

SOL-GEL PREPARATION OF ZIRCONIUM OXIDE

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INTRODUCTION

A sol-gel preparation involves first the formation of a sol, which is a suspension of solid particles in a liquid, then of a gel, which is a diphasic material with a solid encapsulating a liquid. The liquid can be removed from a gel by either conventional drying (such as by using an oven) to obtain a product known as a xerogel, or by drying with supercritical extraction (often referred to as supercritical drying for short) to give an aerogel.

Preparing catalytic materials with the sol-gel method has received increasing attention in recent years because of its versatility and excellent control over a product's properties (1). In fact, there are a host of experimental variables, generally referred to as the sol-gel parameters, which can impact on the physical and chemical characteristics of a sample. To date, most studies have focused on sol-gel parameters that are important in the first step which is the formation of a gel. There has been relatively less work on the subsequent processing steps: aging, drying, and heat treatment. Because these steps are often interrelated (2), one should take a broader viewpoint and consider all of them in fine-tuning a sol-gel product.

In this paper we discuss our recent results on the sol-gel preparation of zirconia with an emphasis on three key parameters: the gel time, the starting precursor, and the drying conditions. In our view these parameters, when fully understood and explored, will put us in a better position to develop materials of desirable properties systematically. We are interested in zirconia because of its potential catalytic applications in general (3) and its effectiveness as a support for superacids in particular (4). Furthermore, the phase transformation of zirconia as a ceramic material is of great interest (5).

EXPERIMENTAL

We used two different precursors in our sol-gel preparation. In the first approach (6), zirconium n-propoxide was mixed with n-propanol and nitric acid. This solution was then mixed with another solution containing n-propanol and water and the mixture was vigorously stirred. The gel time was defined as the time required after mixing for the vortex created by the stirring to disappear completely. The resulting gel, known as an alcogel because alcohol was the solvent, was covered and allowed to age for 2 h at room temperature. The alcohol was subsequently removed either by drying in a vacuum oven to form a xerogel, denoted as X-Zr, or by supercritical drying with carbon dioxide to form an aerogel, denoted as A-Zr. The supercritical drying conditions were usually at ca. 343 K and 2.1×10^7 Pa and the resulting aerogel powder was subsequently vacuum dried. Aerogels that were supercritically dried at a higher temperature of 473 K were denoted as A-Zr-473.

In the second approach (7), three different size zirconia sols, provided by Nyacol Products, Inc., were used: 5-10, 50, and 100 nm. These sols were gelled by the addition of ammonium hydroxide to give samples 10-Zr-0.3, 50-Zr-0.3, and 100-Zr-0.3. The first number refers to the initial sol size in nm and 0.3 is the ratio of ammonium hydroxide to nitric acid (which provides the counter ion in the original sol). These gels were allowed to age for 2-3 h at room temperature and then vacuum dried.

The above vacuum drying steps were performed at 383 K and 3.4×10^3 Pa for 3 h. Finally, all the samples were calcined at 773 K for 2 h in flowing oxygen (24 l/h).

An Autosorb-1 gas sorption system (Quantachrome Corp.) was used to obtain nitrogen adsorption/desorption isotherms. Before analysis, all samples were outgassed at 473 K under vacuum for 2-3 h. Pore size distribution data were calculated with the BJH method (8). X-ray diffraction experiments were performed on a Rigaku D/Max Diffractometer with $\text{Cu-K}\alpha$ radiation.

RESULTS AND DISCUSSION

Effect of Gel Time

At its simplest level, sol-gel chemistry involves the hydrolysis of a precursor (which is a metal alkoxide in our aerogel case) and the condensation of partially hydrolyzed species to form a three-dimensional gel network. The gel structure is thus sensitive to the rate of hydrolysis relative to that of condensation (9), and the two rates can be varied by, for example, adjusting the amounts of water and acid used in the preparation.

In our preparation of zirconia alcogels, we found that the gel time increases significantly when we increase the amount of nitric acid used (6). This observation can be understood in terms of an increased concentration of protonated hydroxo ligands with more acid, thus decreasing the condensation rate and increasing the gel time. The amount of water used also affects the gel time

by changing the concentration of the hydrolyzed species. Qualitatively a decrease in water content slows down the hydrolysis and condensation reactions, thus increasing the gel time. As an example of the effects of changing gel times, Figure 1 shows the variation of surface area and pore volume with gel time for zirconia aerogels calcined at 773 K for 2 h. A gel time of zero corresponds to the formation of a precipitate instead of a gel. This happens when no acid is used and a rapid condensation leads to particle growth. The resultant calcined product thus has very little surface area and pore volume. With increasing gel time, we slow down condensation to allow cross-linking to occur concurrent with particle growth. Hence the product has a large surface area and pore volume upon calcination. Under optimal conditions, we could stabilize a tetragonal zirconia that has a surface area of 134 m²/g and a pore volume of 0.37 cm³/g (see Table 1). However, with further lengthening of the gel time, condensation slows down to form a weakly cross-linked network. The collapse of this network during calcination leads to a decrease in surface area and pore volume. The variation of pore size distribution with gel time, as shown in Figure 2, is also consistent with this explanation.

