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The dynamic surface chemistry during the interaction of CO with ceria captured by Raman spectroscopy

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The interaction of CO with ceria under conditions typically used to measure the oxygen storage capacity (OSC) of automotive three way catalysts (TWC) has been investigated by *in situ* Raman spectroscopy. During exposure of the ceria to CO at 623 K vibrational bands at 1582–1600 and 1331–1340 cm^{-1} appeared; these bands increased with increasing time of exposure to CO. The band positions are consistent with phonon modes of carbon; however, assignment to carboxylate species or carbonate species cannot be excluded. Subsequent exposure to O_2 at room temperature resulted in a decrease in the intensities of the 1582–1600 and 1331–1340 cm^{-1} bands by more than 90%. As well, exposure to O_2 at room temperature also resulted in the appearance of Raman modes characteristic of formate and peroxide surface species. The mechanism by which formate forms upon room temperature O_2 exposure is discussed in the context of the assignment of the 1582–1600 and 1331–1340 cm^{-1} bands to carbon phonon modes which result from the disproportionation of CO on reduced ceria.

KEY WORDS: CO adsorption; ceria; CO disproportionation; carbonates; carboxylates; oxygen storage capacity; *in situ* Raman spectroscopy.

1. Introduction

Ceria is an essential component of the multi-oxide material used to support the noble metals in automotive three way catalysts (TWC). It inhibits thermal sintering of noble metals and promotes CO oxidation by water during fuel-rich excursions [1]. Moreover, because of the facile redox chemistry between the Ce^{3+} and Ce^{4+} oxidation states, ceria also acts as an oxygen buffering agent; viz., ceria has an oxygen storage capacity (OSC). Under oxidizing conditions, the Ce^{3+} ions are oxidized to Ce^{4+} by a stoichiometric reaction with gas phase oxygen. When the automotive emission stream is a reducing atmosphere, the ceria lattice oxygen is utilized to convert CO and hydrocarbons to CO_2, which results in the reduction of Ce^{4+} ions to Ce^{3+} ions. In essence, the oxygen buffering capacity of ceria dampens the oscillations of the engine air to fuel ratio. This improves the overall efficiency of the TWC with respect to oxidation of CO and hydrocarbon emission with simultaneous reduction of NO_x emissions [1]. On the average, the TWC containing ceria operates under conditions closer to optimum than a ceria-free TWC.

The OSC of a catalyst is a property that is measured and assessed in the context of determining the overall performance of a TWC. An established and widely utilized method for measuring the amount of stored oxygen is the pulse technique [2,3]. Typical sequences alternate between O_2 pulses and CO pulses. The total number of O atoms removed from the oxide lattice via CO_2 formation from a single pulse of CO administered after a single pulse of O_2 is termed the OSC [4]. The total number of oxygen atoms removed from a completely oxidized sample during consecutive pulses of CO until CO_2 formation ceases is called the OSC complete (OSCC) [4]. Clearly, the results of measurements to determine the OSC depend on reaction conditions: temperature, reactant partial pressures, and total pressure [2]. Videlicet, the OSC is the amount of labile lattice oxygen available for oxidation reactions *under defined conditions*. Common reaction conditions reported for OSC measurements are with 1–10% O_2 and 1–5% CO in an inert gas at 570–770 K and atmospheric pressure [4–7].

The CO_2 evolved during the OSC measurement is formed via the abstractive reductive adsorption of CO. Oxygen abstraction from the ceria creates defects in the form of Ce^{3+} species and oxygen vacancies [4,8,9]. Additionally, ceria becomes an n-type semiconductor in reducing conditions, which facilitates sorption of electron acceptors [10]. The impact of these factors on the surface chemistry of carbon oxides on ceria remains unclear.

The research put forth in this investigation is directed at understanding the extent to which the interaction of CO with ceria is affected by the degree of ceria reduction. The type and nature of ceria surface species has been probed by *in situ* Raman spectroscopy. Of particular

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interest are reactions which may interfere with OSC measurements such as surface transformations of carbon oxide species and CO disproportionation to form CO_2 and carbon. Raman spectroscopy was chosen for this study because many vibrations of carbon oxide surface species are Raman active. As well, graphite and other carbonaceous moieties are good Raman scatterers with well-established spectra [11–19].

