



Nanometrological Characterization of Heterogeneous Catalysts for the Conversion of CO₂ to High-Value Products

INMETRO has demonstrated that metrologically-driven process control creates a more accurate and efficient CO₂-to-fuel value chain

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The Challenge

The increasing concentration of CO₂ in the atmosphere, combined with the finite reserves of fossil fuels, has driven the urgent search for sustainable alternatives in the global energy matrix. In this context, the catalytic hydrogenation of CO₂ with green hydrogen (H₂) has emerged as a promising technology for carbon capture and utilization (CCU). Through this reaction, a wide range of valuable chemicals and fuels can be produced, including methanol, dimethyl ether (DME), higher alcohols, gasoline, diesel, and sustainable aviation fuel (SAF), all of which are considered low-carbon or “green” when synthesized from renewable hydrogen.

Heterogeneous catalysts are typically composed of a small amount of metal (< 2 wt %, either noble or transition metals) dispersed on a support (e.g., Al₂O₃, carbon, CeO₂). A prominent industrial example is the CuO/ZnO/Al₂O₃ system, in which copper is present at the surface as highly dispersed nanoparticles, usually smaller than 5 nm. The presence of these metal nanoparticles on the catalyst surface is crucial for the efficiency of CO₂ hydrogenation and several other catalytic reactions. However, maintaining the stability of such high-energy nanoparticles against sintering remains a major challenge within industrial processes. Furthermore, their characterization at the atomic and nanoscale level is particularly demanding. In this regard, the application of advanced nanometrology tools is essential to elucidate the reaction mechanisms, identify deactivation pathways, and support the rational development of more effective and durable catalysts.

However, for the efficiency of the process and its scale-up, accurate and metrologically traceable measurements are essential throughout the entire CO₂ hydrogenation process. At the laboratory scale, accurate measurement of gas flows, instrument calibration for material characterization, stable reactor conditions, a controlled laboratory environment, and precise catalyst weighing are essential to ensure reproducible, trustworthy results. Any errors in these steps may negatively affect all processes. Thus, any inaccurate or incomplete measurements at any of these stages can lead to erroneous interpretations and significant losses within the industrial process. At the industrial production level, maintaining metrological control and minimizing errors across these practices directly enable clean energy production from CO₂ and promote industrial innovation and sustainable infrastructure, and enable the transition to a circular carbon economy.

The Solution

This study focused on the metrologically-driven performance of a commercial CuO/ZnO/Al₂O₃ catalyst in the hydrogenation of CO₂ to methanol. The influence of reaction pressure (1, 10, 20, and 30 bar) was systematically evaluated as a function of time on stream (TOS) at 250 °C. Both fresh and spent catalysts were thoroughly characterized using nanoparticle and dimensional metrology techniques to determine the main causes of any deactivation.

The process was metrologically evaluated at all stages using reference materials for mass determinations, laboratory environmental monitoring, various instrument calibrations, and a series of analytical quality assurance processes. The precise weighing of the catalyst extends to the accurate control and measurement of gas flows, and includes the calibration of instrumentation for the reliable detection and quantification of reactants (CO₂ and H₂) and reaction products. Catalyst characterization errors that may introduce bias in the evaluation of sintering and phase distribution were monitored using chemical analysis by XRF and High-Resolution Transmission Electron Microscopy (HRTEM) techniques.

The set of procedures allowed to determine with accuracy the particle size of Cu nanoparticles in the fresh and postreaction sample, the appearance of new crystalline phases resulting in the deactivation during reaction on stream at different reaction pressures (1, 10, 20, and 30 bar) on Cu/ZnO/Al₂O₃ during the CO₂ hydrogenation to methanol.

A Quantifiable Impact

Metrology plays a pivotal role in the successful application of heterogeneous catalytic technology and processes to produce higher-value products. The hydrogenation conversion of CO₂ to methanol, green fuels (green gasoline, diesel, and SAF), and synthetic chemicals has the potential to directly increase the share of renewable energy sources and improve overall energy efficiency. A critical parameter here is the purity of the resultant fuel product, which is achieved only through chemical metrology-based analytical procedures that minimize contaminant content in the product. The metrological intervention described here provides tools to accurately measure the calorific value of synthetic fuels, ensuring that a liter of synthetic fuel delivers the promised energy and making it a reliable and affordable alternative to fossil fuels. Metrological measurements also prevent catalyst poisoning and overextension of operating time and equipment life, thereby lowering production costs.

The hydrogenation process is a prime example of developing infrastructure to make fuels in a more sustainable fashion, and metrological applications are key to its successful development. Through innovations in nanomaterial design, new heterogeneous catalysts with nanosized structures will require metrological characterization at the atomic scale. Advanced characterization will allow measurement science researchers to measure active sites with picometer precision, accelerating the innovation cycle. The integration of sensors directly into hydrogenation reactors provides real-time, traceable data. This will allow automated

adjustments to production processes, reducing waste and increasing safety in industrial plants.

The integration of metrology into the CO₂-to-fuel value chain is also a pillar for job creation. Many specialized roles are needed to calibrate and maintain high-precision sensors in Carbon Capture and Utilization (CCU) plants. Professionals are needed to process the massive amounts of data generated for fuel production optimization, and growth is anticipated in academic and private sector roles for the development and characterization of next-generation catalysts.

Lastly, the accurate measurement of CO₂ flow rates and capture rates as the starting material in such conversion processes will be crucial for carbon credits and for verifying if a process is truly carbon-neutral. Metrology is thus fundamental for establishing trust in technologies that will determine the carbon balance in the market sector, as well as in fuel quality, catalyst development, and process control, as the key components in building a resilient global infrastructure for the energy transition.

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