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Novel alumina ‘KK Leaf Structures’ as catalyst supports

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Abstract

A method has been devised in which alumina can be formed into a layer of thin leaf-like structures that have a thickness of 0.2–0.8 μm. This consists of a process in which aluminium iso-propoxide is transformed into a sol–gel and then: frozen (−195 °C), freeze-dried (−60 °C), and finally calcined (450 °C). These special conditions lead to the formation of a structure that is named: ‘KK Leaves’.

After calcining at 450 °C, the leaves have a specific surface area of 282 m^2/g, an average pore size of 2.8 nm, and exhibit a curly shape. The structure has the appearance of a loosely packed (but ordered) collection of thin curly leaves with fine ribs resembling leaf veins on trees and plants. They would readily act as a support, e.g., for a catalyst, or adsorbents, or act as a membrane filter.

Keywords: Alumina; ‘KK Leaves’; Sol–gel; Catalyst support; Membrane; Filter

1. Introduction

It is well known that aluminium oxide can act as a suitable material for the distribution of catalyst, e.g. [1,2], or as a membrane with ultra fine pores, e.g. [3], and that this can be prepared from alumina sols. A sol is a colloidal suspension of solid particles in a liquid. The dispersed phase is so small (∼1–1000 nm) that gravitational forces are negligible and interactions are dominated by short-range forces (e.g., van der Waals attraction and surface charges) [4]. A sol can be made by a variety of methods and these are well described in the literature. For example [5], the sol could be prepared from an inorganic alkoxide, which is hydrolysed in water/alcohol; and an acid could be employed to catalyse the reaction. It is then normal to allow the sol to ‘age’ for about 24 h.

The term ‘aging’ describes the transformations that take place (slowly with time) in the structure and properties of a sol as it is transformed into a gel. This could occur by a process known as hydrolysis and condensation, in which monomers grow in size and extend throughout a solution. The fluid would then be described as a gel. This could be visualized as consisting of a continuous solid skeleton that encloses a continuous liquid phase [4].

The gel when it is formed is known as a wet gel. If it is dried by a process involving evaporation, then it would be classed as a xerogel. According to Ref. [4], drying under normal conditions gives rise to capillary pressure that causes shrinkage of the gel network, and a reduction in volume by a factor of 5–10 compared to the original wet gel.

In many applications throughout the literature, when an alumina sol is formed to act as a catalyst support, a xerogel is formed that is then calcined and impregnated with catalyst. The alumina is coated/deposited onto a low surface area support structure, which provides the necessary mechanical strength for the final device. An example [6] of the surface of a commercially produced gamma alumina washcoat for a catalytic converter is illustrated in Fig. 1. The image in Fig. 1(b) shows that the washcoat consists of a large number of tightly packed irregular shaped particles of alumina. The particles appear to vary in size from about 1 to 5 μm. When a xerogel is calcined, the structure normally has the appearance of a packed bed of particles.

As summarised in Ref. [4, p. 10 and 501] if a wet gel is dried under supercritical conditions, then during the drying process there is no interface between liquid and vapour, so there is no capillary pressure and relatively little shrinkage. Under supercritical (or hypercritical) drying conditions, the product

