Chromium-free Cu@Mg/γ-Al2O3 an Active Catalyst for Selective Hydrogenation of Furfural to Furfuryl Alcohol

Arundhathi Racha, Panyala Linga Reddy, Chanchal Samanta and Bharat L Newalkar

Corporate Research & Development Centre, Bharat Petroleum Corporation Limited, Greater Noida, Uttar Pradesh-201306, India.

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India.

Contents

1 General remarks 2
2 Experimental (Catalyst Preparation) 3
   2a Mono metallic supported catalyst preparation 3
   2b Various bimetallic supported catalyst preparation 4
3 Catalyst Characterization 5
   3a BET surface area, Pore Volume, Pore Size and Particle Size 5
   3b Temperature Programmed Reduction (TPR) 7
   3c Temperature Programmed Desorption (TPD) 9
   3d High Resolution Transmission Electron Microscopy (HR TEM) Analysis 11
   3e XPS and AES analysis of Cu@Mg/γ-Al2O3 14
   3f XRD analysis of synthesized catalysts 16
4 General Procedure for the Hydrogenation Reaction 20
5 Reaction Kinetics for the Hydrogenation Reaction 20
6 Inductively Coupled Plasma-Atomic Emission Analysis (ICP-AES) 21
7 1H and 13C NMR spectrum of Furfuryl alcohol: 22
8 References 23
Experimental

1) General Information

All reagents were purchased from commercial suppliers and used without further purification. All hydrogenation experiments were carried out under hydrogen (purity: 99.95%). Column chromatography was carried out with Merck silica gel 60-120 mesh and the products were visualized by GC detection. $^1$H NMR and $^{13}$C NMR (Bruker (Germany) Avance III) spectra were recorded in CDCl$_3$. Chemical shifts ($\delta$) are reported in ppm using TMS as an internal standard, and spin -spin coupling constants ($J$) are given in Hz. $^1$H NMR and $^{13}$C NMR of the compounds were proved either by comparison to the known compounds or the synthesized compounds according to the literature. BET surface area was obtained with N$_2$ as adsorbate at liquid nitrogen temperature in Micromeritics ASAP-2020 plus. Hydrogen Temperature Programmed Reduction (H$_2$-TPR) and Carbon dioxide Temperature Programmed Desorption (CO$_2$-TPD) analysis of the prepared copper catalysts were performed on Autochem II 2920. The particle size and external morphology of the samples were observed on a JEOL JEM-2100 high resolution transmission electron microscope (HR-TEM). XPS spectra were recorded on a Kratos AXIS supra with a dual anode (Mg and Al) apparatus using the Mg K$\alpha$ anode. The pressure in the spectrometer was about $10^{-9}$ Torr. For energy calibration, we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 284.8 eV. The location and the full width at half maximum (FWHM) for a species were first determined using the spectrum of a pure sample. The location and FWHM of the products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Auger electron spectroscopic (AES) analysis is conducted, at a base pressure of $10^{-10}$ Torr, within the K.E. range of 110-700 eV (beam voltage of 3 kV, eV/step 1 eV, time/step 50 ms). Powdered X-ray
powder diffraction (PXRD) data were collected on AERIS PANanalytical diffractometer using Cu Kα radiation.

2.0 Catalyst Preparation:

2a. Mono metallic supported catalyst preparation:

**Cu/γ-Al₂O₃:** In a 250 mL round bottomed flask 100 mL of deionized water was taken and 22.11 gram of Cu(NO₃)₂.3H₂O (0.0915 moles) was added under stirring conditions at room temperature for complete dissolution of copper salt. To this solution, 20 gram of calcined γ-Al₂O₃ support added and stirred at room temperature for 2 hours. The pH of the reaction mixture was maintained constantly (8 to 9) by the continuous addition of the base solution (30% NH₄OH). The resulting slurry was aged at 70 °C for two hours. The solid product was isolated by filtration, washed thoroughly with deionised water (to make the catalyst free from base) and dried at 110 °C for 12 h in oven.

