Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# Selective Oxidation of Methane to Methanol on Dispersed Copper on Alumina from Readily Available Copper(II) Formate.

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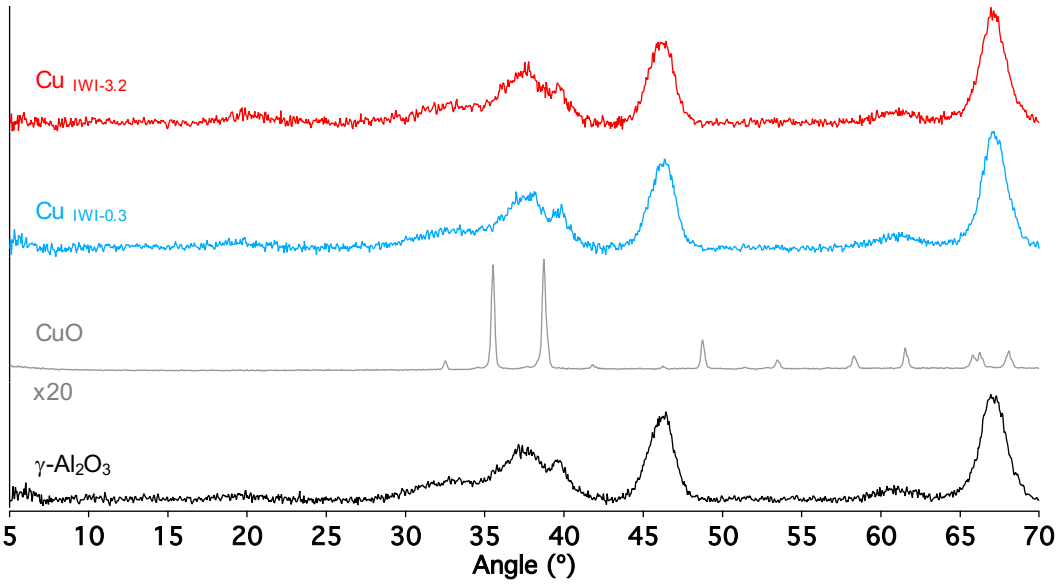


*Figure S1: Powder XRD of γ-$Al_2O_3$ (black), CuO (gray), γ-$Al_2O_3$ after impregnation of 0.3 wt% Cu (blue) and 3.2 wt% Cu (red)*

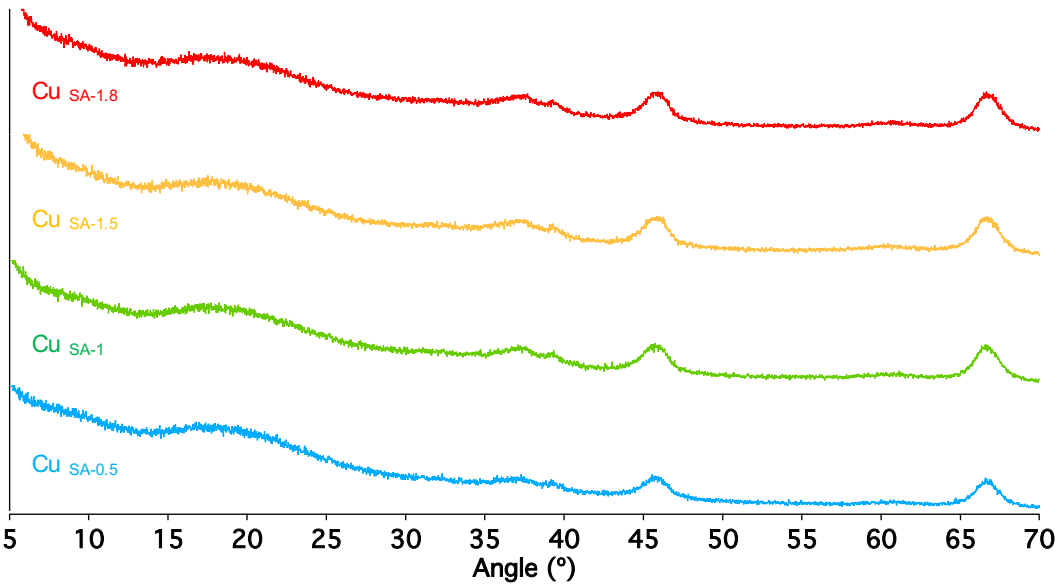


*Figure S2: Powder XRD of γ-$Al_2O_3$ after specific adsorption of 0.5 wt% Cu (blue), 1.0 wt% Cu (green), 1.5 wt% Cu (orange) and 1.8 wt% Cu (red)*

