Isotopic Transient Studies of Sodium Promotion of Pt/Al₂O₃ for the Water-Gas Shift Reaction

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ABSTRACT

The promotional effect of sodium on Pt/Al₂O₃ catalysts for the water-gas shift (WGS) reaction was investigated with *operando* FTIR during steady-state and isotopic transient experiments. The highest turnover frequency (TOF) promotion per surface Pt occurred on a 0.82 wt.% Pt/Al₂O₃ catalyst with a 30:1 molar ratio of Na:Pt. This catalyst exhibited a TOF of 0.35 s⁻¹ at 250 °C and 7% CO, 11% H₂O, 9% CO₂, 37% H₂ compared to 0.43 × 10⁻² s⁻¹ on Pt/Al₂O₃. *Operando* IR revealed that Na addition modifies CO adsorption on Pt to create more strongly bound, multiply-bonded CO species at 1768 cm⁻¹ and 1697 cm⁻¹ compared to predominantly linear CO on Na-free Pt/Al₂O₃ at 2060 cm⁻¹. Transient experiments with ¹²CO/¹³CO isotope switches showed that the number of carbon-containing active intermediates increased from less than 1% of the surface Pt for Na-free Pt/Al₂O₃ to nearly 100% of the surface Pt for 20Na:Pt/Al₂O₃, which indicates that only a small fraction of the Pt surface on the Na-free samples participates in the WGS reaction. From time-resolved IR spectra during transient WGS with ¹²CO/¹³CO and ¹²CO₂/¹³CO₂ isotope switches, we propose that surface formate species are spectators for all Na-promoted Pt/Al₂O₃ catalysts under these WGS conditions. The results suggest that Na promotes Pt/Al₂O₃ for WGS by modifying the local electronic properties of Pt and creating new H₂O activation sites, which provides greater availability of surface OH/H species to react with nearly all CO on the metallic Pt surface through a non-formate pathway.

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1. Introduction

There is a general consensus that the most active WGS catalysts operate in a bi-functional manner with contributions from both the dispersed metal and the support through either a red-ox mechanism [1-12] or an associative mechanism involving formate [13-19] or carboxyl [20-22] intermediate species. In the red-ox mechanism, CO adsorbs on the dispersed metal where it can either diffuse to the metal-support interface [1, 2, 9-12], or react on the surface with labile oxygen from the support to form CO₂ [3-8]. The support is re-oxidized by water and forms H₂ in the process. During the associative reaction pathway, the support dissociates water to form terminal hydroxyl groups at the interface near the metal. These species can then interact with CO adsorbed on the metal side of the interface or migrate onto the metal to create a formate [13-19] or carboxyl [20-22] intermediate. These reactive intermediate species decompose to produce CO₂ and H₂.

Several recent studies report substantial improvement of the TOF for WGS catalysts by the use of alkali metals (Na, K, and Li) as promoters [16, 17, 19, 23-29]. The role of the alkali in the reaction pathway is attributed to either: (i) a way to create sites in close contact with the dispersed metal by modifying the support properties and facilitating the formation of hydroxyl groups [23], (ii) weakening the formate C-H bonds and enhancing the rate of formate decomposition [16, 17, 26, 27], or (iii) providing a film of alkali-OH on the surface to increase the number of H₂O activation sites, as suggested by Kusche et al. [29]. Another possibility, recently proposed by Yang et al. [28], is that the alkali metal disperses ionic Pt species on the catalyst surface as single-atom active sites. However, Ding et al. [30] suggest that only Pt nanoparticles are active for WGS on both alkali-free and alkali-promoted Pt catalysts while single-atom species are spectators.

The use of *operando* IR and isotopic transient experiments is a powerful technique for examining the nature of alkali promotion and gaining insight into the WGS reaction mechanism. These analytical tools combine the evaluation of adsorbate bonding and kinetic performance in a

single experiment under reaction conditions. By introducing an isotopic label into the reactor feed stream via a step change (switch), it is possible to detect the time scale of the evolution of isotopically labeled products and correlate them with evolution of isotopically labeled surface active species as identified in time-resolved FTIR. When the times required for exchange of the surface active species and isotopically labeled product are comparable, it is possible that the monitored species is an intermediate involved in the reaction pathway [31, 32]. Additional information that can be obtained from isotopic transient experiments includes the concentration of adsorbed active intermediates, coverages of the total potential sites available, and surface lifetimes. More details of the fundamentals of the technique can be found elsewhere [33-35]. We have recently developed an economical plug-flow *operando* IR cell [36] with an estimated dead volume of the empty cell around 0.2 cm³. This cell is easy to operate and allows for measurement of intrinsic kinetic information on the reactivity of adsorbed surface species during isotope switching.

In a recent study by Jacobs et al. [18], isotopic transient experiments and diffuse reflectance IR (DRIFTS) were applied to Na-promoted and non-promoted Pt/ZrO₂ to determine whether surface formates are reactive intermediates. They concluded that formate species are likely intermediates for WGS based on finding that these isotopically labeled surface species evolve on a similar timescale with ¹³CO₂ and that their coverage decreases with increasing alkali content on the catalyst. Other experimental evidence shows that the alkali component may weaken the C-O bond [37-39], or that there may a direct interplay with alkali and CO that weakens the noble metal-carbon bond [40]. Based on these findings, along with previously reported results by Pazmiño et al. [24] for alkali-promoted Pt/Al₂O₃, the focus of this investigation is to combine *operando* transmission infrared spectroscopy (IR) and isotopic transient experiments to further understand the underlying reaction pathway and quantify the abundance of carbon-containing active species involved in the WGS reaction by Na-promoted Pt/Al₂O₃. We observed that the addition of Na to Pt/Al₂O₃ modifies the adsorption of CO on Pt from primarily linear CO to multiply-bonded and linear CO on Pt sites near Na. Also, the number of carbon-containing active intermediates increases to nearly 100% of surface Pt on Na-promoted samples compared to non-promoted Pt/Al₂O₃. Furthermore, the results from transient experiments with isotope switching suggest that the majority of surface formates are spectator species for WGS on these catalysts.

