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Step response and transient isotopic labelling studies into the mechanism of CO oxidation over $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ perovskite

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ABSTRACT

The mechanism of CO oxidation over $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ perovskites has been studied using step-response analysis. As these materials pair a high catalytic activity with high hydrothermal stability, perovskites are well-known full oxidation catalysts and form a potential alternative to Pt-Rh based three-way catalysts. Transient isothermal reduction and oxidation studies demonstrate the full reversibility of oxygen uptake at temperatures of 473 K and higher. Using isotopically labelled O_2 , the participation of oxygen from the perovskite lattice could be demonstrated. It is proposed that stable species - most likely bidentate carbonates- are retained on the reduced oxide surface. The highly defective perovskite structure enables rapid exchange between oxygen atoms from surface carbonate and perovskite lattice oxygen. CO oxidation towards CO_2 tentatively proceeds through the ER (Eley-Rideal) followed by LH (Langmuir-Hinshelwood) mechanism. In steady state conditions, the formation of CO_2 is most likely through the formation of intermediate carbonate since considerable amounts of $\text{C}^{16}\text{O}^{16}\text{O}$ and $\text{C}^{18}\text{O}^{18}\text{O}$ are formed.

Keywords: $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$, perovskite, reduction, oxidation, labelled oxygen, CO oxidation, transient

1. INTRODUCTION

Perovskite-type oxides (ABO_3) containing rare earth ions and transition metals are of interest for catalytic oxidation and reduction reactions associated with automotive exhaust emission control [1-4]. They have been tested in oxidation of CO and hydrocarbons [5-8], NO_x reduction [9, 10], and in hydrogenation and hydrogenolysis reactions [11]. By partial substitution of A and B ions of the perovskite with others, a wide variety of mixed oxides $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_3$ can be obtained, allowing the systematic modification of the catalytic properties [6, 12].

CO oxidation has been widely used as a model reaction to shed light on the mechanism of full oxidation over perovskite-type oxides. Early studies on the CO oxidation over perovskites were carried out by Parravano [13]. Research was stepped up in recent years [4,5,8,14-17] in view of the potential application as noble metal free automotive catalysts. For a number of perovskite oxides, it has been attempted to correlate the activity in CO oxidation and the electronic state of the transition metal ions as well as the defect chemistry [17, 18]. It has been postulated that the coexistence of A-sites, oxygen vacancies adjacent to a transition metal ion, and altermetal ions of the same metal form the essential structure for catalytic activity. Studies into the mechanism of CO adsorption have been plentiful [14,15,19-22]. Kawai et al. [14] concluded that CO_2 desorption is the rate-determining step of the overall reaction on the surface of BaTiO_3 in the temperature range 353 K – 493 K. Voorhoeve et al. [15] suggested that oxidation of CO over perovskite-type oxides of 3d transition metals is an example of suprafacial catalysis, in which the electronic band structure near the Fermi level is believed to play a key role. Tascón et al. [19] observed that CO and CO_2 adsorb on the same surface O^{2-} sites while oxygen adsorbs on surface metallic ions of the LaCoO_3 .

A clearer picture of the reaction mechanism may be obtained by separately investigating reduction and re-oxidation, using step response analysis. In this way, information is obtained on the elementary steps of a reaction, since the time-resolved observations allow quantitative assessment of the accumulation of species on the surface [23, 24]. In particular, transient studies have found widespread application in “three-way” catalysis, since these automotive catalysts inherently work under dynamic conditions [23-29].

In this work, the interaction of CO and O₂ with La_{0.8}Ce_{0.2}MnO₃ prepared by co-precipitation is studied by step-response to obtain insight into the elementary steps of isothermal reduction/oxidation of this perovskite with CO and O₂, respectively. This study was extended with the use of labelled and unlabelled oxygen, thereby further elucidating the role of lattice oxygen.

2. EXPERIMENTAL

2.1 Catalyst preparation and gases

The following gases were used (all obtained from Praxair): helium (1% Ar in He, 99.999% pure), carbon monoxide (1% CO in He, 99.95%), unlabelled oxygen (1% O₂ in He, 99.5%), labelled oxygen (5% ¹⁸O₂ in He, 95%) and carbon dioxide (1% CO₂ in He, 99.5%). CO was pre-treated first by active carbon at 373 K to trap the formed iron carbonyl, which can cause the deactivation of the catalyst.

