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Control of mixed oxide textural and acidic properties by the sol–gel method

James B. Miller [1], Edmond I. Ko *

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA

Abstract

Preparation of catalytic mixed oxides by sol–gel chemistry affords a degree of control over the intimacy of molecular-scale mixing – and therefore the important acidic and textural properties that depend upon mixing – that is not available by other methods. Literature examples illustrate how careful control of any one of a number of preparative parameters, including, but not limited to, concentrations, addition order and drying conditions, can lead to changes in the microstructural distribution of the components that are, in turn, related directly to the textural and chemical properties of the calcined sample.

1. Introduction

In this paper we describe the application of sol–gel chemistry to preparation of catalytic mixed oxides. For our purposes, we define mixed oxides to be those materials that approach homogeneity throughout the bulk on a molecular scale. Hence, we specifically exclude a class of materials known as ''supported oxides'' or ''surface oxides'' in which one component is placed on top of another by techniques such as incipient wetness impregnation. While sol–gel preparation of catalytic materials is not as mature as it is in ceramic and glass applications, our focus will remain on the former. Preparative approaches for catalytic materials and glasses share many common features, but the desired properties of the sol–gel product are very different.

We begin by introducing you to the role of mixed oxides in catalysis, using both models and experimental results to illustrate how many significant textural and acidic properties depend upon not only the oxides chosen and their relative amounts, but also the goodness of molecular-scale mixing. Next, we describe sol–gel chemistry and its unique ability to control molecular-scale mixing – and those properties that depend upon mixing. We present literature evidence of sol–gel's ability to form the M–O–M′ bonds (where M and M′ denote two different cations) that are characteristic of a well-mixed sample at ambient conditions.

Finally, we select several examples from the catalytic literature that illustrate: (i) the relative abilities of sol–gel based techniques to promote homogeneous molecular-scale mixing and (ii) the

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* Corresponding author.

[1] Present address: Mine Safety Appliances Company, P.O. Box 427, Pittsburgh, PA 15230, USA.

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types of measures – both spectroscopic and acidic/catalytic – that are used to assess the goodness of mixing in a catalytic mixed oxide.

2. Background

2.1. Mixed oxides in catalysis

Multi-component oxides play a central role in chemical and petrochemical processing as catalysts and as supports for catalytically active species. A major component oxide can be stabilized against degradation of its textural properties upon heat treatment by introduction of even a small amount of a minor component, thereby allowing the material to be used at more severe processing conditions. For example, several authors have reported that addition of less than 10 mol% silica to titania results in significant increases in both surface area and pore volume [1–4]. In addition, silica's presence delays the crystallization of titania to higher temperatures [1,2,5]. These effects have been related to silica's ability to impede titania's normal sintering processes through formation of Ti–O–Si "hetero-linkages" [6].

Combination of dissimilar oxides also presents the potential to create surface acid sites that are not present in either of the pure components. Fig. 1 illustrates how the maximum acid strengths of some example mixed oxides, as measured by indicator methods (these techniques estimate how weak a base can be protonated by a surface Brønsted acid site; see Refs. [7–9] for details), correlate reasonably well with the average electronegativity of the cations [10]. Interestingly, no satisfactory explanation for this correlation has been advanced [7,10].

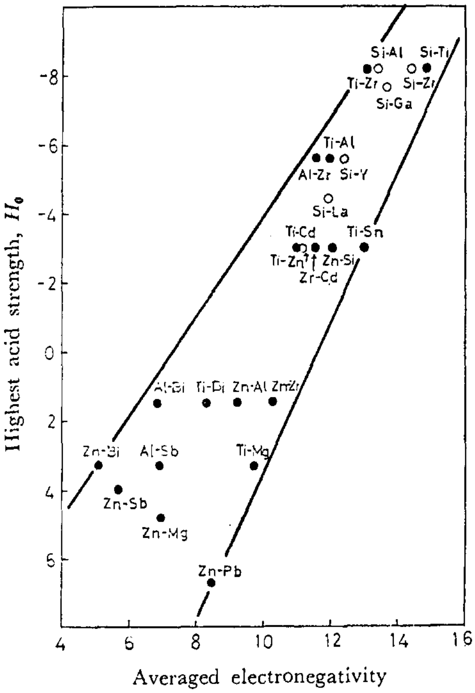


Fig. 1. Acid strength (indicator methods) correlates with mean cation electronegativity for a series of equimolar two-component oxides. All samples calcined at 773 K in air. (Reproduced from Ref. [10] with permission.)

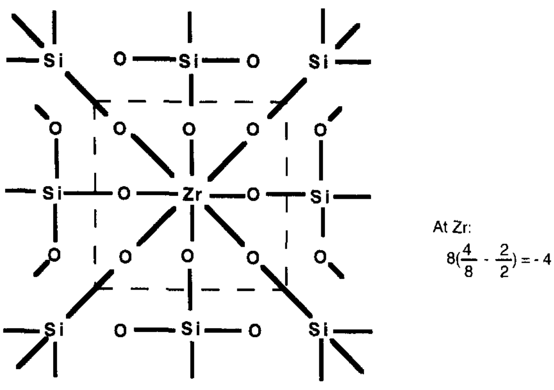
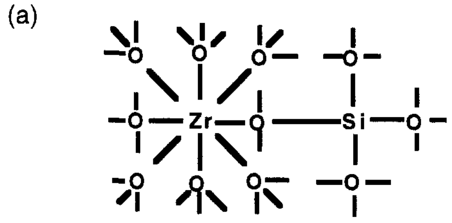
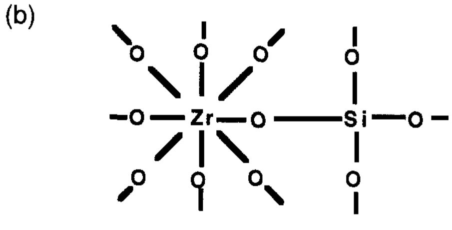


Fig. 2. Thomas' model (Ref. [11]) of acidity development in mixed oxides applied to zirconia–silica.

Several models have, however, been proposed to explain the *appearance* of acid sites in a mixed oxide. In 1949 Thomas proposed a model of acidity to explain the activity of silica–alumina cracking catalysts [11]. Fig. 2 shows a schematic diagram of his hypothesis as applied to zirconia in silica. Zirconium and silicon cations both retain their coordination from the single component oxides (8 and 4 respectively), and all oxygen atoms have 2-fold coordination. The charge excess near the cation of the *minor* component – in this case zirconium – is calculated by distributing each ion's formal charge equally to each bond in which it participates. As the figure shows, the charge excess in this case is −4. It is presumed to be balanced by association with four acidic (Brønsted) protons. Thomas notes



ZrO_2 is major component:
at Si: $4(\frac{4}{4} - \frac{2}{4}) = +2$ Lewis



SiO_2 is major component:
at Zr: $8(\frac{4}{8} - \frac{2}{2}) = -4$ Brønsted

Fig. 3. Tanabe's model (Ref. [12]) of acidity development in mixed oxides applied to zirconia–silica: (a) zirconia is the major component; (b) silica is the major component.

that "maximum activity" should be expected when every oxygen atom is shared by one Zr and one Si – this would occur in a "perfectly mixed" oxide with a Si/Zr atomic ratio of 2.

Tanabe and co-workers have proposed an extension of Thomas' hypothesis which formalizes rules for assigning coordinations in the mixed oxide and allows for generation of Lewis acid sites [12]. Tanabe assumes that: (1) cations retain the coordination that they have in the single oxide and (2) oxygen assumes the coordination it has in the *major* oxide. As in Thomas' method, a "charge excess" is calculated at the site of the minor cation – see Fig. 3. Excess positive charge is associated with a Lewis acid site, excess negative charge with a Brønsted site. As shown in the figure, zirconia in silica is expected to generate Brønsted sites – the same result as Thomas – while silica in zirconia should have Lewis character. The Tanabe model predicts correctly in about 90% of cases [12], but cannot be applied at compositions near equimolar. However, by associating acid sites with hetero-linkages, Tanabe's model establishes a key conceptual relationship between molecular homogeneity and high acid site density.

A model proposed by Kung attributes acid site generation to the difference in electrostatic potential experienced by a cation in its own matrix and that which it sees when substituted into the matrix of a different oxide [13]. Despite its focus on matrix effects, it shares many common features with the Tanabe model, especially in some limiting cases. By presuming a *solid solution* of a dilute oxide component in a host matrix, Kung's model also implies that good mixing is a requirement for acidity.

