Electronic supplementary information

Synergistic activating effect of promoter and oxidant in single step conversion of methane into methanol over tailored polymer-Ag coordination complex.

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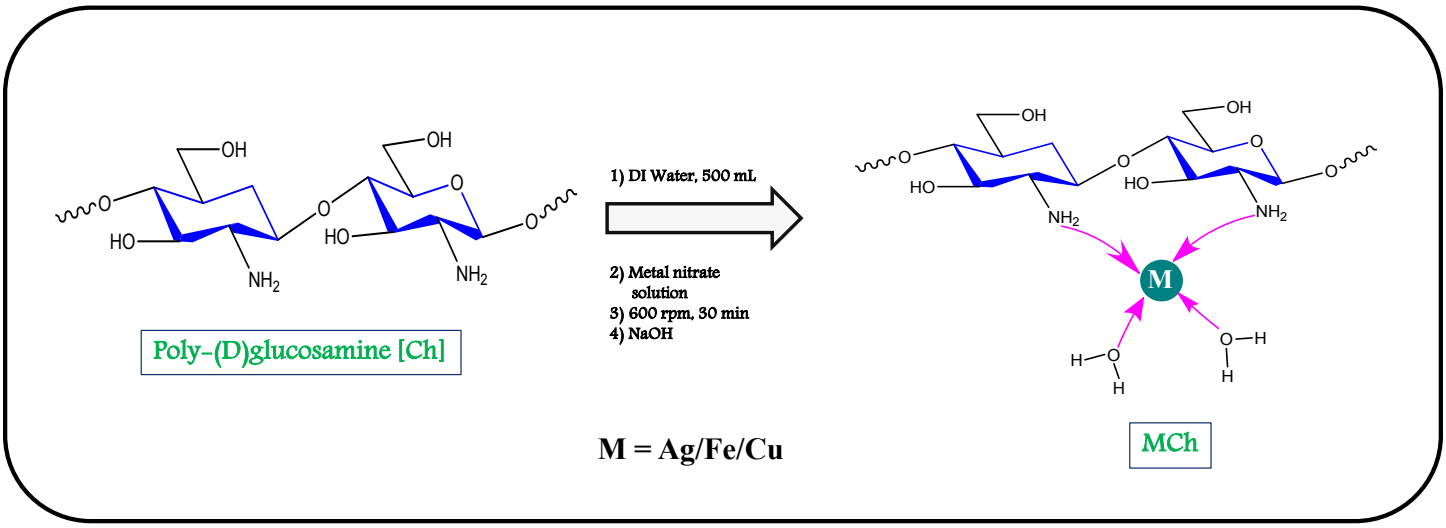