2. Experimental Methods

2.1. Catalyst Preparation and Characterization

Details of catalyst preparation, platinum surface area measurements by H₂ chemisorption, and Pt and Na loadings by ICP are described elsewhere for the Na-promoted and non-promoted Pt/Al₂O₃ catalysts [24]. The H₂ uptake values for the samples used in the present study are shown in Table S1. The incipient wetness impregnation (IWI) method was used with commercially available high-surface-area Al₂O₃ ($100 \pm 15 \text{ m}^2 \text{ g}^{-1}$, Evonik) and an aqueous solution of (NH₃)₄Pt(NO₃)₂ to obtain 0.82 wt.% Pt loading. Next, the catalysts were dried in vacuum at 60 °C for 12 h. Then, alkali was deposited through a second IWI with a solution of NaNO₃ that was prepared in accordance to the desired Na:Pt molar ratio. After a second drying cycle, the catalysts were calcined in air at 250 °C for 3 h. Finally, the catalysts were cooled to room temperature in He and reduced in H₂ according to the following temperature cycle: (i) ramp from RT to 150 °C at 10 °C min⁻¹, hold at 150 °C for 30 min; (ii) ramp to 200 °C at 2 °C min⁻¹, hold at 200 °C for 30 min; (iii) ramp to 300 °C at 2 °C min⁻¹, hold at 300 °C for 2 h; (iv) purge with He at 300 °C for 30 min and cool to RT in He.

2.2. Operando IR and Isotopic Transient Experiments

All IR spectra were collected by using a Bruker Vertex 70 FTIR at a resolution of 4 cm⁻¹ and averaging the data over 100 scans for the background and 50 scans for the sample under steady-state WGS conditions. The IR background spectra for Na-promoted and non-promoted Pt/Al₂O₃ catalysts were collected under 11% H₂O in a He/Ar mixture (50 ml min⁻¹) at each reaction temperature. Spectral measurements during isotopic transient experiments were taken at a resolution of 4 cm⁻¹ in rapid scan mode, which collects data at a rate of approximately 8 spectra

per second. The FTIR transmission cell is composed of a cell body, sample holder, and heater block; the design of which is described in detail elsewhere [36]. The IR cell and gas delivery system are designed to provide a low dead volume with a 95% signal decay time of less than 1.5 s for a step change in gas concentrations at a flow of 50 ml min⁻¹. The 304 SS sample holder consists of two disks with a 1.5 cm diameter hole through the center for the IR beam to pass through along with a 2 cm diameter recess cut around the hole to hold the self-supporting catalyst wafer between the disks. The sample holder also contains inlet and outlet channels to direct the gas flow over the catalyst wafer. Between 65 mg to 85 mg of catalyst sample is pressed into a 2 cm-diameter self-supporting wafer, which is placed between the sample holders and carefully lowered into the cell body. A retainer ring is placed on top of one side of the sample holder, followed by a CaF₂ window, which is placed inside of the retainer ring and directly on top of the sample holder. A custom-made graphite ferrule is placed around the CaF₂ window and in direct contact with the retainer ring to produce a three-way seal inside of the cell. The ferrule backer is set on top of the graphite ferrule and secured with 8 set screws. This method of assembly is repeated for the reverse side of the IR cell with the exception of the sample holder and retainer ring.

The assembled IR cell is placed in the heater block that rests inside the chamber of the Bruker Vertex 70 FTIR and is designed to produce a uniform temperature throughout the cell. Purified air (i.e. H₂O and CO₂ free) is continuously fed to custom-made beam covers throughout the entire IR beam path on either side of the heater block in order to maintain a clean background. The gas delivery system consists of seven mass flow controllers (MFCs), three of which feed directly to the IR cell and deliver H₂, CO₂, and He. Prior to entering the IR cell, these gases are passed through a temperature-controlled water saturator in order to introduce water into the reaction mixture at a desired concentration [36]. The four remaining MFCs feed into a 4-way, fast switching valve (VICI, 2 position, 4 port switching valve, model number A4C4WE), for selection of both CO and Ar (internal standard), or ¹³CO and Ne (tracer) prior to joining the remaining reaction gases, which are then passed into the IR cell. During CO₂ re-adsorption isotopic transient experiments, the 4-way, fast switching valve is used for selection of CO₂ and Ar, or ¹³CO₂ and Ne. The H₂, CO, and He are then passed through the temperature-controlled water saturator prior to entering the IR cell.

The gas feed composition for the WGS reaction was 37% H₂, 7% CO, 9% CO₂, 11% H₂O, 10% Ar, and He as balance at a total flow rate of 50 ml min⁻¹. All feed and effluent lines on the IR cell are heat-traced to prevent condensation of the water vapor. The effluent gas mixture was sent to an HP 5890 Series II Plus gas chromatograph (GC) equipped with a Carboxen 1000 column and measured by a thermal conductivity detector (TCD) for steady-state kinetic analysis. For isotopic transient experiments, an Agilent 5973 N mass spectrometer (MS) was used to measure changes in the gas-phase concentrations of isotopically labeled and non-labeled gases. Changes in the gas-phase composition were measured by MS at a collection rate of 15 scans per second for *m/z* from 15 to 50. Simultaneously, IR spectra were collected in rapid scan mode at a rate of 8 scans per second to capture changes in adsorbed surfaces species during WGS. Since it is crucial for proper data collection to maintain a stable operating pressure and minimize pressure swings during gas switching (i.e. CO + Ar and ¹³CO + Ne), we used two SS bellows-sealed metering valves (Swagelok, SS-4BMW) along with two pressure transducers, (MKS, baratron pressure transducer, model number: 750B13TCD2GA) to regulate and monitor the pressures of the feed to the 4-way fast switching valve and the reactor exhaust.

3. Results

3.1. Reactor Validation

The Koros-Nowak test was used in the previous PFR reactor studies [24] for Na-promoted and non-promoted Pt/Al₂O₃ catalysts to certify the absence of heat and mass transport limitations. Additionally, to ensure an accurate representation of the kinetic data, the temperature gradient between the sample wafer and CaF₂ window on the IR cell was shown to be ± 2 °C from 100 °C to 350 °C [36]. By performing a switch between two inert tracers at 50 ml min⁻¹ total flow, 10% Ar in He and 10% Ne in He, the gas hold-up time for isotopic transient experiments was verified to be less than 1.5 s for 95% signal decay in the MS response curve (Fig. S1).

The total moles of CO adsorbed on Pt was determined by ¹²CO/¹³CO isotope switching to validate previous CO chemisorption measurements [24], as shown in Table S2. To compute the CO uptake from the isotope switching data, the integrated area of the normalized MS signal between Ne and ¹³CO (i.e. rising curve) was multiplied by the flow rate of CO at standard

temperature and pressure (STP), and averaged with the product of the integrated area of the normalized MS signal between Ar and CO (i.e. decaying curve) and the flow rate of CO at STP as shown in Fig. S1.

