High surface area, nanostructured boehmite and alumina catalysts: Synthesis and application in the sustainable epoxidation of alkenes

Warunee Lueangchaichaweng, Bhawan Singh, Dalmo Mandelli, Wagner A. Carvalho, Sonia Fiorilli, Paolo P. Pescarmona

1. Introduction

One-dimensional nanomaterials such as nanorods and nanowires are of great interest commercially and scientifically. They display larger surface area compared to their counterparts with larger size and can also show unique and improved mechanical [1], magnetic [2] and electronic properties [3]. Aluminas (Al₂O₃) are a class of versatile materials with widespread applications as adsorbents, catalysts and catalyst supports [4,5]. Particularly, γ-Al₂O₃ is one of the most employed supports for heterogeneous industrial catalysts [6]. The asset of alumina includes low cost, relatively high surface area and good chemical and thermal stability [7]. Recently, also the aluminium oxyhydroxide known as boehmite ([γ-AlO(OH)]) has found application as support for platinum-tungsten catalysts active in the hydrogenolysis reaction of glycerol to 1,3-propanediol [8]. Boehmite and γ-Al₂O₃ are closely related, as the latter can be obtained by dehydration of the former upon thermal treatment [9]. Boehmite and alumina themselves have also been reported to be active heterogeneous catalysts in the epoxidation of alkenes with H₂O₂ [10,11]. The activity is strongly dependent on the synthesis route used in their preparation [12]. Boehmite and alumina can be prepared by many synthetic routes such as sol-gel [13], hydrothermal [14] and solvothermal methods [15], or by the hydrolysis of aluminium metal [16]. The synthetic parameters involved in sol-gel methods can be tuned, thus allowing a certain degree of control of the structural and textural properties of the resultant aluminium oxide [17]. Also the acidity and hydrophilicity of alumina can be tuned by varying the type of aluminium precursor, the pH and the solvent used in the sol-gel synthesis [18]. An important advantage of these low temperature synthesis methods is the tendency to afford materials with large specific surface area [19]. Many efforts have been focused on the preparation of high surface area one-dimensional alumina nanostructures, e.g. by using surfactants or other structure directing agents [20–22], or sophisticated techniques such as chemical etching of porous anodic alumina [23], electrochemical synthesis [24] or normal and lateral stepwise anodisation [25]. However, a straightforward, highly reproducible sol-gel synthesis
route without employing templating or chelating agents and under mild conditions would still be a rewarding achievement. Therefore, we focused our attention on the discovery of a sol-gel synthesis procedure that does not require the use of expensive reagents or surfactants, with the goal of providing a simple and efficient approach for the synthesis of nanostructured boehmite and alumina with very high surface areas, a well-defined structure with uniquely small dimensions and a large population of coordinatively unsaturated Al sites at the surface. These physicochemical features would be desirable for application as heterogeneous catalysts for the sustainable epoxidation of alkenes using the environmentally benign aqueous hydrogen peroxide as the oxidant, with the target of providing a cheaper alternative to the highly active and selective gallium oxide nanorods, which represent the state-of-the-art transition-metal-free heterogeneous epoxidation catalyst [26].

2. Experimental

2.1. Synthesis of Al2O3·xH2O nanorods

The protocol for the synthesis of boehmite nanorods [γ-AlO(OH)-NR] was developed by adapting the methodology reported by some of us for the synthesis of gallium oxide nanorods [26], and by employing the Al source (aluminium tri-sec-butoxide) that provided an alumina catalyst with optimum epoxidation activity in a previous study [27]. First, aluminium tri-sec-butoxide (1.23 g, 5 mmol) was dissolved by dropwise addition of 2-butanol (1.60 g) within 10 min, and the obtained clear solution was stirred for 30 min. Then, an ammonia solution (25% aqueous ammonium hydroxide) diluted with absolute ethanol (1:1 v/v, ~1.6 mL) was added dropwise until a pH ≈ 9–10 was reached. The white turbid gel was stirred for 1.5 h and then heated at 70°C for 23 h. The obtained material was aged for 3 days at ambient temperature while stirring. Finally, the white powder was collected by centrifugation, washed at least three times with ethanol and then dried overnight in an oven at 80°C in air. This protocol for the synthesis of boehmite nanorods is highly reproducible and efficient, leading to a typical yield of approximately 85%, assuming the product formula to be AlO(OH). The synthesis of the γ-alumina nanorods (γ-Al2O3-NR-T, where T is the temperature of the thermal treatment expressed in °C) was carried out by thermal treatment of the prepared γ-AlO(OH)-NR in a calcination oven in air at 400 or 600°C for 10 h (heating rate: 3°C/min in both cases).

