X AUSE Conference & V ALBA User's meeting

BARCELONA

AUSE ASOCIACIÓN USUARIOS SINCROTRÓN ESPAÑA

ALBA

Spain XFEL HUB

Contribution ID: **63**
Type: **Oral**

Development and commissioning of a capillary flow cell for quasi-simultaneous in situ/operando XAS-XRD catalysis studies: Oxidative de-ligation of atomically-precise supported metal oxo-cluster catalysts as a showcase study

Tuesday, 6 September 2022 09:45 (20 minutes)

Registering dynamic changes in short- and long-range atomic ordering of solid catalysts under operando conditions, i.e. during catalytic action under relevant operation settings, is essential for the rational development of this important class of functional materials. Synchrotron radiation X-ray absorption (XAS) and diffraction (XRD) techniques allow such studies, the challenge being to mimic relevant operation conditions and gas-solid hydrodynamics of flow reactors during spectroscopic studies. A capillary flow cell has been developed through a cooperation between ITQ and ALBA for quasi-simultaneous, in situ, and operando XAS/XRD measurements aimed to be integrated into the recently commissioned NOTOS beamline station, Figure 1a. This versatile cell enables studies under realistic gas-solid operation conditions, i.e. up to 20 bar pressure and 700 °C temperature, under flow of preset gas mixtures, suitable for numerous catalytic reactions of interest to academy and industry.

The setup comprises a quartz glass capillary with tunable wall thickness and external diameter appropriate for XAS applications (adequate X-ray transmittance at relevant incident beam wavelengths). The sample (dp=100–200 µm) is placed at the center of the capillary aligned with the X-ray beam path and packed within a SiC bed, which contributes to the pre-heating and turbulent hydrodynamics of the gases upstream of the catalyst bed, and fixed with quartz wool plugs, Figure 1b. A hot air gas blower (DGB0001, FMB Oxford) equipped with a Eurotherm regulator and a gas flow controller (typical air flow 450 L/h) is used to heat the sample, delivering an isothermal length of 3 mm along the sample packed-bed when positioned at about 2.5 mm, orthogonal to the capillary's axis. The cell is integrated into a flow gas system with a minimized death volume consisting of four main mass flow controllers able to precisely feed reactive (CO2, hydrocarbons, H2) and inert (He, N2, or Ar) gases with volumetric flows ranging from 0.12-6 mL·min-1 and 0.17-8.5 mL·min-1, respectively. An additional bypass line is connected along with a programable 6-way valve that allows pulse dosing of gaseous reactants of interest with micro-volumetric precision through exchangeable µL-loops, Figure 1c. The cell delivers excellent pressure control under flow conditions up to 20 bar (Figure 1d) and 700 °C. The major innovation of the design is a high-speed axial rotation capability (<80 rpm) of the capillary in order to minimize artifacts from preferential orientations during XRD experiments.

As a first showcase application, the cell was tested during the oxidative de-ligation of supported transition metal oxo-clusters via temperature-resolved XAS measurements under in situ conditions in static-capillary mode. For this purpose, a series of innovative organometallic complexes ([MCo3O4]Ln, M=Co, Mn, Ru) with a cubane geometry was used as molecular cluster precursors, Figure 2a. The use of these ligand-protected molecular metal clusters bears significant promise toward the fabrication of new solid catalysts bearing highly undercoordinated metal active sites, on atomically precise metal ensembles, capable of lowering the activation energy for the conversion of molecules in catalytic processes of significance for the transition to more sustainable energy and chemical sectors. As summarized in Figure 2b, immobilization of the molecular cubanes was performed in a one-pot process during the formation of the silica matrix via sol-gel route at room temperature (RT) and neutral pH. The obtained [MCo3O4]Ln@SiO2 composite materials were activated in the capillary cell under oxidative thermal treatment up to 450 °C with a flow of 20%O2/He to decompose the protective organic ligands (Ln). XANES spectra were collected at the Co k and Ru k edges during the heating ramp (5

°C/min) with a temperature resolution of ca. 10 °C/spectrum to track changes in the coordination geometry and oxidation state of the metals M=Co, Ru. Following the temperature-resolved XANES experiments, samples were stabilized at 450 °C for 1 hour and cooled down to RT in order to measure the corresponding EXAFS spectra of the in situ calcined material, as a means to assess the average nuclearity of the metal clusters and coordination environment for Co and Ru atoms. As a strategy to prevent the formation of metal-support compounds, e.g. metal silicates, during the oxidative de-ligation of the oxo-clusters, the silica surface was grafted with thermally stable phenylsilane moieties prior to thermal activation.

