

## Supporting Information

### Elucidating the role of CO<sub>2</sub> in the soft oxidative dehydrogenation of propane over ceria-based catalysts

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**Figure S2.** Selectivity of products in the thermal dehydrogenation reaction. *Reaction conditions:* 37% C<sub>3</sub>H<sub>8</sub>, 67% He; GHSV=6000 h<sup>-1</sup>, T=500 °C. *Legend:* ■:C<sub>3</sub>H<sub>6</sub>, ▲:CH<sub>4</sub>, ▼:C<sub>2</sub>H<sub>4</sub>, ●: CO<sub>x</sub>, □: carbon balance

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**Figure S7.** XPS spectra for the Ce(3d) region for the various 5%Pd/CeZrAlO<sub>x</sub> catalysts, fitted with line-shapes for Ce(IV) and Ce(III) species.

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**Figure S12.** TGA analysis of the fresh and used 5wt%Pd/CeZrAlO<sub>x</sub> catalysts.

### Catalytic performance calculations:

Propane conversion X, was calculated as follows

$$X = \left( 1 - \frac{F_{C_3H_8_{out}}}{F_{C_3H_8_{in}}} \right) * 100\%$$

Where:  $F_{C_3H_8_{out}}$  = flow of propane out of the reactor

$F_{C_3H_8_{in}}$  = flow of propane into the reactor

$$S = \left( \frac{F_{A,out}}{\sum F_{carbon\ prod}} \right) * 100\%$$

Where:  $F_{A,out}$  = flow of carbon in product A out of reactor (\*)

$F_{carbon\ prod}$  = flow of all carbon from products \* out of reactor

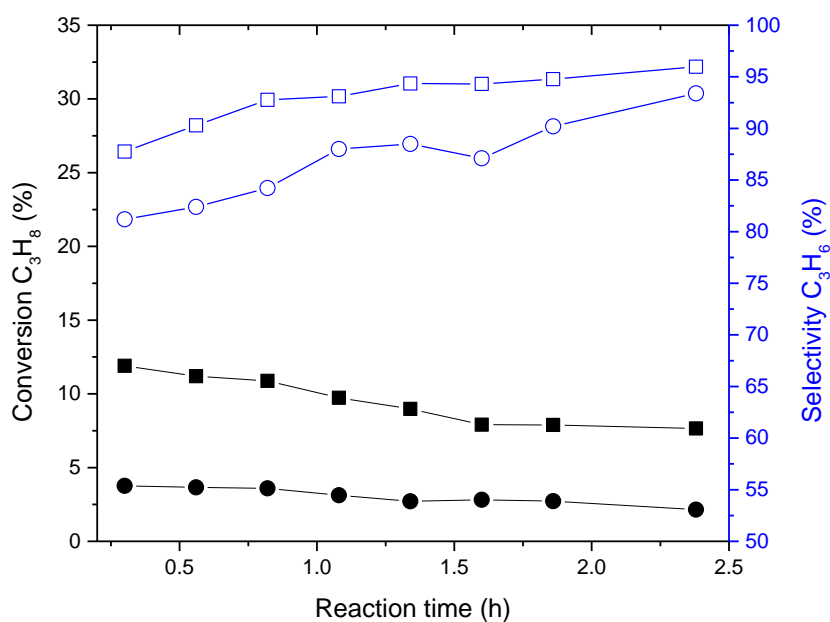
\* *products excluding carbon oxides*

**Table S1.** Propane conversion and selectivity of Pd over various Ce based catalyst formulations.

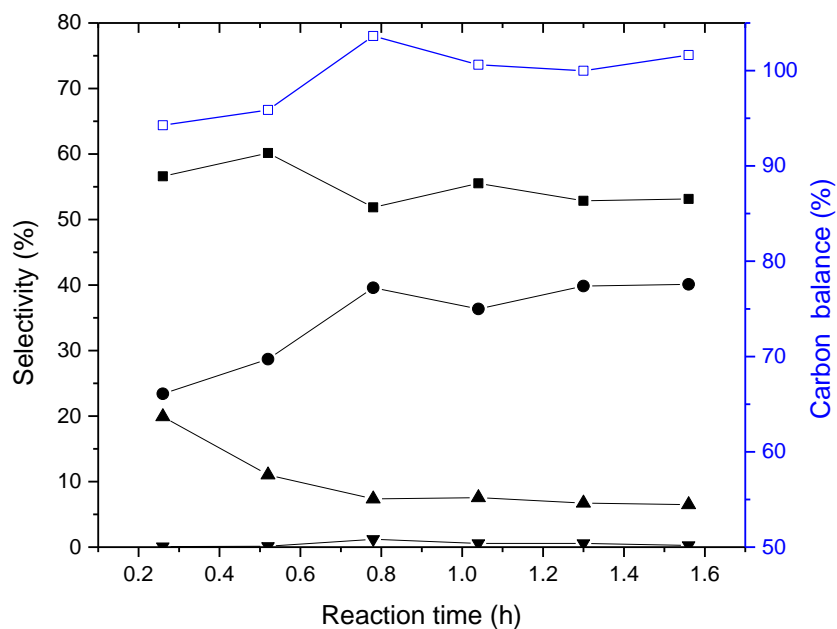
*Reaction conditions:* 37% C<sub>3</sub>H<sub>8</sub>, 37% CO<sub>2</sub>, 26% He; GHSV=6000 h<sup>-1</sup>, T = 500 °C

