

UC Santa Barbara

UC Santa Barbara Previously Published Works

Title

Catalytic Dry Reforming of Methane on Ruthenium-Doped Ceria and Ruthenium Supported on Ceria

Permalink

<https://escholarship.org/uc/item/8fn378rm>

Journal

Topics in Catalysis, 57(1-4)

ISSN

1022-5528

Authors

Derk, Alan R
Moore, George M
Sharma, Sudhanshu
[et al.](#)

Publication Date

2014-02-01

DOI

10.1007/s11244-013-0167-2

Copyright Information

This work is made available under the terms of a Creative Commons Attribution-NonCommercial-NoDerivatives License, available at <https://creativecommons.org/licenses/by-nc-nd/4.0/>

Peer reviewed

Catalytic dry reforming of methane on ruthenium-doped ceria and ruthenium supported on ceria

Alan R. Derk¹, George M. Moore¹, Sudhanshu Sharma², Eric W. McFarland¹, Horia Metiu^{3*}

1. Department of Chemical Engineering, University of California, Santa Barbara CA 93106-5080 USA

2. Department of Chemistry, IIT Gandhinagar, VGEC campus, Chandkheda, Ahmedabad, Gujarat 382424 India

3. Department of Chemistry and Biochemistry, University of California, Santa Barbara CA 93106-9510 USA

* To whom correspondence should be addressed: metiu@chem.ucsb.edu, tel 805-893-2256, fax 805-893-4120

Abstract. Two types of Ru-ceria catalysts were investigated, one prepared by combustion to create an atomically doped metal oxide, and the other, prepared by impregnation, as supported Ru oxide. They have different physical properties (as measured by X-Ray Photoelectron Spectroscopy, X-Ray diffraction, and Infrared spectra of adsorbed CO) but identical catalytic activity for dry reforming of methane. We show that the catalyst for dry reforming is partially reduced using XPS and IR spectroscopy. Furthermore, transient oxidation reaction spectroscopy with oxygen pulses confirms partial reduction of the catalyst is necessary for dry reforming activity.

Keywords: ceria, ruthenium, methane, dry reforming, doped oxide catalysts

1 Introduction

Steam reforming of methane is the preferred commercial process [1,2] for the preparation of syngas. There is, however, considerable interest in “dry reforming” [3-6], which uses CO₂ rather than steam, because large quantities of methane are found mixed with carbon dioxide. The expense of separating methane from CO₂, prior to syngas preparation, makes steam reforming of methane from such sources uneconomical. An efficient dry reforming catalyst would allow us to make use of low-cost CO₂-containing methane to produce syngas. Here we study dry reforming by two catalysts: one which is assumed to be Ru-doped ceria and another which is assumed to be metallic Ru supported on ceria.

Rostrup-Nielsen and co-workers investigated dry reforming catalyzed by silica-supported nickel, ruthenium, rhodium, palladium, iridium, and platinum catalysts [7] and found that the ruthenium performed best, with the highest turnover and minimal coke formation. Safariamin *et al.* studied ruthenium supported on alumina and ceria and combinations thereof [8]. They found that the performance of Ru supported on alumina impregnated with ceria is better than that of Ru supported on alumina. Other studies have found that oxidic ruthenium compounds are also active catalysts. For example, Nakagawa [9] and co-workers suggested that the coexistence of metallic ruthenium and ruthenium oxide was important for dry reforming activity. These results indicate a dual-site mechanism could likely be important. In a similar catalytic system, Gallego [10] and co-workers found Ni/La₂O₃ and the perovskite, LaNiO₃, catalyzed dry reforming via a dual-site mechanism.

We studied Ru-doped ceria for two reasons. (1) Our temperature programmed reaction studies of dry reforming and of partial oxidation of methane, catalyzed by Ru-doped ceria, found that dry reforming (producing predominantly synthesis gas) starts at a lower temperature than partial oxidation (producing predominantly carbon dioxide and water). If interpreted naively this would indicate that CO₂ is a better oxidant than O₂, which is not an acceptable conclusion. We show here that the dry reforming catalyst is the reduced oxide and this reduction is possible because CO₂ is a poorer oxidant than O₂. (2) The combustion method used here is one of the most reliable ways of preparing doped oxides [11]. However, no matter what the preparation method is, one is never completely sure that a doped oxide was prepared. Because of this uncertainty, we also prepared a Ru ceria catalyst by impregnation and reduction, with the intent of preparing metallic supported on ceria. We hoped to show that this catalyst is different from the presumed doped-oxide catalyst. To our surprise we found that the two catalysts have identical catalytic activity even though their physical properties are different.

2 Experimental

2.1 Catalyst Synthesis

Ruthenium-doped ceria was synthesized using the combustion method previously used by Hegde [11]. To begin, 2.50 g of cerium(III) nitrate hexahydrate, 0.06 g of ruthenium(III) chloride, and 0.09 g of urea are dissolved in water (Millipore). A Pyrex dish with this mixture is placed into a furnace, which is heated to 450 °C to induce spontaneous combustion and produce an oxide.

The combustion is very rapid and it is assumed that in this short time the Ru atoms are not able to migrate and make a separate phase, and they get trapped where they were when the combustion started. This is one of the most reliable methods for producing a substitutionally doped oxide (i.e. single Ru atoms replace Ce atoms). In what follows we use for this material the notation $\text{Ru}_{0.05}\text{Ce}_{0.95}\text{O}_2$.

Ruthenium metal supported on ceria was synthesized by wet-impregnation. Cerium oxide powder, prepared by combustion synthesis (as described above, but without RuCl_3), was dried in air at 220 °C after which it was added to an aqueous solution of RuCl_3 . The Ru concentration was such that the ruthenium:cerium mole ratio was 5%, as in the sample prepared by combustion. The mixture was sonicated and dried in air at 80 °C and then heated in H_2 at 400 °C for 6 hours to reduce RuCl_3 . We used a relatively low calcination temperature to minimize Ru diffusion into CeO_2 . Temperature programmed reduction experiments [12-17] have shown that ceria is reduced by H_2 . The temperature at which hydrogen consumption by ceria begins depends on the grain size [17] and also on surface contaminants (some ceria surfaces have hydroxyls or polydentate carbonates [12]) or bulk contaminants (e.g. La is present in ceria used in Ref. [13]). Because of this, different experiments, on different ceria samples, find different temperatures at which ceria starts being reduced by hydrogen (e.g. 200 °C [12], 347 °C [13], 327 °C [14]); these values are below the temperature we used to reduce RuCl_3 . Therefore we expect that the as-prepared catalyst is metallic Ru on a partially reduced ceria support. However, the material was in contact with air for a long time before being used as a catalyst (the shortest time was one day, the longest two weeks). We assume that this exposure to air reoxidized ceria. Perrichon *et al.* [13] found that ceria reduced with H_2 reoxidizes rapidly at room temperature, if it is not reduced too far. In what follows we denote the material prepared by the second procedure by Ru/CeO_2 and will call it metallic Ru supported on ceria.