The copper supported on γ-Al₂O₃ was further calcined at 773 K for 3 h to get CuO/γ-Al₂O₃. CuO@γ-Al₂O₃ was then reduced under 3 bar of H₂ pressure at 350 °C to get the final desired reduced Cu(0)/γ-Al₂O₃ catalyst. Copper(0) anchored on various supports like SiO₂, TiO₂, CeO₂, and MoO₃ were also prepared in similar procedure as described above and their performance were checked in hydrogenation of furfural to furfuryl alcohol.

**Pt/γ-Al₂O₃:** 4 mL of an aqueous solution of H₂PtCl₆ (50 mM) was added to 50 mL of distilled water at 25 °C. Then, γ-Al₂O₃ (1 g) was added to the solution and the mixture was stirred magnetically while maintaining the same temperature for 4 h. Water was removed by rotary evaporation under reduced pressure to give the solid product. The obtained powder was dried at 110 °C for 5 h. Then, calcined at 500 °C for 3 h under a static air atmosphere to obtain Pt/γ-Al₂O₃ as a dark gray powder. ICP-AES analysis determined that the γ-Al₂O₃ had been impregnated with Pt at concentrations of 4 wt%. γ-Al₂O₃-supported monometallic catalysts were prepared by the impregnation method using various noble metal salts. The noble metal
contents were adjusted to 0.02 mol of noble metal/g catalyst. In the case of Pt/γ-Al₂O₃, Pt content was 4.2 wt%.

2b. Various bimetallic supported catalyst preparation:

Step 1: 200 mL of deionised water was taken in a 1 L four neck round bottom flask and equipped with an overhead mechanical stirrer. Mg(NO₃)₂·6H₂O (6.63 g, 0.0447 moles) was dissolved in the solution and 45 grams of γ-Al₂O₃ (45 g, 0.4413 moles) was added to Mg(NO₃)₂·6H₂O dissolved solution. The resulting slurry was kept for stirring for 2 hours and aged at 70 °C for 4h. The solid product was isolated by filtration and dried at 110 °C for 12 h in an air oven. Mg doped alumina catalyst was then calcined at 350 °C in the presence of air for 5 hours to obtain MgO/γ-Al₂O₃ and then cooled to room temperature.

Step 2: In a 250 mL round bottomed flask 100 mL of deionized water was taken and 22.11 gram of Cu(NO₃)₂·3H₂O (0.0915 moles) was added under stirring conditions at room temperature for complete dissolution of copper salt. To this solution, 20 gram of calcined MgO/γ-Al₂O₃ catalyst added and stirred at room temperature for 2 hours. The pH of the reaction mixture was maintained constantly (8 to 9) by the continuous addition of the base solution (30% NH₄OH). The resulting slurry was aged at 70 °C for two hours. The solid product was isolated by filtration, washed thoroughly with deionised water (to make the catalyst free from base) and dried at 110 °C for 12 h in oven.

Step 3: The copper supported on MgO/γ-Al₂O₃ was further calcined at 750 °C for 4 h to get CuO@Mg/γ-Al₂O₃. CuO@Mg/γ-Al₂O₃ was then reduced under 3 bar of H₂ pressure at 350 °C to get the final desired reduced Cu (0)@Mg/γ-Al₂O₃.

Copper and other bimetallic catalyst anchored on γ-Al₂O₃ is prepared in similar procedure and their performance were checked for FF to FA conversion.
Figure 1. Schematic representation of Cu@Mg/γ-Al₂O₃

Table 1. ICP-AES analysis of catalyst Cu@Mg/γ-Al₂O₃.

| S. No | Catalyst                | ICP-AES (Cu & Mg mol%) |
|-------|------------------------|------------------------|
| 1ᵃ    | Cu@Mg/γ-Al₂O₃          | Cu: 0.2001 & Mg: 0.0514 |
| 2ᵇ    | Reaction filtrate      | Cu: 0.0001 & Mg: trace |
| 3ᶜ    | Cu@Mg/γ-Al₂O₃          | Cu: 0.2000 & Mg: 0.0511 |

ᵃFresh catalyst, ᵇReaction filtrate (catalyst removed by filtration), ᵇReaction with fresh catalyst.