2. Experimental

The CO_2 used in this investigation was supplied by Rhodia; the purity of the material exceeded 99.9%. The CeO_2 was calcined in air at 823 K for 12 h in a muffle furnace prior to any experimentation or characterization. Nitrogen physisorption measurements at 77 K were conducted using a Micromeritics ASAP 2010 volumetric sorption analyzer and the results were used to calculate the BET surface area (127 m^2 g^{-1}), the average pore diameter (4.8 nm), and the pore volume (0.20 cm^3 g^{-1}). An average ceria crystallite size of 9.7 nm was determined from the application of the Scherrer equation to the results of (111) and (220) XRD lines broadening experiments.

The Raman spectra were acquired using a Renishaw System 2000 equipped with a Leica DMLM microscope and a 514.5 nm Ar^+ ion laser as the excitation source. The laser power at the source was in the range of 5–25 mW. An Olympus ×50 objective was used to focus the unpolarized laser beam onto a < 3 μm spot on the sample and to collect the backscattered light. For each spectrum ten scans in the 100–4000 cm^{-1} range were acquired at a resolution of 4 cm^{-1} and averaged. The Raman measurements were conducted at atmospheric pressure in an *in-situ* cell (Lincam Scientific). Approximately 100 mg of sample was placed on a thin quartz disc (1 cm dia.), which was then placed in the cell.

A gas mixture of 10% O_2 in He (Praxair, UHP) was used without further purification for all oxidation steps. Reagent grade He (Air Products, $>99.998\%$) was purified of water and oxygen traces by passing it through a deoxidant OxyTrap filter and through a 0.5 nm molecular sieve column (both Alltech). The CO (Praxair, $>99.995\%$) was flowed through a Vista B γ-alumina trap maintained at 573 K to remove any metal carbonyl contaminants. The desired flow rate of each gas (CO, He, and 10% O_2/He) was maintained within ± 1 mL/min using Brooks mass flow controllers (model 5850E). For all treatments and experiments, the total gas flow rate through the cell was 100 mL/min and the heating/cooling rate was always 10 K/min.

The sample pretreatment consisted of heating from room temperature to 673 K in 10% CO/He and maintaining these conditions for 1 h. In one set of experiments, the gas flow was switched to 10% O_2/He, the sample was held at 673 K for 1 h, and then a spectrum was collected. Next, the sample was cooled to 623 K in the 10% O_2/He flow. Next, the sample was purged at 623 K with He, and then exposed to a 10% CO/He flow while Raman spectra were collected as a function of increasing time.

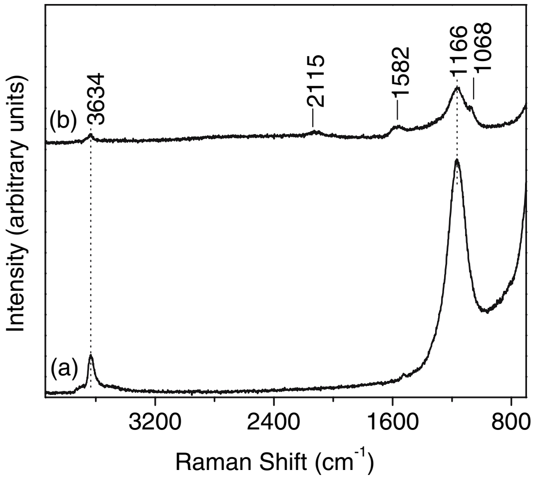

Figure 1. *In situ* Raman spectra of CeO_2 (a) after treatment in 10% O_2/He at 673 K for 1 h and (b) after exposure to 10% CO/He at 623 K for 1 h. All spectra were recorded at 623 K.

In another experiment, the sample was pretreated as described above, except after 12 h CO exposure, the sample was cooled from 623 to 298 K in 10% CO/He and a Raman spectrum was collected. Then, the gas flow was switched to 10% O_2/He and Raman spectra were collected as a function of increasing time.

3. Results

The Raman spectrum of ceria after exposure to 10% O_2/He at 673 K consisted of a band at 1166 cm^{-1} attributed to a combination of A_{1g}, E_g, and F_{2g} ceria lattice vibrational modes [20] and a band at 3634 cm^{-1} assigned to the O–H stretching mode of a ceria hydroxyl group vibration with bidentate coordination [3,21–23] (figure 1(a)). The two bands decreased in intensity by approximately a factor of four after exposure to CO at 623 K for 1 h (figure 1(b)). As well, new bands appeared at 2115 cm^{-1} and 1582 cm^{-1}, and a low-frequency shoulder formed on the 1166 cm^{-1} band at 1068 cm^{-1}. The 1068 cm^{-1} band has been assigned to a vibrational mode of cerium carbonate by several research groups [10,22,24–26].