2.2. Characterisation

Powder X-ray diffraction (XRD) patterns were recorded on a STOE Stadi P Combi diffractometer with position sensitive detector (IP PSD) in the region 2θ = 4.26 to 82°, with internal resolution of 0.03°. The measurements were performed in Debye-Scherrer mode at room temperature using CuKα radiation (λ = 1.54056 Å, selected by means of a Ge (111) monochromator). The ICDD database was employed to assign the phases identified by XRD. N2-physorption measurements were performed on a Micromeritics Tristar 3000 equipment. The samples were outgassed under reduced pressure for 12 h at 120°C (heating rate: 10°C/min) prior to the measurement. The Brunauer-Emmet-Teller (BET) method was applied to calculate the specific surface area [28].

To evaluate the level of hydrophilicity of the synthesised Al2O3·xH2O materials, thermogravimetric analyses (TGA) were carried out under N2 atmosphere with a heating rate of 10°C/min on a TGA Q500 from TA Instruments. The samples were pre-treated overnight in a desiccator containing a saturated aqueous solution of NH4Cl to reach the maximum degree of water adsorption. The number of the water molecules adsorbed per nm2 of surface of the material (nH2O) was estimated from the weight loss between 25 and 150°C using the following equation [29]:
temperature, thus increasing the risks of explosions.

Conversion, epoxide yield and selectivity were determined by gas chromatography (GC) analysis on a Finnigan Trace GC Ultra chromatograph from Interscience, equipped with an RTX-5 fused silica column (5 m; 0.1 mm) [31] or on an Agilent 7890A gas chromatograph, equipped with an HP 5 capillary column (30 m; 0.25 mm). The identification of the by-products of the epoxidation of the various alkenes was performed by gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890N gas chromatograph coupled to an Agilent 5979 MSD mass 4 spectrometer. The GC was equipped with a WCOT fused silica column (30 m; 0.25 mm) coated with a 0.25 mm thick HP-5 MS film.

For the recycling tests, after the reaction in ethyl acetate at 80°C for 4 h, the sample was centrifuged for 10 min at 3500 rpm to deposit the solid catalyst. Next, the reaction solution was removed with a pipette, 5 mL of ethanol were added and the sample was stirred for at least 5 min. The sample was again centrifuged to deposit the catalyst and then the supernatant ethanol solution was removed. The washing procedure was repeated three times. Finally, the samples were dried overnight at 120°C in air and reused in a new catalytic test.

3. Results and discussion

Boehmite nanorods, γ-AlO(OH)-NR, with distinctly small size and high surface area, were synthesised by a straightforward route via a base-catalysed sol-gel method employing aluminium tri-sec-butoxide as precursor. The XRD pattern of the prepared material (Fig. 1a) can be indexed as boehmite phase [γ-AlO(OH)] with orthorhombic structure (JCPDS 021-1307). TEM images reveal that the prepared boehmite indexed as boehmite phase [γ-AlO(OH)] with orthorhombic structure, have high surface area, were synthesised by a straightforward route via a one-step synthesis protocol repeated three times. Finally, the samples were dried overnight at 120°C in air and reused in a new catalytic test.

![Fig. 1. XRD patterns of (a) as prepared γ-AlO(OH)-NR (b) γ-Al2O3-NR-400 and (c) γ-Al2O3-NR-600. The circles indicate the position of the diffraction peaks of boehmite; the asterisks denote the position of the diffraction peaks of the (400) and (440) planes of γ-Al2O3.](image-url)
surface of the three materials, with the purpose of analysing the type and relative amount of surface acid sites. The difference FT-IR spectra in the low frequency region (the spectrum recorded before ammonia dosage was subtracted for each sample) were obtained after ammonia dosage and upon prolonged outgassing at room temperature (Fig. 3B).

