Isotopic Oxygen Exchange Study to Unravel Noble Metal Oxide/Support Interactions: The Case of RuO₂ and IrO₂ Nanoparticles Supported on CeO₂, TiO₂ and YSZ

Y. Hajar, A. Boreave, A. Caravaca, P. Vernoux, E. Baranova

► To cite this version:

Y. Hajar, A. Boreave, A. Caravaca, P. Vernoux, E. Baranova. Isotopic Oxygen Exchange Study to Unravel Noble Metal Oxide/Support Interactions: The Case of RuO₂ and IrO₂ Nanoparticles Supported on CeO₂, TiO₂ and YSZ. ChemCatChem, 2020, 12 (9), pp.2548-2555. 10.1002/cctc.201902187. hal-02544489

HAL Id: hal-02544489

<https://hal.science/hal-02544489>

Submitted on 14 Aug 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Isotopic oxygen exchange study to unravel noble metal oxide/support interactions: The Case of RuO₂ and IrO₂ nanoparticles supported on CeO₂, TiO₂ and YSZ

Yasmine M Hajar,^[a] Antoinette Boreave,^[b] Angel Caravaca,^[b] Philippe Vernoux,^[b] and Elena A Baranova^{*,[a]}

Abstract: The aim of this study is to unravel the mechanism of (noble metal oxide)/(active support) interactions for catalytic purposes. Hence, isotopic oxygen exchange (IOE) tests were performed on Iridium- and Ruthenium-based oxides supported on cerium oxide (CeO₂), titanium oxide (TiO₂), and yttria-stabilized zirconia (YSZ). IOE tests demonstrated the metal oxide support involvement in the propane oxidation reaction, with YSZ-based catalysts showing the highest exchange rate of oxygen, while CeO₂ and TiO₂-based catalysts had a less diffusion of lattice oxygen in that order. This is related to the presence of extrinsic oxygen vacancies in the YSZ-based catalysts and the reduction ability of the CeO₂ and TiO₂ supports. Despite the limitations on oxygen exchange in some of the noble/metal oxide catalysts, their catalytic performance was comparable to the ones that showed a high oxygen exchange. Therefore, active supports result in a higher engagement of oxygen from the support but not in a linear correlation with the catalytic performance of the metal/support.

Introduction

Metal oxides that are considered as active supports (e.g. CeO₂, TiO₂) due to their lattice oxygen mobility are appealing for their use in heterogeneous catalysis [1,2]. For instance, noble metal or noble metal oxide-based catalysts interfaced with active supports are increasingly used in catalytic oxidation reactions [1,3], low temperature solid oxide fuel cells (SOFC) [4–6] and electrochemical promotion of catalysis [7–12]. The oxygen mobility property is of paramount importance, especially when oxygen from the gas phase is scarce or not stable in concentration [3]. As new synthesis methods emerge and result in highly active catalysts, further characterization is required to understand the role of lattice oxygen from the support to attempt in explaining the enhanced catalytic rate. Therefore, the aim of this work is to use experimental isotopic oxygen exchange (IOE) tests to thoroughly understand the interaction that occurs at the atomistic level

between the metal and the active support. These results will be of paramount importance when further designing efficient heterogeneous catalysts.

IOE has been the method of choice for many researchers [13–22]: Doornkamp et al. used IOE tests to find the rate constants for oxygen exchange mechanisms on various group IV metal oxides [13]. IOE experiments are also beneficial as done in Shim et al. to assess the effect of sintering on the grain boundary size of YSZ and its oxygen exchange rate properties [15]. A different form of IOE that can be used is pulsed IOE technique, as presented in Bouwmeester et al. to determine the exchange rates of oxygen on YSZ (Y₂O₃-ZrO₂), BSCF (Ba_{1-y}Sr_yCo_{0.8}Fe_{0.2}O_{3-δ}) and La₂NiO_{4+δ} metal oxides [14].

The oxygen exchange propriety of an active metal oxide is accentuated when interfaced with nanoparticle noble metal acting as a pathway for the oxygen exchange with the environment. Furthermore, it is believed that dispersing noble metals on active metal oxide supports decreases the aggregation rate of the noble metal particles due to the oxygen vacancies formed at the interface [16–18]. The oxygen-vacancy formation is due to the reducible nature of the oxide which allows for a direct charge transfer between the noble metal and the support and the formation of a stable particle with oxygen vacancy around it.

It is important to understand that the ability to exchange oxygen at the interface relies generally on the particle size of the noble metal as it was demonstrated by Dong et al. through their volcano-shaped relationship between the oxygen exchange rate and the noble metal particle size or specific surface area (SSA) [19]. However, one must be critical about the causality relationship and the range of the particle size at which this relationship holds true as a volcano-shaped relationship still means that two catalysts of very different particle sizes and/or SSAs had very similar oxygen exchange rate. Another example of a relationship fitted wrongfully to assign causality is in Acerbi et al. where a linear relationship between the ceria reduction temperature and the work function of metals was assigned [23]. However, few years later, the authors negated the relationship and rationalized the ceria reduction temperature with the d-band metal center position [24].