2.2. *Molecular-scale homogeneity in mixed oxides*

As we have seen, application of the acidity models is often limited to narrow composition ranges. Furthermore, the models' predictions do not always agree with experimental observations. Still, they all suggest that molecular-scale homogeneity is desirable for acidic properties. Indeed, experimental evidence confirms that mixing, along with oxide pair and composition, is a key variable in determining the acidic properties of a mixed oxide. As an example, Tanabe et al. illustrate the importance of homogeneity by comparing mixed 90 mol% titania–10 mol% silica catalysts [14] prepared using two different coprecipitation techniques. In the first method, they used an in situ base introduction technique – thermal decomposition of urea – to eliminate high local hydroxide ion concentrations and promote homogeneous component oxide mixing. They compared this method to a second, more conventional technique in which an ammonium hydroxide solution was added dropwise to a solution of the precursors. As shown in Fig. 4, the sample prepared by in situ base generation – presumably the better mixed material – had weaker acid sites, *but a higher density of sites* (measured by a base titration technique), than the conventionally prepared coprecipitate. Furthermore, the homogeneous sample was twice as active as a catalyst of 1-butene isomerization [14], a reaction that requires weak Brønsted acid sites [15]. This observation illustrates the use of chemical reactions as probes of mixed oxide surfaces. Reactions such as 1-butene isomerization and alcohol dehydration have often been used to characterize acidic surfaces [1,3,14,16–20]. When measured on an appropriate basis – typically reaction rate per area at constant conditions – we can associate high activity with a high density of surface acid sites. In a mixed oxide, where acid sites form at M–O–M′ linkages, activity can be used as a relative measure of the goodness of component mixing [1,14,16–18].

Tanabe et al. also observed that homogeneity differences were reflected in the *textural* properties of their titania–silicas [14]. As shown in Fig. 5, the poorly mixed sample possessed higher surface area at low heat treatment temperatures, but the well-mixed sample was less susceptible to sintering, retaining a higher fraction of its surface area upon heat treatment. Other researchers have also made a connection between homogeneity and the catalytic and textural properties of a mixed oxide [1,16–

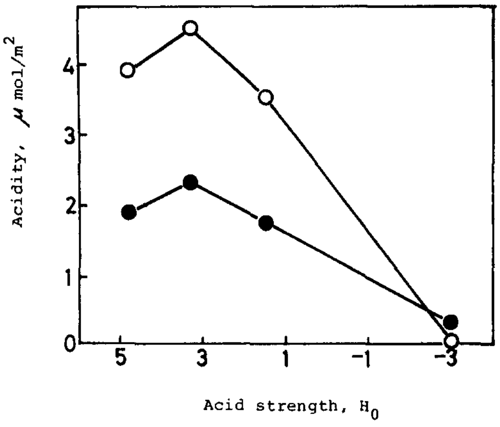


Fig. 4. Acid site density as a function of acid strength (base titration/indicator methods) for titania–silica coprecipitates prepared by in situ base generation (open circle) and drop-wise addition of ammonium hydroxide (closed circle). All samples calcined at 773 K in air. (Reproduced from Ref. [14] with permission.)

18,21–23]. As we will see, many of these examples involve use of sol–gel based preparation techniques.

Conventional mixed oxide preparation methods are very limited in their ability to control component mixing while simultaneously providing the high surface area and pore volume desired for catalytic applications. This makes them poorly suited for studying the important effects of homogeneity upon mixed oxide properties. For example, the practice of high temperature treatment of physical mixtures of component oxides or their solid-phase precursors *can* result in a well mixed multi-component oxide. But the dense product typically has very little surface area or pore volume [24]. And, despite a few successful attempts to promote homogeneity within the framework of the very common coprecipitation technique [14,25], differences among the pHs and rates at which different hydroxides precipitate usually do not allow *fine control* of the goodness of molecular-scale mixing. The sol–gel process, in contrast, provides a low temperature synthesis with excellent control over mixing.

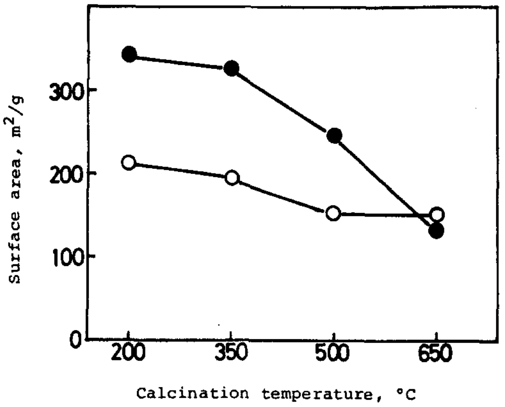


Fig. 5. Surface area (nitrogen adsorption/desorption; BET analysis) for titania–silica coprecipitates prepared by in situ base generation (open circle) and drop-wise addition of ammonium hydroxide (closed circle). All samples calcined at 773 K in air. (Reproduced from Ref. [14] with permission.)

3. Sol–gel chemistry for preparation of mixed oxides

3.1. Basics of sol–gel chemistry

Metallic alkoxides [26–30], inorganic salts [27,29,31], and pre-formed sols [26,27,30] are among the starting materials, or precursors, that can be used in a sol–gel preparation. However, because alkoxides are the most widely used and the most thoroughly understood [27,28,30], we limit our discussion to this precursor class.

Sol–gel preparations with metallic alkoxide ($M(OR)_x$) precursors are typically carried out in an alcohol solvent with a small amount of water as co-reactant. A three-dimensional macro-molecular network is formed by hydrolysis of the precursors followed by condensation of partially hydrolyzed species to form –M–O–M– linkages [28–30,32–34]. In the case of a single oxide preparation, these two important classes of reactions can be summarized as follows:

$$\begin{array}{ll} -M-OR+H_2O = -M-OH+R-OH & \text{hydrolysis} \\ -M-OR+-M-OH = -M-O-M- +R-OH & \text{condensation} \\ -M-OH+-M-OH = -M-O-M- +H_2O & \text{condensation} \end{array}$$

At a characteristic extent of reaction known as the gel point, the growing macro-molecular network spans its container causing a rapid rise in the viscosity of the reaction mixture. The product gel (sometimes referred to as ''alcogel'') is a di-phasic semi-solid material in which the solid gel network encapsulates the alcohol solvent [28,30].

As we illustrate in Table 1, the relative rates of precursor hydrolysis and condensation dictate the structure of the gel network [35]. Many independent variables, known collectively as the sol–gel parameters, are available to manipulate the rates of hydrolysis and condensation – and eventually the nature of the macro-molecular network within the product gel. Most important among these parameters are precursor molecule, its concentration, the solvent, temperature, water concentration, and acid (or base) content [28,30,32,33].

In some cases, the gel is aged before drying. Aging can take the form of a ''redispersion treatment'' which allows dissolution and precipitation of material for a degree of ''fine tuning'' of the network's structure [36]. The solvent is subsequently removed by either (i) evaporative drying or (ii) a supercritical drying step. Supercritical drying has the advantage of eliminating the liquid/vapor interface during drying that could otherwise lead to partial collapse of the network structure – most notably loss of surface area and pore volume – due to high differential capillary pore pressures [28,30,37]. The high area products of supercritical drying are known as ''aerogels''. Sometimes an additional differentiation is made between materials dried with supercritical alcohols (''aerogels'') or by displacement with supercritical CO_2 (''carbogels''). Evaporatively dried samples are called ''xerogels''. Some approaches for retaining area during conventional drying have been developed.

Table 1
How the relative rates of hydrolysis and condensation affect the structure of a gel

Hydrolysis rate	Condensation rate	Result
Slow	Slow	Colloid/sol
Fast	Slow	Polymeric gel
Fast	Fast	Colloidal gel/gelatinous precipitate
Slow	Fast	Controlled precipitation

Adapted from Ref. [35].

These include using solvents with low surface tensions [38,39] and preparing gels with very narrow pore size distributions (recall that it is the *differential* capillary pressure that causes collapse) [28,29]. After drying, the product aerogels/xerogels are heat-treated to prepare catalytic materials.

It is important to recognize that while the details of the aging, drying and subsequent heat treatment steps all have an impact on the properties of calcined sol–gel product, it still bears the signature of the structure that it originally possessed at the gel point. We therefore find that the sol–gel parameters give us substantial control over the textural, structural and surface-chemical properties of even single-component oxides [30,40,41].

3.2. Control of molecular-scale mixing

In the case of a multi-component system, two or more precursors exist in various stages of hydrolysis, resulting in a dramatic increase in the number of possible hydrolysis and condensation reactions. While control of hydrolysis and condensation rates is still important in a multi-component case, it is superimposed upon differences in precursor reactivity. Relative precursor reactivity is a key sol–gel parameter in mixed oxide systems because it can be used to control homogeneity [16,28,30]. In a qualitative manner, we expect the more reactive precursor to hydrolyze and condense first. The less reactive precursor reacts later on, thereby encapsulating or coating the condensation products of the more reactive precursor to form a segregated product. On the other hand, when precursor reactivities are evenly matched, we expect a homogeneously mixed network to develop because M–O–M′ linkages – the signature of a well-mixed sample – have the potential to form at low temperature. It is important to note that homogeneous mixing is not always the desired outcome of a multi-component sol–gel preparation. As we will describe later in this paper, segregated materials are actually better suited for certain catalytic applications.

