

## RESEARCH NOTE

Evidence for Oxidation of Ceria by CO<sub>2</sub>S. Sharma,\* S Hilaire,\* J. M. Vohs,\* R. J. Gorte,\*<sup>1</sup> and H.-W. Jen†

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The oxidation and reduction of Pd/ceria and Pd/zirconia catalysts were investigated using pulse-reactor studies in which products were monitored following step changes in the reactant composition. The results demonstrate that both ceria and zirconia can be partially reduced by CO and partially reoxidized by CO<sub>2</sub>. Steady-state rates for methane reforming by CO<sub>2</sub> were also measured on Pd/ceria, Pd/zirconia, and Pd/silica. The Pd/ceria catalyst was slightly more active than Pd/zirconia and ~10<sup>4</sup> times as active as Pd/silica. The high activities of Pd/ceria and Pd/zirconia are explained as resulting from oxidation and reduction of the supports.

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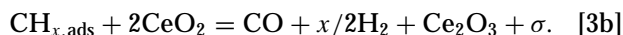
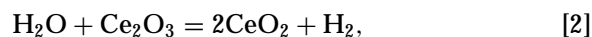
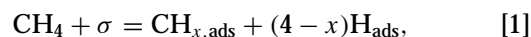
**Key Words:** oxygen storage capacity; ceria; zirconia; Pd; temperature-programmed desorption; CO oxidation; CO<sub>2</sub> reforming of methane.

## INTRODUCTION

Ceria plays a crucial role in three-way, emissions-control catalysts by providing oxygen storage capacity (OSC). OSC is important for controlling the oxygen stoichiometry in the exhaust since the simultaneous oxidation of CO and hydrocarbons and reduction of NO<sub>x</sub> can only be accomplished over a very narrow range of reactant compositions (1–6). It is generally agreed that reduction of ceria does not occur via release of oxygen directly to the gas phase but rather through reaction of a reductant (CO, H<sub>2</sub>, or a hydrocarbon) over a precious-metal catalyst in contact with the ceria (7, 8). It is not known whether this reduction process occurs at the metal–ceria interface or exclusively on the metal after it has been oxidized by ceria.

Two interesting observations have recently been added to this picture. First, the concept that oxygen from ceria can be used to oxidize species adsorbed on a metal which is supported on ceria has been used successfully to explain several reactions which are observed on these catalysts, including a second ceria-mediated process for CO oxidation

(9), water–gas shift (10), and steam reforming (11). The mechanistic picture for each of these reactions is similar to that for the steam-reforming reaction, shown below (11):



In this mechanism,  $\sigma$  represents an adsorption site on the metal. The key step is reaction [3b], which involves reduction of the ceria. This mechanism suggests that water should be treated as an oxidant (reaction [2]) and that the oxidation state of ceria will depend on the partial pressure of water.

Second, the redox properties of ceria are structure sensitive (7, 12–14). In measurements performed on model catalysts formed by vapor deposition of catalytic metals onto ceria films heated to different temperatures, it was found that oxygen from the ceria could not be utilized by reductants on the metal if the ceria had previously been calcined to high temperatures (7, 12). SEM and XRD studies showed that the primary effect of annealing the ceria at high temperature was to increase the particle size. Furthermore, ultra-high vacuum TPD studies of O<sub>2</sub> from ceria films showed that the active form of oxygen in ceria desorbs at lower temperatures, between 800 and 1100 K, compared to that found for O<sub>2</sub> desorption from inactive forms of ceria, where desorption occurs above 1300 K (13, 14) as would be expected based on bulk thermodynamics. The amount of oxygen which desorbs at the lower temperatures correlates with catalytic activity. These observations suggest that the active form of oxygen is more loosely bound in the ceria and that bulk thermodynamic data may not be applicable for predicting redox properties for reactants on ceria.

These results suggest that the presence of H<sub>2</sub>O in the automotive exhaust stream may influence the oxidation state of ceria under operating conditions. One might expect CO<sub>2</sub> to have a similar effect. Indeed, even thermodynamic data

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for bulk compounds indicate that the following reaction,



is favorable at 298 K, since  $\Delta G^\circ$  is  $-85.8$  kJ/mol and  $\Delta H^\circ$  is  $-96.8$  kJ/mol. To investigate this possibility, we examined the redox properties of Pd/ceria catalysts using  $\text{CO}_2$  as the oxidant. From reaction [4] and by analogy to the proposed mechanism for steam reforming, we anticipated that  $\text{CO}_2$  could oxidize a reduced, Pd/ceria catalyst and that Pd/ceria would be a good catalyst for  $\text{CO}_2$  reforming of methane. Using both transient and steady-state rate measurements, we will demonstrate that this is indeed the case.

