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Sols and mixtures of sols as precursors of unique oxides

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Abstract

There is considerable evidence that sols, or colloidal oxides, can play a critical role as precursors to the primary particles of crystalline or amorphous oxides. Sols have been demonstrated to be useful precursors to form microengineered catalysts when adsorbed onto geometric structures, such as monolith honeycombs, or onto macroporous supports capable of allowing entry of the sol structure into the support interior. Sols tend to adsorb only on the exterior of conventional porous catalyst supports, presumably due to plugging of the pores at the exterior of the support particles. Such systems are *microengineered structures* in that the sol forms as a thin coating on the outer surface of the support particles forming a *shell, or rim, configuration* at the individual particle's exterior. However, there is every reason for caution in the assumption that the sol structure(s) are directly translated into the primary particles in the final oxide structure. Even the term sol–gel synthesis, prejudices the case that a sol is the precursor of the gel structure in a formal sense. Evidence presented in this paper makes a compelling case *for some oxide systems* that the sol structure, or sol size, is completely irrelevant to the primary particles which are present in the oxide that is formed during gelation. In these instances, the sol structure simply provides the nutrients which are transported to the growing crystals of the final structure. In contrast, for the case of aluminas formed from preformed sols there is apparently an upper threshold in size of the sol which serves to dictate the size of the primary particles of the crystalline alumina. Alumina sols below this threshold size lead to polymerization within the gel and formation of much more dense alumina structures. It is clear that the primary particles of aluminas are those crystalline particles which give rise to high surface area, and that these crystalline particles are intrinsic to the exceptional surface area stability of the, so-called, transitional aluminas. There are clear examples where the primary nucleation and growth processes, which are critical to the final oxide structure, are independent of the size of the sol precursor. *There is a need to appreciate that each oxide system has unique characteristics of crystallization in regards to the sol structure: sols may be spectators to the crystallization process in some instances, while primary precursor structures of the crystalline particles in others.* This is especially true for the case of mixtures of soluble precursors compared to mixtures of these same precursors as sols prior to gelation. The nucleation processes that occur in such mixed systems, as well as the critical transport of ingredients to these growing nuclei are remarkably sensitive to the state of the precursor phases. Perhaps the best model for thinking about crystallization processes in mixed sol systems is to view the oxide in higher concentration as a ''host'' structure. The liquid-filled voids between the ''host'' particles *within the gel* impart a microcavity which must serve as the reactor vessel in which the ''guest'' sol must undergo transformation to the final structure via nucleation and transport processes imposed by the ''host'' cavities. It will be argued that this concept applies equally well to explain the major differences seen in the final structures of alumina and silica–alumina when crystallization occurs in concentrated as opposed to a ''diluted'' gelation media. This concept provides a novel *microengineering approach* where stable microdomains, or microcrystals, of oxides can be isolated within a secondary structure acting as the scaffolding which provides for unique crystal habits of the ''guest'' oxide.

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1. Introduction

Sols, or colloidal oxides, have had a long history of utility in heterogeneous catalysis [1–3], even though there has only recently been an emergence of interest in the wider application of sols to form the support structure where the sol is formed in situ during the synthesis of the supported catalyst itself [4–6]. This is a rapidly growing area but is not directly related to the subject of this paper. There has been very little information published *on the comparison of oxide's three-dimensional structure* (TDS) when soluble precursors and pre-formed sol precursors are employed *as two distinct classes of precursors* in terms of essential physical properties including surface area, pore volume, and pore size. In fact, there is surprisingly little information on such properties when sols of different size are employed to prepare oxide supports [1,8,9]. One of the prime goals of this paper is to examine the information that is available comparing soluble and sol precursors, and to suggest that there be a systematic reevaluation of the, so-called, sol–gel process where these two distinct classes of precursors to oxide's TDS be examined in future work. There is every reason to expect that by such investigations that sols, and especially mixed sols, will provide avenues to novel catalytic materials. It is also the goal of this paper to point out that sols, and mixture of sols, are materials of choice *in the design of microengineered catalyst structures* due to the fundamental nature of the sol gelation process. Microengineered structures implies the ability to form localized microstructures of oxides with control of the pore size and surface area in a particular "designed" structure, such as a thin film on a geometric substrate, or as isolated units, or as aggregates, within another host structure.

Sols have played a very critical role in the ability to prepare catalytic oxide structures, such as washcoats on monolith structures [8], as the sol structure(s) play a critical role as the binder phase between aggregates of oxides within such structures. In the case of aluminas, sols are believed to be essential in the formation of extruded particles with the strength required in fixed bed applications [1,8]. The sol content may be as high as 30–90 wt% of the alumina content in the slurry in the downstream processing of aluminas [9]. This high sol content is necessary in order to produce the strong extrudate structures necessary in large, vertical reactor applications. In the case of washcoats on ceramic, or metal, honeycomb monolith structures, as little as a few percent of an alumina sol added to a dry milled alumina (or other oxide) of ca. 1–8 μm size, is sufficient to form a strongly adherent washcoat structure [10]. There seems to be little doubt that a significant percentage of the sols in the slurry first form a shell structure on the exterior of the milled particles in the slurry phase, see Fig. 1. This is a structure which depends on the sol forming a fairly strong attachment to the milled particle's surface. Following coating of the slurry mixture, in the drying/calcination steps, the sol units at the surface of particles fuse together to form the strongly adhering bridge structures between particles, Fig. 2. Excess sol in the slurry deposits in the spaces between the milled particles, Fig. 3. Such slurry mixtures coat the monolith channels of metal or ceramic honeycombs. The deposited film coating is principally accomplished in the

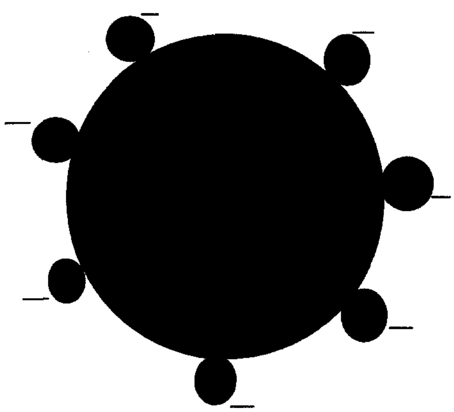

Fig. 1. Diagrammatic representation of charged sol, or colloidal, particles adsorbed as a "shell" structure on to the exterior surface of milled particle of 0.1 μm size, or larger.

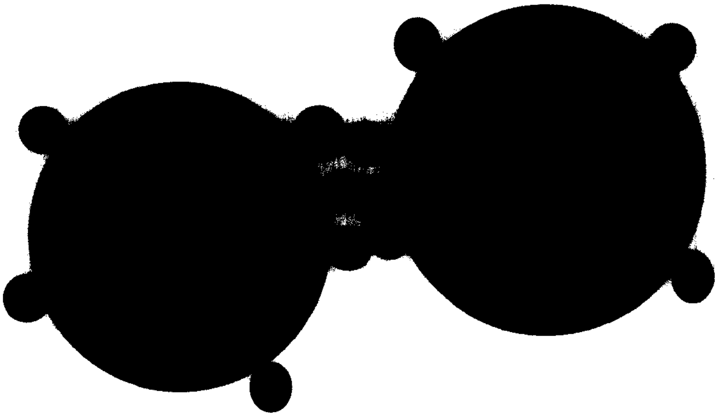

Fig. 2. Diagrammatic representation of bridging of sol particles serving to "glue" coated particles into a coherent three-dimensional structure.

monolith corners, or fillets, due to the surface tension of the coating slurry, even in the case when sols alone are coated onto monolith structures, Fig. 4. Such strongly adherent coatings are essential when employed at high space velocities to prevent spalling of the coating from the channel walls. Higher sol contents beyond a few percent within the slurry mixture of the milled oxide particles force the sol units to fuse together forming a three-dimensional network *filling, or partially filling, the spaces between the milled oxide particles in the coated film structure*. It is only because of the stability of the porous alumina network, formed from alu-

