Preparation and characterization of novel magnetic 
ZrO$_2$/TiO$_2$/Fe$_3$O$_4$ solid superacid

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Abstract

Novel magnetic solid superacids were prepared by introducing TiO$_2$ and magnetic substrates by chemical co-precipitation method. The prepared materials were characterized by means of XRD, FT-IR, DSC and TEM techniques. The results indicated that the introduction of TiO$_2$ and magnetic substrates markedly hindered the phase transformation from tetragonal phase (t-ZrO$_2$) to monoclinic phase (m-ZrO$_2$) even calcined at 1200 °C. Furthermore, the solid superacids doped with magnetic substrates presented the superparamagnetic property. The morphology of the samples showed lamellar crystals with high purity and uniform size distribution, and the (101) lattice plane ($d=0.29$ nm) could be clearly seen in the HRTEM image.

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1. Introduction

Liquid acids (H$_2$SO$_4$, HCl, HNO$_3$, et al.) are conventionally used as catalysts for homogenous reactions such as alkylation, esterization and isomerization [1–3]. But the problems of corrosion, pollution and decrease of selectivity of the desired product strongly limit their industrial applications. Strict environmental norms provide a stimulation to develop novel catalytic materials. Recently, modified solid acid catalysts have gained much attention for isomerization reactions for their high strength of acidity, non-toxicity and high activity at low temperatures [4–6]. Several solid acid catalysts such as inorganic oxides, clays, zeolites, cation-exchange resins have been reported [7–9]. Among these solid catalysts, inorganic oxides especially zirconia have been demonstrated as one of the optimal candidates for solid acid catalyst because of its acid sites on the surface. However, pure zirconia presented low thermal stability and the specific surface area greatly decreased with calcination temperature [10]. Therefore, tetragonal zirconia which possesses high strength of acidity couldn’t be obtained at high temperature. Many efforts have been inducted to increase the thermal stability and acidity by introducing different metals oxide such as SiO$_2$, Al$_2$O$_3$, CaO, Y$_2$O$_3$ and MgO, which formed mixed oxides against surface area loss and crystallization phase transformation upon calcination [11–15]. However, even if the acidity and thermal stability are improved by the above attempts, the separation and recovery of these solid acid mixed oxides from the reaction products are still difficult. So a large amount of separation energy and cost are consumed for the extra equipment and treatments for separation and recovery. In order to extend the application of solid acid and develop green routes, the synthesis of novel solid acid catalyst is necessary.

In this paper, we presented a facile synthetic strategy to design and synthesize ZrO$_2$/TiO$_2$/Fe$_3$O$_4$ solid superacid by chemical co-precipitation method. This material not only has the advantages of a solid acid, but also possesses the following advantages: (1) the introduction of TiO$_2$ and Fe$_3$O$_4$ markedly delays the tetragonal-to-monoclinic phase transformation,
which greatly improved the thermal stability of zirconia and inhibited the crystal growth; (2) the introduction of Fe₃O₄ endowed zirconia with magnetism, which can be easily separated from the reaction media through introduction of a magnetic field. This novel magnetic solid acid material was expected to be used as a green catalyst in the acid-catalyzed reactions.

2. Experimental

Magnetic substrate was prepared by dissolving 2.78 g of FeSO₄ (0.01 mol) and 4 g of Fe₂(SO₄)₃ (0.01 mol) in water under stirring at 45 °C, and the pH value of the solution was adjusted to 10–11 with NH₃·H₂O (20%). The obtained material was recovered, washed several times with deionized water until the pH was neutral, then dried at 80 °C for 24 h.

