Electronic Supplementary Information (ESI)

Simultaneous glycerol dehydration and *in-situ* hydrogenolysis over Cu-Al oxide under an inert atmosphere

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Experimental

X-ray photoelectron spectroscopy (XPS) data were collected on a VG Scientific ESCA-3000 spectrometer using a non-monochromatised Mg Kα radiation (1253.6 eV) at a pressure of about 1×10^{-9} Torr (pass energy of 50 eV, electron takeoff angle 55) and overall resolution ~0.7 eV determined from the full width at half maximum of the $4f_{7/2}$ core level of gold surface. The error in the binding energy values were within 0.1 eV. The binding energy values were charge-corrected to the C_{1s} signal (285.0 eV).

The chemical composition of the sample was determined by Energy Dispersive X-ray spectroscopy (EDX) attached to SEM (JEOL JSM 500).

Gas analysis was carried out using Chemito 8610 GC fitted with Porapac-Q column connected to TCD detector.

The Temperature-programmed desorption of CO_2 (CO_2-TPD) was carried out in a Quantachrome Autosorb -1C sorption unit. 100 mg activated Cu-Al sample was heated at a rate of 10 ^oC min^{-1} to 110 ^oC under He flow (30ml min^{-1}) and maintained at this temperature for 1 h in order to remove the surface impurities. After being cooled to room temperature under He flow, the sample was exposed to a mixture of 30 % CO_2/He for 1.3 h. Subsequently, the sample was purged with He for 30 min and then heated to 700 ^oC at a rate of 10 ^oC min^{-1}. Desorption of CO_2 was monitored by the mass spectrometry.

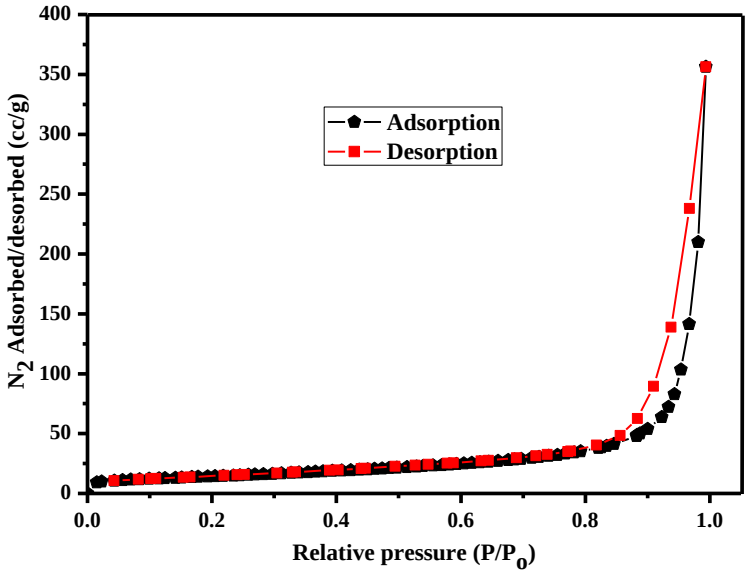


Fig.1 N_2 adsorption/desorption isotherm of activated Cu-Al catalyst.

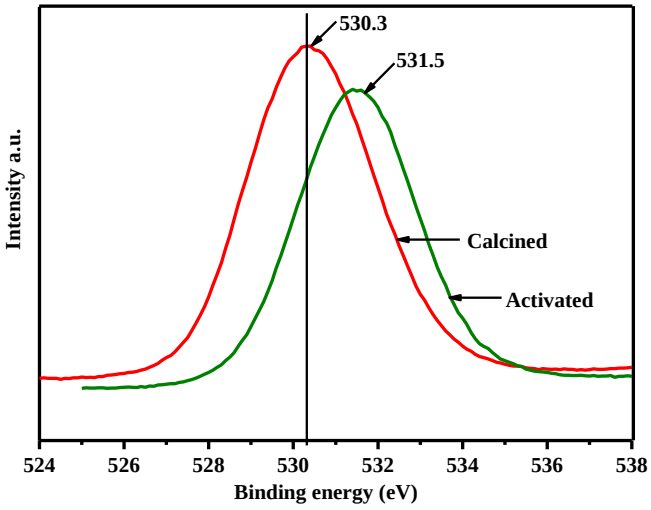


Fig.2 O 1s spectra of the calcined and activated Cu-Al catalyst.

