

Soft X-ray probes of ultrafast dynamics for heterogeneous catalysis

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ABSTRACT

Soft X-ray spectroscopy is one of the best tools to directly address the electronic structure, the driving force of chemical reactions. It enables selective studies on sample surfaces to single out reaction centers in heterogeneous catalytic reactions. With core-hole clock methods, specific dynamics are related to the femtosecond life time of a core-hole. Typically, this method is used with photoemission spectroscopy, but advancements in soft X-ray emission techniques render more specific studies possible. With the advent of bright femtosecond pulsed soft X-ray sources, highly selective pump-probe X-ray emission studies are enabled with temporal resolutions down to tens of femtoseconds. This finally allows to study dynamics in the electronic structure of adsorbed reaction centers on the whole range of relevant time scales – closing the gap between kinetic soft X-ray studies and the atto- to femtosecond core-hole clock techniques.

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1. Introduction

More than 75% of all industrial chemicals are produced in processes using catalysis [1]. Very often pure or compound transition metal surfaces act as a catalyst and the gas phase reactants form novel products through a generic cycle. The process typically starts with the adsorption on the surface, often accompanied by the breaking of a reactant bond. Then the actual product bond is formed on the catalyst surface and the reaction is finished with the desorption of the products from the surface. The catalyst works by providing the potential energy landscape to selectively break the unwanted bonds and form the wanted bonds with lowered energy barriers.

In addition, heterogeneous catalysis is not only important for the large-scale production of chemically relevant molecules. Many challenges for a sustainable energy cycle can potentially be solved with devices where heterogeneous catalysis plays an important role. For example, the direct production of easily storable and transportable fuels with a high energy-density from sunlight and the conversion from the fuels into electric energy are often enabled by processes on catalysts surfaces, e.g. in the production of so called solar fuels and in fuel cells.

Only with the advent of novel methods in surface science, the dynamics driving the reactions on the surfaces have become accessible for experimental studies and more detailed reaction mechanisms could be derived. Detailed total energies for most of the fundamental steps during the reaction can be given. The missing gap between the detailed reaction mechanism and specific reaction

rates (if not limited by the thermal transfer of energy) can nowadays be closed by time-resolved spectroscopies. We are just starting into an era of a much more detailed understanding of chemical reactions by analyzing the fundamental drivers of the chemical reaction directly in the time domain.

The main step during a chemical reaction is the formation or breaking of a chemical bond – a step that is inherently connected with the transfer of charge between the reacting atoms and a rearrangement of their local electronic structure. To analyze charge transfers and local electronic structures, a direct and selective experimental approach with tremendous information depths is given through soft X-ray spectroscopy. In the soft X-ray energy region, the different chemical elements have characteristic energy levels that can selectively be addressed with spectroscopic methods. Furthermore, spectroscopy directly accesses the electronic structure and therefore the determining quantity for the dynamics of a chemical reaction.

The relevant time scales range typically from the low femtosecond to attosecond regime for the transfer of charge and the electronic structure changes, whereas nuclear rearrangements, conformational changes etc. happen on slower time scales reaching into the picosecond regime. Therefore, only ultrafast soft X-ray spectroscopy is able to directly study the quantities and fundamental reaction steps that are ultimately responsible for the existence of a specific chemical reaction on a catalyst surface (determining the selectivity of the catalyst) and the intrinsic time that the chemical transformation needs (determining the efficiency of the catalyst).

The following discussion is centered around dynamics in atoms or small molecules adsorbed on single crystal surfaces – model

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systems for the determining steps in heterogeneous catalysis. A perspective shall be opened how the selectivity of spectroscopy in the soft X-ray region can be applied to study important ultrafast dynamical steps in a heterogeneous catalysis cycle. The line of thought is presented along prominent examples from our work and some references to relevant literature are given without any claim to completeness.

The paper is structured as follows: by introducing resonant inelastic X-ray scattering (RIXS) on adsorbates, one of the most powerful and selective tools to study electronic features during heterogeneous catalysis is presented. The core-hole clock method that addresses ultrafast charge transfer dynamics between adsorbates and the substrate through electron spectroscopy is described along some examples that show the applicability of this method. Unfortunately, the core-hole clock idea has not yet been connected with RIXS on surface adsorbates to study the dynamics of catalytic processes with the intrinsic selectivity. Nevertheless, the direct potential of RIXS for time-resolved studies relating to the core hole life time is illustrated on two examples, where ultrafast processes on the building blocks of an adsorbate system are studied: the vibrational dynamics of free molecules and electron–phonon coupling in the solid state. The discussion is closed with a quick outlook on the possibilities for time-resolved soft X-ray spectroscopy that are opened by the use of novel pulsed X-ray sources in pump-probe setups.

With the combination of the selective information gained with RIXS and the core-hole clock method (able to study processes in the attosecond and low femtosecond region) and pump-probe methods at specialized pulsed X-ray sources (covering the time scales from tens of femtoseconds to pico- and nanoseconds), all the relevant dynamics in surface chemical reactions can be deeply analyzed on their intrinsic time scales.

