

# TAP study on hydrogen production by partial oxidation of ethylene over catalysts derived from LaCoO<sub>3</sub> and LaCo<sub>0.8</sub>Ru<sub>0.2</sub>O<sub>3</sub> perovskites

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## 1 Introduction

Perovskites-type oxides (ABO<sub>3</sub>), such as LaCoO<sub>3</sub>, are attractive catalyst precursors for heavy hydrocarbons reforming since these structures form under reaction conditions highly dispersed Co metallic particles over a matrix of lanthanum oxide which increase hydrogen formation and prevent deactivation by coke and sulphur. To improve the activity and stability of LaCoO<sub>3</sub> derived catalysts for heavy hydrocarbons reforming, structural and electronic modifications can be introduced through partial substitution of Co in the perovskite network by other transition metals. Among them, Ru is highly effective in the catalytic reforming of heavy hydrocarbon fuels. Diesel as a liquid fuel that can be reformed is an interesting option owing to its wide distribution infrastructure, ease of handling and high-energy density [1]. Hydrocarbons of diesel fuel can suffer thermal cracking during pre-heating step at temperatures required to vaporize all the components to reach the reforming reactor temperature. The thermal cracking of fuels starts at temperatures above 350 °C with important ethylene, tar and coke formation for temperatures higher than 500 °C. Therefore, ethylene is a key reaction intermediate product in the reactions involved in the oxidative reforming of diesel fuels. The temporal analysis of products (TAP) has been recognized as a suitable transient experimental method for kinetic and mechanism investigation of adsorption and reaction processes. The low pressures and small pulse quantities in the TAP micro-reactor lead to transport through the packed bed by Knudsen diffusion, thus excluding all gas-phase reactions. This mode of transport also excludes any external mass-transfer limitations, as diffusion is the only mode of transport. This allows extracting information only about the interaction between the reactant with the catalyst surface. The time resolution of TAP experiments is on the order of sub-milliseconds. Moreover, the use of small pulses allows an isothermal reactor operation and heat effects are insignificant due to the use of small amounts of reactants [2].

With this background, the aim of the present work was to make use of the TAP technique to gain insight into the kinetics and mechanism of ethylene oxidation, as key intermediate reaction in the oxidative reforming of diesel, using isotopically labeled oxygen. The influence of the partial substitution of Co by Ru in LaCoO<sub>3</sub> perovskite over the formation rate of the different products and over the participation of the catalyst lattice oxygen in the reaction was studied.

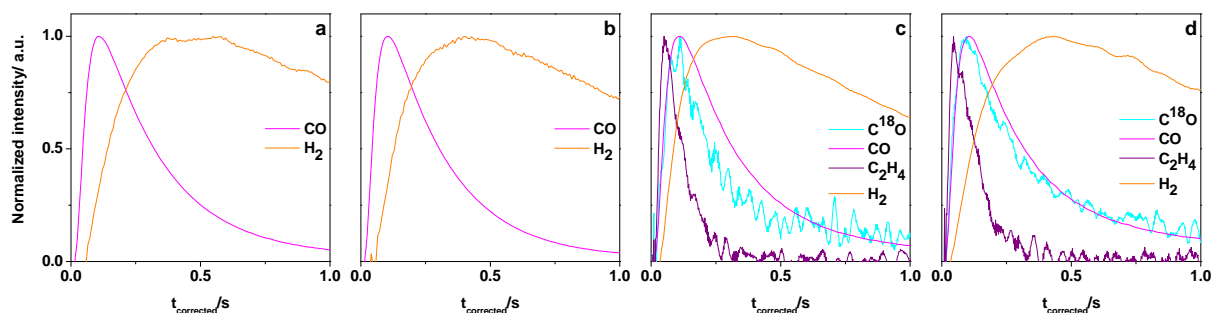
## 2 Experimental/methodology

The perovskite-type LaCoO<sub>3</sub> and LaCo<sub>0.8</sub>Ru<sub>0.2</sub>O<sub>3</sub> precursors were synthesized by a modification of the citrate sol-gel method. The aqueous mixture was stirred and slowly heated to 70 °C for 5 h. The resultant resin which contains the metal cations inside a polymeric network was charred at 300 °C for 2 h with a heating rate of 0.5 °C/min. After that, the resin was milled to obtain a fine powder and calcined under air at 750 °C for 4 h with a heating rate of 2 °C/min. Transient experiments of ethylene oxidation over perovskite precursors was performed in the TAP-2 system [2] at LIKAT. The quartz reactor (6 mm i.d. and 40 mm length) was filled with 33 mg of perovskite particles (250-450 μm) between two layers of quartz particles (250-355 μm). The sample was packed in the isothermal zone of the reactor and had a height of *ca.* 1 mm. The perovskite was pre-treated at ambient pressure with 10% H<sub>2</sub>/N<sub>2</sub> (20 mL/min) at 700 °C for 1 h with a heating rate of 10 °C/min lead to LaCoO<sub>3</sub>-R and LaCo<sub>0.8</sub>Ru<sub>0.2</sub>O<sub>3</sub>-R catalysts followed by cooling down in N<sub>2</sub> flow to 600 °C. After this pre-treatment, the reactor was evacuated to *ca.* 10<sup>-5</sup> Pa. In order to evaluate if lattice oxygen of the activated perovskites takes part in C<sub>2</sub>H<sub>4</sub> oxidation, single <sup>18</sup>O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/Xe = 1/4/4 pulse experiments were carried out. The experiments were performed at 600 and 700 °C. Pulse responses were monitored by means of a quadrupole mass spectrometer at the following atomic