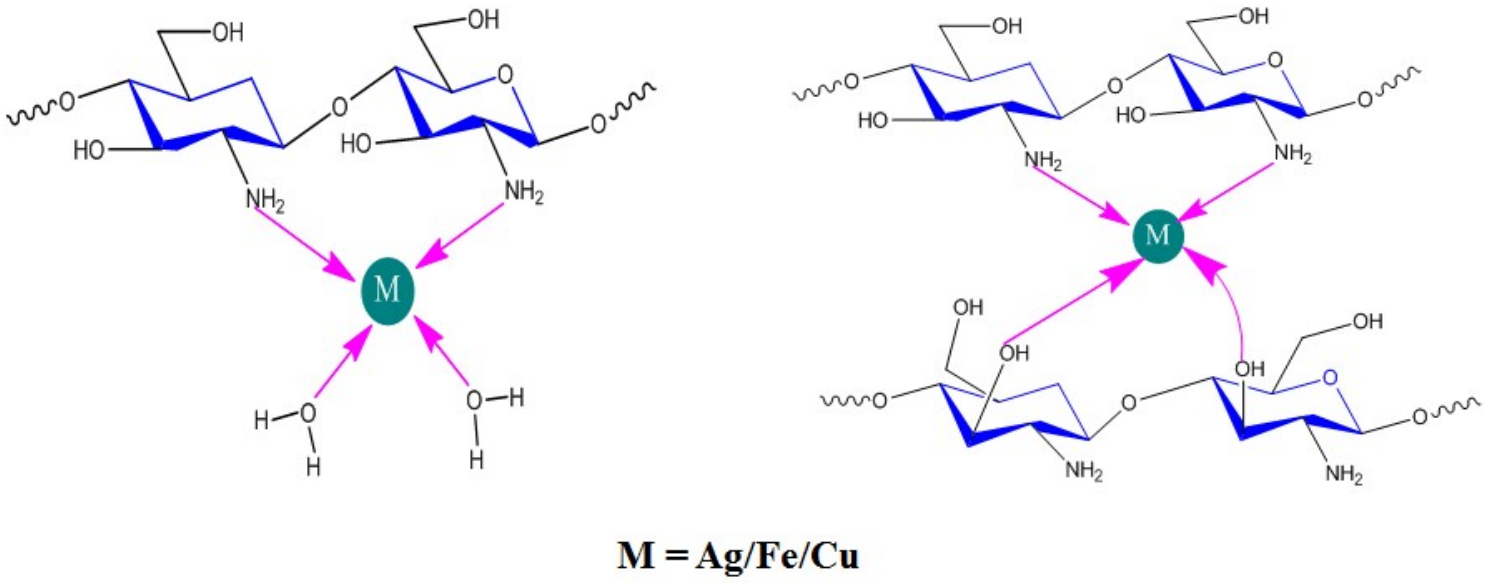

Scheme. S1. Synthetic path way of polymer-metal complexes and their possible structures

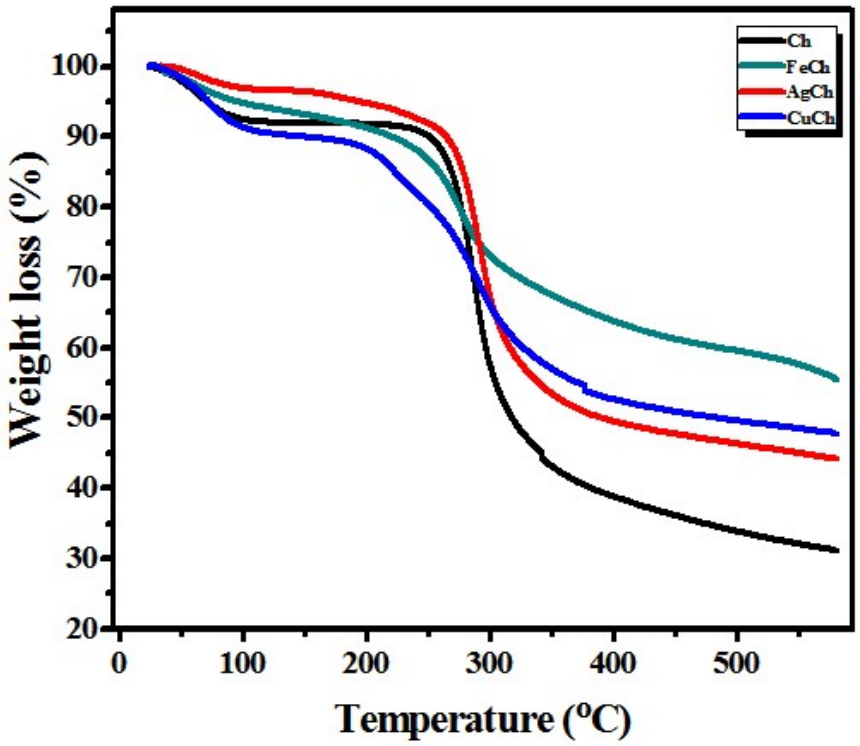

Fig. S1. Thermogravimetric analysis (TGA) spectra obtained for Ch and prepared catalysts

The TGA curve for 'Ch' gave two sharp peaks. One below 100 and other starts at 230 ^{0}C which are attributed to loss of moisture and functional groups respectively. A continues slow degradation of Ch was observed after 400 ^{0}C which informs that the 'Ch' forming carbon at higher temperatures. After complexation the temperature required for functional groups degradation was slightly high. This is because of the strong coordination of functional groups of Ch to metal.

