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CO₂ methanation by Ru-doped ceria: the role of the oxidation state of the surface

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Abstract

Ru₀.₀₅Ce₀.₉₅Oₓ is an active catalyst for methanation of CO₂ with H₂. Under reaction conditions one expects that oxygen vacancies are present on the oxide catalyst surface and that their steady-state concentration depends upon the relative ratio of the oxidant (CO₂) to the reductant (H₂). We show that the activity of the catalyst is sensitive to the degree of surface reduction: a surface that is too reduced or too oxidized loses activity. Exposing the oxidized surface to CO₂ and then to H₂ produces no methane, while on a reduced surface methane is produced by exposure to CO₂ followed by H₂. If the reaction is carried out at steady state, purged, and then exposed to only hydrogen, methane is produced. Methane is formed through the reaction of hydrogen with surface species whose infrared spectrum is associated with a variety of surface carbonates and not through a CO or formate intermediate.

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INTRODUCTION

The methanation reaction of CO₂

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta G_{298K} = \tilde{\eta} 55.8 \text{ kJ mol}^{-1} \]

has been subject of much interest in recent years.\(^1\)\(^{-29}\) Older work has been examined in several reviews.\(^{30,31}\) Previously, we examined and discussed ceria doped with several cations and reported that Ru-doped ceria (Ru\(_{0.05}\)Ce\(_{0.95}\)O\(_{2-\delta}\), where \(\delta\) depends on the degree of reduction) is active and selective for CO₂ methanation. Doped oxides, such as Ru\(_{0.05}\)Ce\(_{0.95}\)O\(_{2-\delta}\), are assumed to be single-phase catalysts\(^{32,33}\) in which some of the cations have been replaced by other cations (e.g. Ru replaces some of the Ce atoms in the lattice of CeO₂).

When the methanation reaction is performed, the oxide catalyst is exposed to a reductant (H\(_2\)) and an oxidant (CO₂). When the reaction is run at steady state the surface will have a steady state concentration of oxygen vacancies. Here we show that the concentration of these vacancies is an important factor in the activity of the catalyst.

In addition, DFT calculations have shown that in many oxides there is a strong interaction between Lewis bases and Lewis acids.\(^{36}\) When an oxygen vacancy is created, two unpaired electrons are left behind, which makes the reduced oxide a very strong Lewis base. The more vacancies created, the stronger the Lewis acidity of the surface. Conceptually, it is possible that an increase in basicity (which is an increase in the ability of the surface to donate electrons \(\tilde{\eta}\) in this case to CO₂) will increase the reactivity of this compound. It is also possible for the surface to be too basic to allow the formation of a hydrogenated product from a carbonate.

Two mechanisms have been proposed for the methanation reaction catalyzed by metals. One assumes that CO₂ is converted to CO which is then converted to methane.\(^{37-41}\) The other mechanism suggests that CO₂ is methanated directly without the formation of a CO intermediate.\(^{42-45}\) The direct hydrogenation of CO₂ on Ni(110) has been supported using density functional theory calculations and ultra high vacuum techniques\(^{46}\) as well as experimentally\(^{47}\) whereby CO₂ forms a formate when adsorbed H approaches and prevents the formation of CO. Previously, we proposed that the direct hydrogenation of a carbonate made from an oxide and CO₂ using a metal that dissociated hydrogen provides an alternate pathway that minimizes the
CO byproduct from CO desorption.\textsuperscript{32} The mechanism is dependent on both the metal and support used. We propose here that CO\textsubscript{2} forms carbonates and these react with hydrogen to produce methane on a single-phase reducible bi-metallic oxide. The rate-limiting step is carbonate formation. A mechanism that proceeds through a CO intermediate is unlikely for Ru\textsubscript{0.05}Ce\textsubscript{0.95}O\textsubscript{2-\textdelta} because exposure of the catalyst to CO + H\textsubscript{2} reduces it and renders it inactive.

**EXPERIMENTAL**

**Catalyst preparation**

Ruthenium-doped ceria was prepared by a combustion method described in previous work.\textsuperscript{33} The XPS and XRD measurements were consistent with Ru atoms substituting the cations in the host oxide but do not prove that the dopants are in the surface layer or near the surface. We assume that this is the case because the catalytic chemistry of ceria doped with Ru is very different from that of ceria.

In this paper, we preconditioned the Ru\textsubscript{0.05}Ce\textsubscript{0.95}O\textsubscript{2-\textdelta} in three different ways: a "steady-state catalyst" (SSC), a strongly reduced catalyst (SRC), and an oxidized catalyst (OC).

