

SUMMARY OF THE THESIS

The thesis consists of two parts. The first part focuses on synthesis, phase relations, crystal structure and magnetic properties of Ruddlesden-Popper type and partially reduced vacancy ordered phases in the La-Co-O system.^{1-4, a} The second part reports on characterization and phase relations for oxidized and reduced compounds in the Co-Al-O system which are viewed as model compounds for Co/ γ -Al₂O₃ catalysts.⁵ The La-Co-O system is relevant for the Co/ γ -Al₂O₃ catalysts since lanthanum is typically used as promotor.

La-Co-O

Phase relations

Samples with nominal composition LaCoO_{3- δ} (0.00 \leq δ \leq 0.05)¹ and La₄Co₃O_{10+ δ} (-1.00 \leq δ \leq 0.00)⁴ were synthesized by isothermal reduction at 673 K in sealed ampoules using zirconium as reducing agent (oxygen getter). For LaCoO_{3- δ} three distinct phases exist. They can be ascribed to a series of compounds La _{n} Co _{n} O_{3 $n-1$} , namely LaCoO₃ (δ = 0.00, n = ∞), La₃Co₃O₈ (δ = 0.33, n = 3) and La₂Co₂O₅ (δ = 0.50, n = 2). La₂Co₂O₅ oxidizes via La₃Co₃O₈ to LaCoO₃. The oxidation proceeds in air at room-temperature, hence inert handling of specimens were required. For La₄Co₃O_{10+ δ} with -1.00 \leq δ \leq 0.00, two distinct phases La₄Co₃O₉ (δ = -1.00) and La₄Co₃O₁₀ (δ = 0.00) exist, the latter with a considerable range of oxidative non-stoichiometry La₄Co₃O_{10+ δ} , 0.00 \leq δ \leq 0.30.³ The reduced, vacancy ordered phases are metastable, and undergo irreversible decomposition reactions to CoO and the Ruddlesden-Popper type phases La _{$m+1$} Co _{m} O_{3 $m+1$} , m = 1 and 3, upon heating under inert atmosphere. Furthermore, none of the reduced, vacancy ordered phases show indications for any larger non-stoichiometry.

Crystal structure

A high resolution powder X-ray diffraction (ESRF) study of La₄Co₃O_{10+ δ} for δ = 0.00 and 0.30 revealed a slightly monoclinically distorted Ruddlesden-Popper type structure, β \leq 90.260°.³ The monoclinic distortion increases, whereas a volume contraction occurs on increasing oxygen content, δ > 0.00. A structural phase transition, monoclinic to tetragonal, possibly via an intermediate orthorhombic state, occurs at 840 K.

The crystal structures of $\text{La}_3\text{Co}_3\text{O}_8$,¹ $\text{La}_2\text{Co}_2\text{O}_5$,² and $\text{La}_4\text{Co}_3\text{O}_9$ ⁴ are determined on the basis of simultaneous refinements of high resolution powder X-ray diffraction and neutron diffraction data. The low temperature reductions of LaCoO_3 and $\text{La}_4\text{Co}_3\text{O}_{10}$, $T < 900$ K, proceeds topotactically, i.e. the cation sublattice of the precursor is retained, whereas an ordered arrangement of oxygen vacancies forms in the oxygen sublattice. For the three partially reduced phases the oxygen vacancy ordering leads to the formation of "layers" with parallel chains of corner-sharing CoO_4 -tetrahedra connecting perovskite type layers of corner-sharing CoO_6 -octahedra. $\text{La}_2\text{Co}_2\text{O}_5$ adopts the orthorhombic brownmillerite type structure with single perovskite type layers,² whereas $\text{La}_3\text{Co}_3\text{O}_8$ is slightly monoclinically distorted ($\beta = 90.144^\circ$) and consists of double perovskite type layers.¹ For $\text{La}_4\text{Co}_3\text{O}_9$ ordering of oxygen vacancies lead to chains of corner-sharing CoO_4 -tetrahedra within the central part of perovskite type triple-layers.⁴ The top and bottom part of each triple-layer retain the perovskite type arrangement of corner-sharing CoO_6 -octahedra.

Magnetic properties

Magnetic properties were studied by powder neutron diffraction ($T < 300$ K) and magnetic susceptibility measurements. All of the studied La-Co-O phases order antiferromagnetically. The ordering temperatures range from $T_N = 13$ K for $\text{La}_4\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2\text{O}_{10}$ to $T_N = 303$ K for $\text{La}_4\text{Co}^{\text{III}}_3\text{O}_9$, which shows that strong antiferromagnetic coupling between cobalt atoms in these compounds are closely connected to a high content of divalent cobalt.¹ Magnetic structures are described on the basis of powder neutron diffraction data taken at 10 K for $\text{La}_3\text{Co}_3\text{O}_8$,¹ $\text{La}_2\text{Co}_2\text{O}_5$,² and $\text{La}_4\text{Co}_3\text{O}_9$.⁴

Magnetic susceptibility data for $\text{La}_4\text{Co}_3\text{O}_{10+\delta}$ ($\delta \geq 0.00$) indicate a temperature induced change from a lower, possibly via an intermediate, to a higher spin configuration for trivalent cobalt, which is comparable to that earlier described for LaCoO_3 .³ Field dependent magnetic susceptibility is observed for $\delta > 0.00$ for $T < 100$ K. For reduced samples, observation of field dependence is ascribed to microscopic Co(s) precipitates.

Co-Al-O

Spinel type samples $\text{Co}_{3-x}\text{Al}_x\text{O}_4$ ($0.0 \leq x \leq 2.0$) were synthesized and used as reference compounds for characterization of a 20% $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ Fischer-Tropsch catalyst. The unit cell expands smoothly upon increasing aluminium content indicating complete miscibility between CoAl_2O_4 and Co_3O_4 . Temperature programmed reduction (TPR) and isothermal reduction of

$\text{Co}_{3-x}\text{Al}_x\text{O}_4$ show the existence of partially reduced Co^{II} -phases having the NaCl-type structure as determined for $(\text{Co}_{5/6}\text{Al}_{1/6})_{0.92}\text{O}$ on the basis of high resolution powder X-ray and neutron diffraction data. Comparative TPR, X-ray diffraction and magnetic susceptibility measurements for the model compounds $\text{Co}_{3-x}\text{Al}_x\text{O}_{4-\delta}$ and the 20% $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ catalyst indicate for the oxidized catalyst the presence of Co_3O_4 supported on $\gamma\text{-Al}_2\text{O}_3$ and a mixed Co/Al-oxide phase, probably existing as an interface layer of $\text{Co}_{3-x}\text{Al}_x\text{O}_4$ with $x \approx 0.5$. The activated catalyst obtained on reduction at 573 K consists of fine particles of ferromagnetic cobalt (*fcc*) and a partially reduced, NaCl-type phase $(\text{Co}_{0.88}\text{Al}_{0.08})\text{O}$ supported on $\gamma\text{-Al}_2\text{O}_3$.