Electronic Supplementary Information

Magnetically retrievable MFe$_2$O$_4$ spinel (M= Mn, Co, Cu, Ni, Zn) catalysts for Oxidation of benzylic alcohols to carbonyls

Anand S. Burange,$^a$ Sandip R. Kale,$^a$ Radek Zboril,$^b$ Manoj B. Gawande,*$^b$ and Radha V. Jayaram$^a$

$^a$Department of Chemistry, Institute of Chemical Technology (Autonomous), N. Parekh Marg, Matunga, Mumbai 400 019, India,
Email: rv.jayaram@ictmumbai.edu.in; Fax +91(22)24145614.4

$^b$Regional Centre of Advanced Technologies and Materials, Faculty of Science, Phys. Chemistry Department, Palacky University, Šlechtitelů 11, 783 71, Olomouc, Czech Republic, Email: mbgawande@yahoo.co.in; manoj.gawande@upol.cz

<table>
<thead>
<tr>
<th>No.</th>
<th>Contents</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Experimental section</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Catalyst preparation and characterization</td>
<td>1-2</td>
</tr>
<tr>
<td>3</td>
<td>GC-MS data of products</td>
<td>3-9</td>
</tr>
</tbody>
</table>
1. Experimental Section

1.1 Materials

All the chemicals were purchased from standard sources and used without further purification. The conversions of reactants oxidation were based on the GC analysis using a capillary column (Chemito1000). Products were identified by GC/MS analysis (Shimadzu QP 2010).

1.2 General experimental procedure for oxidation of benzylic alcohols

To a clean dry 10 mL round-bottom flask containing 1 mmol benzylic alcohol, 3 mmol equivalents of 70% TBHP were added. This was followed by the addition 10 mol% of spinel catalyst and 2 mL solvent. Before reaction, the catalyst was activated by keeping it in oven at 100°C for half an hour minutes.

The mixture was sonicated for 5 minutes in order to disperse the catalyst uniform in the reaction mixture. Further, reaction mixture was stirred at given temperature and time. The progress of the reaction was monitored by TLC and GC. After completion of the reaction, the reaction mixture was cooled to room temperature (25°C) and the catalyst was separated by filtration method. All products were characterized by spectroscopic data.

2. Catalyst preparation and characterization

Preparation of MFe$_2$O$_4$ Spinels (M = Mn, Co, Cu, Ni, Zn)

The catalyst was prepared by reported method by Casbeerand.$^1$ A typical protocol involves the addition of the metal and iron precursors, along with citric acid, to form a gel. The precursors are dissolved in water or ethanol and stirred vigorously at pH 9 until a gel-like material is formed. Citric acid assists in the homogeneous distribution of the metal ions into solution. The gel is dried and then calcined at 650 °C for 3h.
2.1 XRD of MFe$_2$O$_4$ (M= Mn, Ni, Zn): Overlay mode

The X-ray diffraction pattern of synthesized MFe$_2$O$_4$ spinels with various metal (M = Mn, Ni, and Zn) is depicted below.

Figure 1. X-ray diffraction pattern of MFe$_2$O$_4$

The XRD data was obtained using an X-ray diffractometer (Philip 1050). MFe$_2$O$_4$ spinels calcined at 650 °C for 3h showed crystalline nature confirmed by XRD. The XRD pattern shows prominent peaks at 2θ values which corresponds to the spinel structure (Figure 1).

2.2 SEM Images of CoFe$_2$O$_4$ catalyst

The SEM images of CoFe$_2$O$_4$ different magnification shown below, it clearly seen that rough patches are observed with small flakes of particle over the surface of catalysts.

Figure 2. SEM images of CoFe$_2$O$_4$ catalyst

3. GC–MS of some selected products

Benzophenone

![Spectrum of Benzophenone](image)

\[ \text{Benzophenone} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{o-hydroxy acetophenone} \]

![Spectrum of o-hydroxy acetophenone](image)
Acetophenone

Benzaldehyde
Benzoic acid

4-Methyl benzaldehyde
4-Bromo benzaldehyde

4-Bromo benzoic acid
4-Nitrobenzaldehyde

3-Phenoxybenzaldehyde
4-Methoxy benzoic acid

[Chemical structure image]

4-Methoxybenzaldehyde

[Chemical structure image]
Ether of Benzhydrol and ethanol