


Cite this: *RSC Adv.*, 2022, 12, 9036

Elucidation of the reaction mechanism on dry reforming of methane in an electric field by *in situ* DRIFTS†

Naoya Nakano,^a Maki Torimoto,^a Hiroshi Sampei,^a Reiji Yamashita,^a Ryota Yamano,^a Koki Saegusa,^a Ayaka Motomura,^a Kaho Nagakawa,^a Hideaki Tsuneki,^a Shuhei Ogo^{b,c} and Yasushi Sekine^{a,*}

With increasing expectations for carbon neutrality, dry reforming is anticipated for direct conversion of methane and carbon dioxide: the main components of biogas. We have found that dry reforming of methane in an electric field using a Pt/CeO₂ catalyst proceeds with sufficient rapidity even at a low temperature of about 473 K. The effect of the electric field (EF) on dry reforming was investigated using kinetic analysis, *in situ* DRIFTS, XPS, and DFT calculation. *In situ* DRIFTS and XPS measurements indicated that the amount of carbonate, which is an adsorbed species of CO₂, increased with the application of EF. XPS measurements also confirmed the reduction of CeO₂ by the reaction of surface oxygen and CH₄. The reaction between CH₄ molecules and surface oxygen was promoted at the interface between Pt and CeO₂.

Received 19th January 2022

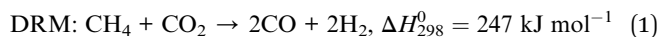
Accepted 14th March 2022

DOI: 10.1039/d2ra00402j

rsc.li/rsc-advances

1. Introduction

As expectations for the achievement of carbon neutrality continue to rise worldwide, the effective use of biomass resources is attracting attention as one means of achieving that goal. Biogas obtained from anaerobic fermentation is composed mainly of methane and carbon dioxide, both of which are known to be greenhouse gases. A promising technology is one that could directly convert methane and carbon dioxide into high value-added substances such as synthesis gas by dry reforming (DRM: eqn (1)).^{1,2} However, because of thermodynamic and kinetic constraints, the conventional catalytic process for dry reforming requires temperatures higher than 1000 K. Moreover, the reaction is known to be prone to carbon deposition.



The reaction mechanism of CO₂ in these reactions has been well-studied through *in situ* DRIFTS measurements. CO₂ dissociates on the active metal *via* carbonyl species^{3–6} and supports oxides using oxygen vacancies *via* intermediates such as

carbonate and formate.^{7–10} Chen *et al.*¹¹ reported that CO was formed *via* carbonate, which is adsorbed species of CO₂ using CeO₂ lattice oxygen defects, in DRM using Pt–Ni supported CeO₂. Bobadilla *et al.*¹² revealed that the reaction proceeds *via* formate species as the key intermediate in RWGS (reverse water gas shift) of Pt-loaded CeO₂.

In addition, various unconventional studies have been conducted in recent years to promote the conversion of CO₂ by application of external stimuli such as electricity, magnetic fields, and light.^{13–17} Wang *et al.* reported that Xe lamp irradiation to Cu-loaded CeO₂ increases the amount of lattice defects of CeO₂ and shows high CO₂ reduction performance.¹⁸ Zhu *et al.*¹⁹ reported that plasma application accelerates the formation and decomposition of the intermediate formate in DRM using Au-loaded CeO₂. Consequently, a process that accelerates the reaction by providing an external stimulus is becoming a more attractive CO₂ conversion technology.^{20,21}

Under these circumstances, our group has proposed a catalytic reaction in an electric field (EF) in which direct current is applied by inserting electrodes at the top and bottom edges of the catalyst layer to promote the reaction.^{22–25} We earlier reported various effects of enhanced activity and lowered apparent activation energy at low temperatures in DRM,²⁶ RWGS,²⁷ and CO₂ methanation.²⁸

However, details of the reactivity of CO₂ and its adsorption ability in the EF have not been clarified. Therefore, *in situ* DRIFTS measurements were taken for this study to confirm EF effects on the CO₂ conversion reaction by examining changes of intermediates when the EF is applied during a DRM reaction.

^aDepartment of Applied Chemistry, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, 169-8555, Japan. E-mail: ysekine@waseda.jp

^bDepartment of Marine Resources Science, Faculty of Agriculture and Marine Science, Kochi University, Nankoku, 783-8502, Japan

^cCenter for Advanced Marine Core Research, Kochi University, Nankoku, 783-8502, Japan

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d2ra00402j



2. Experimental

2.1 Catalyst preparation

The catalyst of 1 wt% Pt-supported ceria (1wt%Pt/CeO₂) was prepared using an impregnation method. We used ceria (CeO₂; JRC-CEO-1) supplied by the Catalysis Society of Japan as a support. Pt was loaded on the support using the following procedure. First, Pt(NH₂)₄(NO₃) (Sigma-Aldrich Corp.) was dissolved in distilled water. The powder of CeO₂ support was added to the solution and was stirred for 2 h. Subsequently, the solution was dried at 393 K for 24 h. The obtained powder was calcined at 773 K for 3 h. The obtained sample was pressed and sieved using 355–500 μ m mesh. Subsequently it was reduced with 20% H₂ diluted with Ar at a 100 SCCM flow rate at 723 K for 30 min.

2.2 *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

In situ DRIFTS measurements were taken with an FT-IR spectrophotometer (FT/IR-6200; Jasco Corp.) equipped with a ZnSe window and MCT-M detector cooled with liquid nitrogen. Spectra were recorded with 4 cm^{−1} resolution and 50–200 times scans. The DRIFT cell was made of PTFE, which is an insulator for inserting two electrodes as described in an earlier report.²⁹ After a pelletized catalyst of 50 mg (without EF) or 110 mg (with EF) was set in the DRIFT cell, the EF was applied with 3 mA of direct current. A schematic image of the DRIFT cell was described in an earlier report.²⁹ The background spectrum was recorded under Ar flow at 90 SCCM at 473 K without EF. During the experiment, CH₄ and CO₂ were supplied respectively at 10 SCCM. They were diluted with Ar at 90 SCCM at 473 K.

