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Low temperature water gas shift: Type and loading of metal impacts forward decomposition of pseudo-stabilized formate over metal/ceria catalysts

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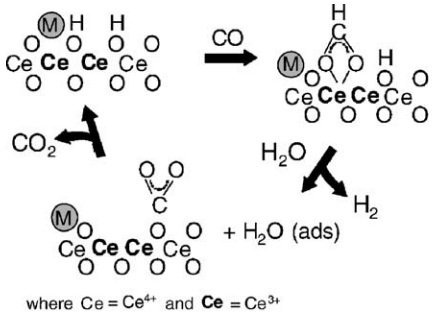
Abstract

A similar degree of surface shell reduction of ceria was obtained for a series of metal/ceria catalysts. Surface formate species were generated by reaction of CO with bridging OH groups associated with the Ce^{3+} defects. Forward decomposition of the pseudo-stable formates was followed in flowing H_2O, leading to the production of surface carbonate species. The forward formate decomposition rate was enhanced changing the promoter from Au to Pt, and by increasing the promoter loading (from 0.5 to 2.5%). Results suggest that formate C–H bond breaking is not only facilitated by H_2O, but it is further enhanced by type and loading of metal promoter. From earlier kinetic isotope effect and isotopic tracer studies, the rate-limiting step of the forward formate decomposition (WGS reaction) was considered to be associated with C–H bond rupture of the formate. The results can explain the promotion in the WGS rates observed for these samples by changing from Au to Pt and by increasing the promoter loading.

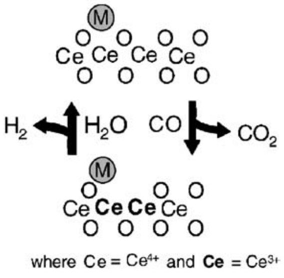
Keywords: Water gas shift; WGS; LTS; Ceria; Pt; Au; Platinum; Gold; Formate; Carbonate

1. Introduction

Past studies have demonstrated that one function of a metal promoter is to facilitate reduction of the ceria surface shell (e.g., [1–15]). The debate continues as to how the WGS mechanism operates and the role of the oxygen deficiencies in the mechanism. Two mechanisms are considered herein, as follows:



Surface formate mechanism



Redox Model

Recently, we found that for a series of well-characterized samples, while Au promoted the surface reduction of ceria to lower temperature than Pt [4,5], ca. 20 times the amount of

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Au/ceria was needed to achieve a similar lightoff curve to Pt/ceria for WGS, on an equivalent loading basis [4], at 250 °C and higher. This indicated that the metallic function probably participates in some way in the surface catalytic mechanism. Many continue to argue in favor of a redox mechanism [6,7]. Although we do not rule out this possibility, it is worthwhile to note that this view is not supported by any of our IR studies carried out in the low temperature regime [4,5,8–14].

Considering the formate mechanism in greater detail, it is clear that the formate decomposition is reactant promoted by H_2O [11,12,15]. Shido and Iwasawa [15] have considered that the role of H_2O is likely to cause a tilting rotation of the formate intermediate, making it amenable to C–H bond rupture. In this contribution, we are attempting to establish if the presence of the metal promoter could also impact the rate of the formate dehydrogenation step. In previous studies, we and others have shown that metal promoter loading and type do impact the WGS rate [4,5,8]. More recently [14], we attempted to determine if the formate dehydrogenation rate was affected by the metal type and loading during thermal decomposition. In that case, the formate C–H bond was cleaved to give the reactants CO and –OH (surface). The decomposition was followed for two loadings – 0.5 and 2.5% – and for two metal promoters – Au and Pt. After appropriate activation, the relative WGS rates at 250 °C followed the order 2.5%Pt > 0.5%Pt > 2.5%Au > 0.5%Au. Interestingly, the thermal decomposition of formate followed precisely the same trend. That work, of course, did not include H_2O. In this study, we examine the rate of the formate forward decomposition to WGS products to determine if the metal can impact decomposition in addition to the promoting effect of water. If so, the results can adequately explain the observed wide differences in catalytic activity observed when the promoter type and loading is varied.

