Project MOSCATo

Cutting-edge X-ray methods and models for the understanding of surface site reactivity in heterogeneous catalysts and sensors

Brief description of the research proposal

Understanding, at the atomic level, the interaction between a specific adsorption site and a target molecule from the gas phase is a key step in the rational design of improved material for: gas separation, heterogeneous catalysis or molecular sensing. We propose the development of a revolutionary instrumentation on the APE-HE beamline @ Elettra synchrotron allowing soft X-ray XAS (in electron yield mode) to be performed under 1 bar at both the K-edge of a typical atom present in the molecule (C, N, O, F) and the L2 and L3 edges of the first row transition metals (from Sc to Zn). At the end of the PRIN project this instrumentation will be available for the whole Italian scientific community working in the field of surface chemistry via standard beamline application @ Elettra. The consortium (4 Uni + 1 CNR lab @ Elettra) will achieve the self-consistent loop that includes sample synthesis, instrumental implementation, structural, electronic and vibrational characterization and modeling. The structure of the adsorbing site will be determined by synchrotron XRPD and confirmed by periodic DFT calculations, which outputs will be used to compute the soft X-ray XAS spectra (APE-HE), the hard X-ray XAS spectra at the metal K-edge (other beamlines) and the IR and UV-Vis spectra (lab.)

1. Abstract

The atomic level understanding of the process of molecular adsorption on surface sites of complex materials will open the possibility to provide a rational improvement of the high-surface area materials nowadays used in relevant applications such as gas storage [1,2] and gas separation [3,4]. When the understanding is further extended to surface reactivity the goal of rational materials improvement can be extended to two relevant fields of applied chemistry such as gas sensing [5-7] and catalysis [8-10]. In spite of the fact that the mentioned applications have a strong impact on everyday life in modern society, there are very few examples of rational design of such class of materials and often a trial and error approach is adopted. This lack is mainly due to the experimental difficulties in characterizing surface sites, that usually represent a minimal fraction of atoms with respect to those of the bulk. One of the major reasons for this is thefact that surface sensitive techniques (e.g. UPS, XPS, Auger spectroscopies) requires ultra-high vacuum (UHV) conditions, preventing the investigation of molecular adsorption and reaction processes.

The consortium presenting this PRIN project is constituted by four academic institutions (Università di Torino, Milano, Pavia and Roma La Sapienza, hereafter UniTO, UniMI, UniPV and UniRoma, respectively) and one CNR unit, the "Istituto Officina dei Materiali" (IOM) in Trieste (hereafter CNR), that has designed, realized and that is running the APE beamline at the Elettra Italian synchrotron.

Herein we propose the development of a revolutionary instrumentation on the APE-HE beamline @ Elettra synchrotron allowing to perform soft X-ray NEXAFS measurements (in electron yield mode) at variable pressure (up to 1 bar) and temperature at both the K-edge of a typical atom present in the molecule (C, N, O, F) and the L2 and L3 edges of the first row transition metals (from Sc to Zn). This instrumentation will allow to bridge the pressure gap between UHV and ambient pressure more effectively with respect to the much more expensive instruments based on differential pumping systems, which make nearly-ambient XPS and TEM experiments possible only in the mbar pressure range. Moreover, the element selectivity of the X-ray absorption technique will allow to measure diluted systems (down to fraction of atomic %), covering many relevant catalytic systems.

Shifting our target from heavy metals to light elements opens unprecedented possibilities in studying the structure of relevant adsorbates in interaction with the solids. XAS spectroscopy of the light elements of the absorber also offer a complementary picture to that gained by conventional hard X-rays techniques. Our efforts will be focused in the investigation of zeolites and functionalized metalorganic frameworks (MOFs) as catalysts, MOFs and functionalized MOFs for gas sorption and separations and oxides and functionalized oxides for gas sensing.

The complementary skills of the 5 units, guarantee to the consortium to fully cover all aspects of the project: samples synthesis, complete structural, electronic and vibrational experimental characterization and related modelling, and final performance testing for catalysts and sensors.