The oxide pairs that are most interesting from an acidic point of view are often the same ones that are most difficult to mix homogeneously. A large electronegativity difference between two cations is desirable for development of an acidic M–O–M′ linkage. However, the same electronegativity difference usually guarantees that the alkoxides of the two cations will have very different reactivities toward hydrolysis and condensation.

Fortunately, sol–gel chemistry provides several chemical strategies for overcoming the effects of precursor reactivity differences to promote intimate molecular-scale mixing. These approaches can be grouped into four broad categories: (1) For most metal atoms, more than one alkoxide precursor exists. And, based on factors such as the inductive capability and the steric hindrance of various alkoxy groups, we would expect different alkoxides of the same metal to display different reactivities [30,32]. In Table 2, we show how the activities of various silicon precursors in hydrolysis reactions vary with the size of the alkoxy ligand; the rate constant decreases with increasing size of the alkoxy ligand [42]. Therefore, simply by switching to a different precursor we can reduce the reactivity

Table 2
Rate constant for acid hydrolysis of tetraalkoxysilanes $(RO)_4Si$ at 20°C

R	k ($l\,mol^{-1}\,s^{-1}\,[H^+]^{-1}/100$)
C_2H_5	5.1
C_4H_9	1.9
C_6H_{13}	0.8
$(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2$	0.3

Adapted from Ref. [42].

mismatch. (2) Prehydrolysis, in which the less reactive precursor (usually a silicon alkoxide) is given a "head start" in the reaction sequence that forms the gel network by allowing it to have first contact with water, is by far the most common reactivity matching strategy. The technique was first developed in the 1970's as a means for promoting homogeneity in sol–gel derived multi-component silicate glasses [43,44]. (3) A reactive precursor can be slowed by replacing some of its alkoxy groups with different ligands in a technique known as "chemical modification" [45]. This approach has been employed most often to control the kinetics of single oxide preparations. Common modifiers are acetic acid and acetylacetone (acac) [46]. (4) *All* reaction rates can be lowered [27,33]. This can be accomplished by introducing hydrolysis water very slowly – by atmospheric humidity, for example [27,33] – or by lowering the temperature of the synthesis [33].

There are literature reports of solution phase NMR studies that demonstrate formation of hetero-linkages – the signature of well-mixed samples – at low temperature by sol–gel chemistry. The alumina–silica system is one of the most widely studied from this perspective [30]. In Fig. 6, we show Pouxveil and Biolot's ^{29}Si NMR data for slow-hydrolysis (atmospheric moisture) of a mixture of tetraethyl orthosilicate (TEOS) and $Al(OBu)_3$ [47]. Note that, at long enough reaction times, the hetero-linkage yield is very high. These authors noted that hetero-linkages can also be formed by addition of the aluminum precursor to *prehydrolyzed* TEOS (1 mol H_2O/mol TEOS "prehydrolysis ratio"). However, the yield is not nearly as good in this case because some TEOS monomers never react and others participate in homo-condensation reactions to form various hydrolyzed TEOS oligomers. Miller and Ko reported similar distributions of "prehydrolysis products" before addition of a zirconium alkoxide in their preparation of zirconia–silica aerogels [17]. They also noted that the details of the distribution, including the extent of oligomerization and the average number of –OH groups per molecule –as well as the properties of the calcined zirconia–silicas – are strong functions of the prehydrolysis ratio. We will discuss Miller and Ko's work in additional detail later in this paper.

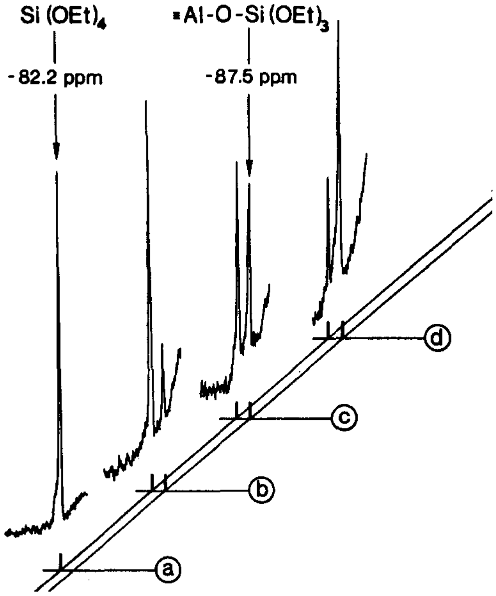


Fig. 6. ^{29}Si NMR spectra for "slow hydrolysis" (50% relative humidity) of TEOS/$Al(OBu)_3$ mixture: (a) at mixing (time = 0); (b) 2 days; (c) 4 days; (d) 5 days. (Reproduced from Ref. [47] with permission.)

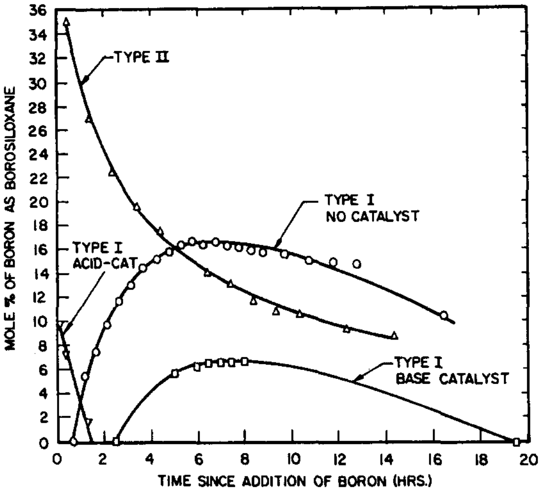


Fig. 7. Borosiloxane (B–O–Si) hetero-linkage yield (% of total boron) as functions of hydrolysis type (type I = ambient temperature, high solvent concentration; type II = 50°C, low solvent concentration) and time. (Reproduced from Ref. [48] with permission.)

Irwin et al. provided a very instructive example of how prehydrolysis conditions affect the yield of B–O–Si bonds in sol–gel preparations using TMOS (tetra*methyl* orthosilicate) and trimethyl borate precursors [48]. They compared two basic methods. In type I, they prehydrolyzed the TMOS precursor (2 mol H_2O/mol TMOS prehydrolysis ratio, ambient temperature) with acid, base or no catalyst, before adding the boron precursor (0.43 mol B/mol Si). As illustrated in Fig. 7, regardless of catalyst choice, the hetero-linkage yield is low, always less than 20% of the total boron content. It also is a function of time. The choice of catalyst in the type I method is another important factor; prehydrolysis with no catalyst delivers the highest yield of hetero-linkages. A type II prehydrolysis procedure, using roughly the same prehydrolysis ratio, but with less solvent and higher reaction temperature than type I, promotes significantly higher hetero-linkage yields at low reaction times. The authors attributed the difference to enhanced TMOS hydrolysis rates promoted by the higher water and precursor concentrations employed in type II.

Evidence of low temperature hetero-linkage formation has also been reported for other oxide pairs of catalytic interest, including zirconia–silica and titania–silica [49]. We also note that addition of titanium alkoxide to prehydrolyzed TEOS has been reported [50] to be more likely to promote homo-condensation among Si–OH species than to form Ti–O–Si bonds. Disparate reports like these undoubtedly reflect differing conditions used in the sol–gel preparations. Our aim is not to interpret all of the available hydrolysis/condensation kinetic data. However, by presenting these examples we hope to have convinced you that (i) formation of hetero-linkages at low temperature using sol–gel chemistry, while not always "simple", can be done, (ii) different approaches for overcoming the precursor reactivity difference are likely to deliver different extents – or perhaps even types – of mixing, and (iii) much more work must be done to firmly establish the relationship between processing conditions, especially at the very start of a preparation, and goodness of mixing.