2. Experimental

High surface area ceria was prepared by homogeneous precipitation of cerium nitrate using urea to slowly release the precipitating agent, OH^- and the preparation procedure is reported elsewhere [2,8]. The ceria was dried and calcined in a muffle furnace at 400 °C for 4 h. Nano-sized gold clusters were formed utilizing the sublimation of dimethyl acetylacetonate gold under vacuum, followed by calcination at 250 °C in O_2 to decompose the ligands, and is reported previously [4]. Incipient wetness impregnation (IWI) was utilized to load Pt via the tetraammine platinum nitrate salt [8], and the catalyst was calcined at 350 °C.

Surface area measurements were conducted using a Micromeritics Tristar 3000 gas adsorption analyzer. In each test, a weight of approximately 0.25 g of sample was used. Nitrogen physisorption was performed at its boiling temperature. Hydrogen temperature programmed reduction (TPR) was carried out on unpromoted, Au promoted and Pt promoted catalysts using a Zeton-Altamira AMI-200 unit equipped with a thermal conductivity detector (TCD). Argon was used as the reference gas, and 10%H_2 (balance Argon) was flowed at 30 cm^3/min as the temperature was increased from 50 to 1100 °C.

X-ray absorption near-edge spectroscopy (XANES) spectra were recorded near the Pt, Au and Ce L_{III} edges at the National Synchrotron Light Source located at Beamline X-18b at Brookhaven National Laboratory, Upton, NY and details are reported in earlier work [4,8]. Samples were treated in situ with H_2. Scans were obtained in transmission mode at 50 °C intervals to explore the reduction of not only the Pt or Au promoter component, but also the partial reduction of ceria. To estimate the extent of reduction of ceria, linear combination XANES fits were carried out using Ce^{3+} and Ce^{4+} references.

A Nicolet Nexus 870 was used, equipped with a DTGS-TEC detector. A chamber fitted with ZnSe windows was utilized as the WGS reactor for in situ measurements. Experimental procedures are provided elsewhere [8]. During a run, the catalyst was first activated at 300 °C in hydrogen and then cooled to 130 °C. The only exception was the unpromoted sample, which was activated at 500 °C (see TPR profiles). Formates were generated by CO adsorption, where the flows were maintained at 3.75 cm^3/min CO and 135 cm^3/min N_2. After the pseudo-stabilized formate was generated, the cell was purged with N_2 and a mixture of $H_2O{:}N_2$ was introduced into the cell at 63:135 cm^3/min. Decomposition of the formate as a function of catalyst metal promoter loading and metal type was investigated.

Steady state catalytic activity measurements were conducted in a fixed bed reactor [8] consisting of a 0.5 in. stainless steel tube with an internal thermocouple. For the Pt/ceria catalysts, experiments were conducted using 33 mg of catalyst diluted to 0.4 g with silica. For the less active Au/ceria catalysts, 660 mg of catalyst was used. Conditions were chosen to mimic those of the low temperature shift reactor of a fuel processor, with the exception that CO_2 was not included in the tests. The gas flows were 3.75 cm^3/min CO, 125 cm^3/min H_2O, 100 cm^3/min H_2 and 10 cm^3/min of N_2. Catalysts were activated in hydrogen at 300 °C.

