Synthesis of Sulfated and Carbon-Coated Al₂O₃ Aerogels and Their Activity in Dehydrochlorination of 1-Chlorobutane and (2-Chloroethyl)ethyl Sulfide

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ABSTRACT

The effect of gel modification with organic and inorganic acids, and β-diketones on the textural and adsorption properties of nanocrystalline alumina synthesized by the modified aerogel procedure was studied. The highest specific surface areas obtained exceeded 1200 m²/g, being 4-5 times higher than those of typically used alumina materials. The activity of high surface area nanocrystalline alumina materials in dehydrochlorination of (2-chloroethyl)ethyl sulfide (2-CEES) and 1-chlorobutane compared favorably with that of other nanocrystalline metal oxides. The temperature of 1-chlorobutane decomposition could be decreased by ca. 100°C in comparison with MgO aerogel extensively studied earlier while maintaining 98% selectivity to butenes. Sulfated alumina aerogels had high surface areas ca. 600 m²/g after calcination at 600°C and showed excellent acidic properties typical for sulfated alumina combined with exceptionally high surface area.

Keywords: Al₂O₃, aerogel, dehydrochlorination, destructive sorption, sulfated alumina

1 INTRODUCION

Aerogels are materials obtained by a sol-gel process followed by supercritical drying of the latter. Under supercritical conditions, the liquid-vapor interface that produces the collapse of the initial gel framework during conventional drying is eliminated. The obtained materials have high surface areas and pore volumes.

Various nanocrystalline aerogel-prepared (AP) metal oxides prepared by the modified aerogel procedure are known to have high surface areas, small crystallite sizes, unusual morphology, and enhanced adsorption properties and have been extensively studied for their use as destructive adsorbents [1-4] and decontamination of vegetative bacterial cells and spores [5] and various catalytic applications [6-9].

The use of these nanocrystalline metal oxides is limited under conditions where liquid water or water vapor is present due to their tendency to adsorb water, and thereby be partially deactivated toward adsorption of the target pollutants. We have earlier shown that coating of a destructive sorbent with an intelligent carbon layer significantly improves the stability of such nanocrystalline material in the presence of water and the possible time of its storage in air in comparison with not coated nanoscale oxide without a considerable loss of activity [4]. In the current publication we discuss the effect of various organic and acidic modifying agents on the textural properties of alumina aerogels and their performance in destructive adsorption of chlorinated hydrocarbons.

2 EXPERIMENTAL

For preparation of modified Al₂O₃ aerogels, aluminum isopropoxide (Aldrich) was dissolved in a desired amount of ethanol and/or other solvent. The modifying agents and hydrolysis water were dissolved in 10 ml of the same solvent each. Then, the solution of the modifying agent was quickly poured into the reaction vessel with aluminum isopropoxide solution and the resulting mixture was stirred for 10 min. Finally, a stoichiometric amount of hydrolysis water dissolved in same solvent was added. The reaction vessel was continuously maintained under nitrogen flow during the whole reaction. The gel formed after adding water was stirred overnight with a magnetic stir bar unless a solid gel was obtained.

The obtained gel was placed into an autoclave (Parr Instruments) equipped with a stirrer and heated in nitrogen atmosphere to 260°C with 1.3 °C/min heating rate. The final pressure and temperature were varied to study their effect on the properties of the obtained aerogels. After reaching the desired temperature the solvents were vented and the autoclave was purged with nitrogen for 20 min.

The resulting materials were calcined under vacuum at 500°C to obtain carbon-coated Al₂O₃ aerogels. The sulfated Al₂O₃ aerogels were calcined at 600°C in air.

Dehydrochlorination of 1-chlorobutane was performed in a flow reactor. 99% 1-chlorobutane (Aldrich) used in the experiments was introduced into the reactor by saturation of the argon flow with C₄H₉Cl vapor at room temperature. 10 μl injections of C₄H₉Cl were used. The volume flow rate was about 2 l/h, the catalyst loading was equal to 0.02 g. The product composition after the reactor was analyzed by gas chromatography. Prior to each experiment the catalyst was activated in an argon flow at 500°C for 1 h for removal of adsorbed water.

Experiments on decomposition of (2-chloroethyl)ethyl sulfide (2-CEES) were carried out in a 25 ml three-necked flask under argon with stirring. Ten milliliters pentane, 15 ml decane as internal standard, and 15 ml 2-CEES were placed in the flask. Then 200 mg of powder sorbent was
3 RESULTS AND DISCUSSION

3.1 Synthesis of C/Al₂O₃ and SO₄²⁻/Al₂O₃ aerogels

Organic groups used for modification of typical metal alkoxide precursors in the sol-gel process can serve two different purposes: i) to control the reaction rates of the reactants as well as the homogeneity and microstructure of derived gels being degraded during subsequent calcination to give purely inorganic materials; or ii) to modify or functionalize the oxide material. The latter approach could be applied for synthesis of oxide nanocrystals coated with carbonaceous structures. Nanostructures of this type can be created very effectively by controlled pyrolysis of organically modified aerogels. In this case organic groups are already located at the surface of the oxide, while their relatively homogeneous distribution can result in a higher number of well-distributed nucleation centers during the pyrolysis leading to smaller carbon particles.