4. Examples of preparing sol–gel mixed oxides

Sol–gel chemistry has been applied to many mixed oxide systems for preparation of glasses, coatings, and other ceramic materials. Table 3 contains a list of mixed oxide glasses that have been

Table 3
Multi-component glasses prepared by sol–gel techniques from alkoxide precursors

Binary glasses	Ternary glasses
SiO_2–B_2O_3	SiO_2–Al_2O_3–La_2O_3
SiO_2–Al_2O_3	SiO_2–ZrO_2–La_2O_3
SiO_2–P_2O_5	SiO_2–ZrO_2–Na_2O
SiO_2–GeO_2	SiO_2–B_2O_3–P_2O_5
SiO_2–TiO_2	SiO_2–MgO–Al_2O_3
SiO_2–ZrO_2	SiO_2–Al_2O_3–CaO
SiO_2–Na_2O	SiO_2–TiO_2–ZrO_2
SiO_2–SrO	SiO_2–CaO–Na_2O
SiO_2–Fe_2O_3	SiO_2–B_2O_3–Na_2O
Multi-component glasses	
SiO_2–B_2O_3–Al_2O_3–BaO–Na_2O	
SiO_2–B_2O_3–Al_2O_3–Na_2O–K_2O	
SiO_2–Al_2O_3–Li_2O–MgO–TiO_2–ZrO_2–ZnO–BaO–CaO–K_2O	
SiO_2–Al_2O_3–P_2O_5–Li_2O–MgO–Na_2O–TiO_2–ZrO_2	

Adapted from Ref. [26].

prepared by sol–gel techniques [26]. We will not review this portion of the scientific literature here. Instead, we refer the reader to excellent reviews by Rabinovich [26] and Thomas [27]. It is important to remember that, while the desired properties of the final sol–gel products are very different (dense ceramics vs. porous catalytic materials), many of the preparative strategies for sol–gel based glasses and catalytic materials are similar. As we described in the last section, for example, prehydrolysis was originally developed for promotion of homogeneous mixing in preparation of multi-component silicate-based glasses. And, because sol–gel chemistry has generally been limited to preparation of *binary* mixed oxide catalytic materials, the glass literature is especially useful when considering systems having more than two components (see Table 3). We therefore encourage you to consult the glass literature when contemplating preparation of a new catalytic mixed oxide. In addition to the reviews we cited above, periodic publications, such as the Journal of Non-Crystalline Solids, Journal of Sol–Gel Science and Technology, and the Materials Research Society Symposia Proceedings, are valuable resources.

Up to this point, we have described sol–gel's potential for delivering catalytic mixed oxides that are better mixed than those prepared by conventional techniques. And, in the previous section, we saw that this advantage is related to the ability to form hetero-linkages at ambient temperatures. In practice, we learn that depending on which reactivity matching scheme – if any – is used, and even upon the details of how a single technique is applied, samples having very different extents of molecular-scale mixing can be prepared. *The idea that component oxide mixing is not a binary*

Table 4
Variations of the sol–gel method (alkoxide precursors) for preparing catalytic mixed oxides [a]

- Slow simultaneous hydrolysis (based on *potential*)
- High ratio prehydrolysis of the less reactive precursor (2–3 mol/mol)
- TMOS for TEOS swap, modification with acetylacetone
- Low ratio prehydrolysis of the less reactive precursor (< 2 mol/mol)
- Rapid, simultaneous hydrolysis
- Complex-agent assisted
- Coprecipitation (for reference)
- Separate hydrolysis, hydrogel kneading

[a] Techniques are listed in order of their ability to deliver well-mixed samples – best mixing at the top, poorest mixing at the bottom.

Table 5
Measures of the goodness of molecular-scale mixing in a multi-component oxide

Acidic/catalytic	
Acid site density, generally by titration or temperature programmed desorption techniques	High acidities imply high hetero linkage densities which are characteristic of a well-mixed sample
Catalytic activity in a reaction that requires an acid catalyst. Examples are alcohol dehydration and alkene isomerization.	High specific activities at constant conditions imply high surface acid site densities
Spectroscopic	
Infrared	(i) Skeletal vibration frequencies matching those of a pure component are a sign of segregation, (ii) in silica-containing samples, features corresponding to Si–O–M vibrations can sometimes be discerned
MAS-NMR ("Magic-Angle Spinning"-Nuclear Magnetic Resonance)	Spectrum displays different chemical shifts for different values of x: $Si(OSi)_x(OM)_{4-x}$
XANES (X-ray Absorption Near Edge Structure)	Estimates coordination numbers/bond lengths –measures goodness of mixing when cation adopts different coordination in homo linkage (M–O–M) and hetero linkage (M–O–M′)
Textural/Structural	
XRD (X-Ray Diffraction)	In general, component crystallization is delayed in well-mixed samples
Surface area	For a given mixed oxide pair, surface area may either increase (e.g., titania–silica) or decrease (e.g., zirconia–silica) as mixing improves

variable – a sample is not either well-mixed or poorly-mixed – is very important. In Table 4 we list a number of variations of the sol–gel method in order of their ability to deliver samples that are homogeneously mixed on a molecular level. At this point, many of the names may be unfamiliar; most are related to either prehydrolysis or chemical modification. Our first goal for the remainder of this paper is to illustrate, using examples from the literature, how we arrive at this rank order.

Establishment of the rank order also implies that we have ways to compare the relative "goodness of mixing" in mixed oxide samples. The second goal of this paper is, therefore, to demonstrate how various methods are used to provide evidence of good mixing. Table 5 summarizes some of the techniques that have been employed by various researchers. Note that the list includes spectroscopic techniques – NMR and IR, for example – that aim to provide information about the atomic environment within the oxide. As we saw earlier, another important class of measures is based on the acidic properties of the sample – acid site densities and activities in reactions that require acid catalysts (see Refs. [7–9] for details). When applying these methods, we infer that high acidity/activity correlates with high surface hetero-linkage populations, which in turn implies better molecular-scale mixing. Some of the most elegant examples employ both chemical and spectroscopic methods.

4.1. Prehydrolysis and "independent hydrolysis" – the range of homogeneities accessible with sol–gel chemistry

One of the most important – and perhaps most unexpected – observations about the entries in Table 4 is that sol–gel techniques can be used to prepare samples that are either better or more poorly mixed than those prepared by the "benchmark" coprecipitation method. Doolin et al. provided key evidence for establishing the mixing rank order by comparing a set of 50 mol% titania–50 mol%

silica xerogels prepared by coprecipitation, prehydrolysis and "separate hydrolysis" [51]. In the prehydrolyzed preparation (called "staged hydrolysis" in the original paper), tetraethyl orthosilicate (TEOS) was first reacted with water (2 mol H_2O:1 mol TEOS "prehydrolysis ratio"). Tetraisopropoxy orthotitanate (TIOT) was subsequently added to the prehydrolyzed silicon precursor, followed by the water required to complete hydrolysis. Using the "separate hydrolysis" technique (called "full hydrolysis"), each precursor was individually hydrolyzed in an excess of water before they were combined.

Total acid site densities, estimated by adsorption of pyridine, of samples calcined to 623 K were 1.0, 0.8, and 0.5 $\mu mol/m^2$ for the prehydrolyzed, coprecipitated and separately hydrolyzed samples. Based on the relationship between homogeneous mixing and acidity suggested by the models described in Section 2, we infer that prehydrolysis delivers the best mixed material among this trio, followed by coprecipitation and finally by separate hydrolysis. This result clearly illustrates that (i) the goodness of mixing can be varied within a sol–gel preparation and (ii) certain variations of the sol–gel method may deliver samples that are poorly mixed relative to materials made by conventional methods. In retrospect, we should have anticipated that samples prepared by separate hydrolysis would be poorly mixed. Precursors that are hydrolyzed individually – especially in a large excess of water – would be expected to undergo a significant degree of homo-condensation before the sols are combined.

Baiker and co-workers [36] prepared 20 mol% titania–80 mol% silica xerogels from TEOS and TIOT precursors by both prehydrolysis (2 mol H_2O/mol TEOS; called "two-stage" in their report) and separate hydrolysis (called "one-stage") techniques comparable to those used by Doolin et al. They also varied the pH used in the silicon precursor hydrolysis step. Unlike Doolin et al. [51], Baiker and co-workers relied upon spectroscopic techniques, primarily infrared (IR) and nuclear magnetic resonance (NMR), to characterize mixing differences among their samples [52,53].

In the infrared spectrum, a feature assigned to the asymmetric Si–O–Si network stretch was observed at higher wavenumber ($\sim$ 1100 cm^{-1}) in separately hydrolyzed samples than in prehydrolyzed materials ($\sim$ 1070 cm^{-1}), suggesting a higher degree of silica crosslinking, or interconnectivity in the former [52]. A second IR feature, located at $\sim$ 950 cm^{-1} and assigned to Ti–O–Si vibrations, was generally more intense in prehydrolyzed samples, illustrating the higher degree of molecular-scale mixing achievable by that technique [52].

