Supplementary Material

Selective Electro-Oxidation of Methane to Methanol at Room Temperature Using a Flow Reactor

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Possible Mechanism of Methane to Methanol

A possible mechanism of OH radical might be in a proton exchange membrane fuel cell with a Nafion membrane, where hydroxyl radicals (•OH) may form in the presence of an Fe^{2+} catalyst. During operation, oxygen reduction may produce hydrogen peroxide (H_2O_2) as a side product. Fe^{2+} reacts with H_2O_2 through a Fenton reaction, generating highly reactive •OH radicals and OH^- ions. These radicals interact with methane to form methanol.

$OH^- + H^+ = OH\bullet + H\bullet$ (1)

$OH^- = OH\bullet + e^-$ (2)

$2\ OH\bullet = H_2O_2$ (3)

Because the generated OH• is more reactive than H_2O_2 and quickly consumed, the addition of Fe^{2+} reagent can effectively break the pre-formed H_2O_2 back into the OH• species to further provide an enhanced oxidation environment through Fenton reaction (equations 6, 7, and 8)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$ (6)

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$ (7)

$2H_2O_2 \rightarrow HO\bullet + HOO\bullet + H_2O$ (8)

The addition of Cl^- in water acts as a spectator ion in the solution. It helps improve the solubility of methane. Methylene chloride (CH_2Cl_2) can react with hydroxide ions (OH^-) through a hydrolysis reaction, in which the hydroxide ion replaces chlorine atoms. During this substitution process, intermediate compounds form and can eventually convert to methanol (CH_3OH).

Gas chromatography Analysis

The GC-FID analysis was performed using a Supelco wax column, 60 m long with an internal diameter of 0.25-0.32 mm. Helium was used as the carrier gas at a flow rate of 1 mL min^{-1}. The oven temperature was held at 70 °C for 2 min, then ramped at 8 °C min^{-1} to 250 °C, with the FID maintained at 250 °C. Blank experiments, including bare graphite felt, water-only, and oxygen in place of methane, were analyzed prior to methane oxidation. All blank chromatograms showed only the water peak at ~6.0 min, confirming the absence of alcohols (Fig. S2).

Gas products analysis

In addition to liquid products, methane conversion generated gaseous species; therefore, the gases were collected in a gas sampling bag and injected into a gas chromatograph coupled with flame ionization detection. The chromatogram shows the CO_2 peak at about 1 minute, Hydrogen at 10 minutes, methane at around 13 minutes, and an additional peak within 1 minute due to purging the gas. The chromatogram is shown in Fig. S3 below.

Before the analysis, Analytical calibration for GC was performed using Argon as an internal standard. Calibration mixtures were prepared by varying the CH_4 flow rate to obtain CH_4 volume fractions of 1–10% while maintaining a constant Ar flow rate. The CH_4 and Ar streams were combined at a T- junction, allowing thorough mixing before direct introduction into the GC. Quantification of CH_4 (and, where applicable, CO and CO_2) was based on the ratio of the target-gas peak area to the Ar peak area. Calibration curves were constructed by plotting the peak-area ratio versus the corresponding concentration ratio, and all target gases showed linear behavior ($R^2 > 0.99$)

Nuclear Magnetic Resonance Analysis

The product samples were analyzed by nuclear magnetic resonance (NMR) spectroscopy on a JEOL ECZLR 600R spectrometer (JEOL Ltd., Tokyo, Japan) operating at 600 MHz. ^1H NMR spectra were acquired in water suppression mode for greater accuracy, using D_2O as the solvent. All spectra were acquired using 128 scans. For each analysis, 0.5 mL of post-reaction sample was combined with 0.1 mL of a dimethyl sulfoxide (DMSO) internal standard solution (10 ppm) and 0.1 mL D_2O. A calibration curve was generated by plotting the concentration of the standard product solution against the integrated areas of the product and DMSO signals. Product quantification was achieved by comparing the ^{1}H NMR signal with this calibration curve. The calibration curves for methanol and ethanol are shown in Fig. S9 below.