3. Results and discussion

The surface areas were very similar for the catalysts studied, about 120 m^2/g, establishing a control parameter allowing for direct comparison of the impact of metal promoter type and loading. Ceria catalysts are covered by a layer of carbonates. With the DRIFTS and TGA-MS experiments it can observed that the metal promoter helps the removal of a fraction of the carbonates during the surface shell reduction process. The characteristic IR bands for the carbonates are in the 1200–1700 cm^{-1} range. During the reduction process, Type II bridging OH groups (3650 cm^{-1})

have been identified on the surface and the cerium atoms associated with them are Ce^{3+}. Type II OH formation is facilitated by the presence of a metal promoter [8,15] and can be described in two ways: removal of surface capping oxygen atoms and dissociation of H_2O at vacancies, or H_2 dissociation via the metal, with subsequent spillover to ceria [8]. Fig. 1 shows there are two main steps for the reduction of the ceria surface shell, a lower temperature surface reduction step and a higher temperature bulk ceria reduction step. Adding a metal promoter catalyzes the surface shell reduction step [1–15]. Based on equivalent loading by weight, Au promotes the reduction of the ceria surface shell to a lower temperature than that of Pt [3–5]. These results are confirmed by XANES. Determining the degree of reduction of ceria using XANES (Table 1) allows one insight into the temperature of Type II OH group formation and perhaps surface density [8]. Another important finding is that the metal–oxide interaction was surmounted at lower temperature with increasing promoter loading, suggesting that the metal promoter was more easily reduced at higher loadings [4,8], most likely the result of a metal cluster size effect.

The samples for this study were reduced at 300 °C, before being cooled to 130 °C for the water addition, because at this temperature, the extent of the reduction after surface shell reduction was approximately 25%. The only exception to this treatment was for the unpromoted ceria, which required a higher temperature of reduction (500 °C from TPR profiles). Even if the extents of ceria reduction observed by XANES were similar, the WGS rates varied, and depended on both metal loading and metal type (Table 2). Increasing the loading led to improved CO conversion on a per gram basis. Also, on an equivalent metal loading basis, the Pt catalysts were far more active than Au [4], as discussed previously.

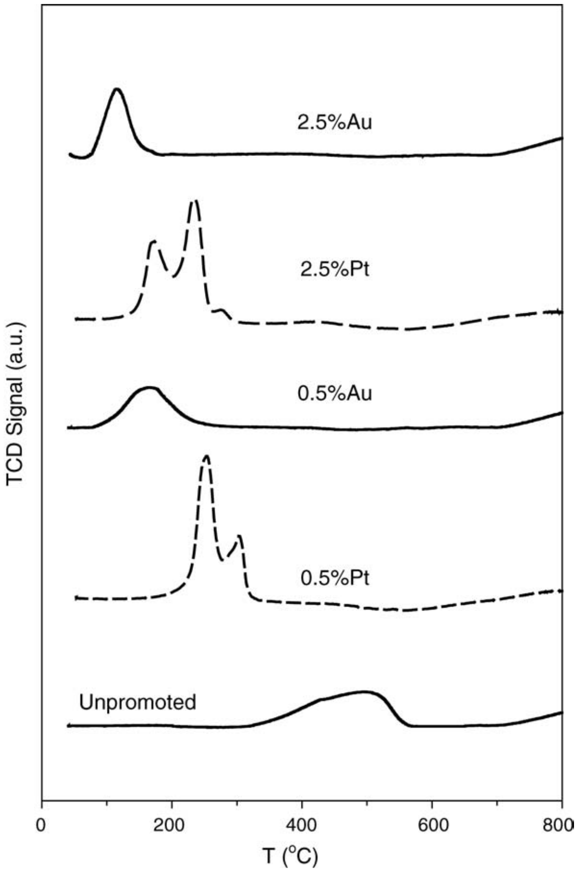

Fig. 1. Hydrogen TPR profiles.

