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SOx trapping performances of cuo based silica mesoporous adsorbents for desulfurization of industrial flue gas stream

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SOx trapping performances of CuO based silica mesoporous adsorbents for the desulfurization of industrial flue gas stream

Industrial SOx emissions

Production of energy

Fossil fuels combustion → Gaseous pollutants

Power Plant (e.g. turbines)
Industrial boilers

SOx (SO$_2$ + SO$_3$)

SO$_x$: negative impact on:
- Environment (acid rain, precursors of secondary aerosols)
- Human health
Industrial SOx emissions abatement

SOx emissions ➞ Strict Regulation at industrial level ➞ SOx emissions abatement

Industrial Emissions Directive (IED) 2010/75/EU

Traditional Desulfurization processes: wet and dry scrubbing

- Efficient
- Non regenerative
- Produce additional greenhouse gas CO₂ and large amount of solid and liquid wastes
- High energy cost

Alternative solution: reversible SOx trapping on solid adsorbents

Promising material: supported CuO

Adsorbent requirements

Oxidation catalyst: \( \text{SO}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{CuO}} \text{SO}_3 \)

SO₃ chemisorption: \( \text{SO}_3 + \text{CuO} \xrightarrow{\text{CuSO}_4} \text{CuSO}_4 \)

Regeneration: \( \text{CuSO}_4 \xrightarrow{\Delta (600-700^\circ C)} \text{SO}_3 + \text{CuO} \)
Elaboration of a regenerable adsorbent with high SOx adsorption performances

- Inert in regards with SOx
- High specific surface area and mesoporous volume
- Easy diffusion of SOx in the porous network

Organized Mesoporous Silica supports

SBA-15

Copper incorporation: wet impregnation in aqueous solution

Characterizations of the adsorbents: N₂ physisorption/XRF/XRD/ and TEM analyses

Study of SOx adsorption capacity during cycling experiments at laboratory scale in fixed bed reactor
Adsorbents synthesis

SBA-15

Copper nitrate

Wet impregnation in aqueous solution: \( T_{\text{ambient}} \)

Drying: 45°C during 12 hours

Calcination step:
500°C during 6 hours (ramp of 1°C.min\(^{-1}\))
in fixed bed reactor under synthetic air flow (60 NL.min\(^{-1}\))

Three metal loadings: 8.8 wt.% - 15.6 wt.% - 31.7 wt.% of CuO

CuO8.8/SBA-15

CuO15.6/SBA-15

CuO31.7/SBA-15
SO\textsubscript{2} adsorption tests

Cycling experiments in fixed bed reactor

SO\textsubscript{2} adsorption conditions:
- reactor: quartz, \( \Phi_{\text{internal}} = 6 \text{ mm} \)
- adsorbent shaping: 250-400 \( \mu \text{m} \),
- mass: 150 to 200 mg
- gas feed composition: 250 ppm SO\textsubscript{2} + 10 vol.% O\textsubscript{2} in N\textsubscript{2}
- GHSV = 25000 h\textsuperscript{-1}
- temperature: 400°C

Regeneration conditions:
Two different procedures at two temperatures:

1. Under N\textsubscript{2} at 600°C
2. Under H\textsubscript{2} (0.5 vol.% in N\textsubscript{2}) at 280°C
   (with regen. 1 under N\textsubscript{2} at 600°C)
Textural characterization

N₂ physioption isotherms

- No alteration of the mesoporous structure after impregnation and calcination steps
- Decrease of the BET surface area, pore size and porous volume after copper incorporation, more pronounced for higher copper loadings
**Adsorbents characterizations**

**TEM analyses**

- **CuO8.8/SBA-15**
- **CuO15.6/SBA-15**
- **CuO31.7/SBA-15**

- XRD analyses: no diffraction peak corresponding to a copper crystalline phase
- TEM analyses: no copper particles observed: copper highly dispersed for all materials, probably formation of Cu-O-Si species\(^a,b\)

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**Synthesis conditions used prevent copper sintering phenomenon and generate copper species in strong interaction with the support SBA-15**