<b>Pd loading (%)</b>	<b>Support composition</b>	<b>Conversion (%)*</b>	<b>Selectivity (%)*</b>
5	Ce <sub>0.33</sub> Zr <sub>0.33</sub> Al <sub>0.33</sub> O <sub>x</sub>	10.2	90
	Ce <sub>0.25</sub> Zr <sub>0.25</sub> Al <sub>0.5</sub> O <sub>x</sub>	9.5	93
	Ce <sub>0.16</sub> Zr <sub>0.33</sub> Al <sub>0.5</sub> O <sub>x</sub>	9.2	80
	Ce <sub>0.157</sub> Zr <sub>0.157</sub> Al <sub>0.66</sub> O <sub>x</sub>	9.3	91
0.1		3.1	90
0.5		3.6	92
2.5	Ce <sub>0.25</sub> Zr <sub>0.25</sub> Al <sub>0.5</sub> O <sub>x</sub>	6.5	92
7.5		13.2	69
10		5.8	31

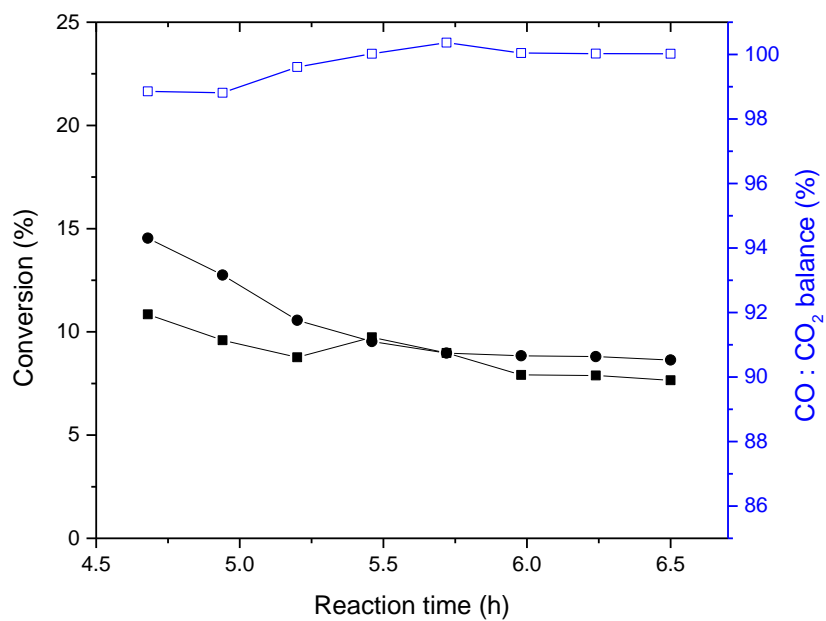
\*Measured after 1 h of stream



**Figure S1.** Comparison of conversion (filled symbols) and selectivity (empty symbols) between Pd/CeZrAlO<sub>x</sub> (■) and CeZrAlO<sub>x</sub> (●) *Reaction conditions:* GHSV=6000 h<sup>-1</sup>, T=500 °C, 37% C<sub>3</sub>H<sub>8</sub>, 37% CO<sub>2</sub>, 26% He.



**Figure S2.** Selectivity of products in the thermal dehydrogenation reaction. *Reaction conditions:* 37% C<sub>3</sub>H<sub>8</sub>, 67% He; GHSV=6000 h<sup>-1</sup>, T=500 °C. *Legend:* ■:C<sub>3</sub>H<sub>6</sub>, ▲:CH<sub>4</sub>, ▼:C<sub>2</sub>H<sub>4</sub>, ●: CO<sub>x</sub>, □: carbon balance.