The same 0.82 wt.% Pt/Al₂O₃ and Na-promoted Pt/Al₂O₃ catalysts used in the previous study of alkali promotion [24] were tested in the *operando* IR reactor to show that the kinetic measurements obtained with the IR cell are similar to those from a regular laboratory PFR. In order to compare the data collected from the two different reactors, the WGS rates measured in the PFR were normalized to WGS conditions at 7% CO, 11% H₂O, 9% CO₂, and 37% H₂ according to the power-law expression:

$$r = k_f [CO]^a [H_2O]^b [CO_2]^c [H_2]^d (1 - \eta) \quad (1)$$

$$k_f = A \exp\left(\frac{-E_{app}}{RT}\right) \quad (2)$$

$$\eta = \frac{[CO_2][H_2]}{K_{eq} [CO][H_2O]} \quad (3)$$

where r is the rate ((mole H₂) (mole Pt⁻¹) s⁻¹); k_f is the forward rate constant; a , b , c , and d are the apparent reaction orders with respect to concentrations of CO, H₂O, CO₂, and H₂, respectively; η is the approach to equilibrium; A is the pre-exponential factor; E_{app} is the apparent activation energy (kJ mole⁻¹); R is the universal gas constant (kJ mole⁻¹ K⁻¹); and T is the reaction temperature (K). This interpolation was carried out because the WGS conditions in the PFR used 22% H₂O instead of the 11% H₂O used in the *operando* reactor. However, in the PFR the H₂O concentration was varied from 11% to 34% in order to determine the apparent reaction order. Thus, the interpolation from 22% H₂O to 11% H₂O is valid since the WGS rates were determined within this range of concentrations. The measured apparent reaction orders for CO, H₂O, CO₂, and H₂ were determined by Pazmiño et al. [24] and are summarized in Table S3 for the catalysts used in the present study.

The kinetic data for the two different reactors are summarized in Table 1 and the Arrhenius plots obtained from the IR cell are shown in Fig. 1. The rate measured on non-promoted Pt/Al₂O₃ at 250 °C was 0.15×10^{-2} (mole H₂) (mole Pt⁻¹) s⁻¹ for the *operando* reactor compared to 0.12×10^{-2} (mole H₂) (mole Pt⁻¹) s⁻¹ as measured in the regular PFR. The highest WGS rate observed was on a Na-promoted catalyst with a 30:1 molar ratio of Na:Pt, which

measured 7.6×10^{-2} (mole H₂) (mole Pt⁻¹) s⁻¹ for the *operando* reactor versus 7.5×10^{-2} (mole H₂) (mole Pt⁻¹) s⁻¹ in the PFR. The CO conversion (X_{CO}) ranged from 1.1% for 0.82 wt.% Pt/Al₂O₃ to 12.4% for 30Na:Pt/Al₂O₃, and the approach to equilibrium (η) ranged from 1.2×10^{-2} for 0.82 wt.% Pt/Al₂O₃ to 0.9×10^{-2} for 30Na:Pt/Al₂O₃ at these reaction conditions. Apparent activation energies, as determined by using the *operando* reactor, ranged from 67 ± 4 kJ mole⁻¹ for non-promoted Pt/Al₂O₃ to 83 ± 6 kJ mole⁻¹ for 60Na:Pt/Al₂O₃. The kinetic results and Arrhenius plots show a promotion of the WGS rate per total mole of Pt with increasing Na content up to a molar ratio of 30Na:Pt.

Table 1

WGS kinetics for 0.82 wt.% Pt/Al₂O₃ and Na-promoted catalysts.

Catalyst	WGS rate ^a (IR cell) / 10^{-2} (mole H ₂) (mole Pt ⁻¹) s ⁻¹	WGS rate ^b (PFR) / 10^{-2} (mole H ₂) (mole Pt ⁻¹) s ⁻¹	Pt disp. ^c / %	TOF ^d (IR cell) / s ⁻¹	E_{app} (IR cell) / kJ mole ⁻¹
Pt/Al ₂ O ₃	0.15	0.12	35	0.43×10^{-2}	67±4
12Na:Pt/Al ₂ O ₃	1.5	1.2	23	6.6×10^{-2}	83±2
20Na:Pt/Al ₂ O ₃	6.2	4.8	26	0.24	82±3
30Na:Pt/Al ₂ O ₃	7.6	7.5	21	0.35	77±4
60Na:Pt/Al ₂ O ₃	3.1	3	15	0.21	83±6

^a WGS rates measured at 250 °C with 11% H₂O, 7% CO, 37% H₂, 9% CO₂, 10% Ar, balance He.

^b WGS rates extrapolated at 250 °C to 11% H₂O, 7% CO, 37% H₂, 9% CO₂, 10% Ar, balance He.

^c Pt dispersion measured by H₂ chemisorption on the same catalyst used after WGS reaction in regular PFR.

^d TOF based on the Pt dispersion measured on the same catalyst used after WGS reaction in regular PFR.

Fig. 1. Arrhenius plots for 0.82 wt.% Pt/Al₂O₃ (●) and corresponding Na-promoted catalysts: 12Na:Pt/Al₂O₃ (□), 20Na:Pt/Al₂O₃ (▼), 30Na:Pt/Al₂O₃ (△), and 60Na:Pt/Al₂O₃ (◆). WGS rates were measured at 250 °C with 11% H₂O, 7% CO, 37% H₂, 9% CO₂, 10% Ar, balance He for catalysts in the IR cell.

3.2. Operando Transmission FTIR

In addition to the kinetic data obtained under steady-state WGS conditions, information on the surface species present on the catalysts was collected and analyzed by using FTIR. The various bands from 2650 cm⁻¹ to 3000 cm⁻¹ were attributed to different formate (HCOO) vibrational modes. Bands in the IR spectra from 1650 cm⁻¹ to 2077 cm⁻¹ were attributed to CO adsorbed on various Pt sites while those from 1300 cm⁻¹ to 1650 cm⁻¹ in the spectra were due to the various vibrational modes of formate and carbonate-like species [14, 15, 19]. IR bands in the 2250 cm⁻¹ to 2400 cm⁻¹ region were assigned to gas-phase CO₂. Integration of the IR band area in each region was performed by using CasaXPS (version 2.3.15) curve-fitting software. Each band was fit by using a pure Gaussian curve shape and optimization of the band position, area, and full width at half-maximum (FWHM) was performed through Levenberg-Marquardt iterations by minimizing the root mean square (RMS) error.

As shown in Fig. 2a., linear and multiply-bonded CO species were observed in the regions of 1900 cm⁻¹ to 2077 cm⁻¹ and 1700 cm⁻¹ to 1900 cm⁻¹, respectively [41-48]. Upon adding sodium to Pt/Al₂O₃ at molar ratios up to 30Na:Pt, the intensity of the linear CO band at

1972 cm^{-1} [4, 48] increased along with multiply-bonded CO bands at 1830 cm^{-1} and 1784 cm^{-1} , which may correspond to CO adsorbed on Pt in bridging and tri-fold configurations, respectively, [41-43]. The main feature of the formate C-H region is the $\nu(\text{C-H})$ stretching mode centered at 2907 cm^{-1} , which red shifted by 7 cm^{-1} upon increasing Na content from 0Na:Pt to 20Na:Pt as shown in Fig. 2b.

