Supporting Information for

Cu-nanoclusters supported on nanocrystalline SiO_2-MnO_2: a bifunctional catalyst for one step conversion of glycerol to acrylic acid

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Materials

Copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), Manganese(II) chloride ($MnCl_2$), Tetraethyl orthosilicate (TEOS), Commercial MnO_2, Cu_2O and CuO were purchased from Sigma-Aldrich. Ethanol, Acetonitrile, cetyltrimethylammonium bromide (CTAB) were purchased from Merck KGaA, Darmstadt, Germany. All the chemicals were used without further purification. Double distilled water was prepared with a BOROSIL® water distillation unit.

Catalyst preparation

In a typical preparation method, a solution of $Cu(NO_3)_2.3H_2O$ (0.0749 g) was added drop wise into a solution of $MnCl_2.2H_2O$ (15.34 g) containing 2.6 g TEOS under vigorous stirring. Subsequently, a solution of cetyltrimethylammonium bromide (CTAB) was added to the reaction mixture of two metal precursors (Cu : CTAB : H_2O = 1 : 0.7: 250 molar ratio). After stirring, until a homogeneous solution was obtained, the resultant mixed species was hydrothermally treated at 150˚C for 24 h in a Teflon-lined autoclave vessel under an autogeneous pressure. The product was washed with distilled water and ethanol, and dried at ambient temperature for 10 h and at 100°C for 6 h. Finally the material was calcined at 500˚C for 6 h in air. The prepared sample was denoted as (Wt% Cu)Cu/SiO_2-MnO_2. Conventional Cu catalysts over MnO_2 and SiO_2 were also prepared as reference using commercial MnO_2 and SiO_2 by incipient wetness impregnation method and denoted as (wt% Cu)Cu/$MnO_2^{comm.}$ & (wt% Cu)Cu/$SiO_2^{comm.}$.

Catalyst characterization

Powder x-ray diffraction (XRD) measurements were performed with a Bruker D8 advance x-ray diffractometer with a Cu Kα radiation (40 kV and 30 mA) in the 2θ range 5-60°. The SEM images are taken on a FEI Quanta 200 F, using ETD detector with an acceleration tension of 10 or 30 kV. All the Samples were analysed by spreading them on a carbon tape and coated with gold to increase the electrical conductivity. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also performed with the same spectrophotometer. The morphology, lattice fringes and crystal boundaries of the samples were examined using a JEOL JEM 2100 high-resolution transmission electron microscope (HRTEM). Samples are mounted by dispersing on ethanol on a lacey carbon Formvar coated Cu grid. X-Ray photoelectron spectra (XPS) of the catalysts were recorded with a Thermo Scientific K-Alpha X-Ray photoelectron equipped with Mg Kα radiation. The C 1s peak at 284.8 eV was used as a calibration peak. Extended X-ray absorption fine structure spectroscopy (XAFS) measurements of Cu-K edge were carried out at the High Energy Accelerator Research Organization (KEK-IMMS-PF), Tsukuba, Japan. The EXAFS spectrum of the fresh catalyst was measured in the transition mode, whereas for the spent catalyst the EXAFS spectrum was measured in the fluoresecence mode using a Lytle detector with Ar gas and spectra were taken at BL-7C and BL-9C at the Photon Factory, Tsukuba, Japan. The electron storage ring was operated at 2.5 GeV and 450 mA; synchrotron radiation from the storage ring was monochromatized by a Si(111) channel cut crystal. Ionized chamber, which were used as detectors for incident X-ray (Io) and transmitted X-ray (I), were filled with N_2 mixture gas, respectively. The angle of the monochromators was calibrated with Cu foil. The EXAFS raw data was analysed with UWXAFS analysis package[1] including background subtraction program AUTOBK [2] and curve fitting program FEFFIT.[3] The amplitude reducing factor, So_2 was fixed at

