Electronic Supplementary Information (ESI) for:

Promotional effect of Fe on performance of supported Cu catalyst for ambient pressure hydrogenation of furfural

Marimuthu Manikandan, Ashok Kumar Venugopal, Atul S. Nagpure, Satyanarayana Chilukuri* and Thirumalaiswamy Raja*

Catalysis & Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr.HomiBhabha Road, Pune - 411 008, India. Fax: (+) 91-20-25902633 ; Tel: (+) 91-20-25902006; E-mail: t.raja@ncl.res.in

Chemicals:

All the chemicals were reagent grade and used without further purification. FAL (99%), FOL (99%), DMTHF (99%), 2-MF (99%), THFA (99%), THF (98%), Furan (99%) were sourced from Sigma-Aldrich. The following materials have been used for the synthesis of catalysts Mg(NO$_3$)$_2$.6H$_2$O, Al(NO$_3$)$_3$.9H$_2$O and Ni(NO$_3$)$_2$.6H$_2$O, NaOH and Na$_2$CO$_3$ were purchased from Merck.

Characterization

X-ray diffraction (XRD) measurements

In XRD analysis, the results were collected with a step size of 0.008°, time per step is 10.8 sec and a scan rate of 0.5° min$^{-1}$. The radiation for analysis used was Cu-K$\alpha$ (1.5418 Å) with Ni filter and the data collection was carried out using a flat holder in Bragg–Brentango geometry.

For in-situ XRD analysis, the most active FC-10 catalyst was analyzed with different temperatures (27-400 °C) in the presence of H$_2$ flow (30 mL min$^{-1}$). The results were collected with a step size of 0.008° and a scan rate of 0.5° min$^{-1}$. The radiation for analysis used was Cu-K$\alpha$ (1.5418 Å) with Ni filter and the data collection was carried out using a flat holder in Bragg–Brentango geometry. The temperatures were kept constant for 2 hours prior to each recording.

Temperature-programmed reduction (TPR)

For TPR experiment, nearly 50 mg of sample was loaded in “U” shaped quartz tube for analysis. The sample was pre-treated from room temperature to 450 °C (5 °C/min ramping) using Helium as a carrier gas. For analysis 5% H$_2$ in Argon mixture was used in a temperature range from room temperature to 1000 °C (10 °C/ min ramping). The H$_2$ consumption was analyzed using a thermal conductivity detector (TCD), which was calibrated before the TPR analysis.
H$_2$-N$_2$O titration

The specific surface area of metallic copper and copper dispersion of the γ-Al$_2$O$_3$ supported catalysts was determined according to H$_2$–N$_2$O titration as described in the reported literatures. $^{1-3}$ Firstly, the sample was treated at 400 °C for 2 hours under He flow (30 mL min$^{-1}$). Then, the sample was underwent a H$_2$-TPR process in a 5% H$_2$/Ar mixture from 50 to 400 °C (2 °C min$^{-1}$ ramping rate) and held the temperature until no more H$_2$ was consumed. The amount of H$_2$ consumption was calculated after this step and named as $A_1$. The sample was allowed to cool down to 40 °C, then the gas was switched to 5% N$_2$O/He mixture and the sample was oxidized at a flow rate of 40 mL min$^{-1}$ for 1 h, followed by Ar gas purging at 60 °C. Finally, H$_2$-TPR was carried out again with a gas mixture of 5% H$_2$/Ar from 60 to 400 °C and held the temperature until no more H$_2$ was consumed. After this step also the amount of H$_2$ consumption was calculated and named as $A_2$. Copper dispersion and copper surface area were calculated as according to the reported literatures. $^{4,5}$ Copper dispersion ($D_{Cu}$), defined as the ratio of Cu exposed at the surface to total Cu, was calculated from the amount of H$_2$ consumed in the two step TPR analysis ($D_{Cu}$ = $2A_2/A_1$). Cu surface area ($S_{Cu}$) determined by assuming spherical shape of the Cu metal particles and a surface concentration of 1.47 × 10$^{19}$ Cu atoms m$^{-2}$.

Transmission electron microscopy (TEM)

The samples for TEM analysis were prepared by placing a droplet of the highly diluted suspension of sample in 2-propanol on a Cu grid coated with a carbon layer and allowed to dry at room temperature.

X-ray photoelectron spectroscopy (XPS)

For in-situ XPS analysis, the pelletized catalyst was placed inside the XPS chamber and heated to different temperatures in the presence of 0.1 mbar H$_2$ pressure. The core level spectrums were recorded at Ultra High Vacuum (UHV) followed by room temperature (RT), 250 and 400°C under 0.1 mbar H$_2$ pressure; the temperatures were kept constant for 2 hours prior to each recording. The photoelectrons are analyzed by using VG Scents R3000HP deferentially pumped analyzer. The XPS spectra were recorded at pass energy of 50 eV and more details about the instrument were can be found elsewhere. $^6$
Figures

$\text{N}_2$ adsorption-desorption isotherms and pore size distribution of the $\gamma$-Al$_2$O$_3$ supported FC-X pre-catalysts

![Figure S1](image)

**Fig. S1** (a) $\text{N}_2$ adsorption-desorption isotherms and (b) pore size distribution of the $\gamma$-Al$_2$O$_3$ supported FC-X pre-catalysts.

XRD patterns of the reduced FC-X catalysts

![Figure S2](image)

**Fig. S2** XRD patterns of the $\gamma$-Al$_2$O$_3$ supported FC-X catalysts after reduction at 400 °C for 2 hours.
Fig. S3 Cu LMM Auger spectra for bimetallic FC-10 sample at different temperatures under UHV and 0.1 mbar H₂.

Fig. S4 GC-MS signals of the product mixture (a), fragmentation of FAL (b) and FOL (c) over C-10 catalyst. Reaction conditions: 175°C, 1 atm. LHSV=1 h⁻¹ with respect to FAL and GHSV=1200 h⁻¹ with respect to H₂, 1 atm. pressure and 1 mL catalyst.
Fig. S5 GC-MS signals of the product mixture (a), fragmentation of FAL (b) and FOL (c) over FC-10 catalyst. Reaction conditions: 175°C, 1 atm. LHSV=1 h\(^{-1}\) with respect to FAL and GHSV=1200 h\(^{-1}\) with respect to H\(_2\), 1 atm. pressure and 1 mL catalyst.

References