Fig. 2. IR spectra under WGS conditions (7% CO, 11% H₂O, 37% H₂, 9% CO₂) at 250 °C: (a) showing linear CO on Pt (CO_L) as well as increased intensities of linear, low frequency CO (CO_{LLF}), bridging CO at 1768 cm^{-1} , and tri-fold CO at 1697 cm^{-1} (CO_{B+T}) upon Na addition, as shown by the rightmost dashed line; (b) appearance of new formate C-H stretching modes at 2794 cm^{-1} , as shown by the rightmost dashed line, and 2696 cm^{-1} .

The deconvolution of CO bands on Pt is shown in Fig. 3. The predominant $\nu(\text{CO})$ stretching frequencies on 0Na:Pt (Fig. 3a) have been assigned to linear CO adsorbed on Pt terrace (2077 cm^{-1}) and step (2059 cm^{-1}) sites [44, 45]. The bands at 2040 cm^{-1} and 2010 cm^{-1} are attributed to linear CO adsorbed on supported Pt catalysts [46, 47]. The lower frequency adsorbed CO band at 1972 cm^{-1} , whose intensity increases upon increasing Na content (Fig.

3b,c), has been observed by others and is assigned to CO adsorbed on sites of exceptional electron-donating properties [4, 48], but may also be attributed to CO on Pt sites near the alkali metal [49]. The band that appears at 1913 cm^{-1} upon Na addition has been assigned to bridging CO on Pt terrace sites [50], but could also indicate CO influenced by interaction with Na. In recent studies of CO oxidation and WGS on single Pt atom sites, researchers have observed CO on $\text{Pt}^{\delta+}$ from 2080 – 2100 cm^{-1} [51, 52]. It is worthwhile to note that no bands from CO adsorbed on $\text{Pt}^{\delta+}$ were observed under our WGS conditions for both Na-free and Na-promoted $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts.

Fig. 3. Curve-fit of IR spectra recorded in the 1600 – 2200 cm^{-1} region ($\text{CO}_{(\text{g})}$ background subtracted) under WGS conditions (7% CO , 11% H_2O , 37% H_2 , 9% CO_2) at 250 °C: (a) 0Na:Pt/ Al_2O_3 ; (b) formation of bridging CO band on Pt terraces at 1913 cm^{-1} , bridging CO at 1769 cm^{-1} , and tri-fold CO at 1692 cm^{-1} on 12Na:Pt/ Al_2O_3 ; (c) increase in area of bridging and tri-fold CO bands on 30Na:Pt/ Al_2O_3 .

Multiply-bonded CO at 1830 cm^{-1} and 1784 cm^{-1} [41-43] increased in intensity and red-shifted to lower frequencies upon increasing Na content, which was also observed by Ding et al. [30] for Na-Pt/ SiO_2 . In a previous study by Crowell et al. [38], thermal desorption (TDS) and high resolution energy loss (HREELS) spectroscopies were used to detect a shift in site occupancy from linear to bridging when CO is co-adsorbed with potassium on Pt (111). They proposed that the presence of alkali lowers the work function of the Pt surface such that the most

energetically favorable site for CO adsorption changes from atop to bridging, thus setting a precedent for a change in surface composition altering the preferred CO adsorption site.

The deconvoluted and normalized IR band areas for adsorbed CO surfaces species were compared to the WGS TOF as shown in Fig. 4. The integrated areas for the bridging and tri-fold CO bands on Pt at 1830 cm^{-1} and 1784 cm^{-1} , respectively, increased along with an increase in the WGS rate. Additionally, there was a positive correlation between the increase in linear CO adsorbed on Pt sites near Na (1972 cm^{-1}) and the WGS rate. The opposite trend was observed for the integrated areas of the linear CO bands on supported Pt (2040 cm^{-1}) and Pt step sites (2059 cm^{-1}), which decreased as the WGS rate increased due to the promotional effect of Na.

Fig. 4. Comparison of WGS TOF (250 °C with 11% H₂O, 7% CO, 37% H₂, 9% CO₂, 10% Ar, balance He) with normalized IR band areas for linear CO on supported Pt (red ●), linear CO on Pt steps sites (green ▲), linear CO on Pt sites near Na (white □), and bridging (including tri-bond) CO on Pt (blue ■).

Deconvolution of the 2700 cm^{-1} to 3000 cm^{-1} region is shown in Fig. 5. Increasing the alkali content also resulted in the formation of two new bands which appear at 2793 cm^{-1} on 12Na:Pt/Al₂O₃ and at 2698 cm^{-1} on 20Na:Pt. Deconvolution of the 2700 cm^{-1} to 3000 cm^{-1} region revealed the IR bands characteristic of $\nu(\text{C-H})$ and $\delta(\text{C-H}) + \nu_s(\text{OCO})$ vibrational modes of formate species (2999, 2968, 2947, 2907, 2891, and 2867 cm^{-1}) [1, 53] as shown in Fig. 5. The areas of the 2793 cm^{-1} and 2698 cm^{-1} bands increased at higher Na content along with an increase in the WGS rate (Table S4).

The asymmetric, $\nu_{as}(\text{OCO})$, and symmetric, $\nu_s(\text{OCO})$, formate OCO vibrational modes gave rise to absorption bands below 1600 cm^{-1} , with the characteristic $\nu_{as}(\text{OCO})$ stretch around 1570 cm^{-1} [14, 18, 19, 53, 54]. However, a large envelope for carbonate species also produced absorption bands in this region, which hindered our ability to completely deconvolute and identify the surface formate, carbonate, and carboxyl species.

Fig. 5. Curve-fit of IR spectra recorded in the $2650 - 3050\text{ cm}^{-1}$ region under WGS conditions (7% CO, 11% H_2O , 37% H_2 , 9% CO_2) at $250\text{ }^\circ\text{C}$: (a) 0Na:Pt/ Al_2O_3 ; (b) red shift of band at 2900 cm^{-1} and formation of new formate C-H band at 2793 cm^{-1} on 12Na:Pt/ Al_2O_3 ; (c) increase in intensity of C-H band at 2798 cm^{-1} and formation of new band at 2698 cm^{-1} on 30Na:Pt/ Al_2O_3 .