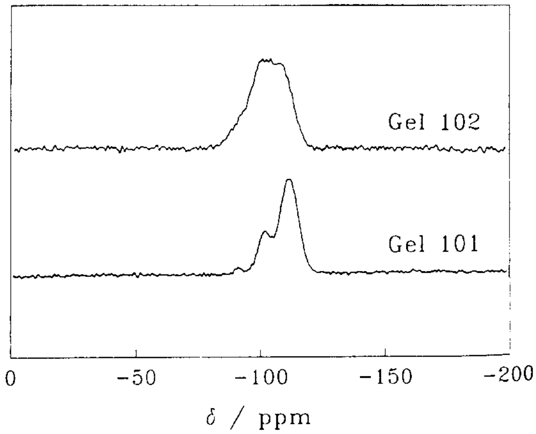


Fig. 8. ^{29}Si MAS-NMR spectra of 20 mol% titania–80 mol% silica xerogels prepared by separate hydrolysis (gel 101) and silicon precursor prehydrolysis (gel 102). (Reproduced from Ref. [53] with permission.)

NMR data also illustrate the lower degree of silica interconnectivity in the prehydrolyzed materials. In Fig. 8, we reproduce Baiker et al.'s ^{29}Si NMR spectra for prehydrolyzed and separately hydrolyzed materials as an example of how solid-state NMR can be used to observe mixing differences [53]. A chemical shift at -110 ppm (relative to tetramethyl silane) corresponds to silicon atoms in an environment of exclusively –OSi nearest neighbors (i.e., $Si(OSi)_4$); it is a signature of "silica-only" regions in the mixed oxide. Broadening towards smaller shifts and/or additional peaks at lower shifts indicate contributions from $Si(OSi)_n(OTi)_{4-n}$ – a measure of improved mixing. In this example we observe that the separately hydrolyzed sample (gel 101) has a more pronounced contribution of the -110 ppm signal, a measure of high silica interconnectivity. The prehydrolyzed sample (gel 102), on the other hand, has more substantial contributions at lower chemical shifts, suggesting formation of Si–O–Ti linkages.

Together, the NMR and IR data indicate that titania and silica exist in largely independent domains with little interaction between the two components in the separately hydrolyzed samples. As a consequence of component segregation, separately hydrolyzed samples allow crystallization of the titania component upon heat treatment at 873 K, while prehydrolyzed materials remain X-ray amorphous [36]. Delay of component oxide crystallization is another very common feature of well-mixed two-component oxides. Based on these observations, Baiker and co-workers proposed the models of component mixing shown in Fig. 9 [52]. The model for the separately hydrolyzed samples is one of titania crystallites embedded in an amorphous silica matrix. Prehydrolyzed samples, on the other hand, exhibit a high degree of interaction (Si–O–Ti bonds) between the two oxide components. In the simplest possible terms, the prehydrolyzed sample is better-mixed on a molecular scale; this is the same conclusion we draw from Doolin et al.'s acidity data.

As we noted earlier, Baiker et al. also varied the pH of the silicon precursor hydrolysis step. Compared to hydrolysis sequence, however, the pH of silicon precursor hydrolysis played a minor role in determining the homogeneity of their titania–silicas. Within separately hydrolyzed samples, the main effect of pH was to fix the type of amorphous silica matrix in which the titania domains are embedded [52,53]. Hydrolysis in a basic environment promoted formation of clusters that packed into a mesoporous structure having less *initial* area than samples prepared with acid hydrolysis, but which *retained* its surface area upon heat treatment.

In contrast, acid catalyzed TEOS hydrolysis delivered linear, weakly linked siloxane chains [52,53]. The open nature of the structure facilitated interaction with the TIOT component to give very well mixed samples, particularly when used with prehydrolysis. However, the fragile nature of the mixed oxide network that formed in the latter case made it especially susceptible to collapse by capillary forces upon drying; a sample prehydrolyzed in acid, in fact, became exclusively *microporous* upon heat treatment to 823 K. Doolin et al. also witnessed their prehydrolyzed sample to be thermally

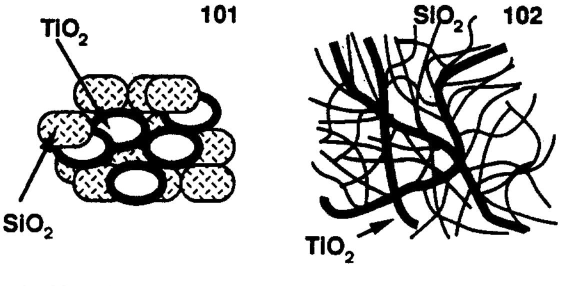


Fig. 9. Models of component mixing in 20 mol% titania–80 mol% silica xerogels prepared by separate hydrolysis (101) and silicon precursor prehydrolysis (102). (Reproduced from Ref. [52] with permission.)

unstable [51]. Upon heat treatment from 623 to 923 K, their prehydrolyzed material lost a higher fraction of its surface area than either the coprecipitate or the independently hydrolyzed sample.

In addition to teaching how preparation variables can be used to control component oxide mixing, Baiker et al.'s work provides an important example of a case where *poor mixing is the desired outcome*. Their titania–silicas were designed to support vanadia as catalysts for selective catalytic reduction (SCR of NO_x by NH_3) applications [54]. They used a successive grafting technique (reaction between surface hydroxyls and vanadyl triisopropoxide) to load vanadia on the samples described in the previous paragraphs. Only a weak interaction – characteristic of pure silica samples – existed between vanadia and the amorphous prehydrolyzed mixed oxides, resulting in catalysts that were relatively inactive for SCR. On the other hand, separately hydrolyzed materials, in which titania existed in large anatase domains, displayed a high ability for stabilizing the two dimensional vanadia overlayers that are required for SCR activity.

Miller et al. reported results of titania–silica aerogels prepared by two different hydrolysis sequences: silica-precursor prehydrolysis (4 mol H_2O/mol Si prehydrolysis ratio) and simultaneous hydrolysis [1]. In simultaneous hydrolysis, the alkoxide precursors are first combined and then hydrolyzed as a single solution; the technique is called ''nonprehydrolyzed'' in the original work. Their prehydrolyzed samples, at various titania:silica molar ratios, all displayed higher activity as catalysts for isomerization of 1-butene, a reaction that requires a weak Brønsted acid catalyst. Miller et al. cited the activity advantage as evidence for improved molecular-scale mixing in the prehydrolyzed materials. They also reported that the prehydrolyzed aerogels had higher surface areas than the corresponding simultaneously hydrolyzed materials. Furthermore, all samples – including those prepared by silicon precursor prehydrolysis – were mesoporous, even upon calcination to elevated temperatures (1173 K). Hence, the Miller et al. prehydrolyzed samples appear to be less susceptible to collapse of their structures than either the comparable Baiker et al. [36] or Doolin et al. [51] materials. This important difference could be due to either (i) use of the structure-preserving supercritical drying step or (ii) the higher prehydrolysis ratio, which could promote formation of an inherently stronger (i.e., more highly crosslinked) siloxane network before addition of the titanium precursor.

Miller et al.'s work introduces us to two new concepts that we will explore in the next section. The first is that the water ratio during prehydrolysis (the prehydrolysis ratio) may also be a key parameter for control of mixed oxide properties. The second is yet another hydrolysis sequence – simultaneous hydrolysis.

4.2. Prehydrolysis ratio for access of a ''continuum of mixing states''

Miller and Ko studied the impact of a single parameter, the prehydrolysis ratio, on the goodness of component mixing in a series of 50 mol% zirconia–50 mol% silica aerogels [17]. They employed a preparative protocol that allowed prehydrolysis ratio to be varied independently of the overall sol–gel parameters. As illustrated in Fig. 10, the activities of their calcined aerogels as catalysts for 1-butene isomerization increased linearly with increasing prehydrolysis ratio (over the range 0.00 – a ''simultaneously hydrolyzed'' preparation – to 3.22 mol H_2O/mol Si; prehydrolysis in acidic environment). They cite the activity improvements, which result from both higher acid site density (ammonia TPD) and higher fractional Brønsted population, as evidence for a ''continuum of mixing states''.