Table 1
LC XANES fits (H_2 flow with temperature)

T (°C)	0.5%Au		2.5%Au		0.5%Pt		2.5%Pt	
	Ce^{4+}	Ce^{3+}	Ce^{4+}	Ce^{3+}	Ce^{4+}	Ce^{3+}	Ce^{4+}	Ce^{3+}
50	99.2	0.8	99.5	0.5	98.9	1.1	99.1	0.9
100	97.9	2.1	98.7	1.3	97.8	2.2	97.1	2.9
150	86.8	13.2	79.1	20.9	–	–	–	–
200	78.7	21.3	76.5	23.5	96.5	3.5	89.3	10.7
250	77.0	23.0	75.1	24.9	92.5	7.5	77.9	22.1
300	74.7	25.3	75.2	24.8	76.0	24.0	75.9	24.1

Table 2
CO conversion during WGS

Catalyst	CO Conversion		
	250 °C	275 °C	300 °C
660 mg cat. (GHSV: 21705 cm^3/h g cat)			
Unpromoted ceria	2.1	3.2	6.2
w/0.5%Au	8.7	14.3	17.4
w/2.5%Au	34.3	52	58.3
33 mg cat. (GHSV: 434090 cm^3/h g cat)			
Unpromoted ceria	4.3	4.8	5.5
w/0.5%Au	10.4	14.9	19.9
w/2.5%Au	36.4	51.1	64.4

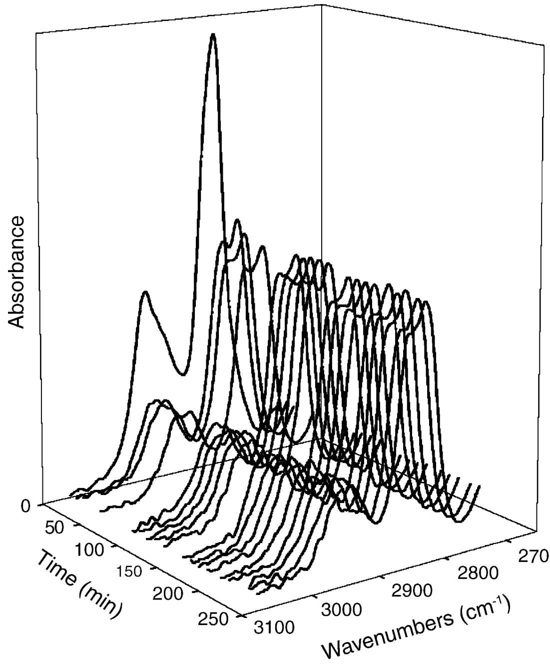

Fig. 2. Unpromoted ceria—response of the stabilized formate to H_2O at 130 °C.

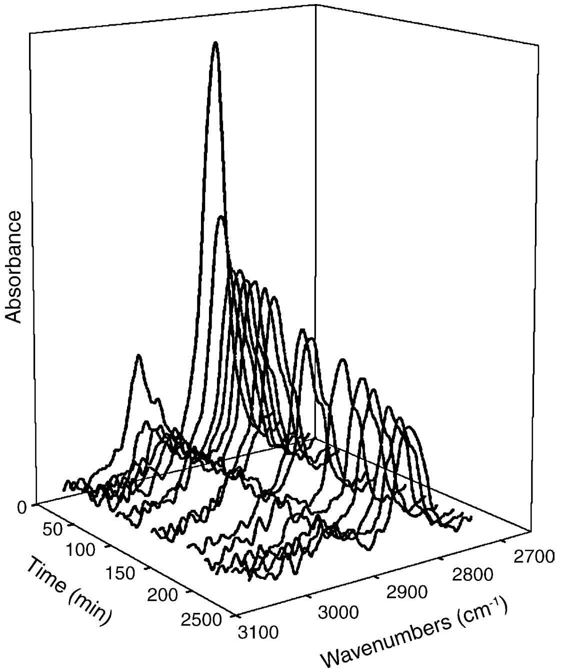

Fig. 3. 0.5%Au/ceria—response of the stabilized formate to H_2O at 130 °C.