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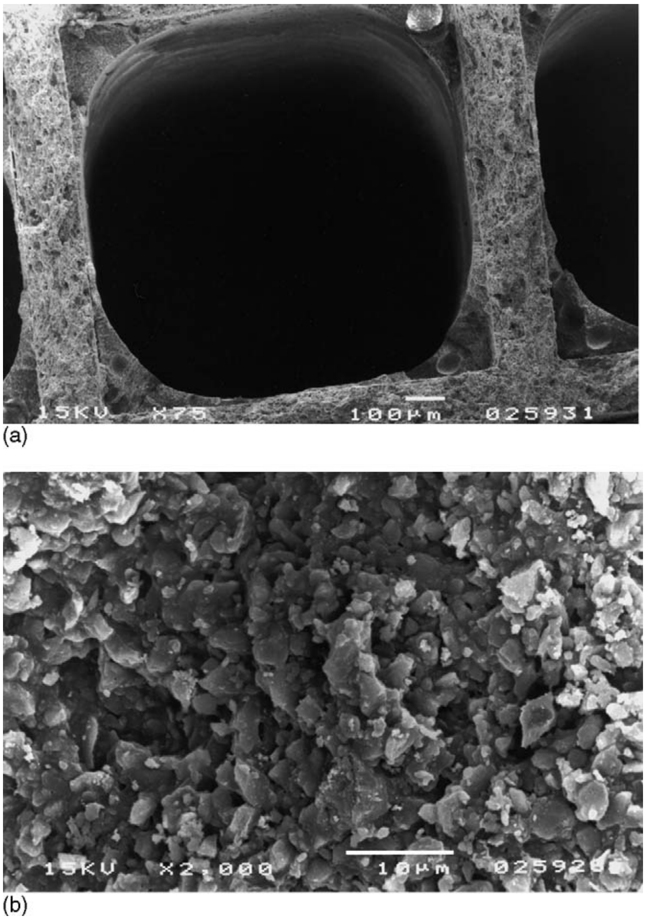

Fig. 1. Scanning electron micrographs, courtesy of Kolaczkowski, University of Bath. 1(a) The face of a catalyst coated monolith [6], showing the point of gas entry. The magnified view shows one of the channels (1 mm × 1 mm) in a multichannel structure. Because of the method of coating, the alumina washcoat adheres more in the corners of the channel, than on the sidewalls. 1(b) Magnified view [6] of the structure of the washcoat in the corner of the cell. The size and shape of the alumina particles vary considerably.

formed is known as an aerogel. The gel has a volume similar to the original sol, and the volume fraction of the solid phase can be as low as ~1%.

On the other hand, if a gel is rapidly frozen by dropping the gel into a liquid nitrogen bath, then it has been reported in Ref. [7] that fine platelets may be formed, whereas in experiments at slower rates of freezing coarser particles were formed. A freeze-dried gel is known as a cryogel. Although there have been a number of studies exploring freezing of aqueous gels, there is relatively little on the potential that this technique could offer to act as a support of catalysts or adsorbents, or act as a membrane filter. In a study by Ref. [8] of the freezing of silica-based sols, the interest centred on the application of the technique to manufacture low-cost ceramic shapes as castings that were ''crack-free and exhibited essentially zero-shrinkage''. In this study of the freezing process, the way in which the ice crystals grew (controlled by cooling rates) was shown to affect the structure and porosity of the final product. According to the literature review in Ref. [9], freeze-drying is widely used for the production of food and pharmaceuticals, and its application to ceramic powders was first described by Ref. [10] in 1968. The application of spray-freezing/freeze-drying to catalysis is described for example in Ref. [11] to illustrate the use of the technique to form porous particles of lanthanum–strontium metal perovskite-type oxides, that act as oxidation catalysts for the combustion of methane. According to Ref. [11], the use of freeze-drying as a method of preparing catalysts ''tends to be neglected in the development of new catalysts''.

In more recent work by Ref. [12], an aqueous solution of magnesium sulphate ($2\ \mathrm{mol\ dm^{-3}}$) was spray-freeze-dried forming spherical shape particles with an average pore diameter of 42 μm. On calcining, the spherical shape was retained but the particle size was reduced to an average diameter of 20 μm. The freeze-dried particles contained mainly macro-pores in the order of 1 μm formed through ice crystal sublimation. When the sample was calcined, a bi-modal distribution of macro-pores in the order of microns and meso-pores <100 nm was formed. The porosity was 87–90%.

From this brief review, the way in which the sol is cooled and ice crystals are formed has a strong influence on the shape of gel formed (e.g., particles/platelets) and the porosity of the structure (which is also influenced by calcining conditions).

