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

Sergei N. Vereshchagin, *[a] Leonid A. Solovyov, [a] Evgenii V. Rabchevskii, [a] Vyacheslav A. Dudnikov, [b] Sergey G. Ovchinnikov, [b,c] and Alexander G. Anshits[a].

Supplementary information

Experimental

1 Samples preparation

Samples of $Gd_{0.2}Sr_{0.8}CoO_{3-\delta}$ with A-site ordered Gd^{3+}/Sr^{2+} ions were prepared by a conventional solid phase ceramic synthesis from Gd_2O_3 (99.99 %, metal basis, Alfa Aesar), Co_3O_4 (99.7 %) and $SrCO_3$ (99.99 %) powders. Thoroughly weighted amounts of compounds were ground in an agate mortar with ethanol, pressed into pellets and calcined at 1200 °C for 12 h in air with intermediate re-grinding and re-pelleting. The final ceramic pellets were ground to the particle size of 100-160 microns, annealed additionally at 1200 °C in air for 1 h and cooled down with cooling rate of 2 $°C\cdot min^{-1}$.

A sample of quenched $Gd_{0.2}Sr_{0.8}CoO_{3-\delta}$ was prepared from the annealed sample, which was additionally calcined at 1200 °C for 1 h in air and quenched from 1200 °C to room temperature, an estimated ramp rate from 1200 °C to 900 °C was about 30 $°C\cdot s^{-1}$.

To ensure the equilibrium oxygen content for the quenched and annealed $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$, the samples were kept additionally in air at 500 °C for 1 h and cooled down to 200 °C with a ramp rate of 2 $°C\cdot min^{-1}$ prior to catalytic experiments or DSC measurements.

2 Perovskite characterization

2.1 XRD

X-ray powder diffraction data were collected on a PANalytical X'Pert PRO diffractometer equipped with a solid-state detector PIXcel using Fe-filtered CoKα radiation over the 2θ range 10–140°. An Anton Paar HTK 1200N high-temperature camera with the sample rotation and automated alignment was used. Powder samples were prepared by grinding with octane in an agate mortar and packed into a flat sample holder for the diffraction measurements in the Bragg-Brentano geometry. The full-profile crystal structure analysis was done using the Rietveld method with the derivative difference minimization refinement [L. A. Solovyov, J. Appl. Cryst. 37 (2004) 743].

2.2 Oxygen content determination

The oxygen content and non-stoichiometry index δ were calculated using the value of mass loss (Δm, %) measured by the thermogravimetric reduction, assuming that the cobalt is reduced to the metallic state (Eqs. (1),(2))

$$Gd_{0.8}Sr_{0.2}CoO_{3-\delta} + ((3-\delta) - 1.4)\ H_2 = 0.4\ Gd_2O_3 + 0.2\ SrO + Co + ((3-\delta) - 1.4)\ H_2O \qquad (1)$$

$$\delta = 3 - \frac{\dfrac{160.48\cdot\Delta m}{1600} + 1.1}{1 - \dfrac{\Delta m}{100}} \qquad (2)$$

The reduction was performed on a NETZSCH STA 449C analyzer equipped with an Aeolos QMS 403C mass spectrometer. All experiments have been done in a stream of argon with 5% H_2, heating the samples up to 900 °C with a rate of 10 $°C\cdot min^{-1}$. The reduction process was carried out in Al_2O_3 crucibles with percolated lid, a sample mass of 22±0.5 mg, The measurements were carried out with correction for the buoyancy force, i.e. blank experiments (base line) have been performed at the same conditions with empty crucibles.

2.3 Simultaneous thermal analysis

STA experiments were performed on a NETZSCH STA 449C analyzer equipped with an Aeolos QMS 403C mass spectrometer. The measurements were carried out in Pt crucibles under argon flow (0.05 % O_2), a sample mass of 25-30 mg, a ramp rate of 10 $°C\cdot min^{-1}$.

2.4 The specific surface area determination.

The specific surface area of the perovskites (S_{BET}) was determined by physical adsorption of nitrogen at 77 K using a Quantachrom NOVA3200 apparatus and evaluated by the BET equation. The values of S_{BET} for annealed and quenched samples fall into the interval of 0.07-0.1 $m^2\ g^{-1}$.Relatively large uncertainties of the specific surface area determination are caused by the very low absolute values of S_{BET} measured.

