Application of Spectrokinetic Techniques for the Understanding of Active Sites and Intermediate Species in Heterogeneous Catalysis

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Introduction

The integration of kinetics with in situ/operando spectroscopy and theoretical calculations such as those based on density functional theory (DFT) is a very powerful tool for the elucidation of intermediate species and reaction mechanisms in heterogenous catalysis. These spectrokinetic methods are commonly based on the application of dynamic and transient spectroscopic techniques since they are richer in kinetic information. They include, for example, jump or stopped-reactant type methods, SSITKA-diffuse reflectance infrared Fourier spectroscopy (DRIFTS), and modulation excitation spectroscopy (MES),[1,2] which have been used for the identification of true reaction intermediates, reaction rate, and rate constant measurements.

Among commonly available spectroscopic techniques, UV-Visible (UV-Vis) spectroscopy has been quite useful to determine the location of adsorbed species, for example, on gold catalysts via Au MaPPS.[3] However, due to its lack of specificity to absorbed species, it cannot be employed for species identification. In this work, we describe several spectroscopic methods based on steady state (e.g., in situ UV-Vis, charge transfer kinetics) and transient (e.g., ME-UV-Vis and ME-DRIFTS) in situ/operando spectroscopic characterizations combined with theoretical calculations and kinetics for the assessment of the location and nature of active sites and true reaction intermediates at conditions relevant for heterogeneous catalysis.

Materials and Methods

In situ DR-UV-Vis and DRIFTS were used to understand active sites and intermediate species in ethanol oxidation reaction. The in situ cells, experimental description, and data analysis have been previously reported,[2,3,4] including catalyst preparation, experimental details, and the description of the gold maximum plasmon peak shift (Au-MaPPS)[3] and modulation excitation spectroscopy (ME)–DRIFTS[2] methodologies. Additionally, a newly developed in situ UV-Vis charge transfer spectrokinetic analysis (CT-SKAn) procedure combines the d-d transition region response to relate charge transfer (CT) processes, DFT charge calculations, and kinetic models to assess the type of adsorbed oxygen species.

Results and Discussion

Figure 1 summarizes sample results of two spectroscopic techniques: Au-MaPPS and ME-UV-Vis for characterizing the location for oxygen adsorption on gold catalysts and to identify the phenomena occurring during ethanol oxidation on Au/TiO_2. Measurements of Au-MaPPS, upon adsorption of alternating and consecutive oxidizing (O_2) and reducing (H_2) species, were correlated to relative CT during these adsorption processes. In combination with models for charge transfer and gold nanoparticles geometry (e.g., truncated octahedron, truncated cuboctahedron), the results showed that the main adsorption sites at reaction conditions are the metal-support interface sites (Figure 1, left).

Moreover, ME-UV-Vis measurement during O_2 modulation showed that at reaction conditions, charge transfer (as evidenced in the d-d transition region, Figure 1, right) to/from the Au nanoparticle occurred to activate the adsorbed oxygen during ethanol dissociation. The rate determining step was found to be the βC-H oxidative dehydrogenation of the adsorbed ethoxy species to form acetaldehyde, as confirmed by KIE. DFT calculations in this limiting step of charge distribution on a model Au/TiO_2 surface with several types of oxygen species and in combination with Langmuir-Hinshelwood expressions (CT-SKAn method) revealed that HO*, O*, and HOO* species were the more likely intermediate species, as also verified via classical kinetic measurements in a fixed bed reactor. Additionally, a more general application of the MaPPS methodology that could be extended to non-plasmonic materials was explored by correlating the derived CT model to CT d-d transition (at ~900-1000 nm) relative intensity changes (CT-TRIC). The CT-TRIC results at ethanol oxidation conditions confirmed: 1) the preferential adsorption on the metal-support perimeter; 2) a decrease in adsorption sites towards higher undercoordinated sites (with increasing temperature); and 3) that only ~1/3 of interface sites are kinetically relevant at reaction conditions.

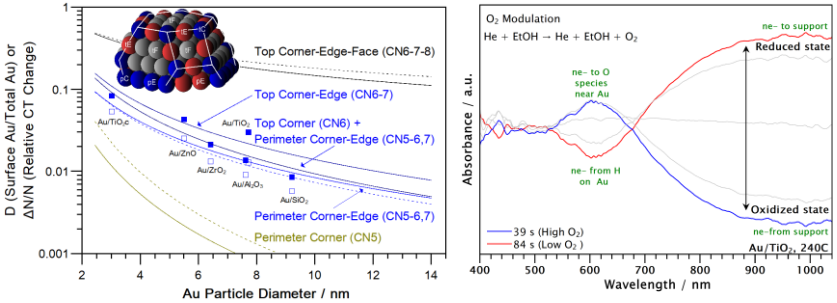

Figure 1. In situ UV-Visible characterization showing application of Au-MaPPS to identify adsorption sites for O_2 on Au catalysts at 125 °C (left) and MES during ethanol oxidation on Au/TiO_2 at 240 °C to show CT processes in the d-d transition region (right). This CT response is used to assess adsorbed oxygen species via CT-SKAn methodology.

Significance

The development of simple in situ spectrokinetic techniques to assess intermediate species nature and adsorption location can benefit catalytic studies by providing insights into the reasons for different catalysts performance and facilitate mechanistic proposals.

References

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