3. Catalyst Characterization.

3a. BET surface area, Pore Volume, Pore Size and Particle Size:

N₂ adsorption–desorption isotherms and pore size distribution of the prepared catalysts are shown in figure 2. The adsorption isotherms of γ-Al₂O₃ and Cu@Mg/γ-Al₂O₃ catalysts are of type IV with a H₂ hysteresis loop at relative pressure ranging from 0.6 to 1.0, which is characteristic of ink-bottle pores. However, the hysteresis loops of Cu@Mg/γ-Al₂O₃ are smaller than that of γ-Al₂O₃ carrier, owning to the insertion of active component in the pore channels (Figure 2D). As shown in the pore size distribution curves, the pore size distributed mainly at 5.0 nm, which is favorable for the diffusion of reactant furfural. The specific surface area and pore volume were decreased after the active component was loaded over the carrier. This is because that the active component can occupy a part of surface area and the pore structure would collapse to a certain extent. The active components could insert into the pore channel of γ-Al₂O₃ carrier, which would transform into metal oxide during the calcination and block a part of pores, resulting in the decrease of specific surface area. In addition, the pores
collapsed partly during the calcination process, which could also decrease the specific surface area. All catalysts have similar surface area and pore volume as they have same active component loading. They all have an average pore size of 6.0 nm, which is favor to the diffusion of reactant during the hydrogenation process. In addition, large surface area can provide much more active sites for hydrogenation, as the reaction mainly occurred on the surface of the catalysts. The overall increase in surface area in Cu@Mg/γ-Al₂O₃ than Cu/γ-Al₂O₃ can be attributed to an increase in specific surface area of the active metal with an addition of Mg as promoter.

Table 2. Textural properties of Cu-Mg/γ-Al₂O₃.

| Sr. No | Catalyst     | BET Surface area (m²/g) | Pore size (nm) | Total pore volume (cc/g) |
|--------|--------------|--------------------------|----------------|--------------------------|
| 1      | γ-Al₂O₃      | 230                      | 7.8            | 0.73                     |
| 2      | MgO/γ-Al₂O₃  | 200                      | 5.8            | 0.70                     |
| 3      | Cu/γ-Al₂O₃   | 180                      | 5.5            | 0.72                     |
| 4      | Cu@Mg/γ-Al₂O₃ | 200                   | 5.0            | 0.69                     |

*MgO/γ-Al₂O₃, Mg: 0.2 mol%; Cu/γ-Al₂O₃, Cu: 0.25 Mol% anad Cu@Mg/γ-Al₂O₃: Cu: 0.25 mol% and Mg: 0.05 mol%

Figure 2. [A] γ-Al₂O₃ [B] MgO/γ-Al₂O₃ [C] Cu/γ-Al₂O₃ [D] Cu@Mg/γ-Al₂O₃.
Table 3. BET analysis of monometallic catalysts on various supports.

| Entry | Catalyst      | BET (m²/g) | ESA (m²/g) | MiPA (m²/g) | TPV (cc/g) |
|-------|---------------|------------|------------|-------------|------------|
| 1     | Cu/γ-Al₂O₃   | 180        | 175        | 5           | 0.7201     |
| 2     | Cu/SiO₂      | 134        | 120        | 14          | 0.495      |
| 3     | Cu/TiO₂      | 29         | 19         | 10          | 0.076      |
| 4     | Cu/CeO₂      | 55         | 53         | 2           | 0.043      |
| 5     | Cu/MoO₃      | 11         | 8          | 3           | 0.076      |
| 6     | Pt/γ-Al₂O₃   | 187        | 182        | 5           | 0.697      |
| 7     | Rh/γ-Al₂O₃   | 192        | 183        | 9           | 0.717      |
| 8     | Ir/γ-Al₂O₃   | 193        | 185        | 8           | 0.698      |
| 9     | Pd/γ-Al₂O₃   | 192        | 187        | 5           | 0.709      |

Table 4. BET analysis of bimetallic catalysts.

