Facile synthesis of zeolite-encapsulated iron oxide nanoparticles as a superior catalyst for phenol oxidation

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1. Microporous ZSM-5 preparation

Microporous ZSM-5 (Si/Al=40) was synthesized hydrothermally with the assistance of active seeds from a gel with the molar ratio of 1SiO$_2$: 0.0125Al$_2$O$_3$: 0.15TPABr: 1EA: 17H$_2$O. The active seeding gel was prepared from a gel with the molar ratio of 1TEOS: 0.36TPAOH: 19H$_2$O by a traditional hydrothermal synthesis route. Typically, the mixture of 15.4 ml TEOS and 16.5 ml TPAOH (1.14 M) was stirred at 308 K for 3 h followed by adding 33 ml distilled water and stirring for another 2 h. The obtained gel was then transferred to 353 K water bath for hydrothermal treatment about 72 h. After cooling, the obtained seeding gel was directly used for the synthesis of ZSM-5 without any treatment. The synthesis of ZSM-5 was conducted by the following procedure. First, TPABr was dissolved with 666.7 g silica solution and afterwards with a solution of 222.6 g C$_2$H$_5$NH$_2$ (65 wt%). The mixture was aged at room temperature for 30 min under mechanical stirring followed by adding a solution of 20.12 g AlCl$_3$•6H$_2$O and 450 g H$_2$O. The as-synthesized active seeding gel was then added into the ZSM-5 precursor. The gel was then introduced to the stainless steel autoclaves (2000 mL, filled volume 1500 ml) with hydrothermal treatment at 443 K for 72 h. The resulting solid was filtered, washed, and dried overnight at 373 K. The as-synthesized zeolite was calcined in static air at 813 K for 6 h to remove the template. The resulting sample was denoted as micro-ZSM-5.

2. Mesoporous ZSM-5 preparation

Mesoporous ZSM-5 (denoted as meso-ZSM-5) was obtained through individual alkaline treatment in sodium hydroxide (NaOH). The treatment was carried out in a round-bottomed flask in which the corresponding aqueous solution, stirred at 400 rpm, was heated to 338 K. The solid was
then added, and the suspension was left to react for 30 min. The ratio of sample weight and liquid volume ($m_{\text{sample}}/V_{\text{solution}}$) was 33 g/L. The treatment was quenched, and the suspension was filtered and washed with distilled water until neutral pH. The resulting solid was dried overnight at 373 K after which calcination was performed at the conditions described above for micro-ZSM-5. The resulting zeolite was brought into ammonium form via three consecutive exchanges in aqueous NH$_4$NO$_3$ at 348 K for 1.5 h. Finally, those samples were calcined in static air at 813 K for 4 h to ensure that the hierarchical ZSM-5 in the proton form, denoted as meso-ZSM-5.

3. **Mesoporous ZSM-5 modified with PEI**

PEI/meso-ZSM-5 was prepared by impregnating methanol solution of PEI (1 g PEI in 100g solution). Typically, 1 g meso-ZSM-5 was added into 10 g methanol solution which contained 0.1 g PEI. The resulting mixture was stirred at room temperature for 12 h and then evaporated by using rotary evaporator. The obtained solid product which was then dried overnight at 373 K was denoted as PEI/meso-ZSM-5.

4. **Iron impregnation**

P, AT, N600 were prepared by using micro-ZSM-5, meso-ZSM-5, PEI/meso-ZSM-5 as supports. Through the incipient wetness impregnation method using aqueous solutions of iron nitrates (Fe(NO$_3$)$_3$•9H$_2$O), to obtain 5 wt% of Fe loading. The desired catalysts were obtained after drying overnight at 373 K followed by calcination in the flow of nitrogen (80 ml/min) at 873 K for 3 h. The obtained catalysts were donated as P, AT, N600, respectively. As a supplement, P, AT and N600 are the final samples used in phenol oxidation evaluation which all contain 5 wt% Fe. “P” and “AT” are acronyms we use for “pristine zeolite” and “alkaline treatment”, respectively. N600 refers
to the sample obtained from using PEI modified mesoporous zeolite as an iron oxide support and
calcination at 600 °C in N₂ atmosphere.

5. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2400 diffractometer,
using nickel-filtered CuKa X-ray source at a scanning rate of 0.02° over the range between 5° and
80°.

Scanning transmission electron microscopy (STEM) images were taken on JEM-2100F
instrument (JEOL Company) with an acceleration voltage of 200 kV. The samples for STEM
analysis were prepared by dipping the carbon-coated copper grids into the ethanol solutions of the
samples and drying at ambient condition.

Ar isotherms at 87 K were measured in a Quantachrome autosorb-iQ2 gas adsorption analyzer.
Prior to the measurement, the samples were degassed in vacuum at 573K for 10h. The Brunauer-
Emmett-Teller (BET) method was applied to calculate the total surface area, while the t-plot
method was used to discriminate between micro- and mesoporosity. In the t-plot, the reported
mesopore surface area (Smeso) consists of contributions from the outer surface of the particles as
well as mesopores and macropores.

