Supplementary Information

$CuCr_2O_4$ derived by sol-gel method as highly active and selective catalyst for the conversion of glycerol to 2,6-dimethylpyrazine: A benign and eco-friendly process

Krishna Vankudoth[a,b], Naresh Gutta[b], Vijay Kumar Velisoju[b], Suresh Mutyala[b], Hari Padmasri Aytam[c] and Venugopal Akula[a,b,*]

[a] Academy of Scientific and Innovative Research, India.

[b] Catalysis Laboratory, Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, Telangana – 500 007, India.

[c] Department of Chemistry, University College for Women, Osmania University, Koti, Hyderabad - 500 095, Telangana, India.

*Corresponding author, Email: akula@iict.res.in Tel. +91-40-27193165;

Fax: +91-40-27160921

Abstract

Vapour phase dehydrocyclization of crude glycerol in conjunction with 1,2-propanediamine (1,2-PDA) was examined over $CuCr_2O_4$ obtained by different preparation methods. High proportion of copper species interacted with Cr_2O_3 in $CuCr_2O_4$ derived from sol-gel route with a low ratio of Cu^{2+}/Cu^0 demonstrated higher dehydrocyclization activity and 2,6-dimethylpyrazine (2,6-DMP) selectivity. X-ray photoelectron spectroscopy analysis of the reduced $CuCr_2O_4$ revealed lower fraction of ionic Cu and high percentage of metallic Cu in the near surface region. The HCOOH and pyridine adsorbed DRIFT spectra of $CuCr_2O_4$ revealed strong basic and moderate Lewis acid sites are responsible for the selective formation of 2,6-dimethylpyrazine which is in consistent with the catalyst poisoning studies on $CuCr_2O_4$ co-feeding pyridine as both Brønsted and Lewis acid site blocker and 2,6-lutidine as a selective Brønsted acid site blocker during the dehydrocyclization reaction. Presence of

isolated CuO and Cr_2O_3 species led to a high selectivity of 2,6-dimethylpiperazine. The high intrinsic activity of $CuCr_{sol\text{-}gel}$ was also concomitant with Cu metal surface areas of the catalysts. The fresh, reduced and some of the used catalysts are characterized by BET – surface area, powder XRD, FT-IR, XPS, TEM, H_2-TPR, TPD of NH_3, pyridine, 2,6-dimethylpyridine and HCOOH adsorbed DRIFT spectroscopy.

1.0 Materials and methods

1.1 Preparation of $CuCr_2O_4$ by different techniques

1.1.1 Sol–gel method

The $CuCr_2O_4$ spinel was synthesized by sol–gel method [1]. In a typical procedure required amounts of $Cu(NO_3)_2.3H_2O$ and $Cr(NO_3)_3.9H_2O$ (at a desired mole ratio of Cu/Cr = 0.5) dissolved in 47 mL ethanol at 60 °C followed by 1 mL of conc. HNO_3 was added to give a clear dark blue solution. About 18 mL Pluronic P123 was instantaneously added to the solution to turn out a dark green transparent gel formed within few minutes. The obtained wet gel was aged in air atmosphere and subsequently dried at 120 °C for 15 h, and the resulting gel was calcined at 550 °C for 5 h. The calcined form of sample (i.e. $CuCr_2O_4$ identified by powder XRD) is denoted as $CuCr_{sol\text{-}gel}$.

1.1.2 Co-precipitation method

The $CuCr_2O_4$ sample was prepared by co-precipitation method using $Cu(NO_3)_2.3H_2O$ and $Cr(NO_3)_3.9H_2O$ with Cu : Cr = 1: 2 (mole ratio) at a constant pH ~ 8 using a mixture of 2M NaOH + 1M Na_2CO_3 (base mixture) as precipitating agent. The gel was washed thoroughly, filtered and oven-dried for overnight at 120 °C and calcined in inactive air at 550 °C for 5 h which is designated as $CuCr_{cp}$. The bulk CuO and Cr_2O_3 samples were prepared by precipitation of their corresponding metal salt precursors [$Cu(NO_3)_2.3H_2O$ and $Cr(NO_3)_3.9H_2O$] at constant pH of 8.0 and the gels were washed thoroughly, followed by filtered and oven dried at 120 °C for 12 h subsequently calcined in inactive air at 550 °C for 5 h.