Substituting standard isopropanol used a co-solvent with ethanol proved to increase the surface area of the resulting material (compare samples Al-11 and Al-22, Al-12 and Al-24 in Table 1). Therefore, the rest of samples were prepared using ethanol.

Unlike AP-MgO synthesis where the addition of toluene (or other aromatic solvent) has a major role and increases the resulting surface area by a factor of 2-2.5 [4], here in has a minor positive effect increasing the resulting surface area by 15-20% (compare samples Al-11 and Al-12, Al-22 and Al-24). Still, the highest specific surface areas exceeding 1200 m²/g that are 4-5 times higher than those of typically used alumina materials were obtained for the samples prepared with an ethanol-toluene mixture used as the solvent.

Therefore, we have carefully investigated the possibility to go to truly supercritical conditions by either eliminating toluene or substituting it with fluorobenzene. In the first case, standard drying temperature of 265°C is above critical for ethanol. The critical temperature of fluorobenzene is 287°C. So, we can go above it if we increase the drying temperature to 295°C. Note that we cannot go above toluene critical temperature with our equipment.

Neither approach is perfect. Aluminum isopropoxide used as a starting material has only moderate solvability in ethanol or other alcohols. So, in this case, we have to deal with a solution containing a precipitate. Increasing the drying temperature generally has itself a negative effect on the surface area of the resulting material.

In order to prepare carbon-coated alumina, we tried to use MAA as a modifying agent. It has a β-diketonate fragment that provides strong binding to the surface, which should survive hydrolysis and high-temperature drying and remain on the surface of dried aerogels. In addition, it has a terminal double bond that can be involved in polymerization reactions. By adding intermediate amounts of MAA we manage to deposit larger amounts of organic groups on the surface and improve the surface area of the material as well (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent/modifying agent</th>
<th>S.A. m²/g</th>
<th>Pore volume cc/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-11</td>
<td>Isopropanol/toluene</td>
<td>1180</td>
<td>1.89</td>
</tr>
<tr>
<td>Al-22</td>
<td>Ethanol/toluene</td>
<td>1290</td>
<td>1.99</td>
</tr>
<tr>
<td>Al-12</td>
<td>Isopropanol</td>
<td>980</td>
<td>0.88</td>
</tr>
<tr>
<td>Al-24</td>
<td>Ethanol</td>
<td>1000</td>
<td>4.46</td>
</tr>
<tr>
<td>Al-25</td>
<td>Ethanol/0.5 mol/mol MAA</td>
<td>1090</td>
<td>2.80</td>
</tr>
<tr>
<td>Al-28</td>
<td>Ethanol/1.0 mol/mol MAA</td>
<td>1040</td>
<td>1.75</td>
</tr>
<tr>
<td>Al-27</td>
<td>Ethanol/1.5 mol/mol MAA</td>
<td>990</td>
<td>1.08</td>
</tr>
<tr>
<td>Al-29</td>
<td>Ethanol/2.0 mol/mol MAA</td>
<td>80</td>
<td>0.25</td>
</tr>
<tr>
<td>Al-33</td>
<td>Ethanol/fluorobenzene dried at 295°C</td>
<td>1040</td>
<td>2.56</td>
</tr>
<tr>
<td>Al-35</td>
<td>Ethanol/fluorobenzene/1.0 mol/mol MAA dried at 265°C</td>
<td>1280</td>
<td>0.75</td>
</tr>
<tr>
<td>Al-36</td>
<td>Ethanol/fluorobenzene/1.0 mol/mol MAA dried at 295°C</td>
<td>1130</td>
<td>2.31</td>
</tr>
<tr>
<td>Al-S51</td>
<td>Ethanol/15wt.% H₂SO₄</td>
<td>1050</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Table 1. Textural characteristics of Al₂O₃ aerogels

We have earlier shown that resorcinol could be used as an efficient modifying agent for synthesis of carbon-coated MgO aerogels [4]. In the case of alumina the resorcinol addition resulted in a continuous decrease of the surface area and pore volume of the obtained aerogels (Fig. 1).

After activation under vacuum at 500°C the surface area of the alumina aerogels without the organic modifying agent was typically between 600 and 700 m²/g. The surface areas of the carbon-coated aerogels was typically somewhat lower, about 400-500 m²/g. HRTEM data (Fig. 2) clear shows that the carbon-coated are nanocrystalline with typical dimensions of the alumina nanoparticles synthesized by this method of several nanometers covered with few layer of graphitic carbon. XRD data did not show any clear peaks indicating that the aerogels even after calcination remained amorphous to x-rays.