It is very appealing to relate the oxygen storage capacity (OSC) of catalysts with their catalytic activity; nevertheless, this relationship does not stand strong as for example CZO (CeO₂-ZrO₂) supporting Rh has a higher OSC than when supporting Pt or Pd as shown in Kai et al. [20], but does not result in a higher catalytic rate. Furthermore, Fortunato et al. showed that using an ionically conducting oxide such as YSZ results in a higher oxygen exchange rate compared to the case of inactive SiO₂ or ZrO₂ when supporting Pt nanoparticles; nevertheless, the latter inert supports resulted overall in a similar catalytic rate to the prior one showing that even though the reaction mechanism was different, the overall catalytic rate was the same [21]. Pt-based catalysts have negligible oxygen exchange rate [25–27] yet similar and/or higher catalytic rate compared to Ir- and Ru- based catalysts. Nevertheless, even though it is well known that Pt has a high catalytic rate as they are used commonly in deep oxidation reactions [28,29], their low oxygen storage capacity (OSC) does not allow their use in applications where high oxygen mobility is required. An emergent application is for example low temperature SOFC where oxygen ions from the support is the only source of oxygen for the deep oxidation of light hydrocarbons [6].

In this work, IOE measurements were used here to quantify the amount of active oxygen engaged in the case of iridium and ruthenium nanoparticle catalysts supported on ionically conducting support (e.g., YSZ) and mixed ionic-electronic conducting support (e.g., CeO₂ and TiO₂). Using iridium and ruthenium oxide catalysts in applications where oxygen exchange is vital is what prompted us to compare their behavior. Furthermore, comparison of the active supports to demonstrate

[a] Department of Chemical and Biological Engineering
University of Ottawa

161 Louis-Pasteur, Ottawa, ON K1N6N5, Canada

[b] Univ. Lyon, Université Claude Bernard Lyon 1, CNRS – UMR 5256, IRCELYON,
2 avenue A. Einstein, 69626 Villeurbanne, France

* Corresponding Author: Elena.baranova@uottawa.ca

the effect of their oxygen exchange capacity on their catalytic performance was similarly imperative.

Isotopic Exchange Principle

During oxygen isotopic exchange, different reactions can occur [30,31]:

- The homomolecular exchange during which oxygen molecules of different labels from the gas phase are scrambled over the catalyst surface (Eq. 1).

- The heteromolecular exchange during which $^{18}\text{O}_2$ is scrambled with lattice oxygen of the oxide solid. A simple heteromolecular exchange involves one atom from the solid (Eq. 2), whereas multiple heteromolecular exchange reaction involves multiple oxygen atoms from the support (Eq. 3).

In this work, simple and multiple heteromolecular exchange is what we focused on. Furthermore, when a fuel is used, three CO_2 isotopes are emitted depending on the source of oxygen: C^{16}O_2 , $\text{C}^{16}\text{O}^{18}\text{O}$ and C^{18}O_2 . We will compare the production of the three isotopes further on.

Experimental and Method Section

Metal oxide nanoparticles (RuO_2 and IrO_2) were prepared using the polyol method to obtain a narrow range of particle size distribution [10,32]. The synthesis involved, 0.11 g of H_2IrCl_6 (Alfa Aesar®, $\geq 99.99\%$) or 0.21 g of RuCl_4 (Sigma-Aldrich®, $\geq 99.99\%$) dissolved in 50 mL of ethylene glycol with 0.08 M of NaOH. The solution was refluxed at 160 °C for 3 h, resulting in a pH drop from 10 to 7.5, indicating nanoparticles formation. The NPs colloid solution was mixed with a pre-calculated amount of the supporting metal oxide powder in deionized water for 72 h [32,33]. The mechanical attachment of the nanoparticles (NPs) to the supporting metal oxides is signaled by the change of the solution's color to clear when the solid phase sediments upon cessation of the mixing. The catalyst sludge is centrifuged and dried in a freeze dryer (LabConco®). The metal oxide supports used were commercial YSZ (8% Y_2O_3 - 92% ZrO_2 , Tosoh®, SSA 13 $\text{m}^2 \text{g}^{-1}$), CeO_2 (Alfa Aesar®, specific surface area 30-50 $\text{m}^2 \text{g}^{-1}$) and TiO_2 (Acros Organics, Aerioxide® P25, SSA 45-55 $\text{m}^2 \text{g}^{-1}$).

Due to pre-treatments and tests under oxygen-based reaction atmospheres, the noble metal nanoparticles are oxidized to RuO_2 and IrO_2 as demonstrated in previous studies using density functional theory (DFT) [34] and X-Ray Photoelectron Spectroscopy (XPS)[35]. Furthermore, to check on the formation of nanoparticle noble metals, transmission electron microscopy (TEM) (JEOL JEM 2100F FETEM operating at 200 kV) was used for the TiO_2 -supported catalysts, and annular dark field Scanning TEM (STEM) (FEI Titan3 80–300 TEM operated at 300 kV) was used for the CeO_2 -based material. Image J software allowed the determination of the average particle size of ruthenium and iridium. The specific surface area (SSA) was determined using the Brunauer–Emmett–Teller (BET) method (Quantachrom®, Mod. Nova 2000) with nitrogen adsorption at -195 °C. The metal loading was checked using X-Ray Fluorescence (XRF) (Olympus®, 40 kV electron beam).

The dispersion of the catalyst was estimated from the average particle size determined from the TEM images:

$$\text{Dispersion (\%)} = (600 \cdot M_{\text{Metal}}) / (\rho(\text{g/m}^3) \cdot d(\text{m}) \cdot a_{\text{Metal}} \cdot N_a) \quad \text{Eq. 4}$$

where M_{Metal} is the molecular weight, a_{Metal} is the atomic surface area, ρ is the metal density, N_a is Avogadro's number, and d is the average particle diameter (m) estimated from TEM or STEM.

