Enhanced γ-phase crystallinity of Al₂O₃ frameworks at the concave surface of PS-b-PEO templated spherical pores
Enhanced $\gamma$-phase crystallinity of Al$_2$O$_3$ frameworks at the concave surface of PS-$b$-PEO templated spherical pores

Md. Saidul Islam, Ryutaro Wakabayashi and Tatsuo Kimura *

The crystallinity of inorganic solids like metal oxides after the porosity design is the crucial factor that should be investigated for enhancing their physicochemical properties. In most cases, metal oxide frameworks around mesopores, that are designed through the supramolecular mediated approach, are resulted to be amorphous. Accordingly, a rational guideline has been required for enhancing the crystallinity of frameworks at such concave surfaces. We have so far surveyed a crystallization behavior of alumina (Al$_2$O$_3$) frameworks to its $\gamma$-phase around spherical mesopores ($\sim$40 nm) and discussed further transition to the $\alpha$-phase around much larger pores ($\sim$200 nm). In this paper, we prepared new and helpful Al$_2$O$_3$ powders having PS-$b$-PEO templated pores ($\sim$25 nm and $\sim$75 nm) smaller than those of our previous case. After careful discussion of the pore size variation by considering the molecular structure of PS-$b$-PEO, we explained the crystallization behavior of the Al$_2$O$_3$ frameworks to enhance its $\gamma$-crystallinity. This knowledge is quite beneficial for designing highly porous Al$_2$O$_3$ powders with abundant crystallinity for use as catalyst supports, which is very useful for assessing synthetic procedures of other mesoporous metal oxides having high crystallinity.

Introduction

The nanostructural design of crystalline alumina (e.g., $\gamma$-Al$_2$O$_3$) containing adjustable pores has been increasingly investigated for applications in research fields including catalysis, adsorption, sensor, energy storage, biomedicines, and so on.1–4 Specifically, extra-large pores can be facilitated for immobilizing/stabilizing bulky guest molecules, metal nanoparticles, quantum dots, etc.5–7 In addition, large mesopores are much favorable for the mass transfer and/or the controlled diffusion of targeted molecules, being useful for optimizing the activity and stability of catalytic components in the pores.8 However, Al$_2$O$_3$ based materials with interior porosity, for example those larger than 20 nm, have so far been synthesized by using techniques such as foaming, emulsion templating, and flame spray pyrolysis so far, but highly porous and well-ordered structures have hardly been found in the resultant structures.9,10 Even in the supramolecular mediated approach, generally famous as soft-templating in the presence of amphiphilic organic molecules,11–14 the synthesis of ordered mesoporous Al$_2$O$_3$ based materials has been limited. A few successful examples have been reported by optimizing the dry-up process of precursor solutions with the evaporation-induced self-assembly (EISA) process.15–19 To prepare highly porous metal oxide powders for use as catalytic supports, aerosol-assisted (spray-dried) self-assembly of poly(oxyethylene)-block-poly(oxypropylene)-block-poly(oxyethylene) (EO$_n$PO$_m$EO$_n$), like Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$) and Pluronic F127 (EO$_{106}$PO$_{70}$EO$_{106}$), has been studied by several groups for obtaining mesoporous Al$_2$O$_3$ based materials.20–23 For expanding such mesopores, several efforts have been reported with the addition of organic swelling agents but a slight increase of the mesopores was only observed for those obtained by such spray-dried approaches.21 To overcome this limitation for the design of large mesopores, asymmetric type diblock copolymers, e.g., polystyrene-block-polyethylene oxide (PS-$b$-PEO), are vital for a drastic increase of the pore size by soft-templating even up to the macroporous region.6,24 Referring to a unique method to obtain well-ordered mesoporous Al$_2$O$_3$ films using PS-$b$-PEO (~35 nm using PS$_{18000}$-$b$-PEO$_{7500}$),24 our study has disclosed the formation of Al$_2$O$_3$ powders having extra-large mesopores (~40 nm using PS$_{35000}$-$b$-PEO$_{17000}$) and much larger macropores (~200 nm using PS$_{85000}$-$b$-PEO$_{17000}$) through a spray-drying process.25,26 Besides, the possibility of increasing the crystallinity of such sol–gel derivative Al$_2$O$_3$ frameworks was found depending on the thickness of the Al$_2$O$_3$ frameworks.
The resultant amorphous frameworks were fully crystallized to its γ-phase without deformation of the porous structure and transformed in part into its α-phase around much larger pores.

