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Final Doctoral Dissertation Defense

Chemical Engineering

In Situ and Operando Tools and Methods for Characterization of Heterogeneous Catalysts

Abstract

In situ and operando spectroscopic characterization of catalysts is a powerful tool to explore the nature of species that may be involved in a heterogeneously catalyzed catalytic cycle. In combination with methodologies to discriminate passive and active species, it can inform researchers on the presence of spectator and true reaction intermediate species. Here, we present an improved design of the commercial Harrick Scientific high temperature reaction cell for use in two different spectroscopic characterization techniques. Firstly, a diffuse reflectance (DR) UV-visible spectroscopic method based on gold surface plasmon resonance (Au SPR) has been developed to characterize oxygen adsorption on gold nanoparticles supported on various metal oxides for understanding activity trends in oxidation with gold catalysts. Also, Drude's free electron model for gold nanoparticles was used to derive a simple correlation between Au SPR and charge transfer from/to gold (a surrogate for adsorbed oxygen) during oxygen adsorption and titration with hydrogen. Additionally, experimental evidence for the preferential adsorption of oxygen on all supports at the gold-support perimeter (from Au SPR) and adsorption of CO on all surface gold atoms (from TOF and Au site statistic trends) was provided.

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Friday, May 3rd
Starts at 8:30am
CEBC, Building A, Conference Room

Committee Chair:
Prof. Juan Bravo Suarez

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Abstract, cont.

A more recent approach to detect surface reacting species has been the combination of in situ/operando spectroscopies and (e.g., concentration, temperature, pressure, etc) modulation excitation (ME) coupled with phase sensitive detection (PSD) analysis to enhance the spectra signal-to-noise ratio of reacting species while avoiding the presence of spectator species. Here, in situ/operando Modulation Excitation-Phase Sensitive Detection-Diffuse Reflectance Fourier Transform Spectroscopy (ME-PSD-DRIFTS) has been used to study the enhanced hydrophobic properties of the Co-Al_2O_3 catalysts during ethanol dehydration. It has been found that the Co-Al_2O_3 catalyst, under identical reaction conditions, could achieve similar ethanol conversion and ethylene selectivity to ethylene at lower temperatures than the original γ-Al_2O_3 support. Analysis of apparent activation energies contributions and water co-feeding tests indicated that the Co-Al_2O_3 was less inhibited by water and that water dimers and trimers were making this catalyst less propense to water inhibition at low to moderate temperatures, allowing more active sites for reaction not accessible in the parent γ-Al_2O_3. Additionally, evidence has also been presented from in situ ME-PSD-DRIFTS for the participation of adsorbed ethanol and ethoxide species as well as terminal and bridging hydroxyls bonded to octahedral and tetrahedral Al on Al_2O_3 (100) and (110) facets as likely reaction intermediates in the conversion of ethanol to diethyl ether and ethylene.