1.0. The backscattering amplitude and phase shift were calculated theoretically by FEFF 8.4 code.[4] ATOMS [5] were used to obtain FEFF input code for crystalline materials. Temperature programmed reduction (TPR) experiment were carried out in a Micromeritics, Auto Chem II 2920 instrument connected with a thermal conductivity detector (TCD). Prior to TPR, the catalysts were also heated at 650°C for 2 h in helium and then placed in 10% H_2/Ar with a flow rate of 40 mL min^{-1} in the temperature range of 40-1000 °C with an increment of 10 °C/min. The amount and strength of the acid site were analysed by ammonia Temperature programmed desorption (TPD) technique using the same Micromeritics, Auto Chem II 2920 instrument. About 0.1 g sample was saturated with NH_3 at 100°C and flashed with He to remove the physically adsorbed NH_3, finally the decomposition of NH_3 was carried at a heating rate of 10°C/ min under He flow.

Glycerol oxydehydration

Glycerol oxydehydration was carried out in liquid phase using a 50 ml double necked round bottom flask containing 0.01 mol (0.92 g) glycerol and 0.046 g of Cu/SiO_2-MnO_2 catalyst in 10 ml solvent (acetonitrile). The reaction mixture was kept at 70°C and H_2O_2 (50 wt. % in H_2O) was added in 0.5 ml portion with a time interval of 15 min. The reaction products were identified by GC-MS (HP 5890 GC coupled with 5972 MSD). The identified product was analysed in an Agilent 7890, fitted with a MXT-WAX (30m X 0.28nm i.d., 0.25 µm film thickness) capillary column and a FID detector. The activity of the catalyst was calculated as:

$$\text{Conversion (C\%)} = \frac{\text{Moles of glycerol reacted (C\%)}}{\text{Moles of glycerol initially used (C\%)}} \times 100$$

$$\text{Selectivity (C\%)} = \frac{\text{Moles of product (C\%)}}{\text{Moles of glycerol reacted (C\%)}} \times 100$$

The presence of perexo intermediate at the end of the reaction was checked using phosphine at the end of the reaction. The product was identified by GC-MS as well as TLC (thin layer chromatography).

1. E. A. Stern, M. Newvill, B. Ravel, Y. Yacoby and D. Haskel, *Phys. B,* 1995, **117**, 208.
2. M. Newvill, P. Livins, Y. Yacoby, E. A. Stern and J. Rehr, J. *Phys. Rev. B: Condens. Matter,* 1993, **47**, 14126.
3. A. L. Aukudinov, B. Ravel, J. J. Rehr and S. D. Conradson, *Phys. Rev. B: Condens. Matter,* 1998, **58**, 7565.
4. A. L. Ankudinov, A. I. Nesvizhskii and J. Rehr, J. *Phys. Rev. B: Condens. Matter,* 2003, **67**, 115120.
5. R. Ravel, *J. Synchrotron Radiat.,* 2001, **8**, 314.

Figure S1

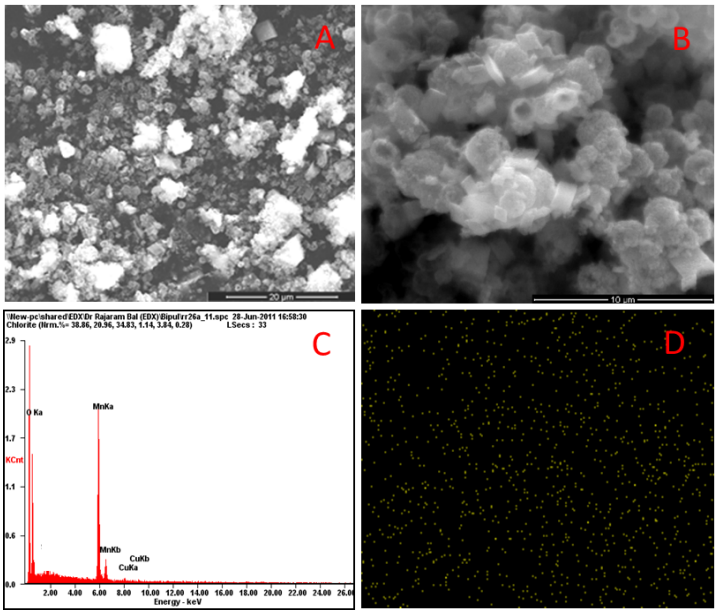

Figure S1 SEM micrograms of Cu/SiO_2-MnO_2 catalyst synthesized by (A) impregnation method and (B) hydrothermal method; (C) & (D) are the EDAX and elemental mapping of Cu of the hydrothermally prepared catalyst, respectively.

