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Preface

This special issue is based on papers presented at the symposium "Spectroscopic Techniques to Elucidate Reaction Mechanism and Structure–Activity Relationships" at the 241st ACS National Meeting in 2011. The symposium focused on advances and new developments of "in situ" and "ex situ" spectroscopic characterization of catalysts. Topics included in situ and operando spectroscopy of catalytic materials, molecular imaging, ab initio DFT computation and spectroscopy.

Examples include the use of vibrational spectroscopy to follow the reactions of methanol over Au/CeO_2 [1], formic acid over TiO_2 (1 0 1) anatase single crystal [2] and ethanol over Au/TiO_2 (anatase) [3]. Over Au/CeO_2 details of methanol oxidation to CO_2 were conducted using IR and on-line mass spectroscopy in which the conversion oscillations observed during the operando analysis were related to local heating effects arising from the IR irradiation of the sample [1]. The kinetic approach also allowed the determination of a zero partial order for methanol associated with a high catalyst surface coverage at steady state. A global kinetic modeling of the reaction found that formate decomposition is the rate-determining step. In related work, the reaction of formate was conducted for the first time using RAIRS over TiO_2 (1 0 1) anatase single crystal [2]. In this work the room-temperature adsorption of formic acid was found to be dissociative (as in the case of powder) yielding two different types of formate species; a mono-dentate formate and a bi-dentate formate; the latter is identified as residing at surface O vacancy sites with one oxygen atom bound to a five-fold coordinated titanium cation and the second to an oxygen defect site. The surface reactions of ethanol over TiO_2 and Au/TiO_2 anatase nano-particle catalysts were investigated by TPD and IR spectroscopy [3]. During ethanol TPD the main desorption product was ethylene, while the main desorption product over Au/TiO_2 was benzene. Infrared spectroscopy indicated that at room temperature both ethanol and ethoxide species are present with the former disappearing faster than the latter. Based on the detailed spectroscopic studies a scheme for the formation of the reaction products on TiO_2 and Au/TiO_2 is proposed in which benzene is formed on Au/TiO_2 by successive condensation reactions.

A detailed imaging study of the interaction of O_2 with TiO_2 (1 1 0) rutile (the most commonly studied TiO_2 surface) by STM, TPD and photoelectron spectroscopy (PES) found that the interaction of O_2 with TiO_2 (1 1 0) depends strongly on the reduction state of the TiO_2 (1 1 0) crystal [4]; for example the energy barrier for the non-vacancy-assisted, O_2 dissociation channel decreases with increasing crystal reduction.

In situ EPR spectroscopy at cryogenic temperatures was used to study paramagnetic products formed when titania photocatalysts are irradiated with UV–visible light in the presence of reactant molecules [5]. Upon irradiation in vacuum with high photon fluxes, in the absence of reactants, EPR signals of trapped electrons (Ti^{3+}) are enhanced dramatically when irradiation is stopped. This process was found to be reversible on restoring the irradiation, and is attributed to a trapping of EPR invisible conduction band electrons once irradiation is stopped. The trapped electrons are excited back into the conduction band when irradiation is resumed. In the presence of adsorbed organic compounds methyl radicals were formed by attack of valence band holes on adsorbed acetic acid. These valence band holes are also able to cleave carbon—silicon bonds, forming methyl radicals from tetramethylsilane.

The mechanism of formation of an Au thin-film electrode made by electroless deposition for in situ electrochemical (EC) attenuated-total-reflection surface enhanced infrared adsorption spectroscopy (ATR-SEIRAS) was studied [6]. It is reported that square-wave treatment of the Au film led to significant surface reconstruction and greatly enhanced oxygen reduction reaction (ORR) activity. This was attributed to the reconstructed sites that could better stabilize the adsorbed ORR intermediates, facilitating the reaction.

In situ NEXAFS spectroscopy and ambient pressure XPS were performed to monitor the oxidation state and structure of CoPt nanoparticles for CO oxidation reaction [7]. Turn over frequency reaction data were correlated with the catalyst oxidation states and structures and results indicated that the chemical state and structure changes of the CoPt nanoparticles during CO oxidation are important factors in determining the rate of the reaction.

The reduction behavior of Cu/SiO_2, Co/SiO_2, and bimetallic CuCo/SiO_2 catalysts was studied by TPR, in situ XRD and XANES [8]. In the case of Cu/SiO_2, a two step reduction process, CuO to Cu_2O to Cu, occurred; the addition of cobalt resulted in formation of an amorphous fraction of CuO that was easily reduced to Cu. Cobalt addition also prevented formation of the less reducible form of Cu_2O. Interestingly the addition of copper to Co/SiO_2 increased the reducibility of Co_3O_4.

Finally, the papers published here include review article on experimental XRPD, EXAFS, Raman, IR, micro-calorimetric data on the adsorption of small molecules like H_2O, NO, and CO on MOF CPO-27-Ni [9]. The review is complemented by a computational study performed at the B3LYP-D*/TZVP level of theory. From both experimental and theoretical results, trends in the framework distances and frequency shifts as a function of the adsorption energy of these different probe molecules are analyzed.

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