Reducibility of $LaNi_xCo_{1-x}O_3$ and $LaFe_xCo_{1-x}O_3$ Perovskites ($0 \leq x \leq 0.5$)

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Nickel and iron substituted lanthanum cobaltates with perovskite-type structure ($LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$) are considered as promising cathode materials for solid oxide fuel cells, as well as automotive exhaust catalysts. One of the factors determining their performance is the reduction stability at high operating temperatures. The reduction of the perovskites is a complex process involving the formation of oxygen-deficient perovskite-type phases before the final reduction to metal and La_2O_3. Irrespective of the intensive studies devoted to the reducibility of perovskites, the appearance of different intermediate phases at the initial stages of reduction is still under controversial discussions.

The purpose of this contribution is to study in details the reducibility of nickel and iron substituted perovskites. In addition, the effect of the synthesis procedure on the reducibility of the perovskites is also examined. For the preparation of $LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$ with $0 \leq x \leq 0.5$, two methods were used: (i) thermal decomposition of La-Co-Ni/Fe citrates obtained by freeze-drying of the corresponding solutions, and (ii) the method of Pechini. Both methods allow preparing between 600 and 900 ^oC well-crystallized $LaCo_{1-y}Ni_yO_3$ and $LaCo_{1-x}Fe_xO_3$ with rhombohedrally distorted crystal structure. The reducibility of the perovskites was tested by thermal programmed reduction with hydrogen (TPR). The products of the partial and complete reduction were determined by *ex-situ* XRD experiments.

The complete reduction of $LaCo_{1-x}Ni_xO_3$ with H_2 proceeds to Co/Ni metals and La_2O_3. Both the Ni content and the synthesis procedure affect the formation of intermediate reduction products. For the Ni-rich perovskites ($x>0.1$) annealed at 900 ^oC, the reduction proceeds via the formation of Brownmillerite-type phases (Ni substituted $La_nCo_nO_{3n-1}$), while for the perovskites obtained at low temperatures the reduction process is more complex and includes the formation of both oxygen-deficient perovskite-type oxides and transition metal. The more non-stoichiometric $LaCo_{1-x}Ni_xO_3$ in respect of oxygen, the easier the Brownmillerite type-phases are stabilized as intermediate products. The loosely bonded nanometric particles and the inhomogeneous distribution of Ni and Co ions favour the one-step reduction of M^{3+} to M^0.

The interaction of $LaCo_{1-x}Fe_xO_3$ with H_2 is not complete up to 700 ^oC. The reaction proceeds by preferential oxidation of Co^{3+} to Co^{2+} without affecting the Fe^{3+} ions. The reduction of $LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$ is less sensitive towards the synthesis procedure as compared to unsubstituted $LaCoO_3$. Iron substituted perovskites display higher reduction stability.

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