The experimental setup used for the isotopic oxygen exchange tests consisted of a U-shape reactor in which 50 mg of the catalyst was introduced. The feed gas consisted of 1% isotopic oxygen (97.37% $^{18}\text{O}_2$, 1.1% $^{16}\text{O}^{18}\text{O}$, 1.53% $^{16}\text{O}_2$ from EURISOTOP®) diluted in Helium (Linde®, 99.999%) or 5% $^{16}\text{O}_2$ (Linde®, 5% $^{16}\text{O}_2$) diluted in Helium, at 30 mL min^{-1} flow rate. Four-port valves were used to switch the feed inlet to the reactor between pre-treatment conditions and reactants feed. Another four-port valve would allow the feed gas to enter the reactor or bypass it before it continues its flow to the Hiden® quadrupole mass spectrometer where the gas composition is detected by following the masses of 18, 20, 28, 29, 32, 34, 36, 42, 44, 46 m/z.

For the temperature programmed IOE, 30 mL min^{-1} of $^{16}\text{O}_2$ (Linde®, 5% in He) was used to pre-treat the sample for two hours at 350 °C. The sample was cooled down, then a feed of 1 % of $^{18}\text{O}_2$ was introduced to the reactor with a balance of He, at a flow of 30 mL min^{-1} . The temperature was increased to 350 °C with a heating rate of 10 °C min^{-1} .

For the isothermal IOE, the sample was pre-treated with the 5 % $^{16}\text{O}_2$ oxygen for two hours at 350 °C. Before starting the experiment, the 1 % $^{18}\text{O}_2$ gas feed by-passed the reactor directly to the MS to find the $^{18}\text{O}_2$ initial threshold; meanwhile, the reactor was purged with helium to remove $^{16}\text{O}_2$ gas from the flow. The two four-port valves were then switched in a way that $^{18}\text{O}_2$ gas feed was directed towards the reactor and then to the MS detection. A blank experiment was performed without any catalyst in the reactor to determine the dead volume and check for leaks.

To determine the source of oxygen in the oxidation reaction of a light hydrocarbon, 0.4 kPa propane (Linde®, 8000 ppm in He) was fed along with 2 kPa $^{16}\text{O}_2$ oxygen (Linde®, 5% in He) for a total flow rate of 40 mL min^{-1} and tested using the aforementioned mass spectrometer at 350 °C. This experiment followed directly the isothermal IOE test with an intermittent purge with He for 5 min.

To perform a titration of the amount of oxygen from the support engaged in the oxidation reaction when no source of gaseous oxygen is provided, an ethylene titration experiment is performed. In this experiment, and following the same conditions performed in a previous study from our previous study [36], the catalysts were pre-treated under 3 kPa of oxygen from room temperature to 400 °C by a step increase of temperature of 25 °C. The temperature was then dwelled at 400 °C for 2 h before cooling it down to room temperature. The temperature was then increased to 350 °C by step change of 25 °C and 10 min at each temperature under the reaction feed of 0.01 kPa C_2H_4 (Linde, 0.5% C_2H_4 in He) and 3 kPa of $^{16}\text{O}_2$ (20 % O_2 , Linde®) with a total flow rate of 100 mL min^{-1} (He balance). The reaction mixture was kept for an hour at 350 °C, then the reaction feed was switched to a flow of ethylene alone with balance of He. The CO_2 produced during the titration test was followed using non-dispersive infrared (NDIR) CO_2 gas analyzer (Horiba®, VA-3000) to quantify the amount of active oxygen emitted from the support.

Results and Discussion

Table 1 shows a summary of the main physicochemical properties of these materials, in particular, the marginal change in the particle size of the noble metals when suspended in their colloidal form versus when deposited on the supports. Furthermore, the

effect of the particle size is shown on the dispersion percentage using eq.1 while similar metal loading was obtained. The Transmission Electronic Microscopy (TEM) and scanning STEM characterizations used to find the average particle size are presented in Fig. 1. The dispersion of iridium oxide on CeO₂ and TiO₂ averaged to a slightly higher number compared to that of ruthenium oxide due to their slightly smaller particle size. A histogram of the range of nanoparticles diameter is shown in Fig. 2. The Specific Surface Area (SSA) of CeO₂ and TiO₂-based catalysts were higher than that of YSZ-based catalysts, which was mainly attributed to the intrinsic SSA values of the pure metal oxide supports.

Table 1. Characteristics of nanoparticles supported on CeO₂, TiO₂ and YSZ.

Catalyst	Average particle size (nm) ^[a]	Dispersion (%) ^[b]	Metal loading (wt.%) ^[c]	Specific Surface Area (m ² /g) ^[d]
RuO ₂	1.4	-	-	-
RuO ₂ /CeO ₂	1.8	33.0	1.03	48
RuO ₂ /TiO ₂	1.4	42.5	1.07	48
RuO ₂ /YSZ	n/a ^[e]	n/a	0.99	12
IrO ₂	1.0	-	-	-
IrO ₂ /CeO ₂	1.0	57.7	1.10	40
IrO ₂ /TiO ₂	1.2	48.1	1.04	46
IrO ₂ /YSZ	n/a ^[e]	n/a	0.91	14

[a] Determined from TEM, [b] from eq. S1 [c] from XRF measurements, [d] from BET measurements. [e] The noble metals on YSZ support were not easily detected due to the limited electronic contrast between the metals and the support in transmission electron microscopy.

