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Reference:

Lueangchaichaweng Warunee, Brooks Neil R., Fiorilli Sonia, Javon Elsa, Bals Sara, Van Tendeloo Gustaaf, et al.- Gallium oxide nanorods : novel, template-free synthesis and high catalytic activity in epoxidation reactions
Angewandte Chemie: international edition in English - ISSN 0570-0833 - 53:6(2014), p. 1585-1589
Full text (Publishers DOI): <http://dx.doi.org/doi:10.1002/anie.201308384>
To cite this reference: <http://hdl.handle.net/10067/1157260151162165141>

Gallium Oxide Nanorods: Novel, Template-free Synthesis and High Catalytic Activity in Epoxidation Reactions

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One-dimensional nanomaterials such as nanorods and nanowires are drawing growing attention for the specific physical properties that they display compared to their bulk counterparts.¹ For a surface-related application such as heterogeneous catalysis, a key advantage of nanomaterials is provided by the increased surface-to-volume ratio that accompanies the decrease in the size of the catalyst particles. Additionally, the surface of one-dimensional nanomaterials is inherently rich in coordinatively unsaturated sites that can play an active role in catalytic reactions. Solution-phase techniques have been shown to be a very advantageous and viable approach for the preparation of metal oxide nanomaterials.² However, these methods typically require the use of templates or other additives to direct the growth of the material towards a specific morphology.

Herein, we present a novel and straightforward method for the fabrication of gallium oxide nanorods with unprecedented small dimensions (length \leq 80 nm). This nanomaterial displays excellent properties as heterogeneous catalyst for the epoxidation of alkenes using the environmentally friendly hydrogen peroxide as oxidant.

Gallium oxide nanorods (Ga₂O₃-NR) were prepared using a precipitation method involving solvolysis of GaCl₃ with 2-butanol, followed by hydrolysis and condensation of the formed species (Fig. 1.A). The method is reliable and accessible, does not require any expensive template or additive, is carried out at very mild temperature and no energy-consuming calcination step is needed prior to catalytic application (see the SI for the detailed synthesis procedure). The material presents rod-like morphology with a length varying from 20 to 80 nm and a width of 3-5 nm (Fig. 1.B-C). The X-ray diffractogram of the nanorods displays two broad Bragg reflections (Fig. 1.F), which are slightly shifted compared to those

of a γ -Ga₂O₃ sample prepared as a reference (γ -Ga₂O₃-lit).³ Although the broadened diffraction peaks of Ga₂O₃-NR suggest a low crystallinity, a local well-defined structural order was evidenced by HR-TEM and SAED (Fig. 1.D-E): the observed planes correspond to the XRD reflections and match well the d-spacings and the orientation of the (100) and (105) planes of the seldom reported ϵ -Ga₂O₃ polymorph.⁴

The nanorod morphology of Ga₂O₃-NR results in the highest specific surface area (192 m² g⁻¹) ever reported for a gallium oxide.^{3,5} The adsorption isotherm of type II with H₃ hysteresis loop (Fig. S1A) indicates the presence of slit-shaped interparticle pores originating from packing of the nanorods.

The generation of nanorods is ascribed to an anisotropic structural feature of the intermediate species, most likely gallium oxyhydroxides, which are formed in the synthesis mixture. Indeed, gallium oxyhydroxides and their better known aluminum counterparts are characterized by orthorhombic unit cells, in which one cell parameter is much larger than the other two.⁶ The conversion of gallium oxyhydroxide into oxide is expected to proceed through condensation steps followed by partial migration of Ga atoms from octahedral to tetrahedral sites.⁷ Accordingly, solid-state ⁷¹Ga NMR of Ga₂O₃-NR shows the presence of Ga atoms in both tetrahedral and octahedral coordination (Fig. 1.G and Table 2), as encountered in ϵ -Ga₂O₃ and in other gallium oxide polymorphs,^{4,5a} but in contrast to oxyhydroxide structures in which all metal atoms are octahedrally coordinated.⁸