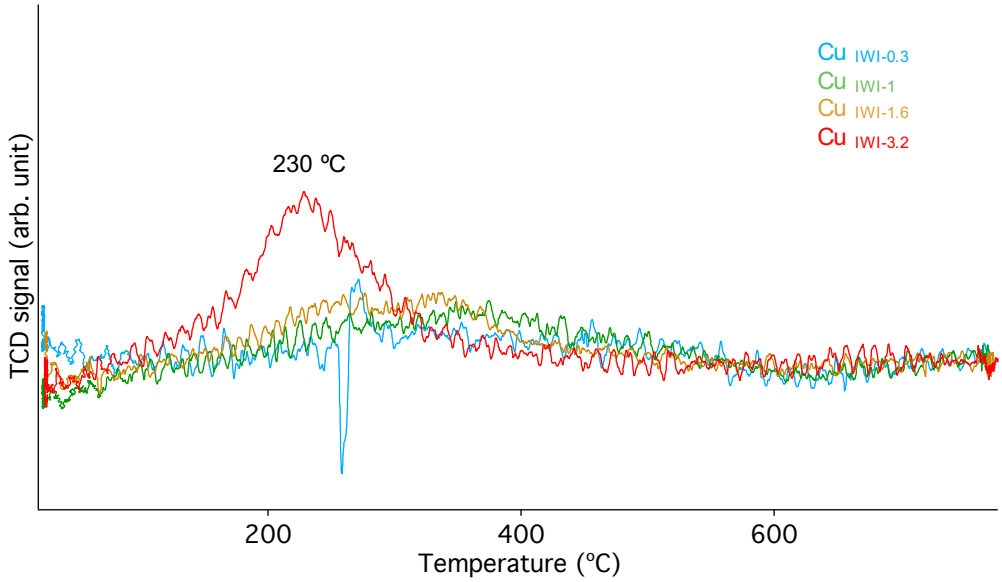


*Figure S3: Temperature programmed reduction (TPR) of the incipient wetness impregnation samples after activation at 500 ºC under synthetic air*

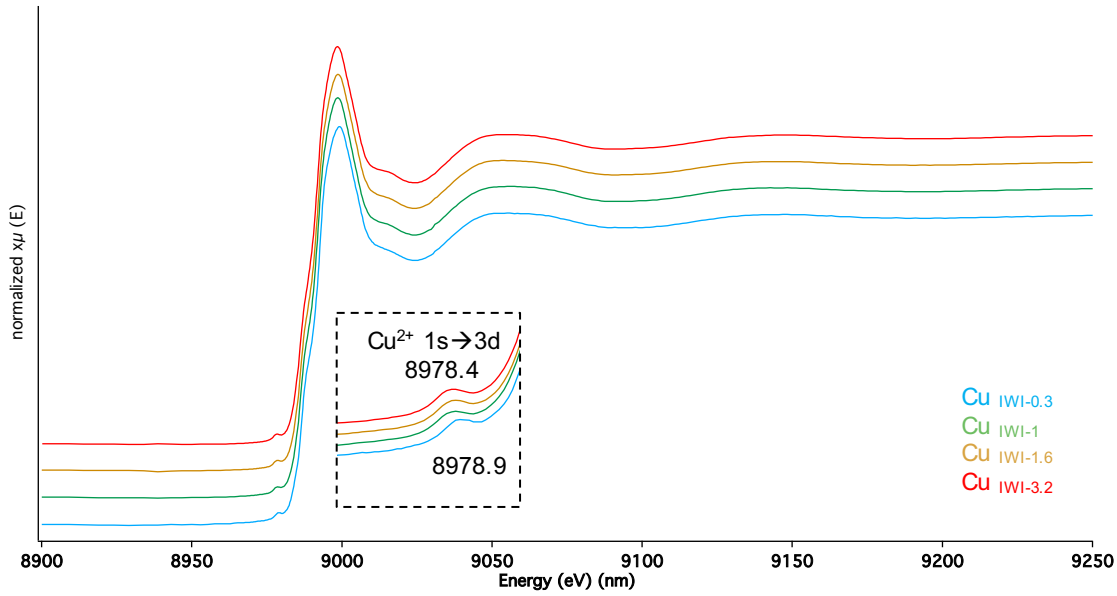


*Figure S4: Cu K-edge X-Ray Adsorption Near Edge (XANES) spectroscopy of γ-$Al_2O_3$ prepared by IWI after calcination at 500 °C*