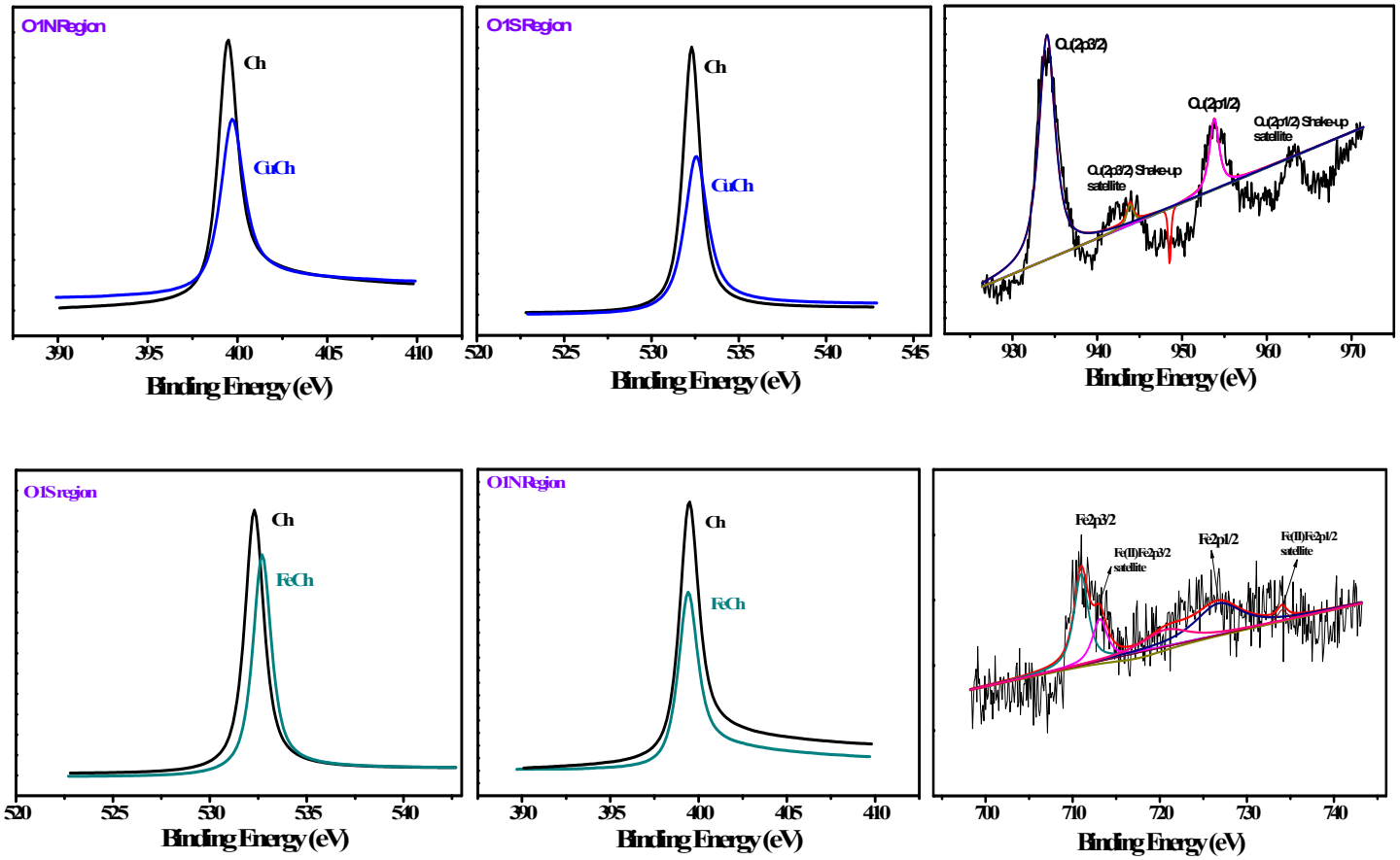

Fig. S2. High resolution XPS spectra for different regions of Cuch (upper row) and FeCh (lower row)