3.3. Isotopic Transient Experiments

The isotopic transient experiments for both $^{12}\text{CO}/^{13}\text{CO}$ and $^{12}\text{CO}_2/^{13}\text{CO}_2$ switches were carried out at $250\text{ }^\circ\text{C}$ on Pt/ Al_2O_3 and Na-promoted catalysts. The IR spectra for WGS at $250\text{ }^\circ\text{C}$ with non-labeled CO at $t \sim 0\text{ s}$ and ^{13}CO after $t \sim 120\text{ s}$ are shown in Fig. 6, indicating the complete exchange of non-labeled and isotopically labeled reactants. Upon switching to ^{13}CO , bands in the adsorbed CO region are red-shifted from 2055 cm^{-1} to 2005 cm^{-1} and from 1954 cm^{-1} to 1911 cm^{-1} . Bands in the formate C-H region shifted from 2798 cm^{-1} to 2791 cm^{-1} with ^{13}CO , on 30Na:Pt/ Al_2O_3 . The experimentally observed isotopic red shifts for C-O and C-H stretches are in agreement with the predicted frequency shift as described by the simple harmonic oscillator model.

Fig. 6. IR spectra under WGS conditions (7% CO, 11% H₂O, 37% H₂, 9% CO₂) at 250 °C for ¹²CO/¹³CO switch on 30Na:Pt/Al₂O₃: (a) shift in adsorbed CO region from ¹²CO (solid line) to ¹³CO (dashed line); (b) shift in formate C-H region from ¹²CO (solid line) to ¹³CO (dashed line).

The normalized transient response curves obtained from the MS signal, F , were overlaid with the normalized IR band area as a function of time as shown in Fig. 7 for 0.82 wt.% Pt/Al₂O₃. The MS signal corresponds to the gas-phase composition at the reactor effluent, while the IR signal represents the adsorbed surface species and IR-active gas-phase species in the reactor. The Ne tracer (F_{Ne} , $m/z = 20$) is the first species to elute from the IR cell, followed by ¹³CO_(g) (F_{13CO} , $m/z = 29$), and finally ¹³CO_{2(g)} (F_{13CO_2} , $m/z = 45$). By integrating the area between the Ne tracer and gas-phase ¹³CO₂ response curves as a function of time, one can

estimate the mean surface residence time of intermediates (τ) without relying on any kinetic assumptions [33].

$$\tau_{13CO} = \int_0^{\infty} (F_{Ne} - F_{13CO_2}) dt \quad (4)$$

Fig. 7. Transient WGS on 0Na:Pt/Al₂O₃ at 250 °C during ¹²CO/¹³CO switch (7% CO, 11% H₂O, 37% H₂, 9% CO₂). Time resolved IR shows correlation of ¹³CO_{2(g)} (solid black line) with linear ¹³CO and bridging ¹³CO at 1995 cm⁻¹ and 1784 cm⁻¹, respectively. The solid lines correspond to the MS signals, while the IR signals are represented by symbols.

The presence of Na on Al₂O₃ in this study leads to two issues regarding CO₂. First, CO₂ adsorption on the support competes with water activation and leads to the observed negative CO₂ reaction order for Na-promoted Pt/Al₂O₃ samples during WGS [24]. Secondly, re-adsorption of CO₂ can interfere with the response curves obtained during isotopic transient experiments and overestimate the mean surface residence time of active intermediates [33]. By performing an isotopic switch with ¹²CO₂/¹³CO₂, we can measure the mean surface residence time of CO₂ due to ¹³CO₂ re-adsorption (τ_{13CO_2}) by the support and define a corrected mean surface residence time [33] as (see Table S5):

$$\tau' = \tau_{13CO} - \tau_{13CO_2} \quad (5)$$

Furthermore, the surface concentration of carbon-containing active intermediates can be calculated as the product of the rate and the corrected mean surface residence time, τ' .

$$N_C = TOF \times \tau' \quad (6)$$

The results of the isotopic transient experiments for WGS on Na-promoted and non-promoted Al_2O_3 at 250 °C are listed in Table 2. The number of carbon-containing active intermediates, N_C , on non-promoted Pt/ Al_2O_3 was $6.2 \times 10^{-3} \pm 0.001$ mole C per mole of surface Pt, corresponding to a TOF of $4.3 \times 10^{-3} s^{-1}$. Adding Na to a 30:1 molar ratio with Pt increased N_C to 0.95 ± 0.2 mole C per mole of surface Pt and yielded the highest observed TOF of $0.35 s^{-1}$. Additionally, by using the corrected mean surface residence time and the abundance of surface intermediates leading to $^{13}CO_2$, and then assuming a pseudo-first-order reaction rate and a single-pool reaction pathway, we can calculate an intrinsic TOF, as:

$$TOF' = \frac{1}{\tau'} = \frac{TOF}{N_C} \quad (7)$$

The intrinsic TOF, TOF' , provides an alternative measure of the absolute turnover frequency because it takes into account a direct measurement of the abundance of surface intermediates leading to the isotopically labeled product [33]. We take this intrinsic TOF as an upper bound of the true turnover frequency, which is the rate normalized by the number of surface atoms that can serve as active sites for the reaction. Since N_C is a measure of the number of sites actually operating at a given instant, the number of possible sites must be greater than or equal to N_C .

When the times required for exchange of an adsorbed surface species and the formation of gas-phase $^{13}CO_2$, which corresponds to the WGS TOF, are comparable, there is strong indication that the adsorbed species is likely an intermediate in the reaction pathway. In the case of Na-promoted Pt/ Al_2O_3 , where the $^{13}CO_2$ response is influenced by CO_2 re-adsorption, we simulate the effective $^{13}CO_2$ transient response based on the corrected mean surface residence time (Eq. (5)) as:

$$F'_{^{13}CO_2} = 1 - \exp\left(\frac{-t}{\tau'}\right) \quad (8)$$

The effective normalized $^{13}CO_2$ response, $F'_{^{13}CO_2}$, in Eq. (8) is obtained from the un-steady-state mass balance on a single-pool of adsorbed intermediates with irreversible reaction [33].

Table 2

Transient kinetics for 0.82 wt.% Pt/Al₂O₃ and Na-promoted catalysts measured in *operando* transmission IR cell with ¹³CO and ¹³CO₂ isotopic labels.

