

Electronic Supporting Information

Hydrogen free hydrogenation of nitrobenzene via direct coupling of cyclohexanol dehydrogenation over MgO/SBA-15 supported Cu nanoparticles

Ravi Kumar Marella,^{*a,b,c} Venkata Rao Madduluri,^c Sivarama Krishna Lakkaboyana,^{*d} Marlia M. Hanafiah^{e,f} and Sarala Yaaratha^g

^a Department of Chemistry, PACE Institute of Technology & Sciences, Ongole 523001, Andhra Pradesh, India. Email: ravikumarmarella@gmail.com

^b Department of Chemical Engineering, University of Cape Town, Rondebosch 7701, Western Cape, South Africa.

^c Catalysis and Fine Chemicals Division, Indian Institute of Chemical Technology, Hyderabad 500007, Telangana, India.

^d School of Ocean Engineering, Universiti Malaysia Terengganu, 21030, Kuala Nerus, Terengganu Darul Iman, Malaysia. Email: svurams@umt.edu.my

^e Department of Earth Sciences and Environment, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Malaysia.

^f Centre for Tropical Climate Change System, Institute of Climate Change, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Malaysia.

^g Department of Chemistry, Chaitanya Bharathi Institute of Technology, Gandipet, Hyderabad 500 075, India.

*Corresponding author. E-mail: ravikumarmarella@gmail.com and svurams@umt.edu.my

Experimental

Materials

Magnesium acetate tetra hydrate ($\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$), (98%, Sigma Aldrich), Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) (puriss. p.a., 99-104%, Sigma-Aldrich), methanol (anhydrous 98%, Sigma-Aldrich) are purchased commercially and used without further purification. SBA-15 support was prepared by following the procedure reported by Zhao et al.¹ In SBA-15 synthesis, triblock co-polymer Pluronic P123 (M/s Sigma Aldrich, USA) used as structure directing agent and tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich) as silica source. High purity Millipore water was used for the synthesis of all catalysts.

Synthesis of mesoporous MgO-SBA15

Initially, mesoporous SBA-15 silica support was prepared by the hydrothermal method according to our previous report.² In a typical synthesis, 20 g of triblock copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) dissolved in 560 mL of deionized water at room temperature. To the above solution, 126 mL of Conc. HCl added and stirred until it produces a clear homogeneous solution. The temperature of the solution increased to 310 K using a hot water bath and 46 mL of TEOS was added gradually. The resulting milky white solution stirred at 310 K for 12 h and hydrothermally treated for 24 h in an autoclave at 373 K. After filtration and drying, the SBA-15 solid was calcined at 823 K for 6 h with a heating rate of 2 K min^{-1} in static air. A required amount of magnesium acetate tetrahydrate and SBA-15 (the molar ratio of Mg/Si is 1) were dissolved in methanol and stirred for 4 h at room temperature. The excess of methanol was evaporated and dried under vacuum at 353 K and calcined at 673 K for 6 h with ramping of 2 K min^{-1} to obtain MgO modified SBA-15 designated as MgO-SBA15.

Dehydrogenation of cyclohexanol

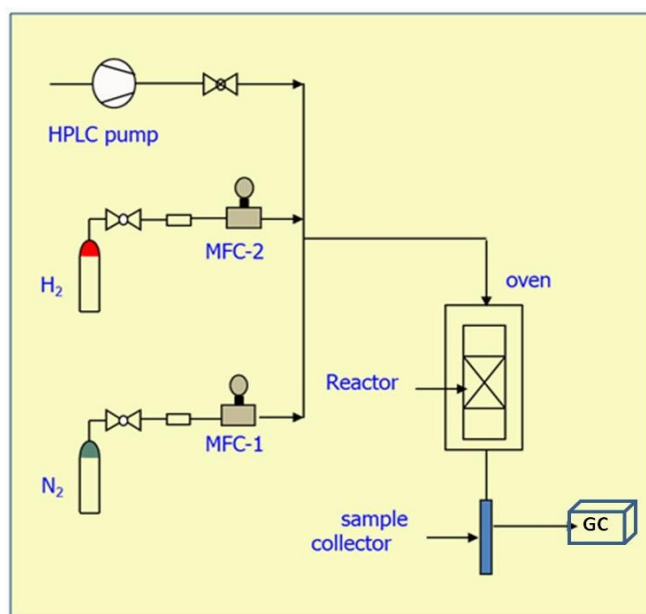
The catalytic dehydrogenation of cyclohexanol was carried out in a fixed bed reactor (14 mm id and 400 mm length) at atmospheric pressure under N_2 flow. About 1 ml of the catalyst is loaded and reduced in H_2 flow at 553 K for 3 h. After catalyst reduction, the reaction temperature was set and the reactant (cyclohexanol) was fed along with N_2 gas at a total flow rate of 1.62 l h^{-1} . The product was collected in an ice cold trap periodically for every 30 min. and analysed by GC-2010 plus (M/s Shimadzu, Japan) equipped with a FID detector and a HP-5 capillary column (30 m \times 0.32 mm \times 0.25 μm). The products were identified by GC-MS QP 2010 (M/s Shimadzu, Japan) equipped with a DB-5 capillary column (30 m \times 0.25 mm \times 0.25 μm).