Indeed, the innovative information on the electronic structure of the adsorption-site/adsorbate pair highlighted by operando NEXAFS spectroscopy, will be supported by several more conventional spectroscopic and diffraction techniques. The structure of the adsorbing site will be determined by synchrotron diffraction and confirmed by periodic DFT calculations, which outputs will be used to compute the soft X-ray XAS spectra (collected at the APE-HE), the hard X-ray XAS and XES spectra at the metal K-edge (collected on other synchrotron beamlines) and the IR, Raman, resonant Raman, XPS collected at (CNR-IOM) and UV-Vis spectra (collected in the laboratory).

The extensive experimental/theoretical multi-technique approach that we are proposing will allow to reach unprecedented understanding on the structural, energetic, electronic and vibrational features of the investigates systems. This will result in a deep understanding of how semiconducting oxides work as gas sensors and of how the active site of a catalyst transform reagents into reactants. These results will be crucial for the development of higher performance materials for next generation gas sensing devices, as well as for the optimization of catalytic processes, that are of fundamental importance for a sustainable future.

It is worth of note that at the end of the PRIN project this instrumentation installed and tested at the APE-HE beamline will be available for the whole scientific community working in the field of surface chemistry via standard beamtime application @Elettra, or via the new European NFFA platform, resulting in a scientific, technological and economic impact at national and international level.

2. Detailed description of the project: targets that the project aims to achieve and their significance in terms of advancement of knowledge, state of the art and proposed methodology

2.1. Molecular adsorption @ surfaces

Molecular adsorption on surface sites is the fundamental key step for relevant applications such as catalysis [8-10], gas storage [1,2], separation [3,4] and sensing [5-7], representing nowadays relevant frontiers in applied chemistry, having a clear impact on everyday life. This project will have direct impacts in the fields of catalysis and gas sensing but it will also deliver relevant outputs in the fields of gas sorption and separation. Gas-surface interactions are studied by several in situ and operando spectroscopic methods. Their design and exploitation in the soft X-ray energy range is currently at the frontier of research.

2.2. NEXAFS spectroscopy at ambient pressure: a breakthrough in the field

We are aimed to achieve breakthrough improvements in the understanding of molecular adsorption and reactivity at surface sites combining the cutting-edge new soft X-ray XAS in total electron yield (TEY) mode under operando conditions (hereafter NEXAFS), presently under development at the APE-HE beamline of the Italian Elettra synchrotron [11], with more conventional but still highly informative spectroscopic and diffraction techniques. This instrumental and methodological effort will provide us unprecedented experimental information on the electronic structure of both metal adsorption center and adsorbed molecule. Moreover, with the support of advanced DFT calculations, the simulation of XAS spectra (NEXAFS or XANES, in the hard X-ray region) has recently become an effective tool to validate the local environment of the excited element on a structural ground [12-19], becoming a reliable structural investigation tool for supporting XRD or EXAFS studies or to substitute them when the samples have no long range order or when the density of adsorbing atoms is too diluted to significantly affect the XRD pattern or to allow an accurate EXAFS data.

The great benefit of hard X-rays, XAS & XES spectroscopies applied to catalyst investigation is related to the high penetration depth of the beam, allowing to study catalysts under operation conditions, i.e. in presence of reactants and products from the gas or liquid phases. The strong connection between catalysis and XAS is testified by the large number of contributions related to catalysis (from 7 up to 19%) presented in the 17 XAS conferences that have taken place in the last three decades (since 1981 in Daresbury, UK, to 2018 in Krakow, PL) and by the number of contributions related to XAS (from 16 to 28%) that have been presented in the 6 conferences on operando spectroscopy (from 2003 in Lunteren, NL, to 2018 in Malaga S), see Ref. [20] for a detailed statistic till 2013.