Catalyst	TOF ^a (IR cell) / s ⁻¹	τ' ^b / s	Pt disp. ^c / %	N_C / (mole C) (mole Surface Pt) ⁻¹	TOF' ^d / s ⁻¹
Pt/Al ₂ O ₃	0.43×10 ⁻²	1.4±0.1	35	6.2×10 ⁻³ ±0.001	0.71±0.05
12Na:Pt/Al ₂ O ₃	6.6×10 ⁻²	1.8±0.5	23	0.12±0.03	0.55±0.1
20Na:Pt/Al ₂ O ₃	0.24	4.0±0.5	26	0.96±0.1	0.25±0.03
30Na:Pt/Al ₂ O ₃	0.35	2.7±0.5	22	0.95±0.2	0.37±0.07
60Na:Pt/Al ₂ O ₃	0.21	4.9±1	15	1.0±0.2	0.2±0.04

^a TOF based on the Pt dispersion measured on the same catalyst used after WGS reaction in regular PFR.

^b τ' is the corrected mean residence time of N_C after CO₂ re-adsorption correction (See Table S5).

^c Pt dispersion measured by H₂ chemisorption for catalysts used after WGS in regular PFR.

^d TOF' calculated according to Eq. 7.

For 0.82 wt.% Pt/Al₂O₃, the normalized MS signal, F , (Fig. 7) shows that both linear and bridging ¹³CO species exchange at approximately the same rate as gas-phase ¹³CO₂, while formates identified by the $\nu_{as}(\text{O}^{13}\text{CO})$ vibrational mode exchange on a slower timescale. Similarly, transient experiments with ¹³CO on 12Na:Pt/Al₂O₃ revealed a correlation between bridge bonded and low frequency linear ¹³CO at 1712 cm⁻¹ and 1925 cm⁻¹, respectively, and gas-phase ¹³CO₂ (Fig. 8a) immediately following the isotope switch. The effective ¹³CO_{2(g)} response, as shown by the dashed line and denoted (¹³CO₂) in Fig. 8a, indicates that a similar rate of formation occurs between the low frequency ¹³CO influenced by Na (1925 cm⁻¹) and the isotopically-labeled product. Subsequent ¹³CO₂ re-adsorption experiments showed that formate species and gas-phase ¹³CO₂ both evolved with a 50% exchange time of less than 2 s (Fig. 8b), which means that the appearance of the ¹³C-labeled surface formate species is the result of equilibration between the gas-phase ¹³CO₂ in the IR cell and the catalyst surface since no ¹³CO reactant was used during the re-adsorption experiment.

Fig. 8. Transient WGS on 12Na:Pt/Al₂O₃ at 250 °C (7% CO, 11% H₂O, 37% H₂, 9% CO₂) during: (a) $^{12}\text{CO}/^{13}\text{CO}$ switch, revealing evolution of bridging ^{13}CO with $^{13}\text{CO}_{2(\text{g})}$ product; (b) $^{12}\text{CO}_2/^{13}\text{CO}_2$ switch, showing formate $\nu_{\text{as}}(\text{O}^{13}\text{CO})$ band but no adsorbed ^{13}CO . The solid lines correspond to the MS signals, while the IR signals are represented by symbols. The simulated $^{13}\text{CO}_2$ response curve, corrected for re-adsorption, is represented by the dashed line.

On 30Na:Pt/Al₂O₃, adsorbed ^{13}CO species exchanged faster than ^{13}C appeared in the gas-phase $^{13}\text{CO}_2$ product, while the $\nu(^{13}\text{C-H})$ and $\nu_{\text{as}}(\text{O}^{13}\text{CO})$ vibrational modes of surface formates appeared to correlate with the gas-phase $^{13}\text{CO}_2$ (Fig. 9a). The simulated $^{13}\text{CO}_{2(\text{g})}$ trace based on τ' in Fig. 9a matches well with the evolution of linear ^{13}CO influenced by Na at 1903 cm^{-1} and bridge bonded ^{13}CO at 1720 cm^{-1} . CO₂ re-adsorption experiments for both 30Na:Pt/Al₂O₃ (Fig. 9b) and 60Na:Pt/Al₂O₃ (Fig. S3b) confirmed that the $\nu(^{13}\text{C-H})$ and $\nu_{\text{as}}(\text{O}^{13}\text{CO})$ IR bands for these samples evolve on a timescale comparable to that for $^{13}\text{CO}_2$, i.e. the MS signal associated with $^{13}\text{CO}_2$ and the IR bands associated with $\nu(^{13}\text{C-H})$ and $\nu_{\text{as}}(\text{O}^{13}\text{CO})$ both exhibit a 50% exchange time of approximately 5.5 s. This finding is discussed further below.

Fig. 9. Transient WGS on 30Na:Pt/Al₂O₃ at 250 °C (7% CO, 11% H₂O, 37% H₂, 9% CO₂) during: (a) ¹²CO/¹³CO switch, showing evolution of formate $\nu_{as}(\text{O}^{13}\text{CO})$ and $\nu(^{13}\text{C-H})$ bands at 1570 cm⁻¹ and 2791 cm⁻¹, respectively, with ¹³CO_{2(g)} product; (b) ¹²CO₂/¹³CO₂ switch, revealing surface formates as spectators due to evolution of $\nu_{as}(\text{O}^{13}\text{CO})$ and $\nu(^{13}\text{C-H})$ bands with ¹³CO_{2(g)}. The solid lines correspond to the MS signals, while the IR signals are represented by symbols. The simulated ¹³CO₂ response curve, corrected for re-adsorption, is represented by the dashed line.

4. Discussion

4.1. Effect of Sodium Promotion

The role of alkali metals, such as sodium and potassium, as promoters for the WGS reaction has been reported in the literature [16, 17, 23-30]. Essentially, the alkali can either create new sites on the metal, or in close proximity with the dispersed metal to facilitate water [24, 29, 30] and/or CO adsorption [24, 30]. Another possibility is that the alkali metal can modify the support properties to weaken the formate C-H bond and facilitate formate decomposition to CO₂ and H₂ [16, 17, 26, 27]. Additionally, researchers have proposed that the alkali metal enhances the dispersion of oxidized Pt as single-atom active species [23, 28].

In the present study, FTIR spectra obtained under WGS conditions in the IR cell support previous findings by Pazmiño et al. [24] that the majority of adsorbed CO is linearly bonded to

metallic Pt clusters for 0.82 wt.% Pt/Al₂O₃ (Fig. 3a), as indicated by the predominant bands at 2077 cm⁻¹, 2059 cm⁻¹, 2040 cm⁻¹, and 2010 cm⁻¹ along with the absence of a band between 2080 and 2100 cm⁻¹ [51, 52]. After Na addition, the linear CO on Pt terraces (2077 cm⁻¹) and steps (2059 cm⁻¹) decreased, while bridging CO species on Pt terraces were formed (1913 cm⁻¹). The band at 1972 cm⁻¹, assigned to CO adsorbed on sites of exceptional electron-donating properties [4, 48], increased when Na was added to Pt/Al₂O₃ at a 12:1 molar ratio of Na:Pt. These high back-donation Pt sites may be characteristic of the coordination unsaturation of perimeter sites, but may also be due to Pt sites near Na that are the result of an electrostatic attraction between linear CO and Na [49]. Furthermore, as shown in Fig. 4., the increase in the WGS TOF correlates with an increase in the intensity of multiply-bonded CO bands at 1768 cm⁻¹ and 1697 cm⁻¹ [41-43] as well as the high back-donation Pt sites at 1972 cm⁻¹, all of which are strongly affected by the presence of Na.

