Temperature Programmed Reduction of cerium oxides with different crystallographic surface terminations.

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Temperature Programmed Reduction (TPR) is a versatile technique to study the redox property of metal oxides relevant to catalytic reactions and many other applications related to oxide materials in general[1,2]. The technique is deceptively simple, imposing a linear temperature ramping on a reducible material inside a reactor and compute for the consumption of hydrogen used during this temperature ramping.

$M_xO_y + y\ H_2 \rightarrow x\ M + y\ H_2O$ Equation 1

where MO is a metal oxide, M is the reduced metal, *x* and *y* are stoichiometric coefficients

Since the amount of molecular hydrogen consumed is equal to the amount of atomic oxygen removed from the solid then one gets the stoichiometry of the reduction knowing the number of moles of a material inside the reactor. Ironically the interpretation of the results is one of the most complex in catalytic systems. It relies on transient kinetics theories and is solved in most of the cases only analytically. Briefly it is as follows.

The gas-solid reaction rate under differential condition is described as follows:

$$\text{rate} = \frac{d[\alpha]}{dt} = k(T)f(\alpha)$$ Equation 2

Where α is the degree of conversion of a solid reactant, t is the time, $f(\alpha)$ is a function of reduction models, and $k(T)$ is the rate constant of the Arrhenius equation:

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right)$$ Equation 3

where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the temperature in Kelvin. In a TPR experiment, the heating rate or ramping rate β is equal to $\frac{dT}{dt}$; therefore, by substituting the ramp rate into equation (2) and combining it with equation (3) the gas-solid reaction rate equation is easier re- written as follows:

$$\frac{d(\alpha)}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) f(\alpha)$$ Equation 4

By plotting the calculated $\frac{d(\alpha)}{dT}$ and fitting it to experimental $\frac{d(\alpha)}{dT}$ one can then analytically obtain the variables (E_a, A, and $f(\alpha)$) in equation (4). The extent of reduction (α) is produced experimentally for each peak in TPR patterns.

Table 1 shows some of the functions used to treat the data.

Table 1. Reduction functions reported in the literatures[3].

Reaction model	$\boldsymbol{f(\alpha)}$
n-dimensional nucleation according to Avrami-Erofeev	$\mathrm{n}(1-\alpha)[-\ln(1-\alpha)]^{\frac{(\mathrm{n}-1)}{\mathrm{n}}}$
n-order reaction	$(1-\alpha)^{\mathrm{n}}$
Phase boundary-controlled	$\mathrm{n}(1-\alpha)^{\frac{\mathrm{n}-1}{\mathrm{n}}}$
1-D diffusion	$\frac{1}{2}\alpha^{-1}$
2-D diffusion	$\frac{-1}{\ln(1-\alpha)}$
3-D diffusion	$\frac{\frac{3}{2}(1-\alpha)^{\frac{2}{3}}}{1-(1-\alpha)^{\frac{1}{3}}}$
Sestak–Berggren	$\alpha^m(1-\alpha)^n(-\ln(1-\alpha))^p$

Information such as activation energy for reduction[4,5], phase composition[6], and differentiation between surface and bulk contribution[7] can be obtained. The technique becomes more powerful for metal deposited on metal oxides as it can also probe into the metal/oxide interface and metal sintering during the reduction process[8].

In a recent work from my previous group, TPR was used to estimate the activation energy of reduction of surface of CeO_2 and its bulk[7] (figure 1). The work gave preliminary information that needs to be revisited. Equally important its application to understand the degree or reduction of CeO_2 in different shapes (nano rods versus nano cubes in particular) is poised to provide quantitative information related to the extent of reduction of surfaces depending on their crystallographic termination ((111) for nano-crystals, (110) for nano rods and reconstructed (100) for nano-cubes)[9].

