenation step requires the physical transfer of two hydrogens from the cinnamyl alcohol to form the water molecule. Such an atom transfer process can only happen in close proximity to the cobalt-oxide site. Considering the relatively large size of the CoO_x particles, we suggest that the active regions are doughnut-shaped volumes surrounding the base of the particles (Figure 4). Oxygen molecules that are activated outside these areas are unlikely to participate in the subsequent dehydrogenation step. Whereas in theory the metal oxide can also be the site of O₂ activation with concurrent hydrogen transfer from the carbon, this is less likely. N-doped carbons are known for their ORR activity,

making them the more likely candidates for the O_2 activation half-reaction in this cooperative catalyst. Thus, we suggest that the 'active doughnut' hypothesis is useful in describing cooperative catalysis on supported catalysts.^[37–39]

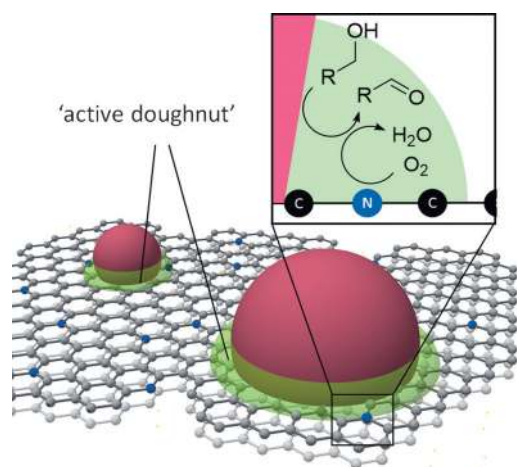


Figure 4. Cartoon showing the 'active doughnut' volume concept in cooperative catalysis: dioxygen activation at a nitrogen-doped carbon surface site combined with oxidative dehydrogenation at the metal-oxide surface.

We further examined the catalytic scope of the MO_x/N -doped materials with various benzylic and allylic alcohols, running reactions for both 16 and 48 h (Table 2). For each substrate, control experiments were run without a catalyst to exclude any possibility of autocatalysis. Oxidation of 1-phenyl-1-propanol gave propiophenone in near-quantitative yields (entry 2). Primary benzylic alcohols (entries 1,3) gave moderate yields, yet still much higher when compared with those of pyridinic or furfuryl alcohols (entries 4 and 5). This may reflect the added stability of the substrate through hydrogen bonding to the ring heteroatom. Reactions with geraniol and the much less active cyclohexanol gave little conversion, confirming the need for an extended π -system.

Overall, we have demonstrated here that the low selectivity problem associated with air oxidation of activated alcohols can be solved by combining an oxygen-activating species and a simple metal-oxide catalyst. The proximity requirement of the two is most likely responsible for suppressing free-radical chain byproducts. By applying a rational screening, we can study the influence of metal oxides on the nitrogen-doped carbon without changing the support morphology. We use no noble metals, and indeed, only minute amounts of first-row transition metals that are present as stable oxides. The good conversions and excellent selectivities obtained in the cases of cobalt and copper show the potential of this approach in alcohol oxidations with oxygen. Considering that this reaction proceeds well under mild conditions ($80^\circ C$ and approximately 1 atm), we foresee opportunities in fine-chemical synthesis, especially for sensitive multi-functional substrates.

Table 2. Oxidation of different benzylic and allylic alcohols. ^[a]				
Entry	Catalyst ^[b]	Substrate	Conversion (Selectivity) ^[c]	
			16 h [%]	48 h [%]
1	a Cu/N:C		19 (92)	27 (96)
	b Co/N:C		27 (91)	34 (94)
2	a Cu/N:C		> 99 (> 99)	> 99 (94)
	b Co/N:C		> 99 (> 99)	> 99 (99)
3	a Cu/N:C		18 (94)	23 (95)
	b Co/N:C		25 (93)	33 (91)
4	a Cu/N:C		8 (83)	15 (74)
	b Co/N:C		8 (38)	38 (65)
5	a Cu/N:C		2 (25)	2 (19)
	b Co/N:C		2 (18)	2 (22)
6	a Cu/N:C		5 (62)	5 (58)
	b Co/N:C		5 (79)	5 (75)
7	a Cu/N:C		1 (83)	2 (74)
	b Co/N:C		< 1 (52)	1 (51)

[a] Reaction conditions: 1 atm O_2 , 1.0 mmol substrate, 20 mg catalyst, 5 mL ethanol; stirred in an autoclave at $80^\circ C$, 16 h. [b] Catalyst notation: [Metal ion]/[dopant]:[support]. Example: Co/N:C designates a cobalt oxide on nitrogen-doped carbon; all metal loadings are $1.3 \pm 0.1 \text{ mmol g}^{-1}$. [c] Selectivity based on GC analysis (*n*-octane internal standard); 16 or 48 h reaction time.

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Keywords: active sites • cooperative effects • heterogeneous catalysts • oxygen • supported catalysts

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