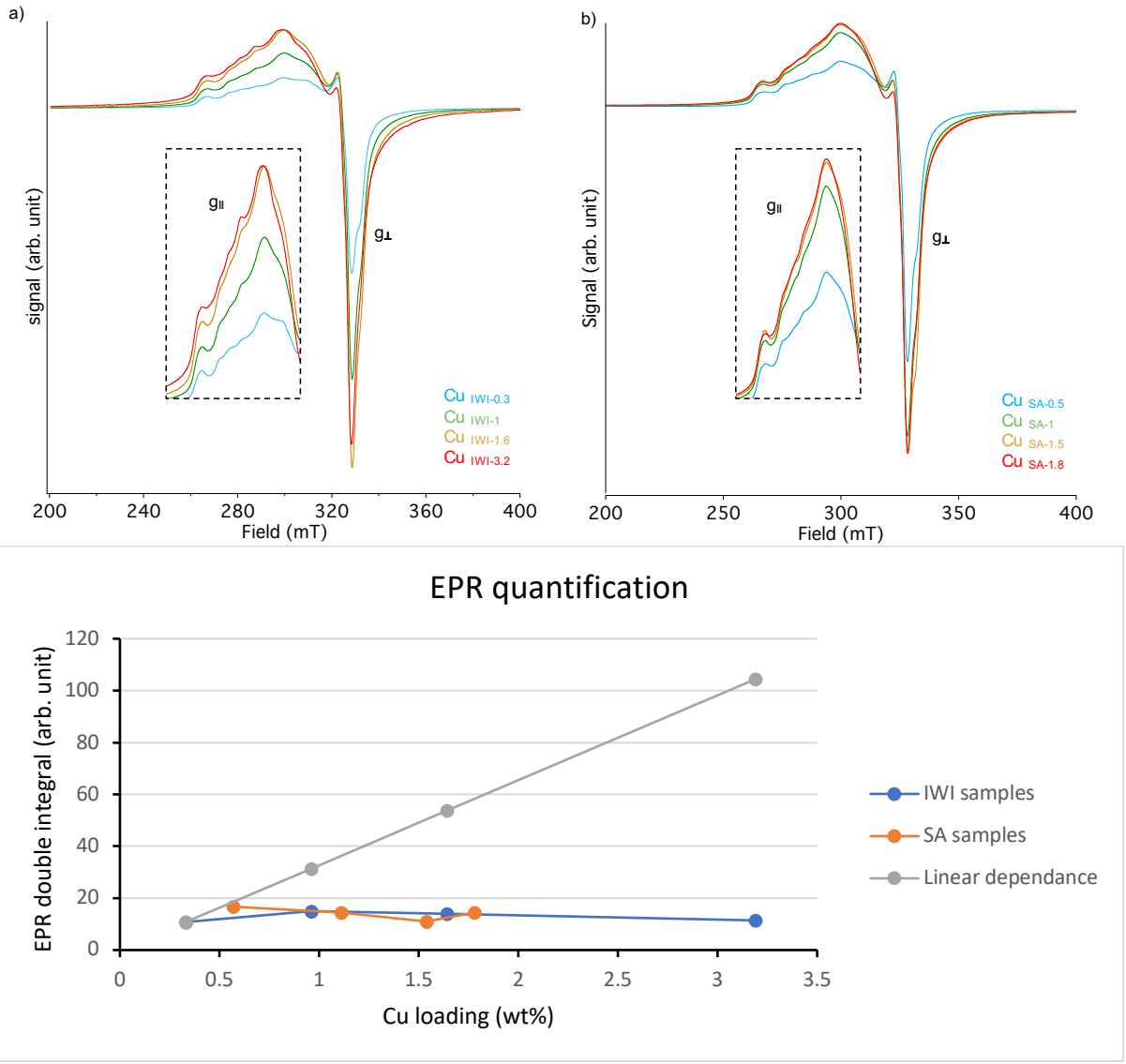


*Figure S5: X-band CW-EPR spectra of the IWI (a) and SA (b) samples after activation at 500 °C under synthetic air*