First, a temperature-programmed isotopic oxygen exchange (TPIOE) was performed (Fig. 3) on the six catalysts to see the temperature effect on the catalysts' oxygen exchange capacity detected through the variation in the atomic fraction (Eq. 5) of ¹⁸O₂, ¹⁸O¹⁶O, ¹⁶O₂ in the gas phase:

$$\alpha_i = \frac{P_i}{P_T} \text{ with } i \text{ being } ^{16}\text{O}_2, ^{16}\text{O}^{18}\text{O}, ^{18}\text{O}_2 \quad \text{Eq. 5}$$

$$\text{and } P_T = P_{^{16}\text{O}_2} + P_{^{16}\text{O}^{18}\text{O}} + P_{^{18}\text{O}_2}$$

YSZ had the highest oxygen exchange capacity, shown by its greatest ability to consume ¹⁸O₂ from the gas as shown by the steepest decrease of the atomic fraction of ¹⁸O₂. This was in parallel with the increase of $\alpha_{^{16}\text{O}_2}$ and $\alpha_{^{16}\text{O}^{18}\text{O}}$ in the gas phase as oxygen molecule was desorbing from the surface by combining two atoms originating from the lattice of the support (resulting in ¹⁶O₂), or one from the support and one from the gas (resulting in ¹⁶O¹⁸O). The desorption of ¹⁶O₂ was more significant than ¹⁶O¹⁸O in the case of YSZ, suggesting that the multiple heteroexchange mechanism (Eq. 3) was more dominant than the simple heteroexchange reaction (Eq. 2) when supporting iridium or ruthenium.

While the same pattern of oxygen exchange was found in the case of iridium and ruthenium supported on YSZ, the oxygen exchange was not similar for the two metal oxides on CeO₂ and TiO₂. This difference shows well the importance of the metal oxide/support interactions. In the case of CeO₂, iridium resulted in a higher oxygen exchange capacity compared to ruthenium. It could be attributed to the slightly higher particle size of ruthenium (1.8 nm) on CeO₂ but also to the bigger size of the CeO₂ particles in the RuO₂/CeO₂ catalyst (Fig. 1) due to an unexpected sintering. Unlike in the case of YSZ, simple heteroexchange mechanism was the dominant one for the oxygen exchange on CeO₂ and TiO₂ based catalysts, showing that either the rate of desorption of ¹⁶O¹⁸O was faster than the full spillover of ¹⁸O₂, or that there is not enough active lattice oxygen in the oxides. Therefore, the temperature-programmed oxygen exchange rate of the catalysts respected the following order: IrO₂/YSZ > IrO₂/CeO₂ > RuO₂/YSZ > RuO₂/TiO₂ > IrO₂/TiO₂ > RuO₂/CeO₂.

Figure 1. STEM of RuO₂ and IrO₂ stand-alone nanoparticles and when supported on CeO₂ (STEM) and on TiO₂ (TEM).

Figure 2. Histograms of the particle size of RuO₂ and IrO₂ as (a) colloidal nanoparticles, and when supported on (b) TiO₂ and (c) CeO₂.

Figure 3. Temperature-programmed isotopic oxygen exchange on IrO₂ and RuO₂ nanoparticles supported on CeO₂, TiO₂, and YSZ metal oxides. P_{18O₂} = 1 kPa and balance of He. Total flow of 30 mL min⁻¹. The support alone (CeO₂, TiO₂ or YSZ) alone had no oxygen exchange capacity in the temperature range used.

During the isothermal IOE test, the multiple heteromolecular exchange (full exchange of ¹⁸O₂ from the gas with two ¹⁶O from the support) was the dominant mechanism for YSZ-based catalysts (Fig. 4) at the beginning of the exchange. This mechanism was followed by a slow drop in its rate as simple heteroexchange was rising. In the case of TiO₂-supported catalysts, comparable simple and multiple heteroexchange reactions occurred, with the former being slightly higher and prolonged. However, in the case of the CeO₂ support, the performance of the two catalysts was not similar. IrO₂/CeO₂ shows a significant oxygen exchange capacity compared to that of RuO₂/CeO₂. The total amount of oxygen exchanged can be better analysed when comparing the time required to saturate ¹⁸O₂ consumption as its flow rate increases to its initial values (Fig. 4). The isothermal oxygen exchange rate of the catalysts followed the order: IrO₂/YSZ > RuO₂/YSZ > IrO₂/CeO₂ > RuO₂/TiO₂ > IrO₂/TiO₂ > RuO₂/CeO₂. It is worth mentioning that the IOE of the active supports alone was negligible at 350 °C similarly to when TPIOE was performed.

The rate of isothermal oxygen exchange was the highest at the initial contact between the gaseous ¹⁸O₂ and the catalyst as was seen in Fig.4 and demonstrated by the peak in ¹⁶O₂

production at t≈2min. Therefore, it is beneficial to compare the initial rate of exchange R_0^e (eq. 1) as a mean to compare quantitatively the catalysts' affinity for surface oxygen exchange. As seen in Table 2, the initial rate of isothermal oxygen exchange was the highest for IrO₂/YSZ at a rate of $1.27 \cdot 10^{-5} \text{ mol } ^{16}\text{O s}^{-1} \text{ g}_{\text{cata}}^{-1}$ while it was the lowest for RuO₂/CeO₂ following the same order from what was observed qualitatively in Fig. 4. R_0^e , which is normalized by gram of catalyst, can also be normalized in a ratio form of moles of ¹⁶O emitted divided by moles of ¹⁶O in the catalyst, giving a value presented as % mol ¹⁶O s⁻¹ mol ¹⁶O_{cata}⁻¹. Since CeO₂ has the lowest molecular weight between the three supports, it was found that R_0^e of IrO₂/CeO₂ was higher than that of YSZ-based catalysts, when normalized by moles of oxygen in the catalyst (% mol ¹⁶O s⁻¹ mol ¹⁶O_{cata}⁻¹). In addition, the total amount of oxygen exchanged within 10 min was calculated as N_0^e (eq. 2) in Table 2., it was found, for example, that 34% of oxygen in IrO₂/YSZ catalyst was exchanged in only 10 min whereas not more than 0.32% of oxygen in RuO₂/CeO₂ was accessible. N_0^e values suggest that oxygen diffusion from the bulk has occurred to a great extent in the case of YSZ-based catalysts and IrO₂/CeO₂ while less engagement in the case of TiO₂-based catalysts occurred and only surface oxygen was consumed in RuO₂/CeO₂.