In the porous materials design using amphiphilic organic molecules, the specific surface area of mesoporous metal oxides can be demonstrated by using the resultant structural features such as pore diameter concerning the size of micelles and wall thickness of frameworks as well as an overall density of the frameworks, indicating that thicker frameworks make the specific surface area smaller. From the viewpoint, to increase the specific surface area of a porous material up to the maximum, the pore size should be reduced by minimizing the thickness of frameworks as far as the frameworks can completely be crystallized with the retention of the porous structure. Thus, we prepared, in this study, a series of highly porous frameworks for enhancing γ-phase crystallinity.

**Experimental**

**Materials**

Anhydrous aluminum chloride (AlCl₃), concentrated hydrochloric acid (HCl, 37%) and dehydrated solvents, such as tetrahydrofuran (THF) and ethanol (EtOH, 99.5%), were obtained from FUJIFILM Wako Pure Chemical Co. Polystyrene-block-polyethylene oxide (PS-b-PEO) type diblock copolymers with different molecular structures, e.g., PS₃₁₀₀₀₀-b-PEO₂₈₀₀₀₀ (Mₚ/Mₚ = 1.07), PS₅₁₅₀₀₀-b-PEO₁₇₀₀₀₀ (Mₚ/Mₚ = 1.10), PS₆₀₀₀₀₀-b-PEO₁₈₀₀₀₀ (Mₚ/Mₚ = 1.08), and PS₅₈₁₅₀₀₀-b-PEO₃₇₀₀₀₀ (Mₚ/Mₚ = 1.15) were purchased from Polymer Source Inc.

**Aerosol-assisted synthesis of alumina powders using PS-b-PEO**

According to our strategy proposed for the rapid optimization of the chemical composition of precursor solution,25,26 a chemical composition was roughly optimized through a rapid spin-coating process and then adjusted to a much better one by spray-drying of the precursor solution with careful monitoring of the formation of a highly porous structure. The chemical compositions after such an optimization process are summarized in Table 1. As a typical procedure, concentrated HCl and H₂O were added to AlCl₃, started to stir immediately, and combined with a PS-b-PEO solution of THF and EtOH under vigorous stirring. The solution was stirred for another 20 min and then spray-dried at 130 °C (Spray Dryer ADL311, Yamato Scientific Co., Ltd) and heated at temperatures in the range from 400 °C to 1000 °C (heating rate; 2 °C min⁻¹) in a N₂ flow for 1 h followed by calcination in an O₂ flow for several hours. Calcination at 400 °C for 3 h was initially conducted for ensuring the formation of a porous structure, that at 850 °C for 3 h was performed for investigating the possibility of crystallizing to the γ-phase with retention of the porous structure, and that at 1000 °C for 3 h was performed for considering further crystallization and/or transformation into the α-phase.

**Characterization**

The formation of a porous structure after calcination at 400 °C and its retention after calcination at 850 °C and 1000 °C were confirmed using a field emission scanning electron microscope (FE-SEM, HITACHI S-4300) and a transmission electron microscope (TEM, JEOL JEM-2010, operated at 200 kV). The crystallization behavior of Al₂O₃ frameworks was traced using X-ray diffraction (XRD, Rigaku RINT 2000 with monochromated Cu Kα radiation) measurements. Nitrogen (N₂) adsorption–desorption isotherms were measured at 77 K of liquid N₂ using a Quantachrome Autosorb-1 system. Prior to the measurements, all samples were degassed at 110 °C for 6 h under vacuum. The specific surface area was calculated from the adsorption branch using the BET method in the range of relative pressure (P/P₀) of 0.025–0.045 and the total pore volume was assessed using the amount adsorbed at the P/P₀ value of 0.997.

