Magnetically-separable Fe₃O₄@SiO₂@SO₄-ZrO₂ core-shell nanoparticle catalysts for propanoic acid esterification


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Abstract:

Monodispersed, sulfated zirconia encapsulated magnetite nanoparticles were synthesized as magnetically-separable solid acid catalysts. Catalyst nanoparticles are prepared via coating preformed 80 nm Fe₂O₃ particles with a 15 nm SiO₂ protective coating prior to growth of a uniform 28 nm ZrO₂ shell. The thickness of the ZrO₂ shell in resulting Fe₃O₄@SiO₂@ZrO₂ nanoparticles was controlled by adjusting the zirconium butoxide to Lutensol AO5 ratio, with 1:10 found as the optimal ratio to produce monodispersed ZrO₂ coated nano-spheres. Sulfation using an ammonium sulfate precursor is less corrosive towards the core-shell structure of Fe₃O₄@SiO₂@ZrO₂ nanoparticles leading to superior sulfated materials compared to those obtained using H₂SO₄. Resulting Fe₃O₄@SiO₂@SO₄-ZrO₂ solid acid catalysts exhibit high activity for propanoic acid esterification with methanol, far exceeding that of conventional sulfated zirconia nanoparticles, while being amenable to facile magnetic separation.

Keywords: magnetic nanoparticles • sulfated zirconia • solid acid • core-shell • esterification

1. Introduction:

Functionalized nano- and microparticles possessing core-shell structures have attracted great interest in recent decades for potential applications in drug delivery, magnetic resonance imagining, bioassays, and catalysis.[1-6] Various approaches have been exploited to synthesize core-shell nanospheres, including the “Stöber” approach,[7] microemulsions/reverse-micelle,[8][9] and aerosol pyrolysis,[10] which enable the fabrication of monodispersed nanomaterials with complex structures including onion-like architectures. In regard of catalysis, magnetic nanoparticles and core-shell variants are particularly attractive since they offer high surface areas, and facile catalyst separation/recycling and product recovery, and hence are ideally suited to liquid phase transformations such as cellulose hydrolysis,[11] fructose dehydration,[12] aldol condensation of 5-hydroxymethylfurfural (5-HMF) with ethanol,[13] oxidation of 5-HMF to 2,5-diformylfuran,[14]

Zirconia is widely used in materials science, notably as a semiconductor,[19] thermal barrier coating,[20] component of oxygen sensors,[21] and a heterogeneous solid acid catalyst wherein its amphoteric Lewis and Brönsted acid character facilitates cascade reactions.[22] Sulfated zirconia (SZ) is generally considered a superacid catalyst that exhibits predominantly Brönsted character and high activity for diverse liquid phase reactions,[23-25] however, conventional synthetic routes to SZ typically result in a low surface area and porosity. Recovery and recycling of such metal oxide heterogeneous catalysts is also problematic, and hence the development of magnetically-separable and highly dispersed SZ nanostructures is especially needed. There are only a few reports on the synthesis of magnetic zirconia nanoparticles,[26-30] and these do not produce well-defined or monodispersed core-shell nanoparticles.

Yin et al recently developed a new, room temperature synthesis of monodispersed zirconia encapsulated polystyrene (PS) nanospheres, PS@ZrO$_2$ employing the PS nanospheres as a hard template.[31] Hollow ZrO$_2$ nanospheres were subsequently fabricated by calcination to remove the PS template. Schüth et al[32] adopted a different approach to create hollow ZrO$_2$ nanosphere utilizing silica nanospheres as the hard template in conjunction with the nonionic amphiphilic surfactant Lutensol AO5; the silica core was subsequently etched by dilute NaOH resulting in high surface area (300 m$^2$.g$^{-1}$) hollow zirconia spheres. A modified protocol allowed the preparation of yolk-shell Au@ZrO$_2$ nanospheres in which the hollow ZrO$_2$ shell protected small Au nanoparticles confined within the internal void against thermal sintering.[32] To our knowledge sulfated analogues of such monodispersed zirconia nanospheres (or core-shell variants) have not been synthesized, while the only report of magnetic sulfated zirconia nanoparticles produced inhomogeneous materials lacking a well-defined magnetic core-SZ shell structure.
Herein, we report the first synthesis and catalytic application of monodispersed magnetic SZ nanoparticles possessing an onion skin structure comprising a magnetite core, encapsulated by a protecting, dense silica shell, which is in turn enveloped by a conformal SZ shell of tunable thickness between 6-28 nm (Fe₃O₄@SiO₂@SZ). These magnetic SZ nanoparticles were subsequently evaluated for propanoic acid esterification, a prototypical solid acid catalyzed reaction employed to upgrade biomass derived pyrolysis-oil[33-35] which are intrinsically unstable and corrosive due to C₂-C₃ acid components.[36]