Figure S2

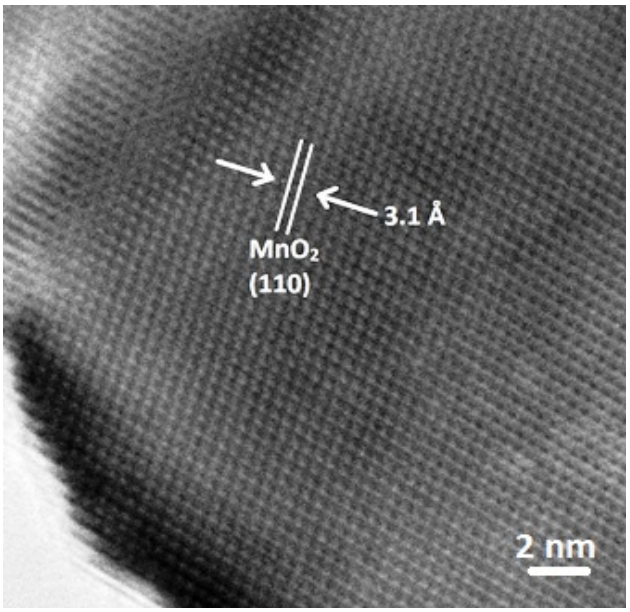

Figure S2. HRTEM image of hexagonal MnO_2 showing lattice fringes with a d-spacing of 110 plane of hexagonal MnO_2.

Figure S3

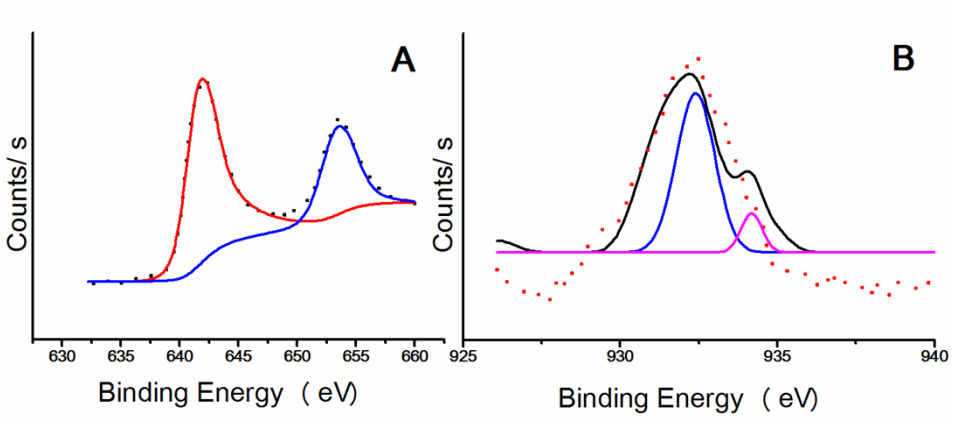

Figure S3. Photoelectron spectra of A) Mn 2p & B) Cu 2p prepared by hydrothermal method (0.9%Cu/SiO_2-MnO_2, fresh catalyst)