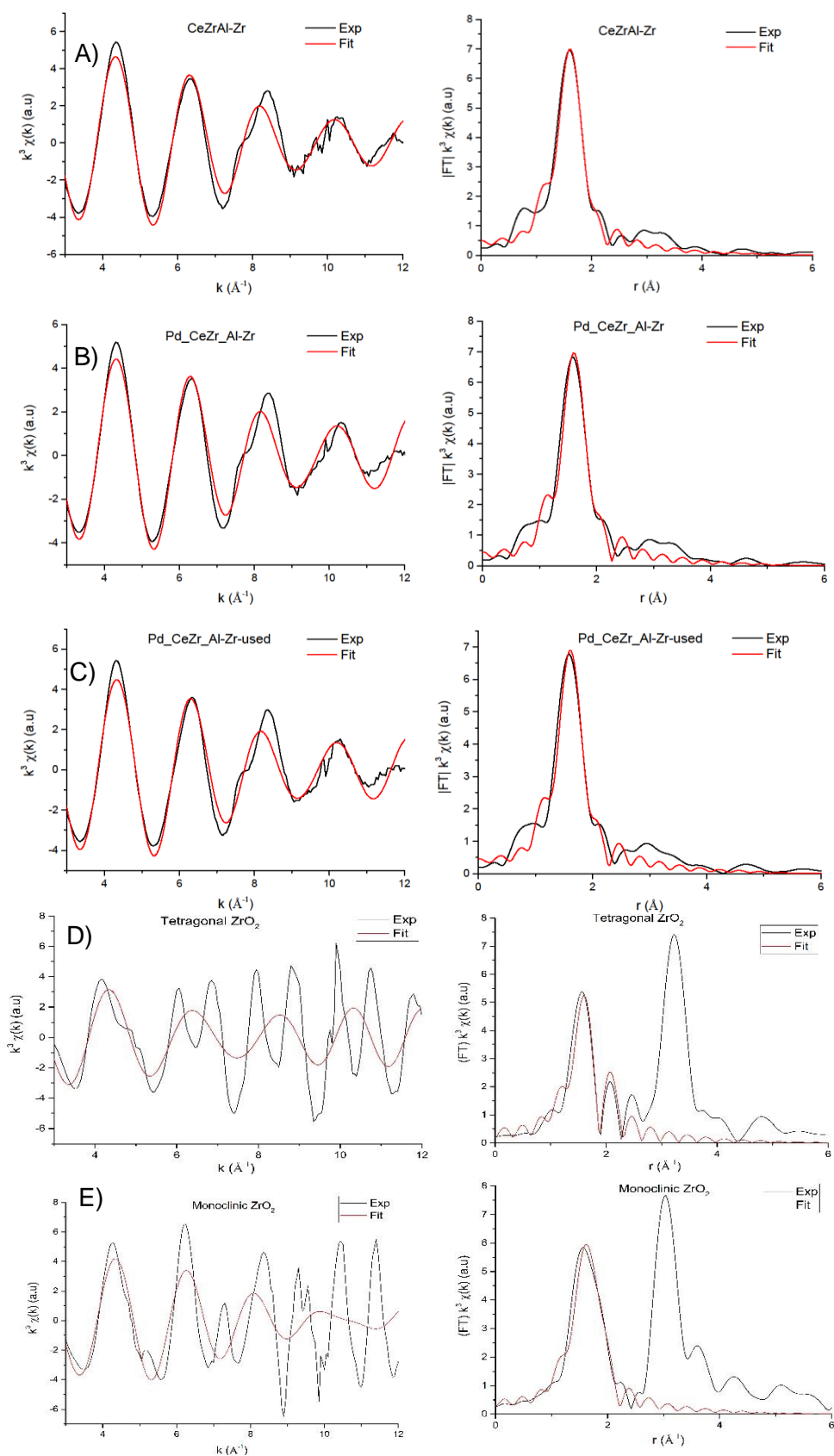


**Figure S3.** Conversion of C<sub>3</sub>H<sub>8</sub> (■) and CO<sub>2</sub> (●) during subsequent oxidative dehydrogenation (37% C<sub>3</sub>H<sub>8</sub>, 37% CO<sub>2</sub>, 26% He) along with CO<sub>2</sub>: CO balance. *Reaction conditions:* GHSV=6000 h<sup>-1</sup>, T=500 °C.