### EXPERIMENTAL TECHNIQUES

Steady-state rates for  $\text{CO}_2$  reforming of methane were measured by placing 100-mg catalyst samples into a  $\frac{1}{4}$ -inch quartz, tubular reactor which has been described in previous publications (11). The total pressure in the reactor was maintained at one atmosphere, but the partial pressures of  $\text{CH}_4$ ,  $\text{CO}_2$ , and He could be controlled by the flow rates to the reactor. In this study, the partial pressures of  $\text{CO}_2$  and  $\text{CH}_4$  were each held at 15 Torr. Differential conversions were maintained for all measurements. Product analysis ( $\text{CO}_2$ , CO, and  $\text{CH}_4$ ) was performed with an on-line Hewlett-Packard 5730A gas chromatograph equipped with a methanator and FID detector. All rates have been normalized to the weight of the catalyst.

The transient pulse experiments were performed on a system for which the product gases could be analyzed by an on-line quadrupole mass spectrometer. Reactant gases were passed over a 100-mg sample in a  $\frac{1}{4}$ -inch quartz tube. Computer-controlled switching valves allowed the composition of the gases to undergo step changes. In all cases, He was the major component of the gas phase, with a flow rate of 30  $\text{cm}^3/\text{min}$ , and the active component ( $\text{CO}$ ,  $\text{O}_2$ , and  $\text{CO}_2$ ) was chosen to be 10% of the total flow rate. This ensured that the step changes in composition did not dramatically change the flow rate. The pulse reactor data were used primarily to determine the amount of oxygen that was added or removed from the catalyst during each oxidation and reduction cycle. Integration of the partial pressure as a function of time allowed accurate determination of the amounts of  $\text{CO}_2$  formed during a CO pulse. Prior to taking the pulse data, we first calcined the samples in flowing air at 673 K for 1 h, which were reduced with 10% CO in He at that temperature for 1 h and then reoxidized in 10%  $\text{O}_2$  for an additional 1 h. The areas under the peaks were reproducible within about 10%.

For all of the catalysts, Pd was added by aqueous wet impregnation of  $\text{Pd}(\text{NH}_4)_4(\text{NO}_3)_2$ . After impregnation, each catalyst was dried, calcined in flowing air for 2 h at 673 K, and then pressed into wafers. Prior to the steady-state rate experiments, the wafers were reduced in a stream of 10%

CO in He for 1 h at 673 K and then cooled in flowing He. A 1% wt loading of Pd was used for all of the catalysts in the pulse experiments, while a 10% wt loading was used for the steady-state reaction measurements. The four supports came from various sources. Ceria was used as received from Johnson Matthey. BET analysis indicated that the surface area was 33  $\text{m}^2/\text{g}$ . The  $\gamma$ - $\text{Al}_2\text{O}_3$  and silica supports were commercial materials obtained from Alfa Aesar and Sigma. Zirconia was prepared by drying an aqueous solution of  $\text{ZrO}(\text{NO}_3)_2$ , then calcining the solid to 673 K in air for 1 h. The BET surface area of this catalyst was 9  $\text{m}^2/\text{g}$ .

### RESULTS

The results for the pulse measurement with CO and  $\text{O}_2$  on Pd/ceria at 623 K are shown in Fig. 1. In this experiment, the oxidized sample was exposed to two pulses of CO ( $m/e = 28$ ), followed by two pulses of  $\text{O}_2$  ( $m/e = 32$ ) and a pulse of CO. For the first CO pulse, a significant amount, 470  $\mu\text{mol/g}$ , of  $\text{CO}_2$  ( $m/e = 44$ ) was formed at the leading edge of the pulse. Essentially no  $\text{CO}_2$  was formed in the second CO pulse, showing that the initial pulse had removed all of the kinetically accessible oxygen from the catalyst. The amount of oxygen removed from this catalyst is similar to that reported in an earlier study of Pd/ceria catalysts (3). For comparison purposes, complete reduction of PdO would result in the production of  $\sim 94$   $\mu\text{mol/g}$  of  $\text{CO}_2$  and complete reduction of ceria from  $\text{CeO}_2$  to  $\text{Ce}_2\text{O}_3$  would provide an additional 2900  $\mu\text{mol/g}$ . Therefore, the majority of the oxygen from this catalyst must originate from the ceria support.