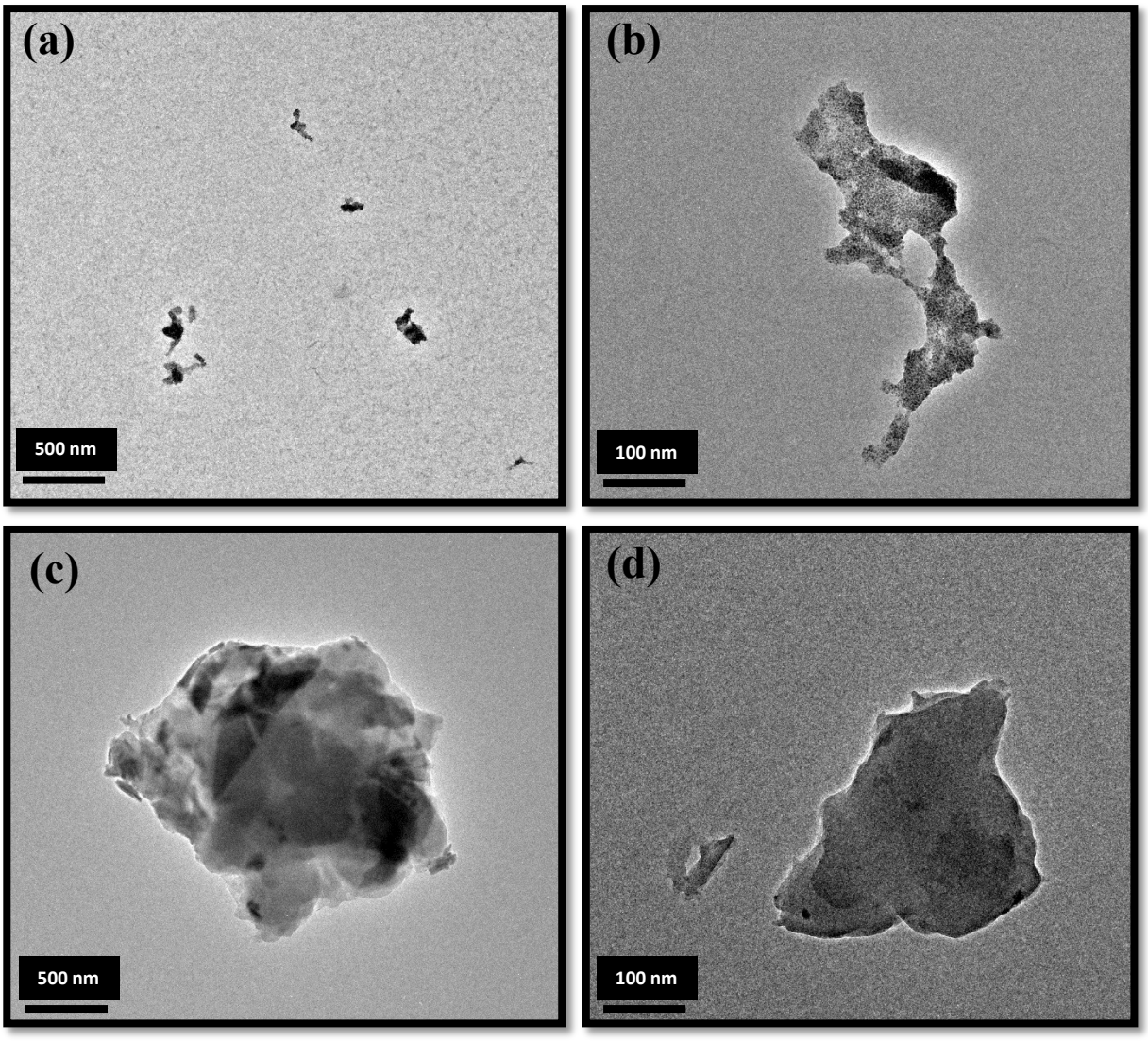

Fig. S3. Transmission Electron Microscopy (TEM) images for (a,b) FeCh and (c,d) CuCh at different magnification

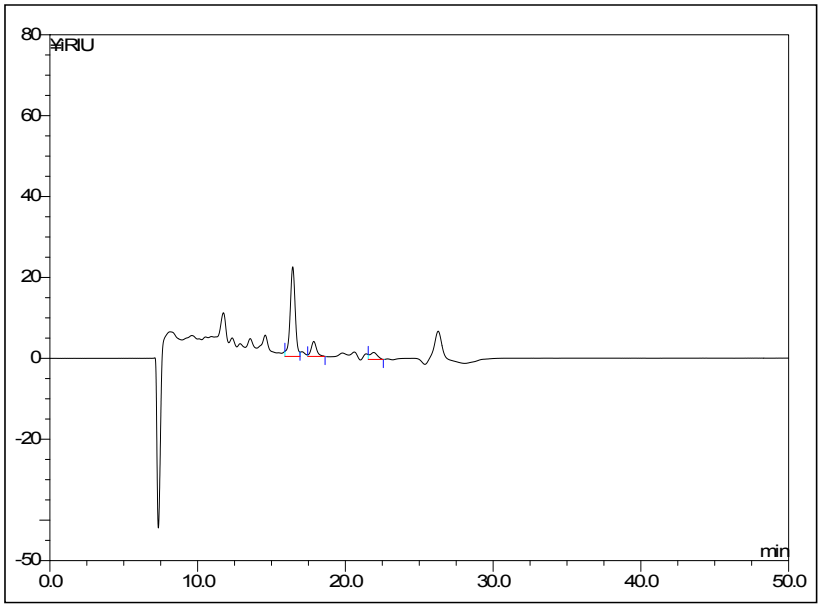

Fig. S4. Ion chromatogram obtained after analyzing liquid products.