Ga₂O₃-NR was tested as heterogeneous catalyst for the epoxidation of alkenes with aqueous hydrogen peroxide (Table 1). This is the preferential path to produce epoxides, which are a family of versatile compounds used in numerous industrial syntheses of fine chemicals.⁹ Ethyl acetate was employed as environmentally acceptable and inexpensive solvent. The catalytic performance of Ga₂O₃-NR was compared both to γ -Ga₂O₃-lit and to titanium silicalite 1 (TS-1), which was chosen as benchmark because this zeolite is considered the optimum heterogeneous catalyst for the epoxidation of small and linear alkenes using H₂O₂ as the oxidant.¹⁰ (See Fig. S2 for TS-1 characterization). Remarkably, the epoxide yield achieved with Ga₂O₃-NR in the conversion of a linear alkene such as 1-octene is comparable to that of TS-1, while the catalytic performance is much superior with bulky cyclic alkenes such as cyclohexene and cyclooctene, which are too large to diffuse through the micropores of TS-1 (pore size of 0.56 nm). The almost complete epoxide selectivity achieved with Ga₂O₃-NR for these alkenes is also noteworthy, particularly in the case of cyclohexene, which is rather prone to the formation of the diol and other side-products.¹¹ In the epoxidation of styrene, Ga₂O₃-NR gave higher conversion and higher epoxide selectivity compared to TS-1. The lower epoxide selectivity observed with styrene is due to the formation of benzaldehyde, which originates from the oxidative cleavage of the

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[**] This work is supported by START1, Methusalem, Prodex, IAP-PAI and ERC (24691 – COUNTATOMS and 335078 - COLOURATOM) projects. The authors acknowledge Dr. K. Houthoofd, G. Vanbutsesele, Dr. C. Klaysom, Prof. J.W. Seo, Dr. T. Korányi and Prof. K. Binnemans for their support in the characterizations, and Dr. C. Özdilek for useful scientific discussion.