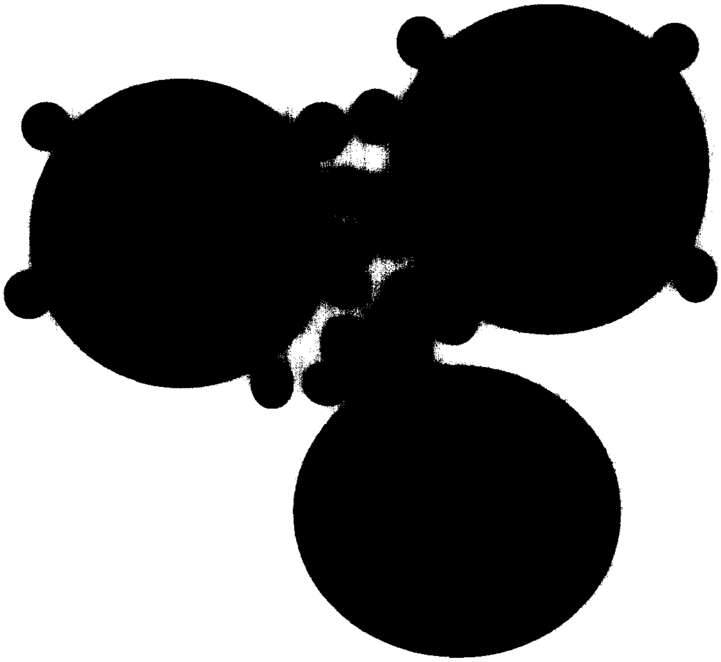

Fig. 3. Picture serving to represent that gelled sol particles between the milled particles can form a pore structure which is independent from that within the milled particles themselves.

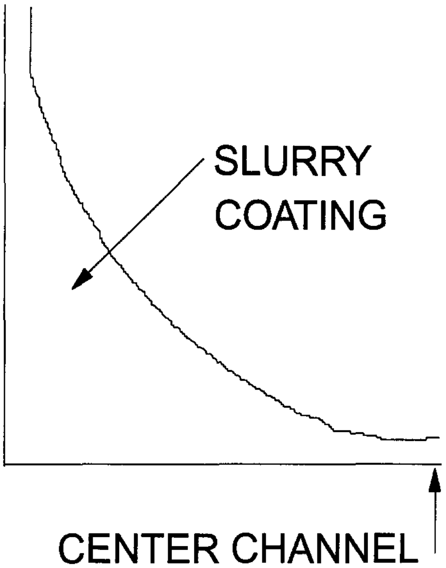

Fig. 4. Diagrammatic representation of the slurry filling of corners of ceramic, or metal monolith structure due tot he surface tension within the slurry.

mina sols, acting as bridges between milled particles that automotive catalysts are stable and useful systems. Other colloids than alumina can serve the same function to fuse the milled particles together upon coating onto a geometric substrate, but only aluminas formed from sol precursors lead to the high temperature stability required in mobile source catalyst applications.

Aluminas formed from sol precursors of different size, and from a soluble aluminum nitrate precursor will be examined in some detail in this paper. Aluminas formed from a sol of a defined size when gelled with either acidic or basic conditions will be compared to the material formed by direct adsorption of the sol onto a monolith structure. It is quite interesting that there is very little difference in the alumina's TDS for any of the gel-forming methods *as long as the alumina sol precursor is of a critical size*. This example provides evidence that alumina's crystallization pathway is strongly dependent on sol size and that gelation conditions, such as pH, are of no consequence for a > 20 nm size alumina sol. Yet another interesting class of materials which will be examined in this paper are aluminas made from gelled aluminum alkoxy precursors. This preparation method will provide yet another dimension into the nucleation and transport requirements in the crystallization pathway that are necessary to occur within the alumina gels themselves in their ultimate transformation into the crystalline boehmite structure. Such boehmite structures are the intermediary phases to the transitional-alumina structures that have been so widely used in heterogeneous catalysis [1,11]. As we shall see, alumina crystalline structures can be formed within preformed, porous supports [12,13], although this is a little studied area of investigation [1,11]. Such examples will provide valuable insights into the conditions required within gels in the transformation of intermediate structures into the primary particles of the final alumina TDS.

Sols have been utilized in still another way to prepare *microengineered catalyst systems* other than as binders for washcoats on ceramic/metallic honeycomb monoliths. Colloidal titanium oxide sols of 100–150 nm diameter have been employed to prepare oxide structures within the large macroscale openings within silicon carbide [14]. These large size sol precursors were ideal in this particular application although transforming to oxides of only 10–20 m^2/g surface area due to the large size of the starting sol. The resulting *macroporous titania support* formed within the silicon carbide host structure, when coated with vanadia, was less prone to undergo surface area transformation under reaction conditions compared to a higher surface titania support. As vanadia is a powerful flux of oxides [15], a high surface area titania support is undesirable in this particular application. In this example, it is advantageous to start out with a lower surface area oxide catalyst than one of higher surface area. The lower surface area titania support will result in a stable vanadia surface structure *on the titania* which will resist transformation under reaction conditions due to the larger size of the titania particles. The large size of the titania particles is a direct consequence of the large size of the titania sol used to prepare the titania "support-within-a-support". These titania crystalline particles are already in a more stable configuration due to their intrinsically larger primary particle size when compared to a titania support formed from smaller particles with a higher surface area. This serves as an example of formation of a microengineered support within a second support phase. This is an interesting case as the support within the host has macropores, i.e., pores > 50 nm diameter. This is a superb example where the microengineered structure of the final catalyst is formed from a sol precursor whose structure transforms directly into the primary particles within the host silicon carbide structure. By the choice of the sol precursor size *alone*, an oxide support is formed which is less sensitive to surface area transformation caused by the catalytic agent introduced onto the oxide support.

In this paper we will examine examples where sols are clearly related in an essential way to the primary particles formed within the final oxide structure. *Sol structures can, however, just as likely be mere spectators in the crystallization processes which form the final structure within gelled sols.* A case can be made that the term sol–gel is very misleading, in that, although sols may be formed as intermediate structures in some cases, they are clearly *not necessarily transformed into the primary particles, or elementary structures*, within the gelled oxide. The nucleation and transport of nutrients at the surface of gels and, in some cases within the solid structure of the gelled oxide, may be independent of the sol which may simply be a transient, intermediate phase. Recent results show clearly that embryo structures can form within the body of the gelled particles themselves, and that the growth of these embryo structures leads to the sequential transformation to the crystalline phase within the gelled particles [16]. In the case of some oxides when formed *from sols of smaller size* than the primary particles in the final oxide structure, dense structures with reduced pore volume can be formed within the gel phase. This transformation then results in undesirable low surface area coupled with low pore volume of the oxide. In fact, recent work from Ko's laboratory [17] demonstrates that for a zirconia sol of 5–10 nm diameter gelation produces a much lower surface area material compared with having this same size zirconia sol "pre-gelled" on the surface of a still larger zirconia sol! An attempt will be made to explain the reason for this most unexpected result.

It is evident to many people working in this area what has often been missing is a set of systematic experiments where a matrix of sols are formed which have well-defined size and size distribution in their own right, and where upon gelation the structure of the oxide phases are compared to that of the sol precursors. It is one of the goals of this paper to provide the evidence that such studies are not only of scientific interest, but will provide a class of novel, and exceptionally stable oxide structures. This is especially true where mixed oxides are prepared from sol precursors compared to soluble mixed oxide precursors. Although only a handful of examples have been published [7,8], there is clear evidence of the value of this type of comparative investigation. High temperature stable microdomains of ceria, zirconia, and titania have been realized by simply co-gelling

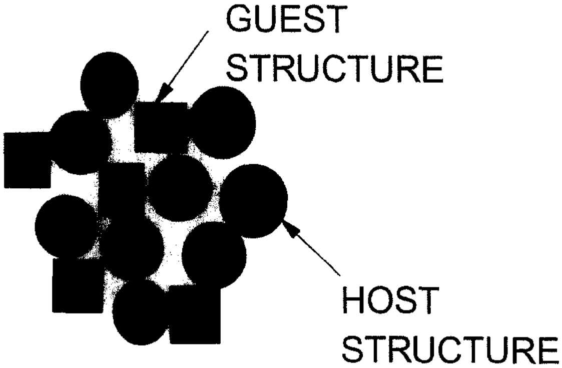

Fig. 5. Diagrammatic representation of gelled mixture of two sols where the sol in excess acts a host structure of the second sol gelled simultaneously with the host sol, thereby serving to trap isolated microdomains of the guest crystals.