Two positive bands at about 1620 cm\(^{-1}\) and 1240 cm\(^{-1}\) are irreversibly formed for all three materials and are attributed, respectively, to the anti-symmetric and symmetric bending vibrations of NH\(_3\) coordinated to unsaturated Al\(^{3+}\) ions in tetrahedral position, acting as Lewis acid sites [39]. The intensity of these signals is higher for γ-Al\(_2\)O\(_3\)-NR-400 (curve b), indicating a higher concentration of Lewis acid centres at the surface of this material. The lower intensities observed for γ-AlO(OH)-NR (curve a) and for γ-Al\(_2\)O\(_3\)-NR-600 (curve c) are ascribable to two different reasons: for the sample treated at 600 °C, the decrease of probed Lewis acid sites is consistent with the observed reduction of surface area upon thermal treatment (Table 1), whereas in the case of the boehmite, the surface is fully hydroxylated, as shown by the related FT-IR spectrum (Fig. 3A.a), thus leading to a relatively low amount of exposed Al (III) cations. The signal at ca. 1465 cm\(^{-1}\) is ascribed to the bending vibration of NH\(_4^+\) species formed by proton-transfer reaction with surface hydroxyls, acting as mild Brønsted sites [40]. The intensity of the signal is substantially higher for γ-AlO(OH)-NR (a) and γ-Al\(_2\)O\(_3\)-NR-400 (b) compared to γ-Al\(_2\)O\(_3\)-NR-600 (c), evidencing a higher concentration of mild Brønsted sites for samples treated at lower temperature, in agreement with their higher population of surface hydroxyl groups.

The physicochemical properties of the prepared nanostructured boehmite and γ-alumina catalysts and of two types of commercial γ-alumina.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m(^2)/g)</th>
<th>nH(_2)O /nm(^2)</th>
<th>Dimensions (nm)</th>
<th>Epoxide yield((^{\circ})) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>w: 2 ± 0.3</td>
<td>Fresh</td>
</tr>
<tr>
<td>γ-AlO(OH)-NR</td>
<td>448</td>
<td>9</td>
<td>l: 23 ± 3</td>
<td>29</td>
</tr>
<tr>
<td>γ-Al(_2)O(_3)-NR-400</td>
<td>376</td>
<td>9</td>
<td>w: 2 ± 0.2</td>
<td>36</td>
</tr>
<tr>
<td>γ-Al(_2)O(_3)-NR-600</td>
<td>305</td>
<td>8</td>
<td>l: 16 ± 1</td>
<td>32</td>
</tr>
<tr>
<td>Commercial γ-</td>
<td>155</td>
<td>8</td>
<td>w: 3 ± 0.6</td>
<td>9</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td></td>
<td></td>
<td>l: 13 ± 1</td>
<td>-</td>
</tr>
<tr>
<td>Commercial γ-</td>
<td>171</td>
<td></td>
<td>w: 3 ± 0.3</td>
<td>16</td>
</tr>
<tr>
<td>Al(_2)O(_3) nanopowder</td>
<td>171</td>
<td></td>
<td>l: 13 ± 1</td>
<td>-</td>
</tr>
</tbody>
</table>

* Estimated by TGA.

\(^{\circ}\) Conditions: 2 mmol of cis-cyclooctene, 4 mmol of H\(_2\)O\(_2\) (as 50 wt% aqueous solution), 40 mg of catalyst, 1 mmol of dibutyl ether (as GC internal standard), 2.0 g of ethyl acetate as solvent, 4 h at 80 °C.

The selectivity towards the epoxide was higher than 99% with all catalysts.

\(^{\circ}\) Activated, neutral, Brockmann I, particle size ~ 150 mesh.

\(\gamma\)-Al\(_2\)O\(_3\) nanopowder, particle size < 50 nm (TEM).

The physicochemical properties of the prepared nanostructured boehmite and γ-alumina catalysts and of two types of commercial γ-alumina.

