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Reaction between nickel hydroxide and cerium(IV) ammonium nitrate in aqueous solution

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Cerium(IV) ammonium nitrate (CAN) has been extensively used as a sacrificial oxidant to study water-oxidation catalysts (WOCs). Although nickel hydroxide has been extensively investigated as WOCs, water-oxidation reaction (WOR), and mechanistic studies in the presence of CAN and nickel hydroxide were rarely performed. Herein, using in situ Raman spectroscopy, in situ X-ray absorption spectroscopy, and in situ electron paramagnetic resonance, WOR in the presence of CAN and β-$Ni(OH)_2$ was investigated. As a WOR mechanism, it is proposed that β-$Ni(OH)_2$ in the presence of CAN is oxidized to α-NiO(OH). α-NiO(OH) in the presence of acidic conditions evolves oxygen and is reduced to Ni(II). In other words, the role of β-$Ni(OH)_2$ is the storage of four oxidizing equivalents by CAN, and then a four-electron reaction could result in WOR with low activation energy. In contrast to β-$Ni(OH)_2$, $Ni(OH_2)_6^{2+}$ (aq) could not be oxidized to α-NiO(OH).

Keywords: Cerium(IV) Ammonium Nitrate, Mechanism, Nickel Hydroxide, Oxygen, Water-oxidation Reaction

References

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