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CO₂ reduction at Pt_{1-x}Fe_x alloys: An experimental and computational study

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Considering the consequences of global warming, and the inevitable depletion of fossil fuels, the case for CO₂ reduction could not be stronger. So far there has been great achievements in developing stable and efficient catalysts for the formation of C₁ products such as CO and formic acid.^{1,2} However, the search for catalysts to promote efficient C-C coupling has been limited to a relatively small number of materials, most notably by Cu catalysts.³ The investigation of bimetallics is one means to modify scaling relations and go beyond the limitations of monometallic catalysts.^{4,5}

A series of Pt_{1-x}Fe_x catalyst have been synthesised using a colloidal “hot injection” method. Their structure, size and composition were characterised using XRD, HR-TEM and EELS.

CO₂ electrolysis experiments were conducted at a series of potentials. ¹H NMR confirms that formate, methanol and acetate is formed at a remarkably low overpotential of -0.16 V vs RHE.

Table 1. Acetate concentration after 30 minute electrolysis held at -0.16 V (vs RHE)

Catalyst	Diameter	Acetate μM mg^{-1}
Pt ₁₇ Fe ₈₃	2.9 ± 0.8	20.6 ± 12.6
Pt ₃₅ Fe ₆₅	2.8 ± 0.6	105.3 ± 6.2
Pt ₅₈ Fe ₄₂	3.7 ± 0.7	32.7 ± 10.1

DFT modelling has been employed to rationalise the observed activities and product distribution. Stark differences appear when comparing models of different complexity. A key finding is that hydrogen bond interactions, which can only be considered in an explicit solvent model, are vital for the calculation of CO₂ adsorption energies and CO₂ activation. Also significant, is a divergence in the

free energy pathways of CO₂ reduction intermediates between the models.

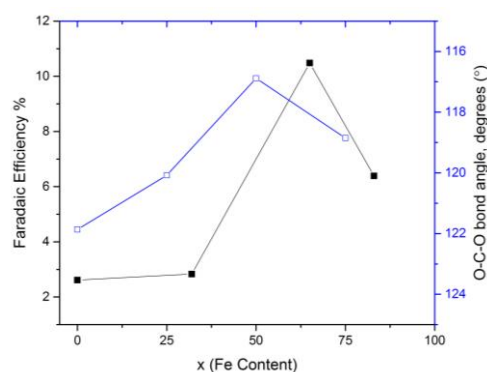


Figure 1. Total CO₂ reduction faradaic efficiency and O-C-O bond angle

On-going experimental and theoretical studies continue to gain further mechanistic insights, ultimately to elucidate C-C bond formation for acetate.

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