2.3 Activity test

Catalytic activity tests were conducted with a fixed bed flow type reactor as presented in Fig. S1.† A 6.0 mm-diameter quartz tube was used, with 300 mg of the catalyst charged in it. A thermocouple was inserted into the catalyst bed at the bottom. The reaction temperature was fixed at 473 K. The temperature was controlled with the thermocouple of the catalyst bed, which includes the Joule heat with EF. For that reason, electrical heating of the catalyst bed is negligible in this case. The feed gas (Ar : CH₄ : CO₂ = 2 : 1 : 1) was supplied with the total flow rate of 80 SCCM. A direct current voltage power supply was used to apply the EF. The current and applied voltage were monitored using a digital phosphor oscilloscope (TDS2100; Tektronics Corp.). After passing a cold trap, the reacted gas was analyzed using GC-FID, TCD (GC-2014; Shimadzu Corp.) with a Porapak Q column and a methanizer. The conversion, yield, and input power were calculated by some equations (see ESI†).

2.4 Characterization

Powder X-ray diffractometry (XRD, RINT-Ultima III; Rigaku Corp.) was used to characterize the crystalline structure of catalysts before and after the activity test. The anode voltage and current were 40 kV, 40 mA, respectively, with Cu-K α radiation.

Fig. S2† shows XRD patterns of catalysts before and after the activity test. The diffraction peaks at 28.6, 33.0, 47.4, 56.4, 69.3, and 76.7° were assigned respectively to the CeO₂ crystal facets of (111), (200), (220), (311), (222), and (400). No significant change in the crystalline structure occurred during the reaction.

The nitrogen physical ad-/desorption isotherm of catalysts was measured using a surface area analyser (Gemini VII; Micromeritics Instrument Corp.) at 77 K. The specific surface area was obtained using the BET method. The specific surface area of the catalyst before the activity test was 158 m² g^{−1}.

The Pt particle size was measured using a field-emission electron microscope (FE-TEM, JEM-2100F; Jasco Corp.) with 200 kV accelerating voltage and 0.1 nm resolution. Fig. S3† shows HAADF-STEM images and EDX mappings of 1wt%Pt/CeO₂. The image of elemental mapping shows that Pt was highly dispersed on CeO₂ and that the particle size could not be estimated. The Pt loading amount on the catalyst was confirmed by ICP-OES. The X-ray photoelectron spectroscopy (XPS) measurements were taken (PHI 5000 Versa Probe II; ULVAC-PHI Corp.) with a monochromatic Al-K α X-ray source. Before the measurement, samples were pretreated with H₂ (H₂ : Ar = 1 : 4; 100 SCCM total flow rate) and O₂ (O₂ : Ar = 1 : 4; 100 SCCM total flow rate) at 693 K for 30 min. Subsequently they were exposed to CH₄, CO₂, and Ar flow, respectively, for 20 min. In each flow, the EF was applied for 10 min at 3 mA. The samples were transported to the instrument using a transfer vessel while avoiding exposure to air. The obtained binding energies were calibrated using C 1s assigned to C–H or C–C (284.8 eV). The peak fittings were conducted using the Shirley method.³⁰ The Ce³⁺ fraction was calculated using the equation shown in ESI.†

2.5 DFT calculation

All Density Functional Theory (DFT) calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) 5.4.4 with the PAW (Projector Augmented Wave) potentials.^{31–33} The Perdew–Burke–Ernzerhof (PBE) of the generalized gradient approximation (GGA) was used as the functional, and the van der Waals force was corrected by DFT-D3.^{34,35} The plane wave cutoff was set to 400 eV, and the on-site Coulomb interaction of Ce 4f orbitals was taken into account using the DFT+*U* method with *U* = 5.0 eV.^{36–41} As reciprocal space sampling, (5 \times 5 \times 5) and (1 \times 1 \times 1) *k*-points were sampled using Gaussian smearing for CeO₂ bulk and slab, respectively, and 0.08 Å^{−1} *k*-points were sampled using the first order Methfessel–Paxton method for Pt bulk.⁴² All sampling points were decided with Monkhorst–Pack method.⁴³

The calculated lattice constant of CeO₂ bulk was 5.437 Å with an error of 0.4% from the experimental value.⁴⁴ The CeO₂(111) slab was represented by the three repeated layers of (3 \times 6) supercells with 20 Å vacuum layers. The lowest layer was fixed during the structural optimization. The calculated lattice constant of Pt bulk was 3.909 Å with an error of 0.4% from the experimental value.⁴⁵ A Pt rod were prepared from the (111) and (100) planes of the Pt bulk as the side and top, respectively, and placed on a CeO₂ slab to express Pt/CeO₂ surface. The O₂

molecules in the gas phase were placed in a $10 \times 10 \times 10 \text{ \AA}$ box and calculated at Γ point. All calculation models were depicted using VESTA.⁴⁶ (Fig. S13 and S14†) In addition, the oxygen vacancy formation energies were calculated according to the following equation.

$$E_{\text{Vox}} = E(\text{Pt/CeO}_2 \text{ without O}) + (\frac{1}{2}E(\text{O}_2) - E(\text{Pt/CeO}_2)) \quad (2)$$

Here, E_{Vox} , $E(\text{O}_2)$, and $E(\text{Pt/CeO}_2)$, $E(\text{Pt/CeO}_2 \text{ without O})$ are the energy of the formation energy of the oxygen defect, the oxygen molecule, the Pt/CeO₂ model, the Pt/CeO₂ model after the oxygen defect formation, respectively.