We emphasize that there is no guarantee that the combustion method produces doped ceria or that all Ru in the sample prepared by impregnation is metallic.

2.2 Catalyst Characterization

X-ray diffraction (XRD) data were collected on a Philips X'PERT diffractometer. Synchrotron XRD patterns were collected in transmission mode at RT on beamline 11-BM at the Advanced

Photon Source, Argonne National Laboratory, with a photon energy of approximately 30 keV. Rietveld refinements were performed using GSAS [18,19].

X-Ray photoelectron spectroscopy (XPS) spectra were obtained with Al K_{α} radiation using a Kratos Axis Ultra X-ray photoelectron spectrometer. In order to account for charging, the XPS spectra were shifted using the C(1s) peak of adventitious carbon to 285.0 eV.

Diffuse Reflectance Infrared Fourier-Transform Spectroscopy (DRIFTS) of adsorbed CO was performed using a Thermo Electron Corporation Nicolet 4700 with DRIFTS accessories by Harrick Scientific. Samples catalyzed dry reforming at 400 °C for an hour, and then cooled to 25 °C in argon. After that, 10% CO in argon was flowed over the sample for 10 minutes. Subsequently, pure argon was flowed to remove CO from the gas phase while adsorbed CO remained bound to the surface. Spectra were collected at each of these steps.

2.3 Reactivity Characterization

The activity of the catalysts was determined in a packed bed reactor with a high flowrate to achieve a very short residence time (differential reactor). The reactor (a quartz tube with 4 mm inner diameter sealed with quartz wool) was filled with 25 mg of catalyst mixed with 50 mg of 200-mesh GC-grade alumina. Gases were delivered using mass-flow controllers (MFCs, supplied by MKS). The CH₄:CO₂:Ar ratios were 1:1:3. The catalyst void-fraction was measured volumetrically with methanol and the gas flowrate was set such that the spacetime was 0.18 s (calculated at 20 °C), unless otherwise noted. This spacetime corresponds to 110 mole of CH₄ / (g-catalyst×second). The reactor effluent was measured by a differentially pumped mass spectrometer (SRS). Frequent calibrations of the mass spectrometer, with mixtures of reactants, products, and argon with known composition, were made. All gases had a purity of at least 99.99%. The temperature was controlled and varied by using a programmable controller (OMEGA CSC32).

Temperature Programmed Reaction (TPR) was used to determine the activity of the catalyst as a function of temperature. With a constant volumetric feed rate, the reactor temperature is varied linearly while the composition of the effluent is monitored. Due to the temperature increase, the space time decreases from 0.18 s at room temperature to 0.06 s at 600 °C. In TPR experiments, the system might not reach steady state during the temperature ramp. Because of this, we also performed Staircase Temperature Programmed Reaction (STPR)

experiments to study the activity of the catalyst at steady state. In STPR, the temperature is increased from 250 °C to 600 °C in 50 °C increments. After each increase the temperature is held constant for 30 minutes to allow the reaction to reach steady state. After reaching 600 °C the temperature is decreased with a reversed stepwise evolution until the temperature is 250 °C.

Transient Oxidation Reaction Spectroscopy (TORS) was used to investigate the dependence of catalyst oxidation state on catalytic activity. In these experiments, the dry reforming reaction is run at steady state, at fixed temperature, and 2-second-wide pulses of O₂ are injected into the reactor feed to observe the effect on reaction products. The pulse shape was approximately square. The height of the pulse was set such that the oxygen and methane concentrations were equal for the duration of the pulse. This is the ratio used in the partial oxidation experiments.

3 Results and Discussion

3.1 Catalyst Characterization

The XRD data obtained in our laboratory are shown in Fig. S1, for Ru/CeO₂ (the figures labeled by S followed by a number are in the Supplementary Information). One observes the diffraction peaks due to CeO₂ and small peaks corresponding to the *hcp*-phase of metallic Ru. The Rietveld-refined, synchrotron XRD data obtained from both as-prepared and post-reaction ruthenium-doped ceria are shown in Figure 1. The refinement included data for wavenumbers between 0.8 and 11.6 Å⁻¹. No diffraction peaks corresponding to RuO₂ or metallic Ru are present in the spectra of Ru_{0.05}Ce_{0.95}O₂. The lattice constant for as-prepared Ru-doped CeO₂ is 5.4214 Å; it is 5.4022 Å after the catalyst was used. Scherer broadening analysis of the ruthenium metal on ceria catalyst indicated that ruthenium crystallites were 19nm in size (accounting for instrumental broadening). Crystallites in this size range are typical for ruthenium wet-impregnated catalysts.

Table 1 gives the binding energies of the 3p_{3/2} orbital in the XPS spectrum of ruthenium atom, published by Ernst [20], for Ru metal and RuO₂. Also included are the binding energies measured by us for Ru_{0.05}Ce_{0.95}O₂ and Ru/CeO₂, for the as-prepared catalysts, and for the catalysts after the reaction. According to the XPS results the Ru atoms in the two catalysts differ from each other: the Ru in Ru_{0.05}Ce_{0.95}O₂ is more oxidized than in Ru/CeO₂ or in RuO₂. It is difficult to understand why the binding energy in Ru/CeO₂ is closer to that of RuO₂ than Ru

metal, even though the XRD measurements detect Ru metallic in Ru/CeO₂. This may be due to a size effect (Ru clusters are small) or to the oxidation of the Ru clusters by atmospheric oxygen prior to taking the XPS spectra. Finally, no chlorine was observed on the catalyst after reaction, indicating chlorine (from the ruthenium precursor) does not likely play a role in activity.