The oxidized catalyst (OC) is preconditioned by exposing the as-prepared catalyst to a flow of 5:1 argon:oxygen for 60 minutes at 450 °C, then rapidly cooled to the reaction temperature while purging. The as-prepared catalyst is described in our previous work, but contains adsorbed water and other molecules when exposed to atmospheric air.

The steady-state catalyst (SSC) is preconditioned by exposing the OC to a mixture of CO\textsubscript{2}, H\textsubscript{2}, and Ar, at 350 °C for one hour at a total flow rate of 10 SCCM, the feed composition Ar:H\textsubscript{2}:CO\textsubscript{2} = 6.5:4:1. The methanation reaction reaches steady state under these conditions.

The strongly reduced catalyst (SRC) is preconditioned by exposing the OC to a flow of 30% CH\textsubscript{4} in argon, for 2.5 hours, at 550 °C. We emphasize that the surfaces of both SSC and SRC are reduced, meaning that they both have oxygen vacancies, but the reduction of SRC is much stronger.
Reactors

Two reactors were used: a packed bed and a commercial reaction cell (The Praying Mantis with high temperature reaction chamber (HVC), Harrick Scientific Corporation) with windows for Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Reactivity data were collected using the packed-bed reactor, and DRIFTS data were collected using a separate DRIFTS reactor (unless otherwise noted).

The packed bed was supported with inert quartz wool in a 0.4-cm diameter quartz tube. 25 mg of catalyst was used with a total flow rate of 10 standard cubic centimeters per minute (SCCM). The feed composition was 6.5:4:1 Ar:H₂:CO₂, unless otherwise noted. The temperature was controlled by a temperature controller (Omega CSC32) using a steel reactor block with heating cartridges that surrounded the reactor tube and pre-heated the gases. A thermocouple in the heating block controlled the temperature and the difference between steady state bed temperature and block temperature was less than 5 °C at all relevant temperatures. This was determined by measurement in an inert bed. All experiments were carried out at atmospheric pressure.

DRIFTS was performed using an FTIR spectrometer (Thermo Electron Corporation Nicolet 4700) coupled to the reaction cell. The reactor unit incorporates two 6X, 90° off-axis ellipsoid mirrors that are arranged to discriminate against specularly reflected radiation. Total flow rate and feed composition in the DRIFTS reactor were the same as in the packed-bed reactor. 256 scans of resolution 4 were taken for all sample and background measurements.

Both reactors used mass flow controllers (MKS) for the reactant and carrier gas (argon) flow, and a mass spectrometer (SRS RGA 200) to analyze the product gases. A small stream of product gas was sent to the mass spectrometer, and mass numbers 44, 40, 28, 18, 15, 4, 3, and 2 were assigned to carbon dioxide, argon, carbon monoxide, water, methane, deuterium, HD, and hydrogen, respectively, with appropriate subtractions for overlapping mass numbers. Argon was used as an inert gas and all pressures are normalized to the known argon flow.

Experimental techniques

In the present paper we use, unless otherwise stated, a total flow rate of 10 SCCM, the
feed composition \( \text{Ar}:\text{H}_2:\text{CO}_2 = 6.5:4:1 \), and a temperature of 350 °C.

To calculate the rate as a function of reactant partial pressures, a given ratio was run for one hour with a flow rate of 10 SCCM and 0.5 mg of catalyst so that the CO\(_2\) conversion was below 5%. Five replicates were performed, varying the ratios randomly. The dependence of the methanation rate on the partial pressure of one reactant was determined by changing the partial pressure of the other reactant while keeping the partial pressure of CO\(_2\) and the total pressure and flow rate constant. To do this, we decreased the partial pressure of Ar when we increased that of the second reactant, so that the sum of these two pressures was constant.

For the isotope experiments, deuterium was simply replaced with hydrogen as a feed gas for the entire reaction. The gases were all from Praxair, purity 5.0, with the exception of deuterium, which was 99.7% pure.

When pulses of hydrogen or carbon dioxide were introduced into the system, a Swagelok fitting with a Thermogreen septum was fitted immediately upstream of one of the reactors. One milliliter of gas was injected into the stream using a syringe. The procedure was standardized using an inert bed so that each pulse was reproducible.

When pulses of formic acid were used, a vessel with argon and liquid formic acid were prepared and heated to 50 °C for a suitable vapor pressure. This vapor with formic acid and argon were then injected directly upstream of the catalyst bed using a warm syringe into a stream of argon flowing at 10 SCCM.