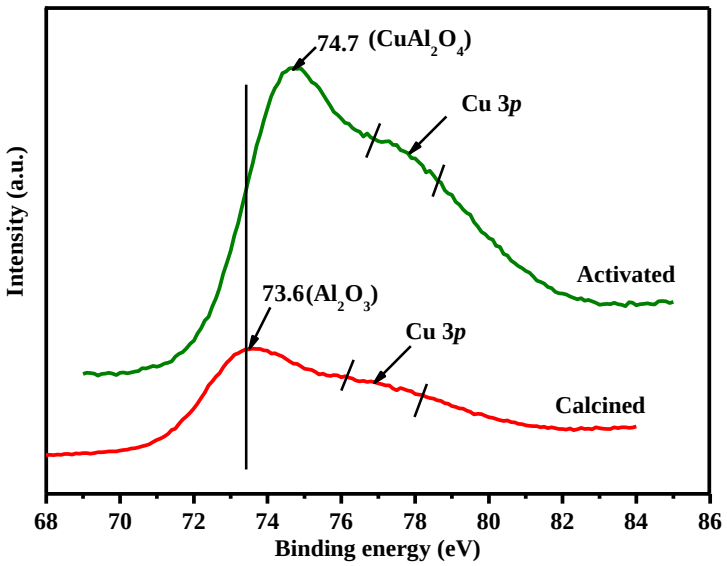


Fig. 3 Al 2p spectra of the calcined and activated Cu-Al catalyst.

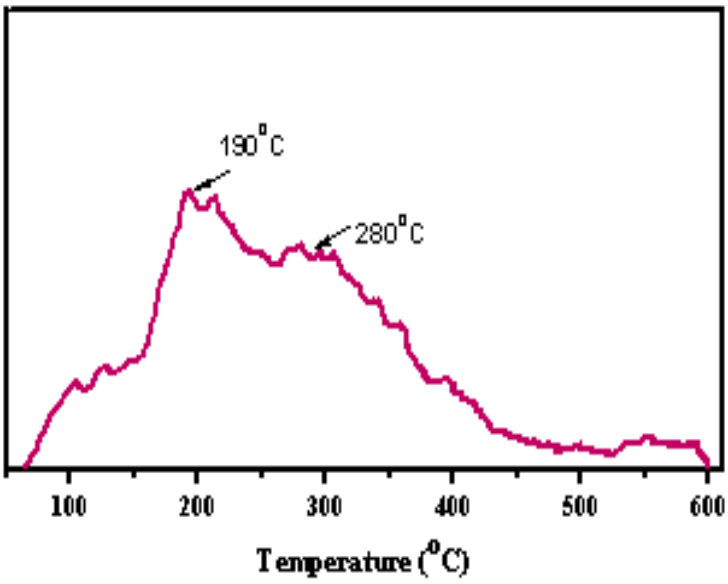
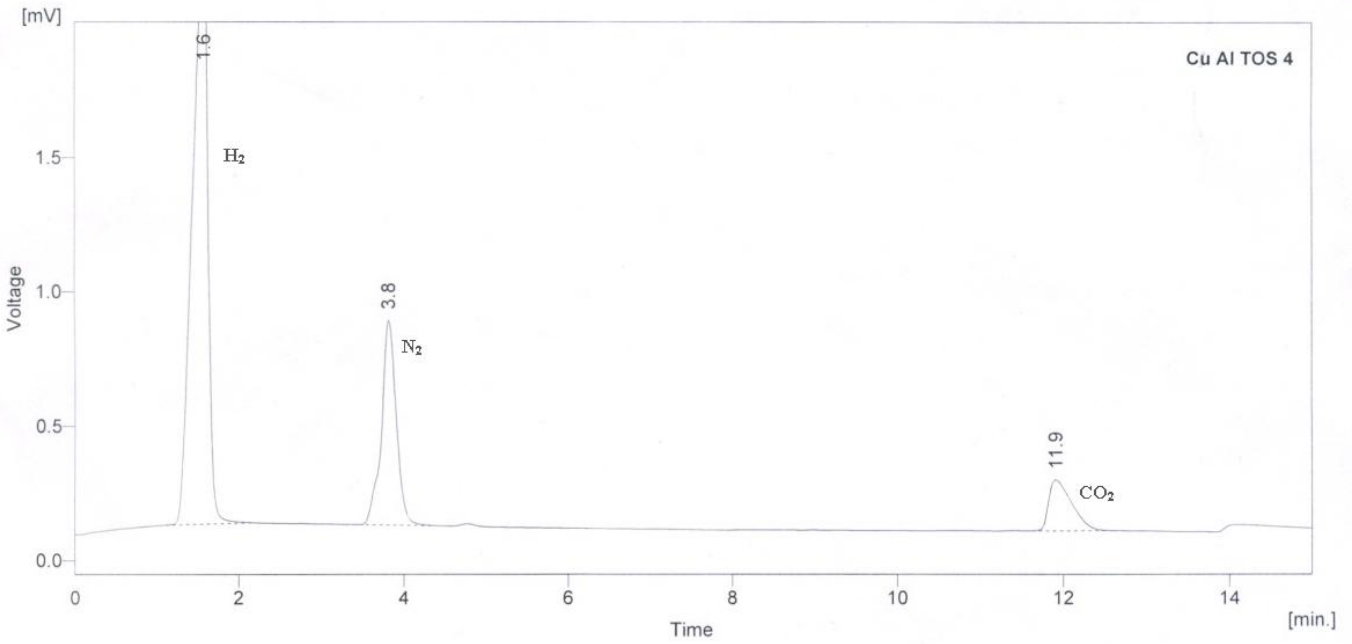