The dynamic nature of the surface chemistry associated with continued exposure to CO at 623 K was evident from the Raman spectra (figure 2). The decrease in the intensities of the bands at 1166 and 3634 cm^{-1} after 20 min exposure to CO (figure 2(b)) in comparison to the oxidized ceria sample (figure 2(a)) was essentially the same as after 1 h exposure to CO (figure 1(b)). Twenty min exposure to CO also marked the appearance of the

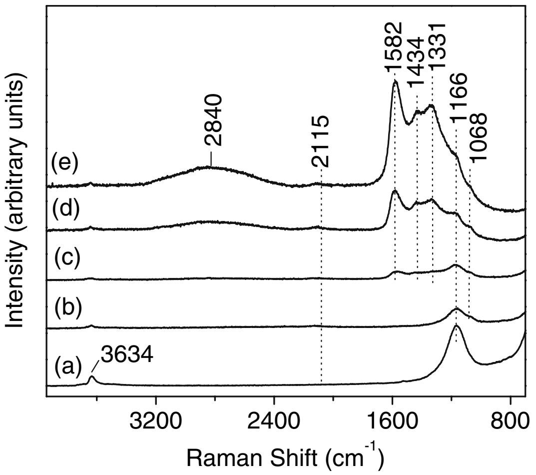

Figure 2. *In situ* Raman spectra of CeO_2 (a) after treatment in 10% O_2/He at 673 K for 1 h, then exposed to a flow of 10% CO/He at 623 K for: (b) 20 min, (c) 3.4 h, (d) 17.3 h, and (e) 21.6 h. All spectra were recorded at 623 K.

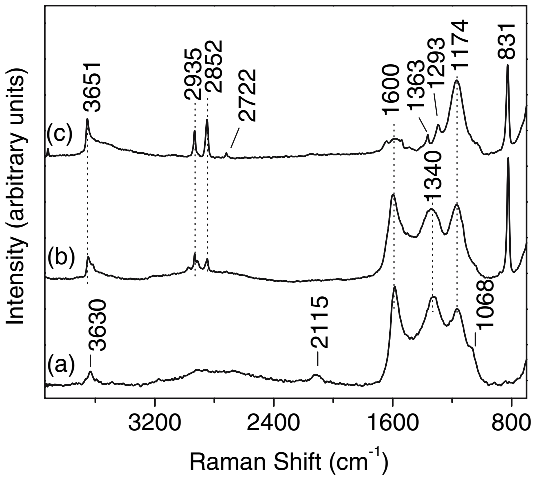

Figure 3. *In situ* Raman spectra of CeO_2 (a) treated in a flow of 10% CO/He at 623 K for 12 h, and after subsequent exposure to a flow of 10% O_2/He at 298 K for (b) 30 min, and (c) 12 h. All spectra were recorded at 298 K.

1068 cm^{-1} carbonate band on the shoulder of the 1166 cm^{-1} band and a band at 2115 cm^{-1}. After 3.4 h CO exposure time, bands at 1582, 1434, and 1331 cm^{-1} were observed (figure 2(c)), and the intensity of these three bands increased throughout the duration of the experiment (21.6 h). In comparison to the intensity increases observed for the 1582, 1434, and 1331 cm^{-1} bands, the intensity of the 3634 and 1166 cm^{-1} ceria bands and the 2115 and 1068 cm^{-1} bands did not change markedly with increasing CO exposure time. It should also be noted that after 17.3 h exposure to CO, a broad band centered at 2840 cm^{-1} was detectable (figure 2(d)), and it became more pronounced after 21.4 h exposure to CO (figure 2(e)).

After exposing ceria to CO for 12 h at 623 K and cooling to room temperature, the position of the ceria lattice vibration was 1174 cm^{-1} (figure 3(a)) [27], in contrast to the spectra collected at 623 K in which the band was centered at 1166 cm^{-1} (figures 1 and 2). The shift to a higher frequency is attributed to the lattice thermal contraction; the accompanying increase in the bond energy caused a shift in the Raman mode [27,28]. Bands at 2115 and 3630 cm^{-1} were also present in the room temperature spectrum, as were bands at 1600 and 1340 cm^{-1} and the 1068 cm^{-1} carbonate band (figure 3(a)). The 1434 cm^{-1} band in figure 2(c)–(e) was obscured in the room temperature spectrum. The position of this vibrational band is consistent with a variety of surface species and vibrational modes. No assignment of the 1434 cm^{-1} band will be put forth herein, as it is considered imprudently speculative.