La_{0.8}Ce_{0.2}MnO₃ perovskites were prepared from known (niet ‘ the corresponding ‘?) molar ratios of La(NO₃)₃·6H₂O (ACROS, 98+ % pure), Ce(NO₃)₃·6H₂O (ALDRICH, 99 %) and Mn(NO₃)₂·6H₂O (MERCK 99 %) solution [30]. Precipitation was carried out by slowly adding the nitrate solution (0.5 N) together with a NaOH (MERCK >99 %) and H₂O₂ (ANALAR, 30 % w/v H₂O₂) solution (0.5 N) into 600 ml of doubly distilled water at pH = 9.1 and 323 K. The precipitate was subsequently dried overnight at 393 K, powdered, filtered

and then calcined at 1073 K for 6 hours. During calcination the colour of the sample changed from brown to black.

X-ray diffraction patterns (XRD) collected on a CPS120 using a primary monochromator with $2\theta = 5 - 125^\circ$, using $\text{CuK}\alpha$ radiation, confirmed the formation of the perovskite structure. The surface area was determined by nitrogen adsorption at 77 K on a Sorptomatic 1990 (CE Instruments) and evaluated using the BET equation. The average particle size was determined by means of Hg porosimetry on a Carlo Erba Porosimeter 4000.

2.2 Set-up for Transient experiments

The step response set-up is represented schematically in figure 1. The apparatus consists of a gas feed, a reactor and an on-line gas analysis section. The gas feed section equipped with mass flow controllers contains two gas-blending systems to allow the generation of two different feed streams. The step change is carried out through a high-speed chromatographic-type 4-way valve (V_1), driven by helium. For the step response experiments, one feed stream contains 1 vol% CO in helium and the other one comprises 1 vol% O_2 in helium. This valve (V_1) allows one feed stream to be fed to the reactor while the other one is directed towards the vent. The gas stream selected by V_1 is directed toward a 6-way chromatographic valve (V_2). The feed entering valve V_2 can then be switched through the reactor filled with the catalyst bed or to the blank reactor. The blank reactor is used for calibration of mass spectrometer with a mixture of a known composition at the reaction temperature, and also for taking the various background signals in the reaction mixture. The back-pressure controller and a U-tube were used to avoid an overshoot in the desired step function at the time of switch.

The catalyst was placed in a quartz reactor with a 5 mm internal diameter. The length of all tubing connecting V_1 , V_2 and the inlet system (i.e., capillary tube) of the mass

spectrometer must be minimised in order to avoid dispersion effects. For the same reason, the catalyst bed was diluted with two times its weight of glass beads ($d_p = 0.15\text{-}0.18\text{ mm}$). In order to create isothermal operating conditions, an inoxida cylinder was placed around the reactor. The inoxida cylinder contains a thermocouple to monitor the temperature in the furnace.

The product gas was analysed by a quadrupole MS (Balzers, QMG 420). The background signal is subtracted from the obtained MS signal. Also the fragmentation contributions (such as $\text{CO}_2 \rightarrow \text{CO}$) and mass spectrometer sensitivity for the different molecules were taken into account. The corrected data are presented here as molar concentrations.

2.3 Experimental procedures in transient studies

The experiments presented here were carried out in a temperature range of 448 K to 523 K, 1.5 bar total pressure and a total flow rate of $100\text{ ml}\cdot\text{min}^{-1}$. First, the samples were pre-treated in-situ: 100 mg of $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ perovskite diluted with 200 mg of glass beads was heated to 773 K ($10\text{ K}\cdot\text{min}^{-1}$) in a He flow containing 1vol% of O_2 and kept at that temperature for one hour, and subsequently cooled to the reaction temperature. This pre-treatment provided fully oxidised catalysts. Subsequently, these catalysts were flushed with He and subjected to the reaction step sequence (figure 2). Both the reducing and oxidising gas mixture as well as the helium were passed over the catalyst bed for 300 seconds.