1.1.3 Mechanical mixing method

For mechanical mixing; CuO and Cr_2O_3 solid powders (obtained by precipitation method see 1.1.2) with a Cu:Cr = 1:2 mole ratio; was ground (using ethanol for wetting) and calcined in static air at 550 °C for 5 h which is designated as $CuCr_{mm}$.

1.1.4 Impregnation method

For impregnation of copper on Cr_2O_3; about 2.0 g of $Cu(NO_3)_2.3H_2O$ dissolved in 5 mL was added to 1.24 g Cr_2O_3. The solution was dried under continuous stirring at 100 °C until H_2O is evaporated. The sample was dried overnight at 120 °C and subsequently calcined in inactive air at 550 °C for 5 h which is designated as $CuCr_{imp}$.

2.0 Characterization of catalysts

The bulk and surface properties of the $CuCr_2O_4$ spinel obtained by various preparation techniques; were analysed by BET-surface area, powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR), temperature programmed reduction (H_2-TPR), X-ray photoelectron spectroscopy (XPS), atomic absorption spectroscopy (AAS), carbon-hydrogen-nitrogen-sulphur (CHNS) analyzer, temperature programmed desorption of NH_3 (NH_3-TPD) and formic acid adsorbed DRIFTS techniques. The specific surface areas were calculated applying the BET method. The temperature programmed desorption of ammonia (TPD of NH_3) of the Cu-Cr samples was measured using an Auto Chem 2910 (Micromeritics, USA). In a typical method 0.1 g of calcined Cu–Cr sample was reduced at 450 °C for 5 h in hydrogen at a flow rate of 30 mL min^{-1}. After reductive pre-treatment the sample was saturated with 10% NH_3 (balance helium) at 60 °C, at a flow rate of 50 mL min^{-1} and subsequently flushed with helium gas at 100 °C for 1 h. The TPD measurements were carried out from 100 to 700 °C at a ramping rate of 10 °C min^{-1}. The amount of desorbed NH_3 was calculated using GRAMS/32 software. The temperature programmed reduction (TPR) analysis was carried out in a quartz micro-reactor interfaced to a GC equipped with a TCD unit. For TPR analysis approximately 50 mg sample was loaded in an isothermal zone of a quartz reactor (i.d. = 6 mm, length = 300 mm) and heated by an electric furnace at a ramping rate of 10 °C min^{-1} to 300 °C in helium gas flowing at a rate of 30 mL min^{-1}, to facilitate the desorption of physically adsorbed water. After degassing the sample was cooled to room temperature and the helium gas was switched to 30 mL min^{-1} of reducing gas (5% H_2 in Ar) and the temperature was increased to 800 °C at a ramping rate of 10 °C min^{-1}. Hydrogen consumption was measured by analyzing effluent gas using a calibration curve of Ag_2O TPR under a similar protocol. The oven dried and calcined form of CuCr samples were characterized by powder X-ray diffraction (XRD) analysis using a Rigaku Miniflex X-ray diffractometer using Ni filtered Cu K_α radiation ($\lambda = 0.15406$ nm) from $2\theta = 20^\circ$ to 80°, at a scan rate of 2° min^{-1} with generator voltage and current of 30 kV and 15 mA respectively.

