Determination of the d-Band Center of Bimetallic Catalysts using XPS

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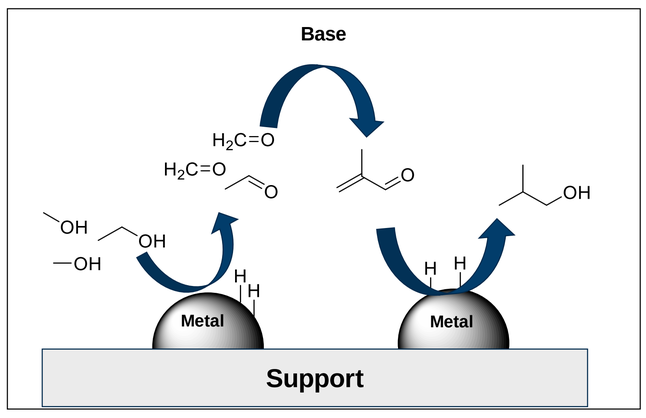
Background

Renewable higher alcohols, especially iso-butanol, are being studied as a promising alternative fuel for transportation. It can be produced from green methanol and ethanol through methylation [1,2]. It has been observed that the catalytic activity of a metal catalyst is strongly correlated with the position of its d-band center [3]. By adjusting catalyst composition, the adsorption strength of reactants can be modified, impacting reaction rates [4]. X-Ray Photoelectron Spectroscopy helps determine d-band center values of catalysts. This information aids in designing efficient catalysts for iso-butanol synthesis.

Objective

- Iso-butanol synthesis via methylation of ethanol on heterogeneous transition metal catalysts.