The exposure of the reduced sample to  $\text{O}_2$  led to a very sharp  $\text{CO}_2$  spike corresponding to 400–500  $\mu\text{mol/g}$ . (Note that the small peak at  $m/e = 28$  is part of the fragmentation pattern of  $\text{CO}_2$  in the mass spectrometer.) One possible explanation for the  $\text{CO}_2$  spike is that  $\text{CO}_2$  formed during the initial CO pulse adsorbs on  $\text{Ce}^{3+}$  sites on the reduced ceria support. This  $\text{CO}_2$  is then displaced when the ceria is reoxidized during the  $\text{O}_2$  pulse. Using the BET surface area of the catalyst and 400  $\mu\text{mol/g}$  for the amount of  $\text{CO}_2$  formed, the surface coverage of  $\text{CO}_2$  was estimated to be  $6 \times 10^{18}$  molecules/ $\text{m}^2$ , which is close to the coverage expected for one monolayer of  $\text{CO}_2$  on ceria. On the basis of this interpretation, the total amount of  $\text{CO}_2$  formed in the CO pulse is the sum of the  $\text{CO}_2$  formed in both events, i.e., more than 850  $\mu\text{mol/g}$ .

Another possible explanation for the sharp  $\text{CO}_2$  spike upon the introduction of  $\text{O}_2$  is that CO or carbon adsorbed on either the Pd or ceria is being oxidized in this process; however, two important observations argue against this assignment. First, the amount is too large for the carbon to be only on the Pd since it would require approximately four carbons per metal atom. The carbon would have to be present in significant amounts on the ceria. This possibility

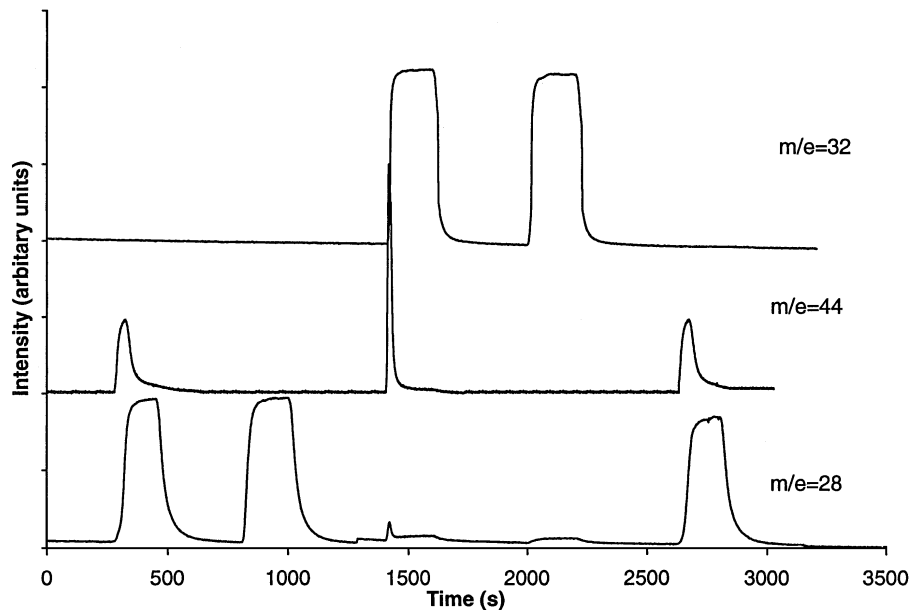


FIG. 1. Pulse measurements on a Pd/ceria catalyst at 623 K. The figure shows two pulses of CO ( $m/e = 28$ ), followed by two pulses of O<sub>2</sub> ( $m/e = 32$ ) and another of CO. Formation of CO<sub>2</sub> ( $m/e = 44$  and 28) is observed.

has been suggested in the literature (15), and a significant number of other papers have reported the dissociation of CO (16) and CO<sub>2</sub> (17–19) on ceria-supported metals. However, because the amount of CO<sub>2</sub> is large, one cannot explain the data based on the metal–ceria perimeter. Furthermore, it would be surprising that carbonaceous species on ceria could be oxidized as rapidly as the sharpness of the CO<sub>2</sub> spike would suggest. Second, the CO<sub>2</sub> formation during the O<sub>2</sub> pulse is only observed with ceria and not with

the other supports. For example, the analogous experiment on Pd/zirconia, shown in Fig. 2, shows no evidence for CO<sub>2</sub> formation at the same point in the pulse sequence.