Methane conversion, methanol selectivity and yield

Methane conversion was calculated by comparing the molar amount of CH_4 before and after reaction: h^{-1}

$$Conversion = \frac{nCH_{4,\,final} - nCH_{4,\,initial}}{nCH_{4,\,initial}} x\ 100\ \% \#1$$

$$Methanol\ selectivity = \frac{n\ CH_3OH}{n\ total\ oxygenates} x\ 100\% \#2$$

$$Yield\ of\ Product\ (\mu molg^{-1}{}_{cat}h^{-1}) = \frac{n\ CH_3OH}{g_{cat}\ *\ t} \#3$$

Faradaic efficiency calculation

The faradaic efficiency (FE) was calculated as:

$$Faradaic\ efficiency = \frac{nCH_3OH\ *\ N\ *\ F}{Q} x\ 100\ \% \qquad 4$$

where n_{CH_3OH} is the amount of methanol produced (mol), $N$is the number of electrons transferred per mole of methanol, $F$is the Faraday constant (96485 C mol^{-1}), and $Q$is is the total charge passed during electrolysis obtained by integrating the chronoamperometry curve.

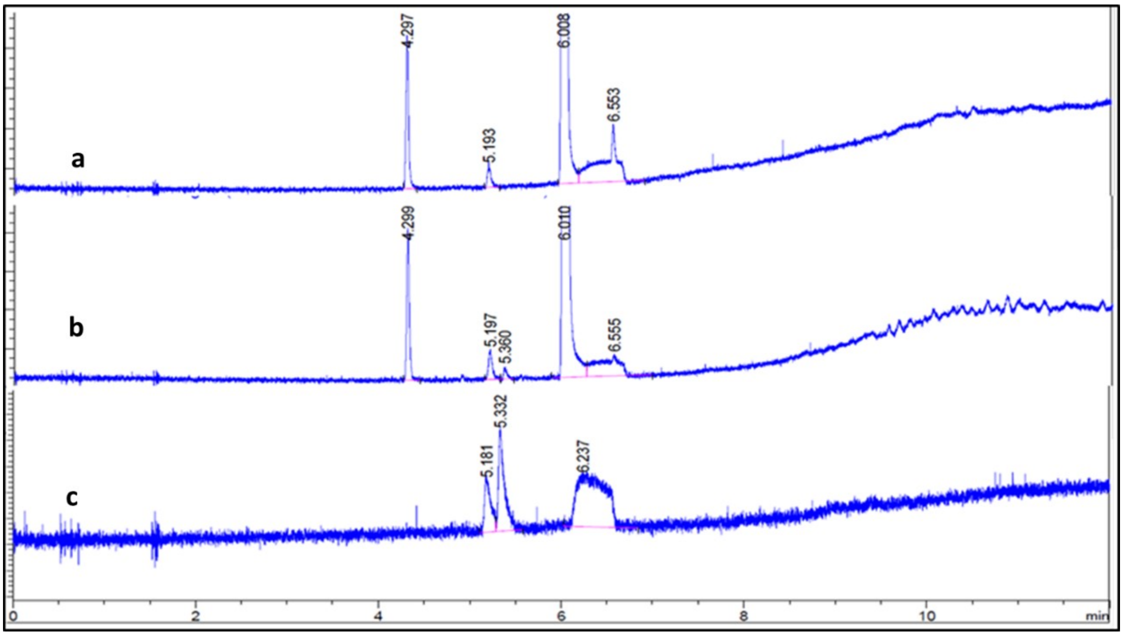


Fig. S1 GC Chromatograms of (a) CH_4 reaction (b) CH_4, O_2 reaction (c) 10 ppm methanol/ethanol standard