The synthesis of magnetic solid superacid is presented as follows: 50 g of tetra-butyl orthotitanate, 50 g of ZrOCl₂·8H₂O and 50 mL of as-made magnetic substrates were dissolved under stirring, and pH was adjusted to 9–10 with aqueous ammonia. The hydroxide was thoroughly washed, filtered and dried in air at 100 °C for 3 h and then immersed in 1 mol mL⁻¹ sulfuric acid solution for 30 min. The sulfated sample was washed, dried at 100 °C overnight and then calcined at high temperature for 6 h. The obtained material was designated as SZT-T (T is referred to as calcination temperature). The pure ZrO₂ solid acid is prepared according to the above process for comparison, which is designated as ZrO₂-T.

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-IIIB diffractometer using Cu Kα radiation (λ = 1.5406 Å). FT-IR spectra were obtained with Nicolet 5DX spectrophotometer using the KBr pellet technique. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) experiments were performed on a PHILIPS CM 200 FEG electron microscope with an acceleration voltage of 200 kV. The samples were dispersed in ethanol, and carbon-coated copper grids were used as the sample holder. Differential scanning calorimetry (DSC) was performed on a NEZSCH STA 409PC thermoanalyzer in the temperature range 40–650 °C with a heating rate of 10 °C/min. Magnetic measurements were performed on a MS-500 magnetometer (England, Oxford University), and the isomer shift values were reported with respect to the α-Fe metal.

The total acidity of the sample was determined by temperature-programmed desorption of ammonia (TPD). A sample of 50 mg was first pretreated in Ar at 700 °C for 40 min,
then cooled to 100 °C and saturated at this temperature with ammonia until equilibrium. The NH$_3$-TPD profile was recorded with a thermal conductivity detector with a heating rate of 10 °C/min from 100 to 650 °C in an Ar flow. The acid strength of the samples was measured using Hammett indicators. The samples were heated under vacuum at 200 °C for 1 h, then connected with the vapor of Hammett indicators. The change in the color of the indicators with different pK$_a$ was observed.

### 3. Results and discussion

Fig. 1 represents the XRD patterns of the samples calcined at different temperatures. As shown in the figure, for the samples SZT-450 and SZT-600 (treated at 450 °C and 600 °C, respectively), a broad diffraction peak implies the amorphous phase of the samples. When the calcined temperature is increased to 700 °C, the characteristic diffraction peak of tetragonal zirconia (t-ZrO$_2$, JCPDS NO 79-1770) appears (Fig. 1c), and the intensity of the characteristic peak (101) increases with increasing temperature up to 1200 °C. However, the pure ZrO$_2$ (Fig. 1g) has almost completely transformed from tetragonal phase to monoclinic phase (m-ZrO$_2$, JCPDS NO 24-1165) when calcined at 450 °C. It is assumed that the strong interaction between zirconia and TiO$_2$ greatly hinders the phase transformation from tetragonal zirconia to monoclinic zirconia. On the basis of the above results, we infer that the introduction of TiO$_2$ significantly improved the thermal stability of tetragonal phase and markedly inhibited the phase transformation from tetragonal to monoclinic zirconia. The characteristic diffraction of t-TiO$_2$ is observed when the sample was calcined above 800 °C, indicating a superfluous amount of TiO$_2$. No characteristic diffraction peak of Fe$_3$O$_4$ is observed in Fig. 1, demonstrating the homogeneous distribution of amorphous Fe$_3$O$_4$ throughout the matrix of ZrO$_2$. The XRD results are consistent with the literature[12].

As listed in Table 1, the total acidity of SZT-700 and ZrO$_2$-700 is 135.2 and 66.3 μmol/g, respectively, showing that the number of acid sites for the sample doped with TiO$_2$ and magnetic substrate is greater than that for undoped sample. This high acidity can be due to the oxide-doping effect, which makes zirconia stable at tetragonal phase as confirmed by XRD (as shown in Fig. 1). And the doping effect of the oxide is related to an increase in the number of surface acidic sites. This is consistent with the results reported by Roh et al.[16]. Both total acidity and acid strength of the samples increase with the increment of calcination temperature up to 700 °C, and then gradually decrease with increasing temperature. The decrease of acidity and acid strength may be the result of the decomposition of sulfate species bonded to the surface of the samples, while the double bond nature of S=O in these sulfate species is usually related with the superacid property of the samples.