Fig. 4 CO_2-TPD profile of the activated Cu-Al catalyst.

Table 1 Gas phase analysis

Catalysts	**Substrate**	**Temperature**	**Gas phase composition (%)**		
			H_2	CO_2	CH_4
Cu:Al (1:1)[a]	Glycerol	220	80	20	0.0
20% Cu/Al_2O_3 [a]	Glycerol	230	0.0	0.0	0.0
Al_2O_3 [a]	Glycerol	230	0.0	0.0	0.0
3%Pt/C [a]	Glycerol	220	86	8	6
Cu:Al (1:1)[b]	Glycerol	220	76	24	0.0
Cu:Al (1:1)[b]	Glycerol	230	80	20	0.0
Cu:Al (1:1) [a]	Acetol	220	0.0	0.0	0.0
Cu:Al (1:1) [a]	1,2-PDO	220	100	0.0	0.0

Reaction conditions: [a] batch operation, reaction time, 3h. [b] continuous operation at GHSV= 513 h^{-1}, LHSV = 1.53 h^{-1}

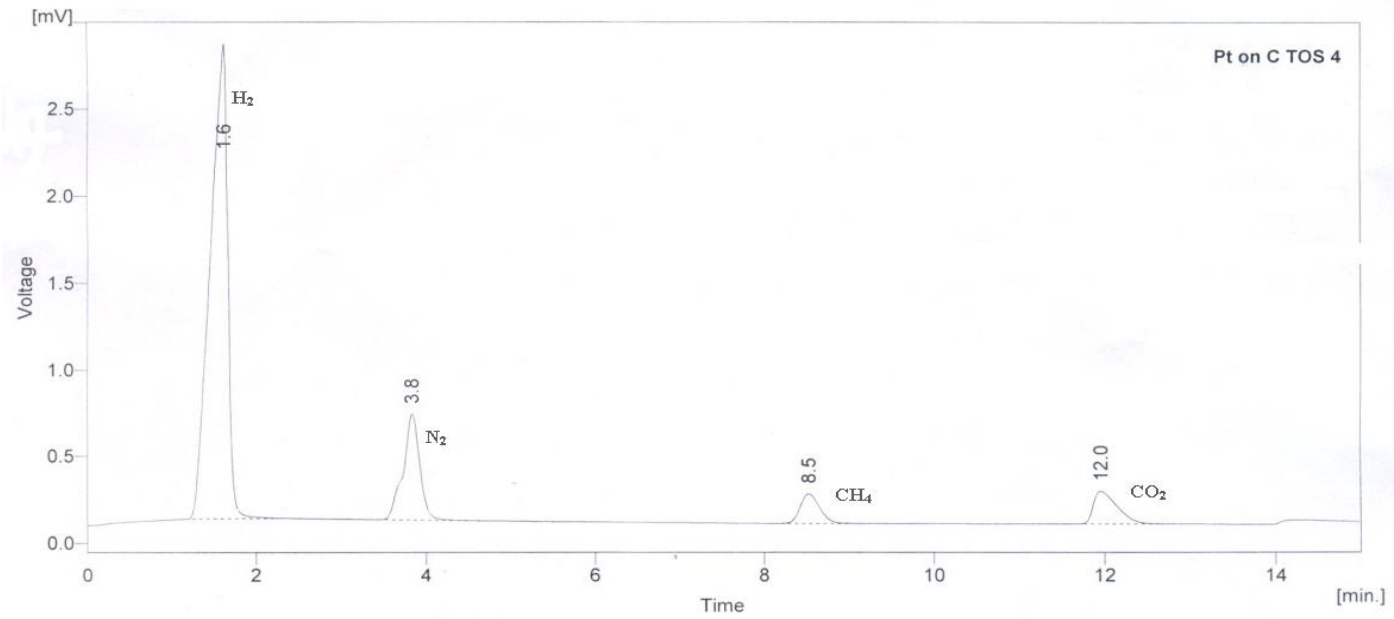


Result Table

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	1.583	575.781	45.897	68.4	70.7	0.20
2	3.820	192.816	15.253	22.9	23.5	0.18
3	11.907	73.018	3.807	8.7	5.9	0.31
	Total	841.615	64.957	100.0	100.0	

Fig. 5 GC of gas phase composition (Cu-Al catalyst).

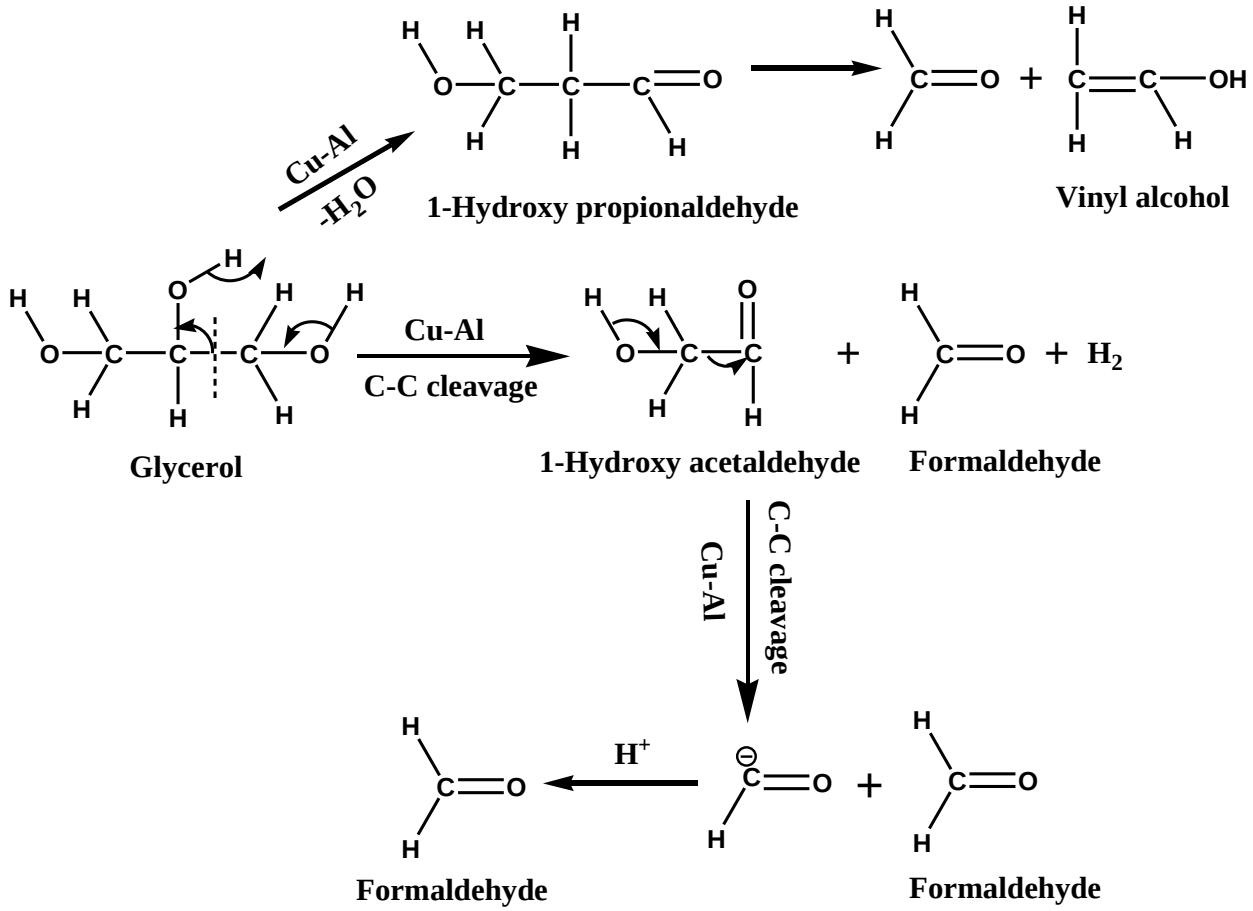
* N_2 was used as an inert in the reaction hence the compositions of other gases were calculated by excluding N_2.