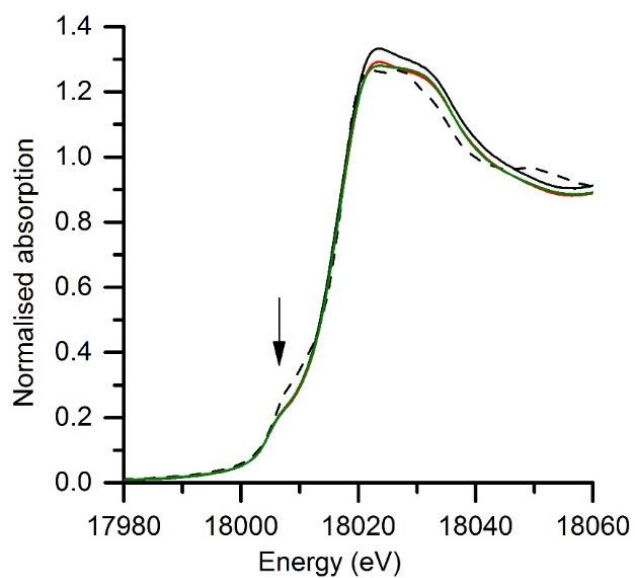
**Table S2.** Zr K-edge derived k3-weighted EXAFS fitting parameters.

<b>Material</b>	<b>bond</b>	<b>N</b>	<b><math>\sigma^2</math> (<math>\text{\AA}^2</math>)</b>	<b>r (<math>\text{\AA}</math>)</b>	<b><math>\Delta E_0</math> (eV)</b>	<b>R-factor</b>
CeZrAlO <sub>x</sub>	Zr-O1	3.2 (7)	0.0019	2.121 (8)	2.385	0.0079
	Zr-O2	2.3 (3)	0.0019	2.275 (14)		
Pd-CeZrAlO <sub>x</sub> fresh	Zr-O1	2.9 (5)	0.0007	2.120 (9)	1.646	0.0155
	Zr-O2	2.2 (2)	0.0007	2.276 (14)		
PdCeZrAlO <sub>x</sub> 4h used	Zr-O1	3.1 (7)	0.0014	2.126 (10)	2.454	0.0172
	Zr-O2	2.2 (3)	0.0014	2.284 (17)		
Tetragonal ZrO <sub>2</sub>	Zr-O1	3.5(8)	0.0041	2.137 (22)	2.802	0.0361
	Zr-O2	2.3(7)	0.0041	2.352 (38)		
Monoclinic ZrO <sub>2</sub>	Zr-O1	2.7(6)	0.0016	2.126 (24)	2.144	0.0217
	Zr-O2	2.7(5)	0.0016	2.272 (26)		