The FT-IR spectra (Fig. 2) of the samples calcined at different temperatures are similar to each other. The broad absorption bands in the region 3400–3600 cm$^{-1}$ can be attributed to O–H stretching vibrations of the physically adsorbed water molecules. The ~1650 cm$^{-1}$ band

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>0</th>
<th>450</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation magnetization $\sigma_s$ (emu/g)</td>
<td>12.5</td>
<td>13.1</td>
<td>14.6</td>
<td>11</td>
<td>9.2</td>
<td>7.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Effect of calcination temperature on saturation magnetization
may be due to HOH bending of the physically adsorbed water. The band centered at 1736 cm$^{-1}$ is related to the C=O stretching vibration of the absorbed CO$_2$ from the air. The band at about 600 cm$^{-1}$ can be related with the vibration of O–Zr, and the band located at 541.34 cm$^{-1}$ is due to the stretching vibration of Fe–O bond.

The DSC–TG results of the as-synthesized sample are shown in Fig. 3. Two endothermic peaks observed at low temperature can be attributed to the desorption of physically adsorbed water, which is accompanied by 20.27% weight loss. And the strong exothermal peak at about 380 °C, accompanied by weight loss of 15.86%, can be attributed to the heat effect of the phase transformation from amorphous zirconia to tetragonal zirconia and from tetragonal zirconia to monoclinic zirconia, respectively. The small exothermal peak for the sample calcined at about 710 °C might be the result of the crystallization of the sample and the evolution of SO$_3$ decomposed from the sulfate species bonded to the surface of the sample. And the gravity doesn’t change with further increasing temperature, implying the complete formation of the stable tetragonal zirconia. The results are supported by the XRD analysis.

Representative TEM and HRTEM images of the sample calcined at 800 °C are shown in Fig. 4a and b, respectively. In Fig. 4a, the micrograph at low magnification shows uniform lamellar crystals of about 110 nm in diameter. The HRTEM image (Fig. 4b) and the corresponding Fourier-filtered transformed (FFT) image (Fig. 4b, inset) can be consistently indexed using the structural data of t-ZrO$_2$ crystals (see Fig. 1d). Representative HRTEM shows clear lattice fringes and the distance between two adjacent planes is measured to be 0.29 nm, corresponding to (101) planes ($d$=0.293 nm) in tetragonal phase zirconia [17].

The hysteresis loop of the solid superacid measured at room temperature is depicted in Fig. 5. The corresponding saturation magnetization and the coercive force of the sample are 11 emu g$^{-1}$ and 0 Oe, respectively. The value of the latter is a typical characteristic of superparamagnetic materials. The emerging of superparamagnetism at room temperature may be due to the Fe$_3$O$_4$ particle with very small particle size [18]. The results are consistent with the XRD results. As displayed in the figure, the magnetic curve increases linearly with increasing field at low magnetization, while the magnetic curve increases slightly with further increasing field, and finally maintains 11 emu g$^{-1}$. The effect of calcination temperature on the saturation magnetization is listed in Table 2. Seen from the table, the value of saturation magnetization decreases with increasing treated temperature, and this may be related with the change of particle size of the magnetic substrates.

A further study on the catalytic application of the sample is being carried out in our group.

4. Conclusion

In summary, a kind of magnetic solid superacid ZrO$_2$/TiO$_2$/Fe$_3$O$_4$ was synthesized by chemical co-precipitation method. The as-synthesized material presented the superparamagnetism. The introduction of ZrO$_2$ and Fe$_3$O$_4$ greatly improved the thermal stability and markedly inhibited the phase transformation from tetragonal ZrO$_2$ to monoclinic ZrO$_2$. Such novel materials could act as green catalysts and have promising applications in catalytic fields.

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References
