Effects of Ir-doping on the transition from oxidative coupling to partial oxidation of methane in La$_2$O$_3$–CeO$_2$ nanofiber catalysts: spatial concentration and temperature profiles

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Spatially resolved temperature and species concentration profiles determined via microprobe sampling and online gas chromatography were used to examine the transition from oxidative coupling of methane (OCM) to catalytic partial oxidation (CPO) as a function of Ir-doping of a La$_2$O$_3$–CeO$_2$ nanofiber fabric catalyst. Experiments were performed at atmospheric pressure at a furnace temperature of 750 °C, feed gas CH$_4$/O$_2$ molar ratio of 5 and at a nominal space time of about 60 ms. Reaction products exhibited a dramatic shift from ethane and ethylene (OCM, C$_2$ selectivity of 54%), in the case of the un-doped catalyst, to exclusively synthesis gas (CPO, CO and H$_2$ selectivity 90+%), at 1% Ir doping. Species concentration profiles obtained in the latter case indicate the formation of H$_2$O, H$_2$ and CO first, followed by the steam reforming of CH$_4$ to produce the balance of the syngas concomitant with a sharp decrease in H$_2$O levels. These findings suggest a CPO mechanism that is different from the literature, calling for the revision of detailed chemical kinetic mechanisms proposed before.

The prevailing mechanism for OCM involves coupled surface and gas phase reactions in which the critical steps are the surface generation, subsequent gas phase diffusion and coupling of methyl radicals to form C$_2$H$_6$.$^{8-11}$

\[
O_2 + 2[^*] \rightarrow 2[O] \tag{1}
\]
\[
CH_4 + [O] \rightarrow CH_3 + [OH] \tag{2}
\]
\[
CH_3 + CH_3 \rightarrow C_2H_6 \tag{3}
\]
\[
[OH] + [OH] \rightarrow [O] + [^*] + H_2O \tag{4}
\]

The formation of C$_2$H$_4$, H$_2$, H$_2$O, CO and CO$_2$ has been proposed to occur via combined surface and gas-phase reactions.$^{8-11}$ Because OCM is highly exothermic, the resulting temperature increase forces the reaction to proceed under transport limitations. Nevertheless, gas phase reactions play an important role in affecting product evolution.$^{14}$ Recently, we also reported that nanofibers of La$_2$O$_3$–CeO$_2$ exhibit excellent OCM activities and selectivities, with combined C$_2$ selectivity (selectivity × conversion) in excess of 22%.$^{15-16}$ In that work, 20–100 nm diameter nanofibers were prepared by electrospinning, which is a versatile technique capable of controlling the surface chemistry of catalysts that will be described further.

On the other hand, no uniformly applicable mechanism seems to exist for the CPO of methane.$^3$ Nevertheless, existing literature can be grouped into two main categories. First is the direct decomposition of methane on the catalyst surface...
followed by the oxidation of surface moieties to form synthesis gas. This is well demonstrated in Pt and Rh catalyzed CPO,\textsuperscript{7,17-20} where the mechanism can be schematically summarized as below:

\[
\begin{align*}
O_2 + 2[^*] & \rightarrow 2[O] \\
CH_4 + 4[^*] & \rightarrow [C] + 4[H] \\
[C] + [O] & \rightarrow 2[^*] + CO \\
2[H] & \rightarrow 2[^*] + H_2
\end{align*}
\]

In the second category, methane CPO has been advocated to proceed via sequential combustion-reformalizing reactions, with the formation of CO$_2$ and H$_2$O first, followed by endothermic CO$_2$ and H$_2$O reforming of CH$_4$ reactions producing CO and H$_2$ in the second step.\textsuperscript{21} This two-step process appears to be the predominant mechanism of syngas production over transition metal based catalysts,\textsuperscript{2,3,21-23} where the overall reactions are:

\[
\begin{align*}
CH_4 + 2O_2 & \rightarrow CO_2 + 2H_2O \\
CH_4 + CO_2 & \rightarrow CO + H_2 \\
CH_4 + H_2O & \rightarrow CO + 3H_2
\end{align*}
\]

