Unravelling the Dynamic Reconstruction of PdIn Intermetallic Nanoparticles during CO_2 Hydrogenation to Methanol by Operando XRD, PDF and XAS

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The hydrogenation of CO_2 to methanol provides a promising route for CO_2 valorisation. Pd-In-based catalysts have shown high activity and selectivity for CO_2 hydrogenation to methanol; however, the structure of the active sites and the role of Pd-In alloys in the catalytic reaction remain debated [1-2]. In particular, it is unclear whether Pd–In intermetallic phases or Pd–InO_x interfaces constitute the main active sites and how the catalyst structure evolves under reaction conditions. Notably, CO_2 hydrogenation typically takes place at elevated gas pressures and temperatures (H_2:CO_2=3:1, 50-100 bar, 200-300°C), where the catalyst structure may differ significantly from that observed in ex situ characterization. Thus, operando characterization becomes essential to capture the structural dynamics and reveal the true active state of a catalyst.

Here, we investigate SiO_2-supported PdIn intermetallic nanoparticles (PdIn/SiO_2) synthesized via a colloidal approach as a model catalyst for the hydrogenation of CO_2 to methanol. Prior to the reaction, the catalyst was activated by H_2 or O_2 treatment. Catalytic testing revealed that O_2 activation is essential for optimal performance, enhancing CO_2 conversion by a factor of 2.5 compared to H_2 activation. We investigate structural dynamics using X-ray powder diffraction (XRD), difference pair distribution function analysis (d-PDF), and X-ray absorption spectroscopy (XAS) under reaction conditions while simultaneously monitoring its catalytic activity.

These operando studies revealed dynamic restructuring of PdIn nanoparticles under activation and reaction conditions. H_2 treatment led to an intermetallic Pd-In alloy phase (B2), as evidenced by diffraction analysis. In contrast, O_2 treatment oxidized the intermetallic phase, forming In_2O_3 together with partially oxidized Pd species. Remarkably, under CO_2 hydrogenation conditions, the B2 PdIn phase fully re-formed after O_2, as evidenced by XRD, pair distribution function (PDF) analysis, and In and Pd K-edge XAS (Figure 1).

These results demonstrate the dynamic reconstruction of PdIn/SiO_2 under activation and reaction conditions and identify the PdIn B2 intermetallic phase as the active structure formed during CO_2 hydrogenation to methanol.

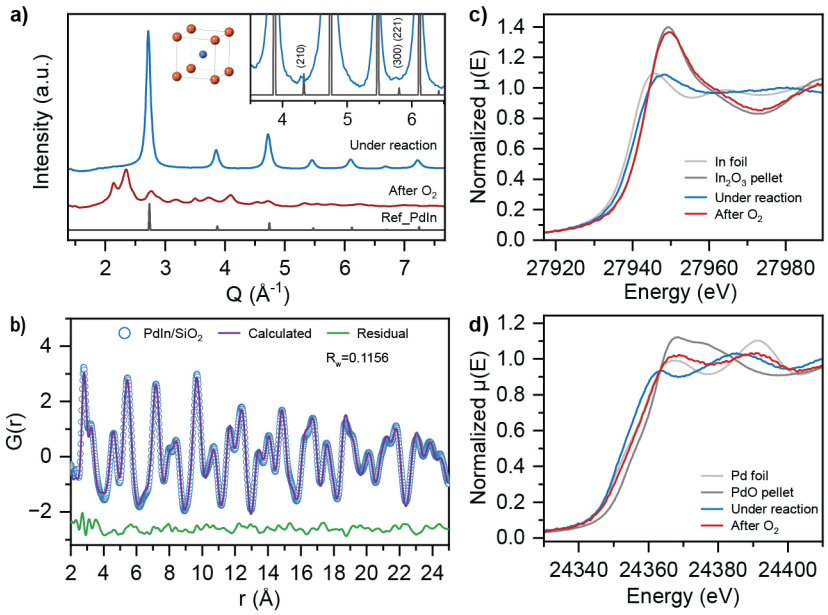


Figure 1. *Operando characterizations of dynamic reconstruction of PdIn intermetallic nanoparticles under CO_2 hydrogenation to methanol after O_2 treatment: (a) XRD, (b) d-PDF, (c)In K-edge XANES, (d) Pd K-edge XANES.*

[1] Araújo et al., Angew. Chem. Int. Ed 2023, e202306563.
[2] Potter et al., Angew. Chem. Int. Ed 2023, e202312645.