3. Results and discussion

3.1 Catalytic activity

First, activity tests were performed to evaluate the activity with EF at low temperatures. Yabe *et al.*²⁶ reported DRM activity with EF: the reaction proceeds at a temperature as low as 473 K for Ni-supported La-doped ZrO₂ with EF. As the catalyst, Pt/CeO₂ was selected because CeO₂ has been studied for other reactions with EF, such as methane steam reforming²⁹ and dehydrogenation of methylcyclohexane.⁴⁷ Then, Pt/CeO₂ catalysts with various supported amounts of Pt were investigated (Fig. S4†), and 1wt%Pt/CeO₂ showed highest activity and was selected for suitable catalyst. Table 1 presents the catalytic activity of 1wt% Pt/CeO₂ at 473 K. The activities at different temperatures are presented in Table S1.† Fig. S5† shows the relation between reaction temperature and conversion in DRM (left), the Arrhenius plot (middle), and H₂/CO ratio (right). The conversion of CH₄ and CO₂ at 473 K was more than 15% (it is conducted in a kinetic region), whereas the reaction did not proceed without EF at this temperature. The cause of catalyst deactivation, the amount of carbon deposition, was negligible because the carbon balance was almost 100%. No carbon formation on the catalyst was apparent after the reaction. The apparent activation energy calculated from the Arrhenius plot (Fig. S5†) without EF was 104 kJ mol^{−1}, but it was markedly lower with EF: only 4.82 kJ mol^{−1}. As reported from an earlier study, the H₂/CO ratio with EF was high in the low-temperature range.²⁶ In addition, the power efficiency, the value obtained by dividing the gained

enthalpy during the reaction by the applied power, was calculated as around 20%. As described above, the 1wt%Pt/CeO₂ showed high activity for DRM at 473 K in the electric field. Therefore, we investigated the reaction pathway related to this process using various methods including DRIFTS.

3.2 Effects of EF on CO₂ adsorption

To elucidate reasons why DRM proceeds effectively even at such low temperatures, *in situ* DRIFTS measurements were performed to observe the changes in CO₂ adsorption state before and after applying the EF. The adsorption of CO₂ on CeO₂-based catalysts has been well-studied. Many reports have assigned the peaks of carbonaceous species. The assignment of carbonaceous species used for this study and their values in the literature are shown in ESI.†^{5,11,48–73} We assigned peaks in the range of 1800–2100 cm^{−1} to carbonyl species adsorbed onto Pt, but they are not shown in the table. In this measurement, we applied the EF to the catalyst in the CO₂ flow and compared the spectra before and after the application of EF. Fig. 1 shows (a) DRIFT spectra before and after the application of EF and (b) the difference spectrum obtained by subtracting the spectrum without EF from that with EF. As shown in Fig. 1(b), the peak area at around 1160 cm^{−1} was increased by the application of EF. The peaks at 1160, 1131, 1074, and 1031 cm^{−1} are assigned

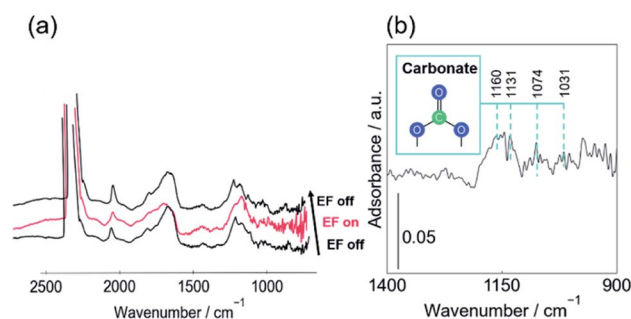


Fig. 1 (a) *In situ* DRIFT spectra with, without EF under CO₂ flow over 1wt%Pt/CeO₂, (b) difference spectra in 900–1400 cm^{−1} region (with EF – without EF); CO₂ : Ar = 1 : 8; 90 SCCM total flow rate; 3.0 mA input current; at 473 K.

Table 1 Catalytic activities over 1wt%Pt/CeO₂ catalyst with/without the electric field (EF)

	Temp./K	CH ₄ conv./%	CO ₂ conv./%	H ₂ /CO/—	Power/W	Energy efficiency/—
With EF	453	15.1	16.4	0.763	2.81	0.186
	473	15.0	16.5	0.754	2.91	0.179
	523	15.9	17.9	0.728	2.74	0.203
	573	16.4	19.2	0.696	2.61	0.223
	623	17.4	20.9	0.667	2.54	0.244
	672	19.1	24.0	0.625	2.63	0.262
	723	27.5	34.6	0.623	2.87	0.347
	723	27.5	34.6	0.623	2.87	0.347
Without EF	472	0	0	—	—	—
	523	0.00	0.01	0.00	—	—
	573	0.03	0.07	0.00	—	—
	623	0.15	0.42	0.00	—	—
	673	0.66	1.60	0.135	—	—
	723	2.21	4.75	0.237	—	—



respectively as monodentate, bridged, polydentate, and bidentate carbonate peaks (see ESI†). The increase of the peak area at around 1160 cm⁻¹ signifies that the number of carbonate species adsorbed onto CeO₂ increased because of application of the EF.

In general, CO₂ adsorbs on metal oxides and forms adsorbed species such as carbonate and bicarbonate.^{71,74} DFT calculations and various experimentally obtained results revealed that lattice oxygen defects enhance the adsorption of gas-phase CO₂.^{75–77} Lattice oxygen in the catalyst support dissociates CH₄ in the DRM reaction, leading to the formation of oxygen vacancies.^{75,78,79}

Consequently, the reaction of CH₄ with lattice oxygen is expected to be an important factor supporting oxygen vacancy formation. Therefore, to investigate the effects of CH₄ on the formation of lattice oxygen defects with or without EF, we took XPS measurements and evaluated the reducibility of CeO₂. We then compared the fractions of Ce³⁺ and Ce⁴⁺ of 1wt%Pt/CeO₂ after exposing catalysts to CH₄, CO₂, and Ar flow, respectively with and without EF at 473 K. Table 2 shows the calculated Ce³⁺ fraction of 1wt%Pt/CeO₂ spent in each condition. Fig. S7† presents the obtained XPS spectra. In the Ce 3d spectrum, three doublet peaks at (u''': 916.6, v''': 898.2), (u'': 907.5, v'': 888.8), and (u: 900.7, v: 882.3) eV are assigned to Ce⁴⁺; two doublet peaks at (u': 903.8, v': 885.2), (u₀: 899.3, v₀: 880.7) eV are assigned to Ce³⁺.⁸⁰ Table 2 shows that the fraction of Ce³⁺, after being kept in the CH₄ flow with EF, was larger than that without EF. The increase in the Ce³⁺ fraction in the CH₄ flow suggests that the oxygen species were removed easily by reaction with CH₄ in the EF, resulting in the formation of more lattice oxygen defects. Fig. S8† depicts changes in DRIFT spectra before and after application of the EF under the CH₄ flow. Fig. S8† (b) shows that the peak area of carbonate species increased. The increase of the carbonate species signifies that CH₄ consumed lattice oxygen, which is the only oxygen source, resulting in the formation of lattice oxygen defects.