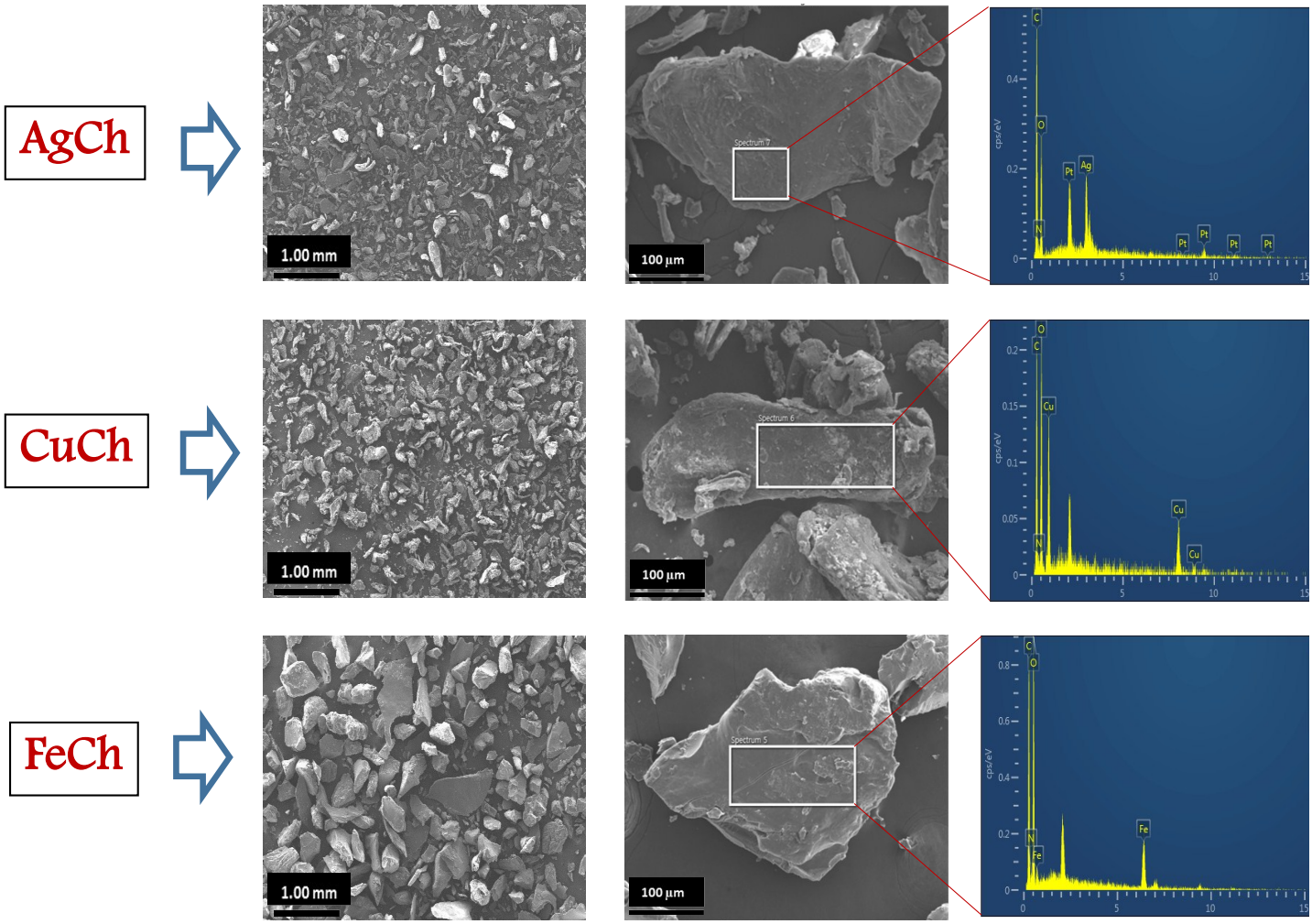

Fig. S5. FESEM- Energy Dispersive X-Ray (EDX) spectroscopic analysis for prepared catalysts.

Field Emission Scanning Electron Microscopy (FESEM) images were recorded using a Sigma Z300 instrument equipped with an energy dispersive X-ray spectrometer (EDS).