Table 1. XPS results for electron binding energy (BE) for Ru. Values in the first two rows are from Ref. 19.

compound	BE Ru3p_{3/2} eV
Ru metal	461.5
RuO ₂	462.7
RuO ₂	462.6
Ru _{0.05} Ce _{0.95} O ₂	
as prepared	464.1
after the dry reforming reaction	464.4
Ru/CeO ₂	
as prepared	462.3
after the dry reforming reaction	462.0

To further test whether Ru_{0.05}Ce_{0.95}O₂ and Ru/CeO₂ are different materials we used CO as a surface probe, performed *in situ* after reaction (without exposure to air). We expect from literature [21] that the CO vibrational energy is different when CO adsorbs on metallic Ru than when it adsorbs on Ru-doped ceria (where Ru is ionic). The DRIFTS spectra (Figure 2) of CO adsorbed on Ru_{0.05}Ce_{0.95}O₂ and on Ru/CeO₂ show that the two materials interact differently with CO. The CO adsorbed on Ru_{0.05}Ce_{0.95}O₂ has an infrared (IR) absorption peak (marked by A1 in Fig. 2) that is absent for CO adsorbed on Ru/CeO₂. The frequency of this peak is very close to that of the gas-phase CO but it is not due to photon absorption by gaseous CO. To prove this we have also taken the IR absorption spectrum of the Ru_{0.05}Ce_{0.95}O₂ catalyst after exposure to CO but prior to purging with Ar. This spectrum (dotted lines in Fig. 2) has the M-shape typical of the R- and P-branches of gaseous CO. Clearly the A1 peak is not due to the gas. We also found that the peak A1 disappears when the sample is heated from 20 °C to 100 °C. This weakly bound CO vibrates roughly at the same frequency as gas-phase CO but it does not have the R- and P- branches because it is not free to rotate. The three peaks observed for the CO adsorbed on Ru_{0.05}Ce_{0.95}O₂ (namely A1, A2, and A3) suggest that on this surface CO has three distinct

binding sites. In contrast, there is almost no CO adsorption (except perhaps for the two small peaks denoted B1 and B2 in Fig. 2) on Ru/CeO₂, which is surprising. We assume that this happens because the Ru clusters in Ru/CeO₂ are oxidized on the surface.

Chin *et al.* [21] assigned the CO IR-absorption peaks to different CO-Ru binding moieties for various Ru oxidation states. While we do not dispute the assignment we prefer not to make use of it here.

In summary: XPS, XRD, and the IR spectrum of CO adsorbed on these catalysts indicate that Ru_{0.05}Ce_{0.95}O₂ and Ru/CeO₂ are different materials, as prepared and after they catalyzed the dry reforming reaction. Nevertheless, they have practically identical catalytic activity, as we show below.

3.2 Catalyst Reactivity

Figure 3 shows methane conversion in two temperature programmed reaction (TPR) experiments: partial oxidation and dry reforming of methane. These results are surprising for two reasons. First, the oxidation of methane by dry reforming starts at lower temperature than partial oxidation with O₂, as if CO₂ is a better oxidant than O₂. Second, dry reforming and methane oxidation with O₂ are supposed to have the same rate-limiting step: the breaking of the C-H bond. If this is true, one would expect, perhaps naively, that the two reactions should take off at the same temperature.

A possible resolution of these two puzzles is that Ru_{0.05}Ce_{0.95}O₂ evolves into two distinct catalysts when exposed to two different feeds (CH₄ + O₂ or CH₄ + CO₂). We show in Section 3.3 that this is the case.

Figures 4a and 4b show the STPR data for dry reforming using Ru_{0.05}Ce_{0.95}O₂ and Ru/CeO₂, respectively. The mass balance for carbon, hydrogen, or oxygen is 100% ± 2%. The dark-blue curve in Fig. 4a shows how the temperature of the reactor was changed with time (the temperatures scale is on the right hand side of the graph). The measurements start at 250 °C and the temperature is held constant at that temperature for 30 minutes. As the purple and the yellow-orange curves show, the concentration of CO₂ and CH₄ in the effluent is the same as in the mixture entering the reactor. A small consumption of CH₄ and CO₂ is observed at 400 °C. The conversion of both CO₂ and CH₄ are largest at 600 °C. If dry reforming were the only reaction in the system then the conversion of CO₂ and CH₄ should be equal, and the amount of

H₂ should equal the amount of CO. This is not what we observe: more CO₂ is consumed than methane and more CO is present than H₂. This indicates that the water-gas shift reaction $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ also takes place in the system.

It is interesting that the data in Fig. 4b, which shows the STPR results for dry reforming on the Ru/CeO₂ catalyst, is practically identical to the data in Fig. 4a, for the same reaction catalyzed by Ru_{0.05}Ce_{0.95}O₂. For example at 600°C, methane conversion respectively is 48% and 46% for Ru_{0.05}Ce_{0.95}O₂ and Ru/CeO₂. We have two materials that have identical catalytic activity but give different XRD, XPS, and CO-DRIFTS signals. We are therefore tempted to conclude that the two catalysts contain identical catalytic sites and that the features that make the spectra different are unrelated to catalysis.

3.3 Why does methane react with CO₂ at lower temperature than with oxygen?

As we have already mentioned we were puzzled by the results shown in Fig. 3 which show the onset of methane conversion, for dry reforming and for partial oxidation, both carried out on Ru_{0.05}Ce_{0.95}O₂. The reaction of CH₄ with CO₂ takes place at a temperature at which CH₄ does not react with O₂. This appears to run counter to two strongly held beliefs. One is that the rate-limiting step is the breaking of the C-H bond by the catalyst, which suggests that CH₄ should react at the same temperature regardless of whether O₂ or CO₂ is present. The other is that methane should react at lower temperature with O₂ than with CO₂, because O₂ is a much stronger oxidant. There is however a third possibility. If we assume a Mars-van Krevelen mechanism, then CH₄ reduces the oxide surface and the reduced surface is reoxidized by O₂ (for partial oxidation) or CO₂ (for dry reforming). Since O₂ is a better oxidant than CO₂, the surface is more reduced when the feed contains CO₂ than when it contains O₂. The results presented in Fig. 3 can therefore be understood if we assume that the more-reduced oxide, present when the feed contains CO₂, is a better methane activation catalyst than the oxidized surface that is present when the feed contains O₂. This hypothesis can be tested by pulsing O₂ through the reactor while we are running the dry reforming reaction at steady state. If the hypothesis is true then the injection of oxygen should lower methane conversion. The results of these experiments (Fig. 5) show that this is what happens.

We flowed through the reactor CH₄:CO₂:Ar = 1:1:3 at 500 °C with a flowrate of 0.07 second, until the system reached steady state. The catalyst was either Ru_{0.05}Ce_{0.95}O₂ (first panel)

or Ru/CeO₂ (second panel). We chose the flowrate so that the reactor is differential, to minimize the complications caused by changes in the catalyst and gas composition along the reactor, which are significant at low flowrates.

The vertical, green, dotted line indicates the moment when the oxygen pulse was sent through the reactor. Prior to that moment the reactor was running the dry reforming reaction at steady state. The dashed horizontal line indicates the concentration of methane and CO₂ at the entrance of the reactor. The yellow and purple lines indicate the concentration of CH₄ and CO₂, respectively, in the effluent. These two lines are below the dashed line because CH₄ and CO₂ were consumed during the passage through the reactor. In the lower part of the graph we show the amount of CO (reddish-brown), H₂O (dark blue), H₂ (cyan), and O₂ (green) in the effluent. The oxygen pulse prior to its entrance in the reactor is not plotted because it is too narrow (2 seconds) to show on the time scale of the plot. The oxygen pulse seen in the lower part of the graph is oxygen that survived passage through the reactor. The pulse is broadened because of different arrival times at the exit.

