Supplementary Information

Green iodination of arenes using sulphated ceria-zirconia catalysts in polyethylene glycol

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A) Experimental

a) Catalyst preparation:

All chemicals were of analytical grade and were used without any further purification. The $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ were prepared by the method described by Lee et al.$^{1-2}$ Precipitate of $\text{Zr(OH)}_4$ was obtained by adding aqueous ammonia into an 0.25 M solution of zirconium oxychloride at room temperature with vigorous stirring until the pH of the mother liquor reached at 8. The preparation of catalyst doped with Ce and modified with sulphate simultaneously was carried out by adding an acidic aqueous solution of cerium sulphate ($\text{Ce(SO}_4)_2.4\text{H}_2\text{O}$) to the $\text{Zr(OH)}_4$ followed by drying at 110°C for 24 h and calcined at 650°C for 2 h. The series of catalysts were prepared by varying mol % of cerium (0.02-0.25) added in the catalyst.

b) Typical experimental procedure:

In typical reaction procedure of iodination, aniline (2 mmol), molecular iodine (2 mmol) were taken in 25 mL round bottom flask. $\text{SO}_4^{2-}/\text{Ce}_{0.07}\text{Zr}_{0.93}\text{O}_2$ (15 wt %) with 2 mL PEG-200 were added to it. The reaction mixture was stirred for 12 h at room temperature (30 °C). The reaction was continuously monitored by using TLC and gas chromatography. After completion of reaction, 10 mL of ethyl acetate was added to the reaction mass and catalyst was separated by simple filtration. The resulting reaction mass was treated with $\text{Na}_2\text{S}_2\text{O}_3$ solution (10 mL) and extracted with ethyl acetate (10 mL). The reaction mixture was then passed through a bed of anhydrous $\text{Na}_2\text{SO}_4$. Evaporation of the solvent afforded the iodo compound, which was purified by column chromatography on silica gel using a mixture of hexane/EtOAc (80:20). All the structures were confirmed by GC-MS.
B) Characterization data of the catalysts

a) FT-IR of the \( \text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{(1-x)}\text{O}_2 \)

![FT-IR spectra of \( \text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{(1-x)}\text{O}_2 \) catalysts.](image)

Figure 1. FT-IR spectra of \( \text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{(1-x)}\text{O}_2 \) catalysts.

FT-IR spectra were recorded for confirming the presence of sulphate ion units on the surface of ceria-zirconia. The intense absorption bands at around 1250, 1222, 1142 and 1096 cm\(^{-1}\) are assigned to the S-O stretching frequency region for bidentate sulphate ions coordinated to the metal. The former and the latter two bands are assigned to asymmetric and symmetric stretching vibrations of the O=S=O and O-S-O groups respectively. The bands at 1625 and 1635 cm\(^{-1}\) are assigned to the deformation vibration modes of the adsorbed water.\(^1\) These characteristic bands of bidentate sulphate ions are absent in
unsulfated ZrO₂ and CeO₂. In sulphated zirconia IR absorption bands were observed at the same region as that of the SO₄²⁻/CeₓZr₁−ₓO₂. In sulphated ceria, slight shift of absorption bands at 1300, 1143, 1196 and 1056 cm⁻¹ was observed.

b) TGA-DSC curve of SO₄²⁻/CeₓZr₁−ₓO₂ catalysts
Thermal stability of SO$_4^{2-}$/CexZr$_{1-x}$O$_2$ (x= 0.2-0.25) catalysts was investigated by DSC-TGA thermal analysis. The first weight loss for all the compositions occurs below 200 °C which is due to the loss of physically adsorbed water. The catalysts exhibit good thermal stability and no remarkable weight loss was observed further up to 700 °C. Next prominent weight loss of the catalysts occurs at 700 °C to 900 °C mainly due to decomposition of sulphate species with the evolution of SO$_3$ (a-f). The endothermic peaks at 712–785 °C observed in the case of SO$_4^{2-}$/Ce$_x$Zr$_{1-x}$O$_2$ (x=0.2-0.25) samples are due to the evolution of SO$_3$ from sulphate species bonded to the surface of Ce-doped ZrO$_2$. The decomposition temperature depends on the amount of Ce and sulphate species present in the catalyst. The decomposition temperature increases (713-785 °C) with increasing Ce content from 0.02-25 mol%, resulting in increased thermal stability of the surface sulphate species.
c) XRD of the Catalysts:

Figure 3. XRD patterns of (a) ZrO₂, (b) CeO₂, (c) SO₄²⁻/ZrO₂, (d) SO₄²⁻/Ce₀.0₂Zr₀.9₈O₂, (e) SO₄²⁻/Ce₀.0₇Zr₀.9₃O₂, (f) SO₄²⁻/Ce₀.1₀Zr₀.9₀O₂, (g) SO₄²⁻/Ce₀.1₅Zr₀.₈₅O₂, (h) SO₄²⁻/Ce₀.₂₀Zr₀.₈₀O₂, (i) SO₄²⁻/Ce₀.₂₅Zr₀.₇₅O₂

The XRD patterns of sulphated metal oxides and mixed metal oxides with different Ce content are shown in figure 3. All the samples were crystalline in nature, wherein CeO₂ forms a solid solution with ZrO₂. SO₄²⁻/CeₓZr₁₋ₓO₂ (x = 0.02-0.25 mol%) show characteristics peaks of catalytically active tetragonal phase (2θ = 30.18° (with 100 as relative intensity) and the peaks located at 34.616°, 35.283°, 50.214°, 50.770°, 59.291°, 60.187°, 62.724° and 74.617°) [d-i]. The oxide of cerium (CeO₂) shows characteristic peaks of fluorite phase whereas ZrO₂ was present in both tetragonal and monoclinic phases (a-b). Sulphated zirconia shows characteristic peaks of tetragonal phase which is supposed to be the catalytically active phase (c). d) BET surface area and number and relative strength of acid sites by potentiometric method
Table 1. BET surface area and number and relative strength of acid sites by potentiometric method with conversion and selectivity

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface area (m².g⁻¹)</th>
<th>Acidity (mmol/g)</th>
<th>(E_i) (mV)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>12</td>
<td>0.8</td>
<td>55</td>
<td>60</td>
<td>93/7</td>
</tr>
<tr>
<td>CeO₂</td>
<td>10</td>
<td>0.3</td>
<td>27</td>
<td>45</td>
<td>91/9</td>
</tr>
<tr>
<td>(\text{SO}_4^{2-}/\text{ZrO}_2)</td>
<td>37</td>
<td>2.07</td>
<td>168</td>
<td>84</td>
<td>96/4</td>
</tr>
<tr>
<td>(\text{SO}_4^{2-}/\text{CeO}_2)</td>
<td>23</td>
<td>1.22</td>
<td>154</td>
<td>54</td>
<td>85/15</td>
</tr>
<tr>
<td>(\text{Ce}<em>{0.07}\text{Zr}</em>{0.93}\text{O}_2)</td>
<td>17</td>
<td>1.54</td>
<td>157</td>
<td>43</td>
<td>100</td>
</tr>
<tr>
<td>(\text{SO}_4^{2-}/\text{CeO}_2+\text{SO}_4^{2-}/\text{ZrO}_2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>65</td>
<td>88/12</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Ce}</em>{0.02}\text{Zr}_{0.98}\text{O}_2)</td>
<td>22</td>
<td>3.17</td>
<td>440</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Ce}</em>{0.07}\text{Zr}_{0.93}\text{O}_2)</td>
<td>53</td>
<td>4.23</td>
<td>560</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Ce}</em>{0.10}\text{Zr}_{0.90}\text{O}_2)</td>
<td>28</td>
<td>3.52</td>
<td>450</td>
<td>82</td>
<td>100</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Ce}</em>{0.15}\text{Zr}_{0.85}\text{O}_2)</td>
<td>14</td>
<td>3.50</td>
<td>460</td>
<td>62</td>
<td>98/2</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Ce}</em>{0.20}\text{Zr}_{0.80}\text{O}_2)</td>
<td>12</td>
<td>2.97</td>
<td>248</td>
<td>57</td>
<td>95/5</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Ce}</em>{0.25}\text{Zr}_{0.75}\text{O}_2)</td>
<td>10</td>
<td>2.17</td>
<td>197</td>
<td>53</td>
<td>95/5</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Y}</em>{0.04}\text{Zr}_{0.96}\text{O}_2)</td>
<td>34</td>
<td>1.23</td>
<td>148</td>
<td>56</td>
<td>92/8</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Y}</em>{0.08}\text{Zr}_{0.92}\text{O}_2)</td>
<td>43</td>
<td>1.64</td>
<td>195</td>
<td>54</td>
<td>90/10</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Y}</em>{0.12}\text{Zr}_{0.88}\text{O}_2)</td>
<td>52</td>
<td>1.93</td>
<td>310</td>
<td>68</td>
<td>90/10</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Y}</em>{0.16}\text{Zr}_{0.84}\text{O}_2)</td>
<td>75</td>
<td>4.19</td>
<td>530</td>
<td>92</td>
<td>94/6</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Y}</em>{0.20}\text{Zr}_{0.80}\text{O}_2)</td>
<td>35</td>
<td>2.91</td>
<td>330</td>
<td>69</td>
<td>99/1</td>
</tr>
<tr>
<td>(\text{SO}<em>4^{2-}/\text{Y}</em>{0.24}\text{Zr}_{0.76}\text{O}_2)</td>
<td>29</td>
<td>2.65</td>
<td>248</td>
<td>60</td>
<td>100</td>
</tr>
</tbody>
</table>