mass units (AMUs): 48 ( $C^{18}O_2$ ), 46 ( $C^{18}O^{16}O$ ), 44 ( $C^{16}O_2$ ), 36 ( $^{18}O_2$ ), 30 ( $C^{18}O$ ), 28 ( $C_2H_4$ ,  $C^{16}O$ ,  $C^{16}O_2$ ), 27 ( $C_2H_4$ ,  $C_2H_4$ ), 26 ( $C_2H_4$ ), 20 ( $H_2^{18}O$ ), 18 ( $^{18}O_2$ ,  $H_2^{16}O$ ), 15 ( $CH_4$ ), 2 ( $H_2$ ) and 132 (Xe). The pulses were repeated 11 times for each AMU in order to improve the signal-to-noise ratio.

### 3 Results and discussion

Figure 1 shows the normalized transient responses of products after pulsing labeled oxygen ( $^{18}O_2$ ) and  $C_2H_4$  ( $^{18}O_2/C_2H_4/Xe = 1/4/4$ ) over  $LaCoO_3$ -R and  $LaCo_{0.8}Ru_{0.2}O_3$ -R catalysts at 600 °C and 700 °C. The transient responses are presented in a normalized form for better comparison of the pulse shapes and time was corrected according to [3].



**Fig. 1.** Transient responses of the reaction products formed after pulsing  $^{18}O_2/C_2H_4/Xe = 1/4/4$  over  $LaCoO_3$ -R catalyst at 600 °C (a) and 700 °C (b) and over  $LaCo_{0.8}Ru_{0.2}O_3$ -R catalyst at 600 °C (c) and 700 °C (d)

Pulses of  $^{18}O_2/C_2H_4/Xe = 1/4/4$  over  $LaCoO_3$ -R catalyst are converted into CO and H<sub>2</sub>. CO<sub>x</sub> compounds containing  $^{18}O$  are not detected indicating that only lattice oxygen of the structure participates in the CO formation oxidizing all  $C_2H_4$  molecules. In order to identify the sequence of the appearance of gas-phase components, the times of maximal concentration ( $t_{max}$ ) were obtained. At 600 °C the  $t_{max}$  of CO and H<sub>2</sub> are 0.108 and 0.549 s, respectively, while at 700 °C the CO and H<sub>2</sub> response are shifted to minor times. This behaviour can be explained by an increase of the oxygen mobility within the crystal lattice with an increase of the reaction temperature. When the mixture is pulsed over  $LaCo_{0.8}Ru_{0.2}O_3$ -R catalyst at 600 °C, on the contrary of  $LaCoO_3$ -R catalyst, the formation of  $C^{18}O$  is observed, suggesting that  $^{18}O$  is adsorbed on an anion vacancy forming these labelled species. These characteristics could be related to the greater surface reduction degree improved with the ruthenium incorporation into  $LaCoO_3$  perovskite. The concentration of non-labeled CO is considerably higher than  $C^{18}O$ . Thus, lattice oxygen of the catalys is mainly responsible for CO<sub>x</sub> formation. The  $C^{18}O$  transient response is played by the  $t_{max}$  of 0.111 s, while the  $t_{max}$  of CO and H<sub>2</sub> are 0.108 and 0.315 s, respectively at 600 °C. This last value points out that the formation of H<sub>2</sub> is faster for the Ru-containing catalyst compared to that of  $LaCoO_3$ -R catalyst. At 700 °C, ethylene conversion and the formation of  $C^{18}O$  and CO are favoured.

### 4 Conclusions

The results obtained by TAP evidence that lattice oxygen of  $LaCoO_3$ -R and  $LaCo_{0.8}Ru_{0.2}O_3$ -R catalysts participate in  $C_2H_4$  oxidation into syngas. The lower participation of lattice oxygen for Ru-containing catalyst is explained by its larger reduction degree. This technique also shows a faster production of hydrogen for  $LaCo_{0.8}Ru_{0.2}O_3$ -R catalyst.

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#### References

- [1] N. Mota, M.C. Álvarez-Galván, S.M. Al-Zahrani, R.M. Navarro, J.L.G. Fierro, *Int. J. Hydrogen Energy* **37** (2012) 7056.
- [2] J.T. Gleaves, G.S. Yablonskii, P. Phanawadee, Y. Schuurman, *Appl. Catal. A: Gen.* **160** (1997) 55.
- [3] C. Berger-Karin, J. Radnik, E.V. Kondratenko, *J. Catal.* **280** (2011) 116.