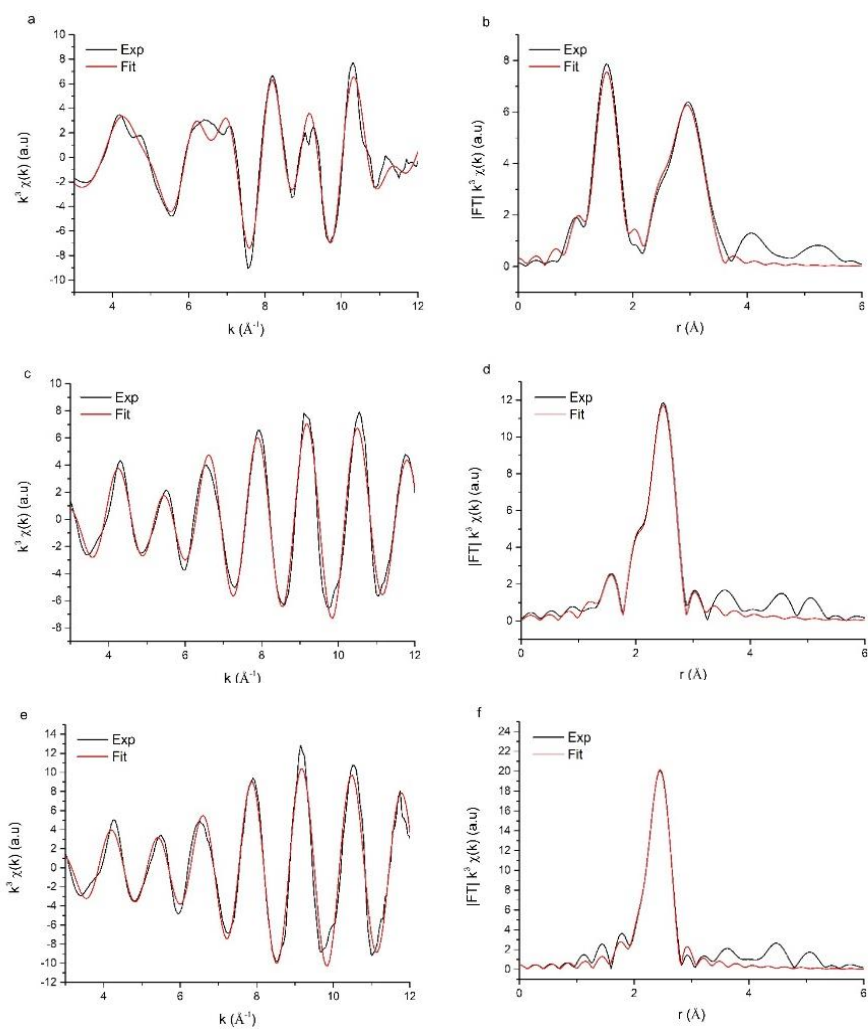


**Figure S4.** Zr K-edge derived  $k^3$ -weighted EXAFS data (left column) and magnitudes of Fourier-transformed data (right column) from A) CeZrAlO<sub>x</sub>, B) fresh Pd-CeZrAlO<sub>x</sub>, C) 4 h used Pd-CeZrAlO<sub>x</sub>, D) tetragonal ZrO<sub>2</sub> and E) monoclinic ZrO<sub>2</sub>.

