

Cr-free, Cu promoted Fe oxide-based catalysts for the High-Temperature Water-Gas Shift (HT-WGS) Reaction

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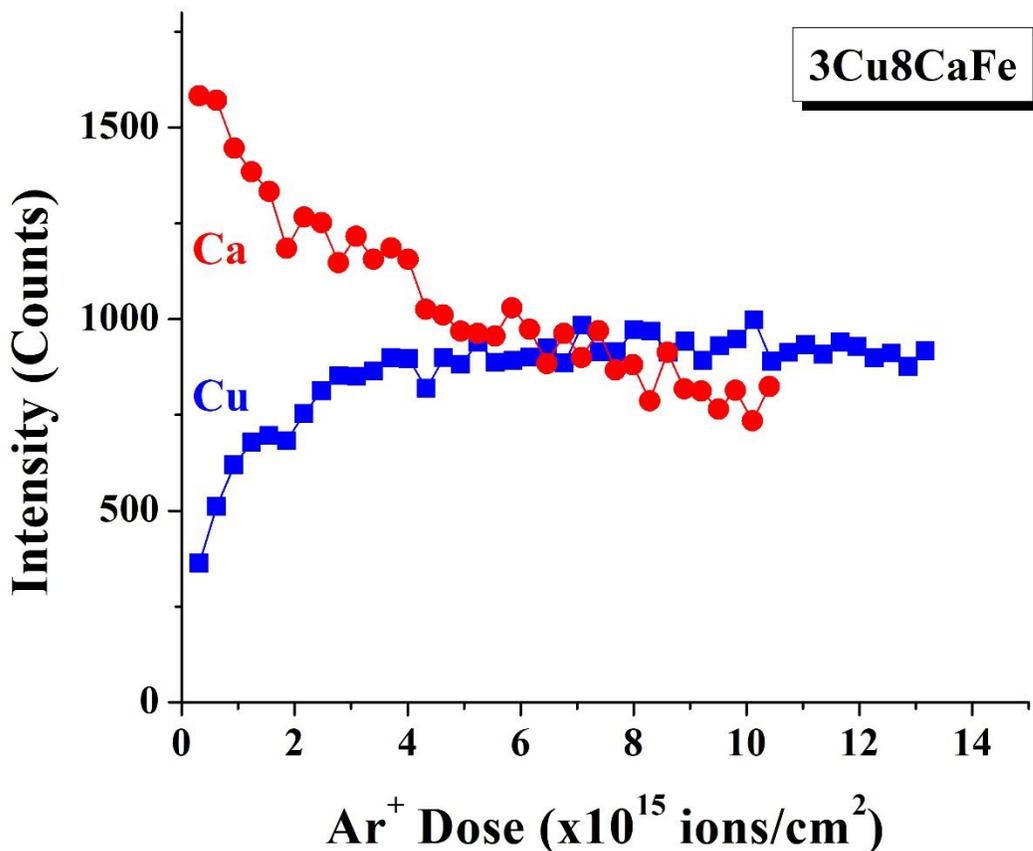


Figure S1: The HS-LEIS intensity of the Cu and Ca signals with depth for the 3Cu8CaFe catalyst after treatment under r-WGS reaction conditions.

The HS-LEIS intensity of the Cu signal increases for about first 3-4 layers and remains constant thereafter until the 14th layer. This suggests that the Cu NPs on the catalyst surface (and up to 4 layers) is covered with other oxide layers, possibly both by Ca and Fe-oxides. More interestingly, after the 4th layer the signal stayed constant suggesting the presence of large Cu NPs. If we consider one atomic layer to be about 0.25-0.3 nm, then the Cu NPs present on the surface of 3Cu8CaFe catalyst will be at least of 4 nm in size.

The Ca signal is much higher near the surface and decreases with depth profiling up to about 8 layers, after which it remains almost constant. This suggests that the Fe₃O₄ bulk lattice also contains Ca.