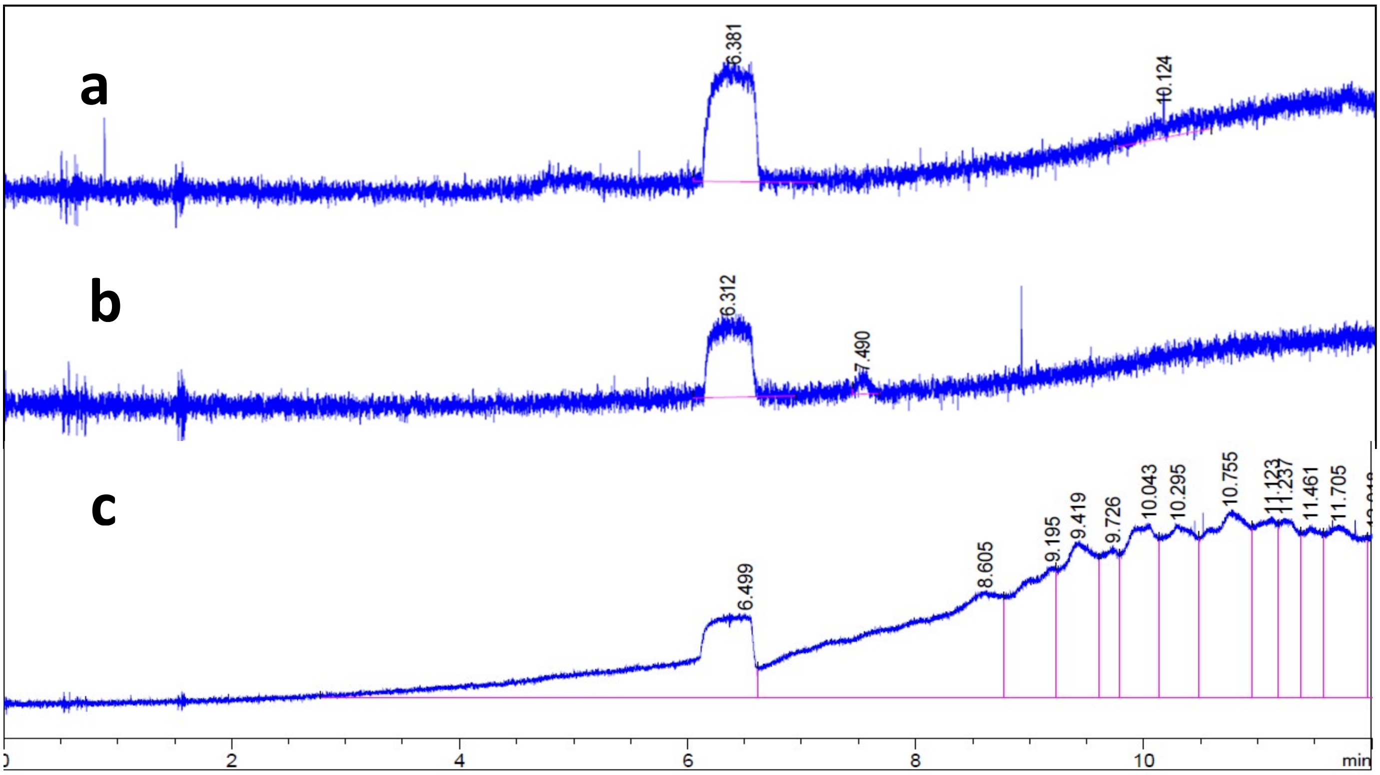


Fig. S2 GC Chromatogram of (a) water (b) O_2 gas instead of methane (c) bare graphite

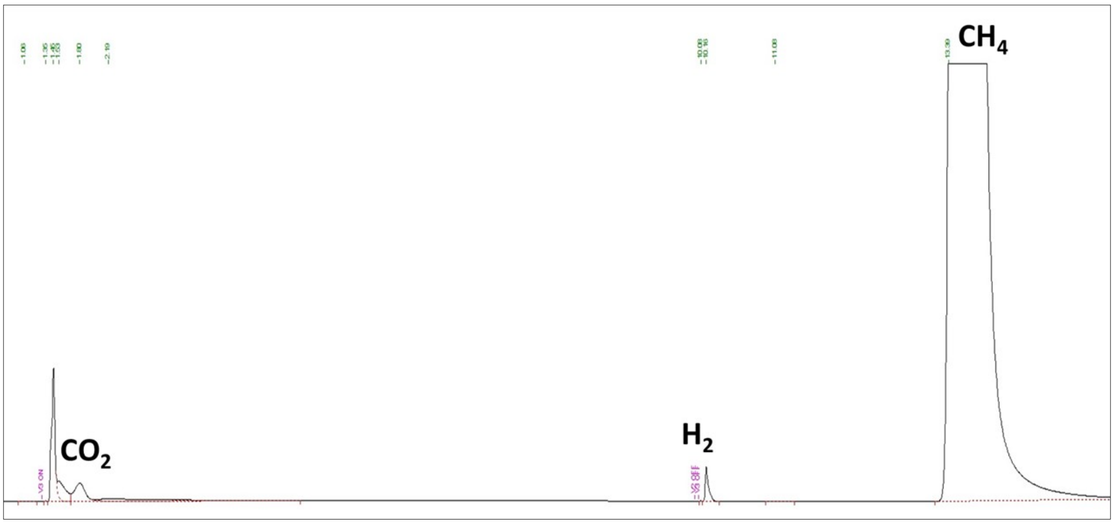


Fig. S3 GC chromatogram of gas samples of the CH_4 reaction under optimized conditions