\(^a\)Sulphated ceria-zirconia catalysts are calcined at 650 °C for 2 h. \(^b\)Total number of acid sites determined by n-butylamine potentiometric titration. \(^c\)\(E_i\)- Initial electrode potential (mV). \(^d\)(%) Selectivity, para/ortho isomers for iodoaniline synthesis.
BET surface areas of the as synthesized \( \text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \) (X=0.02-0.25) catalysts were determined (Table 1). The results indicate that both the surface area and acidity (Figure 4) are dependent on Ce: Zr ratio of the catalyst. \( \text{SO}_4^{2-}/\text{Ce}_{0.07}\text{Zr}_{0.93}\text{O}_2 \) has the highest surface area as compared to other compositions of \( \text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2 \).

**Figure 4.** Potentiometric titration curves for (a) \( \text{SO}_4^{2-}/\text{Ce}_{0.02}\text{Zr}_{0.98}\text{O}_2 \) (b) \( \text{SO}_4^{2-}/\text{Ce}_{0.07}\text{Zr}_{0.93}\text{O}_2 \) (c) \( \text{SO}_4^{2-}/\text{Ce}_{0.10}\text{Zr}_{0.90}\text{O}_2 \) (d) \( \text{SO}_4^{2-}/\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2 \) (e) \( \text{SO}_4^{2-}/\text{Ce}_{0.07}\text{Zr}_{0.93}\text{O}_2 \) (f) \( \text{SO}_4^{2-}/\text{Ce}_{0.20}\text{Zr}_{0.80}\text{O}_2 \) (g) \( \text{SO}_4^{2-}/\text{CeO}_2 \) (h) \( \text{SO}_4^{2-}/\text{ZrO}_2 \) (i) \( \text{CeO}_2 \) (j) \( \text{SO}_4^{2-}/\text{ZrO}_2 \) (k) \( \text{SO}_4^{2-}/\text{Ce}_{0.13}\text{Zr}_{0.87}\text{O}_2 \)
d) Surface morphology of $\text{SO}_4^{2-}/\text{Ce}_{0.07}\text{Zr}_{0.93}\text{O}_2$ catalyst

**Figure 5.** SEM-EDX analysis of $\text{SO}_4^{2-}/\text{Ce}_{0.7}\text{Zr}_{0.93}\text{O}_2$ composition

SEM images were recorded using a Tungsten source on JEOL model JSM-6390 instrument. EDX-XAF analysis showed 7 mol% of Ce and 93.0 mol% of Zr in case of $\text{SO}_4^{2-}/\text{Ce}_{0.7}\text{Zr}_{0.93}\text{O}_2$. The results are in well agreement with the calculations and minimal difference was observed (**Figure 5**).
Table 2. Surface ratio of Ce/Zr and surface density of sulphate for SO$_4^{2-}$/Ce$_x$Zr$_{1-x}$O$_2$