Figure 4. Isothermal isotopic oxygen exchange on IrO₂ and RuO₂ supported on CeO₂, TiO₂ and YSZ metal oxides. The four-way valve is switched to the reactor's inlet at $t = 1$ min. $T = 350$ °C. $P(18\text{O}_2) = 1$ kPa and balance of He. Total flow = 40 mL min⁻¹. The support alone had no oxygen exchange capacity at this temperature.

The initial rate of isothermal oxygen exchange R_0^e (mol O s⁻¹ g_{catal}⁻¹) was calculated as follows:

$$R_0^e = 2 \frac{\dot{V}}{mRT} (P_{32} + 1/2 P_{34}) \quad \text{Eq. 1}$$

where $\dot{V}$ is the volumetric flow rate, m the catalyst weight, R the gas constant, T standard condition temperature. R_0^e was divided by n (mol ¹⁶O_{catal}) instead of m (g catalyst) to find it in ratio form with a unit of mol ¹⁶O s⁻¹ mol ¹⁶O_{catal}⁻¹.

The total amount of oxygen exchanged at time t was calculated as follows:

$$N_t^e = \int_0^t R_t^e \cdot dt \quad \text{Eq. 2}$$

Where R_t^e is the rate of isothermal oxygen exchange at time t in mol O s⁻¹ mol ¹⁶O_{catal}⁻¹.

Table 2. Initial rate of isothermal oxygen exchange R_0^e (mol ¹⁶O s⁻¹ g_{catal}⁻¹ or % mol ¹⁶O s⁻¹ mol ¹⁶O_{catal}⁻¹) and percentage of isothermal oxygen exchange in 10 min N_{10}^e (% mol ¹⁶O) for the different catalyst complexes.

NPs Support	R_0^e (mol ¹⁶ O s ⁻¹ g _{catal} ⁻¹ 10 ⁻⁵ % mol ¹⁶ O s ⁻¹ mol ¹⁶ O _{catal} 10 ⁻¹)		N_{10}^e (% mol ¹⁶ O /mol % mol ¹⁶ O _{catal})	
	RuO ₂	IrO ₂	RuO ₂	IrO ₂
YSZ	1.21 0.82	1.27 0.86	33.6	34.0
CeO ₂	0.11 0.09	1.08 0.94	0.32	18.0
TiO ₂	0.81 0.33	0.56 0.23	3.0	3.1

Furthermore, the catalytic performance of the six catalytic materials was tested for propane oxidation depicted in Fig. 5, while the initial catalytic rate and the accumulated CO₂ production from labeled oxygen are shown in Table 3. The propane oxidation reaction with gaseous ¹⁶O₂ was performed directly after the isothermal oxygen exchange test with a 5 min helium purge in between to remove any remaining ¹⁸O₂ in the gas phase. Propane oxidation at $T = 350$ °C was detected via mass spectrometry, with C₁₆O₂, C₁₆O¹⁸O, and C₁₈O₂ being the main products detected via m/z 44, 46 and 48, respectively. Therefore, CO₂ gas product containing ¹⁸O atoms originates from the catalyst as it was stored in the sample during the isothermal IOE experiment described in Fig. 4. RuO₂/ and IrO₂/YSZ catalysts exhibited the highest production of C₁₈O₂ in good agreement with their highest oxygen exchange rate. The production of C₁₈O₂ strongly suggests a Mars-van Krevelen mechanism such that oxygen from the catalyst is involved in the reaction and is replenished by oxygen from the gas phase [37,38]. While C₁₈O₂ production was dominant at first, C₁₆O¹⁸O production followed for a few minutes, and then the C₁₆O₂ production emerged. This order of CO₂ isotopes production is due to the depletion of the support from the labelled ¹⁸O₂, therefore, differentiation between the gas phase and metal-oxide phase oxygen becomes difficult as both sources of oxygen will be labelled with ¹⁶O as a function of time.

The active nature of YSZ-based catalysts is therefore confirmed by the prolonged C₁₈O₂ production in comparison with

the other supports. TiO_2 -based catalysts had a little C_{18}O_2 production but peaked initially in $\text{C}_{16}\text{O}_{18}\text{O}$ production which is in good agreement with their IOE results of highest $^{16}\text{O}_{18}\text{O}$ desorption. The higher $\text{C}_{16}\text{O}_{18}\text{O}$ production could be attributed to the rapid surface oxygen exchange and the smaller oxygen storage capacity in TiO_2 compared to YSZ. Finally, the divergence in the oxygen exchange behavior of the two CeO_2 -based catalysts was confirmed by the catalytic tests for propane oxidation (Fig. 5). Indeed, $\text{IrO}_2/\text{CeO}_2$ had a significant C_{18}O_2 and $\text{C}_{16}\text{O}_{18}\text{O}$ production whereas only $\text{C}_{16}\text{O}_{18}\text{O}$ production was observed for $\text{RuO}_2/\text{CeO}_2$. This is also presented in Table 3 which shows the initial rate of propane oxidation using labeled ^{18}O , normalized per gram of catalyst as well as per mol of oxygen in the catalyst. Furthermore, the accumulation of CO_2 production using labeled ^{18}O was also calculated at $t=30$ min and presented as n_{30} (% mol ^{18}O / mol O_{cata}). This value, which is found by integration of the CO_2 production rate as a function of time, shows that the highest consumption of labeled oxygen was 17.8 % for the case of IrO_2/YSZ . Overall, the n_{30} values are lower than N_{10}^e found in the IOE experiments. This might be due to the 5 min of He purge that was performed in between, resulting in desorption of some