2.5 Catalytic activity testing.

Tests for catalytic activity were carried out in a fixed-bed 4 mm i.d. quartz reactor under atmospheric pressure, the catalyst bed containing 100±0.5 mg of a catalyst. An on-line gas chromatograph Agilent 7890A was used to analyze the composition of the feed and the product gases. A mixture of CH_4, O_2, and helium (balance) was fed at 200 °C to the reactor at a flow rate of 25 cm^3min^{-1}, all gases were purified separately with suitable filters and their flows were regulated by electronic mass flow controllers. The sample was then heated at a programmed rate of 1 $°C\cdot min^{-1}$. The catalytic runs were repeated two times under increasing and decreasing temperature, the catalytic activity being reproducible within an experimental error.

A rate of methane transformation was calculated at oxygen conversions less than 5 % according to the equation (3). The rate was measured as a function of methane and oxygen partial pressure under experimental conditions of $0.15<P_{CH4}<0.82$ atm, $0.05<P_{O2}<0.30$ atm. To calculate parameters of a kinetic Equation (4) a set of experiments was performed at 500 °C.

$$r_{CH_4} = \frac{10^{-3}F}{0.082\cdot 298}\frac{C_{CO_2}}{100}\frac{1}{m} \qquad (3)$$

$$r_{CH_4} = \frac{kP_{CH_4}(K_{O_2}P_{O_2})^{1/2}}{1+(K_{O_2}P_{O_2})^{1/2}} \qquad (4)$$

Where

r_{CH4} - rate of methane conversion, mol $s^{-1}\ g^{-1}$;
F - gas flow, cm^3s^{-1} at 1 atm, 25°C;
C_{CO2} - CO_2 concentration, % vol;
P_{CH4},P_{O2}- partial pressure of methane and oxygen, respectively, atm;
m - mass of a catalyst, g;
K_{O2} - Langmuir adsorption constant, atm^{-1}.

An equation (5) was used to fit experimental data to the model. The parameter estimates (regression coefficients A and b and the estimated confidence limits for *p*-level 0.05 of those estimates were obtained using a non-linear least squares estimation procedure of STATISTICA software package.

$$\frac{r_{CH_4}}{P_{CH_4}} = \frac{AP_{O_2}^{\ 1/2}}{1+bP_{O_2}^{\ 1/2}} \qquad (5)$$

3 The crystal structure of A-site ordered and disordered $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$.

The crystal structure of the synthesized annealed (ordered) perovskite $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ is the same as that of the tetragonal super-structure phases for $Ln_{1-x}Sr_xCo\ O_{3-\delta}$ ($Ln=Sm^{3+}–Yb^{3+}$) with Ln/Sr and oxygen vacancy ordering[1,2]. The difference in the structure between ordered (Fig.S4,a) and disordered (Fig.S4,b) perovskites $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ is a regularity of distribution of cations Gd^{3+} and Sr^{2+} over the respective crystal lattice A-sites, coupled with oxygen vacancies ordering.

In the ***disordered*** $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ all A-sites are equivalent and Gd^{3+} and Sr^{2+} ions are randomly distributed over these sites, which are statistically occupied by either Gd^{3+} or Sr^{2+} (FigS4, b; dark-blue spheres). Oxygen vacancies are randomly distributed over the recpective O-sites.

In the ***ordered*** $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ there are three distinct crystallographic positions which can accommodate Gd^{3+} or Sr^{2+} ions. Two of these A-sites are occupied exclusively by Sr (Fig.S4, a; shown as green spheres) while the remaining site (A1, shown as dark-blue spheres) may contain both $Gd^{3+}$and Sr^{2+} ions. The regular alternations of pure Sr positions in the ordered state are accompanied, as well, by regularities in the distribution of oxygen vacancies and CoO_6 octahedra tilting. The relative occupation of A-sites in the structure was found to vary as a function of Sr-doping (i.e. with x) and it was shown that for $Ln_{0.33}Sr_{0.67}Co\ O_{3-\delta}$ (x=0.67) A1 sites were fully occupied by Ln^{3+} ions[1].

Therefore, for Sr-rich substituted gadolinium cobaltates the observed order-disorder transition is the process of randomization of Gd^{3+} ions and oxygen vacancies from their respective sites. Evidently, that one can expect the maximum effect of the order-disorder transition for the composition in which all A1-sites are occupied by Gd^{3+} ions, and the rest by Sr^{2+} ions. This is the case for $Sr_{0.75}Gd_{0.25}CoO_{3-\delta}$ because the fraction of A1-sites is equal to 0.25. This assumption determines the motivation to chose $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ as a base system to study because the structure of this compound has been completely refined[1] and its composition is close to the optimum value x=0.75.