The last CO pulse in Fig. 1 demonstrates the reversibility of the redox process on Pd/ceria. The amount of CO<sub>2</sub> produced by this pulse was  $\sim 530 \mu\text{mol/g}$ . The difference between this and the initial pulse can be explained by the 10% uncertainty in our ability to measure the areas under the CO<sub>2</sub> peak.

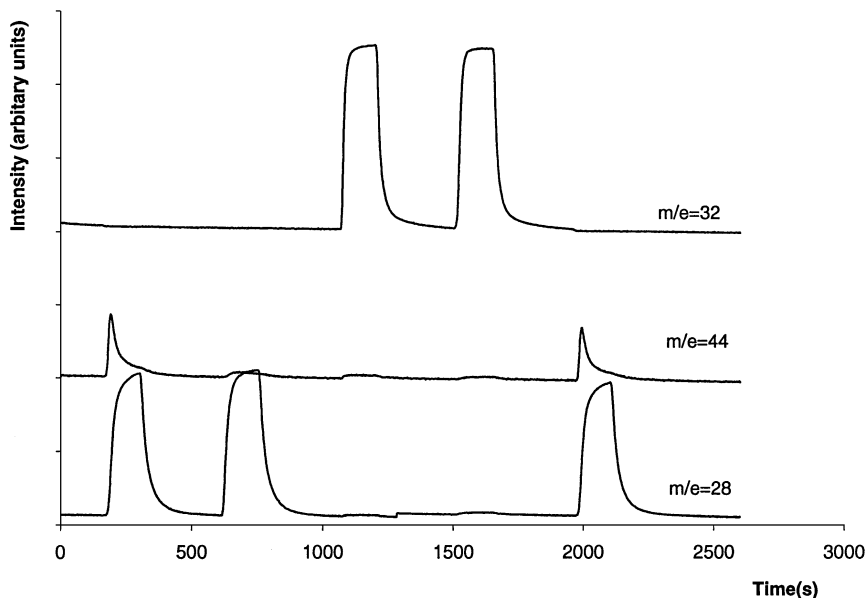


FIG. 2. Pulse measurements on a Pd/zirconia catalyst at 623 K. The figure shows two pulses of CO ( $m/e = 28$ ), followed by two pulses of O<sub>2</sub> ( $m/e = 32$ ) and another of CO. Formation of CO<sub>2</sub> ( $m/e = 44$  and 28) is observed.

The data for alternating CO and O<sub>2</sub> pulses on Pd/zirconia at 623 K in Fig. 2 are qualitatively similar to that for Pd/ceria, with the exception that no CO<sub>2</sub> is formed during the O<sub>2</sub> pulse. What is most interesting about this data is that the amount of CO<sub>2</sub> formed after both the first and last CO pulses is  $\sim 170 \mu\text{mol/g}$ . Again, this amount is too large to be explained by oxidation and reduction of Pd alone. The data for Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd/silica are qualitatively similar to Fig. 2, but the amounts of CO<sub>2</sub> observed at 673 K were 53 and 26  $\mu\text{mol/g}$ , respectively. Oxidation and reduction of the Pd alone can easily explain the CO<sub>2</sub> formed on both Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd/silica. While zirconia is not normally considered to be reducible under normal catalytic conditions, there is mounting evidence that the surface of zirconia powders may nonetheless be reducible (20). Given that the amount of oxygen removed from Pd/zirconia is almost double that which could originate from the Pd alone, at least 100  $\mu\text{mol/g}$  of oxygen must come from zirconia. Based on the BET surface area, this corresponds to  $\sim 6 \times 10^{18}/\text{m}^2$ , a reasonable value for complete reduction of the surface. Note that the interfacial perimeter between Pd and zirconia is still not sufficient to explain the amount of oxygen removed from this catalyst.