The X-ray photoelectron spectroscopy (XPS) of the reduced samples were recorded using a Kratos Axis Ultra Imaging X-ray photoelectron spectrometer, equipped with Mg anode and a multichannel detector. Charge referencing was done against adventitious carbon (C 1s, 284.8 eV). A Shirley-type background was subtracted from the signals. The recorded spectra were fitted using Gauss–Lorentz curves to determine the binding energies of the different elements. The elemental analysis of the samples revealed that there is no loss of metal during the preparation of samples (Table S1 and Table S2). The Cu metal surface area was measured by N_2O decomposition at 80 °C. In a typical method about 50 mg of catalyst was reduced using 5%H_2 balance Ar at 450 °C for 30 min and subsequently the reactor was cooled in helium gas flow (30 mL min^{-1}) from 450 °C to 80 °C. At this temperature, 0.5 mL of N_2O was injected in pulses and the N_2O consumption was monitored using gas chromatograph equipped with thermal conductivity detector (GC-TCD) with Porapak N column [2]. In this investigation, a surface copper density of 1.46 × 10^{19} atoms m^{-2} was used for the copper metal area calculation. The measurements were replicated in order to avoid possible bulk oxidation of catalyst surface due to excess pulses and hence the N_2O pulses were limited to a maximum of 3-4 injections.

The nature and strength of acid-base sites are investigated by pyridine, 2,6-dimethylpyridine and formic acid adsorbed FT-IR (Carry 660, Agilent Technologies) spectra. The in-situ experiments were performed using a purpose made IR cell connected to a conventional vacuum adsorption apparatus. In a typical method the sample powder was pressed into self-supporting wafers (density ~40 mg cm^{-2}) under a pressure of 10^5 Pa. After that, the sample was introduced in the IR cell. Firstly, the sample was pre-treated *in-situ* by heating in dynamic vacuum at a rate of 10 °C min^{-1} up to 450 °C for 1 h. After cooling down to 150 °C, the spectrum (fresh) was collected in the DRIFT mode. Prior to pyridine adsorption, the self supporting wafers were reduced using 5%H_2 balance Ar at 450 °C for 30 min and cooled to 150 °C in N_2 flow. Then the pyridine vapour was injected onto the sample in 3 successive pulses (with a total of ~5 mmol) followed by flushing the sample in N_2 for 1 h and the spectrum was recorded. The pyridine adsorbed DRIFT spectrum was subtracted with that of reduced sample spectrum to obtain the vibrational bands due to pyridine-acid (Brønsted acid site: Py-H^+ and Lewis acid site: Py-M^{n+}) site interaction. Finally, the spectra were quantified with Kubelka-Munk function. The elemental analysis of the samples revealed that there is no loss of metal during the preparation, activation and use (Table S1 and Table S2).

2.1 Dehydrocyclization activity measurements and product analysis

The vapour phase dehydrocyclization of aqueous glycerol and 1,2-PDA was carried out in a fixed bed down flow reactor at atmospheric pressure in the temperature range 300 - 425 °C at various GHSV using ~0.1 g of catalyst loaded in the quartz reactor (i.d = 0.8 cm, length = 46 cm). Prior to the reaction the calcined catalyst was reduced in 5% H_2 balance Ar at 450 °C for 3 h. The aqueous glycerol (10wt %) (Fluka) and 1,2-PDA (Fluka) was used in 1:1 mole ratio was fed using a syringe pump at flow rate of 2 - 10 mL h^{-1} along with N_2 (IOLAR-I grade, BOC, India) as carrier gas at a flow rate of 30 mL min^{-1}. The products were collected each hour in an ice-cold trap and analyzed by gas chromatography (Shimadzu, GC-17A) using ZB-5 capillary column. Simulated feed composition: 10 mmol glycerol +10 mmol 1,2-PDA + 0.2 μmol KOH+ 0.3 mmol CH_3OH + 200 mmol H_2O. All the products were confirmed by GC–MS (QP5050A Shimadzu) using a ZB-5 capillary column with EI mode. **2,6-dimethylpyrazine**: $M^{+\cdot}$ m/z: 108; $(M\text{-}CH_3)^+$ m/z: 93; $(M\text{-}HCN)^+$ m/z: 81; $(M\text{-}C_3H_6)^{+\cdot}$ m/z: 66; $[M\text{-}C_3H_2N_2]^{+\cdot}$ m/z: 42; **Dihydroxyacetone**: $M^{+\cdot}$ m/z: 90; $[M\text{-}H_2O]^{+\cdot}$ m/z: 72; $[M\text{-}CH_2O]^{+\cdot}$ m/z: 60; $[M\text{-}(CO, H_2O)]^+$ m/z: 43; $[M\text{-}(CO, CH_2CH_2)]^+$ m/z: 31; $[M\text{-}C_3H_4O_2]^{+\cdot}$ m/z: 18; **Hydroxyacetone**: $M^{+\cdot}$ m/z: 74; $[M\text{-}CH_2O]^{+\cdot}$ m/z: 43; $[M\text{-}(CO, CH_3)]^+$ m/z: 31; $[M\text{-}C_2H_3O_2]^+$ m/z: 15; **6-hydroxymethyl-2-methylpyrazine**: $M^{+\cdot}$ m/z: 124; $(M\text{-}H)^+$ m/z: 123; $(M\text{-}CH_2O)^{+\cdot}$ m/z: 94; $(M\text{-}CH_3CN)^+$ m/z: 83; $(M\text{-}C_3H_2N_2O)^{+\cdot}$ m/z: 42.