Figure S4

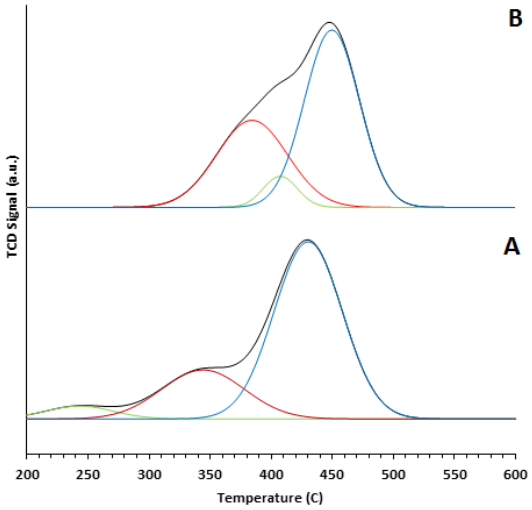

Figure S4. TPR profile of A) 0.9%Cu/SiO_2-MnO_2 and B) 1%Cu/SiO_2-MnO_2^{imp}

Figure S5

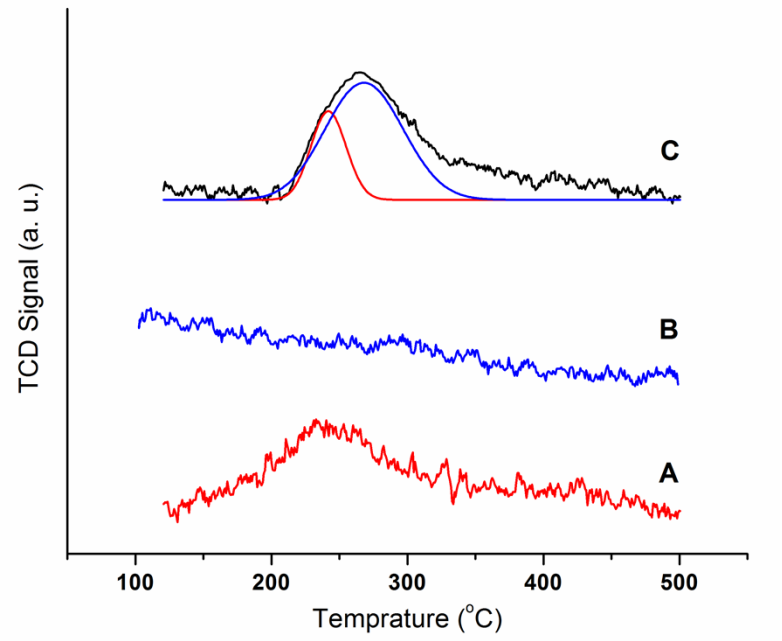

Figure S5. TPD-NH_3 patterns of hydrothermally prepared (A) SiO_2; (B) commercial MnO_2 and (C) Cu/SiO_2-MnO catalysts.

Figure S6

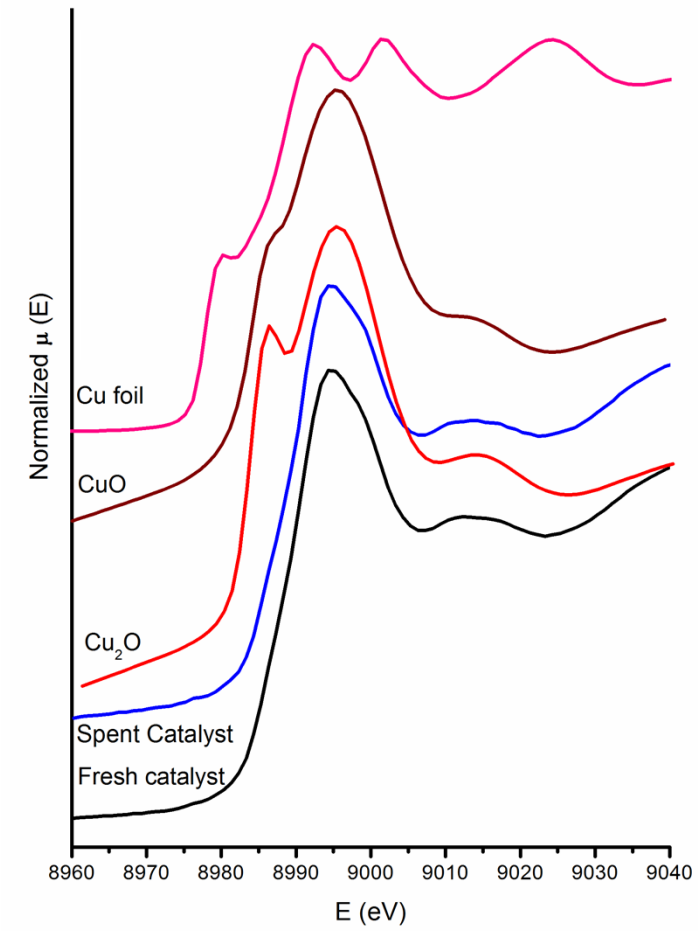

Figure S6. XANES spectra of Cu foil, commercial cuprous oxide, cupric oxide, fresh and spent 0.9%Cu/SiO_2-MnO_2 catalyst.