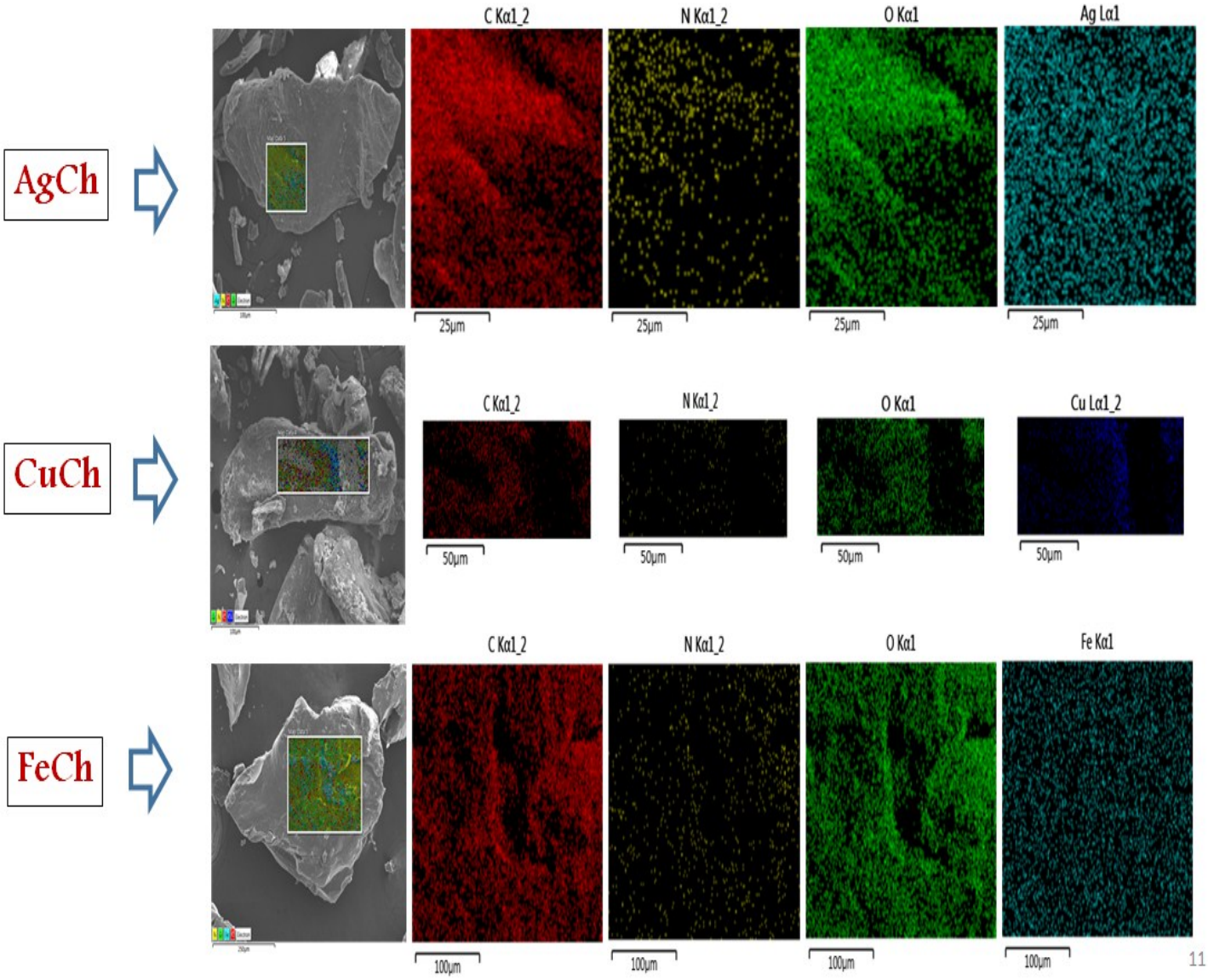

Fig. S6. FESEM elemental mapping for prepared catalysts

Table S1 (a). Metal concentration in catalysts detected by ICP-AES technique

Serial	Sample	Test Item	value	Unit
1	AgCh	Ag	20564.95	mg/Kg
2	FeCh	Fe	86038.45	mg/Kg
3	CuCh	Cu	84970.03	mg/Kg

Table S1 (b). C, H, N & S elemental concentration in catalysts

Serial	Sample	Mass (mg)	N (wt%)	C(wt%)	H(wt%)
1	Ch	1.781	7.45	41.27	7.31
2	AgCh	1.776	7.30	39.48	7.17
3	FeCh	1.768	6.41	34.85	6.26
4	CuCh	1.761	6.31	35.03	6.30

Table S2. Product quantification and percentage of CH_4 conversion for different pristine materials used for catalyst preparation

Entry	Catalyst	oxidant	Product formed (µmol)				CH_4 conversion (%)
			CH_3OH	HCOOH	CH_3COOH	CO_2	
1	$FeNO_3.9H_2O$	H_2O_2	-	24	-	-	0.02
2	$CuNO_3.5H_2O$	H_2O_2	-	264	-	12.3	0.20
3	$AgNO_3$	H_2O_2	-	490	-	15.2	0.38
4	Ch	H_2O_2	12	24	2	0	0.03