**Results and discussion**

**Synthesis of highly porous Al₂O₃ powders using PS-b-PEO**

A new Al₂O₃ based material with large mesopores was prepared using PS₅₁₀₀₀₀-b-PEO₂₈₀₀₀₀ after slight modification of the chemical composition of a precursor solution (see Table 1). SEM and TEM observations of the Al₂O₃ based material were conducted after removing the polystyrene-block-polyethylene oxide (PS-b-PEO) molecules by calcination at 400 °C for 3 h. The SEM image clearly showed the formation of spherical porous whole surfaces of the spray-dried particles (Fig. 1a). The TEM image also proved the presence of such spherical porous whole particles (Fig. 1b). Using the TEM image, the average pore diameter was calculated to be around 25 nm. The N₂ adsorption–desorption isotherm of the highly porous material (see Fig. 2a) was probably type IV, seemed to be a middle type between IV and V due to the presence of large mesopores, with a H-3 type hysteresis loop at relative pressures of 0.4 < P/P₀ < 0.9 and higher uptake at P/P₀ > 0.9.27,28 The values of the BET surface

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The amount (gram) of starting chemicals after optimizing the chemical compositions of precursor solutions</th>
</tr>
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<tbody>
<tr>
<td>PS-b-PEO</td>
<td>AlCl₃</td>
</tr>
<tr>
<td>51000-b-28000</td>
<td>0.10</td>
</tr>
<tr>
<td>60000-b-18000</td>
<td>0.10</td>
</tr>
<tr>
<td>35000-b-17000</td>
<td>0.10</td>
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<tr>
<td>58500-b-37000</td>
<td>0.10</td>
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a The same as those optimized in our previous work.26
area and total pore volume were estimated as 169 m² g⁻¹ and 0.95 cm³ g⁻¹, respectively. Using PS₆₀₀₀₀₋b-PEO₁₈₀₀₀, we can also fabricate much larger pores in the same way as that of Al₂O₃ powders in the presence of PS₅₁₀₀₀₋b-PEO₂₈₀₀₀. The SEM and TEM images of the Al₂O₃ powders (c and d in Fig. 1) exhibited the formation of spherical pores with an average pore size of ∼75 nm. By increasing the pore size, a type of its N₂ adsorption–desorption isotherm (Fig. 2b) was changed into almost V with a H-3 type hysteresis loop at 0.4 < P/P₀ < 0.9 and higher uptake at P/P₀ > 0.9. The BET surface area and total pore volume were 106 m² g⁻¹ and 0.63 cm³ g⁻¹, respectively. For obtaining a series of Al₂O₃ based materials with different pore sizes, we also prepared similar ones using PS₃₅₀₀₀₋b-PEO₁₇₀₀₀ and using PS₅₈₅₀₀₋b-PEO₃₇₀₀₀ that have been used in our previous papers.²⁵,²⁶ The structural features were evaluated through SEM and TEM observations as well as N₂ adsorption–desorption measurements (see c and d in Fig. 2 and 3). For the Al₂O₃ based material prepared using PS₃₅₀₀₀₋b-PEO₁₇₀₀₀, the average pore size, BET surface area and total pore volume were ∼40 nm, 99 m² g⁻¹ and 0.84 cm³ g⁻¹, respectively. Those observed for the Al₂O₃ powders prepared using PS₅₈₅₀₀₋b-PEO₃₇₀₀₀ were evaluated to be ∼120 nm, 82 m² g⁻¹ and 0.32 cm³ g⁻¹, respectively.

Understanding the formation of PS-b-PEO templated pores

Considering the solubility parameter (δ) of polystyrene (8.5–10.3), polar solvents having similar δ values like tetrahydrofuran (THF, δ = 9.1) and dioxane (δ = 9.8) have been frequently used as solvents for dissolution of PS-b-PEO. Although water (H₂O, δ = 21) and ethanol (EtOH, δ = 11.2) are not suitable as solvents to dissolve the PS block but would show better affinity to PEO units. Thus, a mixed solvent of THF and EtOH with H₂O has been applied for the synthesis of a variety of highly porous metal oxides in the presence of PS-b-PEO. During the micellization of PS-b-PEO, a strongly hydrophobic PS chain is assembled as spherical cores and surrounded by a hydrophilic PEO moiety. In the synthesis using block copolymers having a PEO chain, the PEO chain is protonated under acidic conditions and then interacted with soluble inorganic species,²⁹–³¹ revealing that another porosity is integrated in the resultant metal oxide frameworks.³²,³³ As illustrated in Fig. 4, according to the solubility of PS-b-PEO, the PEO chain plays dissimilar roles in working as a part of the core around the PS core and penetrating inside metal oxide frameworks and thus the size of PS-b-PEO templated pores is changed with and without the interior porosity of metal oxide frameworks.