labeled oxygen from the catalyst's surface. Overall, the total CO_2 production rates in the case of the six catalysts were not very different as shown in Fig. 5 even though the consumption of oxygen from the catalyst was majorly different. This results in concluding that the activity of the metal oxide support and thus the metal/support interaction does not have an effect on the catalytic rate as linearly as it was anticipated.

Table 3. initial catalytic rate (r_0 of $\text{C}_{18}\text{O}_2+1/2 \text{C}_{16}\text{O}_{18}\text{O}$) of propane oxidation using oxygen from the catalyst (mol ^{18}O s $^{-1}$ g $_{\text{cata}}^{-1}$ or % mol ^{18}O s $^{-1}$ mol O_{cata}) and percentage of oxygen consumption from the catalyst for production of CO_2 in 30 min for the different catalyst complexes.

NPs Support	r_0 of $\text{C}_{18}\text{O}_2+1/2 \text{C}_{16}\text{O}_{18}\text{O}$ (mol ^{18}O s $^{-1}$ g $_{\text{cata}}^{-1}$ 10 $^{-7}$ % mol ^{18}O s $^{-1}$ mol O_{cata} 10 $^{-4}$)		n_{30} of $\text{C}_{18}\text{O}_2+1/2 \text{C}_{16}\text{O}_{18}\text{O}$ (% mol ^{18}O / mol O_{cata})	
	RuO_2	IrO_2	RuO_2	IrO_2
YSZ	1.03 7.0	1.13 7.7	17.3	17.8
CeO_2	0.27 2.34	1.33 11.6	2.9	7.2
TiO_2	1.00 4.0	0.84 3.4	1.3	1.1

Figure 5. Propane oxidation to the different isotopically labelled CO_2 in the case of IrO_2 supported on CeO_2 , TiO_2 , and YSZ metal oxides. $P(\text{C}_3\text{H}_8) = 0.4$ kPa and $P(^{16}\text{O}_2) = 2$ kPa and balance of He. Total flow rate = 40 mL min $^{-1}$. The experiment is performed consecutively to the isothermal IOE test. The reactive flow is switched to the reactor at $t=3$ min.

To further our studies, the involvement of bulk oxygen from the support in a catalytic reaction was also characterized by “ethylene titration tests” under an oxygen deficient atmosphere. In

such conditions, any resulting oxidation reaction can only be assisted by oxygen from the support material. In previous works, Isaifan et al. have tested Pt supported on YSZ, Sm-doped CeO_2

and CeO₂ for ethylene oxidation in an oxygen deficient environment [39]. Dole et al. tested ethylene oxidation with and without gaseous oxygen and compared the results between Pt, RuO₂ and IrO₂ supported on CeO₂ [36]. In this work, Fig. 6 shows the oxygen storage capacity of the catalysts under an oxygen deficient reaction atmosphere at 350 °C. The catalysts were first stabilized under C₂H₄/O₂ condition before the oxygen feed was interrupted at t= 0 h. IrO₂ and RuO₂ supported on YSZ had the highest and most prolonged ability to provide oxygen for reaction with gaseous ethylene to produce CO₂. It could be attributed to the high mobility of bulk oxygen mobility in YSZ mostly due to the doping factor and the extrinsic oxygen vacancies. TiO₂-based catalysts exhibited a lower reactivity, whereas CeO₂-based materials showed also a divergence in behavior such that IrO₂/CeO₂ had a significant ethylene conversion at the beginning of the reducing environment period, followed by an increase of the ethylene conversion before it decreased to zero. This sudden increase in the ethylene conversion could be attributed to the surface reduction of ceria in the proximity of the metal oxide nanoparticles [40]. A shorter but similar trend occurred in the case of RuO₂/CeO₂ which is in good agreement with its lowest oxygen exchange rate that it demonstrated in the isothermal and temperature-programmed experiments (Fig. 3 and 4). One can notice that the ability of CeO₂ to be reduced might have been limited due to a sintering effect as it was seen in the case of RuO₂/CeO₂. The higher catalytic activity of IrO₂/CeO₂ compared to RuO₂/CeO₂ would be attributed to the smaller particle size of IrO₂ and CeO₂ compared to RuO₂/CeO₂, allowing for a higher dispersion and an enhanced oxygen mobility around the metal oxide nanoparticles.

Figure 6. Ethylene oxidation in the presence and absence of oxygen in the gaseous feed for the case IrO₂ and RuO₂ supported on CeO₂, TiO₂, and YSZ metal oxides. T=350 °C, P(C₂H₄)= 0.01 kPa, P(O₂)= 3 kPa (for t<0 h) and P(O₂)= 0 kPa (for t>0h). Total flow= 100 mL min⁻¹. The “He alone” curve is a reference curve for when no C₂H₄ nor O₂ are flowing in the stream after t=0 h.