The increase of Ce³⁺ fraction by application of the EF in Ar flow was 0.5%, which is much less than that in the CH₄ flow. Therefore, the oxygen species are not released simply by application of the EF, but are released by the reaction with CH₄ in the EF. Therefore, the oxygen of CeO₂ is regarded as activated by the EF. Thus the reaction of lattice oxygen with CH₄ is promoted, thereby forming the oxygen defect.

Table 2 Relative ratio of surface contents of Ce³⁺

Condition	Surface content of Ce ³⁺ /%
CH ₄ flow without EF	16.8
CH ₄ flow with EF	19.4
Ar flow without EF	16.2
Ar flow with EF	16.7
CO ₂ flow without EF	17.5
CO ₂ flow with EF	18.3

The fraction of Ce³⁺ increased from 17.5% to 18.3% after applying the EF in the CO₂ flow, indicating an increase of carbonate species by CO₂ adsorption. According to Yi *et al.*,⁸¹ Ce⁴⁺ decreases along with the carbonate species formation because the carbonate species are formed by oxidization of the adsorbed CO₂ by the surface oxygen of the CeO₂ support. Therefore, the reduction of Ce in the EF in the CO₂ flow also supports enhancement of the CO₂ adsorption.

The enhanced reactivity of oxygen in the EF was confirmed using oxygen isotope exchange test. Fig. S9† portrays results of the oxygen isotope exchange test. For this measurement, the EF was applied to the catalyst in the ¹⁸O₂ flow after the surface oxygen species in CZO were filled with ¹⁶O. Then a mass spectrometer was used to analyze the produced gas. As shown in Fig. S9,† after the application of EF, the amount of ¹⁸O₂ decreased immediately. Simultaneously, ¹⁶O¹⁸O appeared. However, the appearance of ¹⁶O₂ was slight. These results indicate that lattice oxygen is not removed merely by applying EF. Rather, it is removed by reaction with the gas species. This result also supports the increased reactivity of the oxygen in the EF.

3.3 Reactivity of carbonate species

Next, an alternating feed test between CO₂ and CH₄ was conducted to elucidate the behaviour of CO₂ and CH₄ in the DRM reaction with and without EF. In the alternating feed test, CO₂ and CH₄ were switched; GC was used to analyze the produced gas. Fig. 2 shows the calculated formation rate of CO after switching the gas with EF. Actually, CO was not observed without EF, although it was formed with EF. The CO formed after either the CO₂ or CH₄ supply. This CO formation signifies that oxidation of CH₄ and reduction of CO₂ occur on Pt/CeO₂ with EF. In both gas feeds, the amount of the produced CO decreased with the time course. The oxidation and reduction performance of the catalyst decreased with time because of the continuous supply or consumption of oxygen. From earlier results and research, we assumed the role of lattice oxygen in this test. In the CH₄ flow, lattice oxygen was removed by CH₄. Then depletion of the activated oxygen caused the decrease of the produced CO amount. However, CO₂ filled the lattice oxygen defect in the CO₂ flow. The amount of produced CO decreased along with the decrease of the lattice oxygen defects.

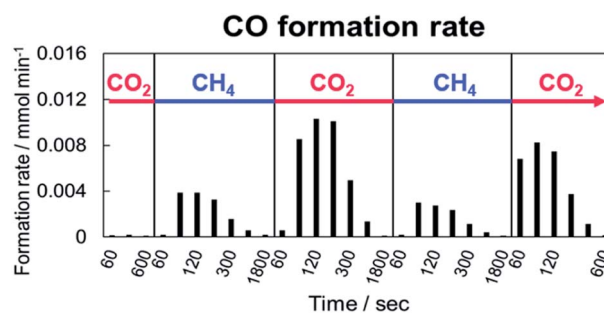


Fig. 2 CO formation rate after switching between CO₂ and CH₄ over 1wt%Pt/CeO₂ catalyst with EF; 80 SCCM total flow rate (CH₄ : Ar = 1 : 3 under CH₄ flow, CO₂ : Ar = 1 : 3 under CO₂ flow) at 473 K.



In situ DRIFTS measurements were conducted in the CO₂, CH₄ alternating feed test to observe the reactivity of the carbonate species. Fig. 3 portrays the change in spectra in the test between CH₄ and CO₂ (a) with EF, (b) without EF, and the difference in the spectrum before and after CH₄ supply (c) with EF, (d) without EF. The peaks assigned to carbonate species decreased by stopping the CO₂ supply, irrespective of the presence of EF. A similar decrease in the carbonate peak was observed when the supply gas was switched from CO₂ to Ar without EF (Fig. S10 and S11†). Without EF, CO was not formed when the CO₂ gas feed was switched to CH₄ or Ar flow, suggesting that carbonate species desorbed as CO₂. However, when the EF was applied, CO was formed, suggesting that some of the carbonate species reduced and dissociated as CO.

3.4 Oxygen release ability of CeO₂

DFT calculations were performed to investigate the tendency of oxygen defect formation on Pt-loaded CeO₂. Fig. S15† shows the calculated oxygen defect locations, and Table S3† shows the oxygen defect formation energy at each location. The formation energy of the oxygen defects became higher as the distance from Pt increased. The results show that the oxygen defects are more easily generated at the interface of Pt and CeO₂ than other locations. This result supports the reaction of CO₂ at the interface of Pt and CeO₂ because the oxygen defects are more easily generated near the interface, and the generated oxygen defects facilitate the adsorption of CO₂ near the interface.⁷⁵ Note that the sign of the value does not mean whether it is spontaneous or not, because the energy of half of the oxygen

molecule is used as the energy of the oxygen atom and the term of pressure, and the temperature is not taken into account in the calculation of the oxygen defect formation energy.

3.5 Discussion

From these results, we consider the effect of EF on DRM and the reaction mechanism.

3.5.1 Effect of EF. *In situ* DRIFTS measurements revealed the effect of the EF on CO₂ adsorption. As shown in Fig. 1, the peak area of carbonate species increased by application of the EF, indicating that application of the EF enhanced the CO₂ adsorption. The XPS measurement results also support the enhancement of CO₂ adsorption on CeO₂ (Table 2).