The main feature of the formate region is the $\nu(\text{C-H})$ stretch at 2907 cm⁻¹ as shown in Fig. 5 for Pt/Al₂O₃. For Na-promoted Pt/Al₂O₃ catalysts, new IR bands appear in the formate region at 2793 cm⁻¹ on 12Na:Pt/Al₂O₃, and at 2698 cm⁻¹ on 30Na:Pt/Al₂O₃. Some studies attribute the band at 2793 cm⁻¹ as a red-shift of the 2907 cm⁻¹ band due to alkali addition, which suggests weakening of the formate C-H bond [26, 27]. However, deconvolution of the formate region IR spectra in our study reveals that the same band at 2907 cm⁻¹ is present on both 0Na:Pt/Al₂O₃ and 30Na:Pt/Al₂O₃. The bands which arise at 2793 cm⁻¹ and 2696 cm⁻¹ have been observed as the $\nu(\text{C-H})$ vibrational modes of sodium formates and we assign them as such [55].

The shift in adsorption of CO from linear at 2060 cm⁻¹ to low frequency linear CO at 1972 cm⁻¹ and multi-bound CO bands below 1900 cm⁻¹ indicates a weakening of the C-O bond and strengthening of the Pt-C bond. CO temperature programmed desorption on 0.82 wt.% Pt/Al₂O₃ and 20Na:Pt/Al₂O₃ was used to infer the relative heats of adsorption of each CO species (linear, bridging, and tri-bonded) based on their change in coverage as a function of temperature according to their characteristic IR bands (Fig. S4a,b). As shown in Fig. S4b for 20Na:Pt/Al₂O₃, the coverages of bridging and tri-bonded CO do not begin to decrease until 100 – 150 °C higher temperatures than on the Na-free sample, which shows that these species are more strongly bound to Pt in the presence of Na. The initial coverage increase for bridging and tri-bonded CO upon increasing temperature may be due to surface restructuring with Na present, or modification of CO adsorption at higher temperatures. Further evidence for the increased binding

strength of CO on Pt is given by the 10 – 15 kJ mole⁻¹ increase in apparent activation energy for the Na-promoted Pt/Al₂O₃ samples shown in Table 1. According to the Temkin equation [56],

$$E_{app} = E_{RDS} + \sum_i n_i \Delta H_i \quad (9)$$

where E_{RDS} is the activation energy (kJ mole⁻¹) of the rate-determining step (RDS) and n_i and ΔH_i are the reaction order and heat of adsorption (kJ mole⁻¹) of species i , respectively, an increase in the heat of adsorption of CO and sign change in the CO reaction order can effectively lead to an increase in the apparent activation energy. Eq. (9) is based on the assumptions that the reaction mechanism is known, the adsorption of reactants is reversible, and that the surface coverages of the reactants vary across the temperature range where E_{app} is valid [56].

Analysis of the IR band shifts for CO adsorbed on Pt is complicated by changing CO coverages and the effects of dipole coupling between adjacent vibrating CO molecules on the catalyst surface. The frequency of the vibration increases as the density of dipoles increases. Isotopic dilution of ¹²CO by ¹³CO results in the two molecules having different vibrational frequencies and prevents the two different isotopic species from coupling. Deconvolution of the time-resolved IR spectra collected during ¹²CO/¹³CO isotope switches allows us to extract the singleton vibrational frequency (ω_s) from the observed stretching frequency for an ensemble of dipoles (ω). As shown in Figs. S5-7, the ¹²CO band positions for linear (Fig. S5), low frequency linear (Fig. S6), and multi-bonded (Fig. S7) CO species are plotted as a function of coverage, as determined by IR, in the isotopic mixture for Pt/Al₂O₃ and Na-promoted Pt/Al₂O₃ catalysts. The data for each sample are extrapolated to zero coverage, or the case of infinite dilution of ¹²CO in ¹³CO, and the y-intercept represents the singleton CO stretching frequency. For the Na-free catalyst, the dipole singleton frequency of 2041 cm⁻¹ for linear CO adsorbed on Pt is in agreement with that observed by Fanson et al. [41] for 0.6 wt.% Pt/SiO₂. Based on the 100% ¹²CO stretching frequency of 2062 cm⁻¹ (Table S6), the resulting dipole shift for Na-free Pt/Al₂O₃ is 21 cm⁻¹.

The results in Table S6 show that the singleton CO frequencies for linear CO on Pt, linear CO on Pt sites near Na, and multi-bonded CO on Pt decrease as a function of increasing Na content. The corresponding dipole shifts for the Na-promoted samples are larger than on Na-free Pt/Al₂O₃, which implies that the presence of alkali modifies CO adsorption on the exposed Pt surface to create sites with stronger Pt-C bonds and a weaker C-O bond via an increase in electron back-donation or an electrostatic attraction between CO and Na near Pt. Although C-O

bond weakening and dissociation steps are not required for WGS, the observed electronic interaction between the alkali and Pt surface confirms that some fraction of the metallic Pt particles must be decorated with Na. A previous ^{23}Na - ^{13}C NMR study by Norcross et al. [57] for Na-promoted Pt/SiO₂ showed that much of the Na remains in contact with the metallic Pt cluster and that CO is bonded only to the Pt surface. In the case of the current study, the fraction of total Pt atoms residing on the surface, and thus, accessible to CO, decreases with increasing Na content from 35% for the Na-free sample to 15% for 60Na:Pt (Table 1) owing to the increased alkali coverage on the metal surface. This finding is further supported by the Pt dispersions for Na-Pt/Al₂O₃ determined by Pazmiño et al. [24] with extended X-ray absorption fine structure (EXAFS). When Na is deposited on Pt/Al₂O₃, the Pt dispersion based on H₂ chemisorption decreases while the estimated dispersion based on EXAFS remains essentially unchanged. Since EXAFS probes all Pt atoms within the sample while H₂ can only access Pt surface sites, the decrease in Pt dispersion based on H₂ chemisorption confirms the migration of some fraction of Na onto the Pt nanoparticles.

