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# NOTE

# Control of Prehydrolysis Ratio for Sol–Gel Preparation of Homogeneous Zirconia–Silica Aerogels

Catalytic researchers have long been interested in the preparation of mixed oxides because of their industrial relevance. Among the different preparation methods, sol–gel synthesis has received increasing attention lately due to its potential in delivering samples that are better mixed on a molecular scale. Within sol–gel chemistry, component mixing is linked to the relative reactivities of the alkoxide precursors in the hydrolysis/condensation sequence that forms the oxide network—evenly matched reactivities generally produce a well-mixed (or homogeneous) oxide; poorly matched precursor reactivities produce segregated materials (1).

Compared to the alkoxides of transition metals, silicon alkoxides are unreactive. Therefore, to promote homogeneity in silica-containing mixed oxides, silicon alkoxide precursors are often allowed to react with water before addition of a transition-metal alkoxide. This approach, known as "prehydrolysis," gives the less reactive silicon precursor a "head-start" in the reaction sequence. Upon their addition, the transition metal alkoxides can condense with prehydrolyzed Si–OH (silanol) groups to form the Si–O–*M* (*M* = transition metal) linkages that are characteristic of a well-mixed sample.

Reports of sol–gel preparations of silica-containing mixed oxides usually involve a single set of prehydrolysis conditions. However, we have noted that researchers often employ very different conditions (2–9). Prehydrolysis ratios (mol of water/mol of silicon precursor)—perhaps the most important prehydrolysis variable—between 1.0 and 2.0 are in most common use, but values as low as 0.8 (2) and greater than 10.0 (3) have also been reported. The disparity among prehydrolysis ratios is interesting because different water amounts have the potential to affect the catalytic properties of mixed oxides as well as the quality of molecular scale component mixing. In this note we present new results showing that prehydrolysis ratio, when varied even over a narrow range of 0.00 to 2.68 mol/mol, significantly affects the textural and acidic properties—and by inference, the homogeneity—of 50 mol% zirconia–50 mol% silica aerogels.

We choose the 50 mol% composition to promote formation of a high density of surface acid sites. Models such as that of Tanabe *et al.* (10) associate acid sites with "hetero" structural units (Si–O–*M*, for example) in mixed oxides, thereby conceptually linking acidity to both composition and molecular scale component mixing. We therefore use the activity of our samples as catalysts for 1-butene isomerization, a reaction catalyzed by weak Brønsted acids (11), as one measure of their relative homogeneity.

In Table 1 we summarize the sol–gel parameters used in preparing the samples described in this work. We have previously described our preparation of zirconia–silica aerogels (8). In brief, for a prehydrolyzed preparation we add the nitric acid (70 w/w, Fisher) and water required for prehydrolysis to a solution of silicon precursor (tetraethylorthosilicate, TEOS, Aldrich) in 1-propanol. After mixing with a magnetic stir-bar for a 10-min prehydrolysis period, we add the remaining nitric acid followed by the zirconium precursor (zirconium *n*-propoxide, 70 w/w in propanol, Johnson Matthey). Immediately thereafter, we pour in a second solution of water in 1-propanol. The amount of water in the second solution is adjusted to maintain an *overall* hydrolysis ratio of 2.24 mol $H_2O$/mol (Zr + Si).

In the "non-prehydrolyzed" preparation, we combine all of the nitric acid and both precursors in a solution with 1-propanol. We then add a second solution of water in 1-propanol (again maintaining the overall 2.24 mol/mol hydrolysis ratio). Note that the same *total* amount of every chemical is used for each preparation; *we simply place more or less of the total water in the prehydrolysis step*. All 4 of our samples gelled in under 30 min.

Each gel was dried via contact with flowing supercritical (343 K, $\sim 2.2 \times 10^4$ kPa) carbon dioxide in a standard autoclave (Autoclave Engineers, Model 08U-06-60FS). After drying and grinding to <100 mesh, samples were heated in vacuum for 3 h at both 383 and 523 K and finally calcined in flowing oxygen (24 liter/h) at 773 K for 2 h. The BET surface area and pore size distribution of the calcined aerogels were determined by nitrogen adsorption/desorption using an Autosorb-1 instrument (Quantachrome Corp.).

Calcined samples were evaluated for their activity as

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TABLE 1

Sol–Gel Parameters Used in Preparing 50 mol% zirconia–50 mol% Silica Aerogels[a]

| Sample ID[b] | Prehydrolysis ratio (mol $H_2O$/mol Si) | Prehydrolysis acid ratio (ml $HNO_3$/mol Si) | BET surface area[c] ($m^2$/g) |
|---|---|---|---|
| A-ZS50-N03[d] | 0.00[d] | 0.00[d] | 244 |
| A-ZS50-P04 | 0.65 | 6.06 | 262 |
| A-ZS50-P03 | 1.13 | 6.06 | 268 |
| A-ZS50-P17 | 2.68 | 6.06 | 186 |

[a] Held constant for all samples: composition (50 mol%), precursor concentration = 1.0 mmol (Si + Zr)/ml 1-PrOH, overall hydrolysis ratio = 2.24 mol $H_2O$/mol (Si + Zr), and overall acid ratio = 10.0 ml $HNO_3$/mol (Si + Zr).