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m(^2)/g)</th>
<th>nH(_2)O /nm(^2)</th>
<th>Dimensions (nm)</th>
<th>Epoxide yield((^{\circ})) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>w: 2 ± 0.3</td>
<td>Fresh</td>
</tr>
<tr>
<td>γ-AlO(OH)-NR</td>
<td>448</td>
<td>9</td>
<td>l: 23 ± 3</td>
<td>29</td>
</tr>
<tr>
<td>γ-Al(_2)O(_3)-NR-400</td>
<td>376</td>
<td>9</td>
<td>w: 2 ± 0.2</td>
<td>36</td>
</tr>
<tr>
<td>γ-Al(_2)O(_3)-NR-600</td>
<td>305</td>
<td>8</td>
<td>l: 16 ± 1</td>
<td>32</td>
</tr>
<tr>
<td>Commercial γ-</td>
<td>155</td>
<td>8</td>
<td>w: 3 ± 0.6</td>
<td>9</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td></td>
<td></td>
<td>l: 13 ± 1</td>
<td>-</td>
</tr>
<tr>
<td>Commercial γ-</td>
<td>171</td>
<td></td>
<td>w: 3 ± 0.3</td>
<td>16</td>
</tr>
<tr>
<td>Al(_2)O(_3) nanopowder</td>
<td>171</td>
<td></td>
<td>l: 13 ± 1</td>
<td>-</td>
</tr>
</tbody>
</table>

* Estimated by TGA.

\(^{\circ}\) Conditions: 2 mmol of cis-cyclooctene, 4 mmol of H\(_2\)O\(_2\) (as 50 wt% aqueous solution), 40 mg of catalyst, 1 mmol of dibutyl ether (as GC internal standard), 2.0 g of ethyl acetate as solvent, 4 h at 80 °C.

The selectivity towards the epoxide was higher than 99% with all catalysts.

\(^{\circ}\) Activated, neutral, Brockmann I, particle size ~ 150 mesh.

\(\gamma\)-Al\(_2\)O\(_3\) nanopowder, particle size < 50 nm (TEM).
catalysts for epoxidation using aqueous \( \text{H}_2\text{O}_2 \) revolved heavily around duct. The initial development of transition-metal-free heterogeneous peroxide towards epoxidation reactions. Aqueous hydrogen peroxide is an asset of this heterogeneous catalyst is the ability to activate hydrogen peroxide. The catalytic performance of gallium oxide nanorods [26]. An important feature of these catalysts is their ability to activate hydrogen peroxide. The initial development of transition-metal-free heterogeneous catalysts for epoxidation using aqueous \( \text{H}_2\text{O}_2 \) is towards metal oxides. All of them present an open and accessible surface, thus allowing for the facile approach of the reactants. Conditions: 2 mmol of alkene, 4 mmol of \( \text{H}_2\text{O}_2 \) (as 50 wt% aqueous solution), 40 mg of catalyst, 1 mmol of dibutyl ether (as GC internal standard), 2.0 g of ethyl acetate as solvent, 4 h at 80 °C. (Y = yield; S = selectivity).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Convaloane (%)</th>
<th>( % ) Epoxide</th>
<th>( % ) Epoxide</th>
<th>Productivity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclooctene</td>
<td>36</td>
<td>36</td>
<td>&gt; 99</td>
<td>2.3</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>23</td>
<td>23</td>
<td>&gt; 99</td>
<td>1.1</td>
</tr>
<tr>
<td>1-Octene</td>
<td>6</td>
<td>6</td>
<td>&gt; 99</td>
<td>0.4</td>
</tr>
<tr>
<td>Styrene</td>
<td>19</td>
<td>12</td>
<td>64</td>
<td>0.7</td>
</tr>
<tr>
<td>Limonene</td>
<td>42</td>
<td>41</td>
<td>97</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Table 2: Epoxidation of selected alkenes catalysed by \( \gamma\text{-Al}_2\text{O}_3\)-NR-400 using 50 wt% aqueous \( \text{H}_2\text{O}_2 \) as the oxidant.

Conditions: 2 mmol of alkene, 4 mmol of \( \text{H}_2\text{O}_2 \) (as 50 wt% aqueous solution), 40 mg of catalyst, 1 mmol of dibutyl ether (as GC internal standard), 2.0 g of ethyl acetate as solvent, 4 h at 80 °C. (Y = yield; S = selectivity).

* Productivity is defined as \( \% \) epoxide/\( \% \) catalyst.

** Total epoxides yield and selectivity, the details of the distribution between the internal-, external- and di-epoxides are presented in Fig. 5.