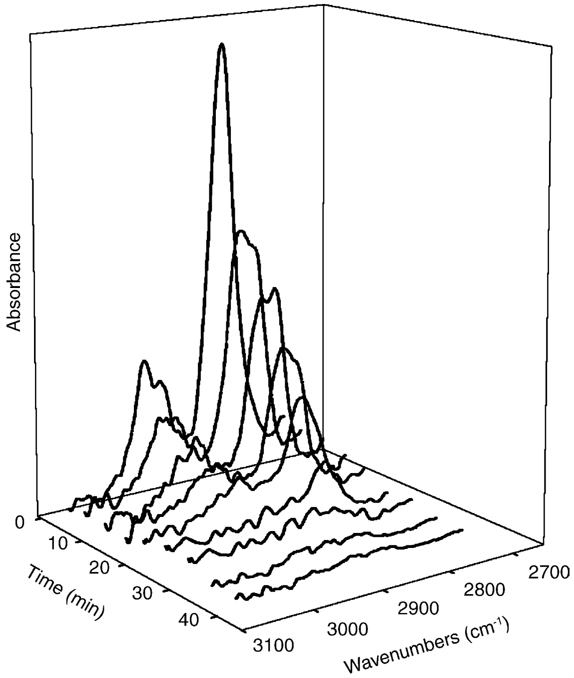

Fig. 5. 0.5%Pt/ceria—response of the stabilized formate to H_2O at 130 °C.

While surface formates are quite stable at low temperature, they decompose in inert gas flow to CO and –OH [11,15] (i.e., reverse decomposition). For a 1%Pt/ceria catalyst, decomposition was complete in 6–8 min at 300 °C [11]. Yet when H_2O is introduced, formates decompose rapidly forming H_2 and unidentate carbonate, the precursor to CO_2 product [11]. With H_2O (for 1%Pt/ceria), formates decomposed in about 8 min at 140 °C [11]. The promoting effect of H_2O on the rate is why H_2O appears in the transition state of the formate decomposition step [15], proposed to be the rate-limiting step from an observed kinetic isotope effect [10,11,15] and isotope tracer studies [12]. Here, we wish to determine if the metal type and loading play an additional promotion from the standpoint of formate C–H bond breaking during decomposition by H_2O. It is very difficult to assess the impact of the metal promoter on the formate

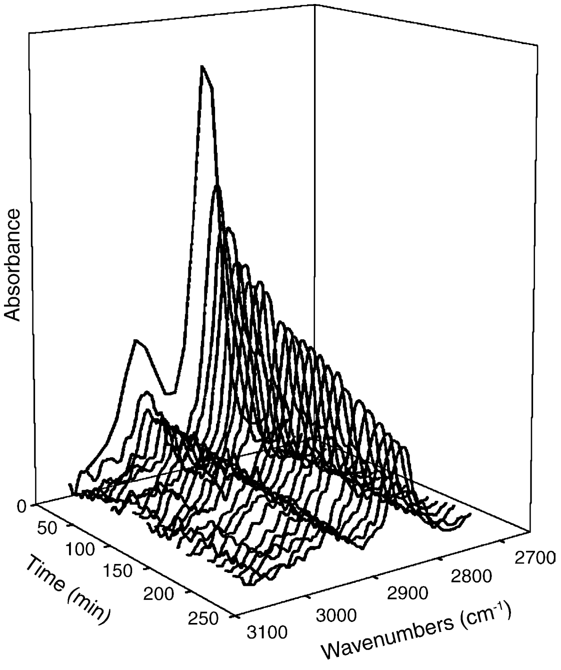

Fig. 4. 2.5%Au/ceria—response of the stabilized formate to H_2O at 130 °C.