Previous methane CPO studies with Ir supported on La$_2$O$_3$ indicate the presence of the latter mechanism.\textsuperscript{23,24} However, this conclusion was indirectly based on separate methane combustion and CH$_4$-H$_2$O and CH$_4$-CO$_2$ reforming studies, in conjunction with CPO experiments that were all accomplished through the measurement of reactor exit gas compositions.\textsuperscript{23,24} In addition, Ir catalysts were prepared by traditional impregnation of a La$_2$O$_3$ support with little control over surface Ir cluster size and dispersion.\textsuperscript{24}

Since the La$_2$O$_3$-CeO$_2$ nanofiber fabric is an excellent OCM catalyst\textsuperscript{25} and Ir-La$_2$O$_3$ is the same for CPO,\textsuperscript{4} it is of scientific and practical interest to explore how Ir doping of La$_2$O$_3$-CeO$_2$ would affect product selectivity. In particular, it is important to understand how the temperature and detailed species concentration profiles evolve inside the catalyst bed at relevant operating conditions and how surface and gas phase kinetics are coupled between OCM and CPO. With ample literature on the materials, lanthanide supported Ir CPO catalysts are of considerable interest for reassessing the relevant kinetic mechanisms using our unique approach. Additionally, electrospun La$_2$O$_3$-CeO$_2$ nanofibers were discovered and extensively studied by the authors as novel, high-performing OCM catalysts. The potential for bridging the OCM and CPO mechanisms in this manner was first postulated when Ir-doped La$_2$O$_3$-CeO$_2$ nanofibers were found to have by far the highest selectivity for CO/H$_2$ in preliminary screenings of dopants, with the original intention of improving OCM performance. Hence, the authors have the expertise in synthesizing, testing and evaluating such catalysts and can easily translate this to thin, uniform and incrementally doped La$_2$O$_3$-CeO$_2$-Ir nanofibers with precisely controlled nanostructures.\textsuperscript{25} Herein we report, for the first time, detailed spatial concentration and temperature profiles in Ir-doped La$_2$O$_3$-CeO$_2$ nanofiber catalysts prepared by electrospinning. These investigations capture the dramatic change in product selectivities from OCM to CPO even at small levels of Ir doping, thus providing useful new data for the development and validation of detailed chemical kinetic mechanisms.

**Experimental section**

**Catalyst preparation**

Experiments were performed using a fixed-bed tubular reactor system as shown in Fig. 1.\textsuperscript{25} The reactor was packed with La$_2$O$_3$-CeO$_2$ nanofiber catalysts, both neat and doped with different levels of Ir. Catalysts were prepared by electrospinning a viscous solution of polyvinylpyrrolidone (PVP; 1.3 MDa, 0.60 g), water/ethanol (~1:1 wt ratio, 9.5 g) in which the metal precursors, as La(NO$_3$)$_3$·6H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O (La/Ce wt ratio = 3, 0.35 g) were dissolved.\textsuperscript{14,15} The required amount of precursor IrCl$_4$ was also dissolved in co-spun samples. The electrospun material was dried and then calcined at 625 °C to form metal oxide nanofiber fabrics.

**Spatial profile acquisition**

The fabric catalyst (20 mg) was loosely packed into a 6 mm diameter quartz tube and sandwiched between two quartz wool plugs (20 mg each, Fig. 1).\textsuperscript{25} The bulk density and void fraction of the catalytic bed were approximately 0.3 g cm$^{-3}$ and 0.94, respectively. The reactor was placed inside a cylindrical tubular furnace, which preheated the feed gas and catalyst. Electronic mass flow controllers (MFCs; MKS Billerica, MA) were used to set the total reactant flow at 120 sccm, corresponding to a nominal space time of about 60 ms. The experiments were performed at atmospheric pressure with a furnace temperature of 750 °C and CH$_4$/O$_2$ ratio of 5.

