

Studies on bimetallic Cu-Ag supported on alumina catalysts for hydrodeoxygenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran

D. Dhana Lakshmi ^{a,b}, Yogita ^{a,b}, B. Srinivasa Rao ^a, and N. Lingaiah ^{a,b*}

^a Department of Catalysis and Fine Chemicals, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India.

^b Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.

*Corresponding author: Email: nakkalingaiah@iiict.res.in; Tel: +91-40-27191722

2.3. Catalyst characterization

BELSorb II Instrument (Japan) was used to measure BET surface area by N₂ adsorption method. The samples were treated at 200 °C for 2 h before the measurement.

X-ray diffraction (XRD) analysis of the catalysts was implemented on an X-ray diffractometer (Ultima-IV X-ray diffractometer of Rigaku Corporation, Japan) at 30 kV in the scan range of 10–80° with 2° min⁻¹ scan speed and 15 mA.

The character of acidic sites of the catalysts was investigated by using pyridine adsorbed FT-IR spectroscopy in DRIFT mode at room temperature. In the typical experiment the degasification was done in vacuum at 200 °C for 3 h followed by suspending dry pyridine. Afterwards the overspill pyridine was evacuated by heating the catalyst sample at 120 °C.

Ammonia TPD was carried on BELCAT-II (Belsorb, Japan) instrument. In a standard experiment about 0.05 g sample was pre-treated in pure helium flow for 1 h at 300 °C. After the pre-treatment, the catalyst sample was soaked with He balanced 10% NH₃ gas for 1 h at 100 °C and He flushing was used to remove physisorbed ammonia at same temperature. Then the TPD profile was carried from 100 °C to 800 °C with the temperature raising rate of 10 °C min⁻¹ and the desorbed ammonia gas was measured.

Temperature-programmed reduction (TPR) was used to measure the reduction temperature of the metal oxides on the catalysts. For each test 50 mg of catalyst dried at 50 °C for 10 min in 5% H₂/Ar gas mixture (35ml/min) and then heated to 800 °C with the ramp of 10 °C/min. thermal conductivity detector (TCD) was used to monitored the hydrogen consumption. Metal surface area, dispersion and particle size of the copper was measured from the N₂O chemisorption method. Prior to the measurement 50 mg of the catalyst was pretreated at 50 °C for 10 min in 5% H₂/Ar gas

mixture (35ml/min) and then reduced to the temperature 350 °C. cooled the reactor to 50 °C and flushed with He for 10 min. copper oxide changes to metallic copper by releasing oxygen. At 50 °C flushed with N₂O for 30 min and again performed same process as mentioned above.

The morphological studies of catalysts were carried out by scanning electron microscope (M/s. JEOL, Switzerland) and TEM images were obtained on a FEI (North America), TALOS apparatus operating between 160 and 180 kV respectively. Prior to TEM analysis, the catalyst sample was ultrasonicated in ethanol and a drop was placed onto a carbon coated copper grid, the solvent was then evaporated in an air oven at 80 °C for 6 hours.

Surface morphology of the catalysts was investigated by field emission scanning electron microscope (FE-SEM) of JEOL JSM-7610F equipped with an energy-dispersive X-ray spectroscopy. FE-SEM pictures were scanned at 2.00 KV voltage with Secondary Electron Image probe (SEI) and the Gentle Beam (GB) mode.

The X-ray photoelectron spectroscopy (XPS) data were obtained with a KRATOS ANALYTICAL, Shimadzu group company, AXIS SUPRA, the 500 mm Rowland circle monochromated Al Ka X-ray source and optimized electron optics contribute to the excellent energy resolution performance.

TGA study was carried on TGA Q500 instrument. In an experiment, 10 mg of sample was loaded into the instrument and an analysis was conducted from RT to 800 °C at 20 °C/min ramp rate under N₂ flow (40 mL/min).