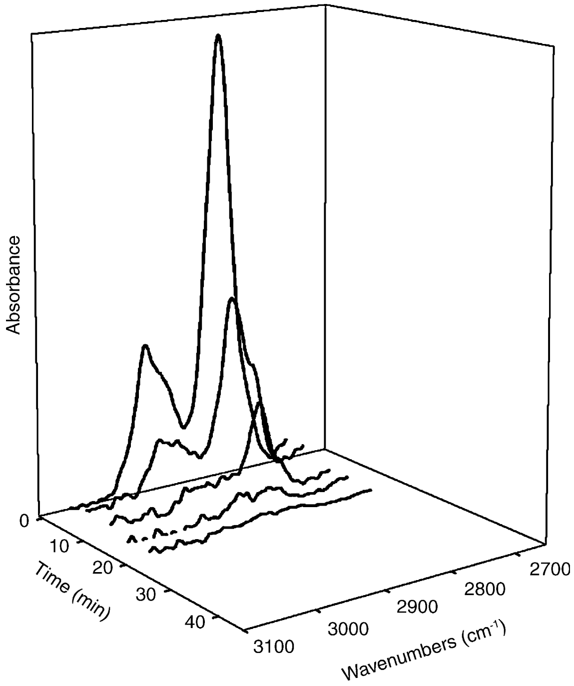

Fig. 6. 2.5%Pt/ceria—response of the stabilized formate to H_2O at 130 °C.

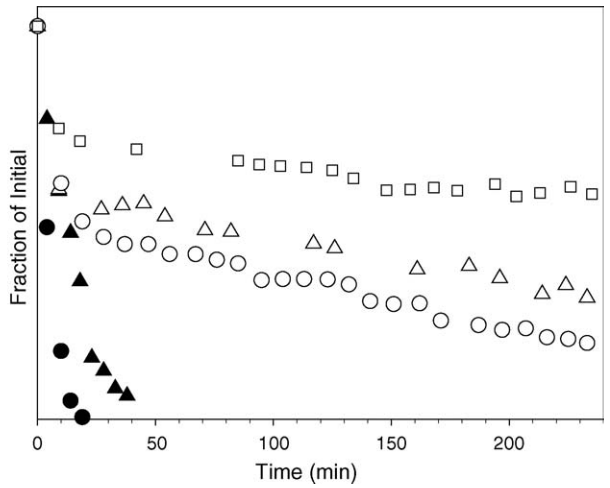

Fig. 7. Ceria catalysts—response of the stabilized formate to H_2O at 130 °C. Unpromoted ceria (open squares) activated at 500 °C. Metal/ceria catalysts include: (filled circles) 2.5%Pt/ceria; (filled triangles) 0.5%Pt/ceria; (open circles) 2.5%Au/ceria; and (open triangles) 0.5%Au/ceria.

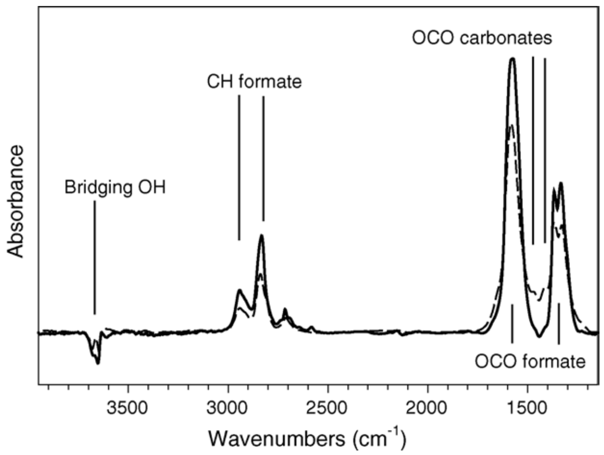

Fig. 8. Unpromoted ceria—(solid) CO adsorption and (dashed) after flowing H_2O from 240 min at 130 °C (purged in N_2). Activated in H_2 (500 °C).

decomposition rate when H_2O is present at normal WGS temperatures, since the formate decomposes so rapidly in the presence of steam [11,12,15]. Therefore, to test the promoting effect of the metallic function on the forward formate decomposition rate, we are monitoring in this work, the forward decomposition (to surface carbonate species) at 130 °C. The implication is that, if the forward decomposition rate of formate is dependent on the metal type and loading, this should also be reflected in the WGS rate during reaction testing.