2.2 Calculations of conversion, rate and specific rate:

$$\%Conversion\ of\ 1{,}2-PDA = \left[\frac{moles_{\ 1,2-PDA\ in} - moles_{1,2-PDA\ out}}{moles_{1,2-PDA\ in}}\right] \times 100$$

$$\%Conversion\ of\ Glycerol\ = \left[\frac{moles_{\ Gly.\ in} - moles_{Gly.\ out}}{moles_{Gly.\ in}}\right] \times 100$$

$$\%\ Selectivity\ = \left[\frac{{P_i}/{C_i}}{\left[\sum_i^n {P_i}/{C_i}\right]}\right] \times 100$$

(where C_i and P_i are the stoichiometric factor and the product concentration, respectively).

$$Yield_{2,6-DMP} = \frac{[Conv._{Gly.} \times Sel._{2,6-DMP}]}{100}$$

$$Yield_{6-HMP} = \frac{[Conv._{Gly.} \times Sel._{6-HMP}]}{100}$$

Rate (r) is defined as

$$r_{2,6-DMP} = \left[\frac{(Yield_{2,6-DMP}) \times (1,2-PDA + Glycerol)\, flow\, rate}{Weight\ of\ the\ catalyst}\right] moles\ g_{cat}^{-1}\, s^{-1}$$

$$r_{6-HMP} = \left[\frac{(Yield_{6-HMP}) \times (1,2-PDA + Glycerol)\, flow\, rate}{Weight\ of\ the\ catalyst}\right] moles\ g_{cat}^{-1}\, s^{-1}$$

3.0 Results

3.1 TEM analysis

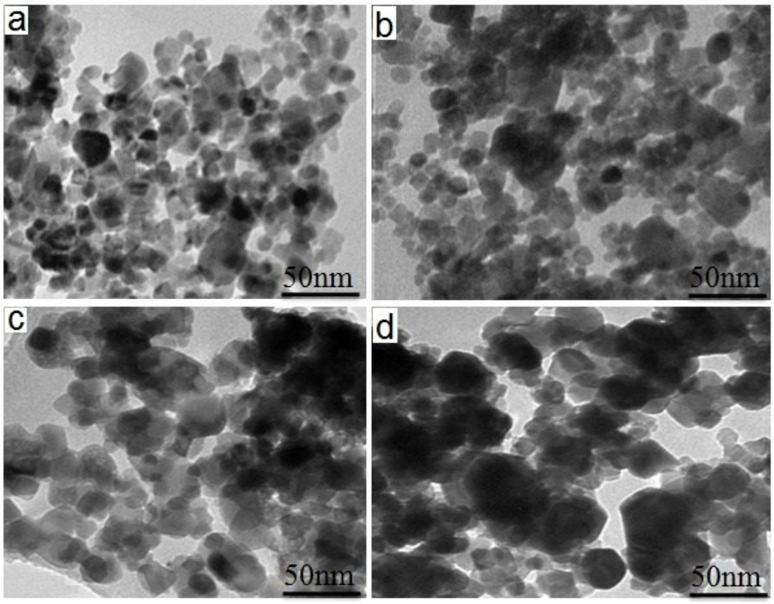


Figure S1: TEM images of calcined (a) $CuCr_{sol-gel}$, (b) $CuCr_{cp}$, (c) $CuCr_{mm}$ and (d) $CuCr_{imp}$ samples.