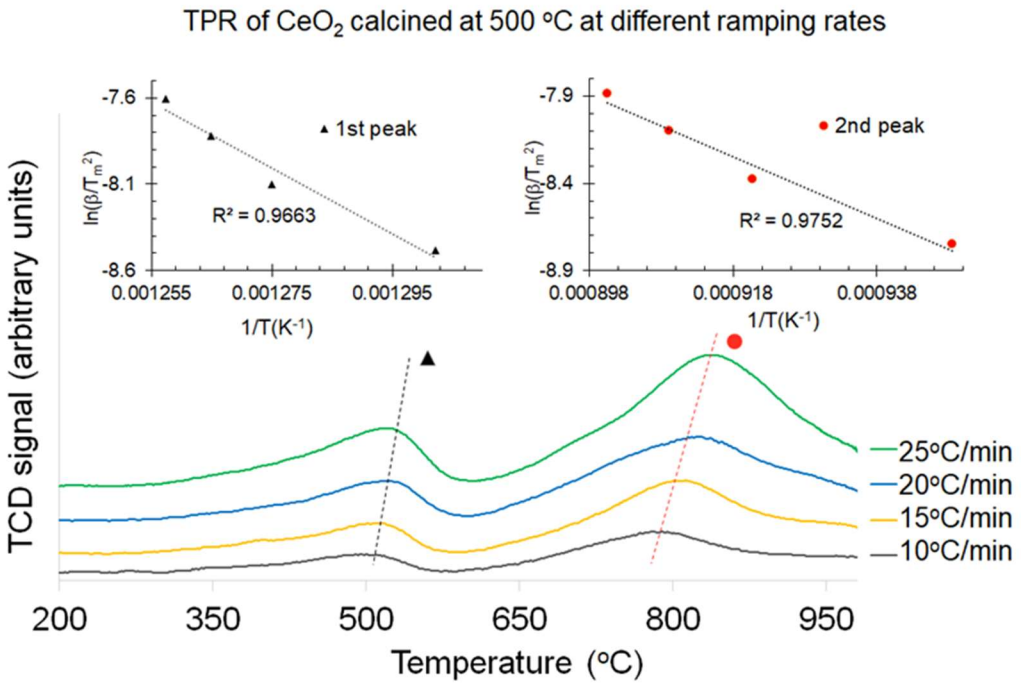

Figure 1. TPR of polycrystalline CeO_2 calcined at 500°C at ramping temperatures, β, equal to 10, 15, 20, and 25°C/min. The insets show the plot of Ln β/T_m^2 as a function of 1/T where T_m is the maximum peak temperature using the Kissinger equation[5].

At the IFG we have a acquired a TPR technique and at present are in need for a student who can conduct research on the reduction of CeO_2 alone in different shapes and crystallite sizes. The student will be asked to prepare the different CeO_2, analyze them by XRD and conduct detailed TPR experiments. The student will also be required to find the most suitable analytical function describing the TPR profile. The project is well suited to a senior level undergraduate student with sound knowledge in chemistry or chemical engineering. Typically, a run takes about three to four hours. Therefore, it is expected that student can do two to three runs per week. Assuming a six months period for the research a good number of studies can be conducted which can be followed by a report. Depending on the quality of the data a manuscript at the end of the training period is expected. The student will be directly supervised by me and will be assisted by a PhD student.

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[1] An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis, Chapter 11, Temperature Programmed Reduction and Sulphiding. Edited by J.A. Moulijn, P. W. N. M. van Leeuwen, R. A. van Santen. Stud. Surf. Sci. Catal. 1993, 79, 401-417.

[2] Temperature Programmed Reduction. Hurst, N.W.; Gentry, S.J.; Jones, A.; McNicol, B. D. Catal. Rev. Sci. Eng. 1982, 24, 233-309.

[3] Investigation on the Kinetic Mechanism of the Reduction of Fe_2O_3/CoO-Decorated carbon Xerogels: A Non-Isothermal Study. M. R. Ghaani, M. Catti. J. Solid St. Chem. 2019, 277, 368.

[4] Thermal desorption of gases. P. A. Redhead, Vacuum 1962, 12, 203.

[5] Reaction Kinetics in Differential Thermal Analysis. H. E. Kissinger, Anal. Chem. 1957, 29, 1702.

[6] Comparative Study on the Formation and Reduction of Bulk and Al_2O_3-Supported Cobalt Oxides by H_2-TPR Technique. Y. Ji, Z. Zhao, A. Duan, G. Jiang, J. Liu. J. Phys. Chem. C 2009, 113, 7186.

[7] Solar thermal hydrogen production over CeO_2 based materials I. Al-Shankiti, F. Al-Otaibi, Y. Al-Salik, H. Idriss, Top. Catal. 2013, 56, 1129.

[8] Extracting Turn Over Frequencies of electron transfer in heterogeneous catalysis. A study of IrO_2-TiO_2 anatase for water oxidation using Ce^{4+} cations. M. Alrushaid, K. A. Wahab, M. A. Nadeem, H. Idriss, Catalysts 2021, 11, 1030.

[9] Surface Faceting and Reconstruction of Ceria Nanoparticles. C. Yang, X. Yu, S. Heißler, A. Nefedov, S. Colussi, J. Llorca, A. Trovarelli, Y. Wang, C. Wöll. Angew. Chem. Int. Ed. 2017, 56, 375.