Figs. 2–7 show the response of the formate during forward decomposition in H_2O. In the 3-D plots, the CH band of the formate is used to establish the formate decay rate (3060–2720 cm^{-1} region). A comparison of the formate decay rates for all the catalysts is depicted in Fig. 7. The formate decomposition rate was found to be impacted by the metal type, as well as the loading. The Pt catalysts exhibit far greater activity for forward formate decomposition than the Au catalysts [4,8], and this activity increases with the loading, which is consistent with WGS results. Figs. 8–10 show a comparison of the initial spectrum after CO adsorption with one after the H_2O assisted formate decomposition experiment. In each case, after reduction of ceria, Type II bridging OH groups are generated (3650 cm^{-1}). These react with CO to produce formates, with identifying bands including C–H stretching bands at ca 2845 and 2950 cm^{-1} and the asymmetric and symmetric stretching characteristic of the OCO vibrations at ca. 1580 and 1350 cm^{-1}, respectively. After the H_2O treatment, formate bands have disappeared completely for the Pt promoted catalysts (lack of C–H stretching bands), while those of carbonates have been formed (OCO bands in the range 1250–1560 cm^{-1}). Very little carbonate is formed after 240 min for the unpromoted ceria, while formates remain with considerable intensity. The Au/ceria catalysts fall between the two.

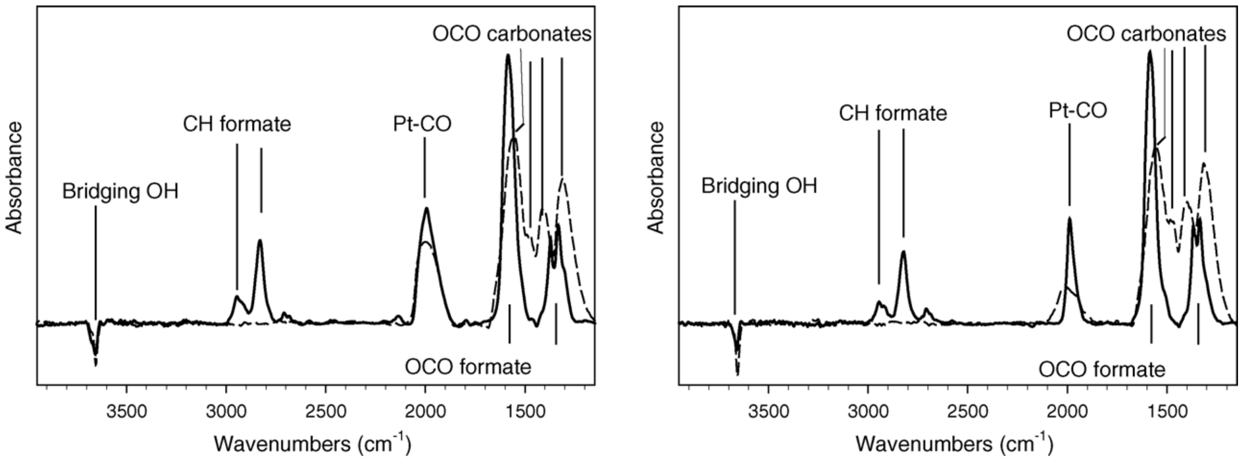

Fig. 9. (Left) 2.5%Pt/ceria, (right) 0.5%Pt/ceria—(solid) after CO adsorption and (dashed) after flowing H_2O for 20 min (2.5%Pt/ceria) or 40 min (0.5%Pt/ceria) at 130 °C, purged in N_2. H_2 activation (300 °C).