It is reported that the enhancement in CO₂ adsorption is related to the oxygen activity of the oxide support. Chen *et al.*⁸² investigated the adsorption and oxidation, redox behaviour of CO and CO₂ on CeO₂ using DFT calculations. They reported that highly reactive surface oxygen, which Ce weakly bonds, lowers CO₂ adsorption and carbonate species formation barriers. In addition, results of several studies suggest that EF promoted the activation of the oxygen in the oxide support.^{83–85} High catalytic activity due to the activated oxygen on supports by applying EF was reported in the OCM reaction using CeO₂,⁸⁵ and in the TWC catalytic reaction of exhaust gases using cerium zirconium oxides (Ce_{0.7}Zr_{0.3}O₂) as support.⁸⁴ Therefore, we considered that lattice oxygen was activated by the EF, and promoted CO₂ adsorption.

The XPS measurements taken for this study revealed that CH₄ molecules react with surface oxygen, consume them, and thereby reduce CeO₂ more with EF than without EF (Table 2). This improved reactivity of CH₄ with surface oxygen might be attributed to the enhanced reactivity of the oxygen by the EF.

Next, the CO₂, CH₄ alternating test shows the CO₂ dissociation ability of CeO₂. When the gas was switched from CO₂ to Ar without EF, the carbonate species desorbed as CO₂ (Fig. S9 and S10†). When the gas was switched to CH₄ without EF, the carbonate species also desorbed as CO₂ and CO did not form. However, CO was formed when the supply gas was switched to CH₄ with EF, indicating that a part of the carbonate species reacted and desorbed as CO (Fig. 2 and 3). These results indicate that the EF promotes dissociation of CO₂ adsorbed on CeO₂.

3.5.2 Active site. DFT calculations showed that oxygen defect is likely to form on CeO₂ at the interface of Pt and CeO₂. Previous research suggest that oxygen defect promotes CO₂ adsorption.⁷⁵ Thus, CO₂ adsorption tends to occur on CeO₂ at the interface of Pt and CeO₂.

On the other hand, CH₄ dissociates on Pt at the interface of metal (Pt) and support (CeO₂) with EF⁷⁵ and without EF.^{86,87} CH₄ and CO₂ with high reactivity at the interface of Pt and CeO₂ suggests that active site of this reaction is the interface of Pt and CeO₂.

3.5.3 Reaction mechanism. From these results, we considered the possible DRM mechanism.

First, with the EF, the reaction of CO₂ is considered to proceed by the Mars–van Krevelen (MvK) mechanism using the lattice oxygen of the support. Yabe *et al.*⁷⁵ have shown that the dissociation of CO₂ proceeds *via* the lattice oxygen in the EF by

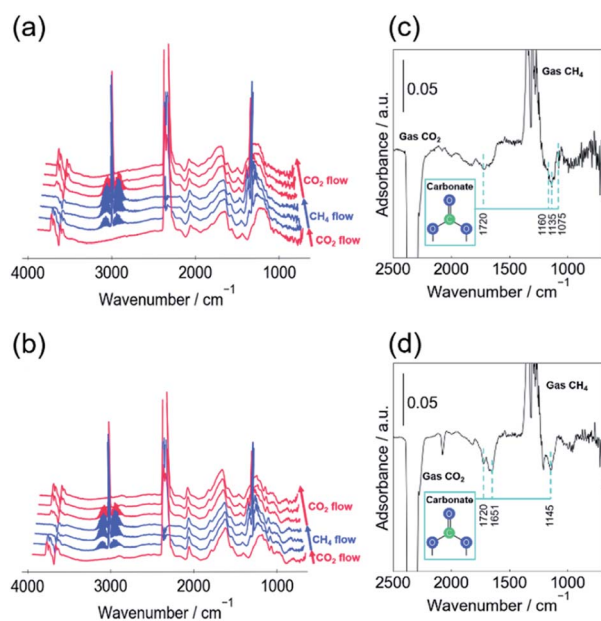


Fig. 3 *In situ* DRIFT spectra over 1wt%Pt/CeO₂ catalyst after switching between CO₂ and CH₄ feeds at 473 K. 120, 600, 1200 seconds after switching to CH₄, 120, 600, 1200 seconds after switching to CO₂. (a) with (b) without EF; difference spectrum in 700–2500 cm^{−1} (CH₄ at steady state – CO₂ at steady state) (c) with (d) without EF; 90 SCCM total flow rate (CH₄ : Ar = 1 : 8 under CH₄ flow, CO₂ : Ar = 1 : 8 under CO₂ flow at 473 K); 3.0 mA input current.

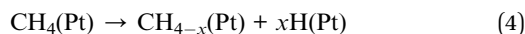
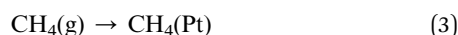


^{18}O isotope test. This indicates that the dissociation of CO_2 by the MvK mechanism proceeds at low temperatures with EF.

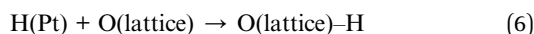
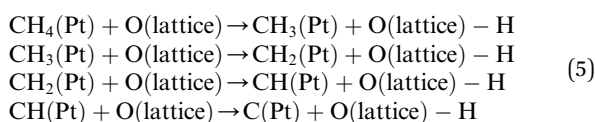
Contrarily, CH_4 dissociation proceeds on Pt. Previously, many reports have suggested the rate determining step (RDS) of the reaction of CH_4 . Otsuka *et al.*⁸⁸ showed that CH_4 dissociation and recombination proceed much faster than the oxidation of CH_4 on CeO_2 and Pt/CeO_2 by the CH_4 , CD_4 exchange test. Wei and Iglesia⁸⁹ also suggested C–H bond activation on Pt is reversible, using the CH_4 , CD_4 exchange test in DRM reaction. Thus, the oxidation of H species formed after CH_4 dissociation is necessary for the reaction to proceed. Das *et al.*⁸⁶ have also reported that reaction of CH_4 and lattice oxygen is the RDS in the DRM reaction. Therefore, we considered that the RDS in this reaction is oxidation of the H species. The EF promotes the reaction to activate lattice oxygen.

