

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.

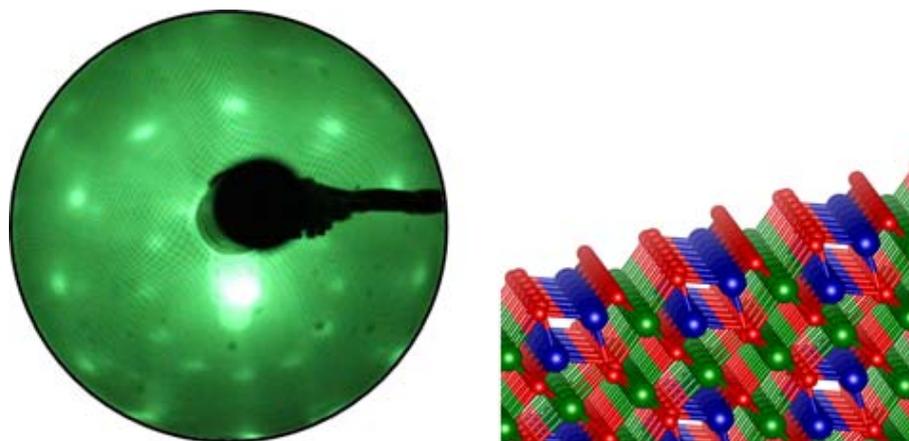


Figure 1: LEED pattern of $\text{Co}_3\text{O}_4(111)$ (left) and surface structure (right; red: O^{2-} , blue: Co^{2+} and green: Co^{3+})

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REFERENCES

- [1] Y. F. Y. Yao, *Journal of Catalysis* 33.1, (1974) 108-122
- [2] X. Xie, Y. Li, Z.-Q. Liu, M. Haruta, W. Shen, W., *Nature*: 458, (2009) 746-749
- [3] G. Marbán, I. López, T. Valdés-Solís, A. B. Fuertes, *International Journal of Hydrogen Energy* 33(22), (2008) 6687-6695
- [4] L. Lukashuk, K. Föttinger, E. Kolar, C. Rameshan, D. Teschner, M. Hävecker, A. Knop-Gericke, N. Yigit, H. Li, E. McDermott, M. Stöger-Pollach, G. Rupprechter, *Journal of Catalysis* 344, (2016) 1-15
- [5] L. Lukashuk, N. Yigit, R. Rameshan, E. Kolar, D. Teschner, M. Hävecker, A. Knop-Gericke, R. Schlögl, K. Föttinger, G. Rupprechter, *ACS Catal* 8(9), (2018), 8630-8641
- [6] K. Shojaee, B. S. Haynes, A. Montoya, *Applied Surface Science* 316, (2014) 355-365
- [7] Z. Tian, N. Bahlawane, F. Qi, K. Kohse-Höinghaus, *Catalysis Communications* 11(2), (2009) 118
- [8] H. Oosterbeek, *Physical Chemistry Chemical Physics* 9(27), (2007) 3570-3576.
- [9] T. Garcia, S. Agouram, J. F. Sanchez-Royo, R. Murillo, A. M. Mastral, A. Aranda, I. Vazquez, A. Dejoz, B. Solsona, *Applied Catalysis a-General* 386 (1-2), (2010) 16-27
- [10] H. C. Liu, S. K. Yen, *Journal of Power Sources* 166(2), (2007) 478-484
- [11] Y. Dou, J. Xu, B. Ruan, Q. Liu, Y. Pan, Z. Sun, S. X. Dou, *Advanced Energy Materials* 6(8), (2016) 1501835
- [12] M. B. Pinson, M. Z. Bazant, *Journal of the Electrochemical Society* 160(2), (2013) A243-A250
- [13] Jansson, J.; Palmqvist, A. E. C.; Fridell, E.; Skoglundh, M.; Osterlund, L.; Thormahlen, P.; Langer, V., On the catalytic activity of Co_3O_4 in low-temperature CO oxidation. *Journal of Catalysis*, 211(2), (2002), 387-397