Soft X-rays have the advantage that their energies cover the range of L or M-edges of most of the transition metals. With respect to XAS at the metal K-edges, L3 and L2 transitions are usually more intense (because formally electric-dipole allowed) and richer in details. L-edges mainly consist of transitions to s- and d-based unoccupied valence density of states (uDOS). Hence, NEXAFS is very sensitive to metal-ligand interactions, and perfectly complementary to XAS at the metal K-edges, that according to the Fermi golden rule, probes mainly the p-uDOS. The d-uDOS is of great importance in understanding the molecular orbitals with the ligands, thus in elucidating the nature of the chemical bonds of the active metal site with the ligands (reactants intermediate states and products), see Fig.1.

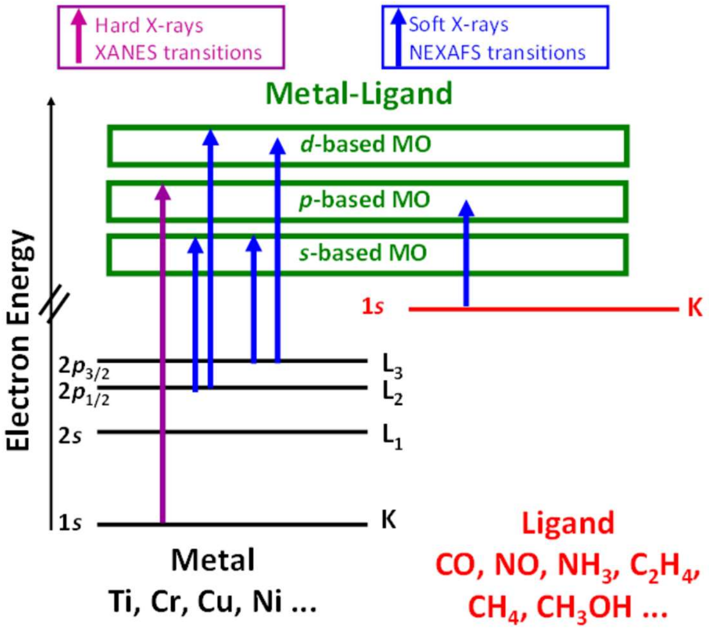

Fig. 1 Schematic, simplified, representation of the different metal-based (black), ligand based (red) and MO (green) electronic levels and of the corresponding electronic transitions observable by conventional XANES (violet) and innovative NEXAFS (blue) spectroscopies. The richness of the latter is evident.

Soft X-rays cover the range of the core level binding energies of light elements (e.g. C, O, N, F) allowing the simultaneous observation of the electronic and structural changes underwent by the ligands or by the adsorbed reactants during the catalytic reaction (Fig.1). Unfortunately, the short attenuation lengths of soft X-rays (and the even shorter of Auger electrons) prevented for a long time the application of NEXAFS in reaction conditions: in the years 2000, the mbar range was reached by the development of differential pumping systems while, only since few years the use of ultrathin SiN membranes permitted to reach 1 bar. This is the reason why NEXAFS spectroscopy appeared in only 232 papers out of 155000 that used spectroscopy to analyse a catalyst, see the bibliometric study in [21].

The CNR unit, in strict collaboration with UniTO and UniPV units, has realized a prototype of operando cell that allows NEXAFS spectra to be collected in TEY mode at ambient pressure [11], Fig.2ab. This is an important characteristic of the instrument allowing a greater surface sensitivity and faster acquisition times with respect to the photon in-photon out acquisition mode, which is by far the most used.

Depending on the atomic content of the absorbing element and on the gas compositions, currents in the pA to nA are currently measured. Fig.2c shows the quality of the spectra collected under different conditions on TS-1, a selective catalyst for partial oxidation reactions using H2O2 as oxidative agent [22,23].