<table>
<thead>
<tr>
<th>No</th>
<th>BET Surface area (m$^2$.g$^{-1}$)</th>
<th>Catalyst</th>
<th>Ce/Zr</th>
<th>Surface density of sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22</td>
<td>SO$<em>4^{2-}$/Ce$</em>{0.02}$Zr$_{0.98}$O$_2$</td>
<td>0.020</td>
<td>3.3</td>
</tr>
<tr>
<td>2</td>
<td>53</td>
<td>SO$<em>4^{2-}$/Ce$</em>{0.07}$Zr$_{0.93}$O$_2$</td>
<td>0.075</td>
<td>8.1</td>
</tr>
<tr>
<td>3</td>
<td>28</td>
<td>SO$<em>4^{2-}$/Ce$</em>{0.10}$Zr$_{0.90}$O$_2$</td>
<td>0.111</td>
<td>7.2</td>
</tr>
<tr>
<td>4</td>
<td>14</td>
<td>SO$<em>4^{2-}$/Ce$</em>{0.15}$Zr$_{0.85}$O$_2$</td>
<td>0.176</td>
<td>5.5</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>SO$<em>4^{2-}$/Ce$</em>{0.20}$Zr$_{0.80}$O$_2$</td>
<td>0.25</td>
<td>5.2</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>SO$<em>4^{2-}$/Ce$</em>{0.25}$Zr$_{0.75}$O$_2$</td>
<td>0.333</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Ce/Zr and surface density of sulphate were determined by EDAX method.

The surface ratio (Ce/Zr) 0.075 showed highest surface density of sulphate in sulphated ceria-zirconia. The highest surface density of sulphate resulted in the increase of total number of acidic sites for SO$_4^{2-}$/Ce$_{0.07}$Zr$_{0.93}$O$_2$ composition. For all the other compositions, the surface densities of sulphate were found to be lower and the total numbers of acid sites are also low.
C) (UV-Vis spectra of I$_2$+PEG).
The value of $\lambda_{\text{max}} = 360$ nm for the diatomic I$_2$ state and whose interatomic distance is a little prolonged by the interaction with solvent molecules$^3$ (PEG-200,400,600 (b to d). The intensity of $\lambda_{\text{max}} = 360$ nm for I$_2$+Ethanol is very small (e).

*Figure 6*, U.V-Vis spectra for (a) PEG-200 (b) I$_2$+PEG-200 (c) I$_2$+PEG-400 (d) I$_2$+PEG-600 (e) I$_2$+Ethanol
D) Spectral data:

**4-Iodo-aniline** (Figure 7)

**GC-MS** (EI, 70 eV): \(m/z\) (%) = 219 (100 %) \([M^+]\), 127 (3 %), 109 (10 %), 92 (51 %), 65 (50 %), 52 (5 %)

**2, 4-Diiodoaniline** (Figure 8)

**GC-MS** (EI, 70 eV): \(m/z\) (%) = 345 (100 %) \([M^+]\), 269 (10 %), 218 (25 %), 91 (45 %), 77 (5 %), 63 (22 %), 52 (18 %), 41 (11 %)

**2-Nitro-4-iodoaniline** (Figure 9)

**GC-MS** (EI, 70 eV): \(m/z\) (%) = 264 (100 %) \([M^+]\), 234 (10 %), 218 (30 %), 107 (8 %), 91 (45 %), 63 (20 %), 52 (17 %)

**3-Nitro-4-iodoaniline** (Figure 10)

**GC-MS** (EI, 70 eV): \(m/z\) (%) = 264 (100 %) \([M^+]\), 234 (10 %), 218 (28 %), 206 (10 %), 151 (20 %), 91 (95 %), 64 (29 %), 52 (30 %)

**4-Nitro-2-iodoaniline** (Figure 11)

**GC-MS** (EI, 70 eV): \(m/z\) (%) = 264 (100 %) \([M^+]\), 234 (50 %), 218 (10 %), 91 (80 %), 63 (26 %).

**3-Chloro-4-iodoaniline** (Figure 12)

**GC-MS** (EI, 70 eV): \(m/z\) (%) = 255 (33 %) \([M^+]\), 253 (100 %), 128 (15 %), 126 (50 %), 99 (28 %), 90 (25 %), 63 (30 %).

**4-Chloro-2-iodo-aniline** (Figure 13)

**GC-MS** (EI, 70 eV): \(m/z\) (%) = 255 (33 %) \([M^+]\), 253 (100 %), 128 (15 %), 126 (45 %), 101 (5 %), 99 (23 %), 90 (25 %), 63 (27 %), 52 (8 %).
4-Iododiphenyl amine (Figure 14)
GC-MS (EI, 70 eV): \(m/z\) (%) = 295 (100 %) [M⁺], 167 (60 %), 139 (15 %), 121 (5 %), 84 (20 %), 65 (5 %), 51 (7 %).