It is considered that the molecular structure of PS₅₁₀₀₀₋b-PEO₂₈₀₀₀ (Nₚₛ/Nₚₑₒ = 0.77) was an intermediate between those of PS₃₅₀₀₀₋b-PEO₁₇₀₀₀ (0.87) and PS₅₈₅₀₀₋b-PEO₃₇₀₀₀ (0.67) with similar PS/PEO ratios where the number of PS (Nₚₛ) is smaller than that of PEO (Nₚₑₒ). As expected, plenty of large mesopores (∼25 nm) can be manufactured in spherical Al₂O₃ par-

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**Fig. 1** (a and c) SEM and (b and d) TEM images of Al₂O₃ powders (calcined at 400 °C for 3 h) prepared using (a and b) PS₅₁₀₀₀₋b-PEO₂₈₀₀₀ and (c and d) PS₆₀₀₀₀₋b-PEO₁₈₀₀₀.

**Fig. 2** N₂ adsorption–desorption isotherms of a series of Al₂O₃ powders (calcined at 400 °C for 3 h) prepared using (a) PS₅₁₀₀₀₋b-PEO₂₈₀₀₀, (b) PS₆₀₀₀₀₋b-PEO₁₈₀₀₀, (c) PS₃₅₀₀₀₋b-PEO₁₇₀₀₀, and (d) PS₅₈₅₀₀₋b-PEO₃₇₀₀₀.

**Fig. 3** (a and c) SEM and (b and d) TEM images of Al₂O₃ powders (calcined at 400 °C for 3 h) prepared using (a and b) PS₃₇₀₀₀₋b-PEO₁₇₀₀₀ and (c and d) PS₅₈₅₀₀₋b-PEO₃₇₀₀₀.
particles by the spray-drying process, the same as that applied in our previous study.\textsuperscript{25,26} It is basically considered that pore size is consistent with the molecular weight ($M_w$) of the PS chain, but we cannot find a direct relationship of pore size to the $M_w$ of the PS unit and/or the total $M_w$ of the PS-b-PEO molecule. This is because the length of the entropy-driven PS core is interrupted by the presence of the PEO unit and the overall pore size strongly depends on the molecular structure of PS-b-PEO like the PS/PEO ratio.\textsuperscript{34} In the case of silica films,\textsuperscript{35,36} spherical mesopores are embedded with a long pore-to-pore distance and a tendency that pore size seems to depend on the PS/PEO ratio has been confirmed using PS-b-PEO. The mesopores are connected by PEO induced micropores.\textsuperscript{37} A similar tendency was also observed for the synthesis of non-siliceous porous materials (e.g., carbon and titania) using PS-b-PEO.\textsuperscript{38-44}

In the case of the preparation of a mesoporous silica (SiO$_2$) film using PS-b-PEO, the resultant size of spherical pores was empirically explained by using PS and PEO lengths (pore diameter ranging from 4 to 22 nm)\textsuperscript{45} and PS/PEO ratios (pore diameter less than 50 nm).\textsuperscript{16} In the latter paper, large mesopores (~40 nm) were very similar but the diameter was not uniform and distributed in the range between about ±5 nm.\textsuperscript{16} Another significant paper on the fabrication of mesoporous titania films using a number of PS-b-PEO (smaller than 20 nm) has also demonstrated the difficulty in obtaining long-range ordered large mesopores using high-molecular-weight PS-b-PEO.\textsuperscript{46}