The reducing and oxidising feed was calibrated with a calibration gas mixture ($\text{CO}/\text{O}_2/\text{He}$, v/v/v = 1/1/98, Praxair). The amount of CO_2 formed in each step was calculated by integrating the area under the CO_2 production curve. The total amount of $\text{CO} + \text{CO}_2$ (ΣCO_x) adsorbed on the catalyst after either step 1 or 3 was obtained by subtracting the integrated area under the CO and CO_2 response curves from that of the CO feed and 1 vol% CO_2 , respectively. The CO and CO_2 concentration were calibrated against a standard gas

mixture. The amount of adsorbed O₂ after step change 2 and 4 was obtained in a similar way.

In order to check whether the reaction is controlled by external mass transport limitations, the catalyst weight (100mg à 50 mg) and flow rate (100 ml·min⁻¹ à 50 ml·min⁻¹) were varied. As at 523 K the CO conversion remains unaffected, external mass transport limitations are clearly absent (not shown). The reaction order in CO was determined by varying the CO concentration (0.5-1.0-1.5-2.0 vol%) in excess oxygen (3 vol%). Similarly, the reaction order in oxygen was determined by changing the oxygen concentration (0.5-1.0-1.5-2.0 vol%) in 2 vol% CO with helium as balance.

The reduction/oxidation behaviour of this perovskite was also studied by using labelled oxygen at 523 K. Finally, CO oxidation experiments were performed using labelled oxygen at 523 K for a gas mixture of 1 vol% CO, 2 vol% ¹⁸O₂ in He with flow rate of 50 ml·min⁻¹.

3. RESULTS

3.1 Catalyst characterisation

The crystallinity of the prepared sample investigated by XRD shows that cerium is not totally incorporated in the perovskite lattice. A small amount of a separate CeO₂ phase is formed beside the perovskite structure (not shown). The surface area was determined to be 25 m²·g⁻¹. Hg porosimetry showed a broad distribution with sizes between 20 nm and 25 µm, with a very strong contribution of dimensions around 1µm. A fractal-like structure has earlier been observed by SEM (not shown), with particles in the order of 120 nm, which constitute the overall structure. Most clusters are thus likely in the order of 1µm.

3.2 Isothermal reduction and oxidation of La_{0.8}Ce_{0.2}MnO₃

3.2.1 Step 1: reduction with CO

The response of the oxidised $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ perovskite to reducing conditions is investigated by a step change from He to a CO/He mixture. CO_2 is formed instantaneously, the CO_2 production reaching a maximum and then slowly declining to zero (figure 3a). The CO concentration increases from zero to the feed CO concentration (figure 3b). The amounts of CO consumed and CO_2 produced are listed in table 1. Notice that not all CO consumed is converted into CO_2 , indicating that some CO has been retained on the catalyst surface, either in the form of adsorbed CO or CO_2 , or in the form of carbonates. When the gas mixture is switched back to He, neither CO nor CO_2 are seen to desorb. The retained CO leaves the oxide surface as CO_2 during heating in helium in a temperature range of 500 K – 700 K, suggesting that CO has become strongly bound to the catalyst in the form of bidentate carbonates.

3.2.2 Step 2: re-oxidation with O_2

Following reduction in CO and a flush with He, the gas mixture was switched to the oxidative feed. During this re-oxidation step, the irreversibly retained CO leaves the catalyst completely as CO_2 (table 1), as the amount of CO_2 produced is almost equal to the amount of CO retained in step (1). No CO desorption is observed. As the amount of oxygen consumed in step 2 is equal to the amount of CO consumed in step 1, the catalyst is entirely re-oxidised. In contrast, at temperatures below 448 K, re-oxidation remains incomplete. A delay in time is observed for both CO_2 production and the oxygen response (figure 4a). Oxygen breakthrough is observed only after the CO_2 concentration has reached a maximum (figure 4b). No oxygen is seen to desorb when the gas composition is switched from oxygen to He.

3.2.3 Step 3 and 4

The CO and CO₂ response in step 3 after re-oxidation in oxygen is fairly similar to that following a step change over the fully oxidised catalyst, step 1. The response to step 4 is identical to that of step 2, indicating that the reduction and oxidation of this catalyst are completely reversible and very quickly in transient experiments a cyclic steady state is reached. Further reduction and re-oxidation cycles demonstrated full reproducibility.