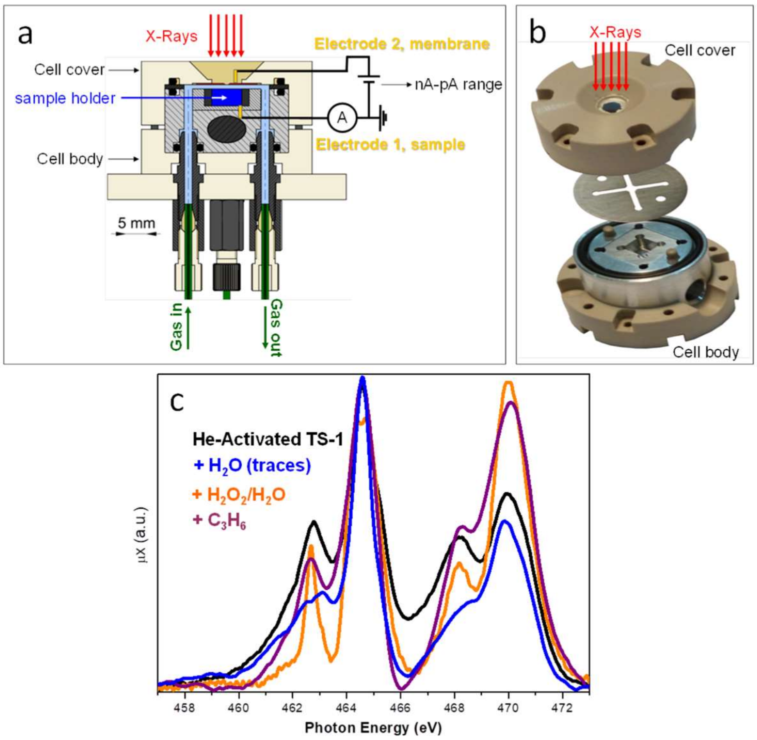

Fig.2. Scheme (a) and photo (b) of the prototype cell. (c): preliminary results showing the quality of the data collected on 1 atomic % Ti catalyst (TS-1) and the sensitivity of the technique to the dosed atmosphere (1 bar).

The first prototype of our cell served as a *proof of concept*, but has several limitations and allows in situ activation only up to 120 C. The working temperature range is an issue as most of the catalysts requires much higher activation temperatures. The same holds for operando experiments, that must be performed at the reaction temperature [24]. Consequently, one of the primary goals of the PRIN is the realization of a II-generation operando cell with improved performances: 500 C during measurements. 2 different solutions relying on a traditional Joule heating or on an innovative laser heating will be considered. Moreover, the gas line will be modified to permit the inlet of several gases at the same time and a gas analysis tool will be added at the exit of the cell to permit the tracking of the reaction during the spectroscopic measurements. The instrument will also be equipped with a new set of ultrathin membranes with different composition. The actual system, based on SiN membranes, prevents the analysis of the N atomic species in samples and adsorbate gases. With a new switch between SiN and SiC membranes, we will be able to analyze all the light elements. These improvements represent the main technological role and the major cost of the CNR unit. The new instrument will allow to fulfil the goals of this project and will also represent an extremely valuable tool available @Elettra facility to the whole
Italian and international catalysis community.

2.3. Parallel characterization techniques and theoretical support

The innovative information on the electronic structure of the adsorption-site/adsorbate pair highlighted by the innovative operando NEXAFS spectroscopy, will be supported by several more conventional, but still highly informative spectroscopic and diffraction techniques. Hard X-ray XANES on metal K-edge will provide insights on the p-based uDOS (Fig.1) [12-14,19,25,26], while the complementary occupied DOS will be investigated at ambient pressure by hard X-rays XES [15, 24, 27-31] and on the naked adsorption site by XPS un UHV [32,33]. The characterization of the electronic configuration will be completed by UV-Vis [17,29,34-36] for zeolites and oxides, while for MOFs it will be further coupled with advanced RIXS to disentangle metal d-d from pi-pi* ligand transitions [37,38].