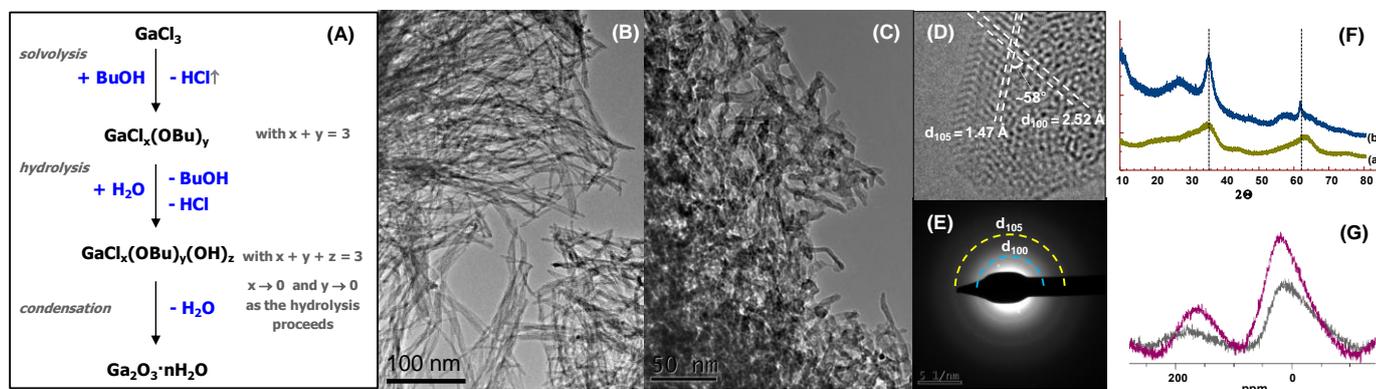


Figure 1. (A) Scheme of the formation of Ga₂O₃-NR (BuOH is 2-butanol). (B-C) TEM images of Ga₂O₃-NR with 40-80 nm length (B) and with 20-50 nm length (C). The size of the nanorods can be tuned by adjustments in the protocol of addition of H₂O (see SI), without affecting the catalytic activity of the material. (D) HR-TEM of a selected nanorod. (E) Selected Area Electron Diffraction pattern of Ga₂O₃-NR. (F) XRD pattern of: γ -Ga₂O₃-lit (a) and Ga₂O₃-NR (b). The vertical lines correspond to reflections of the (100) and (105) planes of ϵ -Ga₂O₃. (G) ⁷¹Ga MAS NMR spectra of Ga₂O₃-NR (grey) and γ -Ga₂O₃-lit (violet), showing Ga in tetrahedral (ca. 150 ppm) and octahedral (ca. 0 ppm) coordination.

vinyl group.¹² The crucial effect of the synthesis method on the catalytic performance of gallium oxides is demonstrated by the strikingly superior activity of Ga₂O₃-NR compared to γ -Ga₂O₃-lit (Table 1), in spite of having the same chemical composition.

Table 1. Catalytic epoxidation of selected alkenes using 50 wt.% aqueous H₂O₂

Alkene	Catalyst	Y _{epoxide} (%)	S _{epoxide} (%)	TON ^a	Productivity
Cyclooctene	Ga ₂ O ₃ -NR	84	>99	266	5.3
	γ -Ga ₂ O ₃ -lit	7	-	56	0.4
	TS-1	0	>99	-	0
	Blank	1	-	-	-
1-Octene	Ga ₂ O ₃ -NR	17	98	55	1.1
	TS-1	21	>99	70	1.3
Cyclohexene	Ga ₂ O ₃ -NR	45	>99	142	2.2
	TS-1	0	0	-	0
Styrene	Ga ₂ O ₃ -NR	20	58	109	1.2
	TS-1	6	23	87	0.4

Conditions: 2 mmol alkene, 4 mmol H₂O₂, 40 mg of catalyst, 2.0 g of ethyl acetate as solvent (acetonitrile for the reactions with TS-1, see SI), 4 h at 80 °C. ^aTON (mol_{alkene converted}/mol_{active sites}) was calculated using the number of acid sites for Ga₂O₃-NR and γ -Ga₂O₃-lit (Table 2) and the number of Ti atoms for TS-1. Productivity is defined as g_{epoxide}/g_{catalyst}.

The origin of the excellent catalytic properties of Ga₂O₃-NR was investigated through a combination of physicochemical characterization techniques. Raman spectroscopy was employed to elucidate the nature of the catalytic site and the mechanism of activation of hydrogen peroxide on Ga₂O₃-NR. The Raman spectrum of aqueous H₂O₂ shows a strong peak at 877 cm⁻¹ (Fig. 2.A(b)), assigned to the stretching of the O-O bond.¹³ A clear shoulder appears next to the peak at 877 cm⁻¹ in the spectrum of Ga₂O₃-NR impregnated with aqueous H₂O₂ (Fig. 2.A(c)), providing for the first time a direct experimental evidence of the interaction of hydrogen peroxide with a transition-metal-free oxide. On the basis of the position of the shoulder at higher wavenumber compared to H₂O₂ alone, and in analogy to related studies on titanium silicates,^{13,14} this signal is assigned to a hydroperoxide complex [Ga(η^1 -OOH)] formed

by reaction of a surface Ga site with H₂O₂. This assignment is supported by the higher epoxide yield obtained over Ga₂O₃-NR with internal alkenes compared to terminal linear alkenes. This evidences a pathway in which H₂O₂ is activated to form a metal-hydroperoxide intermediate, followed by heterolytic cleavage of the O-O bond and transfer of an oxygen atom to the alkene (the double bond in internal alkenes is more electron-rich and thus more prone to undergo electrophilic attack by one of the O atoms).¹⁵ Moreover, a homolytic radical pathway can be ruled out by the negligible formation of products of allylic oxidation in the reaction of cyclohexene (Table 1).¹⁵