Conclusions

In conclusion, noble-metal oxide/support interactions were studied in this work. To that purpose, nanodispersed IrO₂ and RuO₂ based catalysts supported on YSZ, CeO₂, and TiO₂ were investigated by Isotopic Oxygen Exchange (IOE) techniques. Metal oxides supported on YSZ exhibited a very significant metal

oxide/support interaction and the highest oxygen exchange compared to the other supports. It led to CO₂ production that highly involved bulk oxygen from the support. There was no direct correlation between the amount of exchanged oxygen and the catalytic activity, as even when limited exchange occurred such as in the case of RuO₂/CeO₂, the catalyst still showed satisfactory catalytic activity that is comparable to the other materials. This indicates that other factors, such as nanoparticle size, dispersion and oxidation state play an important role in the catalytic activity. Overall, this study demonstrates the high engagement of oxygen from active metal oxides supporting iridium and ruthenium nanoparticles, pointing out that these catalysts can be used in applications where the mobility of oxygen from the support is critical for the performance.

Acknowledgements

The authors acknowledge the financial support from Natural Science and Engineering Research Council (NSERC) Canada through the Discovery Grant (RGPIN05494). Y.H. thanks funding from the doctoral mobility grants (Avenir Lyon Saint- Etienne Program) and the Vanier Canada Graduate scholarship. The authors are thankful to Dr. Yun Liu, Dr. Martin Couillard and Bob Whitehead for TEM, STEM and XRF measurements, respectively.

Keywords: oxygen exchange • isotopes • metal-support interaction • yttria-stabilized zirconia • ceria • titania • iridium • ruthenium

- [1] J. Haber, E.M. Serwicka, The role of Oxygen on Catalysis, *React. Kinet. Catal. Lett.* 35 (1987) 369–379.
- [2] C. Mirodatos, Use of isotopic transient kinetics in heterogeneous catalysis, *Catal. Today* 9 (1991) 83–95.
- [3] L. Liu, A. Corma, Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles, *Chem. Rev.* 118 (2018) 4981–5079.
- [4] S.B. Adler, Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes †, *Chem. Rev.* 104 (2004) 4791–4844.
- [5] Y. Takagi, K. Kerman, C. Ko, S. Ramanathan, Operational characteristics of thin film solid oxide fuel cells with ruthenium anode in natural gas, *J. Power Sources* 243 (2013) 1–9.
- [6] X. Liu, Z. Zhan, X. Meng, W. Huang, S. Wang, T. Wen, Enabling catalysis of Ru-CeO₂ for propane oxidation in low temperature solid oxide fuel cells, *J. Power Sources* 199 (2012) 138–141.
- [7] M.N. Tsampas, F.M. Sapountzi, A. Boréave, P. Vernoux, Isotopical labeling mechanistic studies of electrochemical promotion of propane combustion on Pt/YSZ, *Electrochem. Commun.* 26 (2013) 13–16.
- [8] P. Vernoux, L. Lizarraga, M.N. Tsampas, F.M. Sapountzi, A. De Lucas-Consuegra, J.L. Valverde, S. Souentie, C.G. Vayenas, D. Tsiplakides, S. Balomenou, E.A. Baranova, Ionically conducting ceramics as active catalyst supports, *Chem. Rev.* 113 (2013) 8192–8260.
- [9] C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsiplakides, *Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion, and Metal-Support Interactions*, Springer, New York, 2001.
- [10] Y.M. Hajar, K.D. Patel, U. Tariq, E.A. Baranova, Functional equivalence of electrochemical promotion and metal support interaction for Pt and RuO₂ nanoparticles, *J. Catal.* 352 (2017) 42–51.
- [11] Y.M. Hajar, B. Venkatesh, E.A. Baranova, Electrochemical Promotion of Nanostructured Palladium for Complete Methane Oxidation, *Catalysts* 9 (2019) 48.
- [12] Y.M. Hajar, B. Venkatesh, M.S.E. Houache, H. Liu, R. Safari, S. Prabhudev, G.A. Botton, E.A. Baranova, Electrochemical promotion of Bi-metallic Ni9Pd core double-shell nanoparticles for complete methane oxidation, *J. Catal.* 374 (2019) 127–135.
- [13] C. Doornkamp, M. Clement, V. Poncet, The Isotopic Exchange Reaction of Oxygen on Metal Oxides, *J. Catal.* 399 (1999) 390–399.
- [14] H.J.M. Bouwmeester, C. Song, J. Zhu, J. Yi, M.V.S. Annaland, B.A. Boukamp, A novel pulse isotopic exchange technique for rapid