The structural characterization will be performed with ab initio structure determination from PXRD analysis on data collected by standard laboratory instruments [39-45]; when needed, synchrotron [19,26,46] and/or neutron [47,48] sources will be used. When possible, single crystal XRD will be performed [49,50]. UniMI will develop an in situ/operando cell for XRD collection under controlled temperature and gas atmosphere. The cell will be flexible allowing its use in both powder and single crystals collections using both laboratory and synchrotron sources. Metal K-edge EXAFS will provide short-order structural information [12,24,25,31,35,40,41,49,51-55]. Also DSC/TGA and BET analyses will be used [35,40,42,43].

The vibrational properties [56] will be probed under in situ and operando conditions by IR [16,17,27,36,53,54,57,58] and Raman [54]. The availability of 3 micro-Raman spectrometers, equipped with 5 different excitation wavelengths (from red to far UV), will allow us to exploit, when possible, Raman enhancement effects [22,23,59], particularly suitable to detect diluted surface molecular adducts. When needed, neutron inelastic scattering [32,33] will be performed.

The structural, energetic, electronic and vibrational features of the molecular adducts will be simulated by state of the art quantum chemistry approaches in order to support the experimental findings and to allow the full interpretation of the spectroscopic data. DFT methods will be used, but, for each case, the role of dispersive forces will be evaluated with the empirical Grimme scheme and, if needed, ab initio calculations at MP2 level will be performed [60]. Cluster and periodic calculations will be performed using Gaussian and CRYSTAL17 codes, respectively, the latter developed by the Theoretical Chemistry Group of UniTO. Reverse Monte Carlo scheme will be developed to simulate both NEXAFS/XANES (with MXAN, or FDMNES, when we need to go beyond the muffin-tin approximation [14]) and EXAFS (with FEFF, GNXAS). Simulations of the metal L-edges NEXAFS spectra will be carried out in the framework of crystal field multiplet approach [61]. XES spectra will be simulated with the ORCA code. In the last 5 years UniRoma obtained computational grants form ISCRA-CINECA for more than 1.5 million computational h; 200000 h will be still available in semesters 1-2 of the PRIN, additional grants will be applied for in the future.

The scientists involved in the five units of this PRIN have an outstanding knowledge in the use of all the here mentioned techniques, as testified by the above quoted references; this will allow us to fully cover the experimental and theoretical needs to successfully reach the goals of the project.

2.4. Applications and related materials

2.4.1. Catalysis

Catalysis plays a key role in our modern society because most industrial chemical processes involves the use of a catalyst, that allows to run plants at lower temperature, with higher selectivity.

Among the numerous industrially relevant reactions, we will focus our attention on: 1) selective catalytic reduction (SCR) of NO to N2 by ammonia (NH3-SCR) [15,24,62], 2) methane to methanol [54,63,64] and 3) selective hydrogenation reactions over supported Pd and Pt nanoparticles (NP) [32,51,52,65,66].

Ammonia-SCR plays an important role in the abatement of NOx emissions in the exhausts of diesel engines and power plants. With environmental legislation becoming more stringent in both Europe and US, this reaction is going to play an important role in the development of technologies to meet the emission requirements for exhaust gases [67]. The commercially available catalysts for exhaust gas cleaning by NH3-SCR are based on vanadium oxide supported on titanium oxide, and on Cu or Fe-exchanged zeolites. The traditional zeolites applied in SCR are ZSM-5, and zeolite BEA. More recently, Cu-exchanged chabazites (CHA), in particular SSZ-13 and SAPO-34, have become more important because they are more stable under high temperature conditions.

The direct low-temperature conversion of methane to methanol is heavily investigated, due to its enormous potential uses in the energy and chemicals sectors [68,69]. However, the high energy required for cleavage of the C-H bond and the facile overoxidation to COx, pose great challenges for the realization of such a process. Metal-exchanged zeolites are able to stabilize well-defined metal-oxo sites: different zeolite topologies have been demonstrated to stabilize copper [54,63,70] and iron [71] metal-oxo clusters and all of them have shown activity for stoichiometric transformation of methane to methanol.