Figure S7

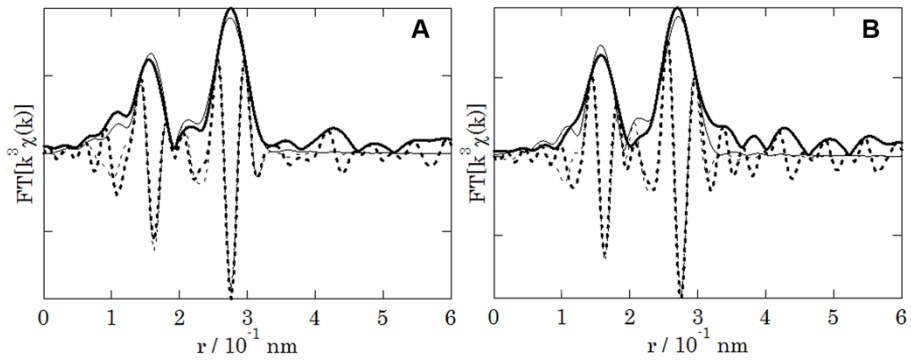

Figure S7. k3-weighted Fourier transform of Cu-K edge EXAFS for the A) fresh catalyst (0.9%Cu/SiO2-MnO2) and B) spent catalyst. Amplitude: solid curves; imaginary part: dotted curves; observed data: thick curves; fitting data: thin curves

Figure S8

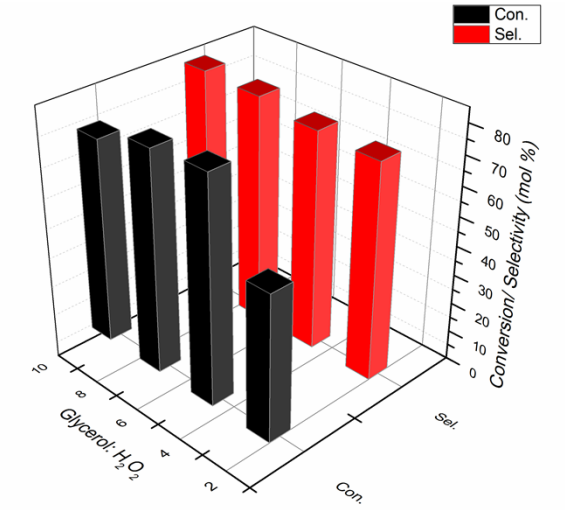

Figure S8. Influence of glycerol to H_2O_2 ratio on oxydehydration of glycerol with 0.046g catalysts, 0.92g glycerol in 10 mL solvent were stirred at 70˚C

Table S1. Summary of the EXAFS fitting results for Cu catalysts.

	Cu-O				Cu_2O crystal				Δk ($10nm^{-1}$)	ΔR (10^{-1}nm)	ΔE_0 (eV)	R_f (%)
	R (10^{-1}nm)	**CN**	**DW** ($10^{-5}nm^2$)	**Path**	**R** (10^{-1} nm)	**CN**	**DW** ($10^{-5}nm^2$)	**Debye temp** (K)				
Fresh	1.954± 0.152	1.9±0.7	1.3±1.8	**Cu-O**	1.906±0. 064	4	27.2	286.0± 6.0	3 – 12	1.2 – 3.2	-5.3±1.5	2.22
				Cu-O-O	2.988	4	37.7					
				Cu-Cu	3.094	12	13.4					
Spent (after 30h)	1.951± 0.113	1.7±0.6	0.4±2.2	**Cu-O**	1.895±0. 013	4	27.1	286.6± 8.5	3 – 12	1.2 – 3.2	-7.4±2.1	4.02
				Cu-O-O	2.989	4	37.7					
				Cu-Cu	3.095	12	13.4					