The injection of oxygen suppresses the dry reforming reaction: the amount of methane coming out of the reactor is nearly equal to the amount supplied at the entrance (i.e. the orange line is close to the dashed horizontal line) and is higher than the amount exiting the reactor when no oxygen is introduced. Also, CO and H₂ production is suppressed immediately after O₂ is injected. It takes approximately 30 seconds for the reactor to reach the steady state it had before the oxygen was introduced. We do not understand why the response of the methane has slight dips, immediately after oxygen introduction and right before the steady state is reached. The slow restoration of the steady state indicates the slowness of the rate of catalyst reduction by methane.

The right-hand panel shows the results of the same experiments on Ru/CeO₂ catalyst. The slight differences between the results on the two catalysts are within the error of our measurements. We conclude that transient response of the two catalysts following oxygen injection is essentially the same.

4 Conclusions

We performed experiments meant to answer two questions. Why does CH₄ react with CO₂ at a lower temperature than with O₂, on a catalyst prepared by the combustion method,

which is assumed to produce Ru-doped ceria? And if this behavior is typical of Ru-doped ceria, does one observe different chemistry on a catalyst prepared by impregnation (which is assumed to be metallic Ru supported on ceria)?

We find that the two catalysts, prepared by different methods, have different physical properties (XRD, Ru-XPS, and the IR spectrum of CO adsorbed on them) but have essentially the same catalytic chemistry and catalytic activity. Obviously catalytic chemistry on these materials does not take place on surface sites that affect the physical measurements we made. We do not have a reliable explanation for this. It is possible that when the Ru/CeO₂ catalyst was prepared, some Ru atoms ended up as substitutional dopants and they are the active sites. We tried to avoid this from happening, by using a low reduction temperature, but we cannot rule out this possibility. Another possible explanation is that the reaction on Ru/CeO₂ takes place at the border of the metallic Ru with the CeO₂ surface and that the reactivity of the oxygen atoms at this border is similar to that of the oxygen atoms surrounding the Ru dopants. A similar dual-site model could explain some of the observed behavior. In such a model, the cerium oxide site could be rate-limiting and the ruthenium site differs between the catalysts. Hence in such a model, the catalysts show stark differences in characterization (due to different ruthenium [oxide] sites), but the cerium oxide site dominates the control of reactivity. The transient oxygen reaction spectroscopy shows that reduction is crucial to the activity. Whatever the active site may be – whether it is on ruthenium, cerium, or both – it is strongly activated by incomplete reduction.

The transient reaction experiments using oxygen pulses suggest strongly that methane is more readily activated by the partially reduced catalyst (for both catalyst preparations). In these two reactions (CH₄ + CO₂ and CH₄ + O₂), methane reduces the oxide surface while CO₂ or O₂ reoxidizes it. Because O₂ is a more effective oxidant than CO₂, the surface exposed to CO₂ + CH₄ has more oxygen vacancies (is more reduced) than the surface exposed to O₂ + CH₄. While we start with the same catalyst (e.g. Ru-doped ceria), by the time the steady state is reached the catalyst performing dry reforming has evolved to a different, more active state than the catalyst performing partial oxidation: one is more reduced than the other.

Acknowledgements. Funding for this work was provided by the Air Force Office of Scientific Research (FA9550-12-1-0147) and the U.S. Department of Energy (DE-FG02-89ER140048). The Advanced Photon Source is supported by the Department of Energy, Office of Basic Energy

Sciences under contract no. DE-AC02-06CH11357. We thank Tom Mates for help in gathering XPS spectra. ARD would like to thank the National Science Foundation for a Graduate Research Fellowship under grant DGE 0707430. Financial support of GMM and the MRL Central Facilities are supported by the MRSEC Program of the National Science Foundation (NSF) under Award No. DMR 1121053; a member of the NSF-funded Materials Research Facilities Network (www.mrfn.org).

References

1. Rostrup-Nielsen J, Christiansen LJ, Concepts in Syngas Manufacture (Imperial College Press, London, 2011)
2. Bartolomew CH, Farauto RJ, Fundamentals of Industrial Catalytic Processes (John Wiley & Sons, New York, 2006)
3. Bradford M, Vannice M (1999) *Catal. Rev.* 41:1-42
4. York APE, Xiao T, Green MLH, Claridge JB (2007) *Catal Rev* 49:511-560
5. Raudaskoski R, Turpeinen E, Lenkkeri R, Pongrácz E, Keiski RL (2009) *Catal Today* 144:318-323
6. Avetisov AK, Rostrup-Nielsen JR, Kuchaev VL, Bak Hansen J-H, Zyskin AG, Shapatina EN (2010) *J Molec Catal A* 315:155-162
7. Rostrup-Nielsen JR, Bak Hansen J-H (1993) *J Catal* 144:38-49
8. Safariamin M, Tidahy LH, Abi-Aad E, Siffert S, Aboukais A (2009) *C R Chimie* 12:748-753
9. Nakagawa K, Hideshima S, Akamatsu N, Matsui N, Ikenaga N, Suzuki T (2002) Chapter 14 (pp. 205-233) In: Song C *et al.*(eds) *CO₂ Conversion and Utilization*, ACS Symposium Series, Washington DC
10. Cimino S, Casaletto MP, Lisi L, Russo G (2007) *Appl. Cat., A* 327:238-246
11. Hegde MS, Madras G, Patil KC (2009) *Acc Chem Res* 42:704-712
12. Laachir A, Perrichon V, Badri A, Lamotte J, Catherine E, Lavelley JC, El Fallah J, Hilaire L, le Normand F, Quemere E, Sauvion GN, Touret O (1991) *J Chem Soc, Faraday Trans* 87:1601-1609
13. Perrichon V, Laachir A, Bergeret G, Frety R, Turnayan L, Touret O (1994) *J Chem Soc, Faraday Trans* 90:773-781
14. De Leitenburg C, Trovarelli A, Kaspar J (1997) *J. Catal.* 166:98-107
15. Singh P, Hegde MS (2009) *Chem. Mater.* 21:3337-3345
16. Bernal S, Calvino JJ, Cifredo GA, Gatica JM, Omil JAP, Pintado JM (1993) *J Chem Soc, Faraday Trans* 89:3499-3505

17. Adachi G, Imanak N, Kang ZC (eds) (2004) Binary Rare Earth Oxides. Kluwer Academic Publishers, Dordrecht, Netherlands
18. Toby BH (2001) J Appl Crystallog 34:210-213
19. Larson AC, Von Dreele RB (2004) Los Alamos National Labs Report LAUR 86-748: General Structure Analysis System (GSAS), <http://www.ncnr.nist.gov/xtal/software/gsas.html>
20. Ernst MA, Sloof WG (2008) Surf. Interface Anal. 40:334-337
21. Chin SY, Williams CT, Amiridis MD (2006) J Phys Chem B 110:871-882

Figure Captions

Fig. 1 Synchrotron XRD patterns of ruthenium-doped ceria (a) as synthesized and (b) after catalyzing dry reforming at 500 °C for 5 hours. Both samples are single-phase fluorite, exhibiting no *hcp*-Ru or RuO₂.

