**Enhancing palladium promotion of indium oxide for CO2-based methanol production through synthetic control.**

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**Highlights**

* Controlled coprecipitation embeds Pd in the lattice leading to low-nuclearity clusters.
* The superiority of this Pd speciation is elucidated by theoretical and empirical methods.
* Record methanol productivity is sustained for 500 h.
* The benefits of nanoscale design for a sustainable large-scale process are demonstrated.

**1. Introduction**

Metal promotion is broadly applied to enhance the performance of heterogeneous catalysts to fulfil industrial requirements. Still, generating and quantifying the effect of the promoter speciation that exclusively introduces the desired property and ensures proximity to the active site and durability is very challenging. Recently, In2O3 was discovered as a highly selective and stable catalyst with the potential to realize green methanol production from CO2 at a commercial scale [1]. Activity boosting with the H2-splitter palladium led to partial success since Pd nanoparticles mediate the parasitic reverse water-gas shift (RWGS) reaction, reducing selectivity, and sinter or alloy with indium, limiting metal utilization and robustness.Herein we introduce a coprecipitation method leading to low-nuclearity Pd clusters anchored to the active site that curtail these limitations.

**2. Methods**

In2O3 and Pd(0.1-10 wt.%)-In2O3 catalysts were prepared by precipitation, and coprecipitation or dry impregnation, respectively, followed by calcination. They were characterized by inductively coupled plasma optical emission spectroscopy, N2 sorption, X-ray diffraction, thermal techniques, electron microscopy, and X-ray photoelectron and absorption spectroscopy. CO2 hydrogenation to methanol was conducted in a continuous-flow fixed-bed reactor setup at 473-653 K, 5 MPa, H2/CO2 = 1.8-5.7, and weight hourly space velocity = 24,000-48,000 cm3STP h−1 gcat−1. Pd speciation and reaction energetics were studied by Density Functional Theory (DFT).

**3. Results and discussion**

Pd-promoted In2O3 featuring palladium atomically dispersed in the oxide matrix was generated by coprecipitation and was benchmarked with dry impregnated systems comprising Pd clusters deposited onto the oxide. The first exhibited a stable activity enhancement compared to bulk In2O3 solely directed to methanol synthesis, while the second displayed a decaying improvement of both methanol and CO formation (**Figure 1**, left). Based on structural, spectroscopy, and microscopy (**Figure 1**, middle) analyses, Pd formed clusters of very low nuclearity attached to the lattice in the coprecipitated sample, whereas aggregated to form defined nanoparticles in the impregnated material. DFT calculations indicated that Pd atoms embedded into the oxide structure serve as effective anchoring sites for the noble metal atoms accommodated onto the surface hindering excessive agglomeration, which provides a molecular-level explanation to the profoundly diverse time-on-stream behaviors of the two catalysts. According to thermal characterization, theoretical simulations, and kinetic data, these Pd clusters do not significantly increase the number of active vacancies but impart an improved H2-dissociation capability without enhancing the RWGS reaction (**Figure 1**, right), leading to a sustained record productivity (0.96 gMeOH−1 h−1 gcat−1 after 500 h on stream). In contrast, Pd nanoparticles supply activated hydrogen that fosters vacancy and methanol formation on In2O3 but also convert CO2 into CO on their own surface.

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**Figure 1.** Methanol space time yield (*STY*) *versus* time-on stream over Pd(0.75 wt.%)-In2O3 catalysts and pure In2O3 during CO2 hydrogenation at 553 K, 5 MPa, and H2/CO2 = 4 (left). EDX maps of In and Pd (middle) and representation of the distinct promotional effect of Pd (right) for the same catalysts after equilibration.

**4. Conclusions**

Controlled coprecipitation enables a fine tuning of the Pd speciation, generating small Pd clusters strongly bound to the oxide that offer a highly effective use of the noble metal and are robust, granting a sustained unparalleled methanol productivity. This permits to operate the catalyst at reduced temperature, with hydrogen-lean feeds, and in the presence of greater amounts of water, implying strong economic and ecologic benefits for a perspective CO2-based methanol synthesis process.

**Reference**

1. Martin, O., Martín, A.J., Mondelli, C., Mitchell, S., Segawa, T.F., Hauert, R., Drouilly, C., Curulla-Ferré, D., and Pérez-Ramírez, J. Angew. Chem., Int. Ed. 55 (2016) 6261–6265.