Sulfated alumina aerogels were synthesized by a similar procedure with sulfuric acid used as a modifying agent. Earlier we showed that this approach yields sulfated zirconia catalysts active in isomerization of n-butane [6]. The introduction of sulfuric acid to the solution before gelation results in a substantial decrease of the pore volume,
whereas the high surface area of the Al₂O₃ aerogels is preserved. The surface areas of the sulfated alumina aerogels after calcination at 600°C usually required to make active acid catalysts was about 600 m²/g. This value appears to the highest ever reported for sulfated alumina catalysts and is 2-3 times higher than those reported in the literature.

Figure 1. Effect of resorcinol on the textural parameters of modified Al₂O₃ aerogels.

Figure 2. HRTEM image of modified alumina aerogel

3.2 Dehydrochlorination of 1-chlorobutane

The catalytic properties of the synthesized Al₂O₃ aerogels were compared in the dehydrochlorination of 1-chlorobutane. Earlier we have extensively studied this reaction for AP-MgO [8] and C/MgO aerogels [4]. We found that the activity of high surface area nanocrystalline alumina materials in dehydrochlorination of 1-chlorobutane compared favorably with that of other nanocrystalline metal oxides. The temperature of 1-chlorobutane decomposition could be decreased by ca. 100°C in comparison with MgO aerogel (Figure 3) while maintaining 98% selectivity to butenes.

Figure 3. 1-Chlorobutane conversion at 250°C over aerogel nanocrystalline MgO, Al₂O₃, sulfated Al₂O₃ and mixed sulfated Al₂O₃ – MgO samples.

Figure 4. Selectivity to 1-butene during 1-chlorobutane dehydrochlorination at 250°C over alumina and sulfated alumina aerogels.

Apparently, the higher activity of alumina in this reaction is related to its higher acidity combined with high surface area. Sulfated alumina has even higher activity due to its higher acidity. In fact, even more active catalysts were prepared by cogelation of MgO and sulfated alumina in 1:1 ratio. The more acidic catalysts were characterized by lower selectivity to 1-butene (Fig. 4), indicating that the reaction
follows E2 mechanism with easy abstraction of the chloride ion with the formation of the carbocation. The latter is than subjected to isomerization to form more stable secondary carbocations.

3.3 Destructive adsorption of (2-chloroethyl)ethyl sulfide

2-CEES is a mustard gas mimic commonly used to characterize the performance of materials developed for destruction of poisonous chlorinated compounds. We found that alumina and carbon-coated alumina aerogels chemisorbed 2-CEES at room temperature from pentane solution even more efficiently than MgO aerogels characterized in detail before [10] (Table 2).

Table 2. 2-CEES conversion at room temperature over various sorbents.

<table>
<thead>
<tr>
<th>Material</th>
<th>S.A., m²/g</th>
<th>Conversion (molec./nm²) in first 5 min (mmol/g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-MgO</td>
<td>660</td>
<td>0.65, 0.020</td>
</tr>
<tr>
<td>C-MgO</td>
<td>370</td>
<td>0.65, 0.037</td>
</tr>
<tr>
<td>AP-Al₂O₃</td>
<td>750</td>
<td>0.65, 0.050</td>
</tr>
<tr>
<td>C/Al₂O₃</td>
<td>510</td>
<td>0.75, 0.040</td>
</tr>
<tr>
<td>SO₄²⁻-Al₂O₃</td>
<td>520</td>
<td>0.96, 0.145</td>
</tr>
<tr>
<td>Act. carbon</td>
<td>1450</td>
<td>0.11, 0.001</td>
</tr>
</tbody>
</table>

The obtained results prove that, like 1-chlorobutane dehydrochlorination, 2-CEES destructive sorption is also more efficient over acidic materials than over basic ones. Most likely, these reactions follow the same E2 elimination mechanism initiated by chloride ion abstraction by very strong acid sites.

4 CONCLUSIONS

We have demonstrated that the textural parameters of alumina aerogels can be effectively controlled by selection of the solvents and modifying agents. Carbon-coated Al₂O₃ with permeable carbon coating can be prepared by adding modifying agents with bulky organic groups during gelation followed calcination under vacuum. The highest specific surface areas exceeding 1200 m²/g that are 4-5 times higher than those of typically used alumina materials were obtained for the samples prepared with an ethanol-toluene mixture used as the solvent. Typical dimensions of the alumina nanoparticles synthesized by this method did not exceed few nanometers.

The activity of high surface area nanocrystalline alumina materials in dehydrochlorination of (2-chloroethyl)ethyl sulfide (2-CEES) and 1-chlorobutane compared favorably with that of other nanocrystalline metal oxides. For example, the temperature of 1-chlorobutane decomposition could be decreased by ca. 100°C in comparison with MgO aerogel while maintaining 98% selectivity to butenes. Sulfated alumina aerogels had high surface areas ca. 600 m²/g after calcination at 600°C and showed excellent acidic properties typical for sulfated alumina. For instance, (2-chloroethyl)ethyl sulfide conversion rate in pentane solution at room temperature over sulfated aerogel alumina was 3 times higher than on Al₂O₃ aerogel and 8 times higher than on MgO aerogel.

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REFERENCES