As background information and to help set the scene for the methodology in this paper, we discovered these 'leaf-like' structures serendipitously. We were exploring methods of coating ceramic monoliths with a gamma alumina washcoat, in which a catalyst would be finally dispersed. Whilst exploring different methods of drying sol–gels, to see if we could produce a washcoat that did not crack on drying, we established this technique. We knew that we had discovered something of novelty, when on examining the coated structure with scanning electron microscopy, we noticed clear and distinct leaf-like structures. This was then confirmed by experts from a major manufacturer of catalytic converters, who had not encountered anything like it before, and they helped with a patent application [13].

2. Experimental

2.1. Method of preparing the sol used to make 'KK' Leaves

First, it was necessary to prepare a sol by hydrolysing an aluminium alkoxide, $Al(OR)_3$. This was then transformed into a sol–gel. The methodology is based on the advice offered in Yoldas [5,14] and follows the three-step procedure, summarised in Fig. 2.

The apparatus consists of a flat bottom flask/vessel that is placed on an electric heater with a magnetic stirring device, and this is operated inside a fume cupboard.

According to Yoldas [5]:

- At the peptization stage at least 0.03 mol of acid per mole of alkoxide must be added, and hydrochloric acid is suitable.
- The slurry must be heated above 80 °C and held until a clear sol is formed.
- Use of closed containers and stirring during the heat treatment significantly enhances the rate of peptization.

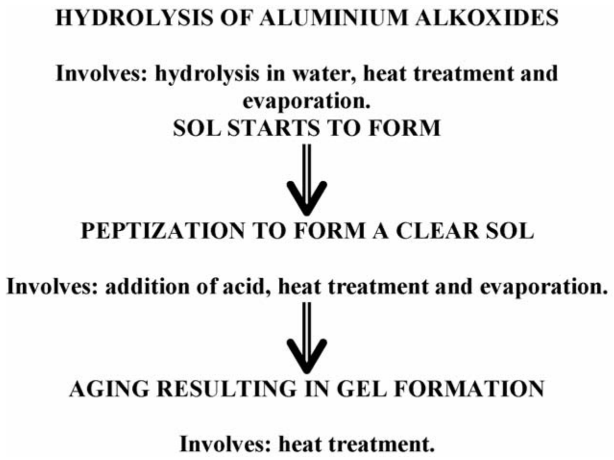

Fig. 2. The three steps in which a clear sol is formed and then transformed into a gel, based on techniques in Yoldas [5,14].

All of this advice was followed and a temperature of 90 °C was selected for this process.

Step 1: *Hydrolysis*—One kilogram of aluminium iso-propoxide (98%, Alfa Chemicals) was added to 5 l of distilled water in a flask. The contents were maintained at a temperature of approximately 80 °C, and they were stirred for about 20 min. As the hydrolysis of aluminium iso-propoxide proceeded, isopropanol was produced, and started to evaporate and was allowed to leave the flask.

The reaction may be represented as:

$$\mathrm{Al(OC_3H_7)_3 + H_2O \rightarrow Al(OC_3H_7)_2OH + C_3H_7OH} \qquad (1)$$

Step 2: *Peptization*—The mixture was then maintained at 90 °C, and HCl was added, amounting to 0.05 moles of HCl per mole of aluminium iso-propoxide. The mixture was stirred and heated, and liquid was evaporated. According to Yoldas [5], the removal of residual (OR) groups in the hydroxide (above 80 °C) significantly enhances the peptization stage. This was allowed to continue until the concentration of the alumina reached approximately 10 wt%.

The reactions may be represented as:

$$a\mathrm{Al(OC_3H_7)_2OH} + b\mathrm{H_2O} \xrightarrow{\mathrm{HCl}} \mathrm{C_3H_7O[(OH)Al{-}O{-}Al(OH)]}_n\mathrm{OC_3H_7} + c\mathrm{C_3H_7OH} \qquad (2)$$

Step 3: *Aging*—A water-cooled condenser was then mounted on top of the flask, and the outlet from the condenser was open to the atmosphere. The contents of the vessel were then mixed and maintained at 80 °C under total reflux for about 48 h. At the end of this operation, an alumina sol–gel had been formed:

$$\mathrm{AlOOH(sol) \rightarrow AlOOH(gel)} \qquad (3)$$

2.2. *Forming 'KK Leaves' in a metal dish*

The sample illustrated in Fig. 3, was prepared using a sol made from aluminium iso-propoxide, with the addition of zirconium nitrate at the peptization step. This was added to give a zirconia content of about 1 wt%. The purpose of adding the zirconia, was to explore if the temperature to which the gamma alumina could be exposed could be increased without the occurrence of a phase change to forms that have a lower surface area.

