Supporting Information

Highly selective transfer hydrogenation of α,β-unsaturated carbonyl compounds using Cu based nanocatalysts†

Nazia Siddqui,[a] Bipul Sarkar, [a,b] Chandrashekar Pendem,[a] Rubian Khatun[a] ,L.N. Sivakumar Konthala, [a] Takehiko Sasaki,[c] Ankur Bordoloi [a] and Rajaram Bal*[a]

[a] *Refinery Technology Division, CSIR- Indian Institute of Petroleum, Dehradun-248005, UK, India, E-mail: raja@iip.res.in*

[b] SKKU *Advanced Institute of Nano Technology, Sungkyunkwan University, Republic of Korea*

c Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, Kashiwanoha, Kashiwa-shi, Chiba 277-8561, Japan

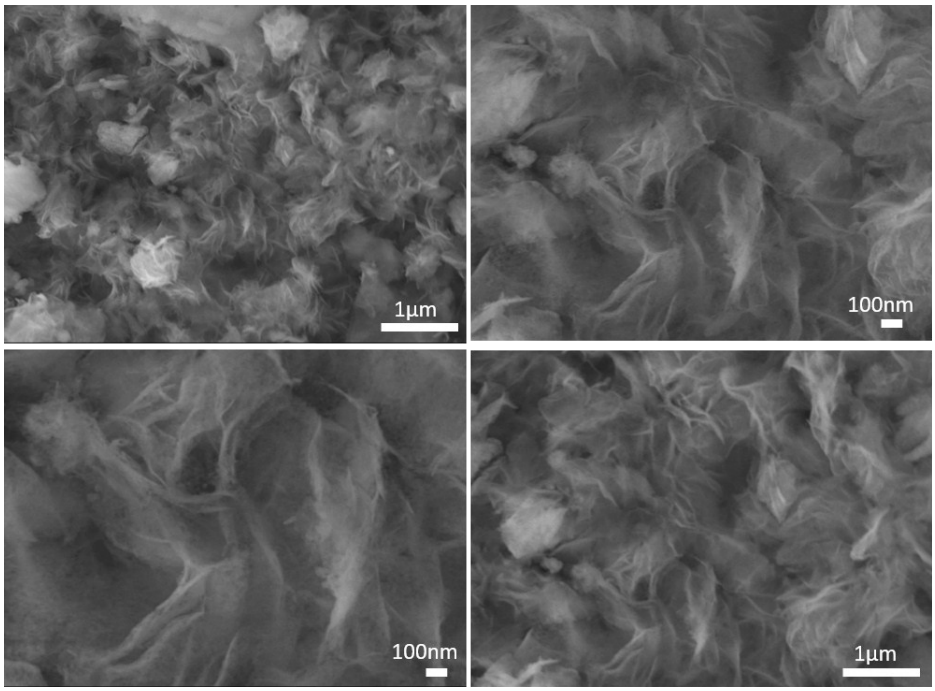

Figure S1. SEM Images and of fresh Cu-MgO catalyst.