From these results, we considered the possible DRM mechanism as follows.

(1) Methane dissociation on Pt⁹⁰



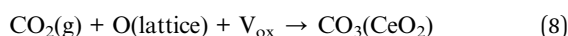
(2) Diffusion of H species^{86,90}



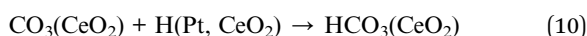
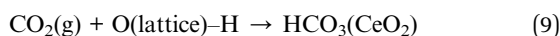
(3) Methane desorption as CO ⁸⁶



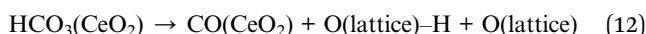
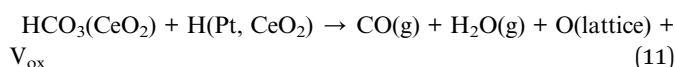
(4) CO_2 adsorption



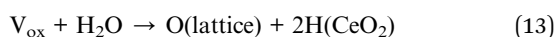
(5) Hydrogenation of CO_2 species



(6) Desorption of carbonaceous species



(7) Refilling of oxygen vacancy



(8) Formation of H_2



Here, V_{ox} and $\text{O}(\text{lattice})$ denote oxygen vacancy and lattice oxygen, respectively.

First, the EF effect is to enhance the oxygen activity of oxide support because the adsorption of CO_2 was promoted significantly by EF application (eqn (8)). The activated surface oxygen reacts easily with C and H species dissociated from CH_4 and forms oxygen defects (eqn (5)–(7)).

The activated oxygen and the oxygen defects of oxide support both contribute to enhancement of the CO_2 adsorption. Finally, the adsorbed CO_2 forms carbonate species, reacts, and desorbs as CO. The remaining oxygen species again work as the oxidant of CH_4 . Consequently, the DRM reaction in the EF proceeds *via* a redox cycle of CeO_2 support.

4. Conclusion

The effect of the electric field (EF) on DRM reaction was investigated using 1wt%Pt/CeO₂ by activity tests, *in situ* DRIFTS, XPS, and DFT calculation. 1wt%Pt/CeO₂ showed high activity for DRM with EF, even at 473 K, at which thermal catalysis proceeds only slightly. *In situ* DRIFTS measurements in CO_2 flow revealed that the adsorbed species of CO_2 increases when the EF is applied. This increase signifies that the adsorption of CO_2 is promoted by the EF. XPS measurements of the catalysts after the treatment in CO_2 atmosphere with EF suggest the enhancement of CO_2 adsorption on CeO₂. In addition, XPS measurements of catalysts after exposure to CH_4 flow with EF confirmed that the Ce^{3+} fraction of CeO₂ increased, indicating that CeO₂ support was reduced after the reaction of surface oxygens and CH_4 molecules in EF, even at 473 K. These results suggest that the oxygen in the oxide support was activated in the EF. Furthermore, the reaction of CH_4 and the surface oxygen was promoted, thereby forming lattice oxygen defects and CO. The activated oxygen in the EF and the resulting lattice oxygen defects by the reaction with CH_4 molecules both promote CO_2 adsorption. The reaction is considered to proceed at the interface of Pt and CeO₂. DFT calculations also support the reaction mechanism of DRM at the interface of Pt and CeO₂.

In summary, the reaction mechanism of DRM in the EF was inferred as presented below. The EF can improve the oxygen activity and can therefore promote the reaction of CH_4 molecules and surface oxygens at the Pt–CeO₂ interface, forming the oxygen defects. Both the activated oxygen and the oxygen defects of oxide support enhance the adsorption of CO_2 , forming more carbonate species on CeO₂ in the EF. Finally, CO_2 molecules dissociate to form CO *via* the carbonate species.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partly achieved through the use of the super-computer system at the information initiative center, Hokkaido



University, Sapporo, Japan. This work was the result of using characterization equipments (JEM-2100F and Versa Probe II: Material Characterization Central Laboratory in Waseda University) shared in MEXT Project for promoting public utilization of advanced research infrastructure (Program for supporting construction of core facilities) Grant Number JPMXS0440500021 and JPMXS0440500022.