Figure S1 shows the TEM images of calcined $CuCr_{sol-gel}$, $CuCr_{cp}$, $CuCr_{mm}$ and $CuCr_{imp}$ samples. It can be seen that CuO-Cr_2O_3 mixed oxides aggregate together and form agglomerates with an average particle size of 17 nm, 25.9 nm and 30.7 nm in $CuCr_{sol\text{-}gel}$, $CuCr_{cp}$ and $CuCr_{mm}$ samples respectively (Figure S1a-c). The $CuCr_{imp}$ sample (Figure S1d) showed a particle size of 41.9 nm could be attributed to aggregates of CuO and Cr_2O_3 together with low dispersion.

3.2 TOS analysis

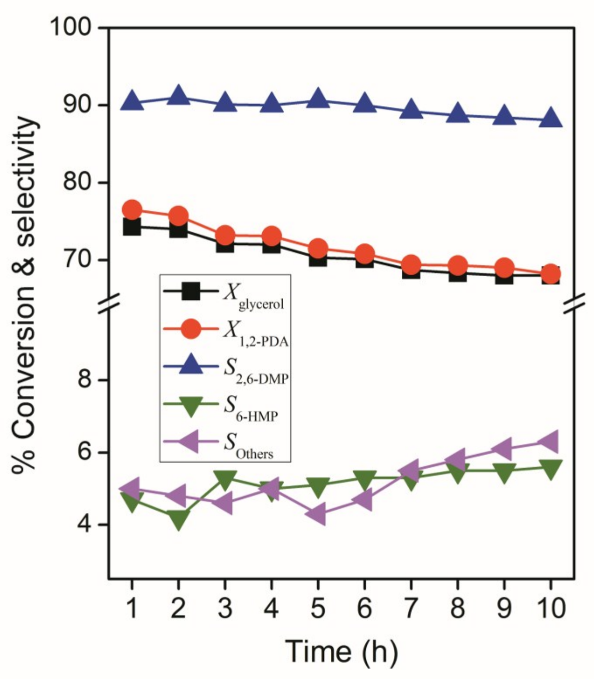


Figure S2: Time on steam on $CuCr_{sol\text{-}gel}$ sample.

3.3 UVDRS analysis of Cu-Cr prepared by different techniques

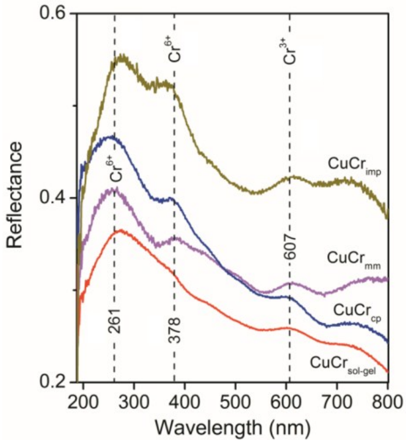


Figure S3: UVDRS analysis of calcined Cu-Cr samples.