4-Iododiphenyl ether (Figure 15)
GC-MS (EI, 70 eV): \(m/z\) (%) = 296 (100 %) [M⁺], 141 (45 %), 115 (35 %), 92 (7 %), 77 (25 %), 63 (13 %), 51 (15 %)

4-Iodo-N, N-Dimethylaniline (Figure 16)
GC-MS (EI, 70 eV): \(m/z\) (%) = 247 (100 %) [M⁺], 231 (5 %), 119 (20 %), 105 (10 %), 91 (5 %), 77 (12 %), 63 (8 %), 42 (13 %)

4-Methyl-2-iodoaniline (Figure 17)
GC-MS (EI, 70 eV): \(m/z\) (%) = 234 (5 %) [M⁺], 107 (3 %), 102 (5 %), 89 (18 %), 87 (73 %), 75 (8 %), 58 (25 %), 45 (100 %), 43 (95).

4-iodo-anisole (Figure 18)
GC-MS (EI, 70 eV): \(m/z\) (%) = 234 (7 %) [M⁺], 107 (17 %), 88 (20 %), 75 (10 %), 71 (100 %), 58 (70 %).

4-methyl-2-iodo-phenol (Figure 19)
GC-MS (EI, 70 eV): \(m/z\) (%) = 234 (100 %) [M⁺], 107 (50 %), 77 (40 %), 51 (20 %).

4-Tert-butyl-2-iodophenol (Figure 20)
GC-MS (EI, 70 eV): \(m/z\) (%) = 276 (28 %) [M⁺], 261 (100 %), 233 (8 %), 134 (30 %)

2-Hydroxy-5-iodobenzaldehyde (Figure 21)
GC-MS (EI, 70 eV): \(m/z\) (%) = 248 (100 %) [M⁺], 229 (6 %), 219 (8 %), 92 (8 %), 75 (10 %), 65 (23 %), 45 (37 %)
4-chloro-2-iodo-phenol (Figure 22)

GC-MS (EI, 70 eV): $m/z$ (%) = 255 (30 %) [M$^+$], 254 (100 %), 127 (30 %), 99 (40 %), 63 (39 %).

2, 4-dichloro-6-iodo-phenol (Figure 23)

GC-MS (EI, 70 eV): $m/z$ (%) = 289 (60 %) [M$^+$], 288 (100 %), 161 (10 %), 133 (40 %), 97 (35 %), 73 (10 %), 62 (30 %).

2,2,4-trimethyl-1,2-dihydroquinoline (Figure 25)

GC-MS (EI, 70 eV): (Figure 4.38) $m/z$ (%) = 173 (9 %) [M$^+$], 158 (100 %), 143 (7 %), 115 (8 %)

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**Figure 7.** Mass spectrum of 4-iodoaniline
Figure 8. Mass spectrum of 2,4-diiodoaniline

Figure 9. Mass spectrum of 2-nitro-4-iodoaniline
Figure 10. Mass spectrum of 3-nitro-4-iodoaniline

Figure 11. Mass spectrum of 4-nitro-2-iodoaniline
Figure 12. Mass spectrum of 3-Chloro-4-iodoaniline

Figure 13. Mass spectrum of 4-Chloro-2-iodoaniline
Figure 14. Mass spectrum of 4-iodo-N-phenylaniline

Figure 15. Mass spectrum of 4-iododiphenyl ether
Figure 16. Mass spectrum of 4-iodo-$N,N$-dimethylbenzenamine

Figure 17. Mass spectrum of 2-iodo-4-methylaniline
**Figure 18.** Mass spectrum of 4-iodo-anisole

**Figure 19.** Mass spectrum of 4-methyl-2-iodo-phenol
Figure 20. Mass spectrum of 2-hydroxy-5-iodobenzaldehyde

Figure 21. Mass spectrum of 4-chloro-2-iodo-phenol
Figure 22. Mass spectrum of 2,4 dichloro-4-iodophenol

Figure 23. Mass spectrum of 4-tert-butyl-2-iodophenol
**Figure 24.** Gas Chromatogram of 2,2,4-trimethyl-1,2-dihydroquinoline (R.T-7.30 min).

**Figure 25.** Mass spectrum of 2,2,4-trimethyl-1,2-dihydroquinoline
References:

