Oxidation of benzylic compounds by gold nanowires at 1 atm O_2 ⁺

Lei Hu,^a Xueqin Cao,^a Jianhui Yang,^b Min Li,^a Haiyan Hong,^a Qingfeng Xu,^a Jianfeng Ge,^a Lihua Wang,^a Jianmei Lu,^{*a} Liang Chen^{*b} and Hongwei Gu^{*a}

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Ultra-thin gold nanowires (GNWs), with uniform surface crystallinity, appear much more active than gold nanoclusters in benzylic compound oxidation. Ethylbenzene oxidation was used as a model reaction and a radical chain reaction mechanism was revealed by the DFT method.

Because of their importance in the manufacture of dyes, flavorants, perfumes, pharmaceuticals and fine chemicals,¹ oxidation reactions involving active gold, such as catalytic alcohol oxidation,² the direct synthesis of azobenzene,³ and low temperature CO oxidation,⁴ have been of considerable interest over the past decade. Lambert's group⁵ reported that ultra-small gold nanoclusters have relatively high catalytic activity and selectivity as evaluated by styrene oxidation under molecular oxygen. Dapurkar et al.⁶ reported that ketone formation from benzylic compounds could be achieved using supported gold nanoparticle catalysts at 1 atm O2. Recently, it has been found that the nanomaterials' catalytic abilities and product selectivity are dependent on the catalysts' surface crystallinity.⁷ Here, we investigated the catalytic performance of ultra-thin gold nanowires (GNWs), a new morphology of active gold with single surface crystallinity, and found that these one-dimensional gold nanocatalysts are more active than gold nanoclusters and that the catalytic cycles undergo a radical chain oxidation mechanism.

GNWs with an average diameter of 1.4 nm were prepared following a reported methodology⁸ with minor modification. HAuCl₄·4H₂O (0.2 mmol) in 3 ml hexane and 1 ml oleylamine was injected into 9 ml oleylamine at room temperature while stirring vigorously. The temperature was raised to 80 °C to remove the hexane and the mixture turned colorless in 5 min. The reaction was maintained at 80 °C for 4 h without stirring. The GNWs were collected by precipitation and centrifugation. Fig. 1A shows representative transmission electron microscopy (TEM) images of the as-synthesized GNWs. The nanowires are a few micrometres in length with an average diameter of approximately 1.4 nm, as calculated from the analysis of high-resolution TEM images in many different regions.

Fringes associated with the gold lattice appear clear, in which the axial direction is (111) (Fig. 1B inset).

The oxidation of styrene was used to evaluate the activity of the GNW catalyst. Table 1 compares the catalytic performance of the GNWs for the partial oxidation of styrene in different solvents at 100 °C for 20 h. The gold content determined using inductively coupled plasma mass spectroscopy (ICP-MS) was 0.0252% (wt%), which was four times lower than the nanocluster catalyst. It was interesting to find that the solvent has an important effect on product formation. Using xylene or chlorobenzene as solvent, aldehyde is the major product with $\sim 70\%$ selectivity. In contrast, epoxy is the major product in DMF or 1, 4-dioxane, with a selectivity as high as 63.3%. In 1.4-dioxane, the styrene conversion is 81.7% and the aldehyde and epoxy yield is 31.4 and 44.0%, respectively. In the styrene oxidation reaction, molecular oxygen was firstly absorbed on the surface of the gold nanowires to form activeoxygen. Both solvent and styrene can react with this activeoxygen through t wo pathways present in the reaction: (1) if the solvent firstly reacted with this active-oxygen, a free radical intermediate would be formed. This intermediate is not stable, and can form peroxide in an oxygen environment. This peroxide acts as an oxidant in the styrene oxidation reaction and an epoxy compound is the major product.⁹ (2) If the solvent is more stable than styrene, styrene can react with the activeoxygen and aldehyde is the major product.⁵ When using xylene as a solvent, methylbenzaldehyde, a new oxidation product, was detected by GC-MS. This product is formed from the partial oxidation of xylene (ESI⁺). A free-radical reaction mechanism was further demonstrated by adding 1-mercaptohexadecane to the reactant. No oxidation products were achieved under the same reaction conditions. 1-Mercaptohexadecane served two important roles: (1) capping on the surface of gold nanowires to inhibit the interaction of oxygen and the nanowire surface; (2) as a free-radical quencher to stop the reaction.



Fig. 1 Transmission electron microscope images of ultra-thin Au nanowires. (Inset: high resolution TEM image of nanowires.) Experiments were performed with a Schlenk system.

^a Key Laboratory of Organic Synthesis of Jiangsu Province, Key Laboratory of Absorbent Materials and Techniques for Environment, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China. E-mail: lujm@suda.edu.cn, hongwei@suda.edu.cn;

Fax: +86-65880905; *Tel:* +86-65880905

^b Institute of Materials Technology & Engineering,

Chinese Academy of Sciences, Ningbo, 315201, China

[†] Electronic supplementary information (ESI) available: Details of GNWs synthesis and catalyst testing; GC spectra; Computational details and the coordinates of GNWs are provided (5 pages). See DOI: 10.1039/c0cc01568g

Table 1 Catalytic performance of GNWs based on the partial oxidation of styrene⁴

Yield $(\%)^c$

а

6.5

31.4

16.0

24.7

2.7

14.5

14.8

b

14.7

44.0

4.4

9.4

1.2

1.6

1.68

Selectivity $(\%)^c$

а

27.9

38.5

70.5

62.5

69.3

50.6

87.2

b

63.3

53.9

19.2

23.8

30.7

5.7

9.9

с

8.8

1.6

10.3

13.7

3.8

0.9

0=0

1 4nm Au NWs $100^{\circ}C.1$ atm O_{2}

Conversion (%)

23.2

81.7

22.7

39.5

3.9

28.6

17.0

Entry^b

2

3

4 5

6

7

^a Reactions are carried out with 1.25 g styrene and 0.4 mg	g GNWs
^b 1. DMF, 2. 1,4-dioxane, 3. <i>m</i> -xylene, 4. <i>p</i> -xylene, 5. chloro	obenzene
6. heptane, 7. toluene; ^c Calculated by GC-MS using deca	ne as ar
internal standard.	