| Material | loading | Site density | $CH_3OH$ yield | $CH_3OH$ yield | EPR quantification |
|---|---|---|---|---|---|
| **IWI** | wt% Cu | Cu.nm-1 | µmol.g$^{-1}$ | mol $CH_3OH$.mol$^{-1}$ Cu (%) | $Cu^{2+}$ reduced (%) |
| **Cu $_{IWI-0.3}$** | 0.33 | 0.1 | 3.0 | 5.8 | 10.8 |
| **Cu $_{IWI-1}$** | 0.96 | 0.4 | 6.8 | 4.5 | 15 |
| **Cu $_{IWI-1.6}$** | 1.64 | 0.7 | 11.8 | 4.6 | 13.9 |
| **Cu $_{IWI-3.2}$** | 3.19 | 1.3 | 14.4 | 2.9 | 11.5 |
| **Cu $_{IWI-0.3}$** | 0.33 | 0.1 | 4.4 | 8.5 | n.d |
| **Cu $_{IWI-1}$** | 0.75 | 0.3 | 6.9 | 5.9 | n.d |
| **Cu $_{IWI-1.6}$** | 1.68 | 0.7 | 11.6 | 4.4 | n.d |
| **Cu $_{IWI-3.2}$** | 2.89 | 1.2 | 14.8 | 3.2 | n.d |
| **SA** | | | | | |
| **Cu $_{SA-0.5}$** | 0.57 | 0.2 | 5.2 | 5.9 | 16.7 |
| **Cu $_{SA-1}$** | 1.11 | 0.5 | 7.9 | 4.5 | 14.5 |
| **Cu $_{SA-1.5}$** | 1.54 | 0.6 | 8.2 | 3.4 | 11 |
| **Cu $_{SA-1.8}$** | 1.78 | 0.7 | 21.0 | 7.5 | 14.5 |

*Table S1: Reactivity summary for the IWI and SA samples for the partial oxidation of methane to methanol*

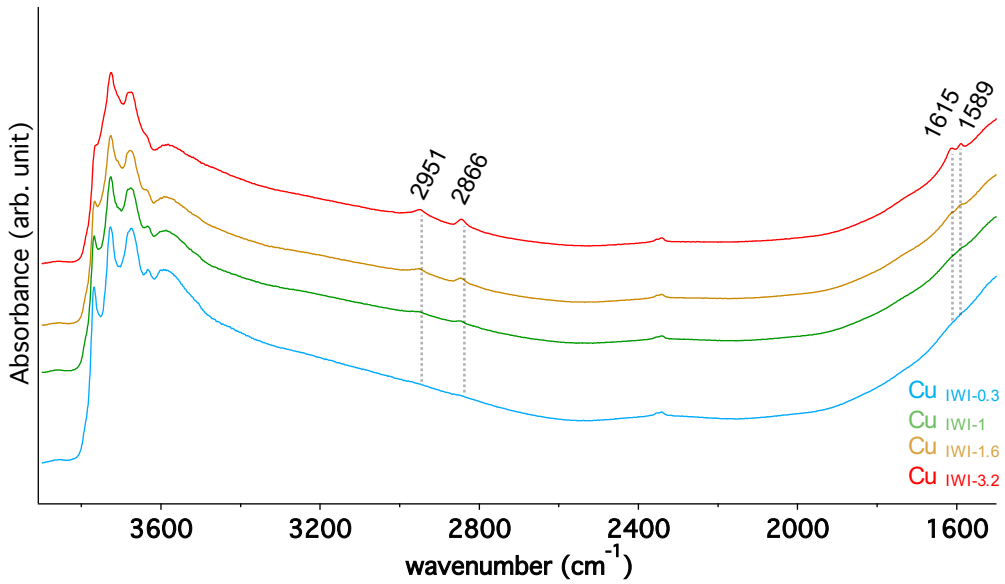


*Figure S6: DRIFT spectra of the incipient wetness impregnation samples after reaction with $CH_4$ (6 bar, 200 °C, 30 min)*