Hydrogenation of nitrobenzene

The catalytic hydrogenation of nitrobenzene was carried out in a fixed bed reactor (14 mm id and 400 mm length) at atmospheric pressure under H₂ flow. About 1 ml of the catalyst is loaded and reduced in H₂ flow at 553 K for 3 h. After catalyst reduction, the reaction temperature was set and the reactant (nitrobenzene) was fed along with H₂ gas at a total flow rate of 1.62 l h⁻¹. The product was collected in an ice cold trap periodically for every 30 min. and analyzed by GC-2010 plus (M/s Shimadzu, Japan) equipped with a FID detector and a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). The products were identified by GC-MS QP 2010 (M/s Shimadzu, Japan) equipped with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm).

Direct Coupling of cyclohexanol dehydrogenation and nitrobenzene hydrogenation

The catalytic coupling of cyclohexanol and nitrobenzene dehydrogenation-hydrogenation reaction was carried out in a fixed bed quartz reactor (14 mm i.d and 400 mm length) as shown in the fig. ESI 1.



ESI. 1 Schematic diagram of the reaction setup for the direct coupling of cyclohexanol and nitrobenzene

Prior to testing, the catalyst was reduced under H₂ flow (99.999% pure) at 553 K for 3 h to obtain higher amount of metallic Cu species, which are believed to be more active and selective compared to oxidised Cu species. The feed consisting of cyclohexanol and nitrobenzene (3:1 mole ratio) was fed at a required flow rate using a HPLC pump along with N₂ (99.999% pure) gas flow. The products were collected periodically for every 30 min in an ice-cold trap, analysed by off-line GC (Shimadzu GC-2010 plus) equipped with FID using HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). The products were identified by GC-MS (Shimadzu QP-2010) equipped with DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm). The conversion, yield and selectivity were calculated in terms of response factors based on the GC results. Reaction rate and turn over frequency (TOF) were calculated using the following expressions.

The fractional conversion of reactant (i) can be expressed as,

$$X_i (\%) = \frac{(A_i)_{In} - (A_i)_{Out}}{(A_i)_{In}} \times 100$$

the product (j) yield is calculated from the following equation, and the selectivity of desired product (j) can be obtained as,

$$Y_j (\%) = \frac{(B_j)_{Out}}{(A_i)_{In}} \times 100$$

$$Selectivity (S_j) = \frac{(Y_j)}{(X_i)} \times 100$$

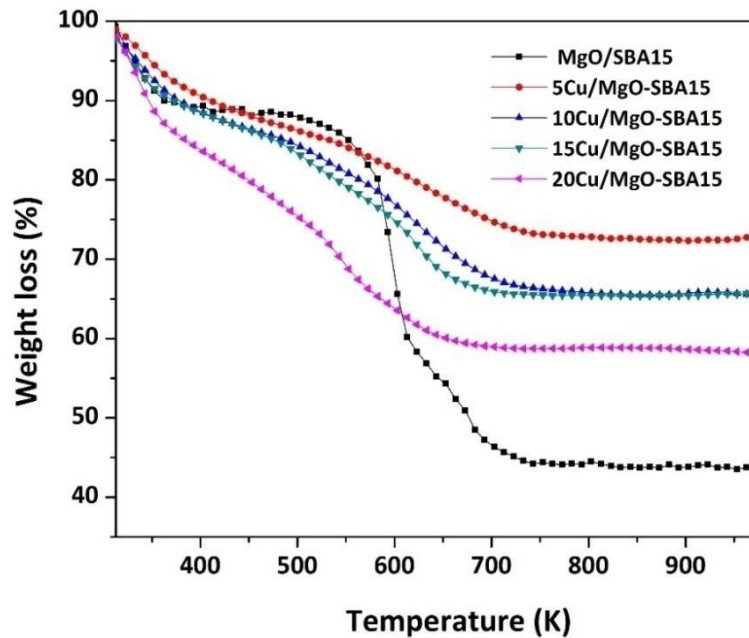
Where, A= number of moles of cyclohexanol (or) Nitrobenzene, B= number of moles of Cyclohexanone (or) Aniline. The subscript "in" and "out" represents the inlet and outlet gases/vapours respectively.