Subsequent exposure to O_2 at room temperature for 30 min resulted in the disappearance of the 2115 cm^{-1} band and the appearance of a band at 831 cm^{-1}, which has been assigned to surface peroxide [29–32], and bands at 2852 and 2935 cm^{-1} (figure 3(b)). The 2852 and 2935 cm^{-1} bands are formate modes. Specifically, the 2935 cm^{-1} is assigned to a C–H stretching mode [33,34] and the 2852 cm^{-1} band is assigned to a combination mode of the C–H bend and O–C–O asymmetric stretch [3,33,34]. Formate also exhibits strong infrared bands at 1599, 1553, and 1542 cm^{-1}, all assigned to the O–C–O asymmetric stretch [33,34]. Thus, a formate mode may be included in the collection of low intensity peaks in the vicinity of 1600 cmcm^{-1} after 12 h O_2 exposure (figure 3(c)) [33–35]. Additionally, the position of the 1363 cm^{-1} band that appeared after 12 h O_2 exposure (figure 3(c)) agrees well with the 1362–1363 cm^{-1} which has been assigned to a formate asymmetric O–C–O stretching vibration [34,35], or alternately, a formate C–H in plane vibration at 1369 cm^{-1} [33].

The intensities of the bands at 1340 and 1600 cm^{-1} decreased substantially during 12 h exposure to O_2 at 298 K (figure 3(c)). The bands at 2852 and 2935 cm^{-1} increased in intensity during O_2 exposure, whereas the intensity of the 831 $^{-1}$ band decreased. After 12 h exposure to O_2, bands were detected at 2722 cm^{-1} and 1363 cm^{-1}. The 2722 cm^{-1} band (figure 3(c)) was assigned previously in infrared spectra of ceria partially reduced in hydrogen at 673 K for 1 h to a formyl species [33–36].

A band in the hydroxyl region at 3651 cm^{-1} was present after 12 h exposure to O_2; it was 21 cm^{-1} higher in frequency than the band present after 12 h exposure to CO. As well, a band at 1293 cm^{-1} was visible after 12 h O_2 exposure (figure 3(c)); assignment to a carbonate vibrational mode is viable [3,26], yet speculative.

4. Discussion

In 1994 Bozon-Verduraz and Bensalem pointed out that the propensity of ceria for non-stoichiometry contributed to significant uncertainty in our understanding of the nature of the species formed when carbon oxides interact with ceria based on IR spectroscopy investigations [10]. Indeed, the IR spectra of ceria exposed to carbon oxides consist of numerous overlapping bands in the C–O, C = O, and C = C vibrational region of 1050–1750 cm^{-1} [24,33]. Efforts to establish the frequencies of the variety of types of surface carbonate and carboxylate have been complicated by the complexity of the spectra – and the propensity of ceria for non-stoichiometry.

The results of this investigation show the increase in intensity of Raman bands at 1582–1600 and 1331–1340 cm^{-1} with increasing exposure time to flowing CO at 623 K (figure 1–3). The position of the bands are in line with reported, albeit generous, ranges for the two asymmetric vibrational modes of a surface carbonate, one high frequency and one low frequency in comparison to the doubly degenerate asymmetric CO stretching mode at 1415 cm^{-1} for a free carbonate ion. The difference in the frequency of the two bands is 250 cm^{-1}. According to the general rule of thumb, asymmetric vibrations of roughly 300 cm^{-1} are indicative of a bidentate carbonate species, 100 cm^{-1} for a monodentate carbonate species, and 400 cm^{-1} or higher for bridged species [37].

The 1582–1600 and 1331–1340 cm^{-1} bands are also in the range reported for the asymmetric and symmetric stretching modes of a carboxylate species are 1510–1570 and 1310–1410 cm^{-1} [26,38–40]. The present research showed that the 1582 and 1331 cm^{-1} bands increased in intensity with continued exposure to CO at 623 K. Under these conditions, the abstractive reductive adsorption of CO to form CO_2 occurs with the concomitant formation of Ce^{3+} ions and oxygen vacancies [1,8,9]. Hence, it is reasonable to suggest that carboxylate formation would be favored as the ceria becomes more reduced and the number of oxygen vacancies increases. The formation of a carboxylate from CO requires only one ceria oxygen whereas formation of a carbonate requires two.

However, the more than 90% decrease the intensities of these two bands after exposure to flowing O_2 for 12 h at room temperature (figure 3) provides a strong driving force to consider alternative assignments to carbonate for the 1582–1600 and 1331–1340 cm^{-1} bands observed in this investigation, even though their formation under conditions similar to those used in the present work has been reported [3,41]. Carbonates of ceria are notoriously stable [10], and no apparent change in the spectra of CO adsorbed on CeO_2 occurs after dosing O_2 on CeO_2 preadsorbed with CO according to Li et al. [26]. In fact, the decomposition of the carbonates require a temperature of roughly 1000 K and an oxygen-free atmosphere [10,26].

