

Metallic Cobalt to Spinel Co_3O_4 : Electronic Structure Evolution by Near-Ambient Pressure Photoelectron Spectroscopy

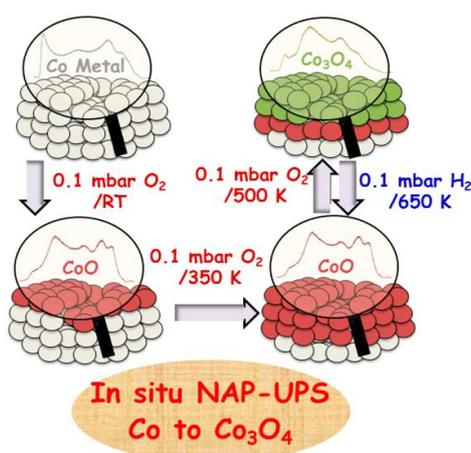
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Abstract:

In the present study, valence band (VB) and core level photoelectron spectroscopy was carried out to investigate the electronic structural changes from polycrystalline Co to spinel Co_3O_4 , via CoO at near ambient pressures ((NAP) ~ 0.1 mbar).¹ O_2 -Co and H_2 -CoOx gas-solid oxidative and reductive interactions, respectively, has been explored with UV photons (He-I) or low kinetic energy electrons (≤ 16 eV) at NAP conditions.² Typical VB features of Co metal, CoO, Co_3O_4 and a mixed phase between any two adjacent features were observed and well corroborated with core level changes. Very significant and characteristic changes were observed with Co 3d features in the VB for each stage from Co oxidation to Co_3O_4 as well as Co_3O_4 reduction to CoO. Co_3O_4 and CoO can be reversibly obtained by alternating the conditions between 0.1 mbar $\text{H}_2/650$ K and 0.1 mbar O_2 at 400 K, respectively. A meaningful correlation is observed between the changes in work function with cation oxidation state; small changes in the stoichiometry can strongly influence the shift in Fermi level and changes in work function under NAP conditions.³ Reversible work function changes are observed between oxidation and reduction conditions. While O 2p derived feature for CoOx was observed at a constant BE (~ 5 eV) throughout the redox conditions, Co 3d band and molecular oxygen or hydrogen vibration feature shifts significantly underscoring the physicochemical changes, such as charge transfer energy and hence changes in satellite intensity. The peak close to E_F originated from the $3d^6L$ final state of the octahedral Co^{3+} 3d band of Co_3O_4 . Present findings have significant relevance to heterogeneous catalysis, as Co and cobalt oxides are important for number of reactions.



References:

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- [3] K.P. Reddy et al., J. Phys. Chem. C. **121**, 21472 (2017).