$$\text{rate } (r), (\text{moles} \cdot \text{g}_{\text{cat}} \cdot \text{s}^{-1}) = \frac{Y_{\text{CHONE}} \times \text{moles of CHOL}}{\text{catalyst weight} \times 3600}$$

$$\text{TOF}, (\text{s}^{-1}) = \frac{\text{rate} \times 63.5}{\text{Cu loading} \times (D_{\text{Cu}})} \times 10^4$$

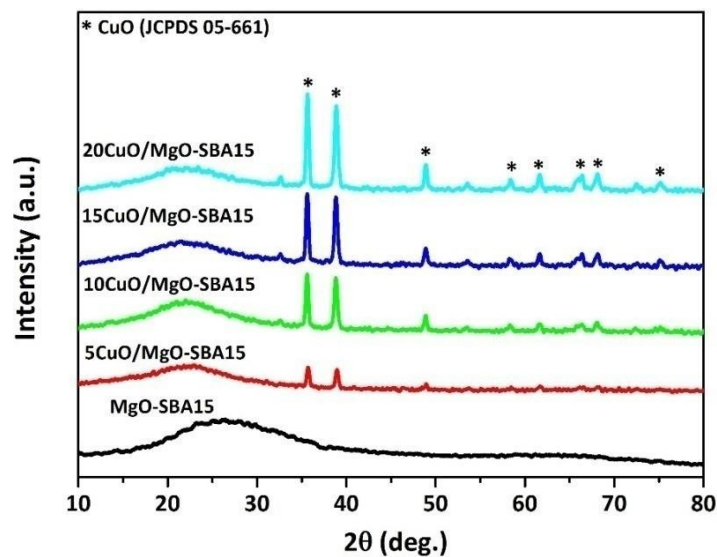
Where D_{Cu} is the Cu dispersion, calculated as the ratio of surface Cu to bulk Cu atoms from N_2O pulse chemisorption^{3, 4}

TG-DTA



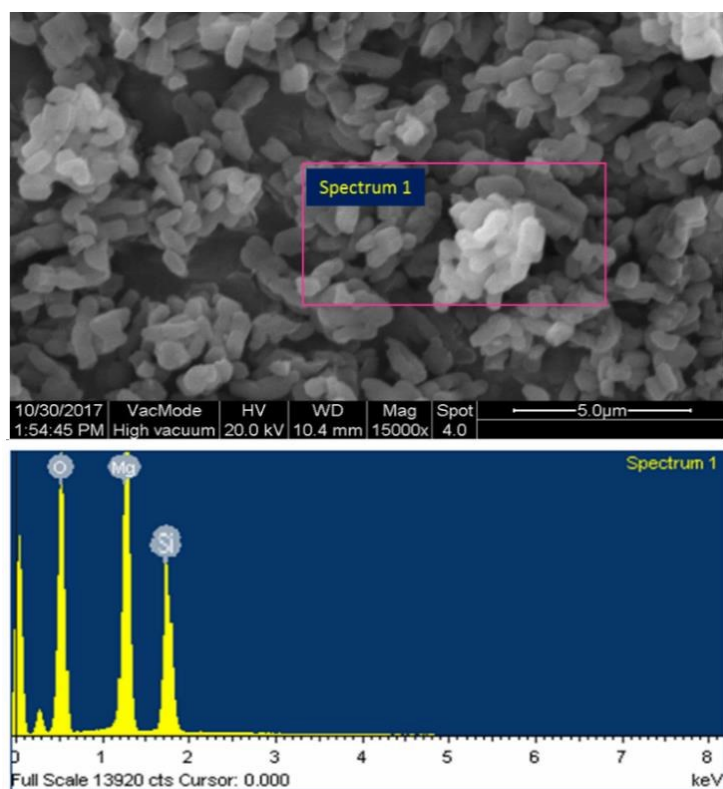
ESI. 2 Thermo-gravimetric (TG) analysis of oven-dried Cu/MgO-SBA15 samples

XRD



ESI. 3 Wide angle X-ray diffraction patterns of calcined samples of MgO-SBA15 and Cu/MgO-SBA15

SEM-EDX



ESI. 4 SEM image and its corresponding EDX patterns of MgO-SBA15 sample

References

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