Metal-Oxide Interfaces and their Role in Methane Conversion to Fuels

M. V. Ganduglia-Pirovano
Instituto de Catálisis y Petroleoquímica-CSIC, Madrid, Spain

Methane dry reforming (MDR), which converts CH_4 and CO_2 into syngas (CO/H_2), is gaining attention for its environmental benefits. Additionally, direct conversion of CH_4 and hydrogenation of CO_2 to CH_3OH are highly sought goals in catalysis. Metal-ceria systems, particularly those involving Ni, Co, and Pt on CeO_2, have emerged as promising catalysts for these processes. This presentation explores recent theoretical and experimental advances in understanding these catalysts, using DFT+U simulations alongside in situ/operando techniques (AP-XPS, XRD, XAFS) and catalytic testing.[1-4]

A key finding is that low metal loading, combined with ceria's ability to stabilize oxidized metal species by re-localizing electrons on *f*-states, is essential for CH_4 activation at room temperature and efficient CH_4 reforming at relatively low temperatures (700 K). Notably, the room-temperature activation of methane on low-loaded metal/CeO_2 deviates from traditional linear scaling relationships, highlighting how this nanomaterial overcomes the "*tyranny of linear scaling.*" This presents a promising strategy for developing active and stable catalysts for methane activation and conversion.

Furthermore, we present evidence that low Ni loadings on CeO_2 can catalyse methanol production at low temperatures (450 K) with high selectivity, using oxygen and water.[5] Additionally, Pd-CeO_2 catalysts modified with carbon (Pd-*i*C-CeO_2) achieve 100% selectivity for methanol in the liquid phase at 350 K using hydrogen peroxide as the oxidant.[6] The role of solvent interactions in enhancing selectivity is also discussed, highlighting the potential of these catalysts to drive cost-effective and selective methane conversion to valuable products. Finally, Cu/MgO is explored for selective hydrogenation to methanol, where the synergy between Cu^+ species and water plays a crucial improving selectivity.[7]

References

[1] Liu Z. et al. *Angew. Chem. Int. Ed.* **55**, 7455–7459 (2016)
[2] Liu Z. et al. *Angew. Chem. Int. Ed.* **56**,13041 –13046 (2017)
[3] Lustemberg, P. G. et al. *J. Phys. Chem. Lett.* **11**, 9131−9137 (2020)
[4] Zhang, F. et al. *ACS Catal.* **11**, 1613−1623 (2021)
[5] Lustemberg P. G., et al. *J. Am. Chem. Soc.* **140**, 7681−7687 (2018)
[6] Jiménez J. D., et al. *J. Am. Chem. Soc.* **146**, 25986−25999 (2024)
[7] Fernández-Villanueva E., et al., *J. Am. Chem. Soc.* **146**, 2024–2032 (2024).