References

- 1 J. R. Rostrup-Nielsen and J. H. B. Hansen, *J. Catal.*, 1993, **144**, 38–49.
- 2 A. Sternberg and A. Bardow, *ACS Sustainable Chem. Eng.*, 2016, **4**, 4156–4165.
- 3 V. T. Sagar and A. Pintar, *Appl. Catal., A*, 2020, **599**, 117603.
- 4 M. A. Álvarez, L. F. Bobadilla, V. Garcilaso, M. A. Centeno and J. A. Odriozola, *J. CO₂ Util.*, 2018, **24**, 509–515.
- 5 Z. Liu, F. Zhang, N. Rui, X. Li, L. Lin, L. E. Betancourt, D. Su, W. Xu, J. Cen, K. Attenkofer, H. Idriss, J. A. Rodriguez and S. D. Senanayake, *ACS Catal.*, 2019, **9**, 3349–3359.
- 6 M. García-Diéguez, E. Finocchio, M. Á. Larrubia, L. J. Alemany and G. Busca, *J. Catal.*, 2010, **274**, 11–20.
- 7 B. Bachiller-Baeza, C. Mateos-Pedrero, M. A. Soria, A. Guerrero-Ruiz, U. Rodemerck and I. Rodríguez-Ramos, *Appl. Catal., B*, 2013, **129**, 450–459.
- 8 M. Németh, Z. Schay, D. Srankó, J. Károlyi, G. Sáfrán, I. Sajó and A. Horváth, *Appl. Catal., A*, 2015, **504**, 608–620.
- 9 C. C. Chong, Y. W. Cheng, H. D. Setiabudi, N. Ainirazali, D. V. N. Vo and B. Abdullah, *Int. J. Hydrogen Energy*, 2020, **45**, 8507–8525.
- 10 S. Das, M. Sengupta, A. Bag, M. Shah and A. Bordoloi, *Nanoscale*, 2018, **10**, 6409–6425.
- 11 H. Chen, S. Chansai, S. Xu, S. Xu, Y. Mu, C. Hardacre and X. Fan, *Catal. Sci. Technol.*, 2021, **11**, 5260–5272.
- 12 L. F. Bobadilla, J. L. Santos, S. Ivanova, J. A. Odriozola and A. Urakawa, *ACS Catal.*, 2018, **8**, 7455–7467.
- 13 L. D. Chen, M. Urushihara, K. Chan and J. K. Nørskov, *ACS Catal.*, 2016, **6**, 7133–7139.
- 14 J. Ran, M. Jaroniec and S. Z. Qiao, *Adv. Mater.*, 2018, **30**, 1704649.
- 15 W. C. Chung, K. L. Pan, H. M. Lee and M. B. Chang, *Energy Fuels*, 2014, **28**, 7621–7631.
- 16 X. Gao, Z. Lin, T. Li, L. Huang, J. Zhang, S. Askari, N. Dewangan, A. Jangam and S. Kawi, *Catalysts*, 2021, **11**, 455.
- 17 X. Zhang, C. S. M. Lee, D. M. P. Mingos and D. O. Hayward, *Catal. Lett.*, 2003, **88**, 129–139.
- 18 M. Wang, M. Shen, X. Jin, J. Tian, M. Li, Y. Zhou, L. Zhang, Y. Li and J. Shi, *ACS Catal.*, 2019, **9**, 4573–4581.
- 19 X. Zhu, J. H. Liu, X. S. Li, J. L. Liu, X. Qu and A. M. Zhu, *J. Energy Chem.*, 2017, **26**, 488–493.
- 20 D. Mei, X. Zhu, Y. L. He, J. D. Yan and X. Tu, *Plasma Sources Sci. Technol.*, 2015, **24**, 015011.
- 21 X. Tu and J. C. Whitehead, *Appl. Catal., B*, 2012, **125**, 439–448.
- 22 M. Torimoto, S. Ogo, Y. Hisai, N. Nakano, A. Takahashi, Q. Ma, J. G. Seo, H. Tsuneki, T. Norby and Y. Sekine, *RSC Adv.*, 2020, **10**, 26418–26424.
- 23 S. Okada, R. Manabe, R. Inagaki, S. Ogo and Y. Sekine, *Catal. Today*, 2018, **307**, 272–276.
- 24 S. Ogo and Y. Sekine, *Chem. Rec.*, 2017, **17**, 726–738.
- 25 M. Torimoto, K. Murakami and Y. Sekine, *Bull. Chem. Soc. Jpn.*, 2019, **92**, 1785–1792.
- 26 T. Yabe, K. Mitarai, K. Oshima, S. Ogo and Y. Sekine, *Fuel Process. Technol.*, 2017, **158**, 96–103.
- 27 K. Oshima, T. Shinagawa, Y. Nogami, R. Manabe, S. Ogo and Y. Sekine, *Catal. Today*, 2014, **232**, 27–32.
- 28 K. Yamada, S. Ogo, R. Yamano, T. Higo and Y. Sekine, *Chem. Lett.*, 2020, **49**, 303–306.
- 29 R. Manabe, S. Okada, R. Inagaki, K. Oshima, S. Ogo and Y. Sekine, *Sci. Rep.*, 2016, **6**, 38007.
- 30 D. A. Shirley, *Phys. Rev. B: Solid State*, 1972, **5**, 4709–4714.
- 31 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **47**, 558–561.
- 32 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **49**, 14251–14269.
- 33 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15–50.
- 34 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 35 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 36 J. J. Carey and M. Nolan, *Catal. Sci. Technol.*, 2016, **6**, 3544–3558.
- 37 K. Murakami, Y. Mizutani, H. Sampei, A. Ishikawa and Y. Sekine, *J. Chem. Phys.*, 2021, **154**, 164705.
- 38 M. D. Krcha, A. D. Mayernick and M. J. Janik, *J. Catal.*, 2012, **293**, 103–115.
- 39 H. T. Chen and J. G. Chang, *J. Chem. Phys.*, 2010, **132**, 214702.
- 40 M. Nolan, *J. Mater. Chem.*, 2011, **21**, 9160–9168.
- 41 A. D. Mayernick and M. J. Janik, *J. Phys. Chem. C*, 2008, **112**, 14955–14964.
- 42 M. Methfessel and A. T. Paxton, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1989, **40**, 3616–3621.
- 43 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Solid State*, 1976, **13**, 5188–5192.
- 44 A. Sundaresan, R. Bhargavi, N. Rangarajan, U. Siddesh and C. N. R. Rao, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **74**, 161306.
- 45 I. N. Leontyev, A. B. Kuriganova, N. G. Leontyev, L. Hennen, A. Rakhmatullin, N. V. Smirnova and V. Dmitriev, *RSC Adv.*, 2014, **4**, 35959–35965.
- 46 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272–1276.
- 47 K. Takise, A. Sato, K. Murakami, S. Ogo, J. G. Seo, K. I. Imagawa, S. Kado and Y. Sekine, *RSC Adv.*, 2019, **9**, 5918–5924.
- 48 M. Daturi, C. Binet, J. C. Lavalley and G. Blanchard, *Surf. Interface Anal.*, 2000, **30**, 273–277.
- 49 L. Fan, J. Zhang, K. Ma, Y. Zhang, Y. M. Hu, L. Kong, A. ping Jia, Z. Zhang, W. Huang and J. Q. Lu, *J. Catal.*, 2021, **397**, 116–127.