Table S1. ICP-AES analysis of the catalysts

Catalyst	Cu (%)		Ag (%)	
	Theoretical	ICP	Theoretical	ICP
CA	10	9.9	0	0
CAA-0.5	10	9.6	0.5	0.4
CAA-1	10	9.7	1	0.8
CAA-2	10	9.6	2	1.7
CAA-5	10	9.3	5	4.1
CAA-7	10	9.2	7	5.3
CAA-10	10	9.3	10	7.6
CAA-2 used	10	9.4	2	1.6

SEM images are displayed in Fig. S1 a-f. The Cu and Ag species were randomly dispersed over the support in all the catalysts. Fig. S1a (CA) shows the congregated CuO species on the support, whereas Fig. S1b (AA) displays the small cubic-shaped Ag particles formation. Fig. S1 c-f represents the mixed Cu-Ag catalysts SEM images. The catalysts with increasing Ag content formed highly agglomerated fibrous clusters.

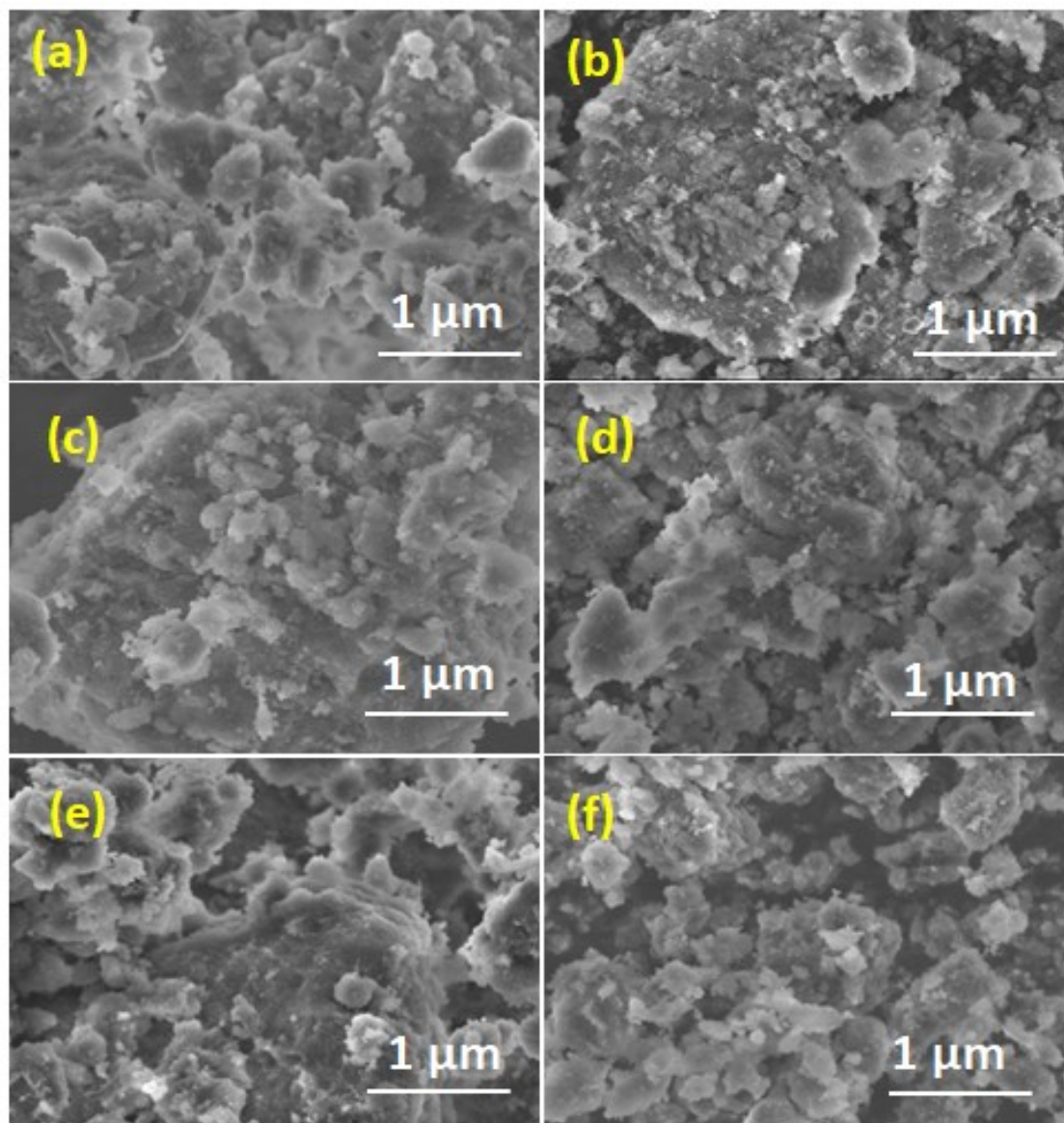


Fig. S1. SEM images of (a) CA, (b) AA, (c) CAA-0.5, (d) CAA-1, (e) CAA-2, (f) CAA-5.

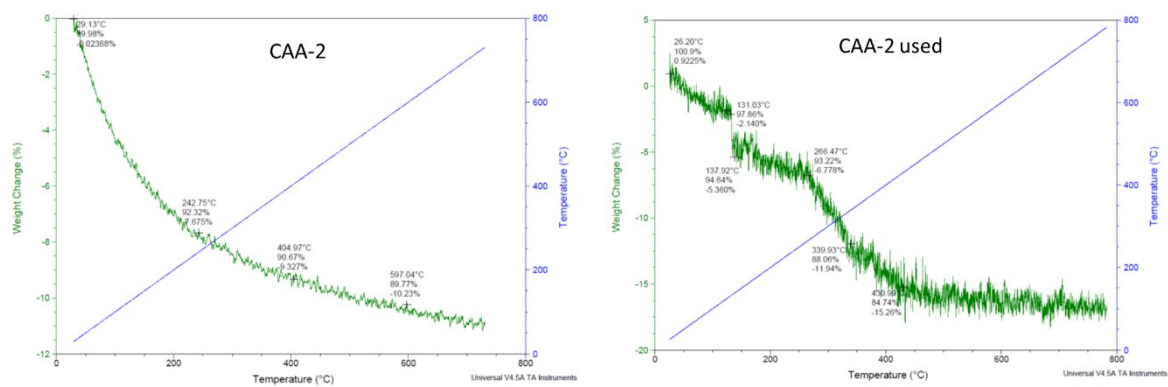


Fig. S2. TGA analysis of fresh and used CAA-2 catalyst.