Microwave (MW) assisted hydrogenation and selective hydrogenation reactions over metal NP functionalized MOFs [52,72] will be performed in UniTO [73,74]. Non-uniform heating at the surface of heterogeneous catalysts along with the production of hot spots by MW irradiation result in non-equilibrium local heating localized at the surface of the metal NP present on the catalysts [75]. MW, as a direct and rapid heating source, can increase the hydrogenation reaction rates. Hence, the combination of MW heating and supported metal NP gives very high reaction rates using very small catalyst amounts, therefore increasing the sustainability of the processes.

2.4.2. Sensors

Semiconductor metal oxides, such as Zn, Sn, Ti, W, Cu, Fe and In oxides have attracted much research interest for applications as resistive gas sensors [5-7]. While a huge amount of literature concerning the sensing mechanisms exists [76-79], general consensus on this point is far to be reached. The mechanisms proposed can be broadly grouped in two groups, i.e., the “ionosorption model” and the “oxygen-vacancy model” [80]. In the former, atmospheric oxygen on SnO_2 surface traps electrons of the conduction band to form molecular (O_2) and atomic (O and O) ionized oxygen species [81-84]. When exposed to reducing gases as CO, the adsorbed oxygen species react with gas molecules, restoring electrons in the conduction band. When the surface is free of adsorbed oxygen, CO is adsorbed as CO^+, and electrons are still injected into the conduction band. In the oxygen-vacancy model, CO is oxidized to CO_2 by removing oxygen from the surface and producing a vacancy that is ionized by injecting electrons in the conduction band; in the presence of oxygen, the vacancy is filled by removing electrons from the conduction band. All these processes influence the density of electrons in the depletion layer, and thus the conductivity of the sensor.

In this context, NEXAFS is expected to give invaluable information: as oxygen states are deeply involved in both the above mechanisms, probing the O K-edge in situ and/or operando conditions will in allow method, that combined with the use of NP, renders the technique intrinsically surface sensitive, and allows to effectively probe the pertinent surface states involved in the adsorption process.

The oxides will be synthesized in form of NP by a recent protocol [85]. In addition, functionalization with a second phase such as noble metal NP or different metal oxides [86] will also be attempted to enhance the selectivity: e.g. Pd based nanomaterials have unique sensing mechanisms toward hydrogen [76]. All the materials will be thoroughly in house characterized concerning structure, grain size, morphology and chemical and phase purity by XRPD and SEM. The surface area will be measured by BET isotherms obtained by thermogravimetry. All the samples will then be checked for their response to external atmosphere and variations thereof by measuring their conductivity using the four-probe method. We will construct pilot devices for applications in medical diagnostics, air quality monitoring, and detection of noxious gases. Particular attention will be devoted to NO_x, which poses a severe environmental problem and whose adsorption onto semiconductor devices was recently investigated [87]. Quantitative determination of these gases and the selectivity of the probe will be evaluated.

2.4.3. Gas sorption and separation

We will apply a rational design for the preparation of MOFs containing exposed metal sites or active organic functionalities, such as bipyridyl linkers, able to react in post-synthetic treatments to introduce novel active metal centers in the pore matrix [43,50,52,72]. The active and functional sites in the surface of the MOFs’ pores are expected to interact efficiently with gases, enhancing their energy interactions.

Promising MOFs, such as UiO-66,67,68 [39,40], CPO-27 [14,38,55], cubic octanuclear Ni(II)-MOF [41] and others, will be selected from the literature, judiciously modified (changing the organic linker or the metal ions) and synthetized by UniMI. Moreover, post-synthetic introduction of structural defects and metal substitution on the inorganic clusters will be done to improve adsorption capacity and selectivity towards specific guests [88].

Preliminary single-component adsorption isotherms will be performed to investigate the gas-matrix interactions. This will lead to a deep understanding of the chemical properties of the materials with and without guest molecules. In these experiments, we will focus on CO_2 separation; olefin/paraffin and ethylene/acetylene separation and capture of H_2S, SO_2, NH_3, NO_x and CO [38,45,89,90]. Advanced adsorption (high pressure) and separation (breakthrough curves) experiments will be done on the best performing materials.