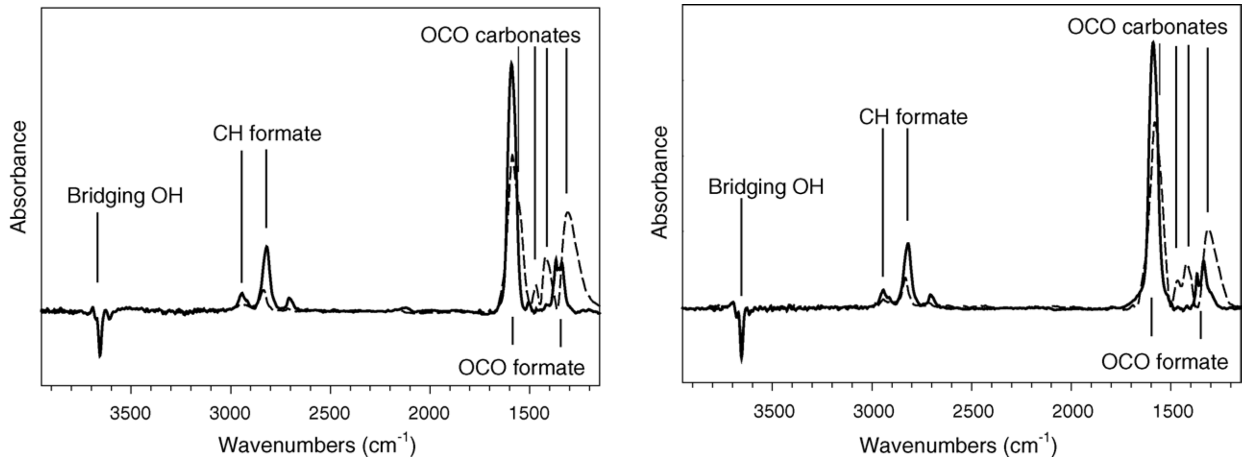

Fig. 10. (Left) 2.5%Au/ceria, (right) 0.5%Au/ceria—(solid) after CO adsorption and (dashed) after flowing H_2O for 240 min (includes both catalysts) at 130 °C, purged in N_2. H_2 activation (300 °C).

The results suggest that the metal likely provides a conduit for H_2 removal during WGS. This is not surprising, since the metallic function typically is utilized for hydrogenation/dehydrogenation reactions. It is important to consider that the promoting impact of the metal is in addition to that of H_2O. Recently, we carried out thermal decomposition of formates over the same catalysts [14] and found a similar trend in rate: 2.5%Pt $>$ 0.5%Pt $>$ 2.5%Au $>$ 0.5%Au $>$ unpromoted. However, the decomposition was in the reverse direction to CO and –OH. Thermal decomposition experiments took place at 240 °C over a similar timeframe to the experiments conducted here. Yet now the temperature is 130 °C, indicating clearly that H_2O imparts an accelerating affect on the decomposition rate, as proposed by Shido and Iwasawa [15]. The promoting effect of H_2O was suggested to be due to a favorable tilting rotation of formate, leading to enhanced forward formate decomposition. The metallic function may also facilitate C–H bond breaking of the formate, most likely via metal-catalyzed abstraction of hydrogen during the formate dehydrogenation step. This follows from two considerations. First, Pt is more active intrinsically [16] than Au for dehydrogenation. Secondly, considering that the formate is likely a mobile species on the surface, it follows that increasing the loading of metal, and therefore, the number of metal particles, should favorably impact the turnover rate of formate on the catalyst surface.

4. Conclusions

After ensuring that the extent of surface ceria shell reduction was similar among a series of metal/ceria catalyst, formates were generated by reaction of CO with the Type II bridging OH groups. Forward decomposition by H_2O of the pseudo-stabilized formate was enhanced by switching from Au promoter to Pt. Likewise, an increase in the formate turnover rate was observed by increasing the promoter loading from 0.5 to 2.5% by weight (both Pt and Au). Carbonate bands were observed after the decomposition, confirming the decomposition was in the forward direction. The results suggest that formate C–H bond rupture is, in addition to the promoting effect of H_2O previously ascertained by Shido and Iwasawa, impacted by the metallic function of the promoter. Therefore, since the rate-limiting step of the forward WGS reaction is strongly suggested, based on earlier kinetic isotope effect and isotopic tracer studies, to be associated with C–H bond breaking in the formate intermediate, the results can explain the enhancement in WGS rates observed by changing from Au to Pt and by increasing the loading.

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