Table 2 summarizes the catalyst activities in the oxidation of various benzylic compounds at 1 atm O₂ where the benzylic compounds were used as both solvent and reactant. Ethylbenzene, 4-nitroethylbenzene and iso-propylbenzene formed a ketone with 21, 23 and 47% conversion, respectively. GNWs show a higher selectivity (100%) as compared with Dapurkar's results⁶ (ethylbenzene oxidation with 85% selectivity).

To establish the reaction mechanisms of ethylbenzene oxidation on GNWs, we performed DFT calculations (Fig. S1[†]) based on a coaxial multi-shell GNW model according to the work of Kondo¹⁰. The saturated ethyl group is too inert to interact with the GNW surface. Ethylbenzene can therefore only be physisorbed on the GNW, with the benzene ring perpendicular to the GNW surface. C-H activation (3.79 eV) in the ethyl group is extremely difficult in the gas phase or on the gold surface and the reaction is expected to be triggered by the endothermic dissociation of O_2 on the GNW with a reaction energy of -0.11 eV. Furthermore, the corresponding activation barrier is 1.01 eV, which is 0.25 eV lower

Table 2 Catalytic results of the partial oxidation of alkylbenzene^a

 $^{HO} Y^{R_2}$

	R	1.4nm ,1	m Au NWs ▲ 1 atm O ₂	R_{\parallel}^{H} $+$ R_{\parallel}^{H}	Ъ	
					Selectivity (%)	
Entry	R	R_1	R_2	Conversion (%)	а	b
1	-H	-H	-H	1.3	95.2	4.8
2	o-CH ₃	-H	-H	4.3	62.1	37.9
3	m-CH ₃	-H	-H	1.3	100	0
4	p-CH ₃	-H	-H	3.4	82.4	17.6
5	p-Cl	-H	-H	1.0	100	0
6	p-OCH ₃	-H	-H	0.6	100	0
7	–H	-H	-CH ₃	21.1	100	0
8	$p-NO_2$	-H	-CH ₃	23.1	83.5	16.5
9	p-OCH ₃	-H	-CH ₃	1.3	70.8	29.2
10	–H	$-CH_3$	-CH ₃	47.9	62.9	37.1

^a Reactions are carried out with 1.25 g alkylbenzene and 0.5 mg GNWs.



Fig. 2 Illustration of ethylbenzene oxidation on the GNWs

than on the Au (111) surface.¹¹ The roughness of the curved surface increases the reactivity of the GNW by altering the electronic structures.¹² The dissociated atomic oxygen on the GNW is highly reactive and is able to activate the C-H bond. Indeed, the extraction of the most active hydrogen atom to form an OH radical turns out to be exothermic, with a reaction energy of 0.12 eV. The required activation barrier is as low as 0.32 eV.

After removal of the first hydrogen, the ethylbenzene radical is able to bind with either the OH adsorbed on the GNW (Fig. 2, cycle 1) or with an O₂ molecule (cycle 2). However, the strong interaction (2.08 eV) between the OH and the GNW reduces the probability of cycle 1 occurring. Furthermore, this step will consume the active oxygen atoms and rapidly terminate the catalytic reactions since O₂ dissociation is rather difficult. On the other hand, O2 molecules can be strongly bound to the ethylbenzene radical, with an adsorption energy (E_a) of 1.23 eV. In return, the O₂ bond strength is significantly weakened, as indicated by the bond length elongation from 1.23 to 1.38 Å. The hanging oxygen in O_2 is activated to interact with the GNW with an E_a of 0.44 eV. Meanwhile, cleavage of the C-H bond is also promoted as the second hydrogen atom can be captured by the OH radical to form an H_2O molecule ($E_a = 1.2 \text{ eV}$). As a consequence, the C–O bond transforms to the C=O double bond, which subsequently dissociates the attached O_2 to yield a new oxygen atom on the GNW. The associated reaction energy is calculated to be 0.94 eV. As such, no net atomic oxygen is consumed in cycle 2. Only trace amounts of initial O₂ dissociation can successfully trigger the catalytic reactions.

Generally, the reactivity of benzylic compounds correlates with their C-H bond strength.¹³ Table 2 shows that toluene or xylene form corresponding aldehydes with low conversions. Compared with the weakest C-H bond strength of ethylbenzene (3.79 eV), the bond strength of toluene is much higher at 3.97 eV. In summary, we successfully synthesized GNWs with single surface crystallinity, and these GNWs show high activities for oxidation reactions at 1 atm O_2 . Our DFT calculations reveal that catalysis proceeds *via* a radical chain oxidation mechanism. Our findings present new opportunities for gold catalysis and should provide significant benefit towards understanding the catalytic mechanisms of nanomaterials.

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