2.5. Risk analysis

We foresee 2 major origin of failure risks in the present project: 1) the most innovative experimental results will came from an experimental set-up that is not operative yet; 2) most of the planned characterizations are based on cutting-edge synchrotron-based techniques, that are subjected to approval by international panels.

Regarding the development of the II-generation cell, its successful realization is likely due to the high technological competence of the CNR unit in the development of new, original instrumentation [91-94].

Moreover, the results recently published [11] and those reported in Fig.2, demonstrate that our team already possess a first-generation cell that will permit the realization of the proposed measurements at ambient pressure but in a relatively low temperature range. In the remote case of failure to reach high temperature in the new instrument, the risks are further mitigated by the collaboration with the group of Dr. D. Payne (Imperial College UK) [95,96] which operates a near ambient pressure XPS able to investigate surface reactivity at few mbar pressure up to 600 C.

For semesters 1,2 the beamtime on the APE-HE is guaranteed by a long-term project (LTP) already granted by Elettra to the PI, in collaboration with the CNR coordinator, covering years 2018-2019. We foresee that such LTP will be extended in the 2020-2021 period, thus covering also semesters 3-6 of the PRIN. In the improbable failure of the LTP extension, the CNR unit will guarantee beamtime via the in-house quota. As far as high energy X-ray experiments are concerned, we plan to submit proposals to Elettra, SLS, MAX-IV, Soleil and ESRF (the last one only for semesters 3-6, being in shut-down before). Reasonably, the probability of success of such applications is very high because of the outstanding experience that all University units have in the use of SR: 210, 130, 100, 10, experiments approved by international panels of the different synchrotrons in the last two decades for UniTO, UniPV, UniRoma and UniMi, respectively (1 experiment consists in 2 to 14 days of data collection).

3. Project development, with identification of the role of each research unit with regards to expected targets, and related modalities of §integration and collaboration

The complementary skills of the 5 units, guarantees to the consortium to fully cover all aspects of the project: samples synthesis, complete structural, electronic and vibrational experimental characterization and related modelling, and final performance testing for catalysts and sensors, see Fig.3. Besides samples synthesized by the consortium units (UniMI, UniTO and UniPV), the project will also benefit of materials developed in the framework of prestigious international collaborations with Oslo [31,35,39], Berkeley [42,48], MIT [18,97], Granada [43-45,88], Kiel [98, 99] Universities and Topsoe [15,24,54,62] and Chimet [32,51,65,66,100] companies. This will not only increase the impact of our study, but it will also prepare our consortium for a European application in the last year of this PRIN.

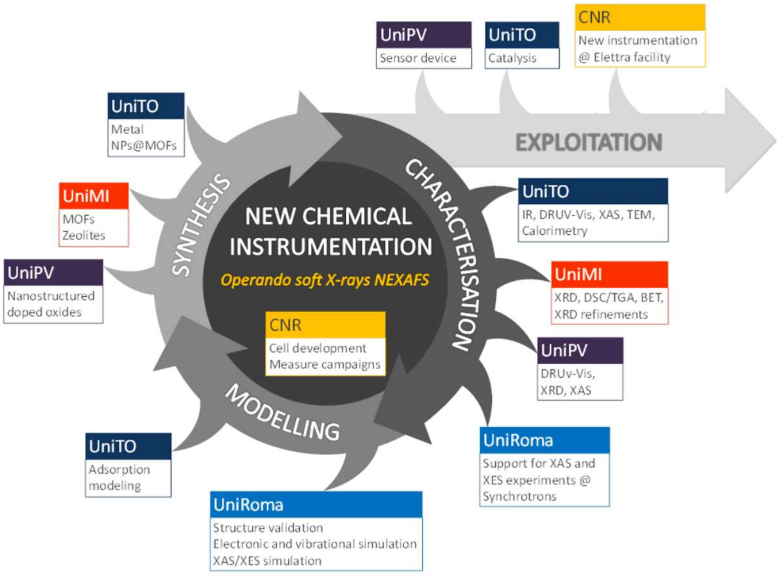

Fig.3. Schematic representation of the specific roles of the different units and of their synergic interaction.