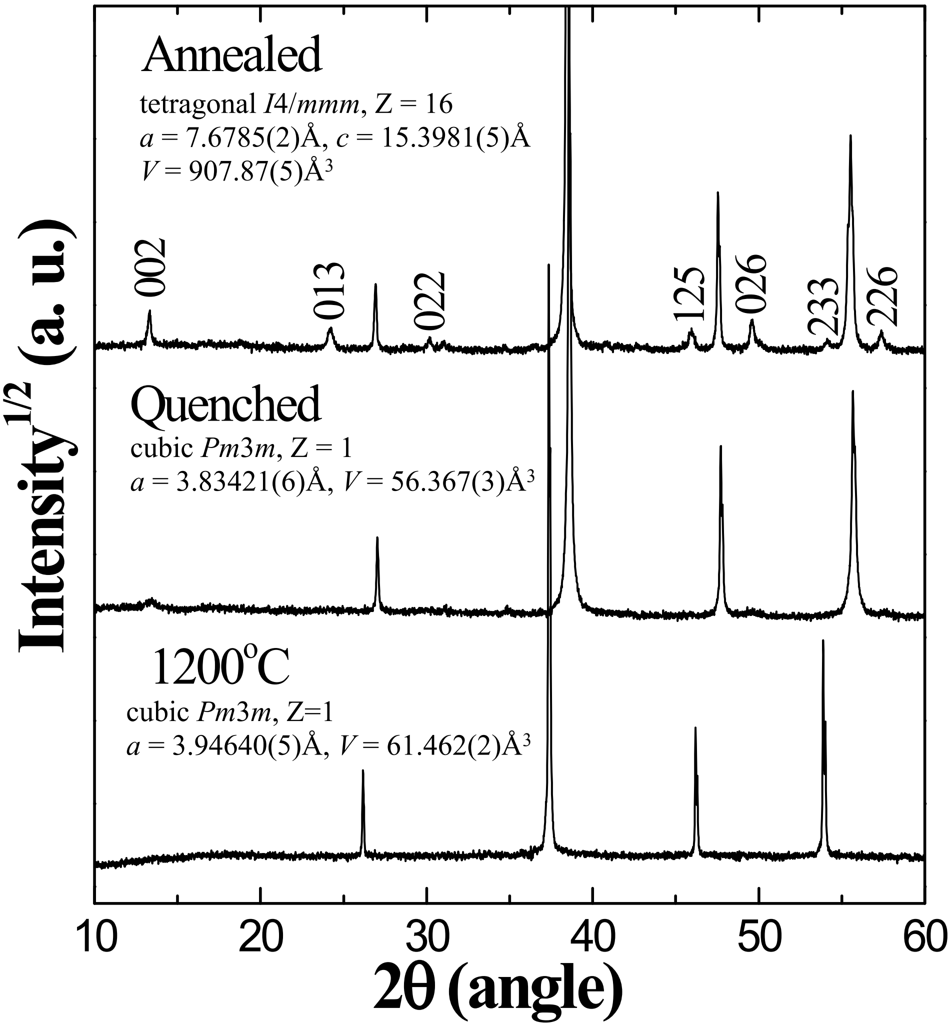

Fig. S1. Characteristic XRD pattern fragments of $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$ in the room-temperature annealed/quenched states and at 1200 °C. Superstructure peaks are indexed. The crystal lattice parameters and unit cell volumes (V) are given in the inserts.

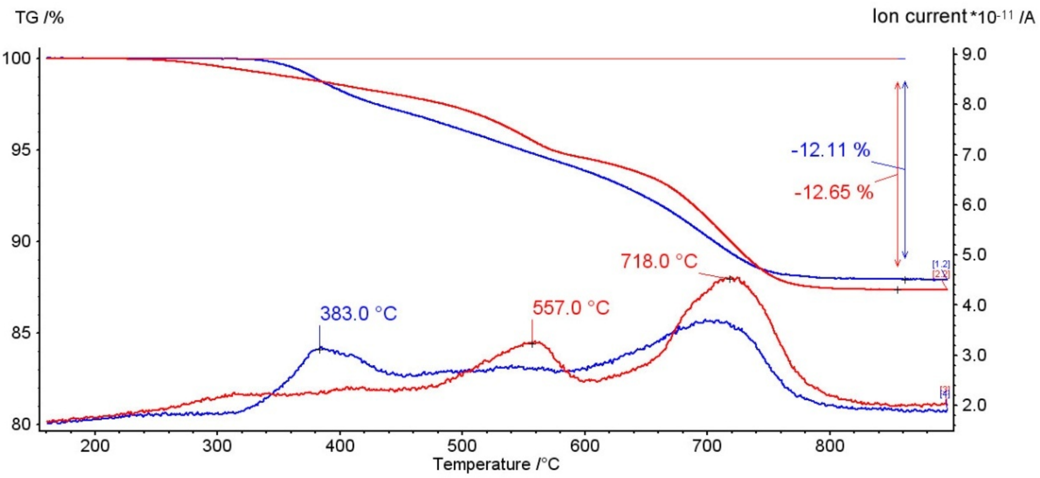

Fig.S2. Thermogravimetric curves of hydrogen reduction of ordered (blue) and disordered (red) $Gd_{0.8}Sr_{0.2}CoO_{3-\delta}$ samples. 5% H_2-Ar, heating rate, 10 °C min^{-1}. The bottom lines show a mass spectrometric signal for water (m/z=18).