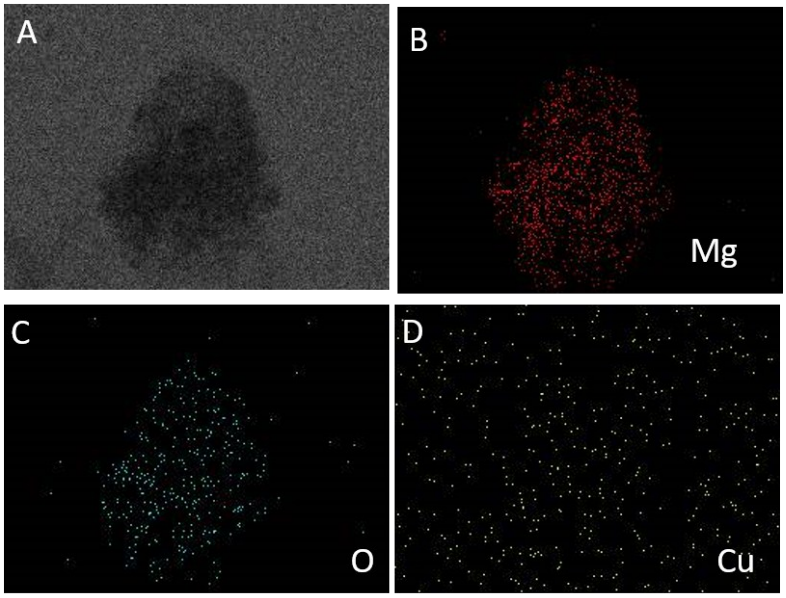

Figure S2. TEM elemental mapping of fresh Cu-MgO.