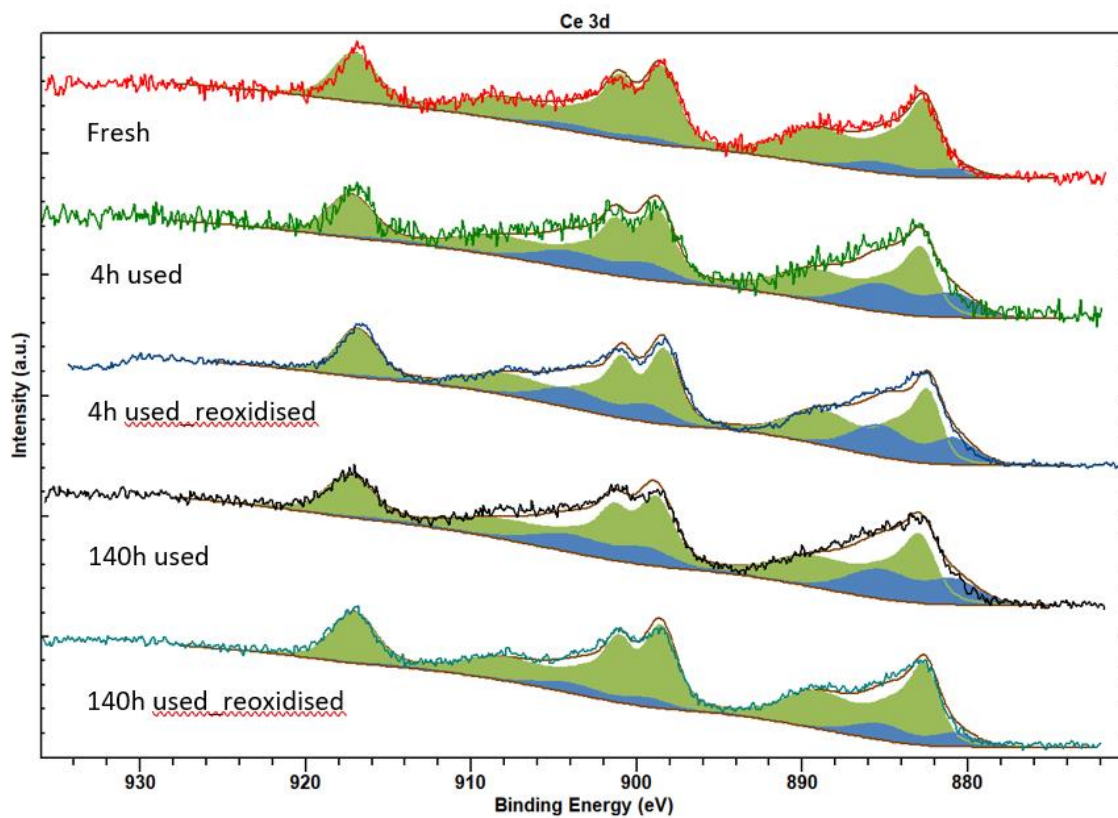


**Figure S5.** Zr K-edge XANES of CeZrAlO<sub>x</sub> support compared with a tetragonal ZrO<sub>2</sub> standard.

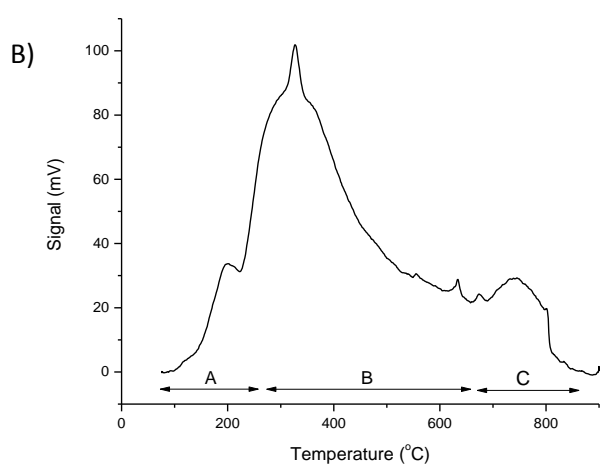
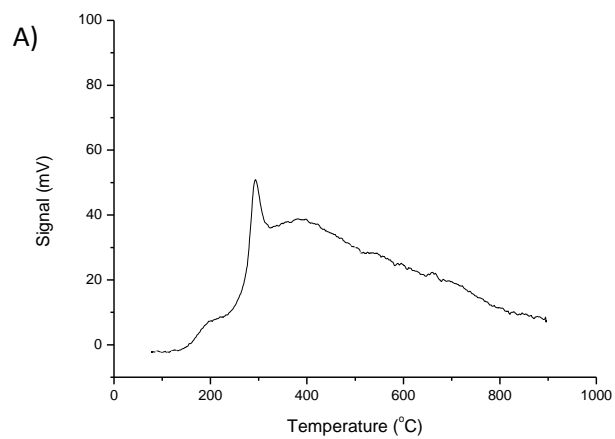
*Key:* Dashed black line: tetragonal ZrO<sub>2</sub>; black solid line: CeZrAlO<sub>x</sub>; red solid line: fresh Pd/CeZrAlO<sub>x</sub>; and green solid line: 4 h used Pd/CeZrAlO<sub>x</sub>. The arrow indicates the position of the 1s to 4d pre-edge transition.



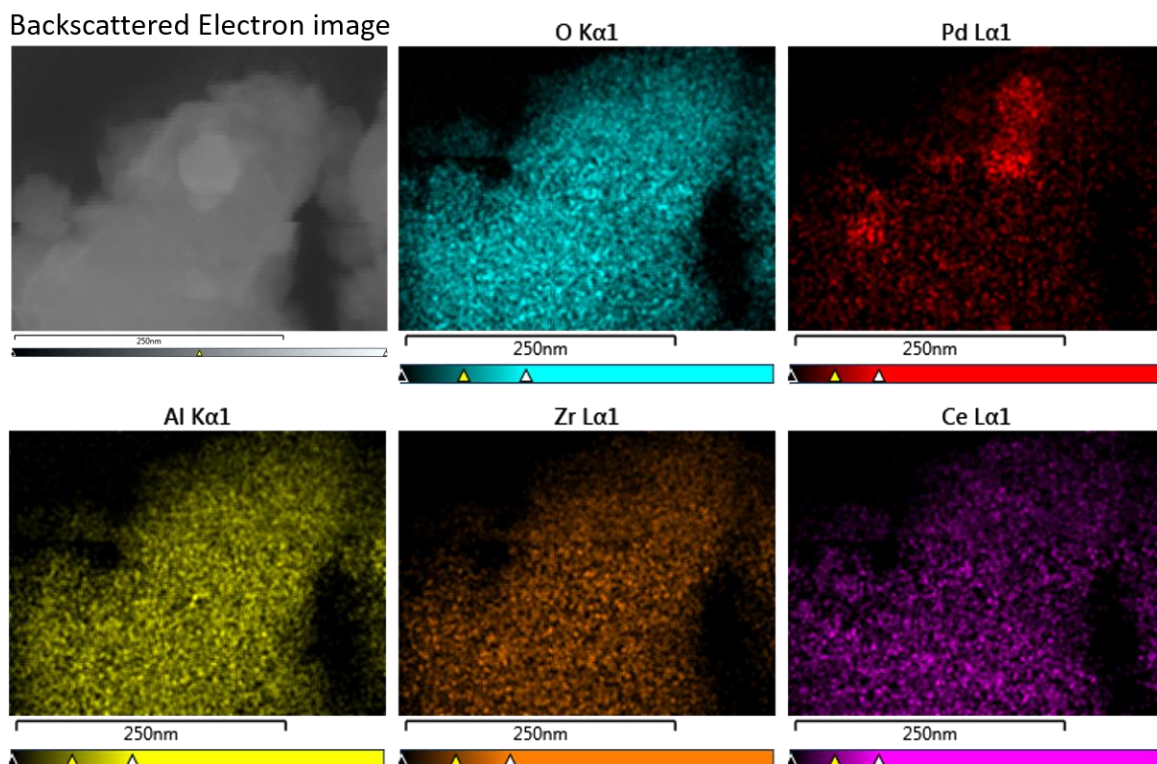
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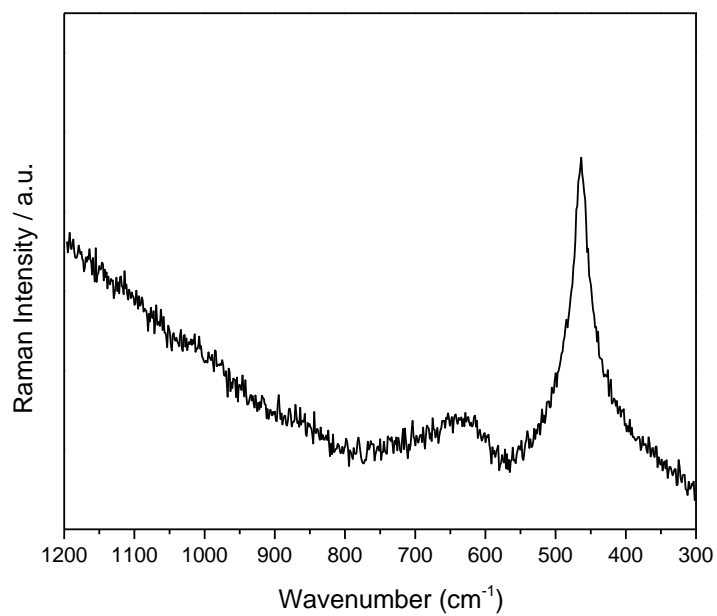
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**Figure S8.** TPD profiles of 5%Pd/CeZrAlO<sub>x</sub> material using different gases: A) NH<sub>3</sub> and B) CO<sub>2</sub>.