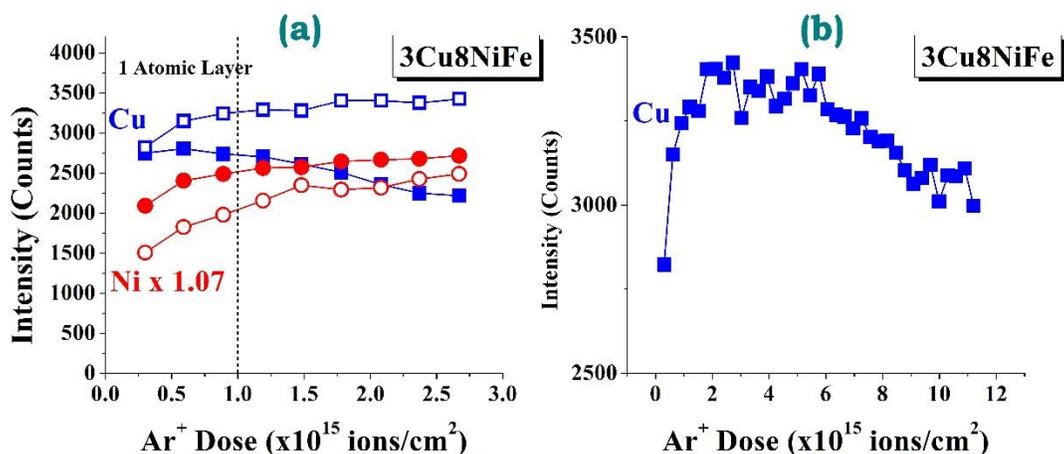


Figure S2: (a) Normalized HS-LEIS signal intensity of Ni and Cu. (b) Cu signal intensity with depth for 3Cu8NiFe catalyst after treatment under r-WGS reaction conditions.

(a) The plot has been corrected to accommodate the difference in signal intensity from the elements registered by the HS-LEIS instrument. After sensitivity correction, Ni/Cu = 1.07, the greater intensity of Cu signal on the surface compared to Ni indicates greater Cu concentration in the topmost layer.

(b) For this catalyst, after activation under r-WGS reaction conditions, the Cu signal increases only in the first 2 layers, suggesting the presence of FeO_x over-layer on the Cu NPs. After that, the signal kept on decreasing up to layer 9 and stayed constant thereafter. This suggests that the Cu NPs are at least 9 atomic layers in size, which is ~ 2.5 nm.