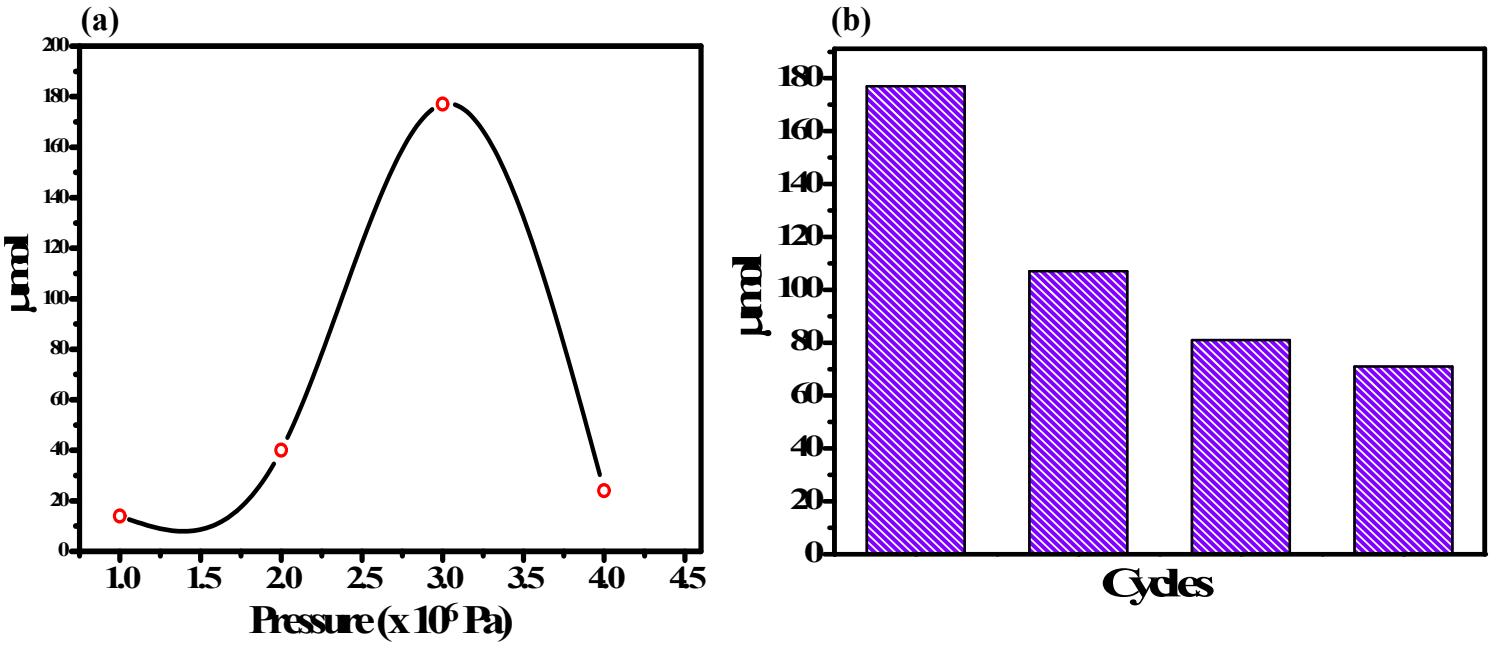

Fig. S7 (a) Effect of CH_4 pressure on the reaction: 150 mg catalyst, 3 hr, 60 ^{0}C (b) reusability data: 30 bar, 150 mg catalyst, 60 ^{0}C

Fig S7 (a) informs that, the 3 × 10^6 Pa pressure is appropriate for the CH_4 to methanol conversion reaction using AgCh catalyst. A pressure higher than this, causes instability in the catalyst to bear pressure. The catalyst appeared to lose the coordination with metal after 3.5 10^6 Pa pressure. A cyclic performance of the AgCh catalyst is shown in Fig.S7 (b). There was continues decrease in catalytic activity. This may be due to loss in active sight which occurs in case of coordination complexes[1].