3.1. Scientific synergy among the units and corresponding role

3.1.1. The synthesis of the crystalline porous materials for catalysis (zeolites and MOFs) will be performed at UniMI, where the coordinator has an extensive experience matured in the labs of Prof. Masciocchi in Como [41,43], Prof. Navarro in Granada [44,45,88] and Prof. Long at Berkeley [42] The same unit will be in charge of the ab initio structural determination from PXRD (and single crystal, when possible) of the synthesized samples. All materials will be tested with laboratory PXRD, while the most promising will be further investigated at synchrotron XRD beamlines. The structural determination will be performed on: 1) as synthesized materials (zeolites with templates and MOFs with solvent); 2) activated samples with empty pores; 3) activated samples in contact with adsorbates to determine the structure of the molecular adsorbing site, this will be possible thanks to the development of the laboratory-scale cell for in situ gas-pressure XRD. UniMI will also perform thermodiffraction experiments to assess stability of the samples under variable-temperature conditions; DSC/TGA and BET analyses. The samples will be fractioned and sent to UniTO and CNR. UniTO will take care of: 1) preparation of metal NPs with non-conventional ultrasound technology [74] and insertion in the MOF prepared by UniMI; 2) IR characterization of adsorbed molecules, as probes for adsorption sites characterization or as reactants for operando catalysis [56,57]; 3) UV-Vis characterization of metal d-d transitions [36,38]; 4) determination of average adsorption enthalpies by microcalorimetry and site specific enthalpies by variable temperature FTIR[101-103]; 5) catalytic tests; 6) hard X-ray absorption and emission experiments at the metal K-edges at synchrotron sources. CNR will provide ambient pressure soft X-ray NEXAFS at the metal L-edges and (C, N, and O) K-edges at the APE-HE@Elettra [11] as well as UHV XPS analysis [33].

All structure refinements will be performed at UniMI and the outputs will be sent to UniRoma, that will validate the stability of the structures by ab initio modeling. Indeed, the ab initio structure solution from PXRD of complex materials such as MOFs, having a cell volume of several thousands of Å^3 is often elusive and several possible structures may be compatible with the observed PXRD patterns. As we have successfully shown in the past [35, 39-41], the synergic loop among PXRD, ab initio refinements and metal K-edge EXAFS will allow correct structure determination in an iterative "self-consistent-like" approach. Besides the crucial structural check, the outputs of the periodic DFT calculations will be used by UniTO to interpret the vibrational features (both IR and Raman [35,40]) and the UV-Vis spectra [34,38]. Finally, UniRoma will use the XRD/DFT optimized structure to simulate metal K-edge EXAFS spectra [15,27] and to simulate metal K-edge XANES [14, 18] and XES [27,29,38,104,105]) spectra and the soft X-ray NEXAFS (C, N, and O) K-edges and metal L-edges.

3.1.2. The synthesis of the nanostructured oxides will be performed at the UniPV unit, that will also take care of the standard structural and band-gap determination as well as hard X-ray metal K-edge XAS.

Samples will be sent to UniTO and CNR. UniTO will take care of the UV-Vis-NIR and IR spectroscopies under in situ and operando conditions with adsorbates [106-108]. At the CNR unit a pre-characterization with XPS [33] will be performed, followed by ambient pressure NEXAFS at the metal L-edges and (C, N, and O) K-edges of the sensed molecule [11]. The most promising materials will be tested in a prototype sensor device for GC detection by UniPV. UniRoma will provide slab periodic calculations of molecular adsorption on the oxide surface [103]. DFT calculations will provide the local geometries of molecular adsorption at the surface allowing to simulate metal K-edge EXAFS and XANES spectra and Metal L-edge and C, N or O K-edge (depending on the sensed molecule) NEXAFS spectra, as well as the vibrational properties investigated FTIR and Raman spectroscopies.

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