[b] Sample nomenclature: A = aerogel, ZS50 = 50 mol% zirconia and 50 mol% silica, N*xx* = non-prehydrolyzed sample number *xx*, P*yy* = prehydrolyzed sample number *yy*.

[c] After calcination at 773 K for 2 h.

[d] A non-prehydrolyzed sample.

catalysts for 1-butene isomerization. Approximately 0.2 g of sample was used as catalyst in a fixed bed, downflow reactor with a feed mixture of 5.7 liter/h helium and 0.3 liter/h 1-butene. We report activity as reaction rate (conversion to *cis*-2-butene and *trans*-2-butene products) per surface area at constant reaction conditions: 1.0 atm, 423 K, 95 min time on stream. We have described the isomerization procedure in detail elsewhere (8, 9).

As isomerization catalysts, all four samples displayed cis/trans product isomer ratios of approximately 1.0, confirming reaction at Brønsted acid sites (11). Figure 1 shows that as prehydrolysis ratio increases, so do the activities of our aerogels. In view of our recent reports associating high 1-butene isomerization activity with homogeneous mixing in both titania–silica (9) and 95 mol% zirconia–5 mol% silica (8) aerogels, this result suggests that high prehydrolysis ratios promote homogeneity.

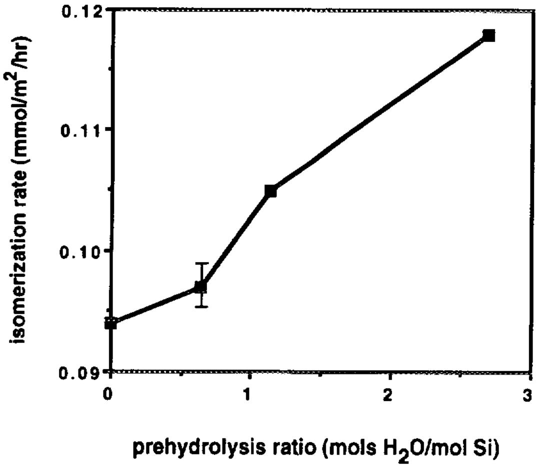

FIG. 1. Effect of prehydrolysis ratio (mol $H_2O$/mol Si) on the 1-butene isomerization activities of 50 mol% zirconia–50 mol% silica aerogels. See text for reaction conditions. Error bar shows range of measured activities in back-to-back trials. All samples calcined at 773 K in oxygen for 2 h before activity testing.

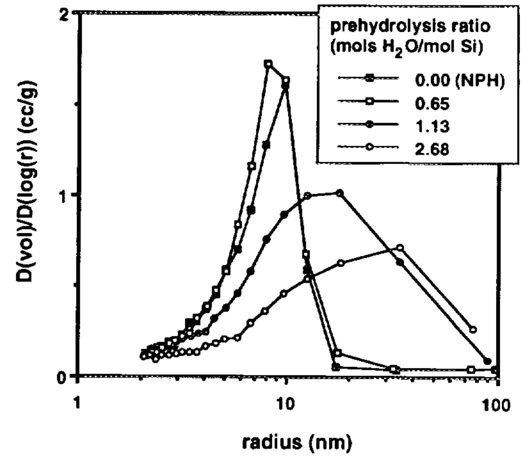

FIG. 2. Effect of prehydrolysis ratio (mol $H_2O$/mol Si, values shown in legend) on the pore size distributions of 50 mol% zirconia–50 mol% silica aerogels. All samples calcined at 773 K in oxygen for 2 h.

Based on parallels between the textural properties of pure zirconia aerogels and well-mixed 95 mol% zirconia–5 mol% silica gels, we recently reported a link between homogeneous component mixing and (i) low surface area, (ii) broad pore size distribution, and (iii) high average pore size (8). In Table 1 we show that the 2.68 mol/mol aerogel has the lowest surface area of the 50 mol% samples, and in Fig. 2 we demonstrate that the pore size distributions of our samples broaden and their maxima shift to higher average pore radii with increasing prehydrolysis ratio. Thus, the textural properties of our 50 mol% aerogels are also consistent with a relationship between high prehydrolysis ratios and homogeneous mixing.

Reports of NMR studies of silicon alkoxide hydrolysis suggest that the potential benefits of high prehydrolysis ratio may be two-fold. As expected, higher water/silicon ratios promote formation of additional Si–OH (silanol) groups (12). However, high ratios can also *preserve* silanol functionality by discouraging participation of the partially hydrolyzed silicon precursor in alcohol-producing self-condensation reactions (12, 13); these reactions have the net effect of consuming hydrolysis water without producing Si–OH groups. Our catalytic and textural data demonstrate that component mixing improves as prehydrolysis ratio is increased beyond 0.65 mol/mol to 2.68 mol/mol, consistent with more effective condensation between zirconium precursors and hydrolyzed silicon species at higher ratios.

Prehydrolysis has long been recognized as an effective strategy in promoting homogeneity in mixed oxides. Our results have shown that the manner by which it is applied, in particular by varying the prehydrolysis ratio, offers another, finer level of control over the properties of the product. Of particular interest for catalytic applications is our observation that the mixing and activity improvements associated with increasing prehydrolysis ratios extend beyond the 1.0 to 2.0 mol/mol range currently in most common use. We believe that similar opportunities exist for optimization of other common sol–gel parameters, such as temperature, pH, and concentration.

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