3.4. XPS analysis calcined $CuCr_{sol\text{-}gel}$ sample

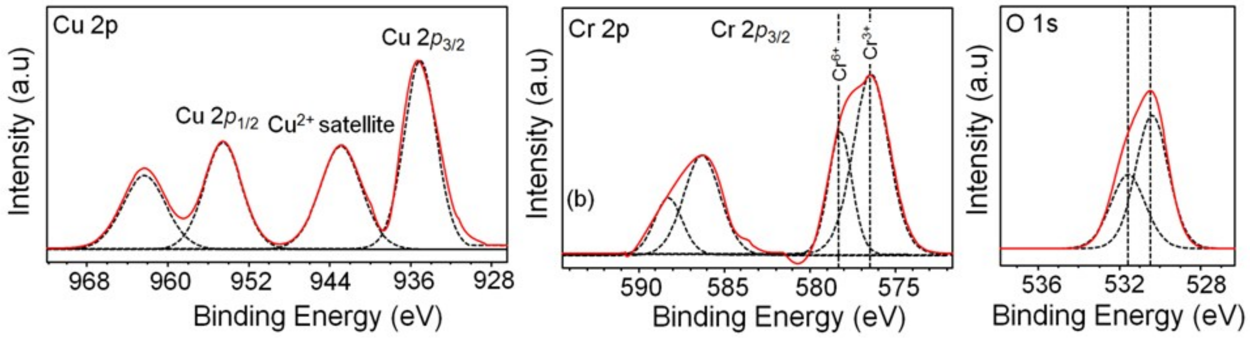


Figure S4: XPS analysis of fresh calcined $CuCr_{sol\text{-}gel}$ sample.

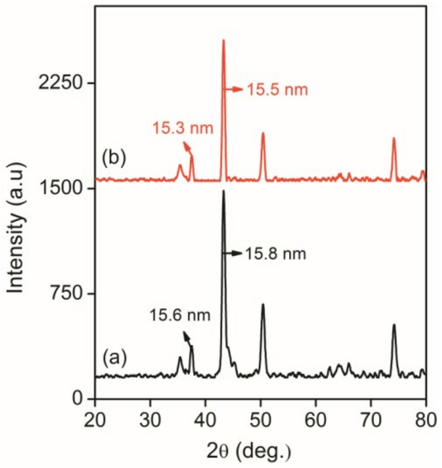


Figure S5: XRD pattern of (a) reduced and (b) spent (10 h) $CuCr_{sol\text{-}gel}$ samples.

Sample	Crystalline size (nm)	
	$CuCr_2O_4$ (202)	Cu^0 (111)
$CuCr_{sol\text{-}gel}$ (Reduced)	15.6	15.8
$CuCr_{sol\text{-}gel}$ (Spent)	15.3	15.5

Crystallite size measured from XRD patterns of reduced and spent catalysts using Scherrer formula and data is reported in table. The crystallite size of $CuCr_2O_4$ (202) and Cu^0 (111)

phases are more or less same in both reduced and spent catalysts. These results are clearly indicating that the sintering is not the cause of decrease in activity.

Table S1: Surface composition obtained by XPS analysis

Catalyst	Cu	Cr	O	Cu/Cr	O/(Cu+Cr)	O/Cu	O/Cr
$CuCr_{sol\text{-}gel}$	27.26	19.69	53.05	1.38	1.12	1.94	2.70
$CuCr_{cp}$	23.50	17.42	59.08	1.34	1.44	2.50	3.39
$CuCr_{mm}$	17.20	14.48	68.32	1.18	2.15	3.97	4.71
$CuCr_{imp}$	9.82	5.92	84.26	1.65	5.35	8.58	14.23

Table S2: Elemental analysis by atomic absorption spectroscopy

Sample	Nominal composition (Cu:Cr) mole ratio	AAS composition (Cu:Cr) mole ratio
$CuCr_{sol\text{-}gel}$	1.0:2.0	0.97:1.95
$CuCr_{cp}$	1.0:2.0	1.06:1.90
$CuCr_{mm}$	1.0:2.0	0.98:1.97
$CuCr_{imp}$	1.0:2.0	0.90:1.86

Table S3: Dehydrocyclization of aqueous glycerol and 1,2-PDA over reduced Cu–Cr prepared by sol-gel; catalyst weight 0.1 g; GHSV = 11.0 mL g_{cat}^{-1} s^{-1}.

