Research Letter

Iron Oxide Doped Alumina-Zirconia Nanoparticle Synthesis by Liquid Flame Spray from Metal Organic Precursors

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The liquid flame spray (LFS) method was used to make iron oxide doped alumina-zirconia nanoparticles. Nanoparticles were generated using a turbulent, high-temperature (Tmax ∼ 3000 K) H2-O2 flame. The precursors were aluminium-isopropoxide, zirconium-n-propoxide, and ferrocene in xylene solution. The solution was atomized into micron-sized droplets by high velocity H2 flow and introduced into the flame where nanoparticles were formed. The particle morphology, size, phase, and chemical composition were determined by TEM, XRD, XPS, and N2-adsorption measurements. The collected particulate material consists of micron-sized aggregates with nanosized primary particles. In both doped and undoped samples, tetragonal phase of zirconia was detected in room temperature while alumina was found to be noncrystalline. In the doped powder, Fe was oxidized to Fe2O3. The primary particle size of collected sample was approximately from 6 nm to 40 nm. Doping was observed to increase the specific surface area of the powder from 39 m2/g to 47 m2/g.

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1. INTRODUCTION

Liquid flame spray (LFS) technique can be used to synthesize the broad spectrum of inorganic oxide nanoparticles like Al2O3, ZrO2, Mn2O3, [1, 2], TiO2 [3], Fe2O3, Fe3O4 [4], and nanoscale metallic particles like Ag and Pd [4]. Liquid feeding-based flame methods also offer a controlled way to synthesize mixed oxides like MgAl2O4, CeO2/ZrO2, Y2O3-ZrO2 [1], and SiO2/TiO2 [5]. In Liquid flame spray (LFS), a high-velocity high-temperature flame is used to produce nanoparticles. Liquid precursor is axially injected into the flame where it evaporates, decomposes, reacts, and finally nucleates to the nanosized particles. Particles can be deposited directly on the substrate as a layer [6], or collected from gas stream by filters [7] or by electrostatic precipitators [3].

The unique properties of nanoscale materials offer several interesting applications in different fields of industry. The remarkable optical, electronic, magnetic, and mechanical properties of nanoparticles and materials made of nanoparticles open up a possibility to modify the functionality of electrochemical, photochemical and structural materials, and coatings [8, 9]. A fractional size and controlled shape of metal and functionalized metal nanoparticles, as well as properties of doped mixed oxides like Al2O3-ZrO2, could provide a unique possibility for highly efficient catalysis [9, 10]. The catalysis provides numerous applications like alkylation and isomerization in the chemical industry [10, 11], catalytic reduction of NO and NH3 [12], or preparation of carbon nanotube-Al2O3 composites with Fe catalysts [13]. Several applications of the catalytic agents together with increasing demand of high-quality structural materials call for new and controllable methods to produce nanoscale building blocks. LFS technique opens up a possibility to produce multicomponent oxide nanomaterials together with additional catalyst for further designing and processing of functional or structural nanomaterials.

The aim of this work was to demonstrate the synthesis of iron oxide doped Al2O3-ZrO2 mixed oxide by an LFS.
The collected particles were analyzed in order to determine resulting particle size, morphology, phases, and chemical composition. The characteristics of iron oxide doped sample were compared to the undoped sample.

2. EXPERIMENTAL

Aluminium isopropoxide (C9H21AlO3), zirconium (IV) n-propoxide (Zr(O(CH2)2CH3)4), and ferrocene ((C5H5)2Fe) were dissolved in p-xylene. Molar ratio of (C9H21AlO3): (Zr(O(CH2)2CH3)4):((C5H5)2Fe) in precursor solution was 52 : 22 : 1. Also in undoped solution, the molar ratio of (C9H21AlO3): (Zr(O(CH2)2CH3)4) was 52 : 22. The precursor solution was fed into turbulent, high-temperature H2-O2 flame. The feed rate was 5.2 mL/min. The gas flows were 20 L/min for H2 and 10 L/min for O2. Liquid precursor was atomized in the high-velocity H2 flow into micron-sized droplets and introduced into oxygen stream and the upwards directed flame where particles were formed. Particles were collected by a cylindrical electrostatic precipitator with a diameter of 100 mm and length of 1000 mm, using 6.0 kV voltage on the central rod, and 0.3 mA current from rod to grounded cylinder. Total amount of collected material was in the order of one gram. LFS-process is schematically illustrated in Figure 1.