Table S3. Catalysts comparison from literature for CH_4 conversion and methanol selectivity

Catalyst	Additives	Temperature (ºC)	CH_4 conversion (%)	Methanol selectivity (%)	Ref.
Al/ZSM-5	Fe	50	0.2	22	[2]
Cu-Fe/ZSM-5	-	50	0.7	85	[2]
Cu/Silicates-1	-	50	0	0	[2]
Fe-Silicate	-	70	10.5	8	[2]
AgCh	$[BMIM]^+Cl^-$	60	4.5	0	This work
AgCh	$[BMIM]^+Cl^-$ O_2	60	4	54	This work
Au^0	2% SO_3	180	0	0	[3]
Au^0	3 M SeO_3 + 2% SO_3	180	28	94	[3]
ZSM-5	-	50	1.1	11.6	[4]

Table S4. Catalysts comparison for CH_4 conversion to its oxygenates in terms of TON

Catalyst	Specifications	TON[a]	Ref.
Cu-ZSM-5	No solvent used	0.02	5
$(Bipym)Pt^{II}Cl_2$	H_2SO_4, Ionic liquid	0.5	6
$Pd(OAc)_2$, $NaNO_2$, O_2,Benzoquinone	CF_3COOH	3~7	7
$FeCl_3$	aqueous	7	8
$PdSO_4$	H_2SO_4	14.2	9
sMMO	--	19	10
AgCh	H_2O_2	22	This work
CuCh	H_2O_2	2	This work
FeCh	H_2O_2	3	This work
$(FetBuPc)_2N/SiO_2$	H_2O_2 , H_2SO_4	209	11
$K_2[PtCl_4]$-CTF	30% Oleum	<250	12
AgCh	H_2O_2, $[BMIM]^+Cl^-$	301	This work
AgCh, O_2	H_2O_2, $[BMIM]^+Cl^-$	266	This work
AgCh	H_2O_2, $[BMIM]^+Br^-$	144	This work
AgCh, O_2	H_2O_2, $[BMIM]^+Br^-$	135	This work

[a] TON = Total moles of oxygenated produced/moles of Ag utilized for the reaction

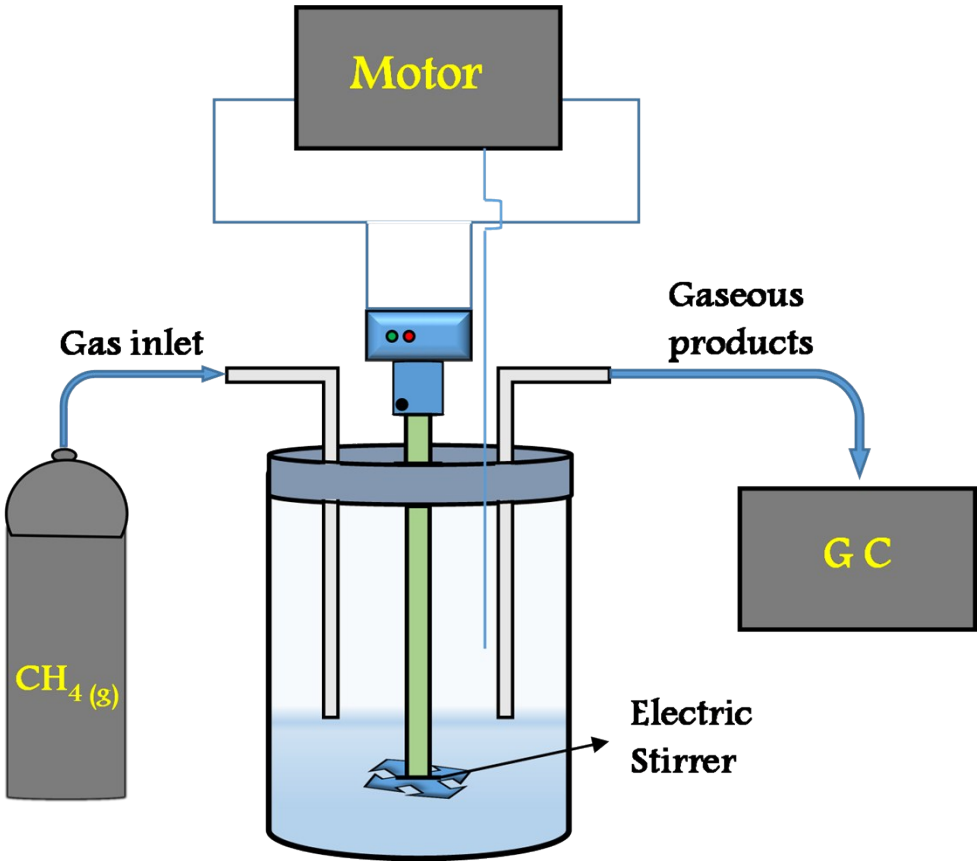

Fig. S8. A rough diagram of the instrumentation used to carry out the reaction

■ Notes and references

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