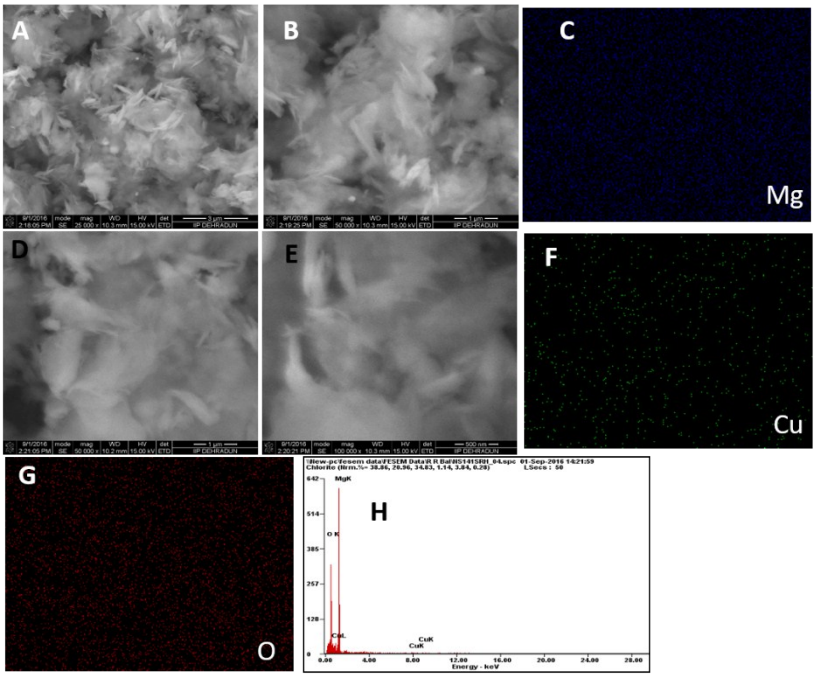

Figure S3. SEM images and elemental mapping of Cu-MgO used catalyst

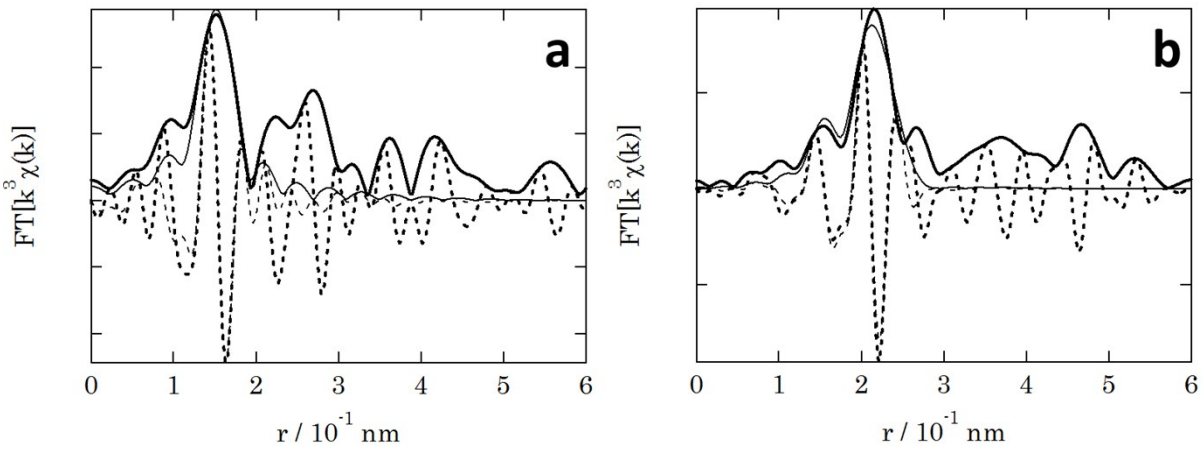

Figure S4. k^3-weighted Fourier transform of Cu-K edge EXAFS for spent 5% Cu-MgO catalyst. Amplitude: solid curves; imaginary part: dotted curves; observed data: thick curves; fitted data: thin curves.

Table S1. Activities of hydrogenation of cinnamaldehyde over different catalyst.

Sl No	Substrate	H_2 donor	Catalyst	χ_c	χ_s
					C-OH
1			MgO ^{commercial}	-	 100
2			MgO	-	 100
3			CuO ^{commercial}	2.1	 100
4			5%Cu-MgO^{imp}	28.4	 100
5			5%Cu-MgO$^{co\text{-}pre}$	20.9	 100
6			5%Cu-MgO	97.2	 100
7			5%Cu-MgO^{a}	96.7	 100

Reaction conditions: 1 g of substrate, 20 ml of cyclohexanol, 0.1 g catalysts, 1 MPa N_2 and 180°C; conversion and product selectivity in mole %; χ_c: hydrogenation of cinnamaldehyde; χ_s: product selectivity. ^{a} after 4 reuse.

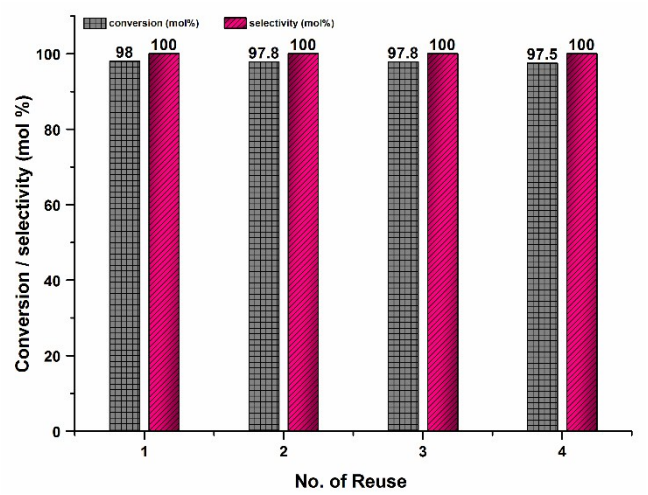

Figure S5. Activity data of consecutive runs with the same catalysts (5%Cu-MgO).

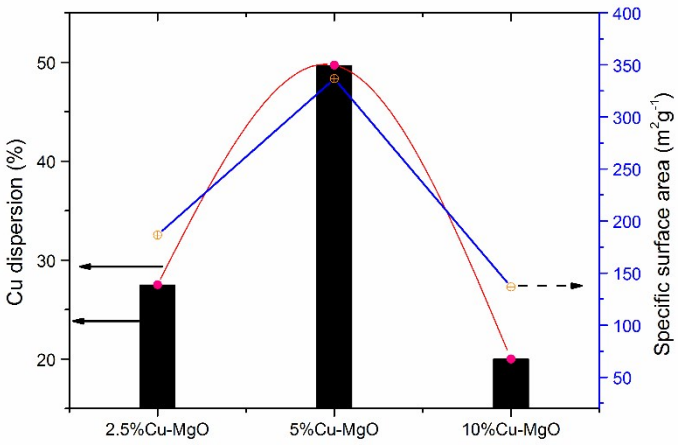

Figure S6. Surface area volcano of Cu-Mgo catalyst with different Cu loading.