**Figure S9.** *Additional* SEM-XEDS mapping data obtained on the 5%Pd/CeZrAlO<sub>x</sub> catalyst showing the excellent homogeneity of Ce, Zr and Al distribution compared to that of Pd.



**Figure S10.** Raman analysis of  $\text{CeZrAlO}_x$  support. The band at  $620\text{ cm}^{-1}$  is clear evidence of the presence of a pseudo-cubic, tetragonal Ce–Zr phase.<sup>1</sup>

## Temperature programmed reduction: simulation of experimental data

Temperature programmed reduction experiments primarily characterise the rate of specific processes that can be thermally stimulated. The rate can be parameterised very simply as a function of temperature  $T$  and the extent of the process  $\alpha$  (which varies from 0 at the beginning to 1 when completed).

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

The pressure of the reactant gas is also a factor in this experiment, but for the purposes of our work it can be ignored as the reactant gases are kept in excess and can be assumed to be constant. The temperature dependence of the rate  $k(T)$  can be parameterised using the Arrhenius equation.

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha)$$

with  $A$  being the Arrhenius pre-exponential factor,  $E_a$  the activation energy,  $R$  the gas constant and  $T$  the temperature. This expression assumes a constant activation energy over the entire process  $\alpha$ . In order to correct for any change in  $E_a$  as the material becomes more reduced, an extra parameter  $\gamma$  can be included in the equation.

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a(1 + \gamma\alpha)}{RT}\right) f(\alpha)$$

The parameter  $\gamma$  describes a linear relationship between the  $E_a$  and  $\alpha$ . A positive value of  $\gamma$  indicates an increase in the distance between the active site for the  $H_2$  dissociation and reduction. The final term to be parameterised is the degree of conversion dependence of the process. It is possible to apply some simple kinetics to parameterise this dependence, but it is found for TPR experiments it is best to use a model free approach outlined by Sestak and Berggren<sup>2</sup> which can represent a large number of reaction models through its kinetic parameters  $m$ ,  $n$ , and  $p$ .

$$f(\alpha) = \alpha^m(1 - \alpha)^n[-\ln(1 - \alpha)]^p$$

The Sestak and Berggren (SB) function is often truncated so that  $p = 0$  as it is found that often only  $m$  and  $n$  are required to describe the TPR reduction processes. These parameters are not



derived from any specific kinetic model and therefore have no true physical meaning, but it is possible to infer information from their values. It can be seen that the shape parameter  $m$  is dominant at higher degrees of reduction, whereas  $n$  is dominant at lower degrees of reduction. For a temperature programmed reduction experiment the relative magnitude of these two parameters can be linked to the influence of the reduced and oxidised material respectively on the shape (which described the kinetics) of the reduction profile (e.g., a higher relative  $m$  value indicates the shape is more dominated by the reduced material, and a higher relative  $n$  value indicates the shape is dominated by the oxidised material). In the past there has been some work to attempt to link these parameters to specific processes occurring during a TPR experiment with moderate success.<sup>3</sup> Finally, for temperature programmed experiments, time can be directly related to the temperature through the following relationship.