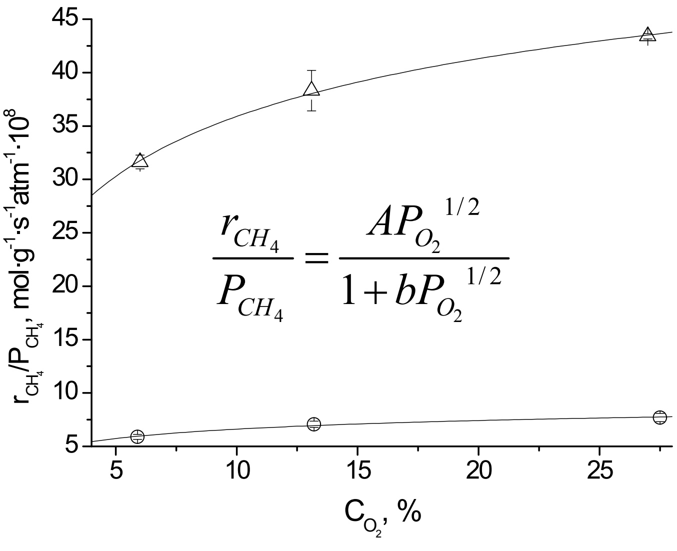

Fig.S3. Experimental (points) and calculated (lines) methane conversion rate as a function of oxygen concentration for annealed (O) and quenched sample (❐). P_{CH4} =27%, He – balance. T = 500 °C.

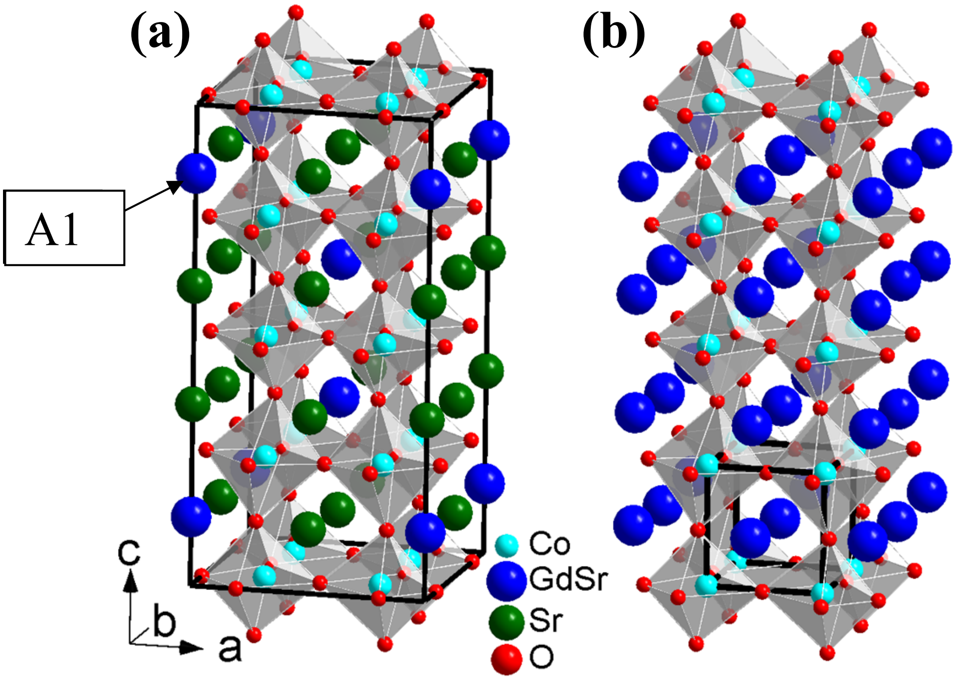

Fig. S4. The refined structure of A-site ordered (a) and disordered (b) perovskites $Sr_{0.8}Gd_{0.2}CoO_{3-\delta}$. The lattice unit cell boundaries are outlined by bold black lines

References

1. *M. James, D. Cassidy, D.J. Goossens, and R.L. Withers, J.Solid State Chem., 177 (2004) 1886–1895*
2. *R.L. Withers, M. James, and D.J. Goossens, J. Solid State Chem., 174 (2003) 198–208*]