2. RIXS for selective valence electronic structure analysis on adsorbates

In this section, the experimental technique is introduced and its selectivity is highlighted. Concentrating on one prominent example of RIXS on an adsorbate, it is shown how this selectivity can be used to study different properties of the valence orbitals of an adsorbed molecule. For a more thorough overview of this field, we refer to a recent book [2] and several review articles [3–6].

The power of soft X-ray spectroscopy is in the energetic difference of the core level binding energies of different elements and even of the same element in different chemical surroundings (the chemical shift). This allows for selective excitations at specific elements by tuning the energy of incoming photons into core resonances. By analyzing the energy of the subsequently emitted photons, typically with a grating spectrometer [7], the valence electronic structure around the selectively excited atom can be studied. In a study for catalytic processes, the dynamically active atoms can be singled out and the evolution of their bonding orbitals can be studied.

The RIXS process can be imagined as a photo-induced excitation of a core electron into an intermediate state (absorption step) and the subsequent radiative decay of the core-hole (emission step). In both steps, dipole selection rules apply and the selectivity of such studies is considerably enhanced. For example, through creation of an *s*-symmetric core-hole, decays from *p*-states can be observed. As dipole radiation along the symmetry axis of the dipole is suppressed, certain orbital orientations can be selectively suppressed by rotating the sample or the spectrometer. After analysis of all inequivalent orientations, the full information of the different orbital orientations can be extracted.

An example making use of the full selectivity of soft X-ray RIXS is shown in Fig. 1, where the valence electronic structure at specific

atoms in an amino acid adsorbed on a surface are addressed through the element specific core level binding energies and their chemical shifts. Through an orientation analysis specific orbital symmetries are projected out [8]. This paves the way for a detailed understanding of the influence of the substrate – the catalyst – on the electronic structure of the molecule and thus the efficiency and selectivity of an induced chemical reaction.

3. The core-hole reference clock for ultrafast soft X-ray studies

Here, the general idea of the core-hole clock method is described before more detailed examples of applications are shown. The focus is first on the core-hole clock method on adsorbates using electron spectroscopy, before the core-hole clock idea is transferred to RIXS measurements. Due to the lack of such studies on adsorbates, examples from the constituents of a surface adsorbate system (free molecules and solid samples) are presented.

The core-hole clock method allows to study ultrafast dynamics with cw soft X-ray sources, enabling highly selective studies of adsorbate dynamics. (Many works on the core-hole clock method have been published, e.g. [9–18]. For reviews see e.g. [19,5] and the more complete references therein.) With this method, it is possible to relate the temporal evolution of specific processes to a system immanent time scale given by the life time of a specifically excited core-hole. The time scales that become accessible with this method in the soft X-ray regime are typically in the hundred attosecond to tens of femtosecond regime. With standard detection efficiencies, one can straightforwardly determine times that range between a tenths and ten times the core-hole life time.

With core-hole clock spectroscopy, processes can be studied that are either static and always present in the sample in a dynamic equilibrium or processes that are induced through or alongside the creation of the core-hole. In the following paragraphs, we will give examples of both.

The main prerequisite to study a process with the core-hole clock method is that it needs to show a specific signature in the core-hole decay spectrum. The intensity of the spectral fingerprint of the process relative to the intensity of the core-hole decay spectrum without the process is then directly related to the rate of the studied process relative to the rate of the core-hole decay.

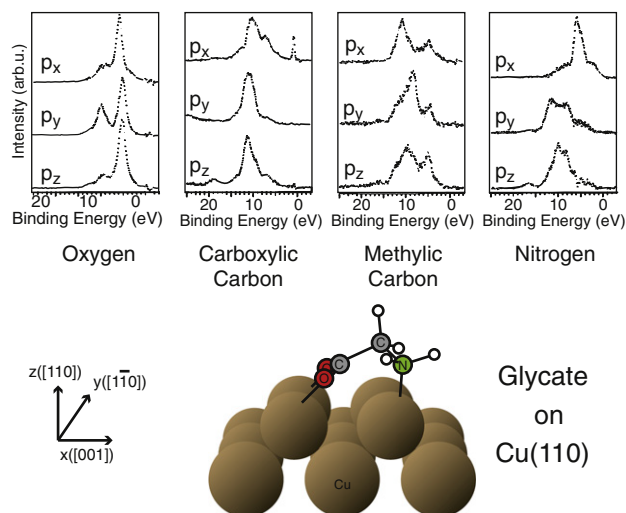


Fig. 1. Specificity of soft X-ray RIXS on adsorbates. Through resonant excitation at the chemically shifted core levels of the nitrogen, oxygen and carboxylic or methyl carbon in a glycine molecule adsorbed on a Cu (110) surface (forming glycinate through partial deprotonation), the local valence electronic structure can be analyzed. An orientation analysis further yields information on the orbital orientation and allows to separate the *p*-symmetric molecular orbitals oriented along the *x*-, *y*- or *z*-axis [8].

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