Efficient Fenton-like La-Cu-O/SBA-15 catalyst for the degradation of organic dyes under ambient conditions

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Experimental

Preparation of catalyst

La-Cu-O/SBA-15 was prepared by impregnation method. Briefly, La(NO\textsubscript{3})\textsubscript{3}·nH\textsubscript{2}O (0.01mol), Cu(NO\textsubscript{3})\textsubscript{2}·9H\textsubscript{2}O (0.01mol), citric acid (0.024mol), de-ionized water (10mL) and ethanol (20mL) were first mixed, and to this solution 2 g of pre-prepared SBA-15\textsuperscript{[1]} was added. The resulting slurry was stirred and heated to 70 °C until it became gel status. The gel was then dried at 100 °C, calcined at 500 °C for 4 h and then at 700 °C for another 4 h in air atmosphere, with a heating rate of 2 °C/min at each temperature-rise stage (RT→500 °C, 500→700 °C). The initial purpose of this procedure is to synthesize a SBA-15 supported LaCuO\textsubscript{3} sample, but later we found, from the XRD patterns, that the oxides produced is not in LaCuO\textsubscript{3} phase, but contains a mixture of La\textsubscript{2}CuO\textsubscript{4} and CuO phase. Therefore, this sample was defined as La-Cu-O/SBA-15 for simplicity.

The synthesis of La\textsubscript{2}CuO\textsubscript{4}/SBA-15 and CuO/SBA-15 was similar to that of La-Cu-O/SBA-15 except that the dosage of metal nitrates and citric acid was used according to the stoichiometric ratio of La\textsubscript{2}CuO\textsubscript{4} and CuO. The loading of Cu-containing compounds was kept to be 55.6%, 67.0% and 28.6% in weight for La-Cu-O/SBA-15, La\textsubscript{2}CuO\textsubscript{4}/SBA-15 and CuO/SBA-15, in order to maintain the same copper content in each sample. Bulk La-Cu-O was prepared as that of La-Cu-O/SBA-15 except the use of SBA-15.

Characterizations.

X-Ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer (Cu Kα irradiation). The 2θ angle ranged from 0.5° to 5° and 10° to 80° for the small-angle and wide-angle measurements, respectively. N\textsubscript{2} physisorption isotherms were determined at liquid-nitrogen temperature (-196 °C) with an Autosorb-1 apparatus. The sample was degassed at 150 °C overnight before measurement. Transmission electron microscopy (TEM) images were obtained on a Tecnai G\textsuperscript{2} 20 S-Twin apparatus with high-resolution transmission electron microscope. Copper grids were used to load the samples for analysis. Thermal gravimetric analysis (TGA) was performed on a NETZSCH TG 209F3 equipment at a heating rate of 5 °C min\textsuperscript{-1} in oxygen using Al\textsubscript{2}O\textsubscript{3} crucibles.

CO\textsubscript{2} produced from RhB degradation was measured as below. The saturated La-Cu-O/SBA-15 (0.1g) was added to a one-neck round bottom flask (50 mL) filled with 50 mL of RhB solution (1 mmol/L). The neck was equipped with a soap film flow meter. After stirring for 30 min (stirring rate of 600 rpm), 1 mL H\textsubscript{2}O\textsubscript{2} (30%, w/w) was added to
the solution to start the catalytic test. The amount of CO₂ produced at different reaction time was evaluated by calculating the volume of the film moved.

**Catalytic tests**

An adsorption procedure was conducted before the catalytic test, in order to exclude that the decrease in the concentration is not attributed to the adsorption of RhB on the catalyst. For this purpose, 0.1 g La-Cu-O/SBA-15 powder was first added to 50 mL RhB solution (0.02 mmol/L) and adsorption procedures were conducted until reaching adsorption/desorption equilibrium (i.e., no change in the absorbance with the adsorption time). The saturated catalyst was then filtered and put into a fresh RhB solution (50 mL, 0.02 mmol/L). After stirring for 30 min (stirring rate of 600 rpm), 1 mL H₂O₂ (30%, w/w) was added to the solution to start the catalytic test. 4 mL aliquots were collected by filtration at a desired reaction time and the absorbance was measured by a spectrophotometer (Model: 722E, Shanghai Spectrum Instruments, China) at wavelength of 550 nm. Both the adsorption and catalytic tests were conducted at room temperature. The concentration of RhB before and after reaction was calibrated using a standard concentration vs. absorbance curve made by an external standard method. The activity was calculated as: % conversion = (C₀ − Cₐ) / C₀ * 100, where C₀ and Cₐ represent the concentration of RhB before and after reaction, respectively.

After the oxidation reaction, the catalysts were filtered, dried in an oven at 100 °C for several hours, and put to a new batch of RhB solution to start the second cycle. This time the sample also underwent an adsorption procedure as the fresh one. The amount of catalyst in each run was balanced to 0.1 g by adding few amounts of used catalysts that were obtained from parallel experiments. This procedure was repeated five times to study the reusability of La-Cu-O/SBA-15.

In evaluating the catalytic efficiency of the catalyst, we referred to the reaction rate, which was calculated as: mol of RhB converted per hour and per total mol of copper.
Table S1. Degradation of RhB over different perovskite-type catalysts under various conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H₂O₂ : Catalyst: RhBᵃ</th>
<th>Reaction Rate (h⁻¹, ×10⁻³)ᵇ</th>
<th>Reference</th>
<th>Remark[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFeO₃</td>
<td>0 : 206 : 1</td>
<td>5.37</td>
<td>[2]</td>
<td>Vis</td>
</tr>
<tr>
<td>porous SrTiO₃</td>
<td>0 : 272 : 1</td>
<td>7.34</td>
<td>[3]</td>
<td>UV</td>
</tr>
<tr>
<td>BiFeO₃</td>
<td>100 : 639 : 1</td>
<td>0.91</td>
<td>[4]</td>
<td>Vis-H₂O₂</td>
</tr>
<tr>
<td>La-Cu-O/SBA-15</td>
<td>9910 : 224 : 1</td>
<td>8.95</td>
<td>This work</td>
<td>H₂O₂</td>
</tr>
<tr>
<td></td>
<td>198 : 13 : 1</td>
<td>109.48</td>
<td>This work</td>
<td>H₂O₂</td>
</tr>
</tbody>
</table>

ᵃ Molar ratio of H₂O₂ : Catalyst: RhB; ᵇ The value was measured at reaction time of 30 min.; ᶜ Reaction conditions used in the catalytic system.

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