2. Experimental:

a) Catalyst synthesis:

(i) Synthesis of silica encapsulated iron oxide nanoparticles (Fe₂O₃@SiO₂): Silica encapsulated iron oxide nanoparticles were synthesized using a modified version of the method of Zhao et al. [37] Uniform hematite (Fe₂O₃) particles were first obtained by aging a 0.02 M aqueous FeCl₃ solution at 100 °C for 48 h, with the resulting Fe₂O₃ nanoparticles isolated by centrifugation, then washed three times with 2-propanol. 50 mg of the resulting Fe₂O₃ nanoparticles were then added to a mixture of 200 mL 2-propanol, 40 mL H₂O, and 5 mL of 35 vol% aqueous ammonia while stirring. To this nanoparticle suspension, 0.15 mL of tetraethyl orthosilicate was added dropwise under vigorous stirring and the resulting mixture aged at room temperature overnight to yield silica encapsulated iron oxide nanoparticles upon centrifugation.

(ii) Preparation of magnetic zirconia encapsulated Fe₃O₄ nanoparticles (Fe₃O₄@SiO₂@ZrO₂): The as-synthesized Fe₂O₃@SiO₂ nanoparticles were added to 100 mL ethanol containing the desired volume (0.25 mL-1.5 mL) of Lutensol AO5 solution (0.43 g Lutensol AO 5 dissolved in 11 g of H₂O). The mixture was stirred for 1 h at room temperature, and then the desired amount (0.05 mL-0.9 mL) of zirconium (IV) butoxide was added quickly. The solution was kept at room temperature and stirred vigorously overnight. The resulting nanoparticles were centrifuged, re-dispersed in water, and then
aged at room temperature for 3 days. Subsequently the nanoparticles were centrifuged and calcined at 900 °C (ramp rate 2 °C/min) for 2 h to yield zirconia encapsulated Fe₂O₃@SiO₂@ZrO₂ nanoparticles. These were finally reduced under flowing H₂ at 450 °C (ramp rate 2 °C /min) for 2 h to convert the hematite core into magnetite (Fe₃O₄).

(iii) Preparation of magnetic sulfated zirconia (nanoparticles) Fe₃O₄@SiO₂@SO₄-ZrO₂: Fe₃O₄@SiO₂@ZrO₂ prepared with a zirconium butoxide:Lutensol AO5 volume ratio of 0.45 mL:0.25 mL were selected as the parent. Sulfation was performed through either wet impregnation with H₂SO₄ or incipient-wetness impregnation by (NH₄)₂SO₄. For wet impregnation, 0.4 g of Fe₃O₄@SiO₂@ZrO₂ nanoparticles were added to 30 mL aqueous H₂SO₄ (0.05-0.20 M) with stirring at room temperature for 5 h. The resulting sulfated nanoparticles were magnetically separated, dried overnight in an oven, and then annealed under flowing N₂ at 550 °C (ramp rate 2 °C /min) for 3 h. Incipient-wetness impregnation was performed by mixing 0.3 g of Fe₃O₄@SiO₂@ZrO₂ nanoparticles with 1 ml of deionized water containing 0.3 g of (NH₄)₂SO₄, followed by drying overnight in an oven, and then annealed under flowing N₂ at 550 °C (ramp rate 2 °C /min) for 3 h.

Prior to use, both types of sulfated Fe₃O₄@SiO₂@ZrO₂ nanoparticles were stirred with methanol at 60 °C for 4 h to remove physisorbed sulfate. Magnetic sulfated zirconia particles prepared with H₂SO₄, are designated xMSZ where x=[H₂SO₄], those prepared with ammonium sulfate are designated NH₄MSZ.