with a large-size alumina sol, i.e., > 20 nm diameter. In these cases, the alumina sol does not aggregate in a fashion that traps the second oxide(s) within the bulk of the ''host'' structure as might be assumed. Rather, the alumina forms isolated units which force the ''guest'' oxide to form isolated domains which contribute to the porous structure of the mixed oxide aggregate. This structure can be visualized as one where the primary particles of the alumina host structure are substituted by crystalline microdomains of the second guest oxide, see Fig. 5. Characterization of such systems makes a compelling case of the validity of this model [7]. This model was subsequently confirmed by high resolution transmission electron microscopy [7]. One of the unique characteristics of this synthesis method is that as much as 50 wt% of the mixed composite is composed of ''guest'' domains which are isolated from each other. In this way, the trapped ''guest'' domains form with a high surface area, and are, also, of unprecedented stability due to their isolation within the ''host'' structure. This amounts to an *in situ* microengineered-catalyst-approach where the ''guest'' oxides are allowed to nucleate and polymerize within the confines of the in situ formed ''host'' structure. The cavities forming *as the host gels* provide unique constraints on crystallization processes. These cavities can result in unique conditions to prepare crystals, or microdomain structures, of ''guest'' crystals which can not be made by any other synthesis method. Examples will be provided to confirm this model of *mixed sol* gelation processes.

There is every reason to expect that *pre-formed, porous structures* can, in an analogous fashion to mixed-sol-syntheses discussed previously, alter nucleation and growth pathways when oxides are grown within the pore voids, or cavities, formed within the confines of the host structure. Pre-formed, porous supports can be expected to alter crystallization processes simply on the basis of the size of the pore voids alone. Examples of this little explored area *where pore void size is systematically varied in order to control the size of crystals formed within the host structure* will be examined in this paper, as well [12–14]. Host cavities have been shown to alter the crystal sizes which are formed within the cavities, whether there is a sol intermediate, or simply an amorphous oxide phase formed from a soluble precursor within the host's cavities. Perhaps the best evidence for the potential to prepare microcrystals with unique properties when grown within a host oxide structure, *which acts as a ''microcavity'' reactor*, stems from unpublished work that Stiles carried out in the early eighties in conjunction with workers at Alcoa [12]. In the case of alumina crystals grown within host aluminas of different pore size, which are clearly crystalline materials [18], it was established that crystals would not form below a threshold pore diameter of ca. 40 nm diameter of the host structure. But what was especially important was the observation that the alumina crystals formed within the > 40 nm diameter host alumina had entirely different chemistry than aluminas grown by traditional sol–gel procedures [19]. This was even true when one compares aluminas of very similar surface area, which must have primary particles of similar size [1,11], assuming that the pore volumes of the different materials have not changed radically. The growth of the alumina crystals within a host support structure exerted such a profound influence on the nature of these alumina crystals that their reactivities toward such metal oxides as nickel and cobalt oxide were unprecedented [19]. In addition, the pore diameter of this alumina was only 3 nm, which is impossible to obtain if not grown within a host structure [1,8]. This is compelling evidence that a host structure alters the nucleation and growth processes of the alumina crystals [1,11]. The case will be made that the same phenomenon can occur in the case of a gels themselves; gels which have formed a transitory porous structure which may function much as the cavities of a preformed support. Other examples will be discussed in this paper which will serve to support this model. Evidence will be presented which will make it clear that cavities in pre-formed porous structures have a very substantial impact on the crystal size of the oxide formed within the ''host'' structure.

Applications of sols to form microengineered thin films will also be discussed. If sols are adsorbed onto the exterior of conventional porous particles, or onto extrudates, a shell of the sol will be formed exclusively [20] on the exterior surface of the oxide particle host as the sol–gel transformation blocks access to the particle's interior. This is a trivial example of the preparation of microengineered ''shell'' structures, but is instructive just the same. Thin films from sols readily form *on the interior* of supports with much larger pores, such as those within the walls of cordierite monoliths. Sequential sol coatings will form ''onion-skin'' layers on the geometric-sized cavities, one layer upon another of constant thickness. The series of onion-like layers is yet another example of a *microengineered structure,* Fig. 6. Layers of different sol precursors will provide, for example, isolation of different microdomain crystals at controllable depth within the multilayer coating on a supporting structure, such as a monolith channel, or a catalyst particle's exterior forming a shell structure.

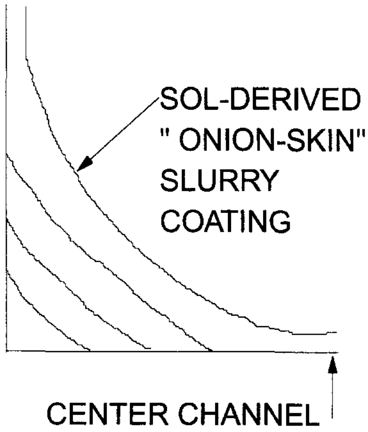

Fig. 6. Picture serving to represent that sequential coatings of a sol slurry can form sequential layers of the gelled oxide structure.

2. Sols as binders and as precursors of microengineered catalysts

As discussed in the introduction, sols act as very effective binders of either wet or dry milled particles to form stable washcoat structures or strong extrudate particles as discussed in a review article [1]. What has often been ignored is that sol slurries can be coated onto geometric substrates to form very strongly adherent coatings in the absence of the milled particles [7]. In this case the thickness of the coated film is usually quite thin due to the fact that the solids content of sol slurries rarely exceeds 20 wt%, except in the case of silica sols. A typical milled particle slurry will often contain between 40–50% solids, and a single coating onto a ceramic honeycomb will deposit a coating of ca. 200 μm thickness in the corners of the monolith channels. A 20 wt% alumina sol will produce in a single coating an analogous coating of 25 μm thickness [7]. This thin, alumina-sol-derived coating is extremely attrition resistance, however. The sol coating can be repeated for eight sequential steps in order to buildup the coated film thickness to 200 μm, similar to that achieved in one coating of a milled particle slurry, see Fig. 6. The milled particle slurry must contain a critical amount of sol as the binder between the milled particles in order to achieve a stable coated film. As little as a few percent of an alumina sol is satisfactory in forming a stable, attrition-resistant coating if the milled particles are of a size between 0.1–2 μm diameter [10]. There is consistent stability of coated films if the particle size is of the order of ca. 8 μm, or less, but much more binder phase is required, on the order of 20 wt%, or higher. No adverse effects on ''coatability'' or attrition resistance were observed if the milled alumina particles had all been milled to ca. 0.1 μm size [10]. The critical parameter is to have the alumina sol content greater than 2 wt% in the slurry mixture, and to have the alumina sol of 2 nm size as the preferred binding agent. An alumina sol of 20–35 nm diameter is satisfactory, but leads to slightly less adherent coatings than those obtained for the smaller sol size at a constant sol-to-milled-particle ratio. This result is very reasonable as the smaller sol size results in a much larger number density of particles in the slurry phase than for the larger sol slurry. The higher density of particles serves to react at the exterior surface of the milled particles in the slurry, or as the slurry is coated, leading to the formation of a large number of bridging groups between the particles.

If higher levels of sol are present in the slurry phase, such as 20 wt%, where the milled solids content is simultaneously reduced, there is no impact on the ease of coating the slurry mixture, or on the stability of the coated film. At the higher sol contents some of the sol gels between the milled particles form a porous matrix for the milled particles. In Transmission Electron Microscope (TEM) cross sections of coated films, on ceramic monoliths, the milled particles are viewed to be imbedded in a plastic-like matrix formed by the gelled alumina sol, see Fig. 7. This is also the consistent image that is observed in the case of wet-milled alumina slurries that have been coated onto ceramic substrates. This indicates that milled slurries contain a substantial amount of sol phase which is the active binder of the milled particles. It is apparent that the high content of the sol-derived matrix must have a stable and porous structure so that there can be access to the catalytically active precious metals, Pt, Pd, Rh, within the milled particles. It was, in fact, demonstrated that catalysts prepared from all sol precursors to form the washcoat structure had analogous activity to those containing the milled particles as the dominant oxide supporting structure within the, so-called, washcoat. Alumina sols form aluminas *under a variety of conditions* whose pore size range is typical of those aluminas used in mobile source applications made by traditional preparation procedures [1,7].

