EXAFS analysis for Cu nanocatalysts active for transfer hydrogenation of α,β-unsaturated carbonyl compounds

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1 Introduction
The selective hydrogenation of α, β Unsaturated aldehydes and ketones to corresponding unsaturated alcohols is of paramount importance in organic synthesis. These unsaturated alcohols are intermediates used in the production of foods, pharmaceuticals and cosmetics. The hydrogen addition to the conjugated C=C bond in an α,β unsaturated carbonyl compounds is both kinetically and thermodynamically favoured over C=O. Therefore research efforts have been made for improving the selectivity of unsaturated alcohols. We report here the preparation of Cu-nanoparticles supported on nanocrystalline MgO for selective hydrogenation of α,β-unsaturated carbonyls compounds to corresponding α,β-unsaturated alcohols via sonication method and this prepared catalyst is highly active for the chemo-selective transfer hydrogenation of α, β unsaturated carbonyl compounds to corresponding α,β-unsaturated alcohols. To best of our knowledge there is no report in the open literature where a single heterogeneous catalyst is used for the dehydrogenation of cyclohexanol to cyclohexanone where this in-situ generated hydrogen is used for selective hydrogenation of α,β unsaturated aldehydes and ketones to unsaturated alcohols. Cu K-edge EXAFS measurements were conducted for the structural characterization for the fresh and the spent catalysts.

2 Experiment
Well dispersed nanocrystalline copper oxide supported on magnesia (Cu/MgO) was prepared by simple ultrasonication assisted synthesis procedure. Starting materials were Mg(NO3)2.6H2O and Cu(NO3)2.2.5H2O. The detailed procedure will be reported elsewhere. The obtained catalyst was found to be the active catalyst for the chemoselective transfer hydrogenation of unsaturated carbonyl compounds to produce corresponding alcohols with very high yield. Transfer hydrogenation of cyclohexanol and cinnamaldehyde produce cyclohexanone and cinnamyl alcohol with 100% selectivity.

EXAFS measurements of Cu-K edge were carried out at KEK-IMMS-PF BL9C.

3 Results and Discussion
Cu K-edge EXAFS measurements were conducted for the structural characterization for the fresh and the spent catalysts as shown in Fig. 1. The curve fitting results are summarized in Table 1. The fresh and spent 5%Cu-MgO catalysts show the presence of CuO (as Cu-O path) clusters. In addition, the spent catalyst showed the formation of metallic Cu (as Cu-Cu path) clusters and we believed that this metallic Cu nanoclusters are the active species for this reaction.

The Cu–O coordination number (CN) in the fresh catalyst was 2.0±0.4 and the Cu–O distance was 1.958±0.012 Å, which is similar to the bond length of CuO oxide. The small CN of Cu–O indicates the formation of nanosized CuO on the MgO surface. The EXAFS data for the spent catalyst indicate no significant change in CuO structures during the catalytic reaction.

Table 1: Summary of the EXAFS fitting results for the fresh and spent Cu catalysts

<table>
<thead>
<tr>
<th>Path</th>
<th>$R_1$ (nm)</th>
<th>CN</th>
<th>$D_W$ (Å$^2$)</th>
<th>$\Delta E_p$ (eV)</th>
<th>$R_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Cu-O</td>
<td>1.958±0.012</td>
<td>2.0±0.4</td>
<td>18.1±1.7</td>
<td>-5.0±2.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Spent Cu-O</td>
<td>1.932±0.032</td>
<td>0.6±0.7</td>
<td>0.66±6.3</td>
<td>-11.2±3.7</td>
<td>8.6</td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>2.553±0.023</td>
<td>8.3±2.9</td>
<td>15.3±3.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Fitting was conducted in the range $\Delta k$ 3.13 (Å$^{-1}$ nm)$^2$ and $\Delta R$ 1.2-2.8 (Å$^{-1}$ nm). Amplitude reducing factor $S_0^2$ was set as 0.95

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