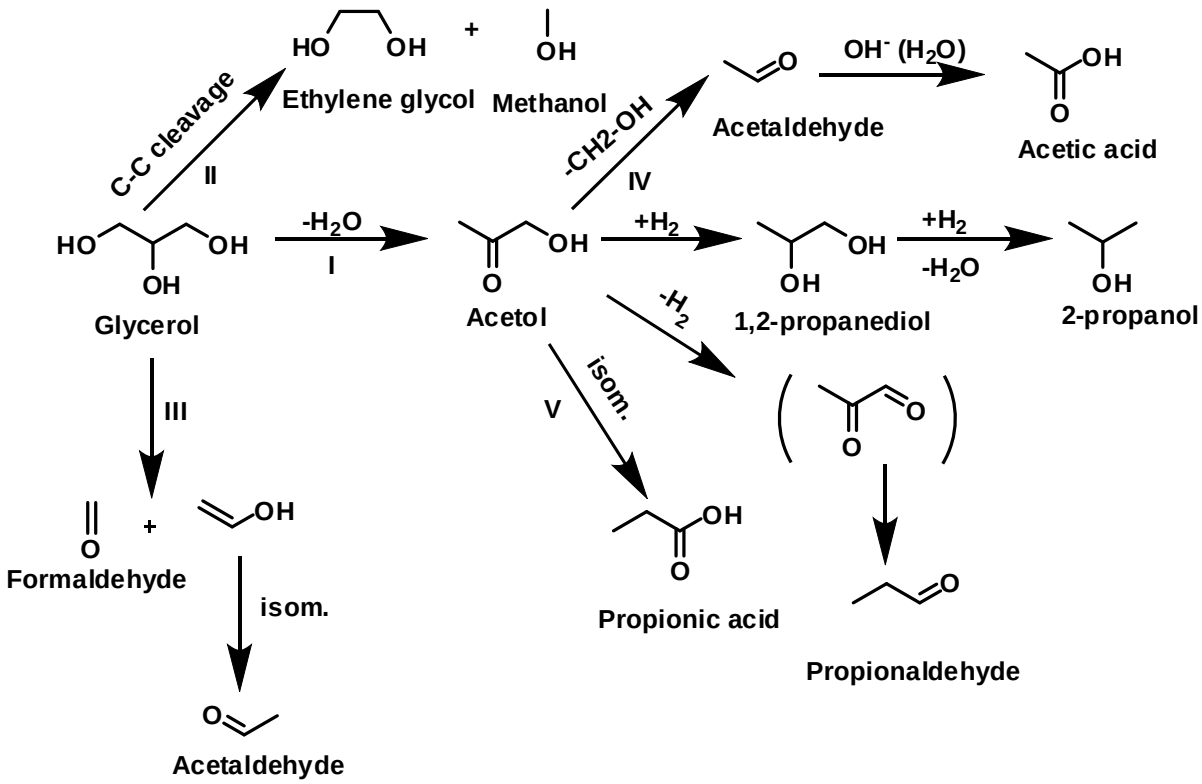
Result Table

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	1.623	787.095	54.745	72.9	73.8	0.24
2	3.833	166.526	12.223	15.4	16.5	0.19
3	8.520	54.057	3.410	5.0	4.6	0.25
4	11.950	72.082	3.757	6.7	5.1	0.31
	Total	1079.761	74.135	100.0	100.0	

Fig. 6 GC of gas phase composition (3% Pt/C) .



Scheme 1 Formaldehyde formation by C-C cleavage of glycerol under dehydration condition



Scheme 2 Schematic representation of reaction pathways during autogeneous hydrogenolysis of aqueous glycerol under inert atmosphere. Pathway I is desirable for glycerol dehydration to give acetol followed by its further hydrogenation to 1,2-PDO and its excess hydrogenation leads to undesirable 2-propanol formation. Pathways II, III, IV present the undesirable C-C cleavage leading to formation of ethylene glycol, formaldehyde, and acetaldehyde. Pathway V is the acetol isomerization giving propionic acid.