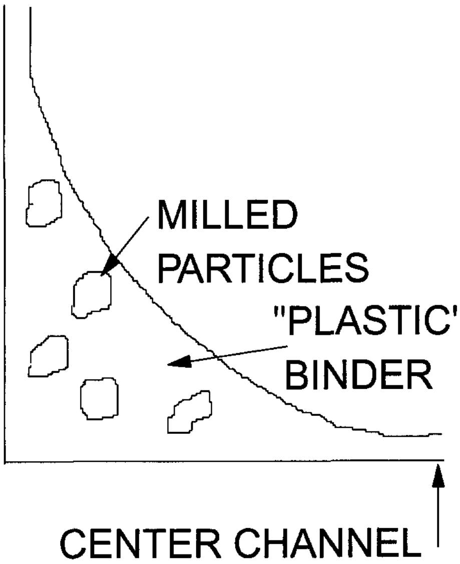

Fig. 7. Picture serving to represent that when the sol is in sufficiently high concentration in a slurry mixture with milled particles that the cross section view of the coated film will have the milled particles appear to be "imbedded" within a continuous structure formed by the gelled sol phase.

There is an excellent example which shows clearly the utility of sols in the synthesis of microengineered catalysts. This example is from the patent literature [14] and shows several key characteristics that sols possess which lead to their utility in the synthesis of well-defined "engineered" structures. Titania sols of very large size were prepared so that the final primary particles of the oxide structure would be in a surface area range that would be stable under partial oxidation reaction conditions. From the size of the titania sol and the surface area of the final catalyst, there is little doubt that the sol structure has translated into the primary structural unit within the final catalyst, see Fig. 8. Due to the partial oxidation reaction being very exothermic the titania sol was coated on a silicon carbide support that has high thermal conductivity. The use of the silicon carbide support allows one to control the level of catalytic surface area that is contained in a given volume of reactor. This "support-within-a-support" concept is particularly of interest as it produces a titania support with ca. 10 m^2/g surface area and which itself has macropores, i.e., > 50 nm diameter, while being formed within, and on the exterior surface of the silicon carbide support. If

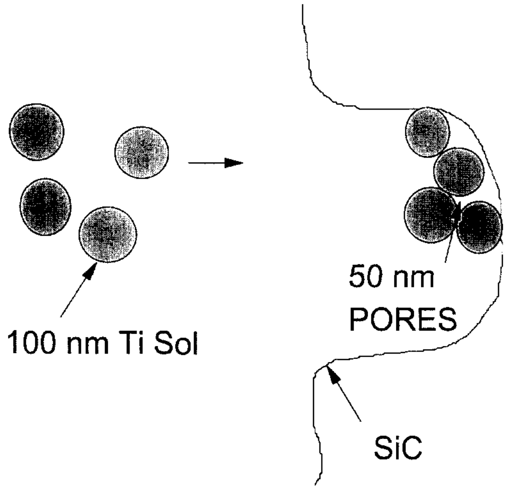

Fig. 8. Diagrammatic representation of large sol particles penetrating into the surface layer of a silicon carbide porous substrate where the pores are suficiently large to accommodate penetration into the surface layer, perhaps to form only a very thin layer of titania within the silicon carbide.

a support had been chosen without the geometric cavities as those within the silicon carbide, the titania coating would have been isolated on the exterior surface of the geometric support. This is due to the fact that the pores would have been blocked by the large titania sol particles during the coating step. By having an inert, but thermally conductive, support which is controllably coated with the catalyst support, the amount of catalyst within the reactor can be carefully controlled and, therefore, the exothermic reaction can be moderated. Since the active component is vanadia supported on the titania surface there is further ability to control the number of active sites in a given reactor volume by "tuning" the vanadia loading on the titania within the silicon carbide to optimize catalyst activity/selectivity.

There is still another advantage to the choice of a large titania sol to prepare the support for this particular system: a low surface area titania support will reduce the tendency of the vanadia to accelerate the transformation of the titania to a lower surface area material under reaction conditions. Vanadia is a potent flux of high surface area supports leading to significant loss of surface area and/or pore volume [20] under fairly mild conditions. As a titania support of 10–20 m^2/g may seem deficient, when compared to conventional aluminas with surface areas from 125–350 m^2/g, it is likely that the large particles in this titania catalyst are more stable than if the initial surface area of the titania was 100 m^2/g. Too high a titania surface area would result in a loss of surface area over time of use in the reaction. This loss of surface area would probably have resulted in encapsulation of the vanadia component within the interior of the titania particles, or formation of undesirable large V_2O_5 particles as surface area loss occurred. By having a low surface area support to start with, a more stable and predictable deactivation for this application was probably realized [14]. Analogous experiments by doping vanadia at different loading levels onto alumina supports showed a marked acceleration of surface area instability as the vanadia content increases from 1 to 3 wt%. In these systems vanadia encapsulation within the bulk of the alumina was observed [20].

3. Gels formed from soluble precursors, and mixtures of soluble precursors

For the systems discussed in this section it is unclear if there was a gel structure which completely filled the volume occupied by the aqueous phase, as opposed to a precipitated phase where a liquid phase clearly separates from the precipitate, following rapid addition of ammonium hydroxide. This ambiguity was due to rapid stirring of the precipitating slurry with a mechanical propeller stirrer during the ca. 30 s required to add the ammonium hydroxide. For all of the systems there was a gelled mass which was a highly viscous liquid which was immediately transferred to a drying oven set at 110°C and allowed to dry to an aggregated cake in a glass drying vessel. For the calcination step the dried mass was broken into ca. 10 mesh size particles and calcined in a muffle furnace in a ceramic dish with flowing air at 500°C.

3.1. Alumina from aluminum nitrate precipitation

Concentrated solutions of aluminum nitrate in water can be readily gelled with the addition of ammonium hydroxide. If excess NH_4OH is added, so that the final pH of the gelled slurry was 9, then the dried and 500°C calcined product from the gelation had a surface area of 170 m^2/g with a pore volume of 0.45 cc/g [21]. X-ray diffraction (XRD) analysis indicated this to be a gamma-alumina phase transitional alumina. This alumina when calcined for 16 h at 900°C had a surface area of 70 m^2/g. This surface area stability, when combined with the observation that no alpha-alumina was present as measured by XRD, was substantial evidence for the complete transformation of the gelled product firstly to a boehmite phase which subsequently converted to the transitional phase during the calcination step. Incomplete transformation of the gelled phase can occur if the final pH is lower than 9, which will result in the formation of an amorphous alumina phase which will convert to alpha-alumina at ca. 800°C with a surface area of < 2 m^2/g [11]. Analogous results were observed in the case of gelation of aluminum isobutoxide where stoichiometric water to cause hydrolysis of the alkoxy groups was used to gel the alumina [11]. At a stoichiometric level of water addition the gelled product was entirely present as an amorphous phase which resulted in complete transformation to an alpha-alumina upon calcination at 800°C. This example of ready transformation of a soluble alumina precursor to a stable boehmite phase is not unprecedented, see for example the excellent paper of Chioba [22] and other examples in a review article [1].