The higher specific surface area of the nanorods compared to γ -Ga₂O₃-lit (Table 2) allows a better contact with the reagents, and its open structure prevents water entrapment that, on the other hand, can occur in the ink-bottle-shaped pores of γ -Ga₂O₃-lit (Fig. S1B). These features result in the lower hydrophilicity of Ga₂O₃-NR, as demonstrated by the lower number of H₂O molecules adsorbed per nm² of surface (Table 2). Too high hydrophilicity is detrimental for the epoxidation as it would hinder the approach of the apolar alkene to the catalyst surface.¹⁶ The nanorod morphology is also favorable for the dispersion of the catalyst particles in solution^{6b,17} Ga₂O₃-NR remains in suspension in the epoxidation mixture much longer upon stopping the stirring (~15 min against 1 min) compared to γ -Ga₂O₃-lit, which consists of large aggregates of particles without a specific morphology (Fig. S3). Although important, these surface and morphological properties cannot account alone for the remarkable superiority of the activity of Ga₂O₃-NR compared to γ -Ga₂O₃-lit.

The correlation between the catalytic activity and the number, type and strength of the surface acid sites on Ga₂O₃-NR and γ -Ga₂O₃-lit was studied by TPD of adsorbed pyridine monitored by FTIR spectroscopy (Fig. 2.B and Table 2).^{5a,c,18} Lewis acid sites in gallium oxides are generally attributed to coordinatively unsaturated Ga³⁺ ions mainly located in tetrahedral sites on the surface,^{5c} while surface Ga-OH are responsible for the mild Brønsted acidity of gallium oxides. These Brønsted acid sites can convert into Lewis acid sites as a consequence of surface dehydration upon thermal treatment at high temperature and tend to reconvert to Brønsted acid sites by rehydration at room temperature.¹⁹ Ga₂O₃-NR displays a much higher number of acid sites per gram of catalyst compared to γ -Ga₂O₃-lit (Table 2). This significant difference is a consequence of the combination of two parameters: the higher surface area of Ga₂O₃-NR, and its higher surface density of acid sites (Table 2).