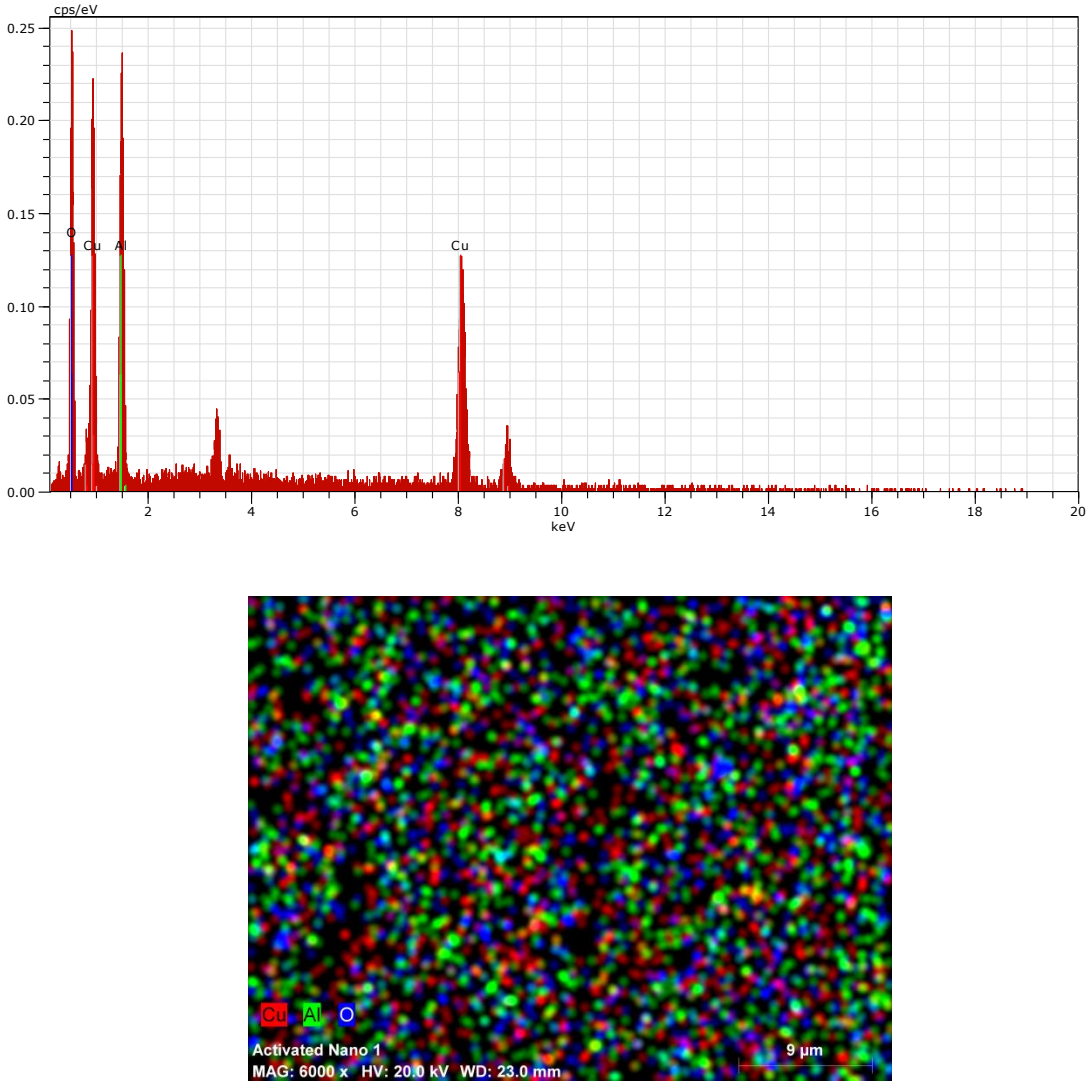


Fig. 7 EDX of Cu-Al catalyst.