| Entry | Support       | BET (m²/g) | ESA (m²/g) | MiPA (m²/g) | MiPV (cc/g) | TPV (cc/g) |
|-------|---------------|------------|------------|-------------|-------------|------------|
| 1     | γ-Al₂O₃       | 230        | 200        | 30          | 0.0060      | 0.7302     |
| 2     | Cu-Co/γ-Al₂O₃| 191        | 166        | 25          | 0.0105      | 0.7317     |
| 3     | Cu-Zn/γ-Al₂O₃| 165        | 157        | 8           | 0.0039      | 0.7219     |
| 4     | Cu-Mg/γ-Al₂O₃| 200        | 189        | 11          | 0.0059      | 0.6905     |
| 5     | Cu-Ga/γ-Al₂O₃| 172        | 159        | 13          | 0.0069      | 0.7095     |
| 6     | Cu-Mn/γ-Al₂O₃| 172        | 168        | 4           | 0.0020      | 0.7388     |
| 7     | Cu-Zr/γ-Al₂O₃| 182        | 166        | 16          | 0.0087      | 0.7598     |

3b. Temperature Programmed Reduction (TPR)

The hydrogen temperature-programmed reduction (H₂-TPR) analysis of the prepared copper catalysts was performed on Micromeritics Autochem II 2920. In a typical experiment, around 0.15 g of catalyst was placed in a quartz sample cell, the sample was then flushed with pure argon at a flow rate of 50 mL min⁻¹ and 573 K for 0.5 h and then cooled down to room temperature. Subsequently, a 10% H₂/Ar (30 mL min⁻¹) was flown through the sample while
the temperature was increased to 600 °C at 10 °C min\(^{-1}\) ramp rate and held at final temperature for 0.5 h. \(\text{H}_2\)-TPR measurement of Cu/\(\gamma\)-Al\(_2\)O\(_3\) and Cu@Mg/\(\gamma\)-Al\(_2\)O\(_3\) catalysts were conducted to study the redox properties of calcined samples and the interaction between the copper species and the support. Obviously, two kinds of copper species exist in the CuO-MgO/\(\gamma\)-Al\(_2\)O\(_3\) sample figure 3. The broad low-temperature reduction peak at ca. 225 °C is assigned to the reduction of isolated highly-dispersed CuO species, while the sharp high-temperature one at ca. 279 °C is associated with the reduction of Cu\(^{2+}\) species having a strong interaction with the matrix.\(^{1-2}\)

Whilst in Cu/\(\gamma\)-Al\(_2\)O\(_3\) sample figure 4 two reduction temperature peaks disappears to one temperature 268 °C and becomes broader. This could be due to the presence of only Cu-containing species and the absence of interaction with MgO matrix, which thus improves the reducibility of copper species. The reduction temperature peak appears well before 350 °C may be due to the reduction of highly-dispersed copper oxide particles. The lower metal loading on the support may have led to the higher dispersion. This is confirmed by TEM images. Chang and coworkers\(^3\) reported that supported samples with low metal loading are easier to reduce.

![Figure 3. TPR spectrum of calcined CuO@Mg/\(\gamma\)-Al\(_2\)O\(_3\).](image-url)
Table 5. H$_2$-Temperature programmed reduction (H$_2$-TPR) of catalysts.

| Sr.No | Catalyst                  | Temperature (°C) | H$_2$ consumption (µmol/g) |
|-------|---------------------------|------------------|----------------------------|
| 1     | CuO-MgO/γ-Al$_2$O$_3$     | 225.4            | 294                        |
| 2     | Cu/γ-Al$_2$O$_3$          | 268              | 138.7                      |

3c. Temperature Programmed Desorption (TPD)

The basic property of the catalysts were measured by temperature programmed desorption of CO$_2$ equipped with TCD detector. 100 mg of the catalysts were placed in a quartz reactor. The sample was pretreated at 400 °C in He of 60 mL/min for 180 min, and cooled down to room temperature. Then the sample was exposed in CO$_2$ (30 mL/min) using a six-way valve for 120 min and then flushed with He (40 mL/min) flow to remove all the physically adsorbed CO$_2$. Once the physically adsorbed CO$_2$ was purged off, the CO$_2$-TPD experiments were started. The data was collected at heating rate at 10 °C/min from room temperature to 750 °C in a flow of He (50 mL/min).