**RESULTS AND DISCUSSION**

**Three states of the \( \text{Ru}_{0.05}\text{Ce}_{0.95}\text{O}_2 \) catalyst**

In the methanation reaction, the catalyst is exposed to \( \text{H}_2 \), which is a reductant, and to CO\(_2\), which is a mild oxidant. As the gases pass through the reactor, the amount of \( \text{H}_2 \) and CO\(_2\) in the gas is diminished and \( \text{CH}_4 \) and \( \text{H}_2\text{O} \) are formed. \( \text{CH}_4 \) is a reductant and water is able to oxidize the reduced oxide. Therefore, all sections of the reactor are exposed simultaneously to a reducing agent and an oxidizing agent. The reductant creates oxygen vacancies and the oxygen annihilates them. At steady state the surface of the catalyst will have some oxygen vacancies;
we know this because a mass balance shows more oxygen leaving the reactor than entering. Vacancy concentration depends on the competition between reduction and oxidation.

Previous work\textsuperscript{33} suggested that the Ru\textsubscript{0.05}Ce\textsubscript{0.95}O\textsubscript{2-δ} catalyst surface is reduced (i.e. it has oxygen vacancies) when the methanation reaction is run under steady-state conditions at 350 °C and a 4:1 H\textsubscript{2}/CO\textsubscript{2} feed composition. Here we investigate further how the presence of oxygen vacancies on the surface of the catalysts affects its activity for CO\textsubscript{2} methanation. To do this we preconditioned the Ru\textsubscript{0.05}Ce\textsubscript{0.95}O\textsubscript{2-δ} in such a way that the catalyst was studied three different states: a “steady-state catalyst” (SSC), a strongly reduced catalyst (SRC), and an oxidized catalyst (OC) as described in the experimental section.

**The mechanism of steady-state methanation reaction on SSC**

At steady state, under the conditions specified above, CO\textsubscript{2} conversion is 40% and the selectivity to methane is 99%.\textsuperscript{33} This subsection describes the chemical and spectroscopic properties of the catalyst’s surface, formed under steady state reaction conditions, by transient chemical experiments and by in situ IR spectroscopy.

The transient behavior of the catalyst was observed using pulse experiments. The surface of the SSC contains carbon-containing compounds that stay on the surface after the reactants are purged. Their reactivity is observed by first preparing the SSC as described in the experimental section. After that, we turned off the flow of the CO\textsubscript{2} and H\textsubscript{2} mixture, then purged the reactor with Ar until there was no CO\textsubscript{2}, CH\textsubscript{4}, or H\textsubscript{2} in the effluent. Throughout these procedures, the temperature was maintained at 350 °C. After purging was completed, we sent seven H\textsubscript{2} pulses through the reactor. Fig. 1 shows that the SSC catalyst produces methane, when exposed to the hydrogen pulses, even in the absence of CO\textsubscript{2} in the gas. Evidently, when H\textsubscript{2} and CO\textsubscript{2} react at steady state, they generate carbon-containing compounds on the surface of the SSC, and these react with hydrogen. There is no methane production when an eighth H\textsubscript{2} pulse goes through the reactor.

After the catalyst is exposed to the seven H\textsubscript{2} pulses, we pass through the reactor CO\textsubscript{2} pulses and find that they produce CO and no methane. The same is true if the reaction is run at steady state, purged, and then only CO\textsubscript{2} is added. This indicates two things. (1) Exposure to the
H₂ pulses did not create surface hydrogen species that react with CO₂ to form methane. (2) After exposure to the hydrogen pulses, the surface is reduced and CO₂ oxidizes it and produces CO.

Finally, after exposure to the CO₂ pulses, we sent H₂ pulses through the reactor and found that methane is produced again. This indicates that the exposure to CO₂ has reoxidized the surface (since CO was formed) and created carbonaceous species that react with H₂ to make methane.

In the hope of gaining some insight into the mechanism of the hydrogenation reaction, we performed CO₂ methanation with D₂ instead of H₂. A clear isotope effect was observed (Fig. 2). The rate of methane production was measured in a differential reactor as described in the experimental section. Methanation with deuterium is faster than methanation with hydrogen, at all temperatures between 200 °C to 350 °C (Fig. 2 insert). Such a "negative isotope effect" has been observed before on metallic catalysts for carbon oxide hydrogenation. Since at least ten elementary reaction steps are needed for methane and water formation and eight of them involve hydrogen, we did not attempt a detailed analysis of these observations.