- determination of the oxygen surface exchange rate of oxide ion conductors, *Phys. Chem. Chem. Phys.* 11 (2009) 9640–9643.
- [15] J.H. Shim, J.S. Park, T.P. Holme, K. Crabb, W. Lee, Y.B. Kim, X. Tian, T.M. Gu, F.B. Prinz, Enhanced oxygen exchange and incorporation at surface grain boundaries on an oxide ion conductor, *Acta Mater.* 60 (2012) 1–7.
- [16] D. Duprez, Study of surface mobility by isotopic exchange: recent developments and perspectives, in: C. Li, Q. Xin (Eds.), *Spillover Migr. Surf. Species Catal.*, Elsevier Science, 1997: pp. 13–28.
- [17] L. Giordano, G. Pacchioni, J. Goniakowski, Properties of MgO(100) ultrathin layers on Pd(100): Influence of the metal support, *Phys. Rev. B - Condens. Matter Mater. Phys.* 67 (2003) 1–8.
- [18] L. Giordano, J. Goniakowski, G. Pacchioni, Characteristics of Pd adsorption on the MgO(100) surface: Role of oxygen vacancies, *Phys. Rev. B - Condens. Matter Mater. Phys.* 64 (2001) 754171–754179.
- [19] F. Dong, T. Tanabe, A. Suda, N. Takahashi, H. Sobukawa, H. Shinjoh, Investigation of the OSC performance of Pt / CeO₂-ZrO₂-Y₂O₃ catalysts by CO oxidation and 18O/16O isotopic exchange reaction, *Chem. Eng. Sci.* 63 (2008) 5020–5027.
- [20] L. Kai, W. Xuezhong, Z. Zexing, W. Xiaodong, W. Duan, Oxygen Storage Capacity of Pt- Pd-, Rh/CeO₂-BasedOxide Catalyst, *J. Rare Earths.* 25 (2007) 6–10.
- [21] M.A. Fortunato, A. Princivalle, C. Capdeillacre, N. Petigny, C. Tardivac, C. Guizard, M.N. Tsampas, F.M. Sapountzi, P. Vernoux, Role of lattice oxygen in the propane combustion over Pt/yttria-stabilized zirconia : isotopic studies, *Top. Catal.* 57 (2014) 1277–1286.
- [22] J. Zhu, J.G. Van Ommen, H.J.M. Bouwmeester, L. Lefferts, Activation of O₂ and CH₄ on yttrium-stabilized zirconia for the partial oxidation of methane to synthesis gas, *J. Catal.* 233 (2005) 434–441.
- [23] N. Acerbi, S.C. Tsang, S. Golunski, P. Collier, A practical demonstration of electronic promotion in the reduction of ceria coated PGM catalysts., *Chem. Commun.* (2008) 1578–1580.
- [24] N. Acerbi, S.C.E. Tsang, G. Jones, S. Golunski, P. Collier, Rationalization of interactions in precious metal/ceria catalysts using the d-band center model, *Angew. Chemie - Int. Ed.* 52 (2013) 7737–7741.
- [25] S. Bedrane, C. Descorme, D. Duprez, 16O/18O isotopic exchange: A powerful tool to investigate oxygen activation on M/Ce_xZr_{1-x}O₂ catalysts, *Appl. Catal. A Gen.* 289 (2005) 90–96.
- [26] H. Over, Surface Chemistry of Ruthenium Dioxide in Heterogeneous Catalysis and Electrocatalysis: From Fundamental to Applied Research, *Chem. Rev.* 112 (2012) 3356–3426.
- [27] H. Over, M. Muhler, Catalytic CO oxidation over ruthenium - Bridging the pressure gap, *Prog. Surf. Sci.* 72 (2003) 3–17.
- [28] T.F. Garetto, E. Rincón, C.R. Apesteguía, Deep oxidation of propane on Pt-supported catalysts: Drastic turnover rate enhancement using zeolite supports, *Appl. Catal. B Environ.* 48 (2004) 167–174.
- [29] A. Boreave, H. Tan, V. Roche, P. Vernoux, J.P. Deloume, Oxygen mobility in lanthanum nickelate catalysts for deep oxidation of propane, *Solid State Ionics.* 179 (2008) 1071–1075.
- [30] G.K. Boreskov, The Catalysis of Isotopic Exchange in Molecular Oxygen, *Adv. Catal.* 15 (1965) 285–339.
- [31] E.R.S. Winter, Exchange Reactions of Oxides. Part IX, *J. Chem. Soc. A.* (1968) 2889–2902.
- [32] Y.M. Hajar, H.A. Dole, M. Couillard, E.A. Baranova, Investigation of heterogeneous catalysts by electrochemical method: Ceria and titania supported iridium for ethylene oxidation, *ECS Trans.* 72 (2016) 161–172.
- [33] Y.M. Hajar, M.S. Houache, U. Tariq, P. Vernoux, E.A. Baranova, Nanoscopic Ni interfaced with oxygen conductive supports: Link between electrochemical and catalytic studies, *Electrochem. Soc.* 77 (2017) 51–66.
- [34] Y. Hajar, L. Treps, C. Michel, E. Baranova, S. Steinmann, Theoretical Insight into Origin of Electrochemical Promotion of Ethylene oxidation on Ruthenium Oxide, *Catal. Sci. Technol.* 9 (2019) 5857–6200.
- [35] R.J. Isaifan, E.A. Baranova, Effect of ionically conductive supports on the catalytic activity of platinum and ruthenium nanoparticles for ethylene complete oxidation, *Catal. Today.* 241 (2015) 107–113.
- [36] H.A.E. Dole, E.A. Baranova, Ethylene Oxidation in an Oxygen-Deficient Environment: Why Ceria is an Active Support?, *ChemCatChem.* 8 (2016) 1977–1986.
- [37] H. Over, Ruthenium dioxide, a fascinating material for atomic scale surface chemistry, *Appl. Phys. A Mater. Sci. Process.* 75 (2002) 37–44.
- [38] P. Mars, D.W. van Krevelen, Oxidations carried out by means of vanadium oxide catalysts, *Chem. Eng. Sci.* 3 (1954) 41–59.
- [39] R.J. Isaifan, E.A. Baranova, Catalytic electrooxidation of volatile organic compounds by oxygen-ion conducting ceramics in oxygen-free gas environment, *Electrochem. Commun.* 27 (2013) 164–167.
- [40] P. Fornasiero, R. Di Monte, G. Ranga Rao, J. Kaspar, S. Meriani, A. Trovarelli, M. Graziani, Rh-Loaded CeO₂-ZrO₂ Solid Solutions as Highly Efficient Oxygen Exchangers: Dependence of the Reduction Behavior and the Oxygen Storage Capacity on the Structural Properties, *J. Catal.* 151 (1995) 168–177.