Fitting was achieved with respect to Cu-O path and three paths of Cu2O crystal, which are repared by ATOMS program and Cu2O crystal structure. Three paths of Cu2O crystal correspond to Cu-O(-Cu), multiple scattering of Cu-O-O(-Cu), and Cu-Cu(-Cu). These four paths are necessary for the good fitting. The simple two paths such as Cu-O and Cu-Cu, or the sole use of Cu2O crystal paths, or the CuO crystal structure failed. The former Cu-O path can be fitted as 0.1951 – 0.1954 nm that can be attributed to the distance of Cu2+- O of the monatomically dispersed Cu2+ species. The crystal size of Cu2O is considered as small, since the inclusion of more distant paths does not improve the fillings.

Figure S9

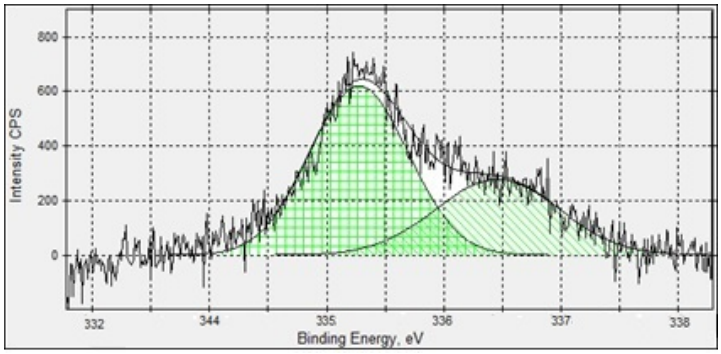

Figure S9. Cu LMM spectra of spent catalyst (after 3 h).

The Cu(LMM) Auger of the catalyst shows binding energies (eV) at 335.3 eV and 336.6 eV, which confirms the presence of Cu(+1) and Cu(+2) in the catalyst surface (without forming any metallic Cu).

Table S2. ICP-AES data of the reused catalyst for the oxydehydration of glycerol.

Sl No	Run	Amount of Cu (wt%)
1	1st	0.912
2	2nd	0.910
3	3rd	0.911
4	4th	0.912

Table S3. Surface composition of 0.9%Cu/SiO_2-MnO_2 catalyst as calculated from XPS.

Sl No		Catalyst	Amount of Cu (At %)	
			Cu^{1+}	Cu^{2+}
1	Fresh	0.9%Cu/SiO_2-MnO_2	90.12	9.88
2	Spent	0.9%Cu/SiO_2-MnO_2	89.23	11.77
Atomic ration of the Cu species was calculated taking all Cu species present in the catalyst as 100%.				

Discussion

Glycerol consumption follow zero order reaction upto 5h and reaches ~64% consumption then reaction rate decreases upto 30h with a maximum glycerol conversion of 77.1%. Additionally, we believe that the decomposition of H_2O_2 is also occurring continuously over our catalyst. Blank experiment was carried out using H_2O_2 over our catalyst (Cu/SiO_2-MnO_2) at reaction temperature and we found that H_2O_2 is continuously decomposing over the catalyst making the peroxide concentration lower with time. So the oxidation of acrolein to acrylic acid become slow with time (after 50 h).

Kinetic study

Glycerol to acrylic acid occurs in two consecutive steps. 1st step is the dehydration step of glycerol, where the glycerol molecule gets converted in to acrolein via intermediate 3-hydroxy propionic acid by the acid sites of the catalyst. While in 2nd step is the oxidation of acrolein with H_2O_2 for the formation of acrylic acid.