To determine whether the rate determining step involved hydrogen and/or carbon dioxide, the dependence of the methanation rate on the partial pressure of hydrogen was determined. A similar experiment was performed to find the rate dependence on the partial pressure of CO₂ (at constant H₂ partial pressure, and constant total pressure). The results are shown in Fig. 3. For the conditions used here, the methanation rate changes with the partial pressure of CO₂ but not with the partial pressure of H₂. Of course the methanation rate would go to zero if the partial pressure of hydrogen goes to zero, but over the pressure range we report, the rate was independent of hydrogen pressure. The independence of the rate on the pressure of hydrogen, seen under the conditions used here, indicates that hydrogen adsorption is very rapid and changing it (by changing the hydrogen pressure) has no effect on the rate of methane formation. This is not the case for CO₂ adsorption. These observations suggest that the methanation rate is controlled by the formation of the carbon containing intermediates that are subsequently hydrogenated.

To further understand the chemistry of H₂, we studied how the SSC catalyst performs the exchange reaction H₂ + D₂ → 2 HD. Fig. 4 shows the results of temperature-programmed isotope-exchange reaction (TPR) performed on the SRC catalyst. The TPR results for the other
versions of the Ru\textsubscript{0.05}Ce\textsubscript{0.95}O\textsubscript{2-δ} catalyst (i.e. strongly reduced or oxidized) look the similar, however there are differences in the light-off temperature and the temperature at which the TPR curves level off. The magnitudes of these temperatures are given in Table 1. We see that SSC catalyzes the exchange reaction at low temperature. The exchange starts below 25 °C (which is the lowest temperature to which the reactor can be cooled), while the oxidized, undoped ceria (made by the same combustion method as was Ru\textsubscript{0.05}Ce\textsubscript{0.95}O\textsubscript{2-δ} and exposed to oxygen for one hour at 450 °C) starts performing the exchange reaction at 325 °C. There is a substantial difference between oxidized CeO\textsubscript{2} (which we take to be CeO\textsubscript{2} with very few oxygen vacancies) and Ru-doped ceria. Doping with Ru changes substantially how ceria affects the exchange reaction. It is customary to assume that the rate of H-D exchange is limited by the dissociation of H\textsubscript{2}. This implies that SSC dissociates H\textsubscript{2} readily. Note, however, that oxidized Ru\textsubscript{0.05}Ce\textsubscript{0.95}O\textsubscript{2-δ} behaves, for the exchange reaction, like the steady-state Ru\textsubscript{0.05}Ce\textsubscript{0.95}O\textsubscript{2-δ} and also like metallic Ru. However, these three catalysts have different performance for methanation. This indicates that these differences do not come from the ability to adsorb and dissociate hydrogen.

**IR detection of surface carbonates**

The IR spectrum in the wave-number range 1700-1200 cm\textsuperscript{-1} is a wide band, and many attempts have been made to deconstruct the spectrum into a sum of various peaks, which were assigned to a variety of carbonate-like species.\textsuperscript{49-51} These assignments were made for undoped ceria and it is not clear that they are applicable to ruthenium-doped ceria. Because of this they are not used with great precision here. Instead, we generally ascribe the carbon containing surface species that absorb between 1700-1200 cm\textsuperscript{-1} as carbonates with multiple structures.

We used DRIFTS measurements to identify the species present on the surface during steady-state methanation of CO\textsubscript{2}. In Fig. 5 we show the IR absorption spectra of the system after it reached the steady state for the methanation reaction with H\textsubscript{2} or with D\textsubscript{2}. There is a shift observed in some of the features in the spectrum when D\textsubscript{2} is used as a methanation reactant compared to H\textsubscript{2}. This indicates that there must be a hydrogen containing species absorbing in the region, possibly bicarbonates.

The evolution of the IR absorption spectra after stoichiometric carbon dioxide and
methane are added is shown in Fig. 6. These data were taken as follows: the OC was prepared and the reactor was completely purged at 350 °C in argon, and IR spectra were taken at 1, 5, 10, 20, and 50 minutes after a mixture of CO₂ and H₂ was introduced in the reactor. When the feed is switched to CO₂ + H₂, it takes 2 minutes for CH₄ production to reach steady state. The carbonate build up is very rapid initially and the spectrum is almost complete after 1 minute. However, additional carbonates are slowly formed (as seen by the increased IR absorption) and it takes 50 minutes, after the reaction has reached steady state, for the IR spectrum to stop changing. We conclude that the additional carbonates, produced after the first minute do not affect the methanation reaction: they are spectators rather than reaction intermediates.