Basicity of reduced supported copper catalysts was determined by CO$_2$-TPD and profiles are shown in figure 5. The CO$_2$-TPD profile of Cu/Al$_2$O$_3$, shows a single desorption at $T_{\text{max}}$ of 108.4 °C was ascribed to the weak basic sites. Whereas, Cu@Mg/γ-Al$_2$O$_3$ catalyst had two CO$_2$ desorption peaks at a $T_{\text{max}}$ of 111 °C and 387 °C, corresponding to the presence of weak and
moderate basic sites, respectively. The basicity is as follows in the decreasing order: Cu/γ-Al₂O₃ 85.8 μmol·g⁻¹ < Mg-Al-HT 94 < Cu-Mg-Al-HT 96.7 < γ-Al₂O₃ 128.3 < MgO/γ-Al₂O₃ 129.5 < Cu@Mg/γ-Al₂O₃ 142.5 μmol·g⁻¹.

Table 6. CO₂-Temperature programmed desorption (CO₂-TPD) of catalysts

| Sr. No | Catalyst                  | Temperature (°C) | CO₂ Consumption (μmol/g) |
|--------|---------------------------|------------------|--------------------------|
| 1      | γ-Al₂O₃                   | 103              | 128.3                    |
| 2      | Cu/γ-Al₂O₃               | 108.4            | 85.8                     |
| 3      | MgO/γ-Al₂O₃              | 116.5            | 82.5                     |
|        |                           | 484              | 47                       |
| 4      | Cu@Mg/γ-Al₂O₃            | 111              | 92.0                     |
|        |                           | 387              | 50.5                     |
| 5      | Mg-Al-Hydrotalcite       | 115.6            | 70.3                     |
|        |                           | 387.0            | 21.8                     |
|        |                           | 677.1            | 1.9                      |
| 6      | Cu-Mg-Al-Hydrotalcite    | 113              | 93.8                     |
|        |                           | 239.5            | 2.9                      |

Figure 5. CO₂-TPD of: γ-Al₂O₃; Cu/γ-Al₂O₃; Cu@Mg/γ-Al₂O₃; MgO/γ-Al₂O₃; Mg-Al-HT and Cu-Mg-Al-HT.
3d. High Resolution Transmission Electron Microscopy (HR TEM) Analysis

HR-TEM analysis of the Cu@Mg/γ-Al₂O₃ catalyst was performed using FEG-TEM-200 kV (JEM 2100F) and found that the copper nanoparticles on the γ-Al₂O₃ are well dispersed with uniform distribution as shown in figure 7. However, the particles are very close to each other can be observed distinguished boundaries of every particle. Further, to check the particle size distribution, we have analysed hundred nanoparticles diameter and plotted the diagram as shown in figure 8. From the images it is also clearly evident that not only dispersion, along with that the size of majority of the nanoparticles are in the range between 3-8 nm with average particle size of 6 nm.
Figure 7. HR-TEM images [A] electron diffraction [SAED pattern, B] and elemental mapping [Cu, Mg and Al from J to L] of Cu@Mg/γ-Al2O3
3e. XPS analysis of Cu@Mg/γ-Al₂O₃

From the XPS analysis, the peak positions observed at 933.3 and 953.3 eV with the corresponding satellite peaks at 942.5 and 963.8 eV confirmed the Cu 2p core level in the +2 oxidation state (Figure 9) of CuO. In contrast, in the case of freshly reduced Cu@Mg/γ-Al₂O₃, the binding energies were observed at 932.6 and 952.3 eV corresponding to the zero oxidation state of copper in the reduced catalyst and no satellite peaks at the corresponding positions were observed which strongly suggest the complete reduction of small amount of CuO present in CuO@Mg/γ-Al₂O₃ to Cu(0)@Mg/γ-Al₂O₃ (Figure 9 and 10). The formation of Cu(0) nanoparticles by reduction was further confirmed with auger electron microscope (AES) analysis. Cu@Mg/γ-Al₂O₃ (fresh) and reused Cu@Mg/γ-Al₂O₃ (recovered after 5th run) were characterized by Auger electron microscopic analysis to confirm the zero oxidation state of the copper and no oxidation of metallic copper of Cu(0)@Mg/γ-Al₂O₃ was found even after successive runs. The kinetic energy for fresh and reused catalyst was found to be 919 eV (figure 11).
Figure 9. XPS spectrum of Cu@Mg/γ-Al₂O₃.

Figure 10. XPS spectrum of freshly reduced Cu@Mg/γ-Al₂O₃.