Metal Dispersion Calculation

Metal dispersion was calculated using the H_2 chemisorption on Micromeritics, Auto Chem II 2920. The formula used is

$$Metal \quad Dispersion = \frac{S \quad M \quad N}{100 \quad L}$$

Where S is a stoichiometric factor of Cu. That means for example in the case of Cu^{2+} and H_2 chemisorption, one molecule of H_2 dissociate to give 2 atoms to be chemisorbed each atom over Cu.

Detail kinetic calculation given below.

$t_{1/2} = 0.03r^2/Dp$ (I)

$t_{1/2} = 0.23r\delta/Df \; x(C_0/Ce)$ (II)

Where
r = Radius of adsorbent in cm
δ = Thickness of water film adhered to the adsorbent in cm (assume = 0.001cm)
Dp = Pore diffusion coefficient in cm2/s
Df = Film diffusion coefficient in cm2/s
C_0 = Concentration of metals on adsorbent in mg/gm
Ce = Concentration of metals in solution at equilibrium in mg/l
$t_{1/2}$ = time required to bring down the metals concentration to half of initial concentration in seconds.
$t_{1/2}$ has been calculated from equation no. (III)

$\square_{1/2} = - [(0.5)]/\square_1$ (III)

To find out the rate limiting step of the overall adsorption the value of first order rate constant

(K1) obtained from the slopes of the straight lines of first order model.
ln (□□ – □□) = ln (□□) – □1□

$qt = (C_i - Ct)V/m$

$q_e = (Ci\text{-}Ce)V/m$

Where Ci and Ce are the initial and equilibrium concentration of cinnamaldehyde, respectively (mg/l), V is the volume of the solution (l), and W is the weight of the catalyst used (g). qe and qt are the amount of cinnamaldehyde adsorbed per gram metal (mg/g) at equilibrium and time t,

K_1 is the slope of graph

Initial concentration of Cinnamaldehyde =1g
Density of Cinnamaldehyde = 1.05 gm/ml
Cyclohexanol = 20ml
Total volume= 20ml Cyclohexanol+ 1ml Cinnamaldehyde
So cinnamaldehyde concentration= (1000*1000)/21
Ci = 47619 mg/l

t	con	Ct	qt	ln(qe-qt)
3600	6	44761.86	599.9994	9.137769
10800	34	31428.58	3399.988	8.779558
18000	73	12857.13	7299.993	7.863266
25200	97	1428.57	9699.99	5.298316
28800	99	476.19	9899.99	#NUM!

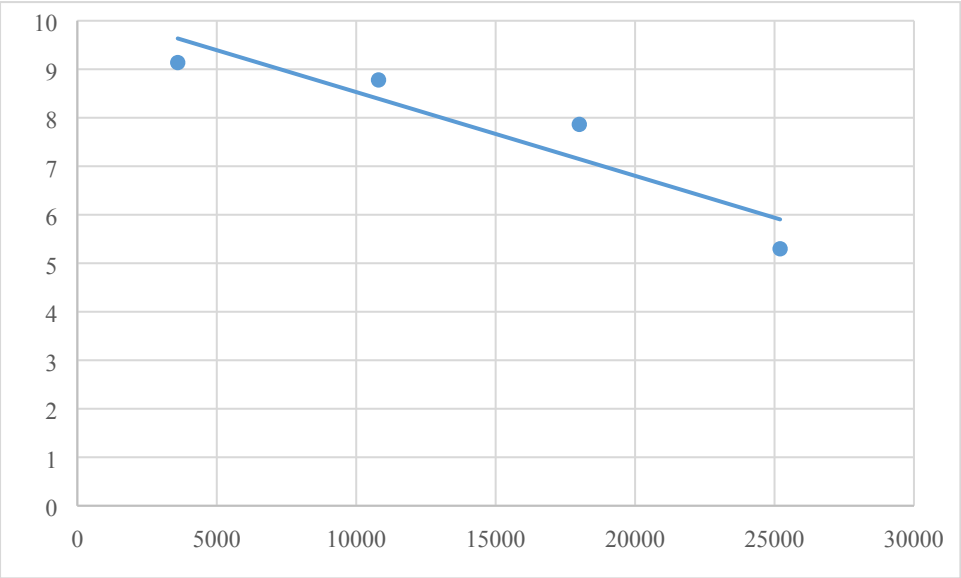

Fig-S7- plot of ln(qe-qt) vs Time.