In this study, the PS/PEO weight ratios were 1.82 (~25 nm, PS$_{510000}$-b-PEO$_{280000}$), 2.06 (~40 nm, PS$_{35000}$-b-PEO$_{17000}$), 3.33 (~75 nm, PS$_{66000}$-b-PEO$_{18000}$), and 1.58 (~120 nm, PS$_{58500}$-b-PEO$_{17000}$) in terms of pore size. However, the last one is not associated with the PS/PEO ratio. In the case of the much larger PS-b-PEO micelle, the relative thickness of PEO corona around the PS core is smaller (crew-cut) than those observed for smaller (star-like) micelles.\textsuperscript{47,48} Accordingly, PS-b-PEO molecules are strongly influenced by a kind of solvent, are much aggregated, and may work as much larger supramolecular templates. For a lower PS/PEO ratio (longer PEO unit), the PS core is surrounded by a thicker PEO unit. The presence of a thick and polar PEO corona reduces the stretching of the PS core, resulting in a decrease in the size of micelles and/or aggregates. In contrast, for a higher PS/PEO ratio (shorter PEO unit), a thin PEO layer allows the diffusion of THF to the PS core up to a constant value. When the entropy of the core is decreased to some critical point, the system is not stable and then a morphological change may occur.\textsuperscript{49} At a constant length of the PS block, a radius of the spherical core is increased with a decrease in the soluble block length, revealing an increase of the pore size.

**Crystallization of alumina frameworks around spherical pores**

For the spray-dried synthesis of highly porous Al$_2$O$_3$ powders, large mesoporous (~75 nm, PS$_{66000}$-b-PEO$_{18000}$) and macroporous (~75 nm, PS$_{58500}$-b-PEO$_{17000}$) structures are the new ones, being different from those reported in our previous work on the creation of an extra-large mesopore (~40 nm, PS$_{126000}$-b-PEO$_{17000}$) and a larger macropore (estimated to be ~120 nm herein, PS$_{58500}$-b-PEO$_{17000}$).\textsuperscript{25,26} Such a series of the diameter of spherical pores, especially novel ones smaller than our previous case, is helpful for improving the γ-crystallinity of Al$_2$O$_3$ frameworks.

After all the samples were calcined at higher temperatures ranging from 700 °C to 1000 °C, the crystallization behavior of Al$_2$O$_3$ frameworks was traced by XRD (Fig. 5). In almost all the XRD patterns, distinct peaks were not found after calcination at 700 °C as well as those (amorphous nature) observed for samples calcined at 400 °C. However, the XRD pattern of the sample prepared using PS$_{58500}$-b-PEO$_{17000}$ only showed the presence of small peaks assignable to the γ-phase of Al$_2$O$_3$. This result is good agreement with our previous work.\textsuperscript{25,26} Al$_2$O$_3$ frameworks start to be crystallized at the surfaces of much larger macropores (lower surface curvature). All the Al$_2$O$_3$ frameworks were crystallized to its γ-phase to some extent after calcination at 850 °C and γ-phase crystallinity was enhanced further after calcination at 1000 °C with the retention of the highly porous structures (Fig. 5 and 6). As a significant insight, we found different behavior during thermal crystallization of similar Al$_2$O$_3$ frameworks around spherical pores. The Al$_2$O$_3$ frameworks at around much larger pores with the lowest surface curvature (~120 nm, PS$_{58500}$-b-PEO$_{17000}$) were crystallized to its γ-phase and already transformed into its α-phase in part through calcination at 1000 °C with the retention of the highly porous structures (Fig. 5 and 6). As a significant insight, we found different behavior during thermal crystallization of similar Al$_2$O$_3$ frameworks around spherical pores. The Al$_2$O$_3$ frameworks at around much larger pores with the lowest surface curvature (~120 nm, PS$_{58500}$-b-PEO$_{17000}$) were crystallized to its γ-phase and already transformed into its α-phase in part through calcination at 1000 °C with the retention of the highly porous structures (Fig. 5 and 6). As a significant insight, we found different behavior during thermal crystallization of similar Al$_2$O$_3$ frameworks around spherical pores. The Al$_2$O$_3$ frameworks at around much larger pores with the lowest surface curvature (~120 nm, PS$_{58500}$-b-PEO$_{17000}$) were crystallized to its γ-phase and already transformed into its α-phase in part through calcination at 1000 °C with the retention of the highly porous structures (Fig. 5 and 6). As a significant insight, we found different behavior during thermal crystallization of similar Al$_2$O$_3$ frameworks around spherical pores.