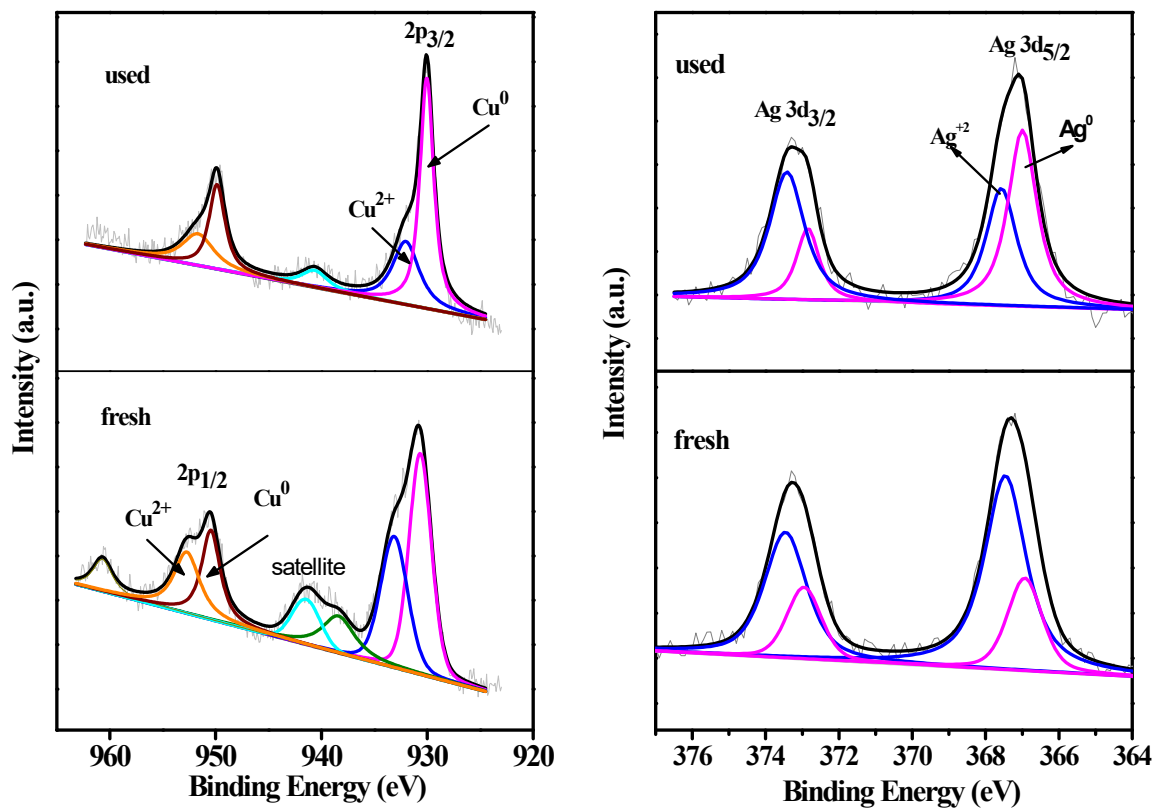


Fig. S3. XPS analysis of fresh and used CAA-2 catalysts

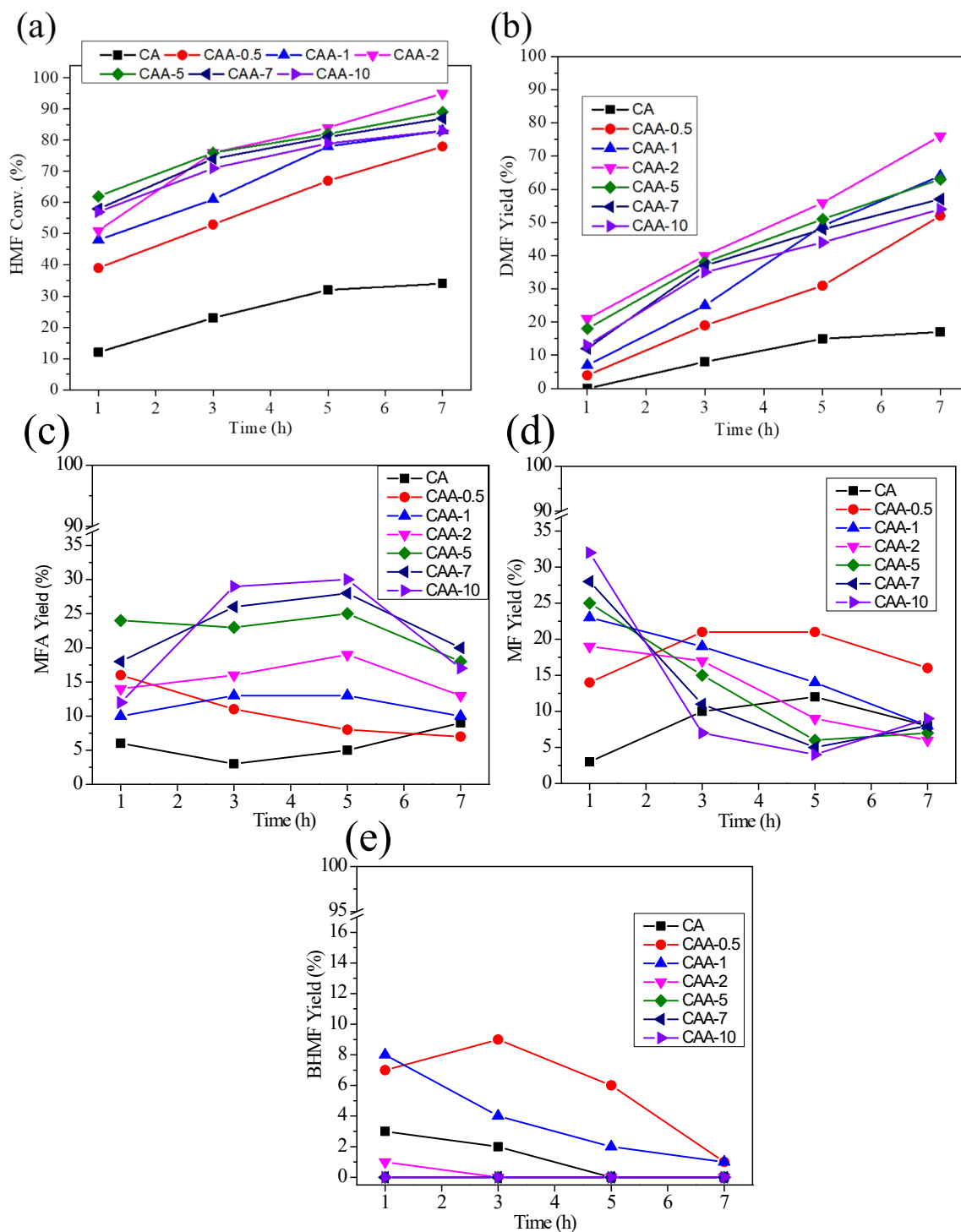


Fig. S4. Influence of Ag addition to Cu/γ-Al₂O₃ on HMF hydrodeoxygenation to DMF. (a) HMF Conversion, (b) DMF Yield, (c) MFA Yield, (d) MF yield, (e) BHMF yield. Reaction Conditions.

