Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2015

Versatile bi-metallic Copper-Cobalt catalyst for liquid phase hydrogenation of furfural to 2methylfuran

Sanjay Srivastava, G. C. Jadeja, Jigisha Parikh^{*} Department of Chemical Engineering, Sardar Vallabhbhai National Institute of Technology, Surat-395007, Gujarat, India.

* Corresponding authors, Tele: + 91261-2251689 E-mail: <u>jk_parikh@yahoo.co.in</u>, Jigisha Parikh

SUPPLEMENTARY INFORMATION

Catalysts Synthesis and Characterization

Bimetallic Cu-Co catalysts having molar ratio (x/y=1) over various supports such as amorphous SiO₂, H-ZSM-5 (Si/Al=25), γ -Al₂O₃, and with molar ratios (x/y=1, 2, and 4) over screened γ -Al₂O₃ were synthesized by impregnation method using an aqueous solutions of (Co(NO₃)₂.6H₂O), and copper nitrate (Cu(NO₃)₂.6H₂O). The doped catalysts were dried overnight at 100±2°C and subsequently calcined at 450±5 °C for 4h to obtain the final oxide catalysts.

X-ray diffraction (XRD) patterns were obtained using high tech XRD (PW-1710, Philips, Netherlands, with Quasar software packages, at SAIF, SVNIT Surat) by using Cu-K α radiation prepared with a PW Bragg - Brentano (BB) goniometer ($\theta/2\theta$), operated at 45 kV and 40 mA. The fresh calcined and used samples were scanned in the range of $2\theta = 5$ to 80° .

BET surface area and pore volume of the prepared catalysts were obtained by the adsorption of N_2 at -196°C at IIT, Delhi. Before analysis, the catalyst was degassed in vacuum at 200±2°C using ASAP 2010, Micrometrics, instrument. Brunauer–Emmett–Teller (BET) method and N_2 adsorption–desorption isotherms were analysed for the surface areas and pore volumes of the synthesized materials. Similarly, Barret–Joyner–Halenda (BJH) method was implemented to calculate the pores of the synthesised catalysts.

Morphology of prepared catalysts has been determined by FE-SEM analytical instrument xT Nova NanoLab 200 (CSIR- Bhopal), by using FE-SEM-EDX analysis. Samples were sonicated in an

ultrasonicator by using acetone (solvent) to disperse the sample uniformly. Thereafter, the small drops of sample were deposited on a carbon holder followed by evacuation at high vacuum (10-5 Torr). Finally, samples were analysed with the average of ten point analysis.

Philips CM-200 model transmission electron microscope (TEM) (SAIF, IIT Mumbai) was used to further assess the morphology and particles size distribution of freshly reduced bi-metallic Cu-Co (x/y=1) catalysts supported on SiO₂, H-ZSM-5 (Si/Al=25), Al₂O₃ and used Cu-Co/Al₂O₃ (x/y=1). For analysis, powder catalyst material was dispersed in ethanol using an ultrasonic bath for 15 min. A droplet of the suspended material was then placed on copper grids followed by vacuum drying.

NH₃-TPD analysis was carried out using the Micromeritics Pulse Chemisorption Chemisorb 2720 analyser at IIT Madras. In order to find the strong and weak acid sites of the supported material ammonia temperature programmed desorption was carried out. Before NH₃-TPD, the samples were activated at 550 °C for 2 h in helium gas (40 ml/min), then cooled down to 100 °C and maintained at this temperature. After 2 h of NH₃ adsorption on the catalysts, the physically adsorbed ammonia was removed by the helium gas flow at 100 °C. NH₃-TPD measurements were performed in the range of 100–700 °C at the temperature ramp rate of 10 °C/ min. The desorbed NH₃ was determined continuously by a thermal conductivity detector (TCD). Also, a water trap was used to avoid the influence of water.

TPR analysis was carried out using the Micromeritics Pulse Chemisorption Chemisorb 2720 analyser at IIT Madras. In a typical procedure, 0.5 g of catalyst was kept in a quartz reactor placed in a furnace. The furnace temperature was increased from ambient to 800 °C with a ramp rate of 10°C/min. 9.9% of H₂ in argon was used for reduction at a flow rate of 30 mL/min. H₂ consumption was measured using a thermal conductivity detector (TCD).

The ex-situ X-ray absorption of both copper and cobalt K-edge (8979 and 7709 eV) were recorded in the transmission mode using two nitrogen gas filled detectors, using beam line-8 at the Raja Ramanna Center for Advanced Technology, Indore, India. The samples were tightly packed in an absorption holder to avoid pinholes and at a thickness close to one absorption length. The X-ray absorption data were analyzed

using the conventional procedure using ATHENA package [42]. After background correction, the XANES spectra were normalized by the edge height. K^2 - weighed EXAFS signal was transformed without phase correction from k-space to r-space. CuO, Co₃O₄ were used as reference compounds for XANES and EXAFS analysis.