Sampling was accomplished by withdrawing gases from within the bed using a closed-end quartz capillary tube (800 μm; Friedrick and Dimock, Millville, NJ) with a 80 μm diameter sampling orifice laser drilled on its side (see inset Fig. 1).\textsuperscript{25-27}

![Fig. 1. Packed bed reactor system and accompanying equipment used for acquiring spatial concentration and temperature profiles within the fabric catalysts.](image-url)
Gas analysis was accomplished by on-line gas chromatography (Varian 4900 Mini GC, with 5 Å molecular sieve and Poraplot U columns). N₂ (1.0 mol%) was used as an internal standard. The location of the sampling orifice and overall probe length were designed such that the capillary tip always remained outside the bed at any sampling position to avoid gas bypass. Samples were withdrawn through the capillary probe at a rate of about 5 sccm; thus, the flow within the reactor was minimally perturbed. Temperature measurements were performed by placing a 250 μm diameter K-type thermocouple inside the capillary probe in the absence of gas withdrawal. The tip of the thermocouple was positioned at the sampling orifice. The temperature and concentration profiles were obtained by moving the capillary (with and without the thermocouple, respectively) in the axial direction using a micropositioning device (Velmex, Bloomfield, NY). Positional accuracy associated with the placement of the capillary probe within the reactor was estimated to be ±0.25 mm. Similar uncertainty would be expected to exist between the temperature and concentration profiles as well.

Catalyst characterization

Catalyst characterization were performed as the following: BET surface areas were determined using Micromeritics ASAP 2020 at 77 K on all fabrics tested in this work. Powder X-ray diffraction (XRD) patterns were obtained on an X-ray powder diffractometer (PANalytical X’Pert PRO) using Cu-Kα radiation, 45 kV and 40 mA, fitted with Ni filter and Soller slit collimator to identify crystalline phases. A scanning electron microscope and an energy dispersive X-ray spectrometer (FE-SEM/EDS, FE-SEM: JOEL JSM-7600F) were used to image the catalyst’s morphology. X-ray photoelectron spectroscopic studies (XPS) were carried out using Al Kα monochromatic radiation, hv = 1486.74 eV with SPECS spectrometer for the X-ray source to determine the surface composition and identify electronic state of the mixing elements.

Results and discussion

Characterization studies

In Fig. 2, a SEM image of the 1 wt% Ir doped La₂O₃–CeO₂ fabric is shown, which was virtually identical to the undoped fabric. As evident from this image, the fibers are long, straight and uniform, possessing diameters of about 100 nm. The BET surface area was about 10 m² g⁻¹, a value that is close to what would be expected for the specific surface area of 100 nm diameter, straight, non-porous cylinders. This suggests that the fibers do not have internal porosity regardless of the level of Ir doping.

In Fig. 3 the XRD spectra of the undoped, 0.05 wt% and 1 wt% Ir-doped La₂O₃–CeO₂ fabrics are presented. The XRD of the undoped fabric exhibits much sharper peaks compared to the doped fabrics but has an overall shape that is similar to that with 0.05 wt% Ir. All three samples, including the 1 wt% Ir, appear to have similar cubic crystal structures. Increasing the level of Ir doping suppresses the XRD peaks. However, the mean crystallite size of the crystals formed remained at approximately 5 nm, based on Scherrer analysis, regardless of the Ir doping level.

It is possible that metal ions can segregate during the solvent evaporation in the electrospinning process and the subsequent calcination steps, and can lead to the establishment of radially non-uniform metal composition, especially Ir, across the fiber. To address this potential problem, we performed XPS studies to determine the surface composition of a 5 wt% (4 atom%) Ir-doped La₂O₃–CeO₂ fiber that has been calcined. We used a higher Ir loading in this test to improve the accuracy of the XPS measurements. The relevant XPS spectra are shown in Fig. 4. The surface atomic metal compositions were estimated by integrating the areas under the La 3d, Ce 3d and Ir 4f curves and computing the fraction that each constitutes relative to the total area, yielding 75% La, 18% Ce and 3% Ir. This measured 3% surface Ir composition is consistent with the calculated bulk atomic composition of 4% Ir for the fiber. Therefore, surface...
enrichment or depletion of Ir relative to the fiber bulk can substantially be ruled out. Evidently, the rapid precipitation of the solid fiber within the liquid jet formed in electrospinning was fast enough to prevent substantial migration of the metal salts across the fiber diameter.