3.2. Aluminum–cerium oxides from aluminum nitrate / cerium nitrate precipitation

The gelation of a soluble alumina precursor, in the presence of a second soluble oxide precursor, was investigated where the second oxide precursor was cerium(III) nitrate. For this example, there was clear evidence that the second oxide precursor completely altered the key nucleation and ion transport requirements that are essential in the final gelled phase. Ceria contents of 20 and 50 wt% were first investigated, as these were the ceria contents that had been used to prepare mixed oxide phases by employing sol precursors [21]. In these investigations, the ceria microdomains, or microcrystals, were shown to be highly dispersed and of a size range that was similar to the ceria sol of 20 nm that was used. Ammonium hydroxide was added by rapid addition to the mixed precursors as in the case of aluminum nitrate alone previously described. In this case, the ceria was not present as an isolated, crystalline phase, and, in addition, the alumina crystalline phase was also absent. Instead the gelled phase was amorphous as measured by XRD. Also, the surface area of the gelled phase after calcination at 500°C was < 2 m^2/g. The presence of the ceria in the gel served to disrupt the nucleation and ion transport processes such that a boehmite phase was not able to form, and, instead, a mixed oxide was formed, probably an inhomogeneous solid solution. This mixed oxide phase exhibited none of the desirable characteristics required of a catalyst support. Crystals with a primary particle size of ca. 20 nm must be formed, and must be isolated from each other, in order to produce

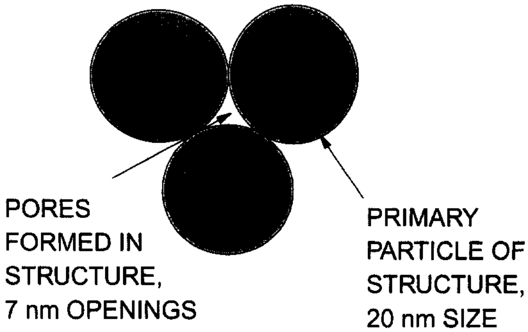

Fig. 9. Picture showing the primary particles within a porous oxide, and the generation of pores between these primary particles.

an oxide where significant surface area and pore volume are generated between the spaces separating the primary particles, see Fig. 9.

This intriguing observation that a second, soluble phase could suppress the intrinsic process of alumina's crystallization [1,11] essential to form a high surface area material was investigated further where the ceria content was reduced to 5 and 10 wt% in the ceria–alumina composite. For both of these compositions, when precipitated as described previously, there was no evidence that either crystals of ceria or alumina were formed. Instead, the $< 2\ m^2/g$ products following calcination at 500°C appeared to be an inhomogeneous mixture of ceria-rich and ceria-deficient amorphous phases as wide variations in the intense yellow color of ceria was observed within the composite oxide. Rapid mixing, and variations in the rate of addition of the ammonium hydroxide to the low ceria content mixed phase slurries failed to generate any evidence that alumina crystalline particles were forming when the ceria precursor was present in the gelation step. The ceria must be interfering with the nucleation and growth processes that are essential for isolated crystals of ceria and alumina to form. The ceria component may be so basic that bridging of the alumina units into chains, which may be required for transformation into the crystalline alumina phases, has been disrupted by the presence of ceria units along the alumina chain. Another possible explanation is that ceria ties up the molecular migrating species of $AlO_x(OH)_y$ structure that are essential to diffuse along the surface of the gelled, and highly charged amorphous particles as the nucleation occurs. It is also possible that ceria, in some way, interferes with the nucleation step itself, where a critical number of nuclei must form in order to guide the gelation process. Formation of an amorphous, mixed oxide structure occurs as a consequence of a limited number of nucleation sites. As we shall see, a soluble tungsten oxide precursor has no impact on the alumina gelation process over a wide range of compositions, in marked contrast with the ceria–alumina system discussed in this section.

3.3. Aluminum–tungsten oxides from aluminum nitrate / ammonium meta-tungstate precipitation

There are many examples in the literature where mixed oxides are formed over the entire composition region where the goal was often the generation of unique acidity in the mixed composite oxides compared to the individual oxides [23]. Many of these systems that were examined had surface areas of ca. $10\ m^2/g$ due to the intrinsic instability of the oxides when calcined at temperatures in the range of 400–600°C. The solid acid systems that we investigated over many years of research at Exxon [24] had high surface areas, combined with high surface area stability, when treated to extreme high temperature conditions, even in steam-containing atmospheres. The most acidic system was tungsten oxide dispersed at monolayer capacity on an alumina surface. The question was asked if it was possible to generate the acidic tungsten oxide surface phase structure simultaneous with the formation of the alumina crystals formed in situ in a gel phase. The protocol of these studies was quite similar to the ceria–alumina composite oxides discussed previously, except that the tungsten content in the composite was investigated in the range of tungsten oxide contents of 5–25 wt% of the composite oxide, as this was the range of tungsten levels that would react with the alumina surface to give a range of acidities [24]. These studies were done well before their comparison to the behavior of ceria–alumina composites formed from soluble precursor was of interest. These results for Al–W composite oxides were not published, but, in retrospect, are of some interest to the present discussion.

For the case of Al–W systems, gelled to a final pH of 9 by rapid addition of NH_4OH, the surface area and pore volume were quite similar over the composition range 5–25 wt% tungsten oxide after drying at 110°C and calcination at 500°C. The surface areas were measured to be between 190–210 m^2/g with a pore volume of ca. 0.5 cc/g. Little attention was directed at the time to investigate subtle shifts in the pore size distribution that might have occurred as a result of the presence of the second oxide being present during the gelation of the soluble precursors. In retrospect, the examination of the pore size distribution could have provided some clues as to the behavior of the second oxide component on the crystallization pathways of the majority alumina component. However, the acidity of these systems was examined [24], and was shown to be entirely consistent with the tungsten oxide phase being highly dispersed on the alumina crystallite surface, with very little material encapsulated within the bulk of the alumina crystals. The failure of the tungsten oxide to be trapped within the alumina crystals may explain why there was little impact of the tungsten oxide phase on the ability of the alumina gel to undergo the nucleation and growth processes which are necessary in the conversion into the final boehmite phase, also. The fact that the tungsten precursor is present as a polyanion structure may help explain why there was no impact on the transformation of the alumina gel into the final crystalline structure. It is also possible that the tungsten oxide component may have reacted with the surface of alumina gel particles during the calcination step at 500°C. This is a real possibility in that bulk tungsten oxide was found to readily disperse onto the surface of alumina particles when calcined in this same temperature range. This process led to identical surface acidity as if a soluble tungsten precursor was added to the porous alumina and then decomposed by calcination at 500°C [25]. These results have a number of different explanations which must be considered. It may be that during the transitory gelation process, the tungsten oxide phase aggregated into separate, large domains of tungsten oxide, which would subsequently be readily dispersed, during the calcination step of the gel transformation. The tungsten oxide particles would disperse to form the surface phase structure bonded to the transitional, gamma-alumina phase. This might explain the failure of the tungsten oxide phase interfering with the alumina gelation process. This gelation process is well established [18] to form the porous structure composed of primary particles of ca. 20 nm diameter which are so ubiquitous in alumina systems [1,7]. Future studies of the gelled mixed phases with XRD may resolve the issue of pre-aggregation of the tungsten component in the gel itself. There is clearly a major difference in the impact that a cerium oxide phase has compared to a tungsten oxide component in the co-gelation with a soluble aluminum nitrate precursor. Formation of a highly dispersed Pt–O surface phase structure was recently reported when a soluble platinum precursor was added to a ceria sol prior to the sol gelation with added ammonium hydroxide [8]. The comparison to the tungsten oxide–alumina composite system forming a surface oxide structure during gelation is striking.

4. Alumina sols as precursors of porous aluminas: impact of sol size on primary particles in porous structures

As discussed in the introduction, there are very few examples where sols of different size were used to form porous oxide structures where the goal was *to compare the primary particle size distribution in the oxide to the size distribution of the sol precursor to the oxide.* Such a study can be quite informative as it can provide information on the transformation in the sol structure as the gel transforms into the final oxide structure. This is not to say that excellent work does not exist on the control of the pore size distribution in the final alumina structure, see for example the excellent paper from the Chioba laboratory [22]. In this paper the primary particles of boehmite crystals were transformed in a systematic fashion where the pore voids between the primary particles were varied from 7 to 100 nm diameter within the formed alumina structure by an in situ procedure where the pH was alternated, or "flipped", over a narrow range. This alternating pH technique allowed the primary particles to grow in a systematic fashion to produce materials with a very narrow distribution of pore sizes. What was especially interesting in this work was the fact that a high pore volume alumina, ca. 1 cc/g, with pores of 7 nm diameter could be induced to transform to an alumina with 100 nm diameter without loss of pore volume within the structure.

If a commercially available alumina sol with a size of 2 nm is gelled using ammonium hydroxide then the alumina produced has pores with an average size of 5.5 nm diameter [1,7]. This material has a surface area of 177 m^2/g, and, although similar to many commercial aluminas, has only about a third the pore volume of a traditional alumina. This example is a clear case where the sol structure has undergone a quite significant polymerization during the gelation process. Sols can be reactive in some cases where the pores within the final oxide have no relationship to the final structure within the gelled and calcined oxide. This alumina sol did provide excellent binding characteristics when added to a dry-milled alumina of 0.1 μm size, however. In this case, the amount of sol required to act as an effective binder was of the order of only 2–5 wt% of the milled alumina in the slurry mixture [21]. At such small levels of sol to the milled alumina there is little concern that the sol can polymerize to such an extent that the milled particles would be encapsulated within a low pore volume phase. In this case, the 2 nm size sol is gelling while in contact with the surface of the milled particles.

In the investigation of another commercially available alumina sol of 20–35 nm diameter, it was found following gelation that an alumina was produced which was virtually identical to traditional aluminas made by aqueous gelation processes [1]. The pore size distribution in the calcined alumina was quite consistent with the alumina sol precursor structure remaining intact during the gelation process. In other words the sol, in this case, transforms apparently intact to form the structures of the primary particles in the alumina. This interesting result was confirmed for both acidic, as well as basic, gelation conditions. The pore size was independent of the solution pH during the gelling process. In fact, the same sol was deposited as a series of eight sequential layers onto a ceramic monolith and the pore size and pore volume was identical to the aluminas produced by gelation from aqueous solution. This raises a very intriguing possible model of alumina crystallization from aqueous media, in general, where the critical factor may be a plateau in the size of the sol stability in aqueous conditions of ca. 20 nm size which is very difficult to grow to a larger size. In the case of the Chioba work discussed previously the size of the pores of the alumina was 7 nm diameter. Interestingly, this is exactly the pore diameter that one would expect to be formed from a sol of ca. 20 nm diameter. Work published by Soled makes a very convincing case that the primary particle size within traditional aluminas are indeed formed from crystals of this 20 nm size range. It was shown that an alumina sol of 2 nm diameter led to a quite dense phase compared to that produced by the 20–35 nm size sol [7]. It is by comparison of the physical properties of the aluminas from these two extremes of alumina sol size that one can conclude with some confidence that:

1. alumina sols can be transformed by aggregation into dense boehmite phases if the sol size is ca. 2 nm diameter.
2. alumina sols of a critical size range, ca. 20 nm, can transform into the final alumina structure without significant aggregation occurring which would otherwise produce a dense alumina structure.

Work to be discussed in subsequent sections will show that there are very interesting pathways to transform alumina primary particles by manipulation of the gelation processes within the pores of a pre-formed support, or by altering the crystallization conditions within the gel phase itself. In these cases to be discussed subsequently, the pre-formed pore structures of an oxide or a gel may be producing a ''micro-cavity reactor'' for the gelation process which acts in fundamental ways to alter the crystal transformations that are constrained by the environment provided by the pore walls.

5. Oxides formed from aluminum alkoxide hydrolysis: synthesis conditions impact on physical properties

This section will only briefly review published observations [11] that point out the pronounced reactivity of an alumina gel that had been previously precipitated to form a gel phase. In this work the formation of a continuous gel structure throughout the entire solution was observed to occur upon water addition. This observation is distinctly different from the Chioba investigation because in that work the transformations were from a boehmite structure into another boehmite structure [22]. If aluminum iso-butoxide is precipitated using the stoichiometric amount of water necessary to hydrolyze all of the alkoxy groups the dried and calcined phase has very high surface area, ca. 600 m^2/g with pores of less that 3 nm diameter when calcined at 500°C [11]. XRD showed this to be an amorphous phase. When this gel was calcined at 800°C complete transformation to an alpha-alumina occurred with transformation to a very low surface area. This poor stability is characteristic of an amorphous alumina, but is not characteristic of transitional-aluminas [1,7]. This calcination treatment is even effective in detecting the presence of small amounts of an amorphous alumina phase in the presence of a majority transitional-alumina phase in a mixed composite sample. It was discovered that this amorphous gel was porous even in the state where the initial hydrolysis had occurred [11]. When water was added to the amorphous gel a remarkable re-crystallization took place. If the water was added to fill the voids within the gel phase, similar to a capillary pore impregnation, then transformation of the material into a high pore volume and large pore diameter boehmite was observed. Due to the high pore volume, upon calcination the boehmite transformed into a high pore volume and high surface area transitional-alumina. This transformation took place because of the limited amount of water added to the pores of the amorphous gel [11]. This intriguing result suggests that the limited amount of water added to the gel in some way limits the number of nucleation centers, which then transform into the large primary particles which transform to the final structure upon calcination. To the best of the author's knowledge this is the only method that a transitional-alumina can be formed with these large pores combined with this high a pore volume without resorting to the ''flip-pH'' method described in the Chioba paper [22]. If the amorphous alumina gel had a 10-fold higher amount of water added than necessary to just fill the pore voids in the gel, then transformation of the gel produced a very similar alumina to conventionally prepared transitional-aluminas which have a surface area of 200 m^2/g [1,7]. Both of these alumina gel transformations occurred in situ with the only difference *being the amount of water added to the amorphous gel.* These results prove that the amount of water added to a previously gelled phase can result in the immediate transformation into a boehmite support, but with very different physical properties depending to a remarkable extent on the amount of water added to the gel phase. One can picture the gelled amorphous gel as a ''host'' structure which undergoes transformation within the gel phase to form the ''guest'' structures which are the primary particles in the final structure. In this model the cavities within the gel structure provide a unique environment not unlike the pores within a conventional support where recrystallization must occur. This in situ crystallization can be envisioned to have occurred within the cavities of the gel itself. In this way the gel may

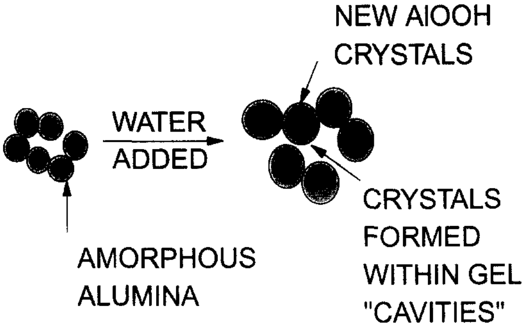

Fig. 10. Diagrammatic representation of pores within and amorphous alumina and how water addition fills these voids where restrained crystallization must take place.

be providing ''microcavities'' which in some fashion regulate nucleation and perhaps transport of nutrients to the growing crystals while at the same time provide the nutrients of the growth process. Such transformation might be referred to as crystallization processes which occur within a ''microcavity reactor'' which is provided by the gel pore structure itself, Fig. 10. Analogous transformation which have been carried out by the in situ recrystallization within crystalline, transitional aluminas of widely different macropore size show very clearly the remarkable impact that cavity, or pore size, has on the crystallization processes for aluminas gelled within the porous alumina structure.

Additional investigations were extended to the investigation of high alumina silica–aluminas and it was discovered that uniquely acidic solid acids were formed by this in situ gelation process. The silica phase was largely isolated on the surface of the boehmite crystals, not unlike the results found for the aluminum–tungsten mixed oxide synthesis described previously. There was a close parallel in the physical properties including surface area and pore volume in the case when water was added to the gel containing up to 20 wt% SiO_2. Clearly, the presence of this high a silica level in the amorphous gel phase does not interfere in the nucleation and growth of the crystals that give rise to the unusual combination of large pores combined with high surface area. It appears by limiting water contact with the amorphous alumina, or silica–alumina, gel phases that a limited number of nuclei are formed which transform into the large primary particles which are necessary to produce the large pores observed. What is intriguing about the materials formed by the limited-water crystallization procedure within the amorphous gel phase itself, is the fact that similar materials can not be formed to the best of the author's knowledge from pre-formed sol intermediates. This appears to be a case where transformation within the pores, or cavities, generated by a precipitated gel are giving silica–alumina catalysts that can not be produced by any other method of synthesis. There are other examples to be discussed subsequently of *unique aluminas being formed* [12,19] when the crystallization is restricted to occur within the cavities of a previously formed alumina phase.