3.3 Isothermal reduction/oxidation of La_{0.8}Ce_{0.2}MnO₃ using ¹⁸O₂

Reduction/oxidation behaviour of the catalyst was further investigated using labelled oxygen in subsequent reduction/re-oxidation experiments at 523 K. Figure 5a shows the CO and unlabelled CO₂ concentration at the reactor outlet in time at a period of 300 s. The amount of CO consumed and CO₂ produced in first step change is identical to the first cycle in the previous experiment, since the same CO concentrations were used and the oxidation in the pre-treatment was carried out with unlabelled oxygen. During the oxidation step with labelled oxygen, mostly C¹⁶O¹⁶O is produced (figure 5b). Smaller amounts of C¹⁸O¹⁶O and C¹⁸O¹⁸O were formed as well, their response being somewhat delayed with respect to the C¹⁶O¹⁶O response.

The second reduction cycle (figure 6a) provides insight in the oxygen exchange during re-oxidation. C¹⁶O¹⁶O, C¹⁸O¹⁶O and C¹⁸O¹⁸O are formed instantaneously after the step change. When the C¹⁶O concentration in the outlet returns to its original level, the release of C¹⁶O¹⁶O, C¹⁸O¹⁶O and C¹⁸O¹⁸O decline to zero. Surprisingly, a significant amount C¹⁶O¹⁶O is still present during the second reduction step, while re-oxidation of the surface has been carried out with labelled oxygen.

The second re-oxidation step is in essence similar to the first re-oxidation step (figure 6b). A slightly larger amount of labelled CO₂ can however be observed in an early stage, along with C¹⁶O¹⁶O production.

3.4 CO oxidation with labelled oxygen

The response of CO oxidation for a $\text{CO}/^{18}\text{O}_2/\text{He}$ mixture is shown in figure 7. The background signal is subtracted from the obtained MS signal and subsequently corrected for the inlet pressure, using Ar as a reference gas. Following the step change from He to the gas mixture, $\text{C}^{16}\text{O}^{16}\text{O}$ is formed in two steps. The labelled oxygen response curve shows an increase to a maximum value and a subsequent decrease, accompanying the appearance of $\text{C}^{18}\text{O}^{16}\text{O}$ and $\text{C}^{18}\text{O}^{18}\text{O}$ in the outlet gas. Surprisingly, the formed $\text{C}^{16}\text{O}^{16}\text{O}$ approaches a constant value after going through a maximum, instead of decreasing to zero, as would be the result of the exhaustion of the available unlabelled oxygen. The signals have been followed for more than 600 s, but no changes were observed after the first 100 s.

Under the applied conditions, i.e. near the stoichiometric CO/O_2 ratio, we found first order reaction rates in CO and near-zero order in O_2 .

4. DISCUSSION

4.1 Reduction/oxidation with C^{16}O , $^{16}\text{O}_2$ and $^{18}\text{O}_2$ of $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$

Involvement of subsurface oxygen in the reduction steps can be concluded, since the amount of oxygen consumed is 6 times higher than that expected for the reduction of Mn^{4+} à Mn^{3+} . The tail in the response curves of CO_2 appearing in the reduction steps can be explained by a slower reaction with these subsurface oxygen atoms.

Highly thermally stable carbonate species i.e., bidentate carbonates are formed on the partially reduced oxide surface, since retained carbon species desorbs as CO_2 at a temperature higher than 500 K. Similar stable carbonate species have been reported by Tejuca et al. [21] on LaMnO_3 . Formation and decomposition of carbonate structures have also been found for LaCoO_3 [11, 31].

The existence of carbonate species on the reduced surface of catalyst is further confirmed by using labelled oxygen. The formation of $C^{18}O^{16}O$ during either reduction or oxidation can be explained by dissociate adsorption of labelled $^{18}O_2$ (equation 1). However, the formation of both $C^{16}O^{16}O$ and $C^{18}O^{18}O$ in re-oxidation step can only be explained by decomposition and desorption of the carbonates. The presence of $C^{16}O^{16}O$ indicates a rapid exchange between oxygen from the carbonates with lattice oxygen. A delay in CO_2 production suggests that desorption of CO_2 from the reduced surface is the rate-limiting step here. The formation of both $C^{18}O^{16}O$ and $C^{18}O^{18}O$ indicates that the oxygen in the carbonate bond can either be replaced by surface/subsurface oxygen or by adsorbed-labelled oxygen, as described in equations 2-5, in which “g” represents the gas phase and “s” the surface site.