- 50 L. Atzori, M. G. Cutrufello, D. Meloni, B. Onida, D. Gazzoli, A. Ardu, R. Monaci, M. F. Sini and E. Rombi, *Front. Chem. Sci. Eng.*, 2021, **15**, 251–268.
- 51 Z. Wu, A. K. P. Mann, M. Li and S. H. Overbury, *J. Phys. Chem. C*, 2015, **119**, 7340–7350.
- 52 Z. Wu, M. Li and S. H. Overbury, *J. Catal.*, 2012, **285**, 61–73.
- 53 T. Shido and Y. Iwasawa, *J. Catal.*, 1993, **141**, 71–81.
- 54 S. Y. Zhao, S. P. Wang, Y. J. Zhao and X. Bin Ma, *Chin. Chem. Lett.*, 2017, **28**, 65–69.
- 55 Z. Wu, M. Li and S. H. Overbury, *J. Catal.*, 2012, **285**, 61–73.
- 56 K. Yoshikawa, H. Sato, M. Kaneeda and J. N. Kondo, *J. CO₂ Util.*, 2014, **8**, 34–38.
- 57 Y. Wang, Z. Liu, M. P. Confer, J. Li and R. Wang, *Mol. Catal.*, 2021, **509**, 111629.
- 58 O. Pozdnyakova, D. Teschner, A. Wootsch, J. Kröhnert, B. Steinhauer, H. Sauer, L. Toth, F. C. Jentoft, A. Knop-Gericke, Z. Paál and R. Schlögl, *J. Catal.*, 2006, **237**, 1–16.
- 59 P. A. U. Aldana, F. Ocampo, K. Kobl, B. Louis, F. Thibault-Starzyk, M. Daturi, P. Bazin, S. Thomas and A. C. Roger, *Catal. Today*, 2013, **215**, 201–207.
- 60 P. Bea, A. L. Camera, A. Hornes and A. Martinez-Arias, *J. Phys. Chem. C*, 2009, **113**, 10689–10695.
- 61 S. M. Lee, Y. H. Lee, D. H. Moon, J. Y. Ahn, D. D. Nguyen, S. W. Chang and S. S. Kim, *Ind. Eng. Chem. Res.*, 2019, **58**, 8656–8662.
- 62 F. C. Meunier, D. Tibiletti, A. Goguet, D. Reid and R. Burch, *Appl. Catal., A*, 2005, **289**, 104–112.
- 63 G. Busca and V. Lorenzelli, *Mater. Chem.*, 1982, **7**, 89–126.
- 64 S. Hilaire, X. Wang, T. Luo, R. J. Gorte and J. Wagner, *Appl. Catal., A*, 2004, **258**, 271–276.
- 65 T. Tabakova, F. Boccuzzi, M. Manzoli and D. Andreeva, *Appl. Catal., A*, 2003, **252**, 385–397.
- 66 C. Li, Y. Sakata, T. Arai, K. Domen, K. I. Maruya and T. Onishi, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 1451–1461.
- 67 L. Chen, S. Wang, J. Zhou, Y. Shen, Y. Zhao and X. Ma, *RSC Adv.*, 2014, **4**, 30968–30975.
- 68 M. Wang, M. Shen, X. Jin, J. Tian, Y. Shao, L. Zhang, Y. Li and J. Shi, *Chem. Eng. J.*, 2022, **427**, 130987.
- 69 Q. Pan, J. Peng, S. Wang and S. Wang, *Catal. Sci. Technol.*, 2014, **4**, 502–509.
- 70 G. Finos, S. Collins, G. Blanco, E. Del Rio, J. M. Cies, S. Bernal and A. Bonivardi, *Catal. Today*, 2012, **180**, 9–18.
- 71 C. Li, Y. Sakata, T. Arai, K. Domen, K. I. Maruya and T. Onishi, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 929–943.
- 72 A. Yee, S. J. Morrison and H. Idriss, *J. Catal.*, 1999, **186**, 279–295.
- 73 C. Binet, M. Daturi and J. C. Lavalley, *Catal. Today*, 1999, **50**, 207–225.
- 74 G. Ramis, G. Busca and V. Lorenzelli, *Mater. Chem. Phys.*, 1991, **29**, 425–435.
- 75 T. Yabe, K. Yamada, K. Murakami, K. Toko, K. Ito, T. Higo, S. Ogo and Y. Sekine, *ACS Sustainable Chem. Eng.*, 2019, **7**, 5690–5697.
- 76 B. Liu, C. Li, G. Zhang, X. Yao, S. S. C. Chuang and Z. Li, *ACS Catal.*, 2018, **8**, 10446–10456.
- 77 Z. Ma, P. Li, L. Ye, Y. Zhou, F. Su, C. Ding, H. Xie, Y. Bai and P. K. Wong, *J. Mater. Chem. A*, 2017, **5**, 24995–25004.
- 78 K. Kousi, D. Neagu, L. Bekris, E. I. Papaioannou and I. S. Metcalfe, *Angew. Chem.*, 2020, **132**, 2531–2540.
- 79 K. Sutthiumporn, T. Maneerung, Y. Kathiraser and S. Kawi, *Int. J. Hydrogen Energy*, 2012, **37**, 11195–11207.
- 80 L. Óvári, S. Krick Calderon, Y. Lykhach, J. Libuda, A. Erdohegyi, C. Papp, J. Kiss and H. P. Steinrück, *J. Catal.*, 2013, **307**, 132–139.
- 81 Y. Yu, B. Mao, A. Geller, R. Chang, K. Gaskell, Z. Liu and B. W. Eichhorn, *Phys. Chem. Chem. Phys.*, 2014, **16**, 11633–11639.
- 82 F. Chen, D. Liu, J. Zhang, P. Hu, X. Q. Gong and G. Lu, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16573–16580.
- 83 A. Sato, S. Ogo, Y. Takeno, K. Takise, J. G. Seo and Y. Sekine, *ACS Omega*, 2019, **4**, 10438–10443.
- 84 Y. Omori, A. Shigemoto, K. Sugihara, T. Higo, T. Uenishi and Y. Sekine, *Catal. Sci. Technol.*, 2021, **11**, 4008–4011.
- 85 K. Sugiura, S. Ogo, K. Iwasaki, T. Yabe and Y. Sekine, *Sci. Rep.*, 2016, **6**, 25154.
- 86 S. Das, A. Jangam, S. Jayaprakash, S. Xi, K. Hidajat, K. Tomishige and S. Kawi, *Appl. Catal., B*, 2021, **290**, 119998.
- 87 J. H. Bitter, K. Seshan and J. A. Lercher, *Top. Catal.*, 2000, **10**, 295–305.
- 88 K. Otsuka, Y. Wang, E. Sunada and I. Yamanaka, *J. Catal.*, 1998, **175**, 152–160.
- 89 J. Wei and E. Iglesia, *J. Phys. Chem. B*, 2004, **108**, 4094–4103.
- 90 A. P. Ferreira, I. Rodriguez-Ramos, J. A. Anderson and A. Guerrero-Ruiz, *Appl. Catal., A*, 2000, **202**, 183–196.