Reaction studies

Before the results are presented, an important issue related to the catalyst selection must be noted. Although a large number of Ir doped catalysts were prepared and tested, only the results with undoped, 0.05% Ir and 1% Ir doped La2O3–CeO2 will be presented for the following reasons. At 0.05% Ir loading the reaction process exhibits both the features of OCM and CPO. At lower Ir loadings OCM dominates the reaction process. At 1% Ir, the reaction process becomes virtually CPO, with only trace OCM products. CPO remains the only reaction process at Ir loadings higher than 1%.

Shown in Fig. 5 are the axial temperature and concentration profiles for the reactor packed with the undoped La2O3–CeO2 fabric catalyst. These profiles exhibit behaviors similar to those reported in our earlier OCM studies with the important conclusion that C2 hydrocarbons are the principal products. As evident from Fig. 5, the peak temperature of 970 °C occurs 4 mm within the catalytic zone. It is worth noting that C2H4 and C2H6 both peak at about same depth within the catalyst (3 mm) at values of 3.4 and 1.9% respectively. At higher CH4/O2 ratios, e.g. 7 or higher, substantial lag time is observed for the formation of C2H4 relative C2H6.

The level of H2 peaks at 5.8%, 2 mm deep within the catalyst bed and levels off to about 5%, after 5 mm. The CO2 concentration increases and levels off at about 7.4%, 3 mm deep. The profile of CO also peaks at 4.0% at 3 mm within the catalyst and levels off at 2.4%, 11 mm into the catalyst. The water concentration, as calculated by O balances, increases uniformly reaching 15.6% at 2 mm, concomitant with the complete consumption of O2. Here, methane consumption also ceases, leveling at 62.1%.

It is widely accepted that OCM is induced by a surface oxygen atom (eqn (2)), activating CH4, generating a CH3 radical and [OH]. Ethane is then created in the gas phase by combination of two CH3 radicals (eqn (3)). The catalyst is regenerated through the formation and desorption of H2O (eqn (4)) and subsequently by the dissociative chemisorption of O2 (eqn (1)). The generation of C2H6, however, may be initiated on the catalyst surface or in the gas phase, but either way is strongly influenced by the presence of O2. In the catalytic route, [O] may abstract hydrogen from C2H6 in a manner similar to CH4 activation. Ethane may then interact with other species to form C2H4. This is summarized in eqn (12)–(15) below:

\[
\begin{align*}
C_2H_6 + [O] & \rightarrow C_2H_4 + [OH] \quad (12) \\
C_2H_3^+ + HO_2^- & \rightarrow CH_3^+ + CH_3O + OH^- \quad (13) \\
C_2H_3^+ + M & \rightarrow C_2H_4 + H^+ + M \quad (14) \\
C_2H_5^- + O_2 & \rightarrow C_2H_4 + HO_2^- \quad (15) \\
\end{align*}
\]

C2H6 dehydrogenation is also feasible in the gas phase by eqn (16):

\[
C_2H_6 + OH^- \rightarrow C_2H_4^+ + H_2O \quad (16)
\]

Clearly, the rates of above reactions are impacted by the concentration of O2 in the feed gas, consistent with the lag of C2H4 relative to C2H6 diminishing at lower CH4/O2 ratios.

In Fig. 6, the temperature and concentration profiles are presented for the La2O3–CeO2 catalyst doped with 0.05 wt% Ir, the addition of which most dramatically impacts the concentration profile for water. Instead behaving as an ultimate reaction product as is the case for OCM (Fig. 5), H2O, here in Fig. 6, exhibits a distinct peak of 12.7% at 3 mm in the catalyst bed and then decreases sharply, ultimately leveling off at 7%. This behavior supports the methane steam reforming reaction, an expected result for Ir based catalysts as reported in the literature.

