

SURFACE SCIENCE STUDIES OF Li AND Co₃O₄(111) THIN FILMS

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INTRODUCTION

Over the past decades, cobalt oxides have served as inexpensive key materials for many applications. These range from heterogeneous catalysis of important oxidizing reactions (e.g. low-temperature CO oxidation^[1, 2], preferential oxidation of CO (PROX)^[3-5], Ostwald synthesis of nitric acid by oxidation of ammonia^[6], and oxidation of hydrocarbons^[1, 7]), to the Fischer-Tropsch synthesis of hydrocarbons and liquid fuels^[8], and the conversion of volatile organic compounds (VCOs)^[9]. Recently, Co₃O₄ has also been investigated as potential anode material for Li ion batteries (LIBs)^[10, 11], featuring high theoretical discharge capacities. However, the formation of a solid electrolyte interface (SEI) competes with reversible Li⁺ ion intercalation and thus reduces the capacity of LIBs^[12]. A similar behavior is observed in solid-state batteries where metallic Li anodes are used.

EXPERIMENTAL

The most effective approach to explain and improve the functionality of cobalt oxides is to conduct experiments at a microscopic or even atomic level. This can be achieved by preparation and study of model-systems. Therefore, Co₃O₄ and Li thin films were prepared by physical vapor deposition (PVD) under ultrahigh vacuum (UHV) conditions. Film growth was monitored visually in real-time using low energy electron microscopy (LEEM). Afterwards, thin film characterization was carried out by X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and temperature-programmed desorption (TPD).

RESULTS AND CONCLUSION

The catalytic activity of Co₃O₄(111) thin films was investigated under working conditions using CO oxidation as test reaction. Experiments were performed within a flow reactor supplying a stoichiometric mixture of reactants (CO:O₂ = 2:1) at mbar pressure while the catalyst was heated stepwise over a wide temperature range. Product (CO₂) formation was observed *via* mass spectrometer (MS), starting at roughly 200 °C, which agrees well with previous results reported in the literature^[13]. Regardless of morphology (cobalt oxide thin films, powders, nanorods), the stability of the Co₃O₄ phase, particularly the presence of Co³⁺ at the surface, defines the temperature window of catalytic activity. Moisture (even trace amounts) in the feed led to a decrease of CO conversion due to water dissociation (formation of hydroxyl groups) and blocking of active sites. However, this deactivation process is reversible upon heating to higher temperatures.

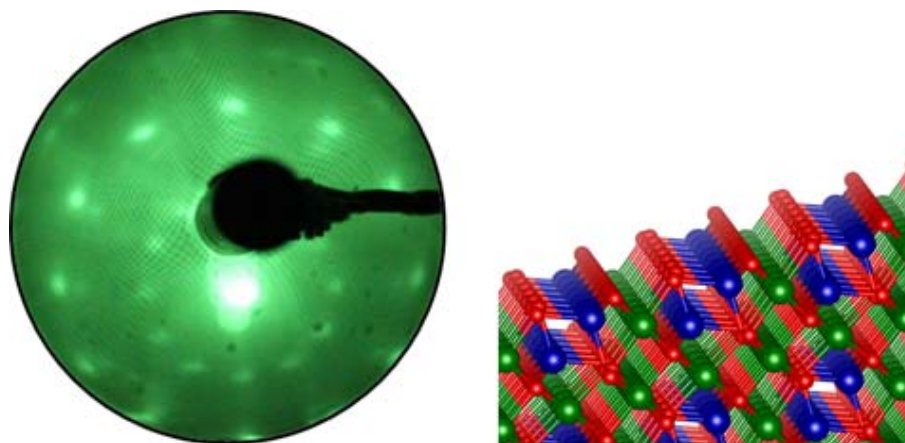


Figure 1: LEED pattern of $\text{Co}_3\text{O}_4(111)$ (left) and surface structure (right; red: O^{2-} , blue: Co^{2+} and green: Co^{3+})

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