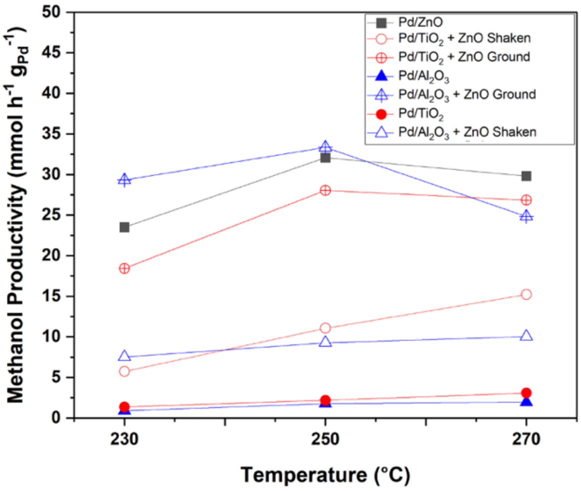
Pd and ZnO Physical Mixtures for CO_2 Hydrogenation to Methanol

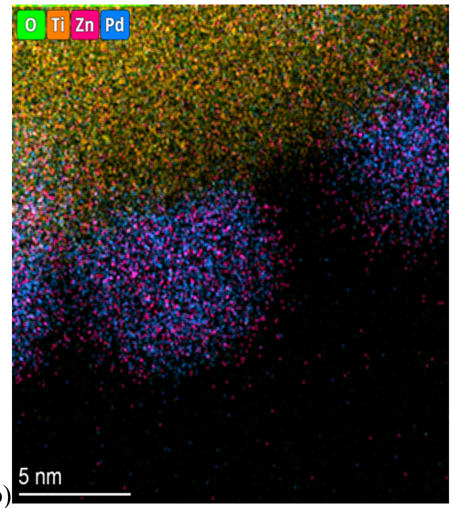
Samantha P. Fagan, Nicholas F. Dummer, Louise R. Smith, Kieran J. Aggett, Thomas S. Davies, Stuart H. Taylor, Michael Bowker and Graham J. Hutchings

Max Planck Cardiff Centre – Fundamentals of Heterogeneous Catalysis FUNCAT, UK Translational Research Hub, Cardiff University, UK

Carbon dioxide is getting released into the atmosphere in increasing quantities since the industrial revolution, contributing to the increase in global temperatures.[1] Many products can be made from CO_2 instead, one beneficial product is green methanol, which can be used as a fuel, as a solvent, as hydrogen storage, or as a chemical intermediate, specifically for formaldehyde and acetic acid.[2] Pd/ZnO has been found to be a good catalyst for this reaction, due to formation of the ß-PdZn alloy.[3] This study focuses on whether the ZnO has a role aside from alloy formation, using physical mixtures of ZnO and Pd supported catalysts of different contact areas of mixing on two different supports. It was found that lower contact areas of mixing showed little change in activity, but at higher contact areas of mixing Zn migrated onto the Pd nanoparticles shown in the AC-STEM imaging in Figure 1b, forming the PdZn alloy, and enhancing the methanol productivity (Figure 1a). The Zn migrated after reduction of the ZnO, where the reduction temperature of ZnO is impacted by the interaction with the Pd nanoparticles. The H_2-TPR analysis showed similar reduction temperatures of ZnO for both a reducible and non-reducible support for the same contact area of mixing, indicating the reducibility of the support was not a major factor. However, when comparing the different contact areas of mixing for one support, H_2-TPR analysis showed that the reduction temperature of ZnO decreases with increasing contact area of mixing. This finding compliments the reactor results, as a lower reduction temperature of ZnO, means a greater amount of ZnO reducing at 400˚C, this leads to more Zn migrating, so more PdZn alloy formation and hence a larger enhancement in activity. Therefore, the differences in contact areas of mixing highlights how important the PdZn alloy is, regardless of the support.



a)



b)

Figure 1 a) Methanol productivity for different contact areas of mixing between 5wt% Pd/Al_2O_3 or 5wt% Pd/TiO_2 with ZnO. Catalysts reduced in-situ at 400°C, 5°C/min for 1hr, then tested for CO_2 hydrogenation (0.5g catalyst, 3:1 H_2 : CO_2, 230-270°C, 2.0 MPa and 30 mL min^{-1}) and b) AC-STEM HAADF imaging of 5wt% Pd/TiO_2 + ZnO ground post-reactor

[1] Climate Change, http://www.climate.gov/news-features/understanding-climate/climate-change-global-temperature, (accessed 26 April 2024). [2] M. Bowker, ChemCatChem, 2019, 11, 4238–4246. [3] M. Bowker, N. Lawes, I. Gow, J. Hayward, J. R. Esquius, N. Richards, L. R. Smith, T. J. A. Slater, T. E. Davies, N. F. Dummer, L. Kabalan, A. Logsdail, R. C. Catlow, S. Taylor and G. J. Hutchings, ACS Catal., 2022, 12, 5371–5379.