Organic Ligand-Mediated Electronic Modification of Au/TiO_2 and its Impact on H_2 Adsorption Properties

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Catalytic H_2 activation is crucial in energy storage[1], hydrogenation[2], dehydrogenation[3], hydrodesulfurization[4], methanol synthesis[5], water gas shift reactions[6], and several other transformations. Most well-known hydrogenation catalysts (e.g., Pd, Pt, Ir) exhibit strong H_2 adsorption activity through dissociative chemisorption, whereas H_2 adsorption on extended Au surfaces is thermodynamically unfavorable.[7] In the case of Au/TiO_2, H_2 adsorbs weakly through a quasi-heterolytic mechanism at the metal-support interface (MSI), followed by rapid Au-H deprotonation resulting in weakly coupled proton-electron pairs on TiO_2 where the proton is on hydroxyls and electrons located in the conduction band edge.[8] This weak, fast, and reversible H_2 adsorption on Au/TiO_2 gives a rare opportunity to probe the kinetics and thermodynamics of H_2 adsorption and activation using *in-situ* FTIR and chemisorption. The fundamentals of H_2 activation on Au/TiO_2 have received less attention and are poorly understood despite its significance. Herein, we investigate the electronic effects caused by modifying Au/TiO_2 using PPh_3 ligands on the kinetics and thermodynamics of H_2 adsorption and activation. This project can give a clear idea about the preferred electronic distribution in the presence of electron-donating PPh_3 on Au/TiO_2 and its impact on the H_2 adsorption properties. PPh_3 modification was done using a solution adsorption method probed using UV-Vis absorbance spectroscopy. The UV-Vis absorbance and ^{31}P NMR data suggest that PPh_3 is predominantly absorbed on TiO_2. The preliminary H_2 adsorption studies delineate that the electron density from PPh_3 is potentially localized in the conduction band of TiO_2 and acts to destabilize the electrons from H_2 adsorption rather than increasing the basicity of support hydroxyls and stabilizing the protons from activated H_2. This result provides valuable insights into the behavior of Au/TiO_2 under deliberate electronic perturbations, and it can be leveraged to engineer catalysts for enhanced H_2 adsorption activity by tailoring the electronic and support environment of Au/TiO_2.

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