Fig. 7 shows the IR spectra taken as follows: we ran the reaction of CO₂ and H₂ at 350 °C for one hour and then we shut off the supply of CO₂ and H₂, then injected eight H₂ pulses, followed by a steady stream of hydrogen gas in argon. The system produces methane when the first seven pulses pass through the reactor, after which methane production stops. The further introduction of a steady stream of hydrogen does no produce any more methane, however the intensity of the carbonate spectrum continues to decrease during this time as indicated by the dotted lines in Fig. 7. If all carbonates on the surface reacted with H₂ to make methane there should be no IR absorption at the frequencies assigned to carbonates. However, the IR spectrum shows that at the time when pulsing H₂ through the system makes no methane, there is a substantial amount of carbonate left on the surface. This experiment shows that most surface carbonates are spectators and that the methane is formed by the reaction of H₂ with a minority carbonate species.

It is also interesting to note that upon introduction of H₂ to the SSC, the intensity of the carbonate peaks between 1600 cm⁻¹ and 1300 cm⁻¹ decreases uniformly. The peaks below 1300 cm⁻¹ behave in the opposite manner: they absorb more light as the hydrogen reacts with the surface. We do not have a reliable explanation for this; a possibility is that some carbonates are converted to bicarbonates.

When the reaction is run at steady-state and then purged, the concentration of carbonaceous surface intermediates must be equal to or greater than the amount of methane subsequently produced by hydrogen pulses. Using the data from the experiment in Fig. 1, the amount of methane produced from seven hydrogen pulses is 1.9×10⁶ mol. This corresponds to
5.7×10^{16} moles of carbonaceous surface intermediates per square meter of catalyst if the intermediates are not stacked. This would be equivalent to a cross-section of 0.29 nm² per molecule. This high carbonate surface density may be due to more than one adsorption layer and suggests that the late-forming "spectator" carbonates (above) can be mobilized into the reaction pathway.

Discussions of CO₂ methanation on other catalytic systems often invoke a mechanism that has a formate intermediate. To test whether such an intermediate is present on our catalyst, we exposed the oxidized catalyst (OC) to formic acid, at 25 °C. When the surface is heated, the compound formed by formic acid adsorption decomposes, at 150 °C, into CO₂ and water (observed downstream in the mass spectrometer). This suggests that a formate would not be stable at the methanation temperature. If we pass formic acid through the reactor at 350 °C, the formic acid decomposes into CO₂ and water, and the IR spectrum shows the presence of carbonates but not of a formate. We assume that the carbonate is formed by the CO₂ produced by the decomposition of the formic acid. Running formic acid and hydrogen through the SSC bed, at 350 °C, produces methane. We assume, given the fact that the formic acid decomposes at 150 °C, that the methane is formed by the reaction of H₂ with the CO₂ produced by formic acid decomposition.

The IR spectrum of the compound formed by exposing the oxidized catalyst (OC) to formic acid at 115 °C (before decomposition) is shown in Fig. 8 together with the IR spectrum of the catalyst during steady-state methanation reaction. The compound formed by exposing the oxidized catalyst to formic acid has peaks at 1544, 1369, 1355, and 1292 cm⁻¹. When heated to desorb the carbonates, no formate peaks were observed, and the initial surface species were not characteristic of formate. When the spectra before and after addition of hydrogen to the surface species to make methane are subtracted, the result did contain absorbance peaks at the values we observed for formate. While the IR spectra do not rule out the presence of the formate, the fact that the formate decomposes at temperatures much lower than the steady-state methanation temperature suggests to us that the formate is not likely to be a methanation intermediate.
**The chemistry of the oxidized catalyst (OC)**

The oxidized catalyst exposed to a mixture of H$_2$ and CO$_2$ produces very little methane initially, at 350 °C. However, in time the hydrogen reduces the surface and the performance of the system drifts towards that of the steady-state catalyst. This is of course expected. The OC surface does not adsorb CO$_2$ at 350 °C and no carbonates are formed by exposure to CO$_2$. This was verified by pulsing carbon dioxide onto the OC - the IR spectrum showed no carbonates.

However, if the OC is exposed to CO (to reduce it), carbonates appear. We think that this takes place in two stages. Initially CO reduces the surface to form CO$_2$ and oxygen vacancies. Once oxygen vacancies are present, the CO$_2$ produced by the oxidation of CO is able to form carbonates. The IR spectrum of these carbonates is very similar to that observed when the methanation is carried out at steady state. The main conclusion drawn from these experiments is that the fully oxidized Ru$_{0.05}$Ce$_{0.95}$O$_{2.0}$ surface does not act as a methanation catalyst unless the surface is sufficiently reduced.

**The chemistry of the SRC surface**

We have shown that the surface of Ru$_{0.05}$Ce$_{0.95}$O$_2$ is reduced when the methanation reaction is performed at steady state and that if it is not reduced it is not active i.e. the OC is not active. Next we show that the degree of reduction matters: if the catalyst is too reduced (i.e. it has too many oxygen vacancies), its performance is poor.

