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## Methane oxidation over A-site ordered and disordered $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ perovskites†

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A tetragonal phase $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ with ordered $Gd^{3+}/Sr^{2+}$ ions and oxygen vacancy sites is found to be about five times less active in the reaction of methane combustion than a quenched cubic perovskite phase with randomly distributed (disordered) $Gd^{3+}/Sr^{2+}$ ions over the A-sites of the crystal lattice.

Substituted rare-earth perovskites with the general formula $A_xA'_{(1-x)}B_yB'_{(1-y)}O_3$ (A – rare-earth; A′ – Ca, Sr, Ba; B, B′– Mn, Co, Fe, Ni) display a wide variety of fascinating electric, magnetic and optical properties.[1] They are also particularly promising for a number of catalytic applications: total and partial oxidation of hydrocarbons,[2,3] as oxygen conducting media for catalytic membrane reactors,[5] CO and hydrogen generation,[4] electro-, photocatalysis and fuel cells.[6,7]

From a crystallochemical viewpoint, the perovskite structure allows a large number of ionic substitutions to form new compounds as well as solid solutions amongst the various oxide or complex oxide compositions. Such substitutions may result in the formation of either A/B-site ordered or completely/ partially disordered states giving rise to specific properties not inherent to normal unsubstituted perovskites. In particular, lead-based complex perovskites belong to a special family of substituted materials (called "relaxors") which have extraordinarily high dielectric constants due to the formation of nanoscale ordered regions in a disordered matrix.[8] There are numerous papers considering the interrelation between the cation order–disorder phenomena and physico-chemical properties of solids,[9] however, to the best of our knowledge, there have been no reports so far on correlations between the A/B-site ion ordering and catalytic performance of perovskites. Herein, we report for the

first time the comparison of catalytic properties of A-site ordered and disordered rare-earth cobaltates in the reaction of methane oxidation.

It is known, that single-phase rare-earth cobaltates $Ln_{1-x}Sr_x-CoO_{3-\delta}$ have a modulated tetragonal perovskite-based superstructure for rare-earth ions smaller than $Nd^{3+}$ (Ln = $Sm^{3+}$–$Yb^{3+}$).[10] Within this structure Ln/Sr ions are located on three different A-sites – A1–A3 (Fig. 1, see the ESI† for details). The relative occupation of these sites in the structure was found to vary as a function of Sr-doping (*i.e.* with *x*) and for the $x \geq 0.8$ compositions, the A2 and A3 sites were found to be fully occupied by $Sr^{2+}$ ions, while the A1 sites were found to contain both $Ln^{3+}$ and $Sr^{2+}$ ions.[10] Based on these data, a sample of $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ with A-site ordered $Gd^{3+}/Sr^{2+}$ ions was prepared by a conventional solid phase ceramic synthesis from $Gd_2O_3$, $Co_3O_4$ and $SrCO_3$ powders at 1200 °C in air with intermediate re-grinding and re-pelleting. The final ceramic particles (size of 100–160 microns) were cooled down from 1200 °C with a cooling rate of 2 °C min$^{-1}$.

An XRD pattern of the sample thus prepared (Fig. S1, ESI†) and denoted as annealed a-$Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ hereafter, corresponded well to the $I4/mmm$ superstructure with ordered Gd/Sr sites.[10] DSC measurements of the sample reveal a reversible

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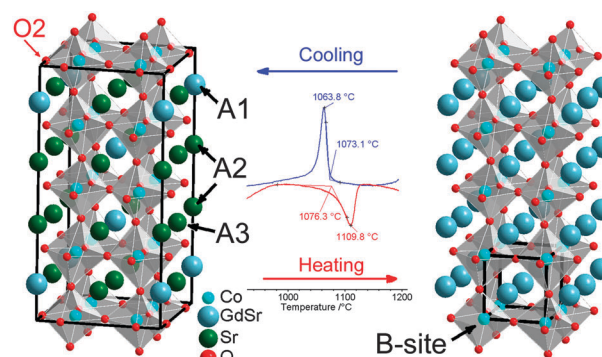
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Fig. 1 DSC curves near the transition and the structure of ordered (left) and disordered (right) $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$. Heating (red) and cooling (blue) ramp rate of 10 °C min$^{-1}$, 20% $O_2$–Ar.
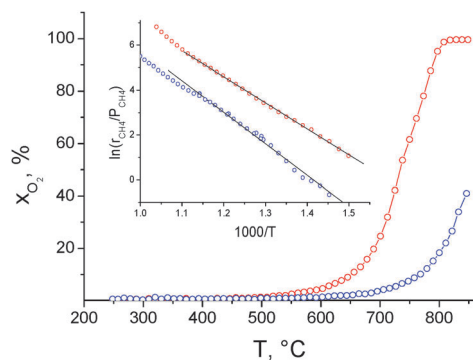
**Fig. 3** Light-off temperature curves for the oxidation of methane over ordered (blue) and disordered (red) $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$. Feed, $CH_4 : O_2 : He = 27 : 13 : 60$. Inset: the Arrhenius plot of the apparent constants of $CH_4$ oxidation.

the annealed $Sr_{0.8}Gd_{0.2}CoO_{2.63}$ agrees with the lower reactivity of this system.

