Realistic Catalysts at Work: APXPS Insights into Surface Transformations for Sustainable Energy Applications

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ABSTRACT

CO_2 methanation ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) is of significant environmental interest as a sustainable pathway for energy production and storage [1]. Ni-based catalysts are widely used in this reaction due to their low cost and high CH_4 selectivity. These systems typically consist of nanoscale Ni particles dispersed on high-surface-area oxide supports such as Al_2O_3, SiO_2, or CeO_2. The support plays a crucial role in controlling Ni particle dispersion, morphology, and stability through metal–support interactions. However, stabilizing Ni nanoparticles under reaction conditions remains challenging, as they tend to agglomerate, leading to performance degradation. In this context, exsolution? a high-temperature process that drives metal species initially dissolved in the parent oxide to emerge as nanoparticles at the surface, has attracted significant attention as a route to generate strongly anchored particles with enhanced resistance to sintering [2].

In this presentation, we focus on Ni-doped CeO_2 and $LaNiO_3$ perovskite as precursors that, upon thermal activation, generate the active surface phase [3-5]. To elucidate the structural and chemical evolution of these materials, we combine a suite of advanced in situ and operando spectroscopies, spanning a wide pressure range (from mbar to bar) and probing depths (from nanometers to micrometers), across five European synchrotron facilities. We will show how the integration of ambient-pressure soft and hard X-ray photoelectron spectroscopies (static and time-resolved APXPS, HAXPES) with X-ray absorption spectroscopy (XAS) enables direct monitoring of key surface transformations during activation and under working conditions. Beyond capturing the chemical state of the catalyst, these techniques provide crucial insights into adsorbed species and their mechanistic role during CO_2 methanation. We further examine how controlled oxidative and reductive thermal treatments influence the formation, stabilization, and reactivity of the active phase. Overall, while the talk will focus on the unique capabilities of APXPS, it will also illustrate its inherent limitations and show how an integrated multitechnique operando approach, combining multiple probing depths and pressure regimes, is essential to fully unravel structure–function relationships and guide the rational design of next-generation Ni-based catalysts for efficient and durable CO_2 methanation.

REFERENCES

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