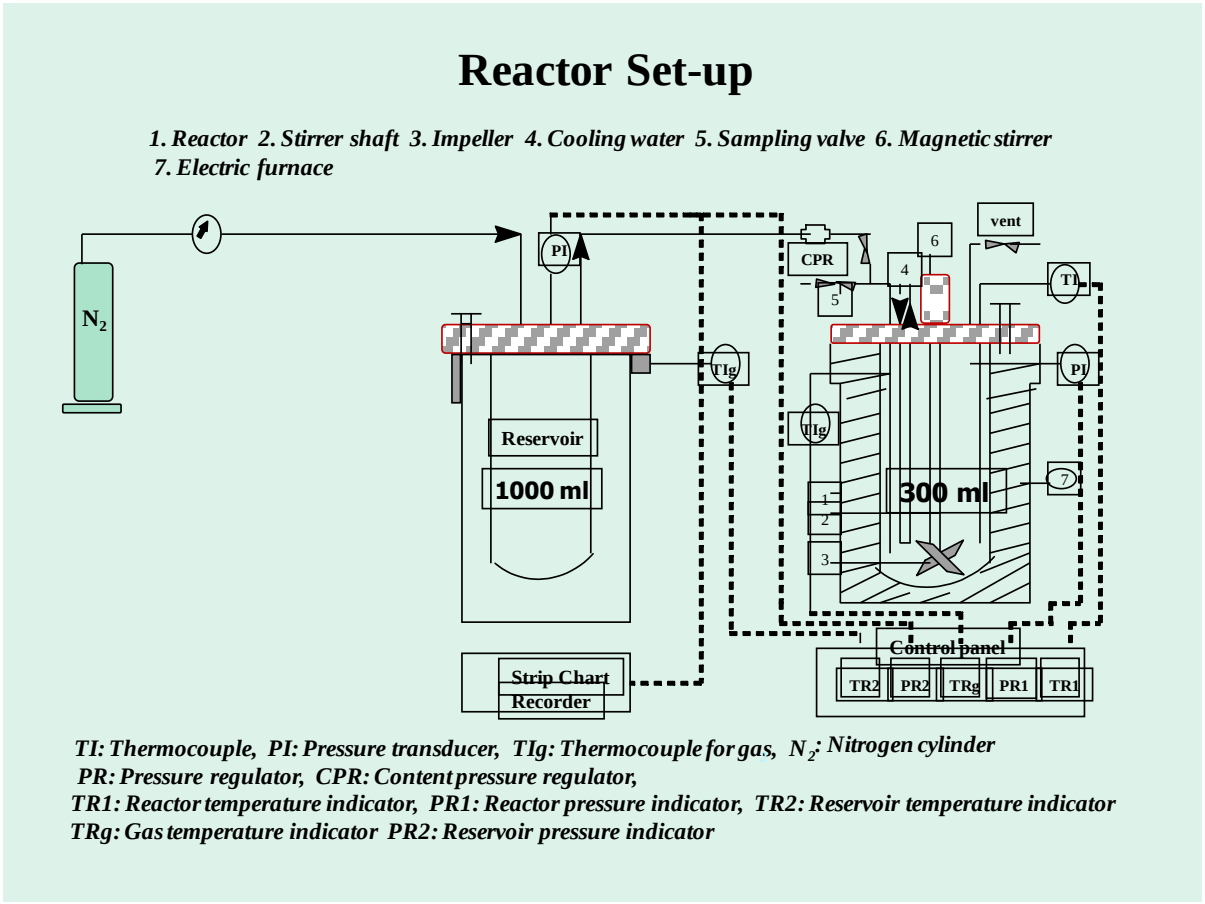


Fig. 8 Schematic of a batch reactor set-up.