At 0.05 wt% Ir loading, some OCM products are also observed, albeit at lower levels than the undoped case. The reactor effluent concentrations of C2H6 and C2H4 were 1.80% and 0.02% respectively in Fig. 6, compared to the 3.4 and 1.9%
values observed in the undoped catalyst experiments (Fig. 5). This reduction in C₂ products could also be due to their steam reforming reactions. Carbon monoxide and H₂ levels were 10% and 15%, respectively, both of which are substantially higher than the undoped experiments that were 2.4% and 5%, respectively (Fig. 5); this again is an expected result for the reforming process. Carbon dioxide increases and levels off at 6.2%, slightly lower than the 7.4% with the undoped experiments that were 2.4% and 5%, which are in harmony with the reaction stoichiometry of methane CPO (i.e. eqn (9)-(11)). Both H₂ and CO are produced early in the catalytic reaction zone, although there was some delay in CO production. However, earlier H₂ detection can be attributed to diffusion due to its very steep gradient and high diffusivity. In fact the measurement of significant levels of H₂ upstream outside of the catalytic zone is a clear manifestation of such diffusion effects.

The concentration profiles for H₂O and CO₂ exhibit several new and significant mechanistic insights. First, as seen in Fig. 7, the H₂O profile initially rises to a peak of about 9% at 2 mm and then sharply decreases to levels of about 0.2%, 3 mm in the catalyst bed, which is consistent with the two-step combustion-steam reforming reaction mechanism discussed before. On the other hand the CO₂ concentration profile does not exhibit such a peak (Fig. 7). Instead, the CO₂ concentration profile exhibits an initial low level reaching a plateau of about 1.7% at 2 mm in the catalyst bed, coincident with the H₂O peak. The absence of a peak in the CO₂ profile creates questions regarding the validity of the two-step mechanism for methane CPO over Ir-based catalysts as reported earlier. The results in Fig. 7 clearly suggest a hybrid mechanism, i.e. a composite of the two previous reaction mechanisms suggested for methane CPO. That is, the CPO of methane over Ir appears to involve first its catalytic fragmentation, concomitant with the formation of abundant levels of H₂O (combustion) and CO, employs different mechanistic steps, in which gaseous CH₃ radicals serve as precursors to syngas generation. For example, the possible fragmentation of CH₃ radicals and all other OCM intermediates and products should not be ruled out and would suggest the mechanism for CPO over Ir-based catalysts is not exclusively explained by the proposed two-step combustion-steam reforming path. Follow-up investigations are clearly called for in which novel DCKMs for methane CPO are formulated against the spatial profiles presented in this work.

Fig. 7 shows the temperature and concentration profiles for the catalyst doped with 1 wt% Ir. As can be seen from this figure, the product composition is exclusively that of CPO with no OCM products. Exit H₂ and CO levels are 42% and 20%, respectively, which are in harmony with the reaction stoichiometry of methane CPO (i.e. eqn (9)-(11)). Both H₂ and CO are produced early in the catalytic reaction zone, although there was some delay in CO production. However, earlier H₂ detection can be attributed to diffusion due to its very steep gradient and high diffusivity. In fact the measurement of significant levels of H₂ upstream outside of the catalytic zone is a clear manifestation of such diffusion effects.

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together with $H_2$. This step is then followed by the steam reforming of methane reaction producing the balance of the CO and $H_2$. The low levels of $CO_2$ subsequently produced in the reactor can be explained by the water gas shift reaction (eqn (17)). Also, the reappearance of $H_2O$ from between the $11 – 15$ mm positions may be due to temperature drop pushing steam reforming in the reverse direction. Although the needed consumption of $H_2$ appears to be absent in Fig. 7, it could easily be masked by the high diffusivity of $H_2$ effectively flattening the concentration profile. Methane also experiences a slight net rise in concentration in this same region. Similar artifacts are also present in Fig. 6.