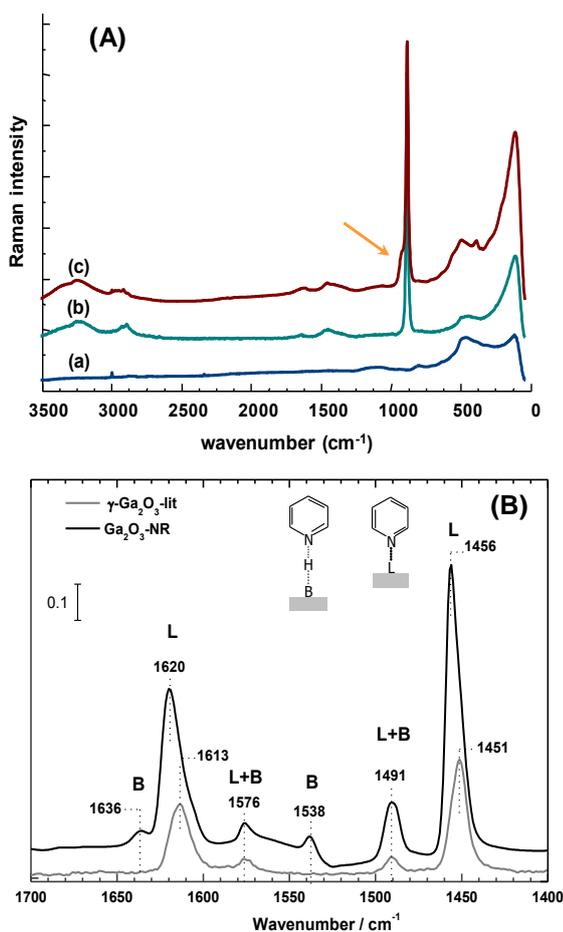


Figure 2. (A) Raman spectra of Ga₂O₃-NR (a); 50 wt.% aq. H₂O₂ (b); and Ga₂O₃-NR impregnated with H₂O₂ (c) measured at room temperature. In agreement with the observed signal in the Raman spectrum, Ga₂O₃-NR is able to activate H₂O₂ towards the epoxidation of cyclooctene also at 25 °C (though with lower yield, 5% after 24 h). (B) FTIR spectra of pyridine chemisorbed on Ga₂O₃-NR and on γ-Ga₂O₃-lit (measured at 150°C). L and B indicate pyridine adsorbed on Lewis and Brønsted acid sites, respectively.

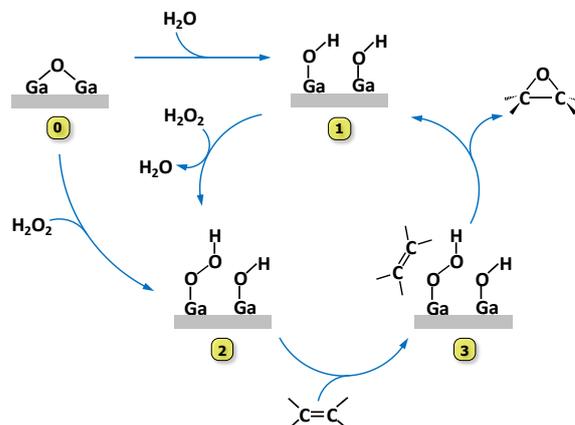
Table 2. Physicochemical properties of Ga₂O₃-NR and γ-Ga₂O₃-lit.

Catalyst	Surface area (m ² /g)	Ga _{tetra} :Ga _{oct} ^a	n _{H₂O} /nm ² ^b	Acid sites (mmol/g) ^c	L:B ratio ^c	Density of acid sites (sites/nm ²) ^c
Ga ₂ O ₃ -NR	192	1 : 10	26	0.16	18:1	0.63
γ-Ga ₂ O ₃ -lit	98	1 : 5	36	0.06	only L	0.38

^a Determined by ⁷¹Ga MAS NMR. ^b Estimated by TGA. ^c Based on FTIR spectroscopy of adsorbed pyridine at 150°C. Prior to the IR measurement the samples were subjected to an evacuation at 400°C, implying that the measured ratios of Lewis to Brønsted acid sites are expected to be higher than in the materials used as catalysts.

Both these features stem from the nanorod morphology of the catalyst: the higher surface area is a direct consequence of the higher surface-to-volume ratio that is characteristic of nanosized materials, while the higher surface density of acid sites is attributed to the intrinsically defective nature of the nanorods and the consequent higher density of coordinatively unsaturated sites on their surface compared to materials consisting of larger particles. Moreover, the Lewis acid sites in Ga₂O₃-NR are stronger than those in γ-Ga₂O₃-lit, as proven by the shift to higher wavenumbers of the peaks due to pyridine adsorbed on this type of acid sites (Fig. 2.B).^{5c,18} This is in

line with the higher chemical shift of the ⁷¹Ga NMR signal of tetrahedral Ga sites in Ga₂O₃-NR compared to γ-Ga₂O₃-lit (Fig. 1.G). Ga₂O₃-NR displays also a small amount of Brønsted acid sites that are strong enough to protonate pyridine, while this type of acid sites is absent in γ-Ga₂O₃-lit (Fig. 2.B).^{5c} However, these sites are weaker compared to the Lewis acid sites in Ga₂O₃-NR, as shown by the easier disappearance of their IR signal with increasing temperature (Fig. S4). The lack of strong Brønsted acid sites, which would promote further reaction of the formed epoxides, is in agreement with the high epoxide selectivity over Ga₂O₃-NR (Table 1).