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT}$$

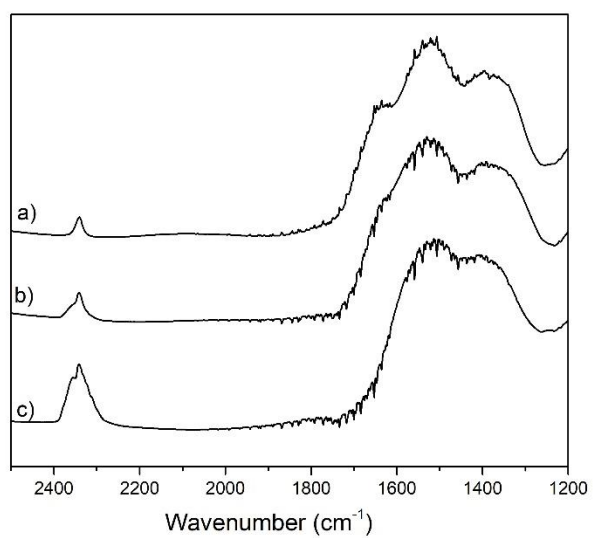
with  $\beta$  being the heating rate of the experiment, the final form of the function can then be expressed using

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{E_a(1 + \gamma\alpha)}{RT}\right) \alpha^m (1 - \alpha)^n$$

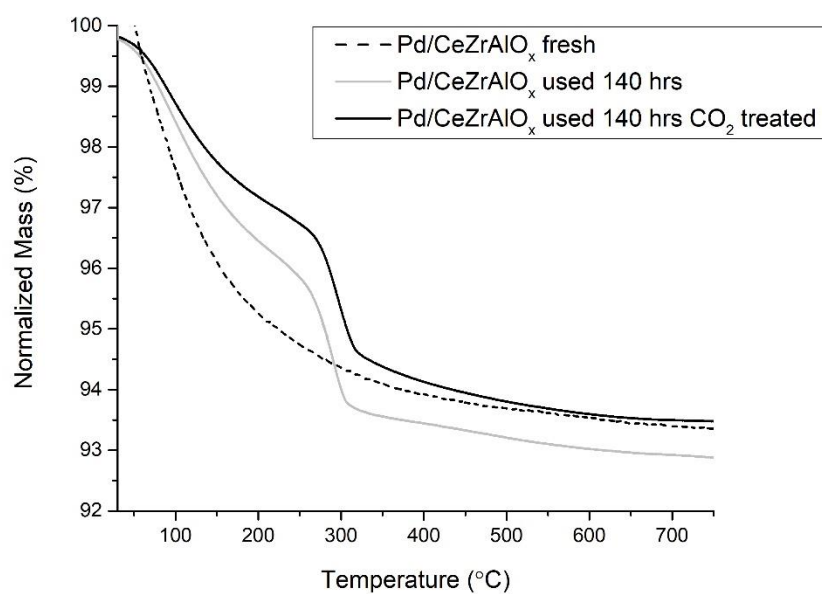
For a complex reduction profile such as the ones measured in this paper, it becomes pertinent to express the total reduction profile as a simple sum of individual processes, such that

$$\frac{d\alpha}{dT} = \sum_{N=1}^N \frac{d\alpha_N}{dT}$$

with  $N$  being the number of individual reduction processes which make up the total profile. As one can imagine as you increase  $N$ , the goodness of overall fit to the experimental thermogram will increase, therefore for this work a value of  $N$  was selected to the minimum value which would still enable us to describe the major features of the thermogram, while also making sense physically.



**Figure S11.** DRIFT analysis of calcined CeZrAlO<sub>x</sub> support a) when fresh, b) under N<sub>2</sub> flow and c) under CO<sub>2</sub> flow.



**Figure S12.** TGA analysis of the fresh and used 5wt%Pd/CeZrAlO<sub>x</sub> catalysts.

## References:

1. Lan, L.; Chen, S.; Cao, Y.; Gong, M.; Chen, Y., New insights into the structure of a CeO<sub>2</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite and its influence on the performance of the supported Pd-only three-way catalyst. *Catal. Sci. Tech.* **2015**, *5*, 4488-4500.
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3. Munteanu, G.; Ilieva, L.; Nedyalkova, R.; Andreeva, D., Influence of gold on the reduction behaviour of Au-V<sub>2</sub>O<sub>5</sub>/CeO<sub>2</sub> catalytic systems: TPR and kinetic parameters of reduction. *Appl. Catal. A: Gen.* **2004**, *277*, 31-40.