The sol was then poured into a metal container and immersed in liquid nitrogen (for about 3 min at −195 °C) where it was frozen. It was then placed into a freeze drying unit (at −60 °C and 0.133 Pa, for 15 h), using phosphorous pentoxide as a drying agent to remove water, forming a cryogel. The sample was then dried at room temperature, and then it was calcined at 450 °C for about 5 h. Heating of an alumina based gel (γ-AlOOH) causes dehydration and rearrangement leading to a series of transitional aluminas and finally α-$\mathrm{Al_2O_3}$ as follows [4, p. 600].

$$\mathrm{AlOOH} \xrightarrow{300\,^\circ\mathrm{C}} \gamma\text{-}\mathrm{Al_2O_3} \xrightarrow{850\,^\circ\mathrm{C}} \delta\text{-}\mathrm{Al_2O_3} \xrightarrow{1100\,^\circ\mathrm{C}} \theta\text{-}\mathrm{Al_2O_3} \xrightarrow{\geq 1200\,^\circ\mathrm{C}} \alpha\text{-}\mathrm{Al_2O_3}.$$

A temperature of 450 °C was selected to ensure that the high surface area γ-alumina phase was formed. By calcining the sample the structure of the material is also fixed. Had it just been dried at room temperature and left in the open atmosphere, then it would have absorbed moisture from the atmosphere and could have swelled and changed its form.

The specific BET surface area of samples was determined from nitrogen adsorption experiments using an ASAP 2010 unit, supplied by Micrometrics Instrument Co., USA. The same instrument was also used for pore size measurements. In addition, mercury porosimetry was used to check for the presence of macro-pores, using an AUTOPORE II 9220, supplied by Micrometrics Instrument Co., USA.

Scanning electron microscopy (SEM) was used to examine the structures formed. To obtain a cross-sectional view of a sample, it was set in Epoxy cold-setting resin (supplied by Struers A/S, Denmark). This was then ground to obtain a flat surface, using silicon carbide paper on a Motopol 12 machine (supplied by Buehler Ltd., USA). The sample was then ground for 2 min using a Perftex surface with a 30 μm diamond slurry,

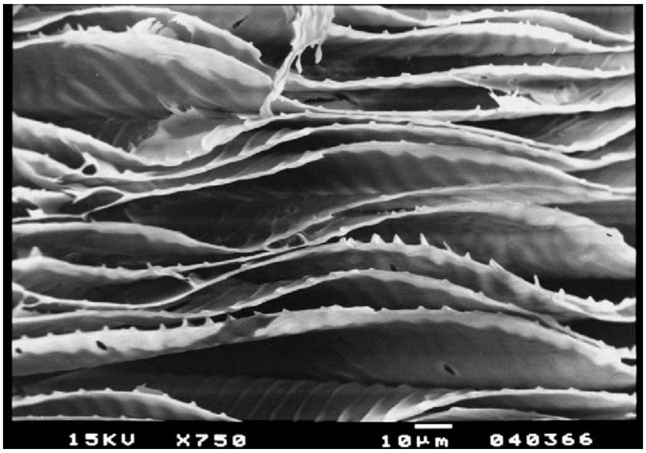

Fig. 3. SEM image showing the loosely packed 'KK Leaves' on the surface of a sample that was formed in a dish, courtesy of Kolaczkowski.

and then for 4 min with a 6 μm diamond slurry. The sample was then polished for 2 min on a Texamet 1 cloth with 1 μm diamond slurry, and then with colloidal silica (0.3 μm). To make the surface of the sample electrically conductive, a gold coating was added in an Edwards 5150B Sputter (supplied by BOC Edwards, UK).