Carbon phonon modes are Raman active, and it is plausible that the 1582 and 1331 cm^{-1} bands are attributed to carbon–carbon vibrations. Specifically, the band position corresponds well with the 1575–1585 cm^{-1} band frequency of the doubly degenerate E_{2g} Raman-active phonon mode (G band) of sp^2 hybridized carbon materials such as graphite, charcoal and coke [11,14,16,17,42,43]. And the position of the band at 1331 cm^{-1} is comparable with the 1343–1360 cm^{-1} band position of a disorder-induced carbon A_{1g} phonon mode (D band) of graphitic and glassy carbons measured experimentally using a 514.5 nm excitation source [11,17,19, 44], as was used in this investigation. The broad band centered in the vicinity of 2840 cm^{-1} after prolonged exposure to CO at 623 K (figure 2(d)–(e), 3(a)–(b)) is consistent with the assignment of the 1331–1340 cm^{-1} band to the D band of carbon, as it is in the position [11,14,18,45] and is of the shape [17,43] of a D band overtone.

The dissociation of CO must occur in order for surface carbon to form. To this end, it must be noted that the carbon–oxygen bonds of CO and CO_2 readily cleave on ceria at 673 K, as evidenced by isotope exchange experiments with $C^{18}O$ and $C^{18}O_2$ [3]. In fact, the rate of exchange was faster on ceria than on Pt supported on ceria. Additionally, the band at 2115 cm^{-1} (figure 2 and 3) is characteristic of Ce^{3+} species. The band has been assigned to the CO stretching mode of a CO–Ce^{3+} species [46] (although earlier investigations assigned it to the symmetry-forbidden $^2F_{5/2} \rightarrow {}^2F_{7/2}$ electronic transition of Ce^{3+} [10,25]). In contrast to CO adsorbed on Ce^{4+} in which the CO vibrational frequency is 5–24 cm^{-1} higher than gas phase CO [46], the frequency of CO adsorbed on Ce^{3+} is 28 cm^{-1} lower in frequency than the gas phase. A donation of electron density from the Ce^{3+} ion to the CO is consistent with the shift, as is the interpretation that the reduced cerium cations sites favor CO dissociation.

In contrast to an earlier IR investigation in which it was shown formate species form on partially reduced ceria upon exposure to CO at room temperature [33], the results of this investigation show upon exposure to room temperature O_2 formate species form to on ceria that was exposed to CO at 623 K (2852 and 2935 cm^{-1} bands in figure 3(b)–(c)). One possible mechanism to account for the formate formation is the reaction of a dioxygen surface species with carbon followed by a reaction with a hydroxyl group. The formation of surface peroxide species up addition of O_2 is evidenced by the 831 cm^{-1} band (figure 3).

It may be inferred from the presence of a D band of carbon (1331–1340 cm^{-1}) in addition to a G band (1582–1600 cm^{-1}) that the carbon is highly reactive. The presence of the D band demonstrates that the carbon particle size is small. Based on an empirical relationship that relates the ratio of the band intensities (I_G/I_D) to the graphite particle size [16,17] and intensity data obtained from spectrum e of figure 2 by the deconvolution and peak fitting method described by Nistor *et al.* [47], the average particle size was roughly 1.7 nm. This calculated value is smaller than the 2 nm experimentally verified lower limit [48] of the $I_G/I_D = 44Å/L_a$ empirical relationship for disordered carbon spectra, in which L_a is the crystalline size of the graphite plane [16,17]. Most importantly, the surface of such small particles is comprised largely of carbon atoms that are coordinatively unsaturated. Thus, the interaction of coordinatively unsaturated carbon sites with surface peroxides is a viable model for room temperature carbon oxidation.

5. Conclusions

Prolonged exposure of ceria to CO at 623 K generates reactive lattice defects and carbon-containing surface species. It may be inferred from the increase in intensity of the vibrational bands at 1582–1600 and 1331–1340 cm^{-1} with continuing CO exposure that accumulation of one or more surface species occurs. Although carbonates and carboxylates remain viable species to which the bands may be assigned, the band positions are also in line with carbon phonon modes. It has been suggested that carbon may form by CO disproportionation, and this suggestion is supported by the formation of formates upon subsequent exposure to O_2 at room temperature.

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