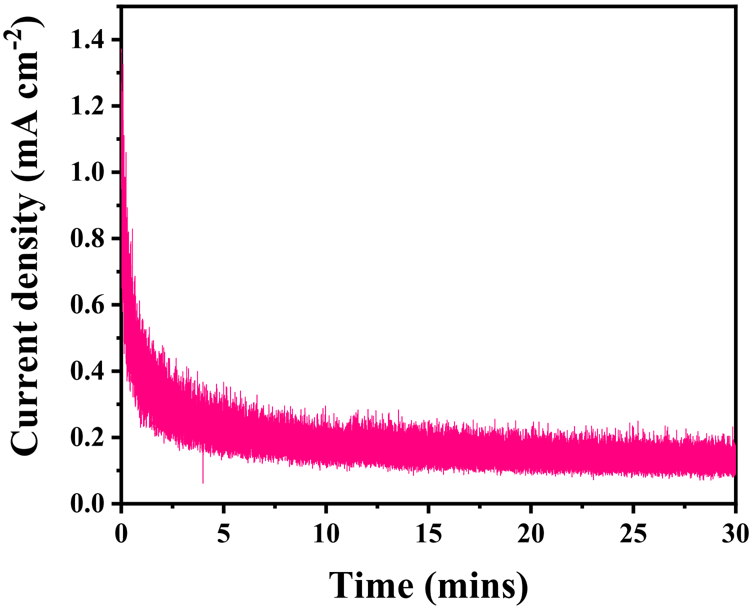
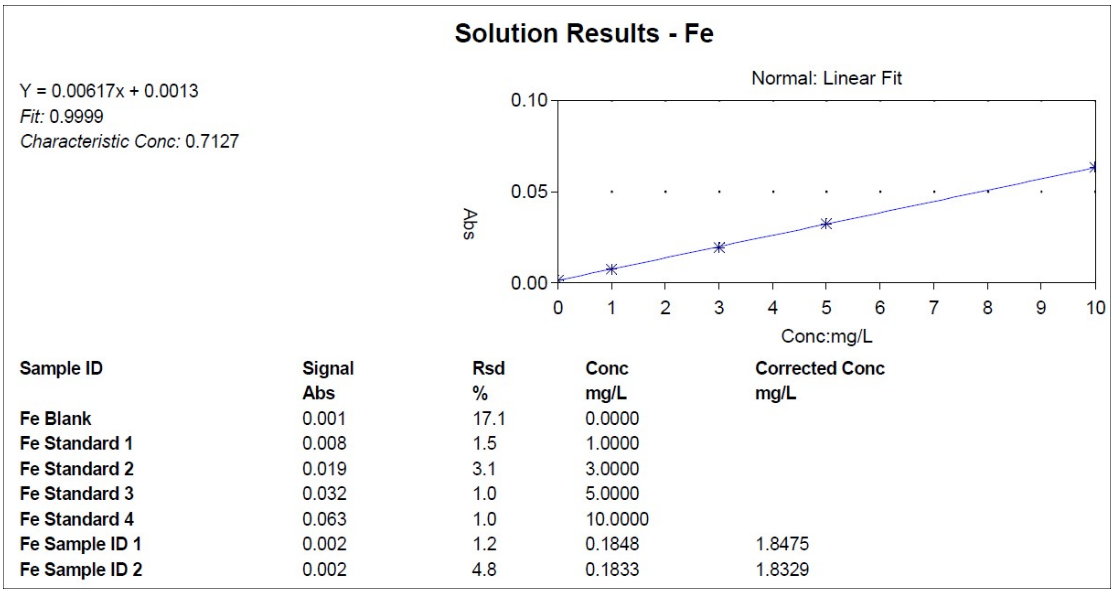


Fig. S4: Methane conversion current density at 0.9 V. Constant current density clearly shows the steady conversion of methane to methanol.



