ABSTRACT

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Title: Electronic Modification of Platinum and Palladium Alloy Catalysts and the Consequences for Dehydrogenation Selectivity
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Dehydrogenation is the catalytic process of removing hydrogen from a saturated hydrocarbon to produce an olefin. Olefins are important feedstocks for the petrochemical industry and can potentially be used to produce fuels through oligomerization. Alloys containing an active metal such as platinum and palladium and a non-catalytic metal offer improved selectivity towards the olefin. This body of work seeks to further the understanding of how heteroatomic bonds in alloys change the rate and selectivity of alloy catalysts used for dehydrogenation.

In the first study, a series of Pt-V bimetallic catalysts are synthesized, which are highly selective propane dehydrogenation catalysts. The bimetallic nature of the nanoparticles was verified by in-situ XAS and the formation of the Pt3V alloy phase was shown by in-situ synchrotron XRD. A reduction-oxidation difference XAS method was used to examine the surface stoichiometry and found that a shell layer of the alloy phase forms when the particles are platinum rich. Electronic modification of Pt was studied by Pt L3 edge XANES, XPS, RIXS and DFT. The spectral changes observed were shown to be due to changes in the energy of the filled and unfilled 5d density of states, and not due to electron transfer. The electronic modifications cause a weakening of adsorbate binding and destabilization of deeply dehydrogenated hydrocarbons, which contributes to the dehydrogenation selectivity.

In the second study, alloys between palladium and five different promoters were synthesized and tested as propane dehydrogenation catalysts. The structure of the alloy catalysts was characterized by in-situ XAS and in-situ synchrotron XRD. Zinc and indium form alloy structures with site isolated palladium, while gallium, iron and manganese do not. All of the alloys have improved propane dehydrogenation selectivity compared to monometallic palladium. The propylene production turnover rate of the alloys increased by almost an order of magnitude compared to monometallic Pd, but among the alloys the turnover rates only varied by a factor of

two despite the different structures and electronic modifications inherent to each phase. The site isolated alloys had higher propylene selectivity than those that were not site isolated. The site isolated alloys showed stronger electronic modification: both in binding strengths and in Pd pDOS by DFT than did the non-site isolated alloys. The commonly used computational selectivity descriptor for dehydrogenation, which is the difference in energy between alkene desorption and alkene C-H bond activation energy correctly predicts that the site isolated alloys will have high selectivity but shows weaker trends for alloys without site isolation. A modified selectivity descriptor, involving the C-C bond breaking barrier in the adsorbed alkyne more accurately reflects the high selectivity of the non-site isolated alloys.

In a third study, resonant inelastic X-ray scattering (RIXS) and x-ray photoelectron spectroscopy (XPS) are used to examine trends in the electronic modification of platinum alloys with transition metal and post transition metal promoters. All alloys show an increase in the energy transfer maximum, showing that alloying modifies energy the filled and unfilled density of states. The increase in the energy transfer maximum in platinum alloys with 3d metals gets larger for early transition metals, which by DFT show larger shifts in the d-band center. The post transition elements show larger shifts than to the transition elements, partially due to the lack of orbital overlap between the valence p orbitals and Pt 5d orbitals. Platinum has the same number of valence d electrons regardless of promoter or structure, and redistribution of the 5d electron energy brought about by heteroatomic bonds leads to the observed electronic modifications. The positive binding energy shifts measured by XPS reflect these energy changes, which occur due to changes in the Fermi energy of the alloy, initial state effects and intra and extra atomic relaxation (final state effects). The calculated initial state effect shift is correlated to descriptors of the valence d band, such as the d band center.