Table 2 shows the performance of the Ru$_{0.05}$Ce$_{0.95}$O$_{2-d}$ having different degrees of reduction. When a mixture of H$_2$ and CO$_2$ is run through the reactor with a SRC catalyst, CO$_2$ is converted to CO, and hydrogen is converted to water, and the methane yield is 3% (Table 2). If SRC is exposed to a flow of 10% CO$_2$ in argon, at 350 °C for one hour, CO is produced and the surface is partially reoxidized. The catalyst obtained in this way was used for methanation, and the methane yield was 10% (Table 2). SRC exposed to 10% CO$_2$ in argon, at 550 °C for one hour (Table 2), has a methane yield of 30%; this is better than SRC but not as good as SSC. These experiments show that over-reducing the Ru-doped oxide diminishes its catalytic activity severely, but the reduced catalyst can be reactivated by oxidation with CO$_2$. However, if we run through the SRC bed a mixture of CO$_2$:H$_2$=1:4, at 350 °C for one hour, only very small amounts
of methane are produced. This indicates that in the presence of H₂, carbon dioxide is very slow to reoxidize the surface. This is not surprising since H₂ acts as a reductant.

The variation of methane yield with degree of reduction might be related to a change in structure of surface intermediates. To investigate this we have taken a DRIFTS spectrum of SRC exposed to CO₂ + H₂. This is shown as a red dotted line in Fig. 9. The double peak at ~2100 cm⁻¹ is typical of gas-phase CO and consistent the fact that the reduced catalyst converts CO₂ to CO. If the reactor purged, this double peak decreases with the same rate as the other gas-phase peaks due to methane. As discussed above, this double peak is not present on the SSC. For these reasons, we conclude that these peaks are mainly gas-phase CO. The carbonate band is visible and the spectrum has peaks at 1523 cm⁻¹, 1373 cm⁻¹, and 1267 cm⁻¹. In all spectra shown in Fig. 9, we have subtracted the spectrum of SRC that has not been exposed to CO₂.

Next we oxidized partially the SRC by exposing it to CO₂, for 30 minutes, at 350 °C. This limited exposure to CO₂ does not oxidize the catalyst to completely recover its activity towards CO₂ methanation (see Table 2). After having exposed SRC to CO₂ (as described above), we ran CO₂ + H₂ through the reactor, at 350 °C, and took the spectrum shown in the middle of Fig. 9. The intensity of the carbonate band is increased and its peaks are shifted to 1485 cm⁻¹, 1373 cm⁻¹, and 1018 cm⁻¹. Therefore this partially reoxidized surface, which is more active for methanation than SRC (see Table 2), makes different carbonates on its surface.

In a third experiment we exposed SRC to CO₂ (10% CO₂ and 90% Ar), at 350 °C for one hour. After that we introduced CO₂ and H₂ into the reactor, at 350 °C, and took the IR spectrum shown in the top of Fig. 9. The catalyst oxidized with CO₂ for one hour is practically as active as SSC. The absorption band of the carbonates on this surface is the most intense and its peaks are shifted again (as compared to the other two spectra). The peaks are at 1454 cm⁻¹, 1467 cm⁻¹, 1126 cm⁻¹, and 1009 cm⁻¹.

Although it is difficult to assign these peaks to specific structures on the surface, it is clear that different carbonates are present on the surface depending on the degree of reduction of the surface. This suggests that the carbonates present in the bottom spectrum cannot be hydrogenated to methane, those in the middle spectrum are hydrogenated slowly, and those in the top spectrum are more readily hydrogenated (see Table 2 and Fig. 9).
The hydroxyl peaks in the 3600-3700 cm$^{-1}$ region indicate that running the methanation reaction of the SRC produces fewer hydroxyls than on the more oxidized surfaces. In particular, in the top spectrum in Fig. 9, the hydroxyl band is much larger and it extends to lower wave number than in the other two spectra. This is natural since there is less oxygen on the reduced surface and the oxygen that is present is likely to make strong bonds with the reduced oxide and be less reactive towards hydrogen. Although the hydroxyls are present, they do not react with CO$_2$ (according to the experiments described above, in which turning off the H$_2$ flow during methanation reaction stops the production of methane).

In summary, too much reduction of the Ru$_{0.05}$Ce$_{0.95}$O$_{2-\delta}$ catalyst diminishes its activity. It is likely that this happens because on this system CO$_2$ forms different, less reactive carbonates. The reduced catalyst is also less active for H$_2$/D$_2$ exchange but this is not likely to limit its methanation activity because the exchange does occur at 75 °C (see Table 1).