In addition to macroscopic physical properties, gel time affects the microscopic "quality" of the material in terms of defect density. We found that zirconia aerogels prepared at different gel times exhibit different behavior with respect to their tetragonal-to-monoclinic phase transformation. Specifically, at a calcination temperature of 973 K, the ratio of tetragonal to monoclinic phase is a strong function of gel time. Samples with short gel times transform more readily into the monoclinic phase because they have higher defect densities (6). In sum, gel time is an important parameter in controlling the initial gel structure which impacts on all subsequent sol-gel processing steps.

Effect of Starting Precursor

In changing the rates of hydrolysis and condensation of metal alkoxides, one is balancing the growth of particles and the cross-linking of these particles. The particle size in a sol is thus a key parameter in controlling the initial gel structure. To probe this idea, we have used preformed zirconia sols as alternate precursors in order to study the effect of sol size independently. Table 1 summarizes the physical properties of zirconias prepared with three different starting sol sizes.

When solid spherical particles are packed together, the external surface area varies inversely with particle size. This trend is opposite to the data in Table 1, which shows that the sample made with the largest sol also has the highest surface area. This observation is due to the fact that the starting sol particles are not dense, but contain internal micropores which are the primary contributors to the surface area and pore volume of the resulting materials. In fact, we have found that all three zirconia samples have similar pore size distributions and are primarily microporous (7). Recall that zirconia aerogels are mesoporous (see Figure 2) and have pore volumes that are a factor of 3-5 higher (see Table 1).

Table 1 shows that the crystal structure of the 10-Zr-0.3 sample is the same as the zirconia aerogels. On the other hand, both the 50-Zr-0.3 and 100-Zr-0.3 samples contain monoclinic domains. This difference can be explained in terms of a bimodal size distribution in the two larger sols, which contain about half by weight particles in the indicated size and the other half in the 5-10 nm size range (7). Apparently the small particles crystallize into the tetragonal phase upon heat treatment while the large particles are in the monoclinic phase.

These results clearly demonstrate that using a different starting precursor (metal alkoxide versus preformed sols) is a simple and effective way to change the textural and structural properties of a sol-gel product. At the same time they teach us that a careful characterization of preformed sols, in particular their particle size distribution and porosity, is necessary for their applications as precursors.

Effect of Drying Conditions

The basic idea of supercritical drying is to eliminate the liquid-vapor interface in a pore in order to avoid differential capillary pressure in a gel network. Results in Table 1 show that physical properties of a zirconia aerogel (A-Zr) and xerogel (X-Zr) are indeed very different, with the latter having a much lower surface area and pore volume. Furthermore, the xerogel is primarily microporous. However, we note that we intentionally did not take great care in minimizing the capillary pressure in preparing the xerogel to illustrate the effect of drying conditions. There are many effective approaches, such as using a solvent with a low surface tension (10), in obtaining high-surface-area, low-density xerogels that are of catalytic interest.

We have found that varying the temperature while using a single drying agent, carbon dioxide, can also change the properties of a zirconia aerogel (11). We prepared two zirconia aerogels by supercritically drying them at 343 and 473 K. The two samples have similar surface areas, pore volumes, and crystal structures after calcination at 773 K for 2 h, but a more careful examination reveals interesting differences. First, the sample dried at 473 K has a pore size distribution that is shifted towards larger pores. The resulting larger average pore diameter explains why this sample has a larger pore volume but a smaller surface area than the sample dried at 343 K. Second, the sample dried at 473 K crystallizes into the tetragonal phase at a lower heat treatment temperature. Figure 3 shows that after calcination at 673 K for 2 h, the sample dried at 343 K remains X-ray amorphous whereas the one dried at 473 K shows a diffraction peak of tetragonal zirconia.

Our results highlight the fact that a gel is not static during supercritical drying. Indeed, drying should be considered as part of the aging process during which polymerization, coarsening, and phase transformation occur (2). While supercritical drying may be more effective in preserving a gel's network in comparison with evaporative drying, supercritical drying nonetheless accelerates aging because its operating temperature is above ambient. Along this line, we should expect aerogels that are prepared with different supercritical drying agents to have different properties. An example is the finding of Beghi et al. (12), who showed that anatase crystallization in titania-silica is more extensive when the sample is dried in alcohol (which has a higher critical temperature) than in carbon dioxide. Clearly, there are a lot of research opportunities in using supercritical drying conditions to vary the properties of aerogels.