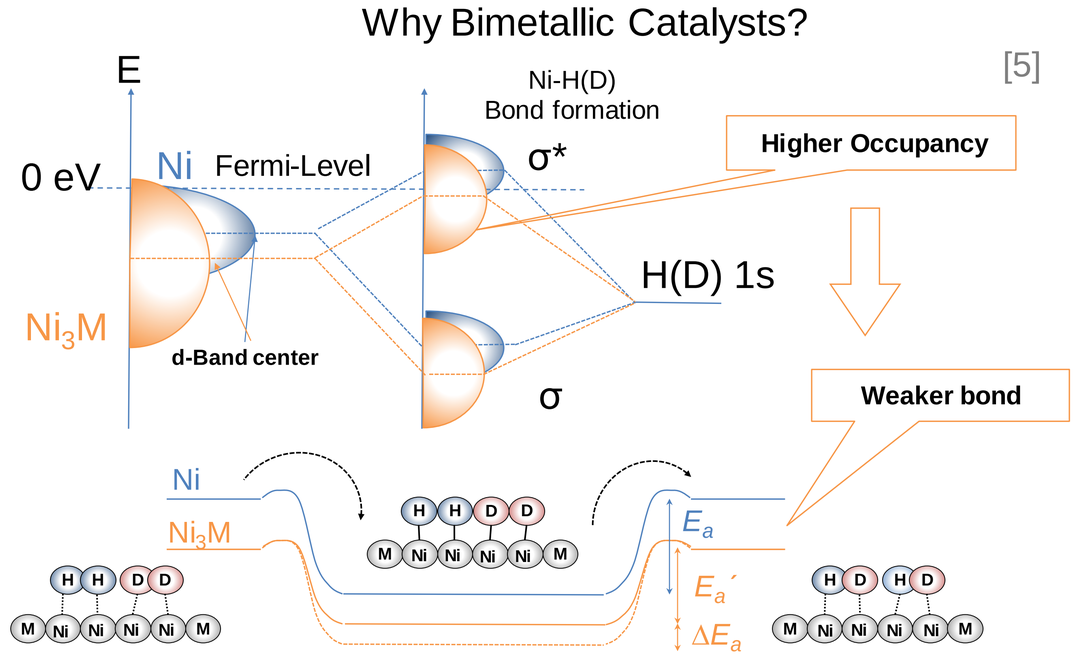


Theory: d-band center effect on catalytic activity

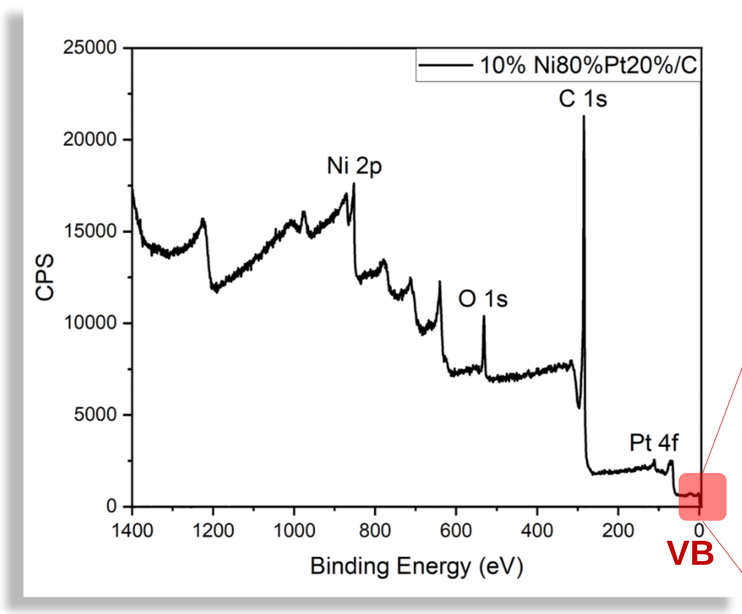
- D-band center position - center of gravity of d-orbital in transition metals - in relation to the Fermi-Energy is connected to the strength of the transition metal-adsorbate interaction.
- Interaction of adsorbate with d states will lead to generation of bonding and antibonding states.

Shift in the position of d-band center (Up/Down):
- Higher/Lower antibonding states energy
- Lower/Higher antibonding states occupancy
- Strengthen/Weaken surface-adsorbate interaction
- More/Fewer activated molecules for reaction

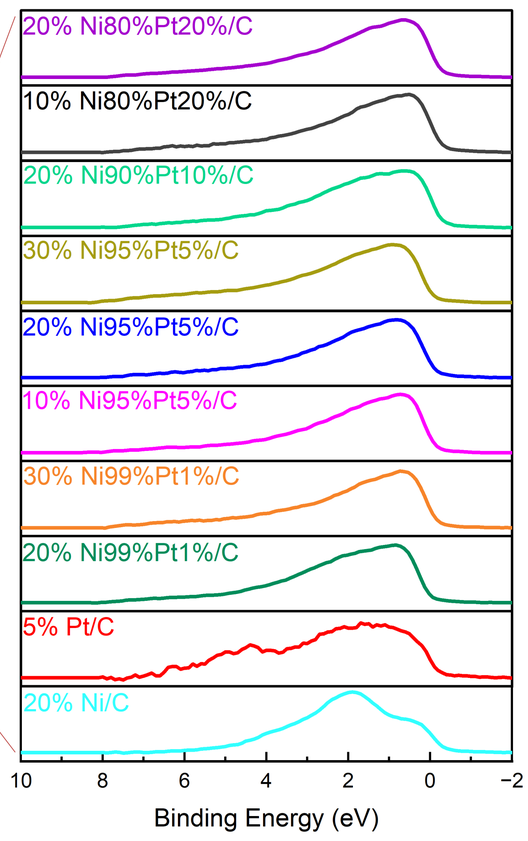
Why Bimetallic Catalysts? [5]



Determination of d-band center of NiPt/C Catalysts



Monochromatized Al kα XPS survey Spectra of 10% weight loading on Ni80%Pt20%/C reduced (H_2 flow for 1 h at 250°) catalyst



Experimental XPS valence band spectra of different NiPt/C catalysts after subtraction of Shirley background

Catalysts d-band Centers (eV) derived from XPS

Catalyst composition	d-band center values
20% Ni80Pt20/C	-2.03
10% Ni80Pt20/C	-2.02
20% Ni90Pt10/C	-2.04
30% Ni95Pt5/C	-2.38
20% Ni95Pt5/C	-2.29
10% Ni95Pt5/C	-2.13
30% Ni99Pt1/C	-2.15
20% Ni99Pt1/C	-2.27
5% Pt/C	-2.54
20% Ni/C	-2.12

- D-band centers derived from weighted average energy of the VBs. For accurate comparison, the upper level of integration of background subtraction is fixed at 10 eV.
- Small introduction of Pt to the catalysts, results in observable differences in geometry of VBs and values of d-band centers.
- Comparable d-band center values to literature.
- Further experiments will include other bimetallic compositions to investigate the correlation to their d-band centers with the catalytic activity.

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[2] Pasel, J. Catalysts 2020, 10 (10), 1151
[3] Häusler, J. et al. Elucidating the Influence of the d-Band Center on the Synthesis of Isobutanol. Catalysts
[4] Hammer, B.; Nørskov, J.K. Theoretical surface science and catalysis—calculations and concepts. In Impact of Surface Science on Catalysis; Gates, B.C., Ed.; Academic Press: San Diego, CA, USA, 2000; pp. 71–129. ISBN 9780120078455.
[5] S. Furukawa, K. Ehara, K. Ozawa, T. Komatsu; A study on the hydrogen activation properties of Ni-based intermetallic: a relationship between reactivity and the electronic state. Phys Chem. Chem. Phys, 2014, 16, 19828-19831