During the second reduction step, $C^{16}O^{16}O$, $C^{18}O^{16}O$ and $C^{18}O^{18}O$ appear instantaneously. Appearance of large amount of $C^{16}O^{16}O$ indicates again rapid exchange between surface and subsurface oxygen (equation 6), in which “ss” represent the subsurface site.

The high mobility of oxygen in the perovskite lattice can be explained by its highly defective structure due to the presence of incorporated Ce ions [30]. A small amount of labelled CO_2 desorbs during an earlier stage in the second re-oxidation step, indicating that some ^{18}O has already been built into the lattice.

4.2 CO oxidation with labelled oxygen $^{18}\text{O}_2$

The oxidation of carbon monoxide over perovskite-type oxides has widely been studied [11, 32-35]. The reaction scheme for the catalytic CO oxidation over $\text{LaCo}_{1-t}\text{Cr}_t\text{O}_3$ according to Tilset et al. [35] must involve reduction and re-oxidation of the catalyst, which is also confirmed by our work.

The appearance of $\text{C}^{16}\text{O}^{16}\text{O}$ in outlet gas stream immediately after switching from inert to reactants is the result of the reduction of the oxide via an ER (Eley-Rideal) mechanism, as shown in equation 7. It seems that the desorption of CO_2 is very fast. Subsequently, CO can adsorb on the partially reduced surface and react with surface oxygen to form CO_2 , followed by CO_2 desorption, as described in equation 8 and 9 through a LH (Langmuir-Hinshelwood) mechanism. (Labelled) $^{18}\text{O}_2$ adsorbs dissociatively on a partially reduced surface (equation 1), and it may also adsorb on the same active site as CO, since the $^{18}\text{O}_2$ concentration in the outlet gas increases after switching from He to reactants and decreases when the CO_2 concentration rises in the off-gas stream. Desorption of formed CO_2 may regenerate the active site for oxygen adsorption.

$\text{C}^{18}\text{O}^{16}\text{O}$ can be formed through a LH mechanism (equation 10). The appearance of $\text{C}^{18}\text{O}^{18}\text{O}$ indicates that CO can adsorb on surface oxide ions, leading to a labile species that interacts with adsorbed atomic oxygen, producing a carbonate structure that then decomposes into (adsorbed) CO_2 and oxygen (equation 11 and 12).

The formation of $C^{16}O^{16}O$ might again be explained by the involvement of oxygen in the perovskite, through an interfacial process due to high oxygen mobility. This is confirmed by the finding of a near-zero reaction order in oxygen for CO oxidation at 523 K, which is a direct indication of the involvement of lattice oxygen. It is in accordance with results of Yao et al. [5] and Chuah et al. [32], and confirms our previous finding [30]. Yao and Chuah found a near-zero reaction order in the partial pressure of oxygen, which suggests the involvement of lattice oxygen from $LaMnO_3$. Finally, CO oxidation via the formation and decomposition of carbonates is likely to be important under steady-state conditions (equation 13 and 14), since the concentration of $C^{16}O^{16}O$ is relatively high, and remains constant after 100 s.

4.3 Kinetics of catalytic CO oxidation

The Arrhenius plot obtained from the initial rate of CO_2 formation during isothermal transient reduction step shows an apparent activation energy of $12.5 \text{ kJ}\cdot\text{mol}^{-1}$ (figure 8), assuming an Arrhenius temperature dependence for the reaction rate at maximum peak height. This value is close to the apparent activation energy of $16\text{-}19 \text{ kJ}\cdot\text{mol}^{-1}$ on $LaMnO_3$ in the temperature range of 333 K – 573 K at low oxygen pressure [32]. However, an activation energy of $63.0 \text{ kJ}\cdot\text{mol}^{-1}$ was found for the CO oxidation reaction over the perovskite in a temperature range of 348 K to 498 K under stoichiometric conditions (figure 9). This activation energy is of the same order as that observed by Chan et al. [33] for $LaMnO_3$ ($66.1 \text{ kJ}\cdot\text{mol}^{-1}$) in the temperature range of 373 K – 523 K.