H₂-TPR measurements were carried out with ChemBET Pulsar TPR/TPD equipment
(Quantachrome, USA) to analyze the reducibility of the calcined catalysts. Prior to the reduction,
the calcined sample (0.10 g) was placed in a quartz tube reactor in the interior of a controlled oven.
The sample was flushed with high purity argon at 573 K for 1 h to remove water and other
contaminants then cooled down to room temperature. A gas mixture containing 5 vol% H₂ in Ar
was passed through the sample at a total flow rate of 30 ml min$^{-1}$. The temperature and detector signals were then continuously recorded while heating at 10 K min$^{-1}$ up to 1173 K. A cooling trap was also placed between the sample and the detector for removal of released water formed during the reduction process.

TG analysis was conducted on a TGA/SDTA851e thermo-balance (Mettler Toledo). The thermal analysis data were collected in the range of 308-1073 K in a nitrogen flow. The heating rate was 10 K min$^{-1}$ at a flow rate of 25 ml min$^{-1}$ while the sample weight was between 7 and 10 mg.

6. Catalytic testing

All catalyst evaluations were conducted in a 100 ml tubular flask equipped with a magnetic stirring bar. In a typical procedure, 20 mg catalyst, 50 ml phenol solution (1 g L$^{-1}$), 10.76 ml H$_2$O$_2$ solution (0.69 M) were added together into the flask followed by maintaining at 308 K or 323 K to react for the appropriate time and analyzed by liquid chromatography.

7. XRD patterns of P, AT, and N600

Fig. S1 XRD patterns of P, AT, N600.

Fig. S2 Ar adsorption and desorption isotherms at 87 K and pore size distributions of sample P, AT, and N600 (inset). The pore size distributions were determined by non-local density functional theory (NLDFT).


Table S1 Textual properties of P, AT, N600.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$S_{\text{micro}}$</th>
<th>$S_{\text{meso}}$</th>
<th>$S_{\text{BET}}$</th>
<th>$V_{\text{micro}}$</th>
<th>$V_{\text{pore}}$</th>
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</thead>
<tbody>
<tr>
<td>P</td>
<td>293</td>
<td>125</td>
<td>418</td>
<td>0.11</td>
<td>0.32</td>
</tr>
<tr>
<td>AT</td>
<td>131</td>
<td>240</td>
<td>371</td>
<td>0.05</td>
<td>0.70</td>
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<tr>
<td>N600</td>
<td>121</td>
<td>222</td>
<td>343</td>
<td>0.05</td>
<td>0.62</td>
</tr>
</tbody>
</table>

[a] t-plot method  [b] BET method  [c] $p/p_0=0.99$

Fig. S3 H$_2$-TPR curves of P, AT and N600.

11. Fe 2p XPS spectra of P, AT and N600

Fig. S4 Fe 2p XPS spectra of P, AT, and N600.


Table S2. Parameters of $^{57}$Fe Mossbauer spectra of P, AT and N600.
<table>
<thead>
<tr>
<th>Sample</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>Magnetic Field (T)</th>
<th>IR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.37</td>
<td>-0.21</td>
<td>52.17</td>
<td>100</td>
</tr>
<tr>
<td>AT</td>
<td>0.37</td>
<td>-0.22</td>
<td>51.71</td>
<td>41.2</td>
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<td></td>
<td>0.34</td>
<td>0.82</td>
<td>/</td>
<td>58.8</td>
</tr>
<tr>
<td>N600</td>
<td>0.31</td>
<td>-0.05</td>
<td>49.37</td>
<td>22.6</td>
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<tr>
<td></td>
<td>0.33</td>
<td>1.13</td>
<td>/</td>
<td>77.4</td>
</tr>
</tbody>
</table>

13. Thermo gravimetric analysis results of P, AT, and N600.

![Fig. S5 Thermo gravimetric analysis results of P, AT, and N600.](image)

14. High resolution transmission electron microscopy (HRTEM).
Fig. S6 HRTEM images of sample P, AT and N600.

15. Ar adsorption/desorption isotherms of samples Micro-ZSM-5 and Meso-ZSM-5.
Fig. S7 Ar adsorption and desorption isotherms at 87 K and pore size distributions of Micro-ZSM-5 and Meso-ZSM-5. The pore size distributions were determined by non-local density functional theory (NLDFT).

Table S3 Textual properties of Micro-ZSM-5 and Meso-ZSM-5.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>$S_{\text{micro}}$</th>
<th>$S_{\text{meso}}$</th>
<th>$S_{\text{BET}}$</th>
<th>$V_{\text{micro}}$</th>
<th>$V_{\text{pore}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro-ZSM-5</td>
<td>391</td>
<td>67</td>
<td>458</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>Meso-ZSM-5</td>
<td>204</td>
<td>152</td>
<td>358</td>
<td>0.08</td>
<td>0.61</td>
</tr>
</tbody>
</table>

[a] t-plot method  [b] BET method  [c] $P/P_0=0.99$. 