Component mixing improvements attributed to increasing prehydrolysis ratio were accompanied by significant changes in textural properties, including lower surface area and delay of the zirconia component's crystallization to higher temperatures (see Fig. 11). Earlier we noted a similar link

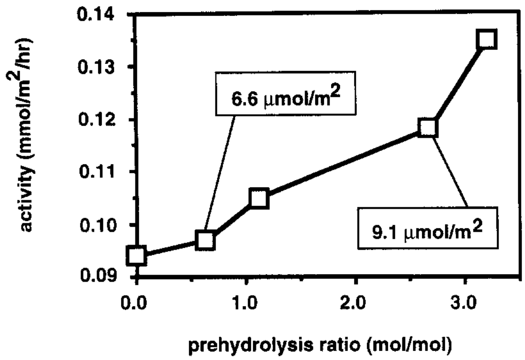


Fig. 10. Activity of 50 mol% zirconia–50 mol% silica aerogels as catalysts for 1-butene isomerization (423 K, 1 atm, 95 sccm He, 5 sccm 1-butene, 200 mg sample, 95 min on-stream) as a function of prehydrolysis ratio. Figures in boxes are total acid site densities estimated by ammonia TPD. All samples calcined at 773 K in oxygen.

between homogeneous mixing and stabilization against component crystallization in sol–gel prepared titania–silicas. However, Miller et al. reported differing effects of improved mixing upon the surface areas of their titania–silicas [1] and zirconia–silicas [16–18]. This observation underscores another important concept: *the textural property changes that accompany mixing improvements can depend on the oxide pair.*

Miller and Ko explained their zirconia–silica results in terms of differences in the types of products that form during the prehydrolysis step of the preparation at different water ratios [17]. As shown in Fig. 12, low prehydrolysis ratios produce primarily hydrolyzed TEOS monomers, but leave much of the TEOS completely *unhydrolyzed.* At higher ratios, (i) TEOS is eventually consumed, (ii) hydrolyzed dimers and higher oligomers form, and (iii) the average degree of molecular hydrolysis

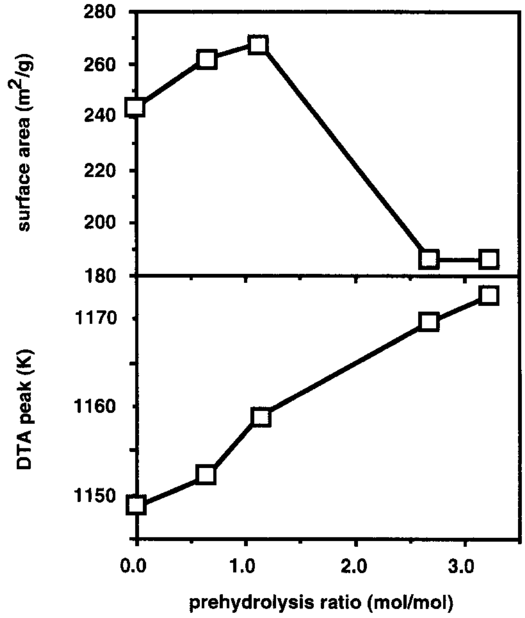


Fig. 11. Surface area (BET analysis of nitrogen desorption data; top panel) and zirconia's crystallization temperature (estimated by location of DTA exotherm that corresponds to the amorphous-to-tetragonal transformation; bottom panel) of 50 mol% zirconia–50 mol% silica aerogels as functions of prehydrolysis ratio. Samples calcined at 773 K for surface area measurement, dried at 523 K for DTA.

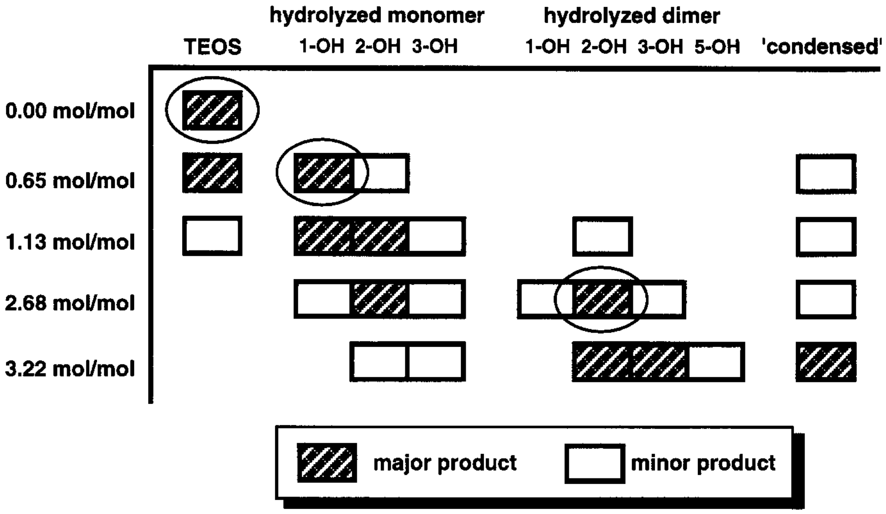


Fig. 12. Relative prehydrolysis product distributions, measured by ^{29}Si NMR, at different prehydrolysis ratios (TEOS, propanol, nitric acid amounts held constant; water varied to adjust PH ratio). "Condensed" products are TEOS trimers and higher oligomers.

(number of OH groups per molecule) increases. They associate the non-hydrolyzed TEOS that remains after low ratio prehydrolysis with formation of loosely interconnected (low Si–O–Si wavenumber in the IR spectrum) surface patches that have the ability to stabilize high surface areas (Fig. 13). At high enough ratios, the hydrolyzed TEOS dimers begin to crosslink to form an "embedded siloxane network" (high Si–O–Si wavenumber) in the calcined mixed oxides that stabilizes zirconia against crystallization (Fig. 13).

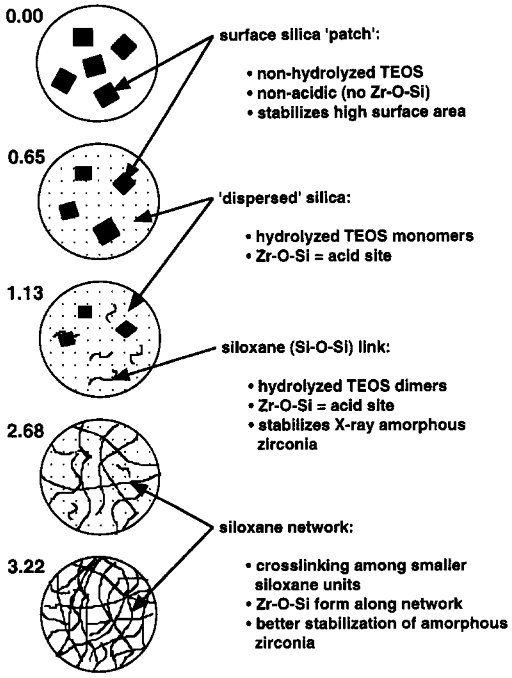


Fig. 13. Models of component mixing in 50 mol% zirconia–50 mol% silica aerogels prepared at different prehydrolysis ratios. Silica/siloxanes are shown in black, zirconia in white. Numerical values are prehydrolysis ratios (mol H_2O/mol Si).

Table 6
Comparison of literature reports of zirconia–silicas prepared by different methods

Reference/sample type	Composition (mol% silica)	Surface area (m^2/g @ temp.) [a]	Acidity ($\mu mol/m^2$ @ temp.) [a]	Comments
Miller and Ko [17]	67	430 @ 773 K	5.1 @ 773 K	
Prehydrolyzed	50	186 @ 773 K	9.1 @ 773 K	Crystallizes at ~ 1170 K [c]
Miller and Ko [17]	67	498 @ 773 K	N/A [b]	
Simultaneous	50	244 @ 773 K	7.0 @ 773 K	Crystallizes at ~ 1149 K [c]
Toba et al. [21]	83	~ 400 @ 823 K	~ 0.77 @ 823 K	Last to crystallize [d] in this group;
Sol–gel/complex'n	50	~ 250 @ 823 K	N/A	Best mixed by NMR
Toba et al. [21]	83	~ 390 @ 823 K	~ 0.77 @ 823 K	Second to crystallize in this group;
Coprecipitate	50	< 50 @ 823 K	N/A	Second best mixed by NMR
Toba et al. [21]	83	~ 320 @ 823 K	~ 0.74 @ 823 K	First to crystallize in this group;
Kneaded hydrogels	50	< 50 @ 823 K	N/A	Poorest mixing by NMR
Sohn and Jang [55]	83	507 @ 673 K	~ 0.60 @ 673 K	
Coprecipitates	48	280 @ 673 K	~ 0.50 @ 673 K	

[a] Calcination temperature.
[b] Not available.
[c] Estimated from results of differential thermal analysis.
[d] Based on results of X-ray diffraction experiments.

Placement of samples prepared by varying the prehydrolysis ratio over the range 0 to 3 mol/mol within the "mixing hierarchy" (Table 4) is an important issue. Toward this goal, Miller and Ko recently compared literature reports of acidities of zirconia–silicas prepared by a series of different methods [18]. Some of their key findings appear in Table 6. Note that the simultaneously hydrolyzed materials (prehydrolysis ratio = 0), while slightly less acidic than prehydrolyzed samples, are significantly more acidic (and, by inference, better-mixed) than materials prepared by conventional coprecipitation techniques. The simultaneously hydrolyzed samples are also more acidic that materials made by another variation of sol–gel preparation called "complex-agent assisted". The appearance of another sol–gel technique provides us with a starting point for the next section.

4.3. Other variations of the sol–gel technique

Toba and co-workers examined zirconia–silica, titania–silica, and titania–alumina xerogels made by "complexing-agent assisted sol–gel", coprecipitation and hydrogel kneading [21–23]. Complex-agent assisted sol–gel is a variant of chemical modification in which hexylene glycol is used as the modifier. Hydrogel kneading is a close relative of "separate hydrolysis", in which gels formed from completely hydrolyzed precursors are physically mixed. Within all three mixed oxide systems, solid-state NMR analysis of the calcined products uncovered the following mixing rank-order: sol–gel (best mixed) > coprecipitate > kneaded hydrogels [21–23]. We reproduce their ^{29}Si NMR spectra for the zirconia–silica sample set in Fig. 14 [21]. As the figure shows, especially at lower silica contents, the sol–gel sample displayed the highest contribution from the smaller chemical shifts, indicating that it is the best mixed of the group.

The mixing differences are reflected as differences in the acidic properties of their samples. Within all three mixed oxide pairs, Toba et al. observed acidities (ammonia adsorption/desorption techniques) that decrease in the order sol–gel > coprecipitate > kneaded; they attributed enhanced acidity to a higher density of hetero-linkages present in the better-mixed samples [21–23]. However, as we

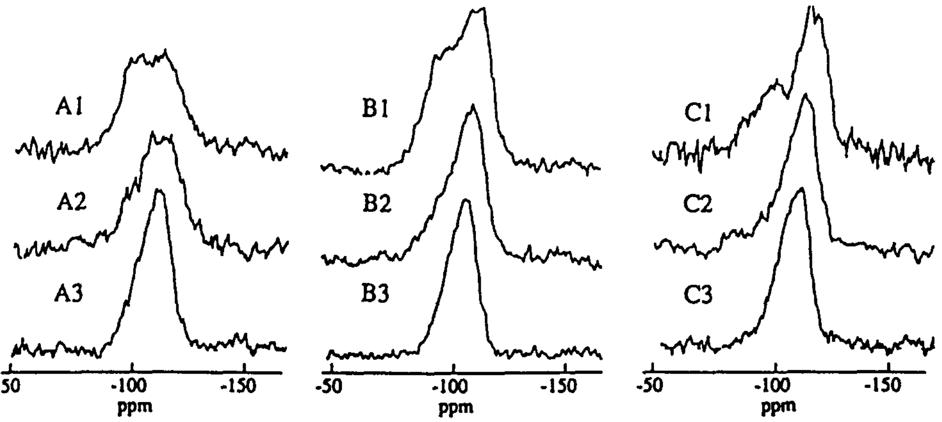


Fig. 14. ^{29}Si MAS-NMR spectra of zirconia–silica xerogels prepared by different methods: complex-agent assisted sol–gel (A, left column); coprecipitation (B, center); hydrogel kneading (C, right). Compositions: $ZrO_2/SiO_2 = 2$ (1, top row); $ZrO_2/SiO_2 = 1$ (2, middle); $ZrO_2/SiO_2 = 0.2$ (3, bottom). All samples calcined at 823 K. (Reproduced from Ref. [21] with permission.)

noted in the previous section, the acidities of their zirconia–silicas prepared by complex-agent assisted sol–gel are considerably lower than those of prehydrolyzed or even simultaneously hydrolyzed materials. We therefore place the complex-assisted technique below the others in the mixing rank order (Table 4). Hydrogel kneading and separate hydrolysis share a common place in the rank order based upon both (i) the similarity of their preparations and (ii) their inability to deliver materials that are better-mixed than conventional coprecipitates.

Toba et al. reported some important contrasting behaviors among the three oxide pairs, reinforcing our earlier observation that the benefits of improved mixing can be system dependent. For example, they found that acidity enhancement attributable to improved mixing is largest, especially on a per-area basis, in titania–silica [22]. And, while BET surface area was not a strong function of mixing in either zirconia–silica [21] or titania–silica [22], it was considerably larger for the sol–gel (well-mixed) titania–aluminas [23], especially at low titania content.

For all three of their oxide pairs, Toba et al. linked good mixing to delay of component oxide crystallization. This result is consistent with many previous examples described in this paper. We reproduce data from their titania–alumina series in Fig. 15 to illustrate that crystallization of *both* pure titania and pure alumina phases are delayed to higher temperatures in samples that are better-mixed [23]. Note that calcination to 1273 K is necessary to eliminate the effects of the mixing differences.

Miller et al. [16] examined a set of 95 mol% zirconia–5 mol% silica aerogels prepared by four different techniques; (i) prehydrolysis (2 mol H_2O/mol TEOS), (ii) simultaneous hydrolysis, (iii) a TMOS (more reactive) for TEOS (less reactive) precursor swap, and (iv) chemical modification of the zirconium precursor by pretreatment with acetyl acetone. Based on improved activity for 1-butene isomerization, they concluded that all three of the matching techniques delivered samples that were better mixed than those prepared by simultaneous hydrolysis. However, they reported that the techniques are not interchangeable, with each resulting in a different distribution of silica within the zirconia matrix. As shown in Fig. 16, these mixing differences are reflected in subtle differences among textural, structural and acidic properties of the calcined aerogels.

Interestingly, Miller and Ko observed that *poorly mixed* 95 mol% zirconia–5 mol% silicas provided better stabilization against zirconia crystallization than did well-mixed materials [16]. This result contrasts with the general relationship between good mixing and stabilization of high tempera-

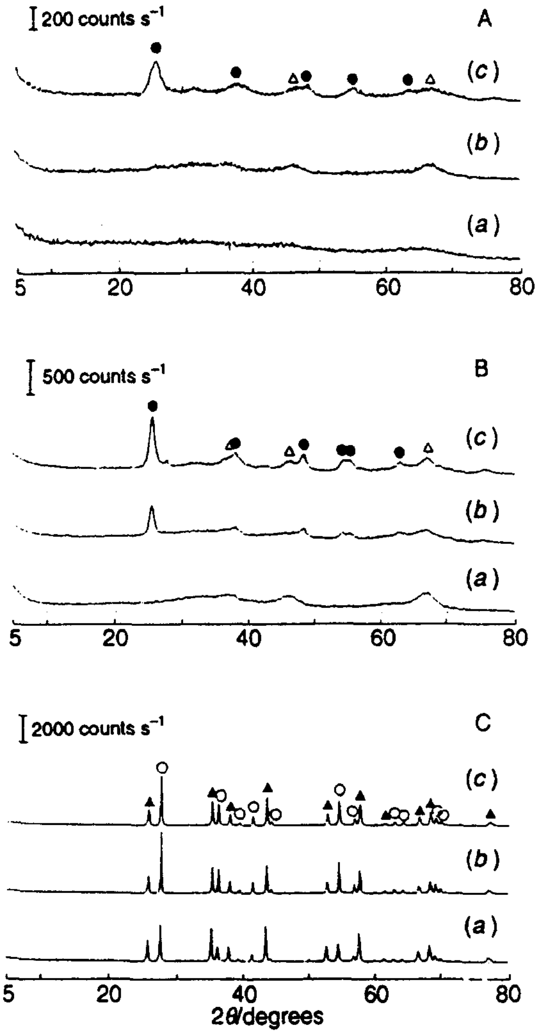


Fig. 15. Effect of calcination temperature on titania–aluminas (TiO_2:Al_2O_3 = 0.2) prepared by different methods: complex-agent assisted sol–gel (a, bottom pattern in each panel); coprecipitation (b, center); hydrogel kneading (c, top). Calcination temperatures: 823 K (A, top panel); 1073 K (B, center panel); 1273 K (C, bottom panel). Crystalline phases: anatase titania (closed circle) rutile titania (open circle), α-alumina (closed triangle), γ-alumina (open triangle). (Reproduced from Ref. [23] with permission.)

ture forms, including Miller and Ko's results at 50 mol% zirconia–50 mol% silica [17]. They attributed this difference to the inability to form a penetrating siloxane network to stabilize zirconia at such low silica contents [17]. Earlier we noted that some effects of mixing improvements depend on the oxide pair; *this result illustrates that the effects can also be composition-dependent.*

Lastly, we address the preparative method that appears at the top of the "mixing hierarchy" in Table 4. As we illustrated earlier (Section 3.2, Fig. 6), slow, simultaneous hydrolysis of two precursor alkoxides – aluminum butoxide and TEOS, in this case – can provide a higher yield of Al–O–Si hetero-linkages than prehydrolysis. We are not, however, aware of any catalytic materials having been prepared using this approach. Its position in the rank order reflects its *potential* and should be therefore viewed as tentative.

4.4. Post-gelling processing steps that can effect component mixing

At the beginning of this paper, we noted that processing steps that take place after the formation of a gel can affect the properties of a single component oxide prepared by a sol–gel technique. Post-gelling treatment can also affect the goodness of component mixing. Baiker and co-workers demonstrated, again relying upon NMR and IR evidence, how redispersion of a ''wet'' gel in a basic medium can break some of the weaker homo bonds (Si–O–Si and Ti–O–Ti), allowing them to reform as hetero-linkages for improved molecular-scale mixing [52,53]. Furthermore, by promoting additional condensation at high pH redispersion of acid catalyzed prehydrolyzed samples improved their resistance to pore collapse upon heat treatment [36].

Calvino et al. used a set of 10% titania–90% silicas prepared with both prehydrolysis and chemical modification (acetic acid) to illustrate how the details of the drying step can affect the goodness of component mixing in calcined mixed oxides [56]. They prepared a set of three identical gels, but dried them in three different manners: (i) 10 days in air at 300 K to form a xerogel, (ii) supercritical drying in alcohol at 600 K yielding an aerogel, and (iii) supercritical drying with CO_2 at 315 K to produce a carbogel. As expected, the calcined (773 K) xerogel possessed the lowest surface area of the trio: 832 m^2/g for the aerogel, 515 m^2/g for the carbogel and 459 m^2/g for the xerogel.

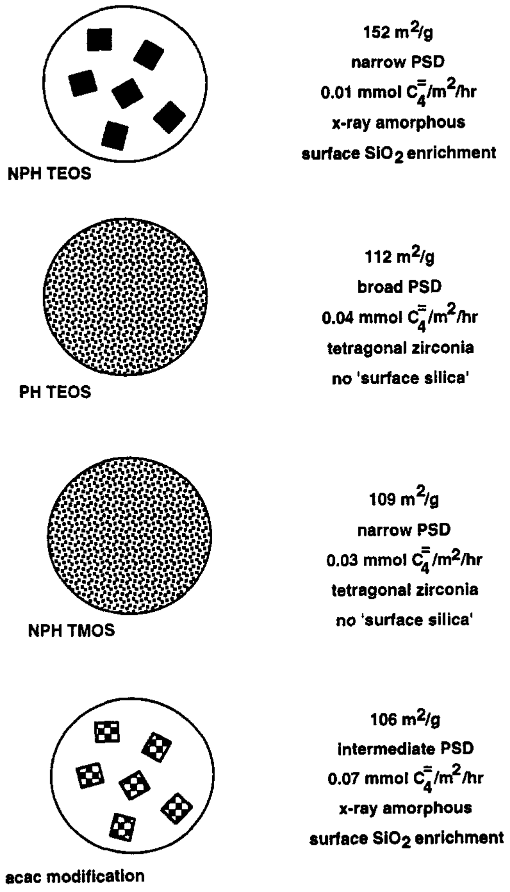


Fig. 16. Models of component mixing in 95 mol% zirconia–5 mol% silica aerogels prepared by different reactivity matching techniques. Silica/siloxanes are shown in black, zirconia in white. From top to bottom: simultaneous hydrolysis; silicon precursor prehydrolysis; TMOS for TEOS precursor swap; chemical modification of the zirconium precursor with acetylacetone (acac).

Significantly, Calvino et al. reported that the *xerogel* was the best mixed sample of the group. As shown in Fig. 17, the xerogel displayed the highest IR intensity of the 950 cm^{-1} feature that is associated with Si–O–Ti linkages. The titanium near-edge X-ray absorption spectrum (XANES) of the xerogel suggested that most of its titanium atoms are tetrahedrally coordinated, a signature of titanium atoms that participate in Ti–O–Si linkages. In contrast, the aerogel had no tetrahedrally coordinated titanium atoms and the carbogel exhibited intermediate behavior. X-ray diffraction confirmed the superior mixing of the xerogel: upon calcination to 773 K, both the carbogel and the aerogel show an anatase titania peak, while the xerogel remains X-ray amorphous.

The various drying techniques also deliver different activities for *t*-butanol dehydration. The xerogel that, based on IR, XANES, and XRD data, was the best mixed of their sample set displayed the highest specific activity for the dehydration reaction.

Calvino et al. explained that while many Ti–O–Si bonds are present in the alcogel, they can be rearranged – and "demixed" – depending upon the specific drying conditions [56]. At 600 K, the temperature necessary to obtain supercritical alcohol, component segregation by titanium leaching (dissolution in the warm supercritical alcohol solvent) and subsequent redistribution in narrow pores takes place. In the carbogel they suspect that sintering that occurs near hot spots upon "burnoff" of residual carbon species contributes to component segregation.

Brodsky and Ko have shown how the temperature during drying by displacement of the alcohol solvent by supercritical CO_2 can affect textural properties of the calcined titania aerogels [57]. Compared to samples dried at 343 K, those dried at 473 K displayed (i) a higher average pore radius (upon calcination to 773 K) and (ii) a lower crystallization temperature. These authors noted that the gel's network does not remain intact during drying and that high temperature drying facilitates particle growth and crystallization. Brodsky and Ko reported similar observations for titania–silica aerogels [58], thus establishing supercritical drying temperature as an important parameter in affecting the mixing of two-component oxides.

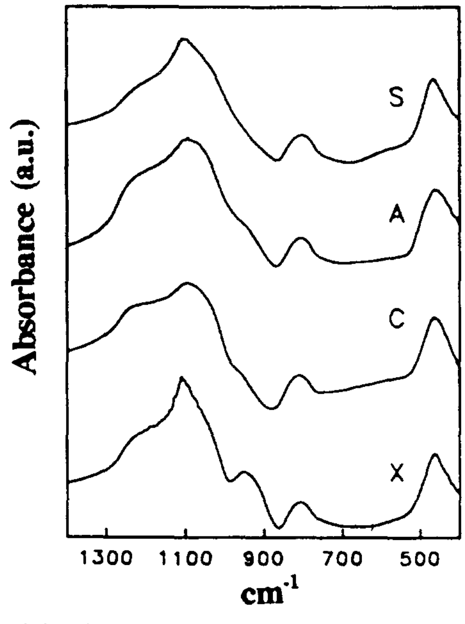


Fig. 17. "Skeletal vibration" region of the infrared spectra of titania–silica gels dried by different methods: xerogel (X); carbogel (C); aerogel (A); silica xerogel (S). All samples calcined at 773 K. (Reproduced from Ref. [56] with permission.)

An important consideration of post-gelling treatment, especially high-temperature calcination, is the phase diagram of the multi-component system. Most often, sol–gel prepared mixed oxides are kinetically stabilized in forms that are not at thermodynamic equilibrium. When thermodynamically stable compounds or one-component crystalline phases exist near temperatures used during heat treatment, kinetic constraints can be overcome allowing atomic rearrangements (sintering) that ''demix'' the sample.

As we have seen throughout this paper, well-mixed two-component oxides, being more kinetically constrained than comparable poorly mixed materials, generally require more severe heat treatment temperatures for their crystallization. The examples described in this section illustrate that differences among the relatively mild processing temperatures used in the gel drying step also have some important contributory effects.

5. Conclusions

By providing control of the relative reactivity of the alkoxide precursors, sol–gel chemistry allows preparation of two component oxides with controlled homogeneity. Throughout this paper, we have seen sol–gel applied in many different ways; in Table 4 we have ranked the various methods according to their ability to deliver intimately mixed catalytic materials.

We find some very common characteristics among well mixed samples, including high acid site densities, high activities in reactions that require acid catalysts and stabilization against crystallization. The response of textural properties to homogeneity changes can, on the other hand, vary with both oxide pair and composition. Another important observation we have made is that ''good mixing'' is not always the goal of a sol–gel preparation. As we saw, Baiker et al.'s poorly mixed titania–silicas were the best supports for vanadia in the SCR application.

We have also demonstrated how homogeneity, at least in a relative sense, can be measured. High acidity/catalytic activity provides one simple measure. X-ray spectroscopy, solid state NMR and analysis of skeletal vibrations in IR spectra can provide a more fundamental insight into atomic arrangements.

Needs for future research in this area include better characterization of the link between the molecular processes that occur in the initial stage of the preparation and properties of the calcined oxide using techniques like NMR. Likewise, the mechanisms by which post-gelling treatments, especially drying conditions, impact homogeneity are not well understood. Application of the lessons of homogeneity control in two component mixed oxides can also be extended to preparation of multi-component catalytic materials. Here we anticipate that even more complex hydrolysis sequences than those described in this paper or perhaps a combination of different techniques will be required to control the goodness of molecular-scale mixing.

Future applications-oriented activities will include extension of the lessons learned about mixing to more conventional preparation techniques. As mentioned at the outset, traditional methods do not allow the same degree of control over mixing as does sol–gel. However, sol–gel samples can be used to define the accessible range of homogeneity, thereby providing a standard against which the success of efforts to improve mixing by traditional methods can be measured. Another area of interest is sol–gel preparations using non-alkoxide precursors – preformed sols, for example – that are less costly and easier to handle than alkoxides.

Acknowledgements

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