Fig. 2 DRIFTS spectra of ruthenium-doped ceria (dashed line) and ruthenium supported on ceria (solid line), after exposure to CO followed by purging with Ar to remove gaseous CO from reactor. The catalyst was exposed to CO after it was used for dry reforming (see text). The dotted line shows the IR spectrum of Ru-doped ceria after exposure to CO and prior to purging with Ar.

Fig. 3 Methane partial oxidation using oxygen or carbon dioxide on a ruthenium-doped CeO₂ catalyst. The catalyst bed contained 25 mg of Ru_{0.05}Ce_{0.95}O₂, diluted with 50 mg of alumina. The temperature ramp was 10 °C/min. Feed composition was 1:1:3 (molar) for CH₄:CO₂:Ar (for dry reforming) and 2:1:3 for CH₄:O₂:Ar (for partial oxidation). Spacetime was 0.18 second at 20 °C. Dry reforming produced predominately synthesis gas and the methane partial oxidation produced predominately carbon dioxide and water.

Fig. 4 The steady state composition of the reactor effluent for methane reacting with carbon dioxide on (a) Ru_{0.05}Ce_{0.95}O₂ and (b) Ru/CeO₂, at various temperatures. The plug reactor contained 25 mg of Ru_{0.05}Ce_{0.95}O₂ diluted with 50 mg of alumina. Temperature was varied from 250 °C to 600 °C and back to 250 °C in steps of 50 °C. After each step the temperature was held constant for 30 minutes. Mass balances were approximately 100%. The feed molar composition was 1:1:3 for CH₄:CO₂:Ar. Total volumetric flowrate corresponded to a spacetime of 0.18 seconds at 20 °C.

Fig. 5 Transient oxidation reaction spectroscopy of methane dry reforming on ruthenium-doped ceria and ceria-supported ruthenium metal. Temperature was maintained at 500 °C. Feed molar composition was 1:1:3 for CH₄:CO₂:Ar. Spacetime was set to 0.07 second, calculated at the reactor temperature of 500 °C. The square O₂ pulse had a width of 2 seconds. The oxygen

flowrate equaled that of the methane (overall composition of 1:1:1:3 of O₂:CH₄:CO₂:Ar).
Further details are given in the text.

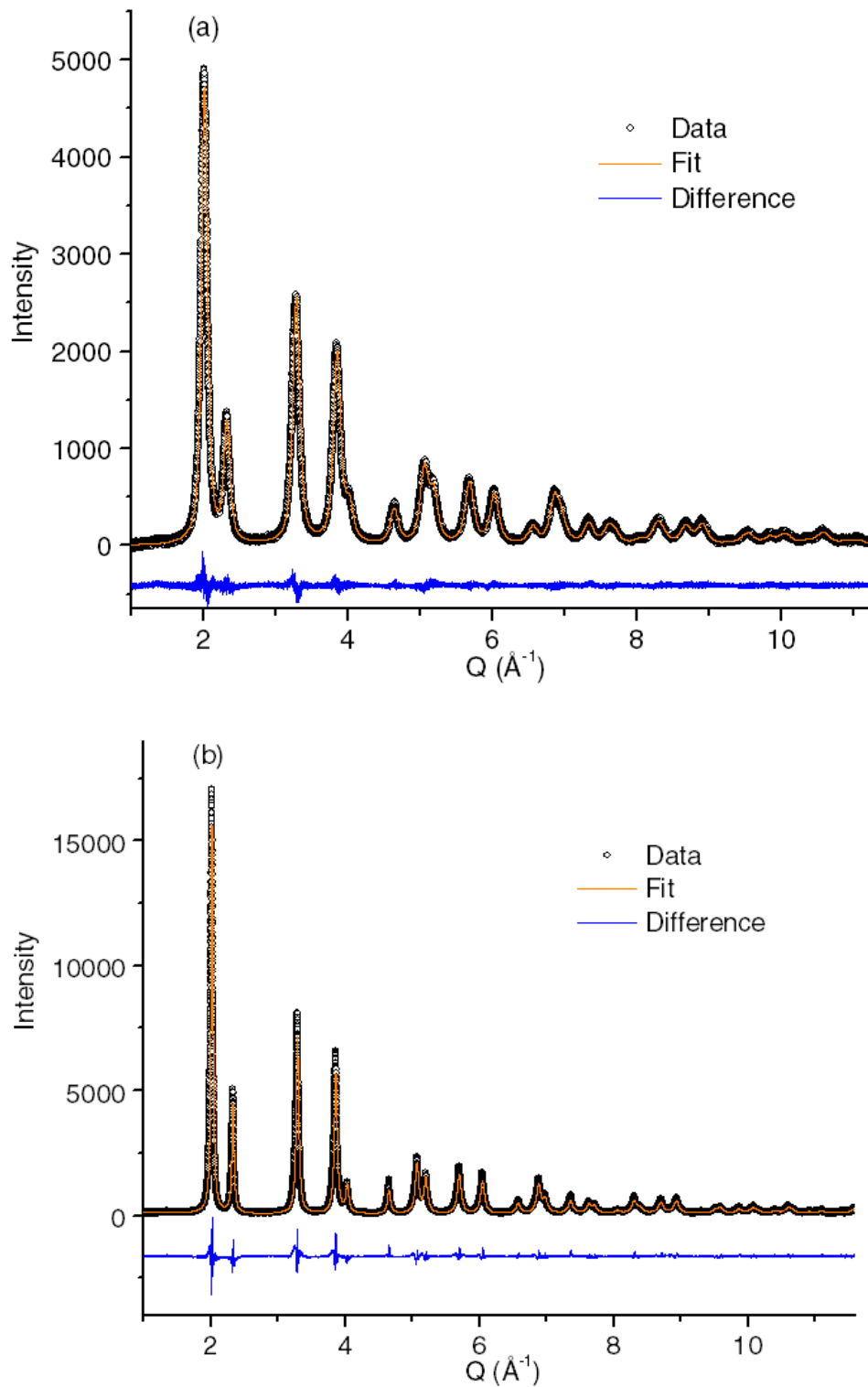


Fig. 1 Synchrotron XRD patterns of ruthenium-doped ceria (a) as synthesized and (b) after catalyzing dry reforming at 500 °C for 5 hours. Both samples are single-phase fluorite, exhibiting no *hcp*-Ru or RuO₂.