Temperature (°C)	Conversion (%)		Selectivity (%)				$^{b}r_{2,6\text{-DMP}}$ /10^{-8} mol $(g_{cat})^{-1}$ s^{-1}
	$X_{glycerol}$	$X_{1,2\text{-PDA}}$	$S_{2,6\text{-DMP}}$	$S_{6\text{-HMP}}$	$S_{2,6\text{-DMPip}}$	$^{a}S_{others}$	
300	24.8	26.4	85.3	8.2	1.6	4.9	239.7
325	35.3	37.7	87.2	7.4	2.0	3.4	348.8
350	50.6	52.3	87.5	5.0	2.4	5.1	501.7
375	74.3	76.5	90.3	4.7	2.6	2.4	760.3
400	76.1	78.2	88.7	5.2	2.7	3.2	765.0

425	77.8	78.5	87.3	5.4	3.1	4.2	769.7

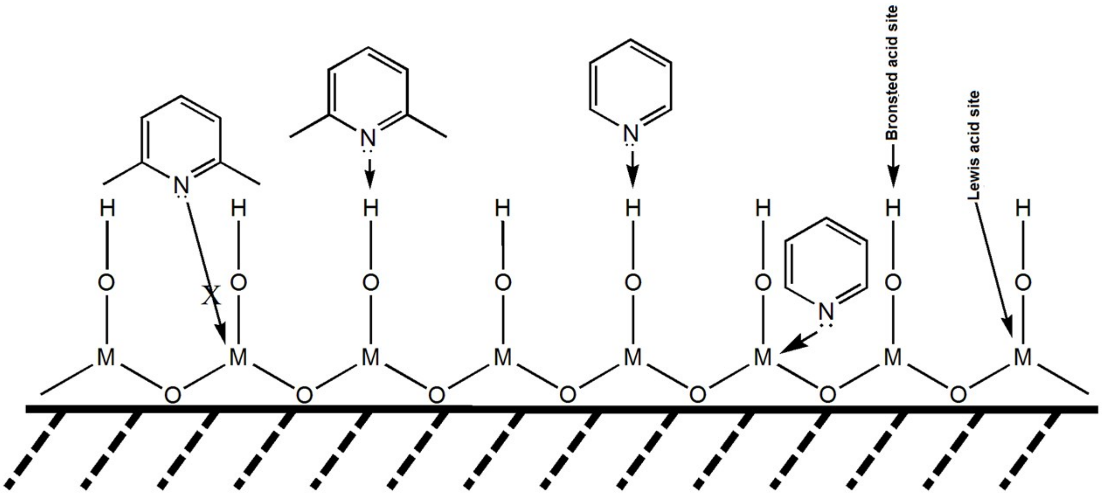
[a] Others include 2,5-DMP and 5-HMP.

[b] Rate of 2,6-DMP measured with respect to glycerol conversion and 2,6-DMP selectivity.

Table S4: CHNS analysis of used CuCr catalysts recovered after 6 h run time.

Catalyst	N_2 %	C %	H_2 %	S %
$CuCr_{sol\text{-}gel}$	0	2.0	0	0
[a]$CuCr_{sol\text{-}gel}$	0	2.3	0	0
$CuCr_{cp}$	0	2.1	0.2	0
$CuCr_{mm}$	0	3.8	0	0
$CuCr_{imp}$	0	2.3	0.3	0

[a] CHNS analysis of used CuCr catalyst recovered after 10 h run time.



Scheme S1: Surface poisoning of Brønsted and Lewis acid sites using pyridine (both Brønsted and Lewis site blocker) and 2,6-dimethylpyridine (a selective Brønsted acid site blocker) as probes.

4.0 References

[1] Z. Ma, Z. Xiao, J. A. van Bokhove and C. Liang, *J. Mater. Chem.,* 2010, **20**, 755–760.

[2] A. Venugopal, J. Palgunadi, J. K. Deog, Oh-Shim Joo and C. H. Shin, *Catal. Lett.* 2008,**123**, 142-149.