CHNS analysis of used catalysts was performed using Flash EA 1112, Thermo finnigan, Italy at SVNIT Surat. 0.8 g of used Cu-Co/Al₂O₃ (X/Y=1) was placed in a combustion chamber. The combustion products are separated by a chromatographic column and detected by the thermal conductivity detector (TCD), which gives an output signal proportional to the concentration of the individual components of the mixture.

Catalyst	Cu/Co	EDX	Surface area	Pore	Pore	Avg. Particle
	molar		(m^{2}/g)	volume	size	Size (nm)
	ratio(x/y)			(cm ³ /g)	(A°)	
γ-Al ₂ O ₃			166.1	0.54	66	
Cu-Co/	1	10.4:9.9	113.5	0.28	46	20
γ-Al ₂ O ₃	2	10.5:5.2	118.0	0.31	52	17
	4	10.3:2.4	125.1	0.34	56	15

Table-S1 Effect of Cu/Co molar ratio(x/y) on textural and structural characteristics of Co-Cu/y-Al₂O₃

Table S2. Acidity of bi-metallic Cu-Co catalysts supported on SiO₂, H-ZSM-5, and γ -Al₂O₃, using ammonia-TPD method

Supports/ Catalysts	Cu/Co=1	Amount	Total Acidity		
		mmol/g.c	(mmol/g.cat)		
		<200	<250-450>°C	>450 °C	
γ-Al ₂ O ₃					0.28
H-ZSM-5	-				0.66
(Si/Al=25)					
Cu-Co/SiO ₂	1	0.07	0.02	0.00	0.09
Cu-Co/ y-Al ₂ O ₃	1	0.13	0.21	0.14	0.49
Cu-Co-HZSM-5	1	0.0	0.72	0.36	1.08

Table S3. Effect of Cu/Co molar ratio(x/y) on acidity of bi-metallic Cu-Co/y-Al₂O₃ using ammonia-TPD method

Supports	Cu/Co(x/y)	Amount	of ammonia de	sorbed in	Acidity
		mmol/g ca	(mmol/g cat)		
		<200 °C	<200-450>°C	>450 °C	
Cu-Co/ y-Al ₂ O ₃	1	0.13	0.21	0.14	0.49
Cu-Co / y-Al ₂ O ₃	2	0.11	0.15	0.21	0.52
Cu-Co / y-Al ₂ O ₃	4	0.09	0.12	0.31	0.53

Table S4. CHNS analysis of bi-metallic Cu-Co/ɣ-Al₂O₃ after reaction (third cycle) and dried at 150 °C

Catalyst	C (%)	H (%)	N (%)	S (%)
Cu-Co/ y-Al ₂ O ₃	5.57	1.05	0.004	0.001

(Reaction Conditions: T= 220 °C, P= 4.0 MPa, furfural concentration = 2.25 M, Time = 4 h)



Figure.S1 Wide angle X-ray diffraction pattern of bi-metallic Co-Cu/ γ -Al₂O₃ (x/y) catalysts (# CuCo₂O₄, *Co₃O₄, Δ CuO)



Figure.S2 Wide angle X-ray diffraction pattern of bi-metallic Co-Cu/y-Al₂O₃ (x/y=1) fresh calcined and used (dry in air at 150 °C) catalysts



Figure S3. SEM micrographs for Cu-Co/ γ -Al₂O₃ (Cu/Co = 4, 2, and 1) catalysts (d, e, f)



Figure S4. NH₃- TPD patterns of Cu-Co/ y-Al₂O₃ with various Cu/Co ratios



Figure S5. XANES derivative spectra of Cu-Co (x/y=1) over various supports (a) Fresh calcined 450 °C, (b) Reduced at 280 °C, and Cu-Co/ γ -Al₂O₃ with various Cu/Co ratios (x/y=1, 2, and 4) (c) Fresh calcined 450 °C, (d) Reduced at 280 °C



Figure S6. Fourier transform Modulus of Cu-Co (x/y=1) over various supports (a) Fresh calcined 450 °C, (b) Reduced at 280 °C, and Cu-Co/ γ -Al₂O₃ with various Cu/Co ratios (x/y= 1, 2, and 4) (c) Fresh calcined 450 °C, (d) Reduced at 280 °C



Figure S7. Co-Kedge XANES Spectrum of Cu-Co/γ-Al₂O₃(x/y=1) (fresh calcined and reduced at 280°C)