For comparison, a pure sulfated zirconia (SZ) was prepared by conventional wet impregnation with H₂SO₄.[22] 2.5 g of Zr(OH)₄ (MEL Chemicals-XZO 880/01) was added to 25 mL aqueous H₂SO₄ (0.2 M). The resulting slurry was stirred for 5 h at room temperature, filtered, and dried at 80 °C overnight, prior to calcination in air at 550 °C (ramp rate 2 °C /min) for 3 h.

b) Catalyst characterization:

Textural and structural properties of parent core-shell nanoparticles and the corresponding sulfated
nanoparticles were measured by a combination of N\textsubscript{2} porosimetry and transmission electron microscopy (TEM). Nitrogen physisorption was undertaken on a Quantachrome Nova 1200 instrument, with samples degassed at 120 °C for 6 h prior to recording N\textsubscript{2} adsorption/desorption isotherms. Brunauer–Emmett–Teller (BET) surface areas were calculated over the relative pressure range 0.01–0.2 (P/P\textsubscript{0}), while pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) method applied to the desorption branch of the isotherm. Transmission electron microscopy (TEM) images were recorded on an aberration corrected JEOL 2100-F electronic microscope operating at 200 kV; equipped with a Gatan Orius SC600A CCD camera. Samples were prepared by dispersion in ethanol and drop-casting onto a copper grid coated with a holey carbon support film (Agar Scientific Ltd). Images were analysed using ImageJ 1.41 software.

Bulk sulfur elemental analysis was performed on a FLASH 2000 CHNS/O organic elemental analyzer. XPS was performed on a Kratos Axis HSi X-ray photoelectron spectrometer fitted with a charge neutralizer and magnetic focusing lens employing Al K\textalpha\ monochromated radiation (1486.7 eV); spectral fitting was performed using Casa XPS version 2.3.15, with spectra energy-corrected to the C 1s peak of adventitious carbon at 284.6eV.

Acid site loadings were quantified by propylamine decomposition via the Hoffman reaction, using a thermo-gravimetric mass spectrometry analysis (TGA-MS) method.[38] Prior to thermogravimetric analysis, samples were impregnated with propylamine and then dried in the vacuum oven at 40 °C overnight. TGA was performed on a Mettler Toledo, TGA/DSC2 Star system with a heating rate of 10 °C·min\textsuperscript{-1} from 40-800 °C with flowing N\textsubscript{2} (30 mL·min\textsuperscript{-1}). In parallel, evolved gas analysis was performed with Pfeiffer ThermoStar mass spectrometer, connected to the outlet of the TGA apparatus. Mass channels were recorded for m/z values of 17 (NH\textsubscript{3}), 41 (propene) and 59 (propylamine), with the evolution of reactively propene a product from propylamine decomposition over acid sites.

Brønsted/Lewis acid character was determined pyridine DRIFT, carried out by impregnation of
diluted samples (10 wt% in KBr) with neat pyridine. Excess physisorbed pyridine was removed in a vacuum oven at 30 °C overnight prior to sample loading in the environmental cell. DRIFT spectra of the pyridine-saturated samples were recorded at room temperature under vacuum using a Nicolet Avatar 370 MCT with Smart Collector accessory, mid/near infrared source and a mercury cadmium telluride (MCT-A) photon detector at -196 °C.

c) Propanoic acid esterification:
Esterification was carried out on a Radleys Starfish carousel at 60 °C using a stirred batch reactor at atmospheric pressure. Reactions were conducted with 10 mmol of propanoic acid in 12.5 mL of methanol (molar ratio \( n_{\text{MeO}}/n_{\text{PA}} = 30 \)), 50 mg of catalyst and 0.59 mL of dihexylether as an internal standard. Samples were withdrawn periodically, separated with a strong magnet and diluted with methanol prior to analysis on a gas chromatograph (Varian 450-GC, Phenomenex ZB-50 15 m × 0.53 mm ×1.0 μm capillary column, FID detector).

3. Results and discussion:
The multistep synthesis of magnetic SZ core-shell nanoparticles illustrated in Scheme 1 was as follows (details provided in the Supporting Information). Monodispersed, 80 nm hematite (Fe₂O₃) nanoparticles were first prepared following the hydrothermal route of Matijević and Scheiner.[39] A dense silica layer was subsequently deposited by a classical Stöber method, to protect the iron core from corrosion and leaching during catalytic application, with the resulting Fe₂O₃@SiO₂ nanoparticles exhibiting a sharp core-shell interface and uniform 15 nm silica shells (Figure S1 in the Supporting Information). The silica shell thickness could be adjusted by varying the concentration of TEOS (tetraethyl orthosilicate) precursor.
Scheme 1. Stepwise synthesis of magnetically-separable Fe₃O₄@SiO₂@SO₄-ZrO₂ core-shell nanoparticle catalysts.

A zirconia shell was then grown around the Fe₂O₃@SiO₂ nanoparticles following the protocol of Schüth and co-workers, in which zirconium (IV) butoxide was hydrolysed in dry ethanol over the particles (whose surfaces were pre-modified by the adsorption of Lutensol A05 surfactant), prior to aging in water at room temperature for three days and 900 °C calcination to obtain Fe₂O₃@SiO₂@ZrO₂ onion-skin structures (Figure 1a and b). The ZrO₂ shell was uniform and approximately 28 nm thick, however the shell thickness and morphology could be adjusted by varying the ratio of zirconium (IV) butoxide to Lutensol AO5. Fe₂O₃@SiO₂@ZrO₂ nanoparticles agglomerated for high Zr:surfactant ratios (3.6:1 by volume), as seen in Figure 1c, possibly due to poor conformal zirconia growth. Decreasing the Zr:surfactant ratio reduced the zirconia shell thickness, improved its uniformity, and suppressed particle agglomeration (Figure 1d-e). The reduction in shell thickness to only 6.5 nm for the optimal 1:10 Zr:surfactant volumetric ratio could be reversed without any negative impact on particle morphology by simply increasing the concentrations of both zirconium (IV) butoxide and Lutensol AO5, while maintaining this optimal ratio, to achieve an outer shell of 10.6 nm (Figure 1e). Fe₂O₃@SiO₂@ZrO₂ nanoparticles exhibited high surface areas spanning 63-111 m².g⁻¹ (Table S1 in the Supporting Information). Fe₂O₃@SiO₂@ZrO₂ nanoparticles were then subject to a 450 °C treatment under H₂ to reduce the hematite core to magnetite (Fe₃O₄)[37] and hence facilitate their magnetic separation (Figure 1k). The resulting magnetic core-shell nanoparticles exhibited significant mesoporosity (BJH analysis revealed ~2.9 nm diameter mesopores, Figure S2 in Supporting Information). Following reduction,
the zirconia shell comprised solely tetragonal ZrO$_2$ crystallites of ~6.4 nm diameter (Figure S3 and Table S2 in the Supporting Information).

**Figure 1.** a) TEM image of Fe$_2$O$_3$@SiO$_2$@ZrO$_2$ prepared with a zirconium butoxide (mL):Lutensol AO5 (mL) ratio of 0.90: 0.25, and b) corresponding elemental line profile highlighting layered structure. Impact of changing zirconium butoxide (mL):Lutensol AO5 (mL) ratio on morphology of the core shell structure: c) 0.9:0.25, d) 0.3:0.25, and e) 0.15:1.5. f) magnetic separation of NH$_4$MSZ post-reaction.

The final step involved sulfation of the zirconia shell via wet impregnation with dilute H$_2$SO$_4$[24] (xMSZ, where x=[H$_2$SO$_4$]) or incipient-wetness impregnation with aqueous (NH$_4$)$_2$SO$_4$[40] (NH$_4$MSZ), followed by annealing at 550 °C under N$_2$. For this, Fe$_3$O$_4$@SiO$_2$@ZrO$_2$ nanoparticles were prepared using a 2:1 ratio of zirconium butoxide:Lutensol AO5 in order to provide the optimum balance between zirconia film thickness, uniformity and surface area. Sulfation by H$_2$SO$_4$ had negligible effect on the shell crystallinity, with zirconia remaining in tetragonal form as 5-6 nm particles (Figure S3 and Table S2 in the Supporting Information), but increased the surface area and pore volume relative to the unsulfated parent, possible reflecting corrosion of the zirconia and underlying silica shells. The latter hypothesis is supported by TEM, which evidenced numerous hollow nanoparticles following sulfation by H$_2$SO$_4$ (Figure S4 in the Supporting Information) consistent with leaching of iron from the Fe$_3$O$_4$ cores. In contrast, the NH$_4$MSZ material exhibited a significant decrease in surface area relative to the parent Fe$_2$O$_3$@SiO$_2$@ZrO$_2$, but retained magnetic Fe$_3$O$_4$ cores (Figure S5 in the Supporting Information), presumably due to the weaker acidity of the ammonium precursor. **Zr 3 XP spectra (Figure 2)** confirmed that the local zirconium chemical
environment in the sulfated shell of the magnetic nanoparticles was identical to that observed within nanocrystalline sulfated zirconia, with a binding energy of 182.5 eV.[25, 41, 42]

**Figure 2.** Zr 3d XP spectra of magnetic sulfated Fe₃O₄@SiO₂@ZrO₂ nanoparticles.

The sulfur content of all sulphated core-shell nanoparticles was subsequently quantified by bulk and surface elemental analysis (**Table 1**), and for the H₂SO₄ impregnated materials was directly proportional to the sulfate concentration, with bulk values increasing from 0.21→0.47 wt%.

**Table 1.** Surface and bulk properties of parent and sulphated magnetic Fe₃O₄@SiO₂@ZrO₂ nanoparticles

<table>
<thead>
<tr>
<th>Sample [a]</th>
<th>SO₄²⁻ precursor / mmol</th>
<th>Surface area [b] / m².g⁻¹</th>
<th>Pore volume [c] / cm³.g⁻¹</th>
<th>BJH pore diameter [c] / nm</th>
<th>Surface S content [d] / at%</th>
<th>Bulk S content [e] / wt%</th>
<th>Acid site loading [f] / mmol.g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄@SiO₂@ZrO₂</td>
<td>-</td>
<td>93</td>
<td>0.14</td>
<td>3.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.05MSZ</td>
<td>1.5</td>
<td>112</td>
<td>0.23</td>
<td>3.9</td>
<td>0.25</td>
<td>0.21</td>
<td>0.25</td>
</tr>
<tr>
<td>0.1MSZ</td>
<td>3</td>
<td>123</td>
<td>0.23</td>
<td>1.5</td>
<td>0.47</td>
<td>0.27</td>
<td>0.32</td>
</tr>
<tr>
<td>0.2MSZ</td>
<td>6</td>
<td>130</td>
<td>0.24</td>
<td>3.9</td>
<td>1.19</td>
<td>0.47</td>
<td>0.42</td>
</tr>
<tr>
<td>NH₄MSZ</td>
<td>2.3</td>
<td>42</td>
<td>0.19</td>
<td>1.5</td>
<td>4.19</td>
<td>7.29</td>
<td>2.75</td>
</tr>
<tr>
<td>SZ</td>
<td>-</td>
<td>172</td>
<td>0.24</td>
<td>3.4</td>
<td>-</td>
<td>3.23</td>
<td>0.78</td>
</tr>
</tbody>
</table>

[a] MSZ and NH₄MSZ refers to Fe₃O₄@SiO₂@ZrO₂ nanoparticles sulphated using H₂SO₄ or (NH₄)₂SO₄ respectively, the prefix refers to the [H₂SO₄] employed; [b] BET analysis; [c] from desorption branch of N₂ physisorption isotherm; [d] from XPS; [e] from CHNS elemental analysis; [f] from propylamine TGA-MS.
In contrast, incipient-wetness impregnation with a similar number of moles of (NH₄)₂SO₄ (2 mmoles per 0.3 g of sample) resulted in a S loading of 7.3 wt%. The trends in sulfur content were mirrored by corresponding acid site loadings determined by propylamine TPD (Table 1), increasing from modest values of 0.25→0.4 mmol(H⁺).g⁻¹ for the H₂SO₄ impregnated MSZs, whereas the NH₄MSZ material possessed 2.75 mmol(H⁺).g⁻¹ far exceeding that observed for a pure SZ reference. Acid loadings determined by propylamine temperature-programmed decomposition are extremely surface sensitive, and only titrate sulfur in the outermost surface of the magnetic nanoparticles. In contrast, S 2p XP spectra probe almost all of the sulfur present in the top 3 nm of the sulfated zirconia shell, due to the long inelastic mean free path of ~1300 eV kinetic energy photoelectrons. Table 1 shows that increasing the concentration of sulfuric acid used to impregnate the zirconia encapsulated magnetic nanoparticles resulted in greater penetration of sulfate ions throughout the zirconia matrix (detectable by XPS), but had little impact on the sulfate density in the terminating layer. Switching to an ammonium sulfate precursor increased both the sulfate surface density (and hence acid loading) and the overall degree of sulfation of the zirconia shell (and hence significantly enhanced S 2p XP signal and surface S content). DRIFT spectra of the pyridine titrated, sulfated magnetic nanoparticles shown Figure 3 all display similar strong (predominantly) Brønsted acid features, with a characteristic pure Brønsted band at 1535 cm⁻¹, and hence common acid character; any differences in their reactivity are therefore likely to reflect their differing acid loading (rather than Brønsted/Lewis acid character).
Figure 3. DRIFT spectra of pyridine titrated, magnetic sulfated Fe₃O₄@SiO₂@ZrO₂ nanoparticles with Brønsted and Lewis acid bands indicated.

The performance of MSZ nanoparticles was subsequently evaluated for propanoic acid esterification with methanol under mild conditions. Figure 4 shows the rate of esterification was directly proportional to acid site loading, with the H₂SO₄ impregnated MSZ nanoparticles exhibiting poor activity compared to a pure SZ reference, whereas the NH₄MSZ nanoparticles were approximately four times more active than SZ (165 versus 44 mmol.h⁻¹.g⁻¹) and achieved 93 % conversion in only 1 h. Recycle data on the most active NH₄MSZ catalyst revealed a modest loss of activity loss between a first and second reaction (propanoic acid conversion after 6 h falling from 100 → 71 %) possibly due to leaching of weakly bound sulfate species or poisoning of strong acid sites by organic residues.
Figure 4. Activity of conventional SZ and magnetic sulfated Fe$_3$O$_4$@SiO$_2$@ZrO$_2$ nanoparticles for propanoic acid esterification with methanol. Reaction conditions: 60 °C, 12.5 mL MeOH, 50 mg catalyst, molar MeOH:propanoic acid (30:1).

Corresponding Turnover Frequencies (TOFs) normalised per acid site reveal a monotonic increase from 5→52 h$^{-1}$ with [H$_2$SO$_4$] for the H$_2$SO$_4$ impregnated MSZs (Figure 5); this is attributed to a concomitant increase in acid strength, as previously observed for both pure SZ and SZ conformal monolayers grown on mesoporous silica frameworks. However, the NH$_4$MSZ TOF of 113 h$^{-1}$ was comparable to that of pure SZ possessing strong acid sites, while offering the benefit of facile magnetic separation post-reaction. Since TOFs do not convey information regarding the number of active sites, which is critical to their potential industrial exploitation, due consideration must be given to the specific activity (mass normalised rates of propanoic esterification) when benchmarking against commercial catalysts. Figure 4 highlights the clear superiority of our NH$_4$MSZ catalyst versus pure SZ in this regard.
Figure 5. TOFs of magnetic sulfated Fe$_3$O$_4$@SiO$_2$@ZrO$_2$ nanoparticles and conventional SZ for propanoic acid esterification with methanol. Reaction conditions: 60 °C, 12.5 mL MeOH, 50 mg catalyst, molar MeOH:propanoic acid (30:1).

4. Conclusions:

A new method for the preparation of magnetically-separable Fe$_3$O$_4$@SiO$_2$@SO$_4$-ZrO$_2$ core-shell nanoparticle catalysts has been developed. The thickness of the ZrO$_2$ shell in parent Fe$_3$O$_4$@SiO$_2$@ZrO$_2$ nano-particles could be controlled by adjusting the zirconium butoxide to Lutensol AO5 ratio, with 1:10 is confirmed to be the optimal ratio to give rise to mono-dispersed ZrO$_2$ nano-spheres. Sulfation of Fe$_3$O$_4$@SiO$_2$/ZrO$_2$ nanoparticles using (NH$_4$)$_2$SO$_4$ is less corrosive towards the ZrO$_2$ shell, generating materials with higher acid sites loadings (2.75 mmolg$^{-1}$) than achievable with H$_2$SO$_4$ (0.42mmolg$^{-1}$). All Fe$_3$O$_4$@SiO$_2$@SO$_4$-ZrO$_2$ samples were active for propanoic acid esterification, with the NH$_4$MSZ sample exhibiting a TOF of 113 h$^{-1}$, comparable to that of pure SZ but with the added advantage of magnetic separation. Future work will explore the use of mesoporous silica priming layers to further increase the surface area of the central Fe$_3$O$_4$@SiO$_2$ nanoparticle[15] prior to ZrO$_2$ grafting.[42]
Acknowledgements

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5. References