6. Aluminas formed by acid addition to aluminas with 20–80 nm diameter pore size

One of the very best examples of the profound impact that pore cavities have on alumina nucleation and growth come from work that Al Stiles reported in the mid-eighties which unfortunately has not been published [12]. In this work, aluminas with low surface area with pores of a size range from 20 to 75 nm diameter were synthesized. Then acids were added to peptize the alumina which resulted in 7–15 wt% of the alumina being solubilized. It was found that acid addition was of no consequence for aluminas with a pore size < 40 nm diameter. However, when the pore size shifted to between 40–75 nm, a major transformation within the alumina phase was observed with an increase in the surface area from ca. 30 to > 350 m^2/g. This high surface area alumina phase is believed to be formed on the pore walls formed by the large particles of alumina which were responsible for the large pore diameter aluminas originally present prior to acid addition [12]. This new alumina phase was very different from conventional aluminas [19]. Firstly, all of the pores of the high surface area phase were present in a very narrow distribution at 3.0 nm diameter. Secondly, the high surface area alumina reacted with nickel oxide to form a high temperature stable alumina phase where the nickel could not be reduced in hydrogen up to 600°C. Additional levels of nickel, beyond this particular level which was established to be non-reducible in hydrogen, and was believed to form a stable, and interactive nickel–alumina phase, showed normal reduction behavior. This reducible nickel phase was also effective in forming active hydrodesulfurization catalysts for deep levels of sulfur and nitrogen removal despite the fact that the alumina had small pores of only 3 nm diameter. Addition of cobalt oxide to this narrow pore alumina material also exhibited unusual redox and catalytic activities when combined with molysulfide. There is no example that this author is familiar with where aluminas can be formed with a narrow distribution of pores centered at 3 nm. An alumina sol of 2 nm diameter when gelled leads to an aggregated phase with much larger pores centered at ca. 6 nm diameter. It appears that by adding acid to wide-pore-size aluminas that *intermediate-size sol phases, ca. 6 nm in size,* were formed *within the cavities of the alumina phase.* These sol structures form the 3 nm diameter pores which bring about the increase in surface area by an order of magnitude, Fig. 11. Apparently, pores of < 40 nm could not sustain the formation of the sol structure necessary to generate the high surface area alumina phase. This is a very good example of using pore size alone to ''microengineer'' the crystallization pathways that occur within a porous structure. We have extended this concept to the gelation of titania, niobia, and tantala structures within the macro-sized cavities of a ''foamed'' alumina structure with 50–200 nm diameter pores [21]. For these three oxides the crystal size was found to be ca. 30–40 nm diameter formed within the cavities of the foamed support. The treatment of these three ''supports-within-a-support'' at 900°C failed to cause loss of the surface area of ca. 20–30 m^2/g for these structures. All of these oxides transform to < 1 m^2/g surface area if not stabilized within the cavities provided by the host ''foamed'' alumina phase. It appears that a general concept of stabilization of smaller crystals when formed within macroporous supports has emerged from the pioneering work of Stiles and co-workers.

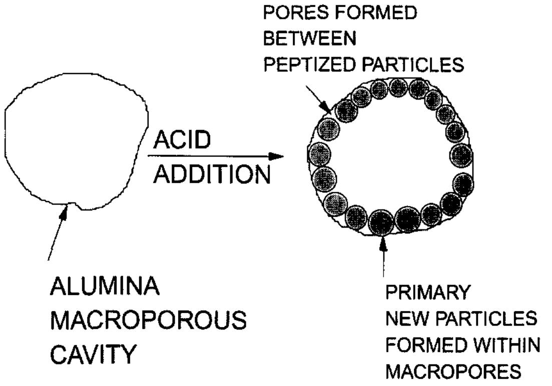

Fig. 11. Picture showing a cross sectiion view of a macropore within an alumina, and the formation of small crystals which produce a high surface area ''support-within-a-support'' upon peptizing the alumina.

7. Ceria formed from sol precursors

It has been determined [7] that ceria sols from 1 to 20 nm diameter obtained from PQ Corporation when gelled with ammonium hydroxide forms an oxide structure whose physical properties are not greatly different from a ceria when gelled in an analogous manner using soluble $Ce(NO_3)_3$ as the precursor. The structures present in all of these gel phases were determined by TEM to be cubic structures with a size of 5.5 nm. The pore size was found for all of these gels to be a narrow distribution centered at 3.3 nm diameter, which is in good agreement with the primary cubic particles detected by TEM. There is clear evidence from these studies that the ceria sol of 20 nm diameter is consumed in the gelled oxide to form a smaller primary particle in the gelled phase. It is also apparent that the smaller 1 nm diameter ceria sol has undergone polymerization, or growth, to form the 5.5 nm cubic structures established to be present in the gelled ceria phase. This result is quite similar when compared to the 2 nm diameter alumina sol when gelled in an analogous fashion to form a transitional-alumina phase where the primary particles in the alumina were ca. 10 nm diameter. The surface area of these gelled ceria phases were 100 m^2/g regardless of the precursor sol phase. In order to account for these surface areas for an oxide with 3 nm diameter pores it is essential that a relatively dense phase is formed upon gelation. This was in fact confirmed in that a pore volume of 0.20 cc/g was obtained. This is a very interesting example where a large sol precursor is of little consequence in preserving a high pore volume within the gelled oxide. One can picture this gelation process as one where the sol phase must be digested essentially completely to form a dense, crystalline phase. The only role of the sol phase is to provide nutrients for transformation into the final structure. The formation of a dense phase is of interest as this suggests that the number of nucleation centers which grow into the cubic 5.5 nm primary structures of ceria are unaffected by a sol phase where the sol surface area in the gel must vary over a very wide range immediately following the gelation step where ammonium hydroxide is initially added [7]. Apparently, the surface of the sol does not trigger the formation of nucleation sites at the surface which would have resulted in very different crystalline phases for sols of 1 or 20 nm diameter. Some zeolite systems have been found to readily form nucleation centers at the surface of larger crystals [26–28]. As we shall examine in subsequent sections the ceria sols of 1 and 20 nm diameter lead to very different ceria structures when gelled with a second sol which serve to isolate the sol particles from one another. The second sol phase interferes with the crystallization process to such an extent that thin rods or shorter cylinder structures of ceria were formed instead of the ubiquitous cubic structures of 5.5 nm size observed in virtually all ceria gels.

8. Preparation of oxides from mixed sols

The preparation of ceria from gelation of a 20 nm size ceria sol results in the formation of a low pore volume phase with very narrow pores centered at ca. 3 nm diameter as discussed in the previous section. It was found that this same size ceria sol when gelled with a Ti sol of similar size formed a much higher pore volume material with separate ceria and titania domains for a 50 wt% fraction of each oxide. The size of these two different domains corresponded quite well with the size of the starting sols of ca. 20 nm size. This serves to show that the pore volume of ca. 0.5 cc/g and a surface area of ca. 200 m^2/g is due to formation of crystalline titania and ceria domains which are the primary particles within the structure.

This work was extended in much greater detail [7] to the formation of ceria domains when gelled with an alumina sol of 20 nm size. In this case three ceria sol sizes were investigated: 1, 14, and 20 nm diameter. Ceria contents from 2.5 to 50 wt% were investigated. In all of these systems the pore volume and surface area corresponded to that which one would expect from the sol domains transforming into the primary particles within the structure of the calcined oxide structure. This was especially important as the host alumina sol of 20 nm diameter acts as the "host" structure of the ceria domains. In the case of the 14 and 20 nm size sol the domains of ceria were found by TEM investigation to be small cylinders whose size varied over a small range but whose volume corresponded very closely to the sol size of 14 or 20 nm diameter. This is convincing evidence that the ceria domains for these two sols are "trapped" during the gelation process to form isolated domains of ceria which correspond to the sol used in the synthesis. These ceria domains substitute for the primary alumina particles within the structure such that pore volume and surface area are very similar to that formed by gelling the alumina sol itself, Fig. 12. These ceria domains have the shape of ''rice grains'' as they substitute for the alumina crystals within the three-dimensional structure. Temperature Programmed Reduction (TPR) showed that the ceria formed as separate domains within the alumina host and were highly dispersed as the ca. 20 nm domains established by TEM studies. In addition, TPR studies of these sol-prepared mixed oxides when calcined at 900°C showed that the ceria domains were stable to high temperature treatment unlike the corresponding bulk ceria system [11]. Other work also confirmed the ability of the ceria domains to bond strongly to all of the Group VIII precious metals leading to stabilization of highly dispersed M–O structures bonded to the surface of the ceria domains after calcination at 900°C [8].