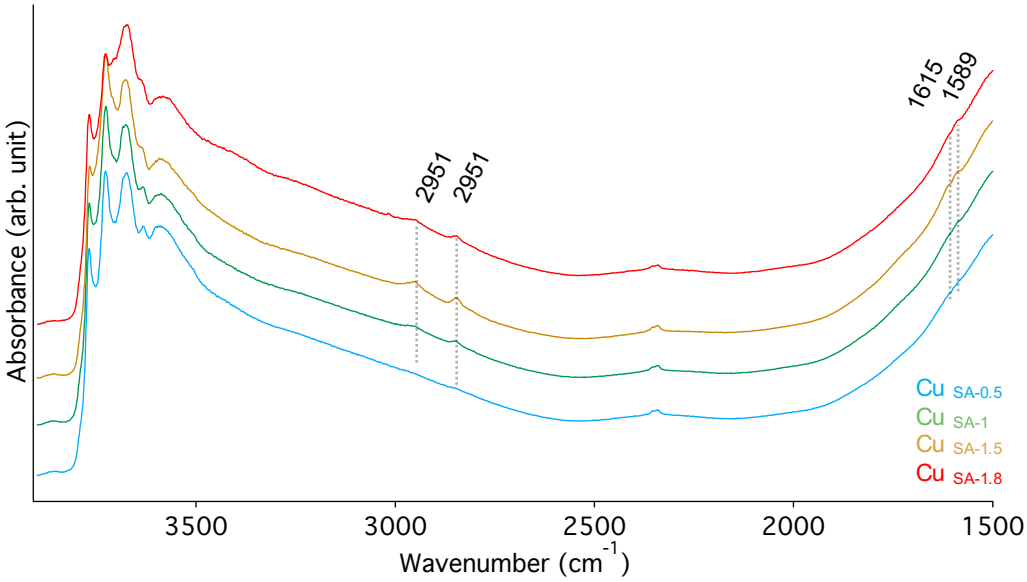


*Figure S7: DRIFT spectra of the specific adsorption samples after reaction with $CH_4$ (6 bar, 200 °C, 30 min)*

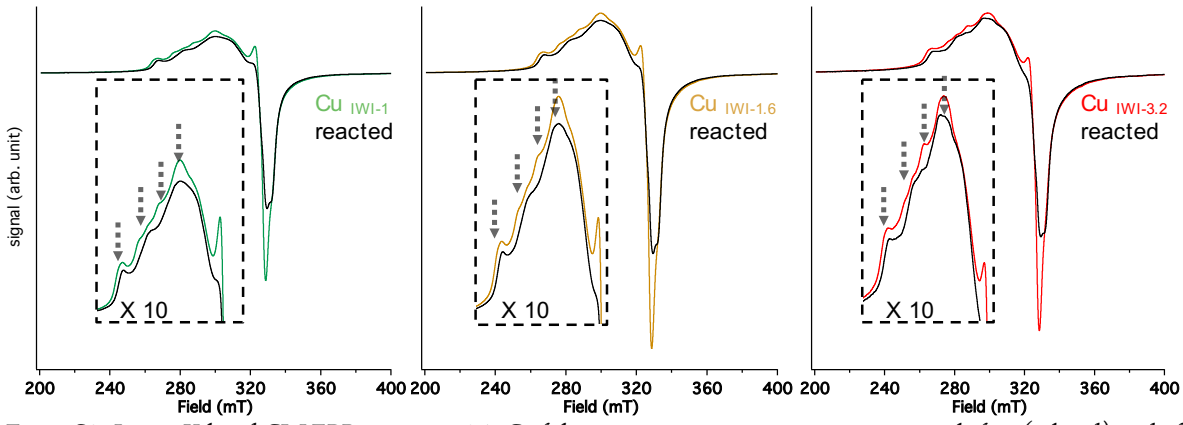


*Figure S8: In situ X-band CW-EPR spectra at 25 °C of the incipient wetness impregnation series before (colored) and after (black) reaction with 6 bar of $CH_4$ at 200 °C for 30 min. The insert shows a magnification of the parallel transition region and the grey arrows indicate the Cu hyperfine coupling that decrease after reaction with $CH_4$.*