Thus, the A-site ordered and disordered states of the strontium–gadolinium–cobaltates differ in their reducibilities, oxygen stoichiometries and the amount of mobile oxygen evolved under the TPD conditions. Evident distinctions in the catalytic behaviour of these samples are the rates of carbon dioxide formation (at $T < 650\ ^\circ C$) and the selectivity of $C_2$-production, along with the similar trends of the activities on the Arrhenius plot, closely spaced values of $E_a$ and Langmuir adsorption constants $b$ (Table 1).

The observed behaviour agrees with the generally accepted concept of "intrafacial" type of catalytic transformations over perovskites. From a viewpoint of oxygen species participating in catalysis, adsorbed (and/or surface) oxygen and lattice oxygen are supposed to contribute to suprafacial and intrafacial catalysis, respectively. The intrafacial catalysis proceeds preferably at relatively high temperatures, according to the combination of a reduction–oxidation cycle of the catalysts,[3] which seems to be valid for both ordered and disordered samples. In this case, two main factors should be considered to explain the catalytic performance of $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$. These are the rates of the surface re-oxidation (which is directly connected with the oxygen mobility) and the properties of surface oxygen interacting with molecules of methane. The results of $O_2$ TPD (Fig. 2a) and $H_2$ reduction (Fig. S2, ESI†) suggest that the chemical properties of surface oxygen for the ordered and disordered states are not identical but very similar. This assumption agrees with the same type of the transformation kinetics, closely spaced values of the activation energies and Langmuir adsorption constants. Identical chemical compositions of the single-phase perovskites under study allow one to assert that it is the structural peculiarities that are responsible for the activity variations.

Our structural XRD analysis and the literature data[10] show that there is a substantial difference in the oxygen vacancy distributions for the samples under study besides the Sr/Gd ordering. In the A-site ordered structure of $Sr_{0.8}Gd_{0.2}CoO_{2.63}$, the vacancies primarily reside on specific O2 sites (Fig. 1) in the basal planes at $z = 0$ and $1/2$, whereas in the disordered sample they are randomly distributed over all O-sites. Furthermore, the amount of oxygen vacancies in the ordered sample is larger as

revealed by the thermogravimetric reduction (Fig. S1, ESI†) in agreement with the difference in the specific unit cell volumes $V/Z$ of 56.742 and 56.367 $Å^3$ for annealed and quenched $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$, respectively.

The oxygen mobility is known to be one of the most important factors governing the activity of catalysts according to the intrafacial mechanism. It was shown that the catalytic activity in methane oxidation over $La_{1-x}Sr_xCoO_{3-\delta}$ was determined by the mobility of oxygen ions in the structure.[13] The activity of the $LaFeO_{3-\delta}$ phase in $CH_4$ combustion was explained in terms of the catalyst's ability to uphold very large amounts of oxygen in the O-vacancies.[12] The activity of $(La_{1-x}Nd_x)CoO_3$ systems also correlate with the amount of mobile oxygen: the temperature corresponding to the 50% conversion of $CH_4$ increased as a result of a decrease of the amount of adsorbed oxygen.[14]

Theoretical and experimental investigations show that oxygen mobility is tightly coupled with the vacancy distribution. It is known that cation ordering may be accompanied by oxygen/vacancy ordering (*e.g.* in $Ln_{1-x}Sr_xCoO_{3-\delta}$[10] and $(Ba_{0.5}Sr_{0.5})CoO_{2.5}$[17]) and that structures with ordered vacancies are less favourable for ion conduction and oxygen permeability compared to disordered perovskites as shown for Sr–ferrite–titanates,[15] $SrCo_xFe_{1-x}O_{3-\delta}$[16] and (Ba, Sr) cobaltates.[17] Therefore, we may assume that the substantial catalytic activity enhancement of the quenched A-site disordered $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ sample may result from the structure-directed increase in both the amount of mobile oxygen and its mobility in the crystal lattice.

In conclusion, $Gd^{3+}/Sr^{2+}$ ion site ordering in $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ results in the oxygen vacancy ordering coupled with the reduction of the mobile oxygen amount and, in turn, decreases the rate of methane deep oxidation, the effect being also observed for Sr-rich substituted gadolinium cobaltates of other compositions ($x = 0.5, 0.9$). This phenomenon allows tuning of the contribution of the deep oxidation reaction route to the overall conversion without a modification of the chemical composition of the catalyst, at least for intrafacial reactions. The results obtained in this study may serve as a guide for improving the performance of existing catalytic materials and as a tool for developing new ones expanding our knowledge on the structure-reactivity/selectivity relationships.

## Notes and references

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