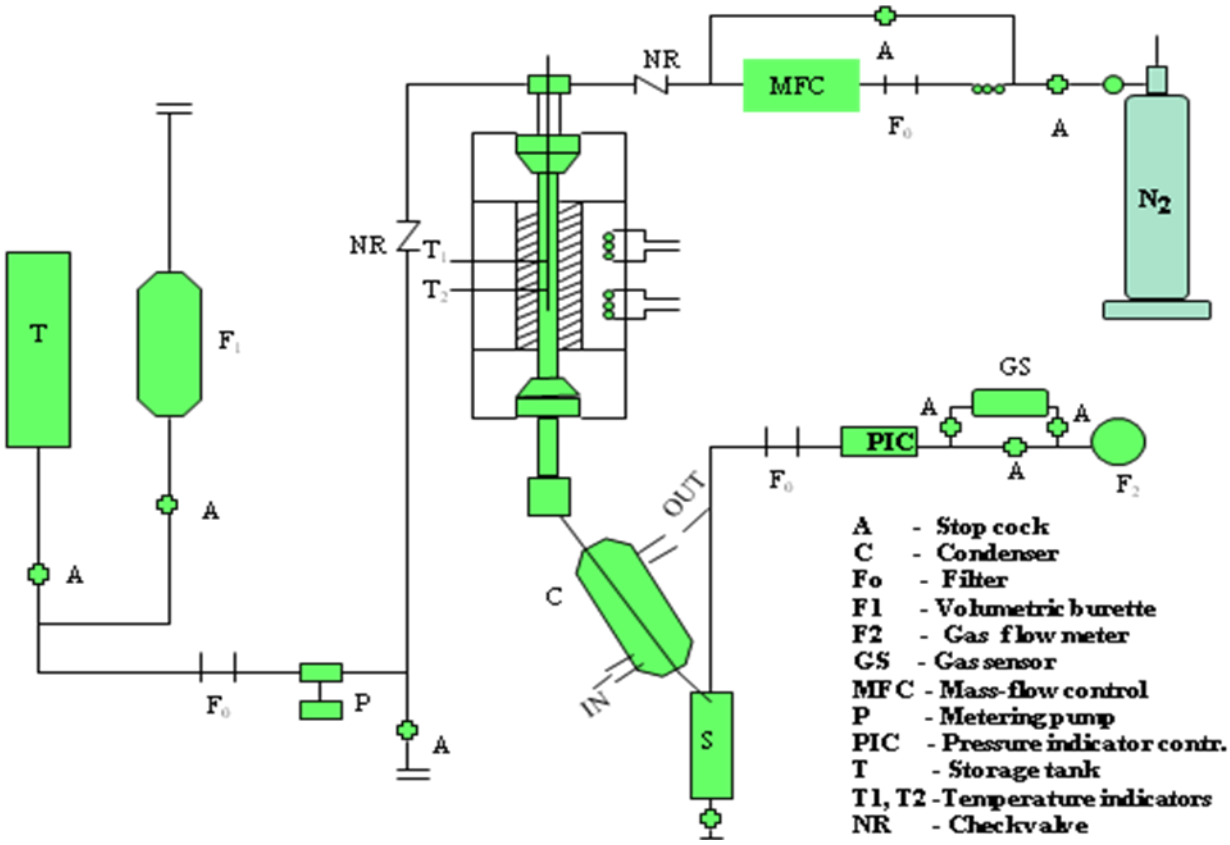


Fig. 9 Schematic of a continuous fixed bed reactor set-up.