Slop = -2x10^{-4}

K_1= 2x10^{-4}

$\square_{1/2}$ = –[□□(0.5)]/ 2x10^{-4}

=3465

r = 3 Nm

=3x10^{-7}cm

$t_{1/2}$ = 0.03r^2/Dp

Dp = 0.03x (3x10^{-7}cm)^2 /3465

Dp =7.79x10^{-19}

$t_{1/2}$ = 0.23rδ/Df x(C_0/Ce)

Co =Concentration of metals on adsorbent in mg/gm

Ce = Concentration of metals in solution at equilibrium in mg/l

Ce = 476.19

Co = (47619-476.19)/(.021/.1)

= 9899.99 mg/gm

Df = $0.23x3x10^{-7}x0.001x9899.99/(3465x476.19)$

= $4.14x10^{-13}$ Cm^2/s

Here we concluded that Df value is very small so this reaction is not a control reaction.

Calculation for activation energy is given below,

At different temperature the values of rate constants were calculated (Fig S7), and Arrhenius plot was used for the calculation of activation energy (Fig-S8). The amount of activation energy was around 8.9 kJ/mol.

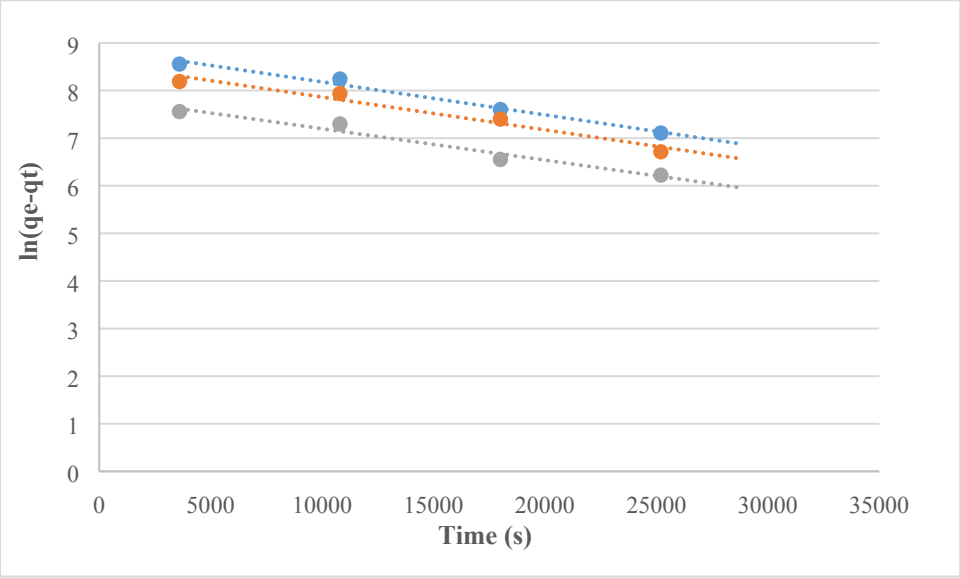

Fig-S8 Plot of different ln(qe-qt) vs Time

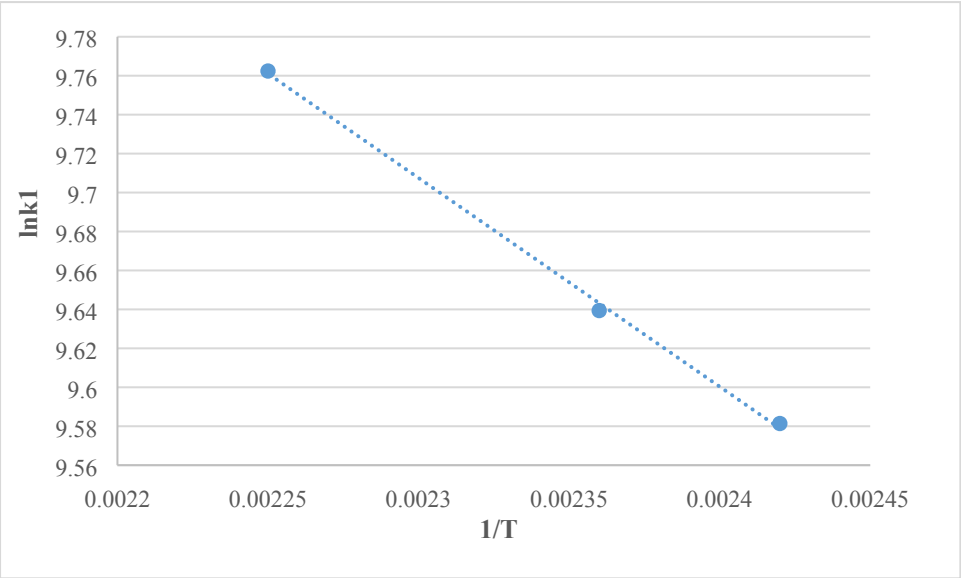

Fig-S9 Arrhenius plot for transfer hydrogenation reaction.

TOF Table -S2

S.No	Catalysts	Reaction condition	H_2 Source	Selectivity of Unsaturated alcohol (%)	TOF (h^{-1})	Ref.	Remark
1	2% Pt/CeO2	50°C,2h,20 MPa	2-propanol	83.5%	7.3	[1]	Expansive metal used
2	0.75%Pd–WN/SBA-15	40°C,2h,1.0 MPa	IPA+10 bar H_2	0.7	757	[2]	Selectivity of Cinnamyl alcohol is low and Expansive metal used