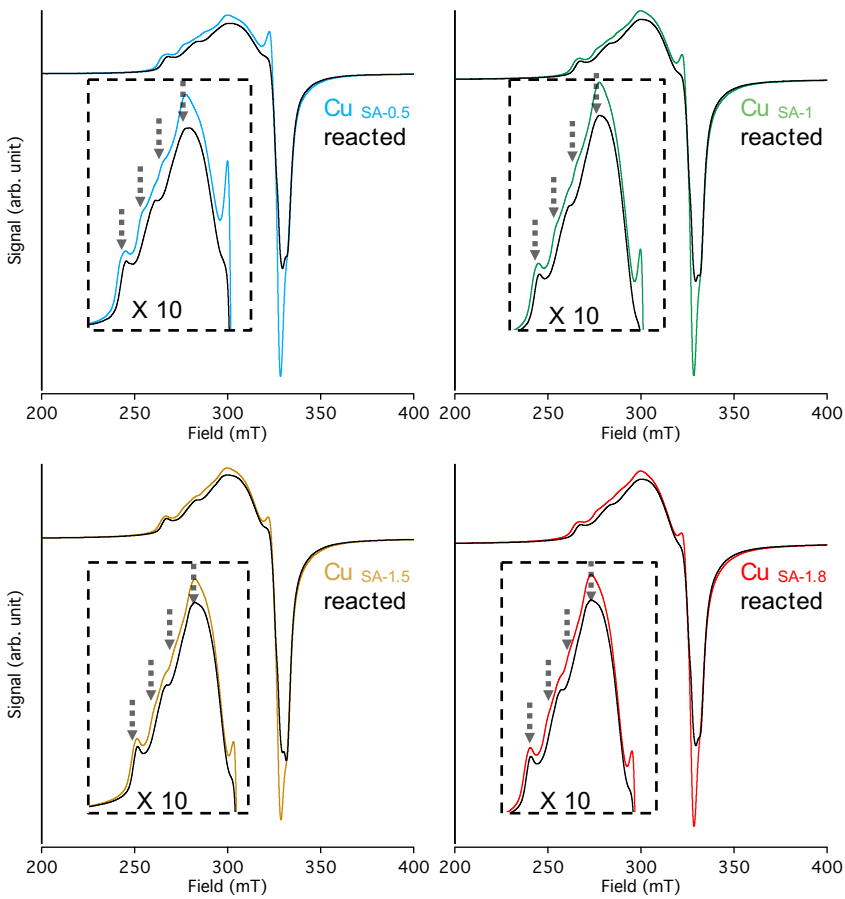


*Figure S9: In situ X-band CW-EPR spectra at 25 °C of the specific adsorption series before (colored) and after (black) reaction with 6 bar of $CH_4$ at 200 °C for 30 min. The insert shows a magnification of the parallel transition region and the grey arrows indicate the Cu hyperfine coupling that decrease after reaction with $CH_4$.*

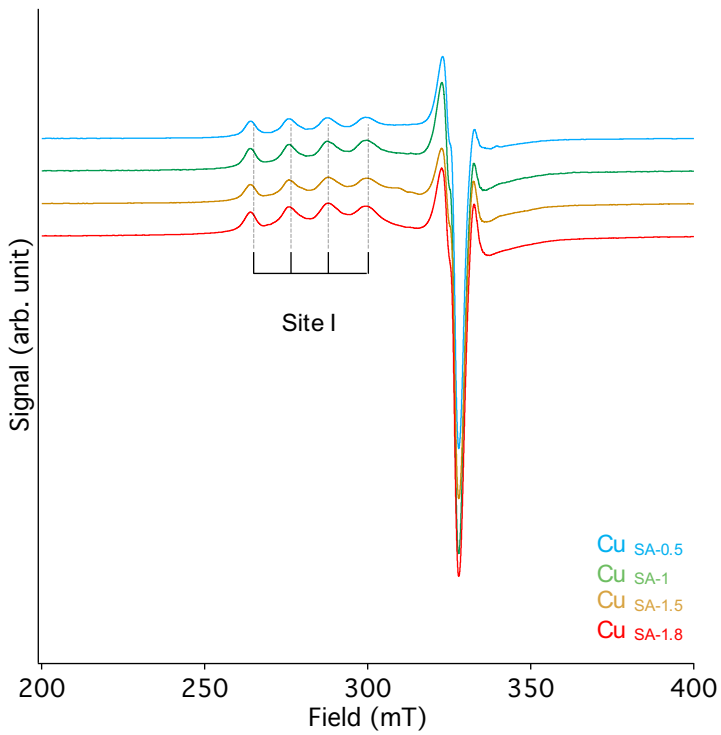

*Figure S10: Resulting difference spectra for the specific adsorption series showing the same spectral signature of the monomeric $Cu^{2+}$ active site in all samples.*