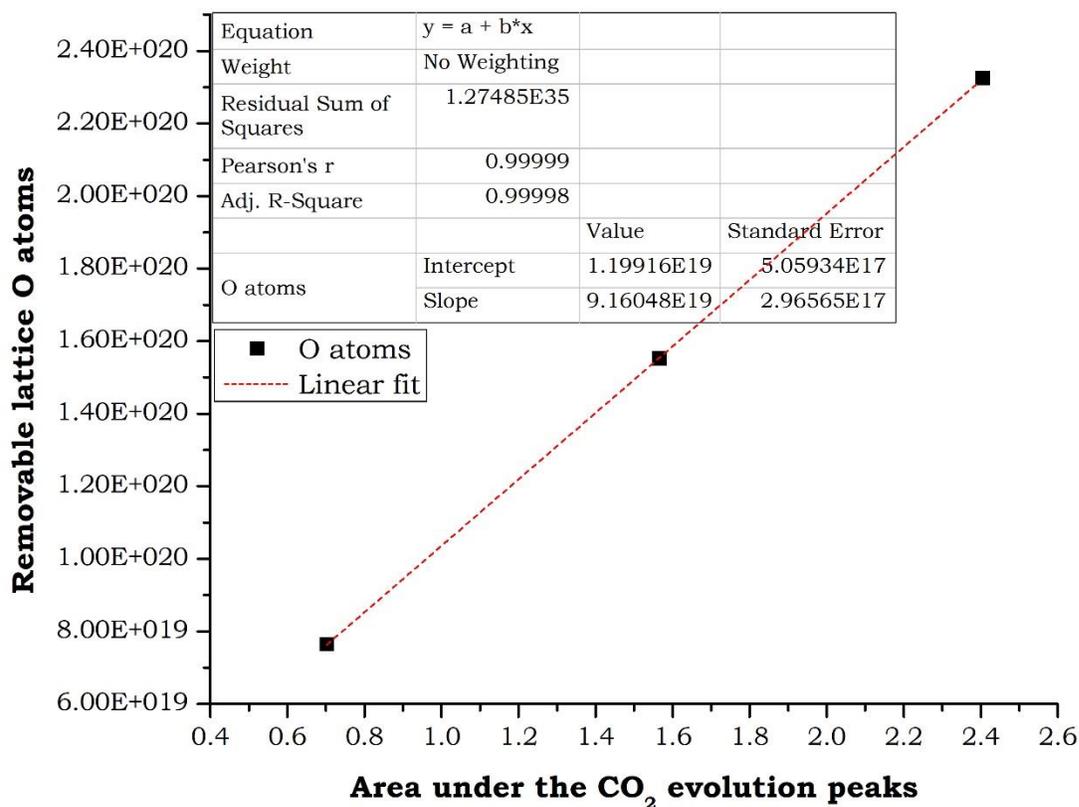


Figure S3: Calibration curve for counting lattice O atoms removed corresponding to the area under CO₂ evolution peaks.

Three different loadings (10 mg, 20 mg and 30 mg) of CuO were reduced during CO-TPR from 50°C to 450°C at 10°C/min. The samples generated CO₂ between 100°C and 250°C by completely reducing CuO to metallic Cu. From the sample loading, the amount of lattice oxygen removed was calculated and the corresponding area under the CO₂ evolution curve was also determined. For all the three loadings, the area *vs.* the removed O atoms was plotted and shown above in **Figure S3** (fitting parameters are given in the inset Table). From the above calibration curve, the number of reduced O atoms was calculated for the CO-TPR spectra (shown in **Figure 3**) of all the catalysts.