The catalytic performance of gallium oxide nanorods [26]. An important asset of this heterogeneous catalyst is the ability to activate hydrogen peroxide towards epoxidation reactions. Aqueous hydrogen peroxide is a highly attractive oxidant for a number of reasons: it is cheap, safely handled and stored, and is a mild and environmentally benign reagent with a high content of active oxygen, and forms water as only by-product. The initial development of transition-metal-free heterogeneous catalysts for epoxidation using aqueous \( \text{H}_2\text{O}_2 \) is to the formation of surface hydroperoxide species [26]. Benzaldehyde (7% yield), which formed by the oxidative cleavage of the vinyl group of the styrene oxide product [47], was identified as the only side product. The relative activity in the conversion of different alkenes follows the same trend previously observed for gallium oxide nanorods under the same reaction conditions [26] with the latter being consistently more active (both in terms of epoxide yield and productivity). On the other hand, aluminium is a much more abundant and cheaper element compared to gallium (Al is ca. 4000 times more abundant than Ga in the earth crust and ca. 300 times cheaper) [48,49], making this catalyst an attractive alternative for the sustainable epoxidation of alkenes with hydrogen peroxide.

In the case of cyclohexene and limonene, the epoxidation over \( \gamma\text{-Al}_2\text{O}_3\)-NR-400 was monitored over the course of time. With cyclohexene as substrate, an epoxide of yield of 52% was reached after 28 h (Fig. 4), while retaining a very high selectivity (97%) towards the epoxide with only minor amounts of 2-cyclohexene-1-one and 1,2-cyclohexanediol, thus confirming the very low tendency of this catalyst to promote allylic oxidation or hydrolysis of the epoxide, respectively. The epoxidation of (R)-(+)limonene was studied in detail because there is growing interest for the utilisation of this bio-based product, which can be obtained from waste peel generated as abundant side product of juice extraction from orange and other citrus fruits [50]. Particularly, the selectivity between the three possible epoxide products (internal-, external- and di-epoxides, see Fig. 5) is worth being studied, as each of these compound can find different applications. For example, the internal limonene oxide has been employed as monomer for copolymerisation with \( \text{CO}_2 \) to produce fully renewable polycarbonates [51], whereas limonene di-epoxide is used as reactive diluent in cationic UV-curing applications [52] and is employed in the synthesis of limonene dicarbonate, which can be used as monomer for the production of polyurethanes [53]. The internal limonene oxide is the major product throughout the whole reaction (Fig. 5, left plot). The total yield of epoxides reached 78% after 26 h of reaction, with a ratio internal: external: di-epoxide = 90:7:3. On the other hand, the selectivity towards the internal epoxide gradually decreased as the reaction proceeded, that \( \gamma\text{-Al}_2\text{O}_3\)-NR-400 has similar concentration of Brønsted acid sites and higher concentration of Lewis acid sites compared to \( \gamma\text{-AlO(OH)}\)-NR.
while the selectivity towards the external epoxide, the di-epoxide and the minor side products (mainly diols) gradually increased (Fig. 5, right plot). This indicates that the di-epoxide is mainly formed by further reaction of the internal limonene oxide, which is possibly also more prone to hydrolysis of the epoxide ring with formation of the corresponding diol.

Hydrogen peroxide is generally available as an aqueous solution and in this work most experiments were performed with commercially available 50 wt% aqueous H$_2$O$_2$. The nature and amount of solvent in which H$_2$O$_2$ is diluted can play an important role on the catalytic performance in epoxidation reactions, as water can compete with hydrogen peroxide for adsorption on the catalyst surface. In this context, it is relevant to investigate the catalytic behaviour of γ-Al$_2$O$_3$-NR-400 employing hydrogen peroxide sources with a lower water content, and namely 70 wt% aqueous H$_2$O$_2$ and 24.5 wt% anhydrous H$_2$O$_2$ in ethyl acetate. This study was carried out on three different substrates: cis-cyclooctene, cyclohexene, and 1-octene (Fig. 6 and Table S1). With all the tested alkenes, higher epoxide yields were obtained switching from 50 to 70 wt% aqueous H$_2$O$_2$, while retaining analogous very high selectivity towards the epoxide product. A further, though less marked, improvement in epoxide yield was achieved when using the 24.5 wt% anhydrous hydrogen peroxide in ethyl acetate, also in this case without loss of epoxide selectivity. It is worth noting that the increase in epoxide yield was more marked in the epoxidation of cyclohexene and, particularly, 1-octene, reaching more than a two- and three-fold increase, respectively. The enhancement in epoxide yield upon decrease of the water content in the hydrogen peroxide source confirms the detrimental role of water molecules, which can interact with the active sites at the catalyst surface and thus decrease their availability for activating hydrogen peroxide towards the epoxidation reaction \[42,54\].