Theg steps can be represented as

$$\underset{(G)}{\text{Glycerol}} \longrightarrow \underset{(A)}{\text{Acrolein}} + \underset{(W)}{\text{Water}} \qquad \text{……equation (1)}$$

$$\underset{(A)}{\text{Acrolein}} + \underset{(O)}{H_2O_2} \longrightarrow \underset{(P)}{\text{Acrylic acid}} + \underset{(W)}{\text{Water}} \qquad \text{……equation (2)}$$

As the peroxide is used in excess so the equation (2) can be simplified as; two consecutive occurrence of two irreversible pseudo-first order reaction.

$$G \xrightarrow{k_1} A \xrightarrow{k_2} \text{product}$$

Where, k_1 and k_2 is the rate constant of the first and second steps of the reaction, respectively. The rate constant of the first step (k_1) can be expressed by conventional equation for 1st order reaction.

$$C_G/C_{G0} = e^{-k_1 t} \qquad (3)$$

Where, C_G and C_{G0} is the final and initial molar concentration of the glycerol at time zero and t respectively.

The rate constant of the second step (k_2) can be expressed in the form of concentration of acrolein (C_A) and acrylic acid (C_P) respectively.

$$d(C_p/C_{G0})/dt = k_2 (C_A/C_{G0}) \qquad (4)$$

Initially, when the formation of product is too low then the equation (4) can be rewritten as

$$C_p/C_{G0}t = K_2 (C_A/C_{G0})$$

Now the value of k_2 can be determined from the slope of the linear plot of ($C_p/C_{G0}t$) verses (C_A/C_{G0}) and shown in Figure S9. The plot of ($C_p/C_{G0}t$) verses (C_A/C_{G0}) made at 90^{O}C shows the value of k_2 = 0.3575 S^{-1} and exactly fit; thereby it supports our model of pseudo-first order reaction. Based on the model it can be concluded that this is an overall first order reaction.
Figure S10.

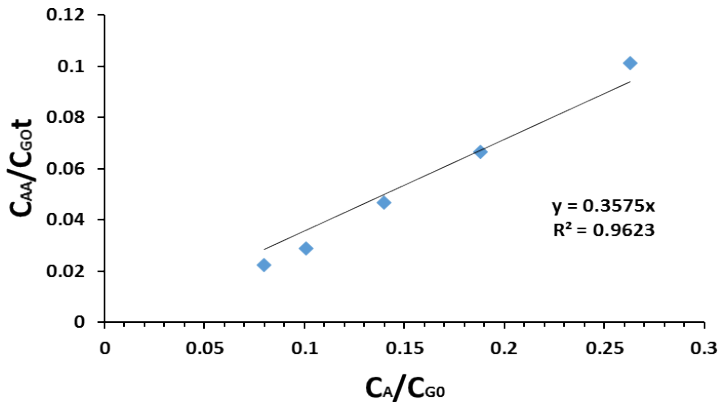

Figure S10. Plot of $C_{AA}/C_{G0}t$ vs C_A/C_{G0}

Thus the plot of ($C_p/C_{G0}t$) verses (C_A/C_{G0}) made at 90^{O}C shows the value of K_2 = 0.3575 S^{-1} is exactly fit; thereby it supports our mode (Figure S10). Based on the model it can be concluded that this is an overall second order reaction. The rate constant (k_2) was calculated in different temperature and Arrhenius plot was used to calculate the activation energy (E_a) for the reaction. From, the plot of lnk_2 versus 1/T (in ^{o}C) (Figure S11), activation energy was calculated and found 1.14 KJ/mol.
Figure S11

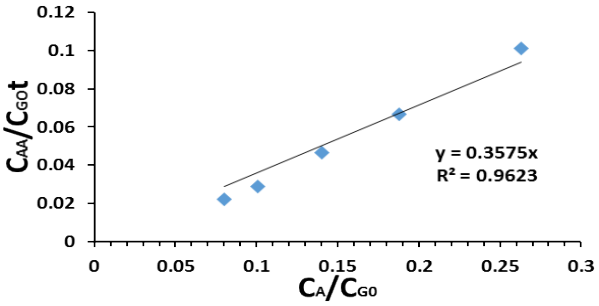

Figure S11. Kinetic Modeling: plot of $C_{AA}/C_{G0}t$ vs C_A/C_{G0}