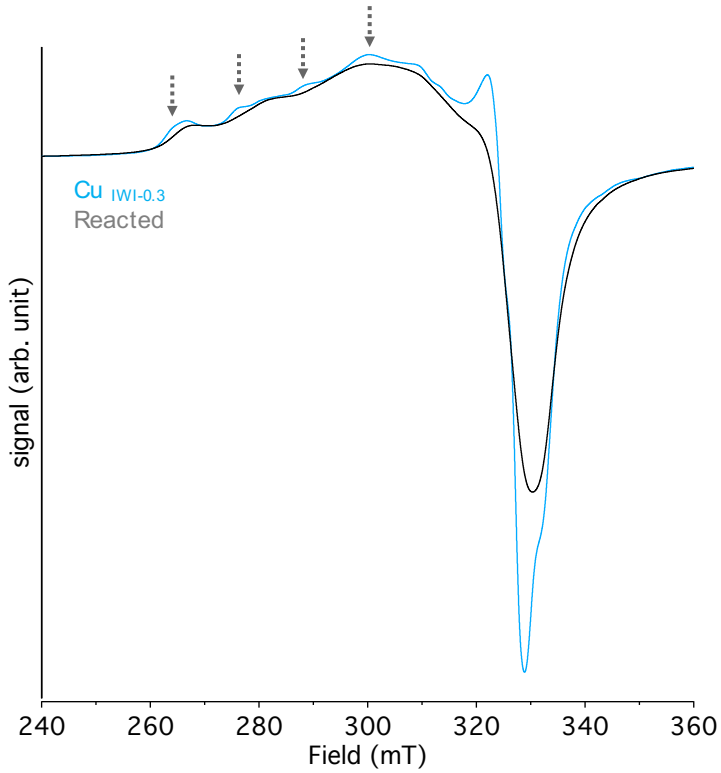


*Figure S11:* X-Band EPR spectrum (−170 °C) for Cu $_{IWI-0.3}$ before and after reaction under 6 bar of $CH_4$ for 30 min at 200 °C. *The grey arrows indicates the Cu hyperfine coupling that decrease after reaction with $CH_4$.*

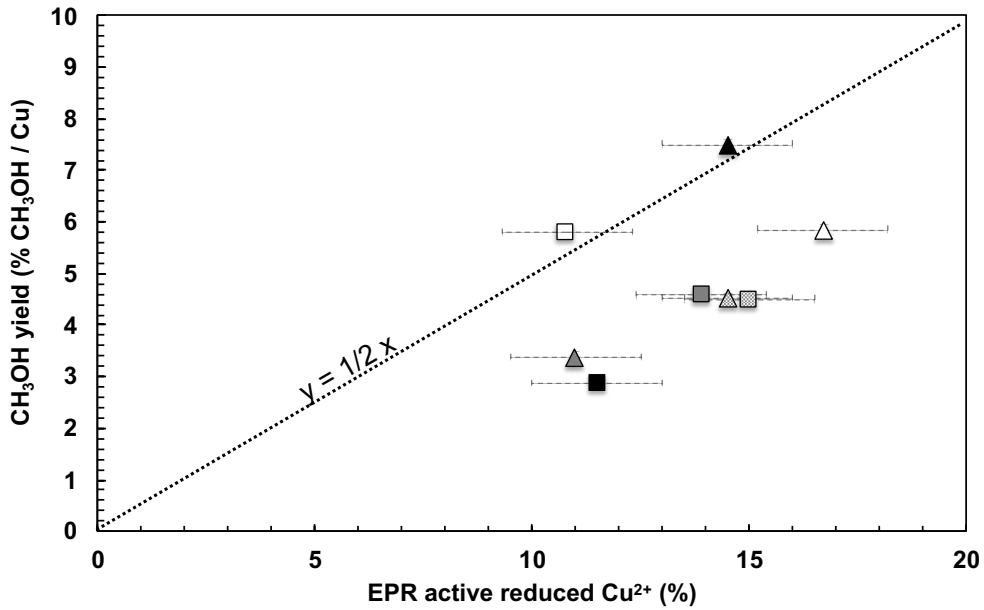


Figure S12: Correlation of the methanol yield in mol% $CH_3OH$. mol%$^{-1}$ Cu with the reduced Cu2+species probed by EPR. IWI samples (■) and SA samples (▲). Grey scale measure for loading with white being the lowest one and black the highest one. The error bar for the reduced $Cu^{2+}$ was determined experimentally by performing the reaction in situ under argon atmosphere with **Cu $_{IWI-1.6}$** and calculated to be 3%.