As evident from Fig. 7, the temperature profile has several important features. First, the temperature profile exhibits two sequential but overlapping peaks. The second peak clearly indicates the presence of a sequential exothermic process, one likely prospect being the water gas shift reaction (eqn (17)). However, without detailed chemical kinetic and reactor modeling studies, definitive conclusions cannot be made regarding the specific reaction processes responsible for this behavior.

Second, the temperature profile in Fig. 7 along the entire catalyst bed is lower than the other catalyst beds discussed above (Fig. 5 and 6). The peak temperature of the 1 wt% Ir catalyst bed is 890 °C, which is significantly lower than the undoped (970 °C, Fig. 5) and the 0.05% Ir doped (950 °C, Fig. 6) catalysts. Evidently the 1% Ir system is an excellent reforming catalyst; that is, as soon as $H_2O$ is produced it undergo endothermic reforming reactions thereby limiting the temperature rise in the catalyst bed. It is also interesting to note that the gases leave the reactor at 733 °C (Fig. 7), substantially lower than the furnace temperature of 750 °C, as a consequence of the endothermic reforming reactions.

In Table 1, key summary features of Fig. 5–7 are provided, namely the peak temperatures and peak and exit product concentrations, and their locations within the catalyst bed.

### Table 1

| Peak value, (location, mm) | Temperature, °C | 970 (4) | Temperature, °C | 950 (4) | Temperature, °C | 890 (5) |
|---------------------------|-----------------|---------|-----------------|---------|-----------------|---------|
| $C_2H_4$, mol%            | 3.4 (3)         | 2.3 (3) | 1.1 (3)         | 0       |
| $C_2H_6$                  | 1.9 (3)         | 1.2 (3) | 9.2 (3)         | 0       |
| $H_2O$                    | 15.8 (3)        | 15.4 (6) | 15.4 (6) | 42 (4) |
| $H_2$                     | 5.8 (2)         | 6.2 (8) | 9.5 (5)         | 20.4 (4) |
| $CO_2$                    | 7.3 (2)         | 6.2 (8) | 9.5 (5)         | 20.4 (4) |
| CO                        | 4.0 (2)         | 1.8     | 0               | 0       |
| Exit                      | $C_2H_6$        | 3.4      | 0.02            | 0       |
|                          | $C_2H_4$        | 1.9      | 0.02            | 0       |
|                          | $H_2O$          | 15.8     | 0.02            | 0       |
|                          | $H_2$           | 5.0      | 0.02            | 0       |
|                          | $CO_2$          | 7.3      | 0.02            | 0       |
|                          | CO              | 2.4      | 0.02            | 0       |

### Conclusions

Detailed species concentration and temperature profiles obtained over La$_2$O$_3$–CeO$_2$ nanofiber catalysts at varying levels of Ir doping, in a fixed bed reactor fed by $CH_4$ and $O_2$ ($CH_4/O_2 = 5$) indicate a clear transition from the oxidative coupling of methane (OCM) to the catalytic partial oxidation (CPO) of methane reaction scheme. With the undoped fabric catalyst, OCM was dominant process with ethane and ethylene as major products. The catalyst doped with 1 wt% Ir produced exclusively synthesis gas (CO and $H_2$). At 0.05 wt% Ir doping, both OCM and CPO processes were operational. Species concentration profiles obtained in the 1 wt% Ir case indicate the formation of $H_2O$, $H_2$ and CO first, followed by the steam reforming of $CH_4$ to produce the balance of the syngas concomitant with the sharp decrease in $H_2O$ levels. These findings suggest a CPO mechanism that is different than the literature, calling for the revisions of detailed chemical kinetic mechanisms proposed before.