Solution Results - Fe

Y = 0.00617x + 0.0013
Fit: 0.9999
Characteristic Conc: 0.7127

Sample ID	Signal Abs	Rsd %	Conc mg/L	Corrected Conc mg/L
Fe Blank	0.001	17.1	0.0000	
Fe Standard 1	0.008	1.5	1.0000	
Fe Standard 2	0.019	3.1	3.0000	
Fe Standard 3	0.032	1.0	5.0000	
Fe Standard 4	0.063	1.0	10.0000	
Fe Sample ID 1	0.002	1.2	0.1848	1.8475
Fe Sample ID 2	0.002	4.8	0.1833	1.8329

Fig. S5: Atomic absorption spectroscopy analysis of Fe concentration on the freshly prepared catalytic surface (sample ID 1) and after multiple times (sample ID 2).

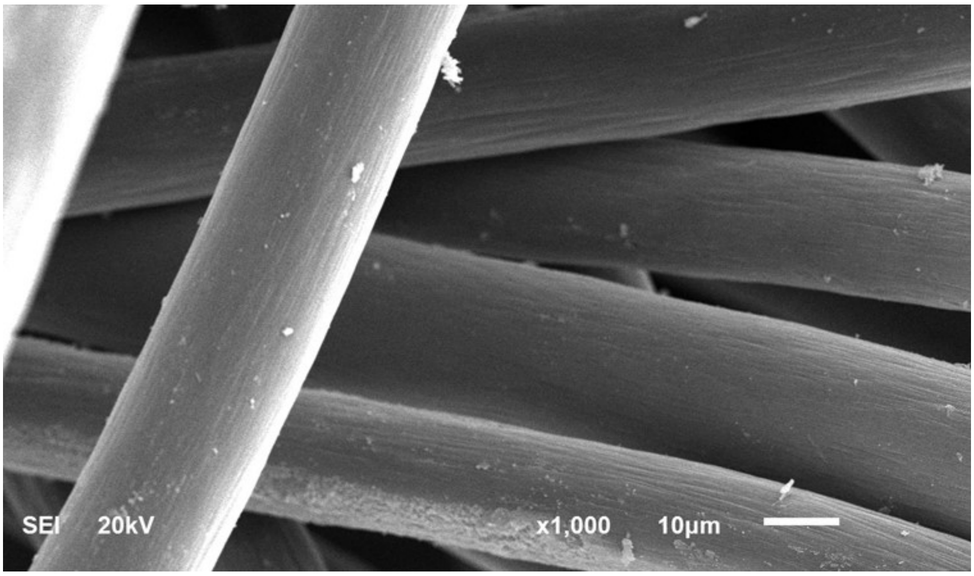


Fig. S6: SEM Image of GF-α-Fe_2O_3 after reaction

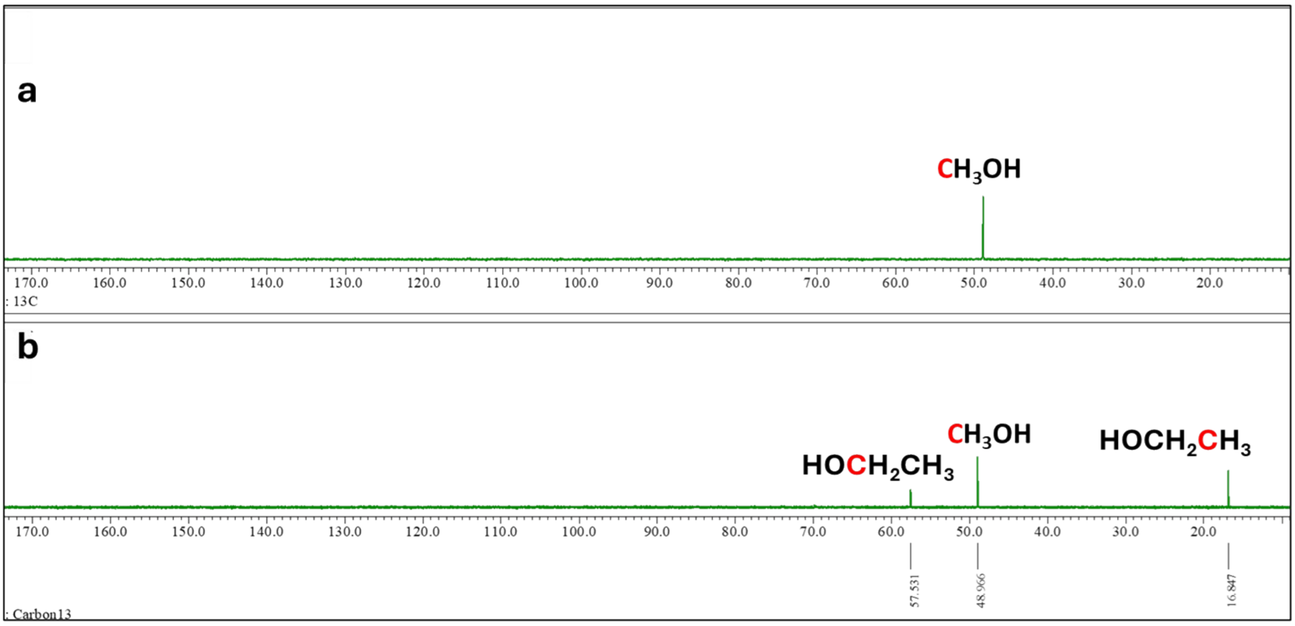


Fig. S7: ^{13}C of the post reaction sample for the reaction of (a) methane (b) methane + O_2 under optimized conditions

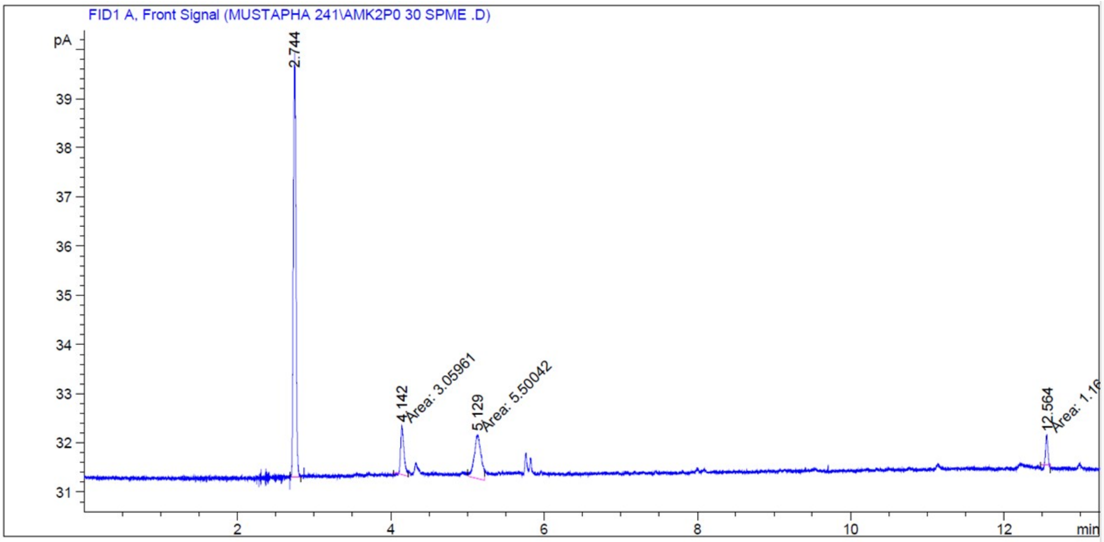


Fig. S8 GC-FID chromatogram for SPME injection of methane reaction

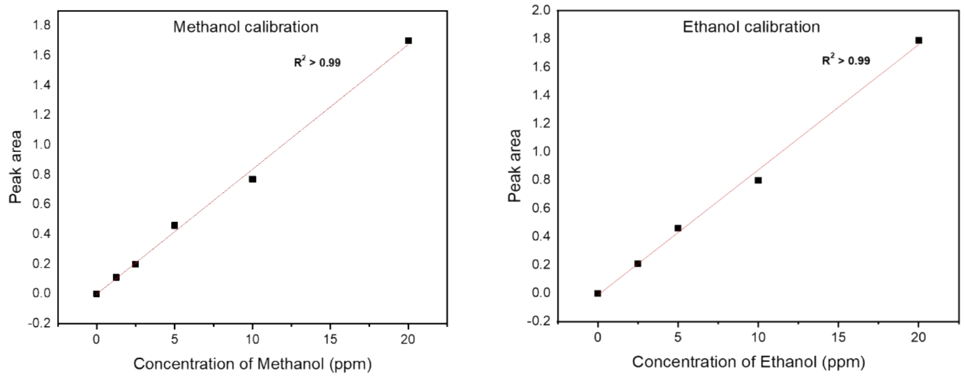


Fig. S9 methanol and ethanol calibration using ^{1}H NMR and DMSO as internal standard