These combined studies show two important conclusions of sol syntheses of mixed oxides:

1. Mixed sols can gel to form isolated particles within oxides where the primary particle size corresponds to the size of the sols from which the oxides were formed.
2. Stabilization of the isolated, ''host'' domains can occur if the second oxide is a stable ''host'' structure, as in the case of alumina as the second oxide.

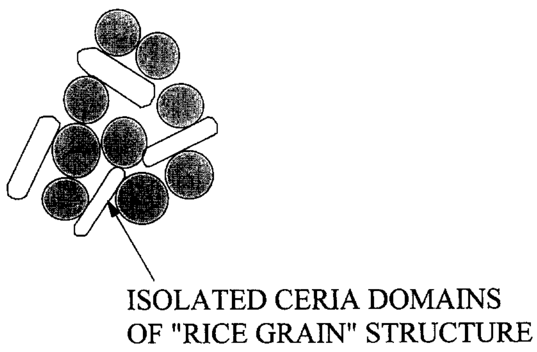

Fig. 12. Diagrammatic representation of formation of ceria microdomains when a ceria sol is co-gelled with an alumina sol which serves as the ''host'' of the ceria domains.

As a note added in proof, calcination of the titania–ceria sol-derived mixed oxide at 900°C caused a collapse of the structure to a surface area to less than 1 m^2/g. The collapse of the mixed oxide structure is undoubtedly due to fact that the titania phase is not as stable a ''host'' phase of the ceria ''guest'' as the case of the alumina crystals serving as the ''host'' phase discussed previously. The corresponding alumina–ceria system would have a surface area of ca. 100 m^2/g which is very similar to that of the sol-derived alumina phase calcined at this high temperature. It was also determined that it was possible to form isolated domains of ceria–zirconia–alumina when prepared from the corresponding sol precursors. The separate domains of ceria and zirconia were clearly in evidence from X-ray diffraction analysis of the gelled and 500°C calcined oxides. Calcination of this three component oxide at 900°C confirmed that the three domains had remained intact as separate phases within the porous structure.

The mixed Ce–Al oxides prepared from the ceria sol of 1 nm diameter was left to this final section for discussion. For this small ceria sol, which has a size similar to a transition metal polyanion structure, there was clear evidence that polymerization occurred during the gelation with the larger 20 nm alumina sol acting as the host structure [7]. The details of the structures formed have been published and will only be referred to here in general terms. If the ceria content was limited to 2.5 wt% within the ceria–alumina composite then thin rod structures of 2 nm diameter by 45 nm were formed within the gel, Fig. 13. As the pores were of a size of 7 nm diameter it is clear that the rod-like structures were not limited to grow within the pores of the host oxide. Instead, the 1 nm size sols crystallized within the formed gel phase forming the thin rod structures prior to the alumina sol forming a rigid structure. This is a very intriguing example where the employment of a

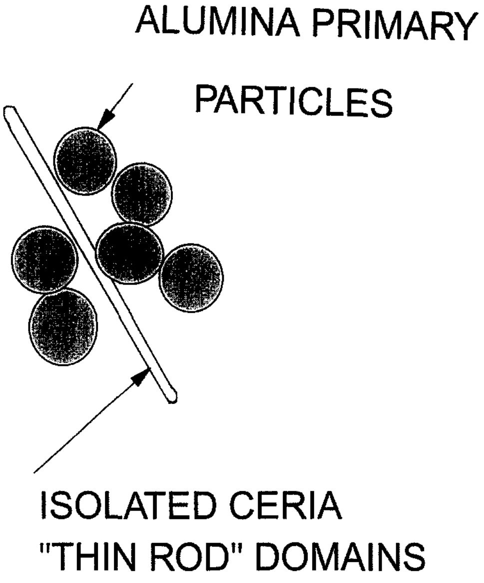

Fig. 13. Picture of thin ceria ''rod'' structures formed by gelling a ceria sol at dilute concentrations with an alumina sol acting as the ''host'' of the rod-like domains.

second sol acting as a host structure guides the formation of a crystalline structure very different from that observed by gelation of the sol itself. If the ceria content was increased to 5 wt% then the ceria domains were of much larger size than in the case of the 2.5 wt% sample. If the ceria content was increased to 50 wt% then ceria domains were obtained of cylinder shape where the size was similar to the case where the ceria sol was of 20 nm diameter. This suggests that the sol content as well as the sol size can play a critical role in the domain size which will form within the framework provided by a second oxide sol phase.

9. Preparation of zirconia from sol precursors

Recent work [17] has shown a quite remarkable difference in the properties of zirconias made from commercially available zirconia sols of nominally different size. In this study, zirconia sols of three different sizes, 5–10, 50, and 100 nm, were gelled and the surface areas, pore volume, and pore distributions were determined after two calcination treatments. The surprising result was that the sol of the smaller size produced an oxide with very little surface area and pore volume. This suggests that the small sol size allowed densification during the gelation process to produce a low pore volume phase, not unlike the case of the 2 nm size alumina sol and the 1 nm size ceria sol discussed previously. The larger sols produced zirconias of much higher surface area and pore volume upon gelation [17]. What was fascinating is the fact that the 50 and 100 nm size sols are made from aggregates of the 5–10 nm sol which produced a material with very little surface area when gelled itself. In some way the pre-aggregation to form an agglomerate of the smaller size zirconia sol serve a very useful role in preventing the densification during the gelation step. This may be explained by the obvious fact that the aggregated sol units serves to bond the elementary sol units one to another to form a thick shell structure in the aqueous phase on a core of sol units which are also bonded one-to-another, see Fig. 14. In this picture, gelation occur without access of the sol units to high levels of water contacting the elementary sol units. The absence of controlled water contact with the isolated, elementary sol units of 50–100 nm size *in some way* facilitates either rapid transport of nutrients from the sol units to form a dense phase, and/or facilitates the formation of large numbers of

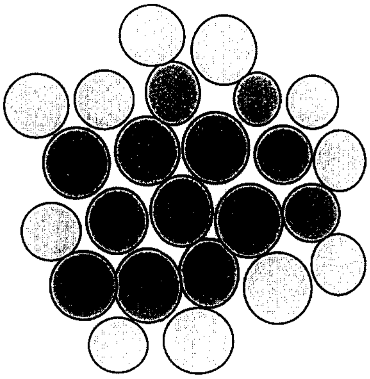

Fig. 14. Simplified representation of a colloidal sol phase that has undergone aggregation to form a larger size sol phase, where the core of the particles is built up of sol particles of similarly size as those that are moore loosely associated with the surface of the colloidal aggregate.

nucleation sites which could also explain the formation of a very dense phase. The pore size appears to be below 2 nm diameter which argues that the 5–10 nm sol units themselves are made from still smaller primary units. Subsequent characterization work suggests that a significant amount of the surface area comes from pores with a diameter of 4 nm size which is entirely consistent if formed from primary particles of 8–10 nm size, clearly similar to size of the zirconia sol itself. The key question is, if this pre-aggregation of zirconia sol units can be employed in a systematic fashion with other oxide systems to prevent densification during the gelation step. If so, then this sol pre-aggregation phenomenon could be a powerful technique to aid in control of surface area retention, and to also aid in the maintenance of large pore sizes between the aggregated units which will lead to large macropores within the structure. As a note added-in-proof an alumina sol from PQ Corporation of 20 nm has been shown to produce a wide range of macropores if diluted in water and allowed to stand for several weeks prior to adsorption onto a metal monolith substrate. Direct adsorption onto a geometric substrate produces a material which shows pores centered at 7 nm diameter. So it appears that there is indeed the possibility to manipulate the macropores formed in sols that have been gelled while at the same time impacting on the fundamental processes which lead to maintenance of pore volume in the mesopore size range, i.e., < 50 nm, which are the principal contributors to the surface areas in catalyst supports. This pre-aggregation of sols prior to gelation is a fertile area for future investigation, which has surfaced from only a very limited number of investigation focused on the employment of preformed sols as oxide precursors [1,2,7,17].

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