The crystal structure of the sample was determined by X-ray diffractometer (Kristolloflex D-500, Siemens) using monochromatized CuKα radiation. The particle morphology was determined by a transmission electron microscope (TEM) (JEOL, JEM 2010). Then the specific surface area of sample was measured by nitrogen adsorption using the Brunauer-Emmett-Teller (BET) method (Coulter Omnisorp 100 cx). The X-ray photoemission (XPS) spectra were recorded using a Physical Electronics Quantum 2000 ESCA instrument. The XPS measurements were performed at a base pressure of 1 × 10⁻⁹ torr using the AlKα X-ray source. Operating power was 12.5 kW and the spot diameter 50 μm.

The low and high resolutions of pass energy in spectral acquisition were 117.4 and 23.5 eV, respectively. Surface concentrations were determined with Multipak 6.1 software using peak areas to give surface concentrations in atomic percent.

3. RESULTS AND DISCUSSION

The XRD diffraction patterns (Figure 2) of LFS particulate materials contained only the peaks of tetragonal ZrO2. Since no other than t-ZrO2 was detected, Al and Fe are probably in amorphous phase.

The XPS spectra of the collected samples are shown in Figure 3. In XPS measurements, iron was detected and the Fe 2p3/2 peak position was around 711 eV, indicating that most of the iron is Fe2O3. The Al 2p peak position was around 73.8 eV and position of Zr 3d3/2 peak around 186 eV which proves that both Al and Zr are oxidized to Al2O3 and ZrO2. The signal at around 285 eV corresponds to adventitious carbon.

The surface concentrations of oxygen, aluminum, zirconium, and iron, in atomic percent, are given in Table 1. From the high-resolution XPS spectra, the calculated concentrations are compared to the theoretical acquisition of named atoms. From XPS spectra, calculated concentrations of oxygen and iron are higher whereas the concentrations of aluminum and zirconium are lower than the theoretical acquisition. It is supposed that there is adsorbed oxygen and meanwhile more Fe2O3 particles on the surface of the sample than inside of it.

The specific surface area of the doped sample was 46.7 m²/g whereas it was 38.8 m²/g for undoped sample. Higher surface area of doped sample refers to small size of Fe2O3 particles. Another explanation for the increase of
Table 1: Calculated surface concentrations in atomic percentage from XPS (1) and theoretical acquisition (2) of oxygen, aluminum, zirconium, and iron of $Fe_2O_3 + Al_2O_3-ZrO_2$ and $Al_2O_3-ZrO_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen at -%</th>
<th>Aluminum at -%</th>
<th>Zirconium at -%</th>
<th>Iron at -%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $Fe_2O_3 + Al_2O_3-ZrO_2$</td>
<td>71.01</td>
<td>22.35</td>
<td>5.87</td>
<td>0.77</td>
</tr>
<tr>
<td>(2) $Fe_2O_3 + Al_2O_3-ZrO_2$</td>
<td>61.91</td>
<td>26.49</td>
<td>11.09</td>
<td>0.51</td>
</tr>
<tr>
<td>(1) $Al_2O_3-ZrO_2$</td>
<td>71.37</td>
<td>22.53</td>
<td>6.10</td>
<td>—</td>
</tr>
<tr>
<td>(2) $Al_2O_3-ZrO_2$</td>
<td>62.23</td>
<td>26.63</td>
<td>11.15</td>
<td>—</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

Iron oxide doped nanoscale $Al_2O_3-ZrO_2$ mixed oxide was prepared by liquid flame spray. The crystal structure, particle and crystal size, specific surface area, and surface concentrations of the elements were analyzed. Analysis using XRD showed that the structure of alumina is not crystalline, whereas zirconia exists in tetragonal phase. According to XPS study, Fe exists mostly in oxide ($Fe_2O_3$). On the grounds of the TEM dissection, the particle size of the sample is in nanometer scale. The calculated crystallite size of zirconia was found to be 7.4 nm. In small particles, the tetragonal structure is energetically favorable. This gives the explanation to the existence of the tetragonal form of zirconia at the room temperature.

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REFERENCES