Returning to Fig. 3, what is particularly interesting about the structure is that when the surface is viewed, it looks like a loosely packed (but ordered) collection of thin leaves, which as a result of the air gaps between the layers would also exhibit a high external surface area per unit volume of packing. In some commercial applications, this could also be exploited. The leaves have a thickness about 0.2–0.8 μm, a specific surface area of about 282 m^2/g, an average pore diameter of about 2.8 nm, and are of a more uniform size although they have a curly shape. They are also loosely packed forming curly layers, with access between the leaves to either of their surfaces. It is the method of transforming the aluminium alkoxide into a gel, conditions of freezing, freeze-drying, and calcination, which gives the final structure its unique appearance and properties.

For comparison, a sample of the same sol was dried in air for a few days forming a xerogel. When this was calcined at 450 °C the measured surface area was 296 m^2/g and the average pore size was 3.2 nm. So, the surface area and average pore size of the formed cryogel and xerogel are similar.

It is important to mention that experiments were not performed in the absence of zirconia, or with varying feed compositions. How these may influence the structures formed is unknown.

Also, in some catalytic applications, the presence of chloride ions in the support may be undesirable. In that case, it may be possible to use a chloride-free acid in the peptization stage. If the key to the formation of the 'KK Leaves' is the formation of a clear sol that turns to a gel, then it is well known [14] that acids such as nitric, acetic and formic could also be used. However, these were not tested in this study.

It is postulated that the pore size, porosity and surface area of the 'KK Leaves' could be controlled by the choice of calcination temperature, however, this aspect was not tested in this study.

2.3. Forming 'KK Leaves' on a cordierite monolith

The sample illustrated in Fig. 4, was prepared by immersing a cordierite monolith for about 2 min into a sol made from aluminium iso-propoxide. The monolith was then withdrawn and the excess sol was blown from the structure with a jet of air. The coated monolith was immersed in liquid nitrogen (about 30 s at −195 °C), and then it was placed in the freeze-drying unit at −60 °C, for about 10 h. Afterwards it was dried at room temperature, then calcined at 450 °C for about 5 h. The coating process was then repeated so that two layers were obtained. A difference in the compactness of the leaves indicates the presence of the layers (in further work it was shown that a number of layers could be built-up in this manner).