3	K_3PO_4	80°C,6h,2.0 MPa	2-Propanol	100	.254	[3]	TOF is very low
4	Co3O4/MC	120°C,50h, 2.0 MPa	2-Propanol	100	1.179	[4]	TOF is very low
5	Au/SiC	visible light irradiation at 20°C,130min.	2-Propanol	100	487	[5]	Expansive metal used
7	Ag/UiO-66	140°C,6h,5.0 MPa	H_2	66	3.3	[6]	Expansive metal used as well as TOF is less
8	(1 : 1) Cu(0)–Ni(0)–	80°C,1h,	H_2	59.6	10.1	[7]	Selectivity of

	AAPTMS@GO						Cinnamyl alcohol is low TOF is less
9	PdNP@PPh2-PEGPIILP	60°C,2h,2.0 MPa	H_2	0	200	[8]	Selectivity of Cinnamyl alcohol is very low Expansive metal used
110	Pd^0-AmP-MCF	20°C,0.5h, 1atm	H_2	14	47	[9]	Selectivity of Cinnamyl alcohol is very low and Expansive metal used
11	Ir-NbO_X/SiO_2	100°C,	H_2	96	25.1	[10]	Expensive metal used and H_2 used
12	Ir-MoO_X/SiO_2	30°C,0.8MPa	H_2	90	217	[11]	Expensive metal used and H_2 used
13	Ir-ReO_X/SiO_2	30°C,0.8MPa.1h	H_2	95	12600	[12]	Expensive metal used and H_2 used
14	$AuIr/Tio_2$	100°C,2.0 MPa.1h	H_2	83.4	17.7	[13]	Expensive metal used and H_2 used
15	Pt-Fe/LDH	60°C,2.0 MPa.2h	H_2	51	10.8	[14]	Expensive metal used and H_2 used. Selectivity of Cinnamyl alcohol is less
16	Ni-OA@SiO_2	60°C, 4.0 bar.	H_2	99	2.8	[15]	TOF is low
17	**This work/5%Cu/MgO**	-	**Cyclohexanol**	**100**	**13.31**		

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