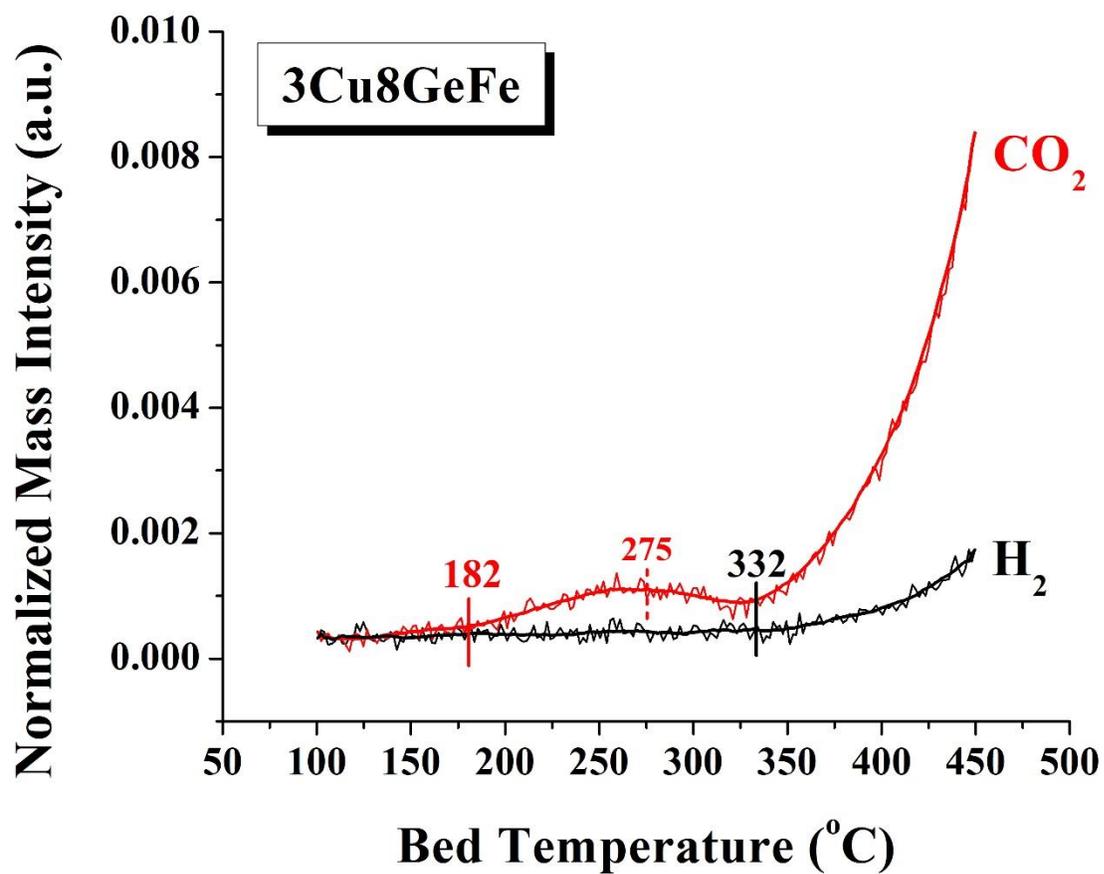


Figure S4: CO₂ and H₂ evolution with catalyst bed temperature for 3Cu8GeFe catalyst.

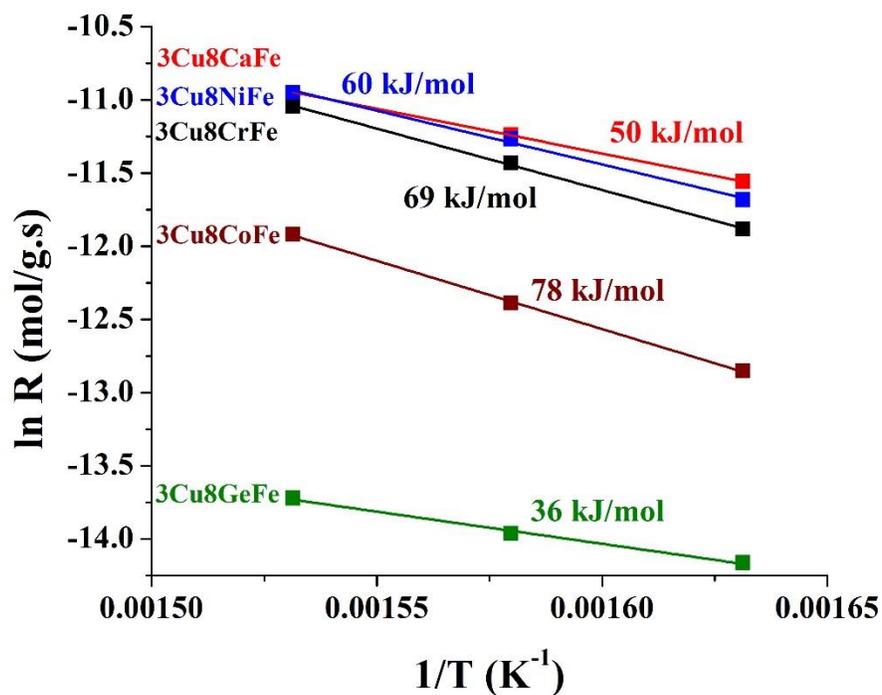


Figure S5: Arrhenius plots and activation energy values for all the catalysts.

Table S1. BET normalized active sites for 3Cu8MFe (M=Cr, Ca, Ni, Co and Ge) catalysts.

Catalysts	N _s (From table 1)	BET surface area after r-WGS treatment (from Figure 1)	N _s /BET
	×10 ⁻³ (mol/g)	(m ² /g)	×10 ⁻⁵ (mol/m ²)
3Cu8CrFe	0.74	34	2.2
3Cu8CaFe	0.22	51	0.4
3Cu8NiFe	0.76	34	2.2
3Cu8CoFe	0.45	17	2.6
3Cu8GeFe	1.52	28	5.4