In situ temperature-resolved XANES measurements (not shown) collected at the Co k edge during the oxidative de-ligation of the supported [MCo3O4]@SiO2 materials indicated that the local geometry around the Co atoms was progressively distorted towards a less centrosymmetric coordination environment, promoting the dielectric dipole transition from 1s electrons to the p component in 3d-4p hybridized orbitals. Fourier-transform of the k3-weighted EXAFS spectra recorded at the Co and Ru k edges for the as-prepared materials and their corresponding de-ligated counterparts is depicted in Figure 3. After thermal treatment of the supported [MCo3O4]@SiO2 M=Co, Ru samples, the development of multiple scattering shells around Co was observed at radial distances about 1.4 Å (Co-O), 2.6 Å (Co-Co), and 4.7 Å (Co-O-Co) (no phase correction), indicating the structural evolution of the oxo-clusters towards the formation of a spinel-like Co3O4 structure (see reference spectrum, Figure 3a,c), which is particularly desirable to drive selective alkane oxidation reactions. However, when these materials were previously surface-functionalized with phenylsilane moieties ([MCo3O4]@SiO2-syl), only the contribution of the first coordination shell was observed, suggesting the formation of smaller Co3O4 domains with a minor, if any, degree of metal aggregation. Interestingly, when Mn was included into the [MCo3O4] cluster the amplitude of the scattering signals remained quite low pointing to the superior thermal stability of this material, Figure 3b. Conversely, measurements at the Ru k edge revealed the segregation of Ru out of the [Ru(O)Co3O4] cluster lattice and the consequent formation of a separate RuO2 phase (Figure 3d), possibly due to the high vapor pressure of ruthenium sub-oxide species at relatively mild temperatures. These results highlight the importance of unraveling the changes in the nuclearity of metal oxo-clusters as a function of factors such as (i) cluster composition, (ii) nature of organic ligands, (iii) activation temperature, and (iv) support surface functionalization to enable a rational design of these type of atomically precise bimetallic cluster catalysts.

In this contribution, preliminary outcomes of the online commissioning of a new multipurpose capillary cell (assembled to the HRPD-XAS end-station of the NOTOS beamline) are presented to the scientific community and industry. The new instrumentation opens a wide range of in situ and operando XAS/XRD studies on the genesis and usage of solid catalysts in gas-solid catalytic processes under technologically relevant operational conditions.

Acknowledgments: RTI2018-096399-A-I00 R&D project, funded by MCIN/AEI/10.13039/501100011033/ and "ERDF A way of making Europe". is gratefully acknowledged.

Would you like to participate in the Poster Prize competition?

No

Primary author: HENAO, Wilson (Instituto de Tecnología Química ITQ-CSIC)

Co-authors: Mr TORREGROSA, Enrique (Instituto de Tecnología Química ITQ (UPV-CSIC)); Dr GUTIÉRREZ-TARRIÑO, Silvia (Instituto de Tecnología Química-ITQ (CSIC-UPV)); Mr HERNÁNDEZ-FENOLLOSA, Juan (Instituto de Tecnología Química-ITQ (CSIC-UPV)); Prof. REY, Fernando (Instituto de Tecnología Química-ITQ (CSIC-UPV)); Dr ESCUDERO, Carlos (ALBA-CELLS Synchrotron Light Facility); Dr OÑA-BURGOS, Pascual (Instituto de Tecnología Química-ITQ (CSIC-UPV)); Dr AGOSTINI, Giovanni (ALBA-CELLS Synchrotron Light Facility); Dr PRIETO, Gonzalo (Instituto de Tecnología Química-ITQ (CSIC-UPV))

Presenter: HENAO, Wilson (Instituto de Tecnología Química ITQ-CSIC)

Session Classification: AUSE A - 6/09/22 I