When the CO₂ desorption is considered to be the rate determining step, the elementary reactions are:

Assuming that the adsorption of O₂ and CO, and the surface reaction are at quasi-equilibrium and the desorption of CO₂ as the rate determining step is irreversible, the following rate equation can be derived:

$$R = \frac{Nk_4 K_1^{\frac{1}{2}} K_2 K_3 P_{CO} P_{O_2}^{\frac{1}{2}}}{(1 + K_1^{\frac{1}{2}} P_{O_2}^{\frac{1}{2}} + K_2 P_{CO} + K_1^{\frac{1}{2}} K_2 K_3 P_{CO} P_{O_2}^{\frac{1}{2}})} \quad (15)$$

Since the reaction is first order in CO concentration, it indicates that K₂ is very small. Thus, K₂ can be neglected. The obtained reaction rate equation is:

$$R = \frac{Nk_4 K_1^{\frac{1}{2}} K_3 P_{CO} P_{O_2}^{\frac{1}{2}}}{(1 + K_1^{\frac{1}{2}} P_{O_2}^{\frac{1}{2}})} \quad (16)$$

For high oxygen concentration in the gas mixture, the reaction rate equation is expressed as followed:

$$R = Nk_4 K_2 K_3 P_{CO} \quad (17)$$

The obtained overall activation energy is then given as:

$$E_{a,overall} = E_4 + (E_2 - E_{-2}) + (E_3 - E_{-3}) \quad (18)$$

For a low oxygen concentration in the gas phase, the reaction rate is:

$$R = Nk_4 K_1^{\frac{1}{2}} K_2 K_3 P_{CO} P_{O_2}^{\frac{1}{2}} \quad (19)$$

The obtained overall activation energy changes to:

$$E_{a, overall} = E_4 + \left(\frac{E_1}{2} - \frac{E_{-1}}{2}\right) + (E_2 - E_{-2}) + (E_3 - E_{-3}) \quad (20)$$

From equations 18 and 20, a decrease of the overall activation energy is found for lower oxygen pressures, which can be attributed to enhanced O₂ adsorption on the perovskite surface. This has been confirmed by findings of Chuah et al., who found a much lower activation energy (16-19 kJ·mol⁻¹) for LaMnO₃ at low oxygen partial pressure (CO/O₂/He, v/v/v = 50/4/46) [32]. At zero oxygen partial pressure, we found even lower apparent activation energies. It is likely, however, that here the mobility of surface/subsurface oxygen through the defective perovskite structure plays a dominant role. The fact that only a weak correlation was observed between the specific surface area and the catalytic activity is also indicative for lattice oxygen migration as the rate-determining step [30].

5. CONCLUSION

Using step response and transient isotopic labelling, the mechanism of CO oxidation over a La_{0.8}Ce_{0.2}MnO₃ perovskite could be partially revealed. Reduction and oxidation of this perovskite have been shown to be completely reversible at temperatures above 473 K. During reduction, CO is retained on the partially reduced perovskite surface in the form of highly stable (most likely bidentate) carbonates. Large amounts of C¹⁶O¹⁶O are formed during the second reduction and oxidation steps when using labelled oxygen. This indicates a rapid exchange between surface and subsurface oxygen. Oxygen can adsorb dissociatively on a partially reduced oxide surface. The adsorption of oxygen is enhanced under reducing reaction conditions, giving rise to a low activation energy. Two reaction mechanisms are involved in CO oxidation: the ER- and LH mechanisms. A considerable

amount of $C^{16}O^{16}O$ is formed, indicating the involvement of lattice oxygen due to the high oxygen mobility through a defective perovskite lattice. This result is in line with the experimentally observed near-zero reaction order in the oxygen pressure under oxygen rich conditions, which is a direct indication of the involvement of lattice oxygen. The formation of both $C^{16}O^{16}O$ and $C^{18}O^{18}O$ under steady-state conditions indicates that the formation of CO_2 over $La_{0.8}Ce_{0.2}MnO_3$ proceeds over an intermediate carbonate species that subsequently decomposes.