Scheme 1. Proposed catalytic cycle for the epoxidation of alkenes with aqueous H₂O₂ over Ga₂O₃-NR.

On the basis of these characterization data, a catalytic mechanism for the epoxidation of alkenes over Ga₂O₃-NR can be proposed (Scheme 1). Both coordinatively unsaturated Ga atoms acting as Lewis acid sites and mainly tetrahedral Ga-OH groups acting as mild Brønsted acid sites located at the surface of the nanorods can be considered as catalytic sites for the epoxidation reaction. These two types of sites are interconvertible by hydration/dehydration. Therefore, Lewis acid sites that are present in the as-synthesized catalyst are expected to convert in contact with either H₂O or H₂O₂ during the epoxidation reaction (0→1 and 0→2). These Ga sites are able to activate hydrogen peroxide (2), as indicated by Raman spectroscopy. The observed stronger acidity of the Ga centers in Ga₂O₃-NR compared to those in γ-Ga₂O₃-lit enhances the polarization of the O-O bond of the hydroperoxide, thus favoring the electrophilic attack on the double bond of the alkene (3),²⁰ which leads to the transfer of an oxygen atom with formation of the desired epoxide product.

This description of the catalytic mechanism and the estimation of the number of acid sites by TPD-FTIR allow calculating the turnover number (TON) for the epoxidation reactions catalyzed by Ga₂O₃-NR (Table 1). High TONs were reached in the epoxidation of all tested alkenes, with a maximum value for cyclooctene (266). Moreover, the productivity of Ga₂O₃-NR (Table 1) is more than double compared to previously reported transition-metal-free oxide catalysts.^{16b} These data confirm the outstanding catalytic properties of Ga₂O₃-NR, which is competitive against TS-1 with a terminal linear alkene as 1-octene but is much more versatile as its nanorod open structure allows the efficient epoxidation of larger substrates. The truly heterogeneous character of Ga₂O₃-NR was demonstrated by a hot-filtration test, which ruled out leaching of catalytically active species during the epoxidation. No acetic acid was detected by GC at the end of the catalytic tests, thus excluding hydrolysis of ethyl acetate, which could have contributed to the epoxidation activity as acetic acid can act as homogeneous catalyst through the formation of a peracid upon reaction with H₂O₂.²¹ Ga₂O₃-NR

retained most of its activity upon recycling in five consecutive catalytic runs (Fig. S5). This represents a remarkable improvement compared to other transition-metal-free epoxidation catalysts, which suffer from relatively rapid deactivation.^{16,22} Ga₂O₃-NR was more efficient than TS-1 in the use of hydrogen peroxide in the epoxidation of 1-octene (60% decomposition against 81% for TS-1). In the epoxidation of cyclooctene with Ga₂O₃-NR, the degree of decomposition of H₂O₂ was lower (34%), corresponding to an enhanced selectivity of H₂O₂ towards the formation of the epoxide (55%), compared to previously reported transition-metal-free oxide catalysts.^{16,22}

In summary, we introduced a template-free, straightforward method for the synthesis of gallium oxide nanorods under mild conditions. The prepared nanorods belong to the seldom observed ϵ -polymorph, have very high specific surface area and uniquely small dimensions compared to previously reported one-dimensional gallium oxides.¹ Ga₂O₃-NR displays excellent catalytic performance in the sustainable epoxidation of alkenes with H₂O₂, achieving high efficiency in terms of activity, selectivity, oxidant consumption, substrate versatility and recyclability. The activity of the nanorods is markedly superior to any previously reported transition-metal-free epoxidation catalyst and is comparable to that of the industrial benchmark TS-1 with linear alkenes and much superior with bulkier alkenes. The attractive features of Ga₂O₃-NR are very promising for a broad range of other relevant applications of gallium oxide that could benefit from a nanorod morphology, both within catalysis and as functional material with semiconducting, optoelectronic or sensing properties.²³

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