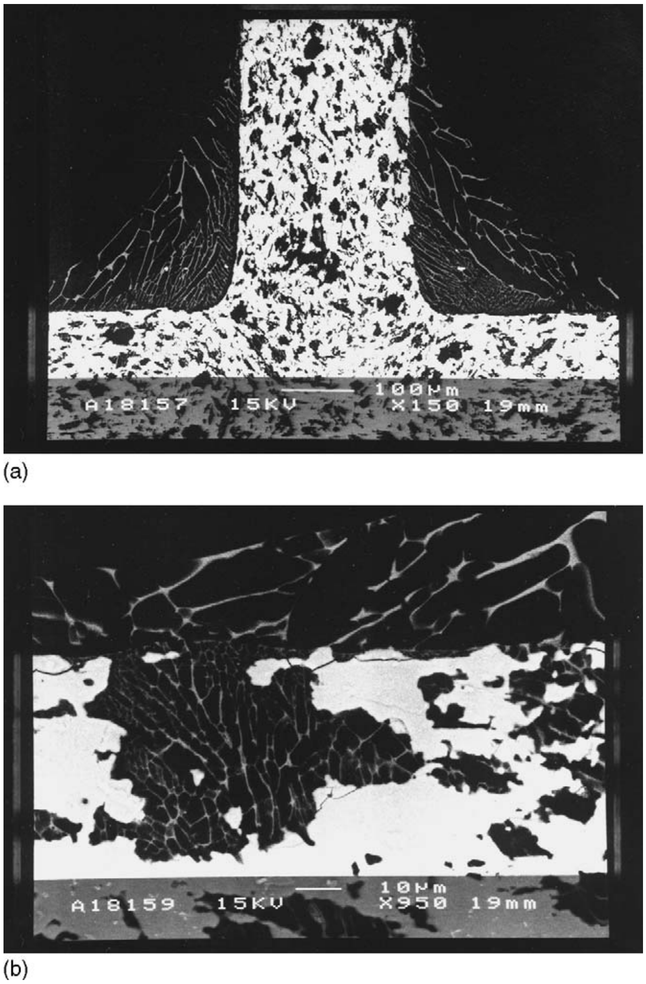

Fig. 4. Scanning electron micrographs, courtesy of Kolaczkowski, University of Bath. 4(a) View of a coated monolith, showing the point of gas entry. The channels are 1 mm × 1 mm, and this view should be compared with Fig. 1(a). The 'KK Leaves' now appear as fine lines or layers of plates, that have voids between them. 4(b) Magnified view of a channel wall, showing the penetration of the 'KK Leaves' into the macro-pores of the support structure.

In samples prepared of coated cordierite monolith it is evident in Fig. 4 that the 'KK Leaves' are penetrating the macro-pores on the surface of the cordierite support, and the leaves are also interconnecting with one another. Have they formed an interface that could act as a barrier? If they have, then this creates a number of interesting opportunities. What is also interesting to note, is that by penetrating the macroporous structure, the 'KK Leaves' are anchoring themselves to the surface—this feature in itself could be highly advantageous. It is also shown that a number of 'KK Leaf' layers can be built-up on a support structure.

As discussed in Ref. [15], an efficient link between the micro- and the macro-world is important as many processes are transport limited. This is evident in nature (branch and leaf systems in plants), and it is important for the design of more efficient porous catalyst and exploitation of nanotechnology. The spaces between the 'KK Leaves' are relatively large providing accessibility to the nano-scale pores in the nano-scale leaf structures.

Although the information in this paper is presented for samples calcined at 450 °C, it is worth mentioning that samples of coated monolith were calcined at 550 °C and supplied to an auto-catalyst manufacurer who impregnated them with Pt catalyst. These were then very briefly tested on a diesel engine and their performance was comparable with conventional washcoated supports. These results were very encouraging and further trials are necessary to explore advantages and any constraints.

3. Concluding remarks

There are a number of potential applications where this technique could be used. The following are offered as examples to stimulate interest.

(a) When coated onto the surface of a porous support, then as the multi-layered structure has the ability to penetrate the larger pores in the support, it could be exploited as a surface that acts as an interface, e.g., acting as a membrane, or a support for a membrane such as palladium.
(b) A coated ceramic monolith could be used to support a wide range of different types of catalysts, e.g., auto-catalyst application.
(c) The catalyst could be incorporated into the gel, and then formed onto the mechanical support.
(d) The leaf-like structure could be used as a filter to trap small particles between the leaves.
(e) The thermal inertia of this structure would be less than that of a washcoated monolith of equivalent thickness.
(f) The thin layers of the leaf would offer less resistance to diffusion than a more conventionally formed catalytic monolith. This could result in applications where a small quantity of catalyst is used to achieve the same outcome.
(g) These fine leaf structure may find applications in the field of nanotechnology.
(h) The method of preparation (with slightly different conditions), may also produce leaf shaped structures for other materials that undergo a transition from sol to gel.

In any new application, it will be necessary to compare the economical aspects of changing to a freeze-drying technique. There may also be practical and operational issues to consider. For example, how securely are the leaves attached to the surface when exposed to high gas flowrates or mechanical vibrations? These aspects are outside the scope of this paper and will very much depend on the application for which the ‘KK Leaves’ are being considered.

As an aside, the thin curly leaves in Fig. 3 have fine ribs resembling leaf veins on trees and plants. Our instincts tell us that besides our own specialist interest in this area, these observations may be even more important to specialists who study the evolution of our planet.

Finally, and unfortunately, after filing the outline application, the financial/operational circumstances of the company changed, and at short notice we lacked the resources to progress the application further. Nevertheless the idea remains exciting, and we hope others will find it of use and acknowledge our discovery of ‘KK Leaves’. If you do decide to try this technique, then please share your experience with Stan Kolaczkowski by e-mail (cesstk@bath.ac.uk).

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