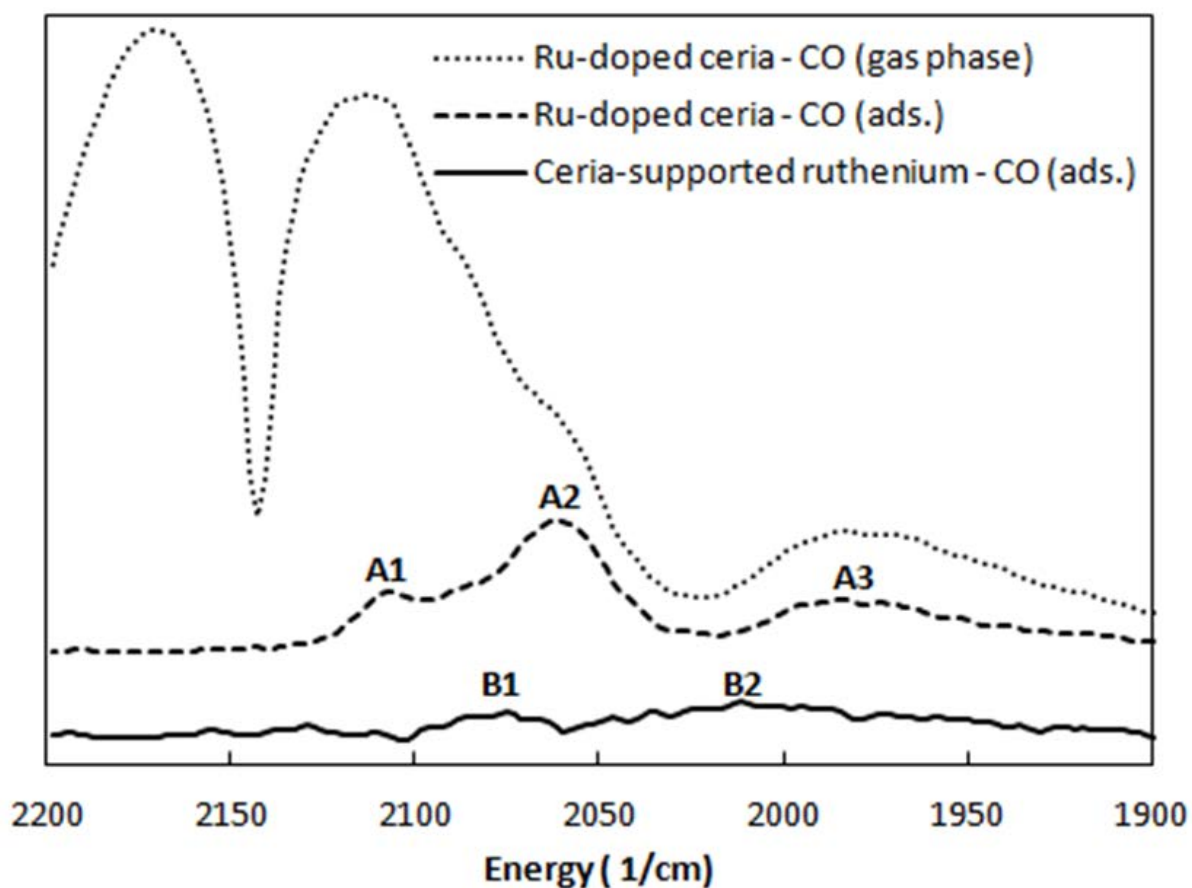


Fig. 2 DRIFTS spectra of ruthenium-doped ceria (dashed line) and ruthenium supported on ceria (solid line), after exposure to CO followed by purging with Ar to remove gaseous CO from reactor. The catalyst was exposed to CO after it was used for dry reforming (see text). The dotted line shows the IR spectrum of Ru-doped ceria after exposure to CO and prior to purging with Ar.