HMF: 2mmol (0.252g), Catalyst: 0.075g, Temp.: 180 °C, Time: 1-7 h, H₂ pressure: 1MPa, THF: 20 mL.

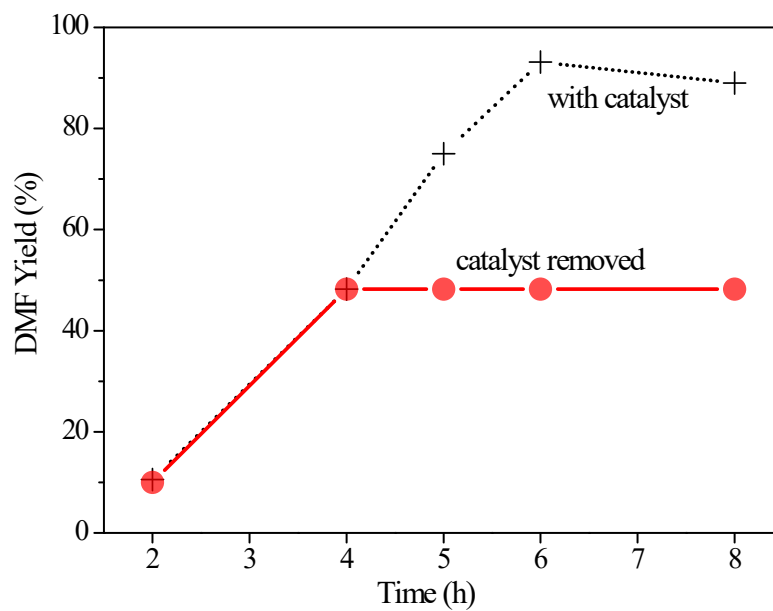


Fig. S5. Catalyst leach test at optimized reaction conditions: HMF: 2mmol (0.252g), Catalyst (CAA-2): 0.15g, Temp.: 180 °C, Time: 1-8 h, H₂ pressure: 1.5MPa, THF: 20 mL.