Figure 11. AES characterization of Cu@Mg/γ-Al₂O₃ [A] Fresh catalyst Cu@Mg/γ-Al₂O₃ and [B] Catalyst after 6th reuse.
Table 7. Effect of Cu/Mg on conversion of furfural to furfuryl alcohol.\textsuperscript{a}

| Sr. No | Cu/Mg | Furfural Conv. (%) | Furfuryl alcohol Yield (%) |
|--------|-------|--------------------|-----------------------------|
| 1      | 4     | 99                 | 90                          |
| 2      | 5     | 99                 | 94                          |
| 3      | 10    | 99                 | 80                          |
| 4      | 15    | 99                 | 65                          |

\textsuperscript{a}Reaction conditions: Furfural (2.6 mol%); catalyst Cu@Mg/\(\gamma\)-Al\_2O\_3 (0.1 g; Cu/Mg = X; where X = 5, 10, 15 and 4 on \(\gamma\)-Al\_2O\_3); H\_2 (2 MPa); Temp (443.15 K); Time 5h.

Figure 12. Effect of Cu/Mg on conversion of furfural to furfuryl alcohol.

Table 8. Comparison of catalyst efficiencies with the present system

| Sr. No | Catalyst          | Solvent   | Temp (°C) | Pressure (bar) | FF Conv (%) | FA Selec (%) | Ref. |
|--------|-------------------|-----------|-----------|----------------|--------------|--------------|------|
| 1      | Ni–Mo–B/Al\_2O\_3 | Methanol  | 80        | 50            | 99           | 90           | 9    |
| 2      | Pt/C              | Butanol   | 175       | 8             | 99           | 50           | 10   |
| 3      | Pd/SiO\_2         | Octane    | 230       | 1             | 69           | 10           | 11   |
| 4      | Pt–Fe/MWNT        | Ethanol   | 100       | 30            | 95.2         | 91.8         | 12   |
| 5      | Pd–Cu/MgO         | Water     | 110       | 6             | 100          | 99           | 13   |
| 6      | Cu/SiO\_2         | Isopropanol | 230   | 10            | 69           | 68           | 4    |
| 7      | Cu/Al\_2O\_3      | Water     | 90        | 2             | 81           | 81           | 5    |
| 8      | Co–Cu/SBA–15      | Isopropanol | 170  | 20            | 99           | 80           | 6    |
| 9      | Cu–Fe oxides      | Octane    | 200       | 60            | 87           | 84           | 7    |
| 10     | CuNiMgAl oxides   | Ethanol   | 200       | 10            | 93           | 83           | 8    |
| 11     | Cu@Mg/\(\gamma\)-Al\_2O\_3 | -------- | 170   | 20            | 100          | 94           | Present work |
### Table 9. Comparison of Cu@Mg/γ-Al₂O₃ activity with hydrotalcite derived copper catalysts in furfural hydrogenation

| S. No | Catalyst          | Cu (Wt %) | Mg (Wt%) | Temp (K) | P (bar) | Time (h) | FF Conv. (%) | FA 2- MF (K) | Yield (%) | Ref. |
|-------|------------------|-----------|----------|----------|---------|----------|-------------|-------------|-----------|------|
| 1     | Cu-Mg-Al         | 17.9      | >28      | 383      | 10      | 6        | 100         | 100         | -         | 14   |
| 2     | Cu-Mg-Al         | 40        | >12      | 423      | -       | 6        | 100         | 100         | -         | 15   |
| 3     | Cu₂Al            | 82        | 18       | 513      | 10      | 1.5      | >99         | 54.7        | 4.7       | 16   |
| 4     | Cu₃Al            | 87        | 13       | 513      | 10      | 1.5      | >99         | 44.9        | 3.7       | 16   |
| 5     | CuMgAlO₃         | 11.2      | >30      | 573      | 10      | 2        | ~50         | ~90         | □10       | 17   |
| 6     | Cu-Fe            | 64        | -        | 433      | 90      | 5        | 91          | 90          | 0.5       | 18   |
| 7     | Cu-Ni-Mg-Al      | 11.2      | 34       | 573      | 10      | 2        | 93.2        | 89.2        | 4.3       | 19   |
| 8     | Cu@Mg/γ-Al₂O₃    | 0.78      | 0.4      | 443      | 20      | 5        | >99         | 94          | 2         | 4    |

3f. XRD analysis of synthesized catalysts:

![XRD patterns of calcined CuO supported on various supports](image)

**Figure 13.** XRD patterns of calcined CuO supported on various supports
Figure 14. XRD patterns of Cu and various noble metals catalysts supported on Gamma alumina
Figure 15. XRD patterns of reduced Copper catalysts supported on various supports
Figure 16. XRD patterns of promoter oxide on $\gamma$-$\text{Al}_2\text{O}_3$.