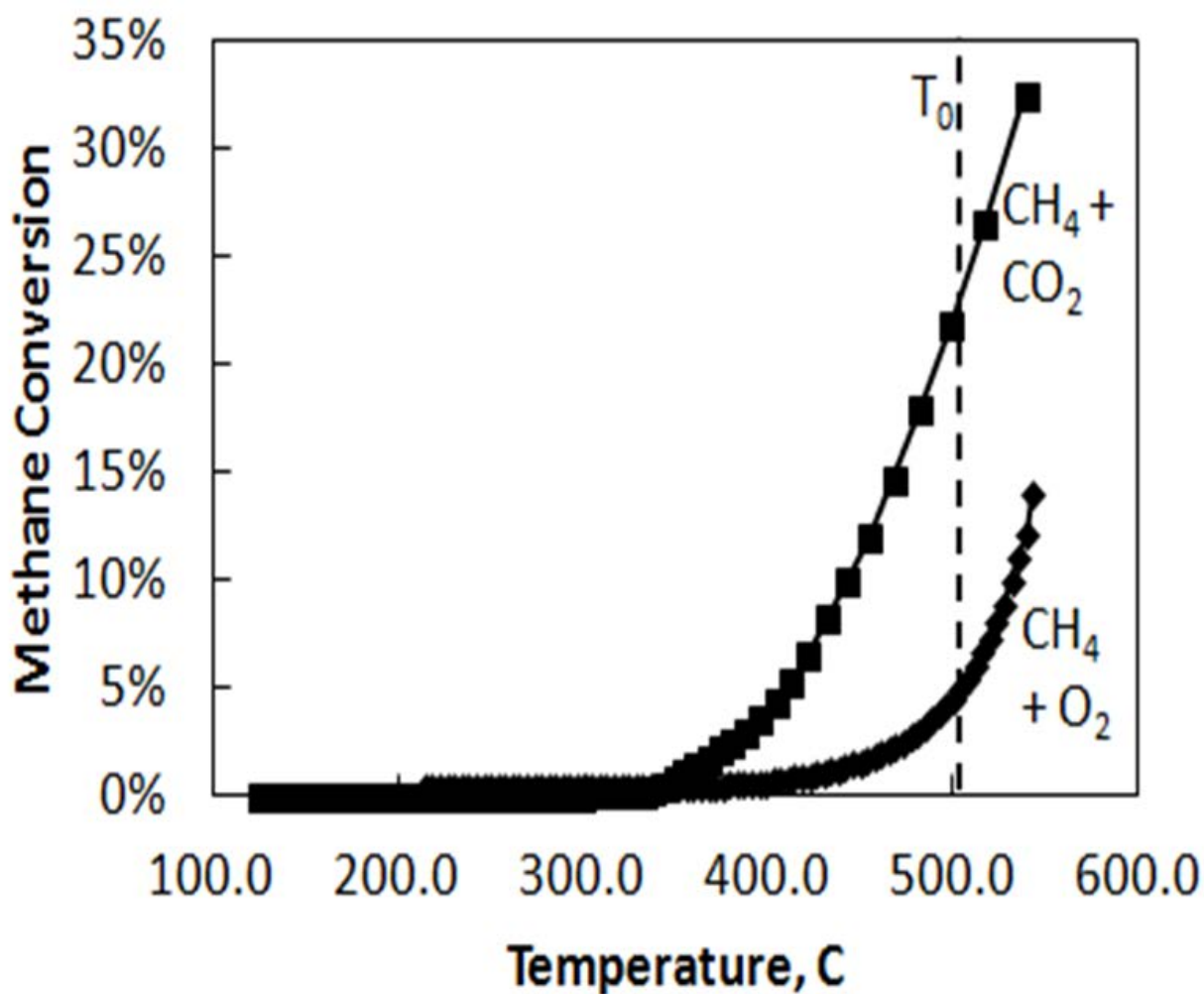


Fig. 3 Methane partial oxidation using oxygen or carbon dioxide on a ruthenium-doped CeO₂ catalyst. The catalyst bed contained 25 mg of Ru_{0.05}Ce_{0.95}O₂, diluted with 50 mg of alumina. The temperature ramp was 10 °C/min. Feed composition was 1:1:3 (molar) for CH₄:CO₂:Ar (for dry reforming) and 2:1:3 for CH₄:O₂:Ar (for partial oxidation). Spacetime was 0.18 second at 20 °C. Dry reforming produced predominately synthesis gas and the methane partial oxidation produced predominately carbon dioxide and water.

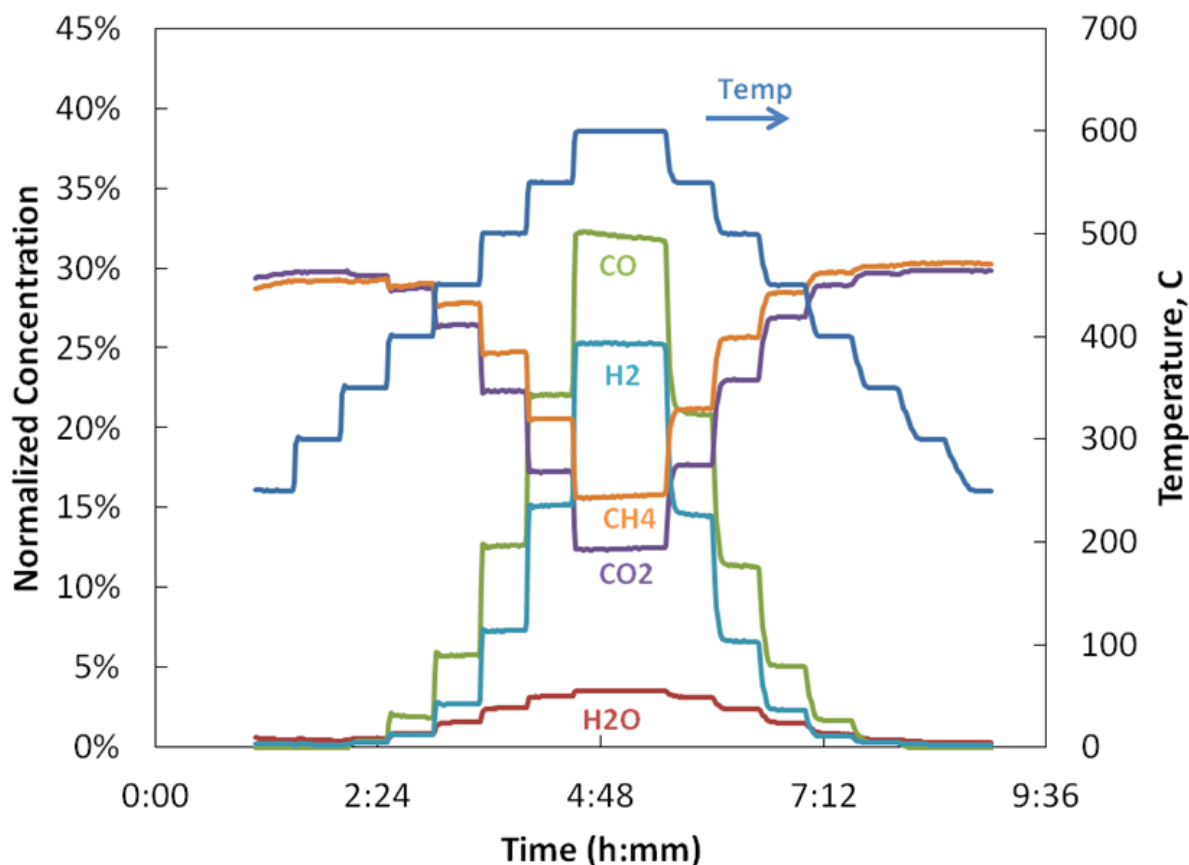


Fig. 4a The steady state composition of the reactor effluent for methane reacting with carbon dioxide on $\text{Ru}_{0.05}\text{Ce}_{0.95}\text{O}_2$, at various temperatures. The plug reactor contained 25 mg of $\text{Ru}_{0.05}\text{Ce}_{0.95}\text{O}_2$ diluted with 50 mg of alumina. Temperature was varied from 250 °C to 600 °C and back to 250 °C in steps of 50 °C. After each step the temperature was held constant for 30 minutes. Mass balances were approximately 100%. The feed molar composition was 1:1:3 for $\text{CH}_4:\text{CO}_2:\text{Ar}$. Total volumetric flowrate corresponded to a spacetime of 0.18 seconds at 20 °C.

