Micro-Spectroscopy for the Investigation of Catalytic Processes under In Situ and Operando Conditions

Abstract: *The proposed research builds on the ongoing activities of the Molecular Spectroscopy Group (MSG) and the Catalysis for Renewable and Innovative Processes (Care in Process) Group at the Department of Industrial Chemistry "Toso Montanari". MSG has extensive expertise in vibrational spectroscopy (Raman and FTIR microspectroscopy) for the study of molecular and solid-state systems, while Care in Process specializes in the synthesis of multifunctional catalysts and the development of innovative catalytic and photo-electro catalyitc processes in liquid- and gas-phase continuous flow systems.*

The project aims to extend these complementary competencies to the investigation of heterogeneous catalysts and catalytic reactions under realistic operating conditions using Raman, FTIR, and photoluminescence spectroscopy. Raman spectroscopy, in particular, enables non-destructive monitoring of catalyst structure, reaction intermediates, and catalyst evolution under in situ and operando conditions, allowing direct correlation between structural changes and catalytic performance.

The spectroscopic investigations will be integrated with complementary characterization techniques, including X-ray diffraction (XRD), electron microscopy (SEM/TEM), X-ray photoelectron spectroscopy (XPS), and catalytic testing, through collaborations with research groups at the University of Bologna and external research institutions.

Project

Heterogeneous catalysis in thermochemical electrochemical conversion processes plays a central role in modern chemical industry and is essential for the development of sustainable processes for energy conversion, environmental remediation, biomass valorization, CO_2 utilization, hydrogen production, and green chemical synthesis.

Catalyst performance strongly depends on the nature and evolution of the active sites under reaction conditions. However, catalytic materials are dynamic systems whose surface composition, oxidation state, crystallinity, and morphology continuously evolve during operation. Conventional ex situ characterization often fails to capture these transformations because the catalyst may significantly change once removed from the reaction environment.

In situ and operando spectroscopic techniques have therefore become indispensable for understanding catalytic mechanisms. Among them, Raman spectroscopy offers several unique advantages:

- non-destructive analysis;
- high chemical specificity;

- sensitivity to crystal structure and phase composition;
- capability of probing metal oxides, carbon materials, zeolites, supported catalysts and adsorbed surface species;
- compatibility with high-temperature and controlled-atmosphere reaction cells.

Operando Raman spectroscopy provides simultaneous information on catalyst structure and catalytic activity, allowing direct identification of reaction intermediates, active phases, catalyst reconstruction, coke formation, and deactivation mechanisms. Recent advances in laser sources, optical components, notch filters, CCD detectors, and environmental reaction cells have greatly expanded the applicability of Raman spectroscopy to catalytic systems operating under realistic conditions in thermochemical and electrochemical processes.

The present project aims to develop advanced Raman methodologies for monitoring catalytic materials during operation and to correlate spectroscopic information with catalytic performance and theoretical modeling. The research will focus on catalytic materials relevant to sustainable chemistry, including transition metal oxides, mixed oxides, supported metal nanoparticles, zeolites, photocatalysts, and catalysts for CO_2 conversion, hydrogen production and utilization, biomass upgrading, and selective oxidation reactions.

Work Plan

As outlined in the project plan, the principal experimental technique will be micro-Raman spectroscopy, with particular emphasis on in situ and operando measurements performed under controlled reaction environments during thermochemical catalysis, electrochemical and photo-electrochemical operations.

The research activity will also include the management, maintenance, and further development of the Raman instrumentation available at the Department of Industrial Chemistry, together with the implementation of dedicated experimental setups and cells for catalytic investigations.

Complementary characterization techniques—including FTIR spectroscopy, XRD, SEM, TEM, XPS, EPR and catalytic testing—will provide structural, morphological, and chemical information before, during, and after catalytic operation.

Specific objectives of the proposal are summarized below.

1) Development of an in situ/operando Raman spectroscopy platform

Design, implementation, and optimization of experimental Raman setups equipped with environmental reaction cells and electrochemical cell allowing precise control of temperature, pressure, and reactive gas atmosphere. The system will enable real-time monitoring of catalysts during thermal treatments and catalytic reactions and electrochemical reaction.

2) Structural and spectroscopic characterization of catalytic materials

Comprehensive characterization of catalyst families, including supported metal catalysts, cluster and nanometal particles, transition metal oxides, mixed oxides, zeolites, electrocatalyst and photocatalysts using Raman spectroscopy together with complementary techniques (XRD, FTIR, SEM/TEM, XPS).

3) Monitoring catalyst activation and structural evolution

Investigation of catalyst activation procedures, oxidation–reduction cycles, phase transformations, and structural reconstruction under reaction conditions. Raman spectroscopy will be employed to identify active phases and monitor their evolution during operation.

4) Operando investigation of catalytic reactions

Real-time Raman measurements will be performed during catalytic reactions to identify adsorbed intermediates, reaction products, carbonaceous deposits, and catalyst modification and deactivation phenomena. Spectroscopic data will be directly correlated with catalytic activity, selectivity, and conversion measured simultaneously through online reaction analysis.