Figure 17. XRD patterns of Cu-catalyst supported on $\gamma$-$\text{Al}_2\text{O}_3$ incorporated with various metal oxides.
4.0 General Procedure for the Hydrogenation Reaction:
Furfural (5.2 mol%), Cu@Mg/γ-Al₂O₃ (0.2 g), were taken in a 600-mL, round-PARR reactor equipped with an overhead stirrer and stirred for an appropriate time. The progress of the reaction was monitored by TLC and on completion of the reaction, the reaction mixture was centrifuged to separate the catalyst, the solid residue was washed with EtOAc (1 X 10 mL) to make the catalyst free from organic matter, the reaction mixture was diluted with water (20 mL), and then extracted with EtOAc (3 X 10 mL). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to yield the crude product. It was then purified by flash chromatography over silica gel (60–120 mesh) column using hexane/ethyl acetate (80:20) v/v as an eluent to afford the pure product. The products were characterized by ¹H NMR, ¹³C NMR and mass spectrometric analysis.

5.0 Reaction Kinetics for the Hydrogenation Reaction:

![Figure 18](image)

**K = 0.2937 hr⁻¹**

*Figure 18. Conversion of furfural vs time for reaction rate constant estimation with Cu-Mg-Al- Hydrotalcite.*
6.0 Inductively Coupled Plasma-Atomic Emission Analysis (ICP-AES): To test if any copper is leached during the reaction, ICP-AES, Inductively Coupled Plasma-Atomic Emission Spectroscopy analysis of the filtrates obtained after solid catalyst separation from reaction mixture to encounter leached metal in the filtrate was conducted. The Cu@Mg/γ-Al₂O₃ catalyst was separated from the reaction mixture by centrifugation, washed with ethyl acetate to make the catalyst free from organic matter, and finally with acetone, dried, and used in the next cycle. Almost consistent activity was noticed even after the fifth cycle. Copper content (0.2 mol%) of the fresh and used (after 5th cycle) catalyst was found to be almost the same (by ICP-AES). To check the heterogeneity of the catalyst, the hydrogenation of furfural was terminated at 16% conversion (after 30 min) and the catalyst was separated by simple centrifugation. The reaction was continued for an additional 4.5 hours and the conversion remained almost unchanged. Moreover, the filtrate was tested for copper by ICP-AES after the 6th cycle and no copper leaching was found for the five consecutive cycles. These studies clearly demonstrate that no leaching of copper from the catalyst was taken place during the reaction. 

![Figure 19. Conversion of furfural vs time for reaction rate constant estimation with Cu@Mg/γ-Al₂O₃](image)
Table 10. Leaching test of catalyst Cu@Mg/γ-Al2O3.

| S. No | Catalyst                  | H2  | Time | FF Conv.[%] | FA | 2-MF | Furan | THF | THFA |
|-------|--------------------------|-----|------|------------|----|------|-------|-----|------|
| 1a    | Cu@Mg/γ-Al2O3            | 2   | 0.5  | 16         | 85 | 0    | 3     | trace | 0    |
| 2b    | Cu@Mg/γ-Al2O3            | 2   | 4.5  | >99        | 94 | 2    | 4     | 0   | 0    |
| 3c    | Cu@Mg/γ-Al2O3            | 2   | 5    | >99        | 94 | 2    | 4     | 0   | 0    |

* Reaction conditions: FF (2.6 mol%), Catalyst (2 g, Cu-Mg: Cu@Mg; Cu 0.2 mol%, Mg 0.05 mol%), 443.15 K. * Reaction continued devoid of catalyst (catalyst removed by filtration). * Reaction with fresh catalyst.