SUMMARY

The sol-gel process has four key steps, gel formation, aging, drying, and heat treatment, each of which consists of a large number of tunable parameters. Furthermore, these steps are interrelated in that what happens in one step usually affects the next step. The initial gel structure will dictate the extent to which it is influenced by drying conditions, differently dried gels will have different structural evolution with heat treatment, and so on. However, it is important to view these complexities as opportunities in using the sol-gel method to prepare catalytic materials with desirable properties. In this paper we have shown the use of three specific parameters in changing the surface area, pore volume, and crystal structure of zirconia. Although these are physical and not chemical properties, results in our laboratory have shown that they have important catalytic implications. We believe more systematic studies are necessary to identify the key parameters in each sol-gel step and to understand the underlying physical and chemical processes. Extension to multi-component systems is of particular interest because of their widespread applications.

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Table 1. Physical Properties of Zirconium Oxides after Calcination at 773 K for 2 h

Sample notation	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Crystal structure ^a
A-Zr ^b	134	0.37	tetragonal
A-Zr-473 ^c	124	0.43	tetragonal
X-Zr	28	0.029	tetragonal
10-Zr-0.3 ^d	17	0.017	tetragonal
50-Zr-0.3 ^d	131	0.087	tetragonal + monoclinic
100-Zr-0.3 ^d	149	0.124	tetragonal + monoclinic

^a Determined by X-ray diffraction; ^b Taken from (6); ^c Taken from (11);

^d Taken from (7).

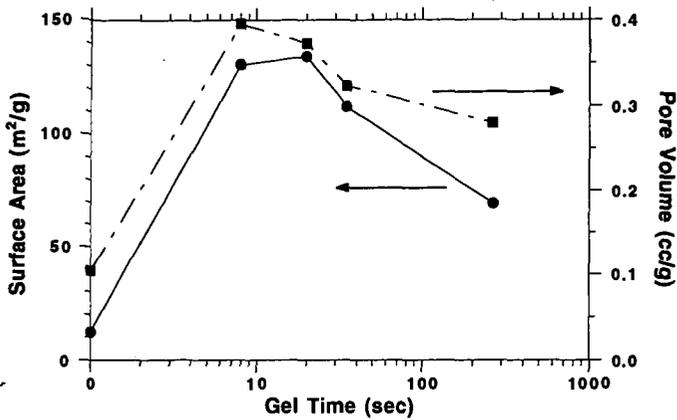


Figure 1. Effect of gel time on the physical properties of zirconia aerogels after calcination at 773 K for 2 h

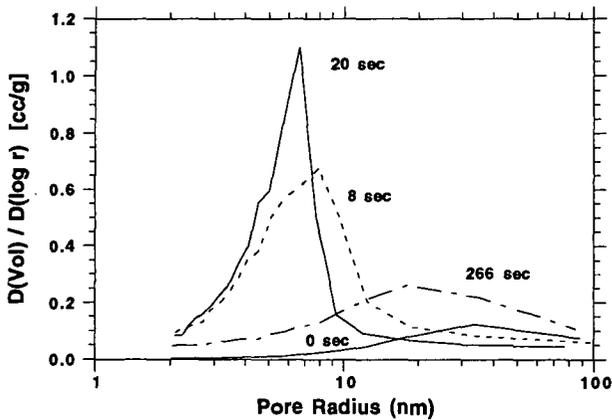


Figure 2. Effect of gel time on the pore size distribution of zirconia aerogels after calcination at 773 K for 2 h

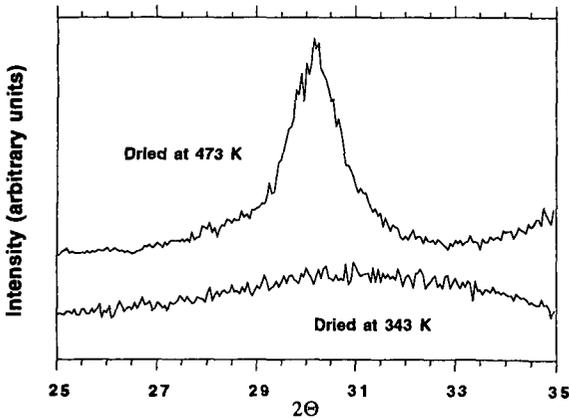


Figure 3. Effect of supercritical drying temperature on the crystallization of zirconia aerogels after calcination at 673 K for 2 h