CONCLUSION

We have investigated methanation on the same combustion-synthesized Ru-doped ceria catalyst preconditioned in three distinct ways. One (OC) was exposed to oxygen for a long time before being used as a catalyst. Another (SSC) was exposed to H$_2$ and CO$_2$ until the methanation reaction reached the steady state. A third (SRC) was prepared by exposure to methane, at 550 °C for 2.5 hours. We performed serial pulse experiments using H$_2$, CO$_2$, and CO and found that OC is inactive when exposed to H$_2$ and CO$_2$ until it is reduced (by H$_2$ or CO); the surface is continually reduced until the surface reaches the proper state of reduction, at which point the methanation reaction reaches a steady state where only methane and water are produced. This means that OC exposed to H$_2$ and CO$_2$ evolves to become SSC. The OC surface reacts readily with H$_2$ and CO and catalyzes the H$_2$/D$_2$ exchange reaction at temperatures below 25 °C. This is a reactive surface but it is not a good methanation catalyst until the surface if properly reduced.

The SRC catalyst does not methanate a mixture of CO$_2$ and H$_2$. It is also less active in catalyzing the H$_2$/D$_2$ exchange. Prolonged exposure of SRC to CO$_2$ will oxidize the surface until it is as good a methanation catalyst as SSC. However, exposure to H$_2$ and CO$_2$ does not oxidize the surface to an active methanation state; CO$_2$ alone can reoxidize SRC but not when H$_2$ is present. When SRC is exposed to CO$_2$ and H$_2$, carbonates are formed on the surface but they are
not active towards methanation. The IR spectra of these carbonates differ from that of the carbonates formed when the reaction is run at steady-state conditions (reached when starting from the oxidized catalyst).

The SSC catalyst has a partially reduced Ru$_{0.05}$Ce$_{0.95}$O$_{2-\delta}$ surface and the degree of reduction is important for determining performance. We observed a similar situation for the dry reforming of methane of the same catalyst. If the reaction is carried out at steady state, then purged, and then exposed to only hydrogen, methane is produced. Methane is not produced if the surface is first exposed to only $\text{H}_2$, and then to only $\text{CO}_2$. We conclude that methane is formed by the reaction of hydrogen with a carbon-containing intermediate formed by the adsorption of $\text{CO}_2$. IR spectroscopy, when the reaction is run at steady state, shows a band in a wave-vector region previously attributed to carbonates. We found that most of these carbonates are not intermediates in the methanation reaction. Spectra taken at various times after the methanation reaction was initiated show that methane production reaches steady state in less than a minute and most (but not all) carbonate spectrum is established in the first minute. However, a slight build-up of carbonates continues long after methane production reaches steady state. If the reaction is run at steady state and then the $\text{CO}_2$ supply is turned off and IR spectra are taken, we find that the hydrogen continues to produce methane for a while, and the intensity of the carbonate band changes: for most wave lengths the absorption decreases but for some wave lengths (corresponding perhaps to bicarbonates) it increases. A strong absorption in the carbonate region is present even after prolong exposure to hydrogen no longer produces methane. These combined experiments suggest that a carbonate is a reaction intermediate, but most surface carbonates are not involved in methane production. The methanation rate depends on $\text{CO}_2$ partial pressure and is independent of the partial pressure of $\text{H}_2$. The lack of $\text{H}_2$-pressure dependence, together with the low temperature at which the $\text{D}_2$-$\text{H}_2$ exchange takes place, indicates that the rate of supplying hydrogen is not a limiting step.

It is possible that an increase in basicity (which is an increase in the ability of the surface to donate electrons) may have something to do with the fact that the catalyst is a reduced (but not too reduced) surface. In particular, it is possible that electron donation to $\text{CO}_2$ to make a negatively charged $\text{CO}_2$ will increase the reactivity of this compound.
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References


Table 1. Results from temperature programmed H$_2$-D$_2$ exchange reaction for various Ru$_{0.05}$Ce$_{0.95}$O$_{2-\delta}$ catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H$_2$-D$_2$ exchange light-off temperature (°C)</th>
<th>Temperature at which HD reaches gas-phase equilibrium (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidized Ru$<em>{0.05}$Ce$</em>{0.95}$O$_{2-\delta}$</td>
<td>&lt;25</td>
<td>45</td>
</tr>
<tr>
<td>Reduced Ru$<em>{0.05}$Ce$</em>{0.95}$O$_{2-\delta}$ (with CH$_4$)</td>
<td>75</td>
<td>125</td>
</tr>
<tr>
<td>Steady state Ru$<em>{0.05}$Ce$</em>{0.95}$O$_{2-\delta}$</td>
<td>&lt;25</td>
<td>45</td>
</tr>
<tr>
<td>Oxidized CeO$_2$</td>
<td>325</td>
<td>N/A</td>
</tr>
<tr>
<td>Ruthenium metal</td>
<td>&lt;25</td>
<td>43</td>
</tr>
</tbody>
</table>