Results

SO₂ adsorption tests: cycling experiments

Regeneration under N₂ at 600°C

CuO8.8/SBA-15

SO₂ breakthrough curves

CuO31.7/SBA-15

SO₂ breakthrough curves

CuO15.6/SBA-15

SO₂ breakthrough curves

 No deactivation, even after 9 cycles
 Strong increase of performances from the 2nd SO₂ chemisorption

 The best SO₂ adsorption capacity during adsorption 1
 Important deactivation from adsorption 2

 Interesting SO₂ adsorption capacities obtained along cycling experiments with a relatively weak deactivation
 The best performances after 5 cycles
### SO₂ adsorption tests: cycling experiments

#### Regeneration under N₂ at 600°C

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>SO₂ adsorption capacity at 75 ppm (mgSO₂·g⁻¹)</th>
<th>Copper sulfation rate at 75 ppm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Cycle</strong></td>
<td><strong>Cycle</strong></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>CuO8.8/SBA-15</td>
<td>21</td>
<td>37</td>
</tr>
<tr>
<td>CuO15.6/SBA-15</td>
<td>44</td>
<td>75</td>
</tr>
<tr>
<td>CuO31.7/SBA-15</td>
<td>162</td>
<td>54</td>
</tr>
</tbody>
</table>

* SO₂ adsorption capacity calculated by integration of the SO₂ curve until the outlet SO₂ concentration reaches 75 ppm
** Ratio of SO₂ chemisorbed at 75 ppm/total Cu content (mol/mol)

#### Adsorbents CuO/SBA-15 behavior strongly depends on copper loading

- **Low and intermediate copper loadings**
  - Formation of Cu⁺ species during the first regeneration, more efficient in the desulfurization reaction

- **High copper loading**
  - High SO₂ storage capacity during cycle 1
  - Strong deactivation during cycle 2 due to strong copper sintering

*The best adsorbent*
Results

**Characterizations after SO\textsubscript{2} adsorption experiments**

**XRD analyses**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO\textsubscript{8.8}/SBA-15</td>
<td>after 9 cycles, copper species remain highly dispersed</td>
</tr>
<tr>
<td>CuO\textsubscript{15.6}/SBA-15</td>
<td>small XRD peaks of CuO</td>
</tr>
<tr>
<td>CuO\textsubscript{31.7}/SBA-15</td>
<td>sharp XRD CuO peaks : presence of large CuO crystallites in high quantity</td>
</tr>
</tbody>
</table>

**TEM analyses**

- CuO\textsubscript{8.8}/SBA-15: Highly dispersed copper species.
- CuO\textsubscript{15.6}/SBA-15: Small XRD peaks of CuO.
- CuO\textsubscript{31.7}/SBA-15: Sharp XRD CuO peaks with large crystallites.
SO$_2$ adsorption tests: cycling experiments

Regeneration under $H_2$ at 280°C

![Graph showing SO$_2$ adsorption over time](image)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>SO$<em>2$ adsorption capacity at 75 ppm (mg$</em>{SO_2}$·g$_{ads}^{-1}$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>57</td>
</tr>
<tr>
<td>6</td>
<td>45</td>
</tr>
</tbody>
</table>

* SO$_2$ adsorption capacity calculated by integration of the SO$_2$ curve until the outlet SO$_2$ concentration reaches 75 ppm

- Regeneration at low temperature (280°C) under $H_2$ (0.5 vol.%) is efficient
- No $H_2S$ is emitted during regeneration under $H_2$
- Energetic and financial advantages
Conclusions

- Synthesis of CuO/SBA-15 based adsorbents with highly dispersed copper species by wet impregnation in aqueous solution

- Interesting SO$_2$ chemisorption capacities along cycling experiments

- Significant increase of the adsorbent efficiency after thermal treatment at 600°C: generation of Cu$^+$ species, more active in desulfurization reaction

- The adsorbents’ behavior strongly depends on copper loading: deactivation increases with copper loading

- Optimum copper loading to ensure sufficient SO$_2$ adsorption capacity and weak deactivation

- Total regeneration under H$_2$ at 280°C without H$_2$S emissions
Thanks for your attention!

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