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CAPTIONS TO FIGURES

Figure 1: Experimental set up for performing step change concentration transient experiments. V_1 : high-speed chromatographic-type 4-way valve; V_2 : high-speed 6-way chromatographic valve; MFC: mass flow controller; BPC: back-pressure controller; MS: on-line mass spectrometer.

Figure 2: Systematic scheme of step sequences (1) à (4) performed over the fully oxidised $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ perovskite; time interval: 300 s.

Figure 3: CO and CO_2 response curves after a step change $\text{He} \rightarrow 1\text{ vol}\% \text{ CO/He}$ over fully oxidised $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ perovskite, (step 1) in a temperature range from 448 K to 523 K. (a): CO_2 ; (b): CO .

Figure 4: O_2 and CO_2 response curves following a step change $\text{He} \rightarrow 1 \text{ vol}\% \text{ O}_2/\text{He}$ over reduced $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ perovskite (step 2) in a temperature range from 448 K to 523 K. (a) CO_2 ; (b): O_2 .

Figure 5: Responses of C^{16}O , C^{16}O_2 , $\text{C}^{18}\text{O}^{16}\text{O}$, C^{18}O_2 and ΣCO_2 after a step change $\text{He} \rightarrow 1 \text{ vol}\% \text{ CO/He}$ (step 1) over fully oxidised $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ perovskite (a), and after a step change $\text{He} \rightarrow 2 \text{ vol}\% \text{ }^{18}\text{O}_2/\text{He}$ over the reduced catalyst (b), both at 523 K.

Figure 6: Responses of $^{18}\text{O}_2$, C^{16}O_2 , $\text{C}^{18}\text{O}^{16}\text{O}$, C^{18}O_2 and ΣCO_2 after a step change $\text{He} \rightarrow 1 \text{ vol}\% \text{ CO/He}$ (step 3) over re-oxidised catalyst (a), and after a step change $\text{He} \rightarrow 2 \text{ vol}\% \text{ }^{18}\text{O}_2/\text{He}$ (step 4) over reduced catalyst (b), both at 523 K.

Figure 7: Response curves of $^{18}\text{O}_2$, C^{16}O_2 , $\text{C}^{18}\text{O}^{16}\text{O}$ and C^{18}O_2 in CO oxidation using labelled oxygen at 523 K.

Figure 8: Arrhenius plot of the apparent reaction rate towards CO_2 at the maximum peak height after a step change from He to $1 \text{ vol}\% \text{ CO/He}$ over fully oxidised $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$.

Figure 9: Arrhenius plot of the apparent reaction rate against reciprocal temperature for $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$; total flow-rate ($\text{He}:\text{O}_2:\text{CO} = 98:1:1$) = $100 \text{ ml}\cdot\text{min}^{-1}$.

TABLES

Table 1: The amount of CO₂ produced, CO retained and O consumed in step sequences (1) à (4) over La_{0.8}Ce_{0.2}MnO₃ perovskite, the concentration of those components is expressed in mol per mol Cerium.

T/K	Step (1)			Steps (2)		Step (3)			Step (4)	
	Heà 1%CO/He			Heà 1%O ₂ /He		Heà 1%CO/He			Heà 1%O ₂ /He	
	CO Cons.	CO ₂ prod.	CO ret.	O Cons.	CO ₂ prod.	CO cons.	CO ₂ prod.	CO Ret.	O cons.	CO ₂ prod.
448	0.19	0.13	0.06	0.14	0.03	0.19	0.14	0.05	0.13	0.02
473	0.25	0.19	0.06	0.25	0.04	0.23	0.16	0.07	0.23	0.04
498	0.29	0.22	0.07	0.28	0.06	0.29	0.23	0.06	0.28	0.05
523	0.31	0.24	0.07	0.31	0.05	0.34	0.26	0.08	0.33	0.07

Figure 1

Figure 2

Figure 3

Figure 4:

Figure 5:

Figure 6

Figure 7

Figure 8

Figure 9

Probeer hier uniformiteit in je figuren aan te leggen, m.n. tussen fig. 8 en 9!