Supporting Information

The details of synthesis, characterization and catalytic reactions, \( \text{N}_2 \) adsorption-desorption isotherms, the calculation of percentage of \{001\} facets and proposed mechanism of reaction are provided here.

**Synthesis of TiO\(_2\)**

5 ml of Ti(OC\(_4\)H\(_9\))\(_4\) was mixed with a certain amount of hydrofluoric acid (40–48 wt.%) (*Caution: hydrofluoric acid is extremely corrosive and it should be handled with extreme care!* ) in a Teflon-lined autoclave with a capacity of 40 ml and subsequently heated to 180 °C at a ramp rate of 2 °C·min\(^{-1}\). The temperature was kept at 180 °C for 24 h. After hydrothermal reaction, the white precipitate was collected, washed with ethanol and distilled water three times, and then dried in an oven at 80 °C overnight. 0.6 ml and 0.2 ml of hydrofluoric acid was added for ST\(_{001}\) and ST\(_{001/101}\), respectively, while, instead of hydrofluoric acid, 0.6 ml of H\(_2\)O was employed for ST\(_{101}\).

The removal of fluorine on surface is described below: 1 g of as-prepared TiO\(_2\) was treated in 50 ml of 0.1 M NaOH solution under magnetic stirring for 10 h. Then the solid sample was washed with distilled water several times until neutral. After centrifugation, the solid was dried at 80 °C overnight.

**Sulfation of TiO\(_2\)**

To obtain the sulfated catalyst, ammonium sulphate, (NH\(_4\))\(_2\)SO\(_4\), was utilized as an initial precursor of sulfate in the catalyst preparation. 1 g of fluorine-free TiO\(_2\) was added into 10 ml of 1 mol·L\(^{-1}\) (NH\(_4\))\(_2\)SO\(_4\) solution to stir for 8 h, and then collected and dried. Afterwards, the dried solid was calcinated at 450 °C for 4 h.

**Characterization**

XRD patterns were recorded on a Bruker D8 Advance diffractometer with Cu \( K\alpha \) radiation (\( \lambda = 0.15418 \) nm) operated at 40 mA and 40 kV. The scanning rate was 3 °·min\(^{-1}\) from 20 to 80°. The FT-IR spectra were recorded in the range of 4000-400 cm\(^{-1}\) with a Nicolet Nexus 470 FTIR spectrometer using KBr pellets. TEM images of the catalysts were taken with a JEOL 2010 transmission electron microscope operating at 200 kV. Samples were dispersed in ethanol and deposited onto a carbon-coated copper grid. Elemental analysis was performed on a Thermo Elemental IRIS Intrepid ICP atomic emission spectrometer. \( \text{N}_2 \) adsorption-desorption isotherms were obtained at -196 °C using a Micromeritics Tristar 3000 apparatus.

**Sample treatment for NMR measurements**

A certain amount of catalyst was placed in a home-made glass tube, which was subsequently connected to a vacuum system. After pretreating the catalyst at 573 K for 1.5 h under vacuum (10\(^{-1}\) Pa), the tube was immersed in liquid nitrogen to introduce a certain amount of adsorbed molecules. Then the tube was carefully flame sealed. Prior to NMR experiment, the sample was transferred into a Bruker 4 mm zirconia rotor with a Kel-F endcap in a glove box under a dry nitrogen atmosphere.
Catalytic activity test

The catalytic activities of sulfated titania catalysts were studied for the synthesis of 5,7-dihydroxy-4-methyl coumarin from phloroglucinol and ethyl acetoacetate under solvent free condition. In a typical reaction, 5 mmol of phloroglucinol was reacted with 10 mmol of ethyl acetoacetate in the presence of 0.1 g of catalyst. The reaction mixture was kept at 130 °C under reflux for a desired time. On completion of the reaction, the mixture was allowed to cool down to the room temperature followed by the addition of ethanol. The reaction mixture was filtered to separate the catalyst and the filtrate was analysed by liquid chromatography (DIONEX U3000). The yield of 5,7-dihydroxy-4-methyl coumarin was calculated as follows:

\[
\text{Yield} \% = \frac{(\text{Obtained weight of product})}{(\text{Theoretical weight of product})} \times 100
\]

The catalyst was recovered by washing with ethanol, centrifugation and drying.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume of HF[^a] (ml)</th>
<th>Crystallite size (nm)</th>
<th>Percentage of {001} facets</th>
<th>(S_{\text{BET}}[^b]) (m(^2)·g(^{-1}))</th>
<th>Content of SO(_4^{2-})[^c] (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST(_{001})</td>
<td>0.6</td>
<td>50×6</td>
<td>80%</td>
<td>67.4</td>
<td>6.6%</td>
</tr>
<tr>
<td>ST(_{001/101})</td>
<td>0.2</td>
<td>25×10</td>
<td>54%</td>
<td>77.3</td>
<td>5.5%</td>
</tr>
<tr>
<td>ST(_{101})</td>
<td>0</td>
<td>10</td>
<td>&lt; 10%</td>
<td>107</td>
<td>5.7%</td>
</tr>
</tbody>
</table>

[^a] Volume of HF employed during the preparation of TiO\(_2\) (with 5 ml of Ti(OC\(_4\)H\(_9\))\(_4\)).

[^b] BET surface area.

[^c] Determined by ICP analysis.

Fig. S1 XRD patterns of TiO\(_2\) parent samples before sulfation treatment.
Fig. S2 TEM images of TiO$_2$ parent samples before sulfation treatment: (a) TiO$_2$-{101}, (b) TiO$_2$-{001}/ {101}, (c) HRTEM image of TiO$_2$-{001}/ {101}, (d) TEM image of TiO$_2$-{001}.

Fig. S3 Simulated shape of the TiO$_2$ anatase single crystal and the calculation process for percentage of {001} facets (AB and CD are considered of the same value approximately, equal to side length of truncated octahedral bipyramid in TEM images, AE is equal to the thickness, θ of 68.3° is the interfacial angle between (001) and (101)).
Fig. S4 N₂ adsorption-desorption isotherms for ST₀₀₁, ST₀₀₁/₁₀₁ and ST₁₀₁.

Fig. S5 Raman spectra of ST₀₀₁, ST₀₀₁/₁₀₁ and ST₁₀₁ and their TiO₂ parent samples.

Fig. S6 Comparison of catalytic activities of ST₀₀₁, ST₀₀₁/₁₀₁ and ST₁₀₁ and their TiO₂ parent samples. Reaction time is 3 h.
Fig. S7 XRD patterns of ST\textsubscript{001}, ST\textsubscript{001/101} and ST\textsubscript{101} after the Pechmann condensation.

Fig. S8 FT-IR spectra of ST\textsubscript{001}, ST\textsubscript{001/101} and ST\textsubscript{101} after the Pechmann condensation.