After removing all the PS-b-PEO molecules, the tension associated with the surface curvature from vacant pores induces the
shrinkage of Al₂O₃ frameworks with a reduction of pore size. As illustrated in Fig. 7, the tension and density strongly influence the shrinking behavior with condensation of the frameworks. The density of Al₂O₃ frameworks is increased with volume shrinkage when the amorphous phase transforms into its crystalline one. Upon shrinking the Al₂O₃ frameworks by thermal treatment, pore surfaces having higher curvatures are denser following condensation and crystallization than those having smaller curvatures, which results in a larger increase of the surface density of the oxide species. Consequently, larger pores with a smaller surface curvature is quite suitable for the transformation from γ- to α-phases.²⁵,²⁶ In addition, during crystallization to γ-Al₂O₃ and subsequent partial transformation into its α-phase, BET surface areas and total pore volumes of all the samples were evaluated by N₂ adsorption–desorption measurements. For example, when the Al₂O₃ based material prepared using PS₅₁₀₀₀-b-PEO₂₈₀₀₀ was calcined by elevating the calcination temperature, the BET surface area and the total pore volume were gradually decreased from 169 m² g⁻¹ and 0.95 cm³ g⁻¹ (400 °C) to 113 m² g⁻¹ and 0.73 cm³ g⁻¹ (850 °C) and 82 m² g⁻¹ and 0.67 cm³ g⁻¹ (1000 °C), respectively. Another tendency that the BET surface area of Al₂O₃ powders having smaller pores is larger than those observed for Al₂O₃ powders having larger pores was also proved, being very important for the design of highly crystallized Al₂O₃ powders showing a high surface area.

Sol–gel derivative amorphous metal oxides are crystallized by heating at a temperature appropriate for a crystalline phase and/or transformed into a high-temperature phase. In our previous study, frameworks composed of titanium, tin and zinc...
oxides (TiO₂, SnO₂ and ZnO) can be almost crystallized by calcination above 400 °C to anatase, cassiterite and wurtzite phases of these oxides, respectively. A thermal phase transformation into the high-temperature rutile phase of TiO₂ was started at around 700 °C.⁵² Temperatures for crystallization and transformation are lower than those investigated in this study (γ-Al₂O₃ at 550 °C and α-Al₂O₃ at 1000 °C). From the viewpoint, metal oxides, such as TiO₂, SnO₂ and ZnO, would be converted to high-end metal oxide based materials arising from higher crystallinity.

**Conclusions**

The design of the interior porous structure of Al₂O₃ particles was investigated at a wide range of the nanometer scale (from ~25 nm to ~120 nm) by utilizing asymmetric diblock copolymers such as PS-b-PEO with different molecular structures. Novel physical properties can be aided through investigation of the porous structure while underlying the self-assembly mechanism of PS-b-PEO for controlling the pore size and framework thickness. The porous structure, especially the smaller one, is quite helpful for increasing the specific surface framework thickness. The porous structure, especially the smaller one, is quite helpful for increasing the specific surface area and is stable even after annealing at higher temperatures (e.g., 1000 °C) that achieve full γ-crystallinity of Al₂O₃ frameworks. The crystallization behavior can be explained by considering the surface curvature of PS-b-PEO templated pores, which is significant for designing highly porous particles composed of other compositions.

Mesopores smaller than 10 nm have been fabricated using EOₙPOₙEOₙ.¹⁵⁻²⁰ Such small mesopores are generally collapsed at higher temperatures (e.g., 1000 °C),²¹,²⁶ revealing that a large surface curvature is not suitable for full crystallization of Al₂O₃ based frameworks. Our recently developed porous Al₂O₃ particles (BET surface area; ~400 cm² g⁻¹ after calcination at 400 °C) are also not stable during impregnation of functional species such as metal species inside the mesopores even after crystallization to its γ-phase.⁵³ Accordingly, the current insight into a stable interior porous structure showing a high specific surface area is a rational guideline for the preparation of a wide variety of highly porous platforms, which contributes to the next challenge to stimulate a variety of research fields such as porous materials design including facile preparation of nanocomposite catalysts, device manufacturing by utilizing highly active surfaces for electrodes and energy storage media, and so on.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**