WI Ru/CeO₂ - Dry Reforming TPR

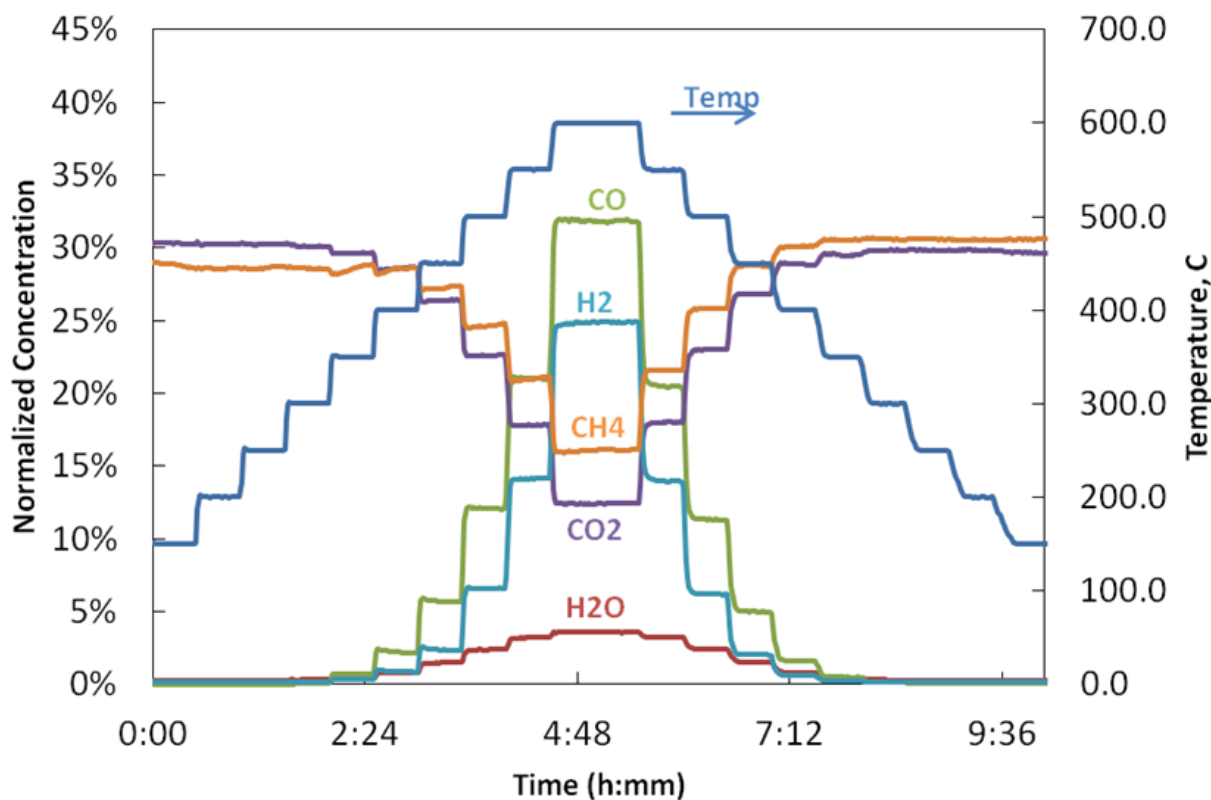


Fig. 4b The steady state composition of the reactor effluent for methane reacting with carbon dioxide on **Ru/CeO₂**, at various temperatures. The plug reactor contained 25 mg of Ru_{0.05}Ce_{0.95}O₂ diluted with 50 mg of alumina. Temperature was varied from 250 °C to 600 °C and back to 250 °C in steps of 50 °C. After each step the temperature was held constant for 30 minutes. Mass balances were approximately 100%. The feed molar composition was 1:1:3 for CH₄:CO₂:Ar. Total volumetric flowrate corresponded to a spacetime of 0.18 seconds at 20 °C.

Transient Oxidation Reaction Spectroscopy

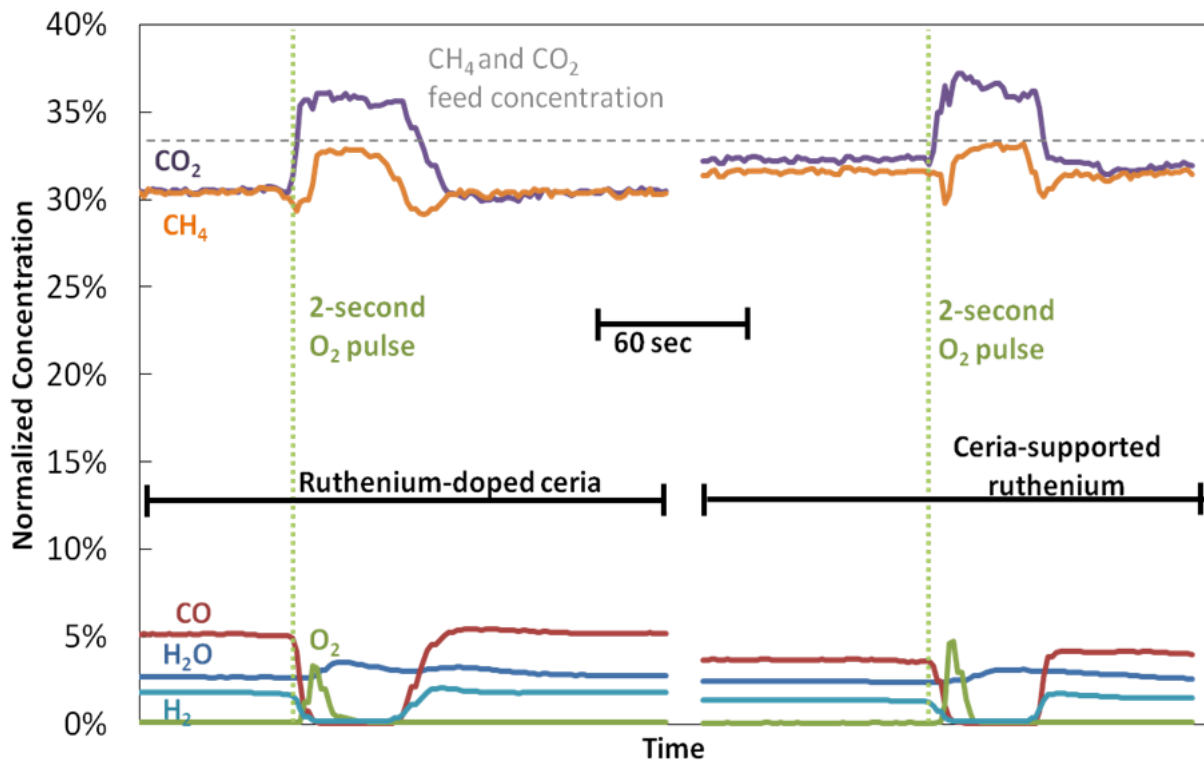


Fig. 5 Transient oxidation reaction spectroscopy of methane dry reforming on ruthenium-doped ceria and ceria-supported ruthenium metal. Temperature was maintained at 500 °C. Feed molar composition was 1:1:3 for CH₄:CO₂:Ar. Spacetime was set to 0.07 second, calculated at the reactor temperature of 500 °C. The square O₂ pulse had a width of 2 seconds. The oxygen flowrate equaled that of the methane (overall composition of 1:1:1:3 of O₂:CH₄:CO₂:Ar). Further details are given in the text.