Finally, we investigated the effect of the nature of the solvent in which the epoxidation reaction is carried out. The performance of a catalyst in liquid-phase reactions can be strongly influenced by the solvent. Identifying the most suitable solvent can drastically accelerate the rate of reaction, selectivity towards a product, and stability of the catalyst by facilitating the access of the reagents to the active sites of the catalyst and stabilising the transition state \[55,56\]. When selecting potential solvent candidates, the use of environmentally friendly compounds with low toxicity is preferred, in accordance with the Green Chemistry principles. Additionally, the solvent should be an...
inexpensive, available compound. Based on these considerations and taking into account that the solvent should be able to dissolve both the relatively apolar alkenes and the polar hydrogen peroxide, we selected a set of relatively polar green solvents, both protic and aprotic (2-propanol, dimethyl carbonate, 1,4-dioxane and 1,3-dioxolane) and we screened them as alternative to ethyl acetate in the epoxidation of cyclooctene, 2-octene, dimethyl carbonate, 1,4-dioxane and 1,3-dioxolane) and we selected 2-propanol, dimethyl carbonate, 1,4-dioxane and 1,3-dioxolane as solvents. On the other hand, the use of 1,3-dioxolane as solvent led to a significant increase in yield (49%) compared to ethyl acetate (35%). The yield could be further improved by employing anhydrous hydrogen peroxide instead of the 50 wt% aqueous H₂O₂, reaching 58% cyclooctene oxide yield with nearly full selectivity. The higher activity by using a 1,3-dioxolane as solvent can be ascribed to the observed good dispersion of the catalysts in the monophasic reaction mixture.

4. Conclusions

A facile and cost effective method was developed for the synthesis of high surface area γ-AlO(OH) (boehmite) nanorods, through a very reproducible sol-gel process in which aqueous NH₃ is dosed into a solution of aluminium tri-sec-butoxide in 2-butanol without the need of any structure templating agent or other additive. γ-Al₂O₃ nanorods were obtained through phase transformation upon thermal treatment, which led a slight reduction in specific surface area relative to the as-prepared boehmite nanorods. A characterisation study by means of XRD, TEM, N₂-physisorption, TGA and FT-IR spectroscopy demonstrated that these nanostructured materials display a combination of properties that are suitable for their application as epoxidation catalysts, and namely a high specific surface area, an open, fully accessible structure, a population of surface acid sites, and a relatively low hydrophilicity. Accordingly, the γ-AlO(OH)-NR and γ-Al₂O₃-NR were found to be active and selective heterogeneous catalysts for the epoxidation of alkenes using the environmentally friendly H₂O₂ as the oxidant. The best catalyst, γ-Al₂O₃-NR-400, achieved good activity, excellent selectivity, broad substrate applicability and enhanced reusability compared to previously reported alumina epoxidation catalysts. The superior activity of γ-Al₂O₃-NR-400 is ascribed to the best balance between surface area and nature and concentration of surface acid sites. Furthermore, the activity of γ-Al₂O₃-NR-400 could be substantially enhanced by using anhydrous H₂O₂ instead of 50 wt% aqueous H₂O₂ as the oxidant and by optimising the solvent in which the epoxidation is carried out. Though the maximum achieved activity is still inferior compared to that of previously reported gallium oxide nanorods, which represent the state-of-the-art among transition-metal-free oxide catalysts, these alumina nanorods are a promising alternative considering that aluminium is much more abundant and cheaper than gallium. Additionally, the high surface area and highly accessible open surface of these distinctively small boehmite and γ-alumina nanorods are desirable features for various other catalytic applications, and particularly for the widespread use of aluminas as support for metal nanoparticles [57,58].

Acknowledgements

The authors acknowledge sponsoring in the frame of the following research programs: START1 from KU Leuven (Belgium), project G09313N from FWO (Flemish Science Foundation, Belgium) and the related project 490043/2013-5 from CNPq (National Council for Scientific and Technological Development, Brazil). We thank Sonia Parres-Esclapez and Gina Vanbutsele for assistance in the measurement of the N₂-physisorption isotherms. We thank Damiano Cani for the TEM measurements, the Flemish Hercules Stichting for its support in HER/08/25 and the MTM Department for technical support.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2018.12.017.

References