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### References

1. M. C. Alvarez-Galvan, N. Mota, M. Ojeda, S. Rojas, R. M. Navarro and J. L. G. Fierro, Catal. Today, 2011, 171, 15–23.
2. U. Zavyalova, M. Holena, R. Schlägl and M. Baerns, ChemCatChem, 2011, 3, 1935–1947.
3. B. C. Enger, R. Lødeng and A. Holmen, Appl. Catal., A, 2008, 346, 1–27.
4 D. A. Wood, C. Nwaoha and B. F. Towler, *J. Nat. Gas Sci. Eng.*, 2012, 9, 196–208.
5 D. A. Hickman and L. D. Schmidt, *Science*, 1993, 259, 343–346.
6 O. Korup, C. F. Goldsmith, G. Weinberg, M. Geske, T. Kandemir, R. Schlögl and R. Horn, *J. Catal.*, 2013, 297, 1–16.
7 K. A. Williams, R. Horn and L. D. Schmidt, *AIChE J.*, 2007, 53, 2097–2113.
8 L. Mleczko and M. Baerns, *Fuel Process. Technol.*, 1995, 42, 217–248.
9 R. Quiceno, J. Pérez-Ramírez, J. Warnatz and O. Deutschmann, *Appl. Catal., A*, 2006, 303, 166–176.
10 J. W. Thybaut, J. Sun, L. Olivier, A. C. Van Veen, C. Mirodatos and G. B. Marin, *Catal. Today*, 2011, 159, 29–36.
11 J. Sun, J. W. Thybaut and G. B. Marin, *Catal. Today*, 2008, 137, 90–102.
12 M. Y. Sinev, Z. T. Fattakhova, V. I. Lomonosov and Y. A. Gordinenko, *J. Nat. Gas Chem.*, 2009, 18, 273–287.
13 Z. Stansch, L. Mleczko and M. Baerns, *Ind. Eng. Chem. Res.*, 1997, 36, 2568–2579.
14 D. Noon, B. Zohour and S. Senkan, *J. Nat. Gas Sci. Eng.*, 2014, 18, 406–411.
15 D. Noon, A. Seubsai and S. Senkan, *ChemCatChem*, 2013, 5, 146–149.
16 B. Zohour, D. Noon and S. Senkan, *ChemCatChem*, 2014, 6, 2815–2820.
17 A. B. Mhadeshwar and D. G. Vlachos, *Ind. Eng. Chem. Res.*, 2007, 46, 5310–5324.
18 D. Dalle Nogare, N. J. Degenstein, R. Horn, P. Canu and L. D. Schmidt, *J. Catal.*, 2011, 277, 134–148.
19 R. Horn, K. A. Williams, N. J. Degenstein, A. Bitsch-Larsen, D. Dalle Nogare, S. A. Tupy and L. D. Schmidt, *J. Catal.*, 2007, 249, 380–393.
20 R. Horn, K. A. Williams, N. J. Degenstein and L. D. Schmidt, *Chem. Eng. Sci.*, 2007, 62, 1298–1307.
21 M. Prettre, C. Eichner and M. Perrin, *Trans. Faraday Soc.*, 1946, 42, 335b.
22 J. R. Rostrup-nilersen and J. H. B. Hansen, *J. Catal.*, 1993, 144, 38–49.
23 G. Postole, K. Girona, J. Toyir, A. Kaddouri and P. Gélin, *Fuel Cells*, 2012, 12, 275–287.
24 K. Nakagawa, K. Anzai, N. Matsu, N. Ikenaga, T. Suzuki, Y. Teng, T. Kobayashi and M. Haruta, *Catal. Lett.*, 1998, 51, 163–167.
25 B. Zohour, D. Noon and S. Senkan, *ChemCatChem*, 2013, 5, 2809–2812.
26 R. Horn, O. Korup, M. Geske, U. Zavyalova, I. Oprea and R. Schlögl, *Rev. Sci. Instrum.*, 2010, 81, 064102.
27 M. Geske, K. Pelzer, R. Horn, F. C. Jentoft and R. Schlögl, *Catal. Today*, 2009, 142, 61–69.