Table 2. Methane yield for the CO$_2$ + H$_2$ reaction on the SSC and SRC as well as the yield on SRC exposed to CO$_2$ prior to running the methanation reaction.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Methane yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steady state CO$_2$ methanation</td>
<td>40%</td>
</tr>
<tr>
<td>SRC (after reduction treatment$^a$)</td>
<td>3%</td>
</tr>
<tr>
<td>SRC (after reduction treatment$^a$) + 60 minutes in 10% CO$_2$ at 350 °C</td>
<td>10%</td>
</tr>
<tr>
<td>SRC (after reduction treatment$^a$) + 60 minutes in 10% CO$_2$ at 550 °C</td>
<td>35%</td>
</tr>
</tbody>
</table>

$^a$30% CH$_4$ in argon at 550 °C for 2.5 hours
Figure 1. The composition of the effluent produced by the exposure of SSC to seven H\textsubscript{2} pulses, followed by exposure to three CO\textsubscript{2} pulses, followed in turn by exposure to five H\textsubscript{2} pulses, all at 350 °C. Prior to exposure to the pulses, the catalyst was exposed to CO\textsubscript{2} + H\textsubscript{2}, at 350 °C until the methanation reaction reached steady state and then it was purged with Ar until no other gases were detected in the effluent. The arrows indicate whether the ordinate scale for a graph is at the left or at the right.
Figure 2. Deuterium isotope effect during CO$_2$ methanation on SSC. The rate of CH$_4$ and CD$_4$ formation for two experiments, one with 4:1 moles CO$_2$:moles H$_2$, and the other with 4:1 moles CO$_2$:moles D$_2$. The rates were determined after waiting one hour to make sure that the steady state was established. The error bars represent 95% confidence interval using four replicates. The inset shows the CH$_4$/CD$_4$ ratio at different temperatures.
Figure 3. The methanation rate as a function of reactant partial pressures. The rates were determined after the reaction ran for one hour to reach steady state. The conversion of $\text{CO}_2$ was below 5%. Error bars represent one standard deviation of five replicates. Reactant ratio was varied randomly.
Figure 4. Temperature programmed H$_2$-D$_2$ exchange reaction on the SRC

Figure 5. DRIFTS of carbonate-like species taken while flowing H$_2$ and CO$_2$ or D$_2$ and CO$_2$ through the reactor at 350 °C.
Figure 6. DRIFTS of CO$_2$ methanation at 350 °C taken at different times after the introduction of H$_2$/CO$_2$ gas into the reactor. The solid line is the spectrum taken at 1 minute, and the spectra above the solid line were taken at 5, 20, and 50 minutes after H$_2$/CO$_2$ introduction. The amount of carbonate increases with time on stream. Background for all spectra was taken after 30 seconds of feed introduction.

Figure 7. Successive DRIFT spectra taken after each hydrogen pulse passed through the reactor containing SSC. Prior to H$_2$ introduction, the catalyst performed CO$_2$ methanation, at steady state, for 1 hour, at 350 °C.
Figure 8. DRIFT spectrum of oxidized Ru$_{0.05}$Ce$_{0.95}$O$_2$-$\delta$ in Ar at 110 °C after injection of formic acid in the reactor, compared to the DRIFT spectrum of the carbonaceous compounds on the SSC performing CO$_2$ methanation at 350 °C.

Figure 9. DRIFT spectra during CO$_2$ methanation at 350 °C of Ru$_{0.05}$Ce$_{0.95}$O$_2$-$\delta$ catalysts having different degree of reduction. Initially, the catalyst was reduced in CH$_4$ at 550 °C for 2.5 hours (to prepare SRC) and cooled to 350°C before H$_2$+CO$_2$ was introduced and a spectrum was taken (red dotted line). In the second experiment SRC was exposed to CO$_2$, at 350 °C for 30 minutes and then the catalyst was exposed to H$_2$+CO$_2$ and the spectrum was taken (middle of the graph). In a third experiment SRC was exposed to CO$_2$ at 550 °C, for 60 minutes and then H$_2$+CO$_2$ was introduced at 350 °C and the IR spectrum was taken (top of the graph). We subtracted from all three absorbance spectra the absorbance spectrum of SRC.