Table 11. ICP-AES analysis of catalyst Cu@Mg/γ-Al2O3.

| S. No | Catalyst                  | ICP-AES (Cu & Mg mol%) |
|-------|--------------------------|------------------------|
| 1a    | Cu@Mg/γ-Al2O3            | Cu: 0.2001 & Mg: 0.0514|
| 2b    | Reaction filtrate        | Cu: 0.0001 & Mg: trace |
| 3c    | Cu@Mg/γ-Al2O3            | Cu: 0.2000 & Mg: 0.0511|

* Fresh catalyst, * Reaction filtrate (catalyst removed by filtration), * Reaction with fresh catalyst.

7.0. ¹H and ¹³C NMR spectrum of Furfuryl alcohol:

![Figure 20. ¹H NMR spectra of fufuryl alcohol](image_url)
Figure 21. $^{13}$C NMR spectra of furfuryl alcohol

8.0 References:

1. Y. Tang, Y. Liu, P. Zhu, Q. Xue, L. Chen and Y. Lu, *AIChE J.*, 2009, 55, 1217-1228.

2. M. Su, R. Yang and M. Li, *Fuel*, 2013, 103, 398-407.

3. F. W. Chang, W. Y. Kuo, K. C. Lee, *Appl. Catal.* 2003, 246, 253-264.

4. S. Sitthisa, D. E. Resasco, *Catal. Lett.* 2011, 141, 784-791

5. (a) M. Lesiak, M. Binczarski, S. Karski, W. Maniukiewicz, J. Rogowski, E. Szubiakiewicz, J. Berlowska, P. Dziugan, I. Witońska, *J. Mol. Catal. A: Chem.*, 2014, 395, 337-348; (b) K. Fulajtárová, T. Soták, M. Hronec, I. Vávra, E. Dobročka, M. Omastová, *Appl. Catal. A.*, 2015, 502, 78-85.

6. M. Audemar, C. Ciotonea, V. De Oliveira, S. Royer, A. Ungureanu, B. Dragoi, E. Dumitriu, F. Jérôme, *ChemSusChem.*, 2015, 8, 1885-1891.

7. K. Yan, A. Chen, *Fuel.*, 2014, 115, 101-108.

8. (a) B. M. Nagaraja, A. H. Padmasri, B. D. Raju and K. S. Rao, *J. Mol. Catal. A: Chem.*, 2007, 265, 90-97. (b) B. M. Nagaraja, V. S. Kumar, V. Shasikala, A. H. Padmasri, B. Sreedhar, B. D. Raju and K. S. Rao, *Catal Commun.*, 2003, 4, 287-293.
9. S. Wei, H. Cui, J. Wang, S. Zhuo, W. Yi, L. Wang, Z. Li, *Particuology*, 2011, 9, 69-74.
10. M. J. Taylor, L. J. Durndell, M. A. Isaacs, C. M. Parlett, K. Wilson, A. F. Lee, G. Kyriakou, *Appl. Catal. B.*, 2016, 180, 580-585.
11. S. Sitthisa and D. E. Resasco. *Catal. Lett.*, 2011, 141, 784-791.
12. L. Liu, H. Lou, M. Chen, *Appl. Catal. A.*, 2018, 550, 1-10.
13. K. Fulajtárova, T. Soták, M. Hronec, I. Vá vra, E. Dobročka, M. Omastová, *Appl. Catal. A.*, 2015, 502, 78-85.
14. M. M. Villaverde, N. M. Bertero, T. F. Garetto, A. J. Marchi, *J. Catal. Today.*, 2013, 213, 87-92.
15. M. M. Villaverde, T. F. Garetto, A. J. Marchi, *Catal. Commun.*, 2015, 58, 6-10.
16. J. Zhang and J. Chen, *ACS Sustainable Chem. Eng.*, 2017, 5, 5982-5993.
17. H. Liangke, X. Chenghua, L. Wenbiao, L. Jianying, L. Jun, D. Xingjie, G. Yan, Y. Yingchun., *Chin. J. of Catal.*, 2010, 31, 461-465.
18. K. Yan, J. Y. Liao, X. Wu, X. M. Xie. *Rsc Adv.*, 2013, 3, 3853-3856.
19. C. Xu, L. Zheng, D. Deng, J. Liu, S. Liu. *Catal Commun*, 2011, 12, 996-999.