Equation [4] suggests that reduced ceria can be oxidized by CO<sub>2</sub>, which has also been suggested earlier [17]. Additional evidence for this is given in Fig. 3, which gives results for alternating CO and CO<sub>2</sub> pulses at 623 K. Prior to this measurement, the oxidized sample was exposed to a series of CO and CO<sub>2</sub> pulses identical to those shown here. Both CO and CO<sub>2</sub> contribute an  $m/e = 28$  signal in the mass spectrum, so that one must consider the ratio of the peaks at 28 and 44 in order to unambiguously interpret the data. The

catalyst is clearly reduced following two CO pulses. What is most interesting is that the first CO<sub>2</sub> pulse exhibits a leading peak at  $m/e = 28$ , which is not observed for the second CO<sub>2</sub> pulse, implying that some CO is formed. Obviously, formation of CO from CO<sub>2</sub> requires oxidation of the catalyst. Evidence for oxidation of the catalyst by CO<sub>2</sub> is also obtained from the final CO pulse. Here, CO<sub>2</sub> is again formed by oxidation of CO. The extent of oxidation is significantly less than that following oxidation by O<sub>2</sub>, with only 100  $\mu\text{mol/g}$  of CO<sub>2</sub> being formed in the last CO pulse. (It was not possible for us to accurately determine the amount of CO which evolved during the CO<sub>2</sub> pulse, but it appeared to be essentially equal to the amount of CO<sub>2</sub> formed in the last CO pulse. The catalyst did not change with continued pulsing of CO and CO<sub>2</sub>.) It should be noted that oxidation of ceria by CO<sub>2</sub> was negligible in measurements using Pd/ceria at 473 K, implying that there are kinetic limitations to the oxidation of ceria by CO<sub>2</sub>. The results for Pd/zirconia were essentially identical, although only 70  $\mu\text{mol/g}$  of oxygen was transferred. Finally, we found no evidence for oxidation of either Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or Pd/silica by CO<sub>2</sub> at temperatures up to 723 K.

Based on the mechanism for steam reforming of methane discussed in the Introduction and the observation that CO<sub>2</sub> can oxidize ceria, one might expect that the role of water could be replaced by CO<sub>2</sub> for reaction on Pd/ceria catalysts. We therefore measured the steady-state rates of the reaction of CH<sub>4</sub> with CO<sub>2</sub> on Pd/ceria, Pd/zirconia, and Pd/silica catalysts. The rates for all three catalysts are shown in Fig. 4 for CO<sub>2</sub> and CH<sub>4</sub> partial pressures of 15 Torr. As expected, the Pd/silica catalyst had essentially no activity and it was not possible to measure rates in the same temperature

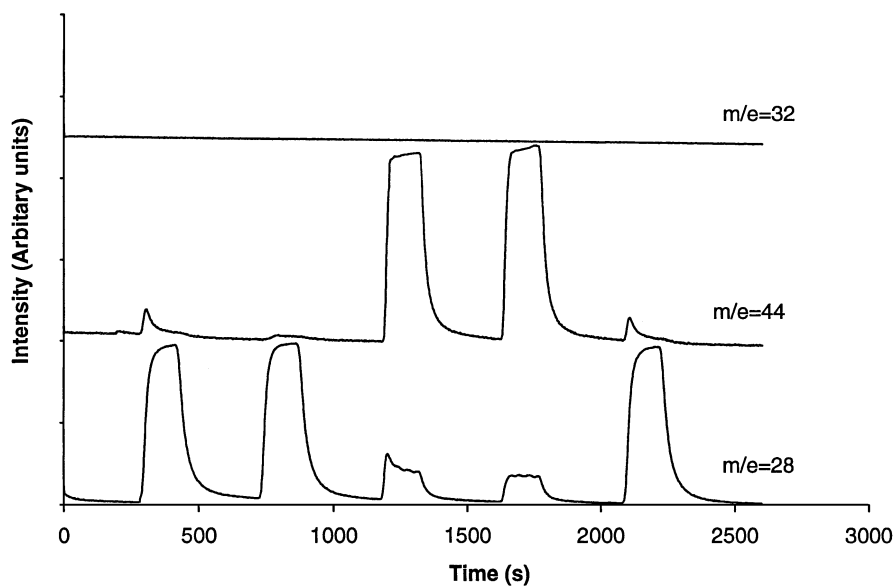


FIG. 3. Pulse measurements on a Pd/ceria catalyst at 623 K. The figure shows two pulses of CO ( $m/e = 28$ ), followed by two pulses of CO<sub>2</sub> ( $m/e = 44$  and 28) and another of CO.

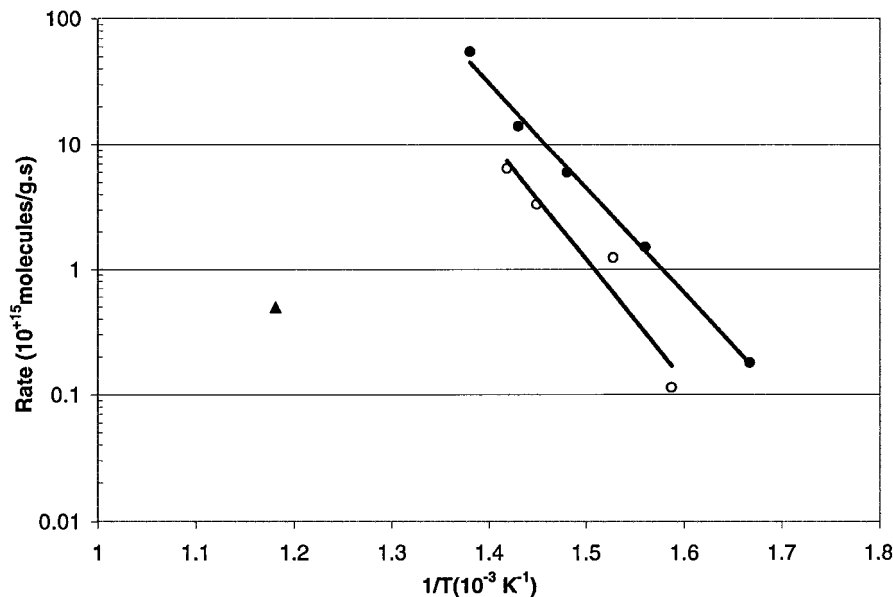


FIG. 4. Steady-state rates for methane reforming by CO<sub>2</sub> on 10% Pd/ceria (●), 10% Pd/zirconia (○), and 10% Pd/silica (▲). The partial pressures were 15 Torr each for CH<sub>4</sub> and CO<sub>2</sub>.

region used for the other two catalysts. Extrapolating the data for Pd/ceria to the same temperature as that used for Pd/silica, the Pd/ceria catalyst was estimated to be a factor of  $\sim 10^4$  times more active.

Previous reports have already indicated that zirconia-supported metals are very active catalysts for this reaction (21–23). The results presented here agree well with these earlier observations, but show that Pd/ceria is even more active than Pd/zirconia. The activation energies calculated from the data in Fig. 4 are 185 kJ/mol for Pd/zirconia and 160 kJ/mol for Pd/ceria. The difference in the activation energies between the two catalysts is within in the uncertainty of the measurement. The fact that the rates are so similar on Pd/ceria and Pd/zirconia, strongly suggests that the mechanisms must also be similar. Based on the data from the pulse experiments, especially that in Fig. 3, the mechanism on Pd/ceria and Pd/zirconia must involve oxidation and reduction of the oxide.

## DISCUSSION

The major conclusion which can be drawn from the results of this work is that CO<sub>2</sub> is able to oxidize reduced ceria or zirconia. Clearly, O<sub>2</sub> is more efficient than CO<sub>2</sub>; still, the pulse reactor data demonstrate that the extent of re-oxidation by CO<sub>2</sub> is significant. These results have obvious implications for the mechanism of methane reforming by CO<sub>2</sub>. They also have important implications for three-way, automotive-exhaust catalysis since the presence of CO<sub>2</sub> and H<sub>2</sub>O in the exhaust environment may affect the equilibrium oxidation state of the ceria component, limiting the extent to which oxygen can be removed. This point requires additional consideration.

The observation that zirconia can be reduced and re-oxidized under the relatively mild conditions used in this study is surprising. It is important to note, however, that others have also reported evidence for surface reduction of zirconia (23). Also, the fact that zirconia-supported metals are active for reactions like CO<sub>2</sub> reforming, while silica- and alumina-supported metals are not, strongly suggests that zirconia plays more than a simple, passive role in the reaction. While it is possible that this role is simply to polarize molecules adsorbed at the metal–zirconia interface, the simplicity of the redox mechanism, along with the fact that both the oxidation and reduction steps are observed directly in the pulse measurements, strongly argues for the redox mechanism.

While we have not definitively proven that the reduced Pd/ceria can adsorb CO<sub>2</sub> and release it upon re-oxidation, the concept is reminiscent of what is observed with sulfur. It is known that SO<sub>2</sub> poisons ceria by formation of a sulfate, with Ce likely in the +3 state as Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (24). Reducing conditions allow the release of the sulfur as H<sub>2</sub>S. While there is probably no relationship between SO<sub>2</sub> adsorption and CO<sub>2</sub> adsorption, the ability of the material to form a sulfate or a carbonate may be related. It would be interesting to determine whether materials which do not adsorb CO<sub>2</sub> are also more tolerant of SO<sub>2</sub>.

## ACKNOWLEDGMENTS

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