From the analysis of the transient kinetics obtained during isotope switching experiments (Table 2), we observe that for the Na-free catalyst N_C is $6.2 \times 10^{-3} \pm 0.001$ mole C per mole of surface Pt, or less than 1 mole% of surface Pt. These results indicate that only a small fraction of CO adsorbed on the Pt surface for the Na-free sample participates in the WGS reaction pathway. At a Na:Pt molar ratio of 20:1, N_C increases to 0.95 ± 0.1 mole C per mole of surface Pt, or nearly all of the exposed surface Pt atoms. A comparison of the intrinsic turnover frequencies (TOF'), which represents the rate per true active site during the reaction, for Na-free Pt/Al₂O₃ and Na-promoted Pt/Al₂O₃ in Table 2 shows that the participating CO sites on Pt/Al₂O₃ turnover faster than those for Na-Pt/Al₂O₃. The TOF' of 0.37 s^{-1} for 30Na:Pt, which exhibits the highest WGS rate for the Na-promoted samples tested in this study, is a factor of two lower than the TOF' of 0.71 s^{-1} for Pt/Al₂O₃. The intrinsic turnover frequencies per active site on the Na-Pt/Al₂O₃ catalysts are comparable to the measured TOF per exposed surface Pt, which indicates that the Na-promoted samples all participate in a similar pathway. The higher TOF' per active site on Pt/Al₂O₃ may be explained by the lower apparent activation energy and weaker bound CO for this catalyst. However, the lower TOF' for Na-Pt/Al₂O₃ is offset by the greater abundance of active sites, which leads to the higher overall WGS rates and higher TOF when normalized per exposed metal surface for these materials.

Although we cannot rule out the presence of some fraction of atomically dispersed Pt on our Na-free and Na-promoted samples, we know from previous X-ray absorption spectroscopy (XAS) experiments under WGS conditions that the majority of active Pt exists as metallic nanoparticles [24]. This finding aligns with recently published results by Ding et al. [30] that identifies metallic Pt nanoparticles as the catalytically-relevant sites on supported Pt catalysts that contain both metal nanoparticles and single Pt atoms. The difference in the observed state of the active Pt for our Na-promoted Pt catalysts compared to those reported by Zhai et al. [23] and Yang et al. [28] may be due to differences in the catalyst synthesis and pre-treatment. For example, Zhai et al. [23] and Yang et al. [28] use NaOH as the alkali source during their second impregnation step to synthesize mono-dispersed Pt catalysts and do not report pre-treatment of Na-free and Na-containing Pt catalysts in H₂. Instead, their catalysts are calcined in air at 400 °C for 4 h, and then heated in He from room temperature to 100 °C prior to performing kinetic measurements.

The role of alkali promotion of Pt/Al₂O₃ has a combined effect through modification of CO adsorption on the Pt surface along with water activation by the alkali metal and/or support based on previous kinetic findings by Pazmiño et al. [24]. In their study, an increase in H₂O order from 0.7 to 1.1 was observed on Na-promoted Pt/Al₂O₃ compared to Na-free Pt/Al₂O₃ (Table S3), which indicates that there is a lower coverage of hydroxyl species, perhaps due to the higher rate of consumption of surface OH/H groups. The interaction of alkali with metallic Pt sites suggests that the Na patches on the surface are able to increase the number of OH/H sites to such an extent that they are able to react with all available CO adsorbed on the exposed surface Pt and enhance the WGS rate. However, in the present study only the carbon-containing surface active intermediates were considered, so we cannot yet address this point directly.

4.2. Mechanistic Aspects of WGS on Na-Pt/Al₂O₃

The simultaneous collection of IR data along with detection of non-labeled and isotopically labeled species by MS allows one to monitor changes in adsorbed surface species and elucidate details of the reaction pathway during the isotope switch. The evolution of the Ne tracer represents the gas hold-up time of the *operando* reactor, while the area between F_{Ne} and

$F_{^{13}\text{CO}}$ corresponds to the capacity of the surface to adsorb ^{13}CO or exchange ^{13}CO for adsorbed ^{12}CO , plus any ^{13}CO that is converted to $^{13}\text{CO}_2$ [33].

For WGS on 0.82 wt.% Pt/Al₂O₃ at 250 °C, as shown in Fig. 7, time-resolved IR shows that both linear bonded ^{13}CO and bridge bonded ^{13}CO at 2052 cm⁻¹ and 1784 cm⁻¹, respectively, evolve at comparable rates to gas-phase $^{13}\text{CO}_2$, while the formate $\nu_{\text{as}}(\text{O}^{13}\text{CO})$ vibrational mode at 1590 cm⁻¹ does not appear until much later and clearly must be a spectator species for this catalyst. Similarly, on 12Na:Pt/Al₂O₃ (Fig. 8) during the $^{12}\text{CO}/^{13}\text{CO}$ isotope switch, the growth of the multiply-bonded and low frequency linear ^{13}CO bands at 1712 cm⁻¹ and 1925 cm⁻¹, respectively, at a comparable rate to $^{13}\text{CO}_{2(\text{g})}$ indicates that these adsorbed CO surface species are likely to be involved in the WGS mechanism for Na-promoted Pt/Al₂O₃ while the formate intermediate is not. The effective $^{13}\text{CO}_{2(\text{g})}$ transient response (Fig. 8a), which takes into account the CO₂ re-adsorption correction, suggests that the dominant active CO species on 12Na:Pt/Al₂O₃ is low-frequency, linear CO that is influenced by the presence of Na. CO₂ re-adsorption on 12Na:Pt/Al₂O₃ via $^{12}\text{CO}_2/^{13}\text{CO}_2$ isotope switching shows that formates are spectators on these catalysts due to the appearance of the $\nu_{\text{as}}(\text{O}^{13}\text{CO})$ band at 1560 cm⁻¹. The formation of this surface species is the result of an exchange with gas-phase $^{13}\text{CO}_2$ and not WGS.

Following complete exchange of the ^{13}CO labeled isotope with CO in the reactor feed stream after $t \sim 120$ s on 30Na:Pt/Al₂O₃ at 250 °C, the IR bands in the adsorbed CO region are red-shifted from 2055 cm⁻¹ to 2005 cm⁻¹ and from 1954 cm⁻¹ to 1911 cm⁻¹, (Fig. 6). To be considered as an active reaction intermediate, one would expect the characteristic IR bands of the surface species to yield the red isotopic shift. Normalized MS – IR analysis of the $^{12}\text{CO}/^{13}\text{CO}$ exchange on 30Na:Pt/Al₂O₃ revealed that the formate $\nu(^{13}\text{C-H})$ and $\nu_{\text{as}}(\text{O}^{13}\text{CO})$ vibrational modes at 2971 cm⁻¹ and 1570 cm⁻¹ evolved at a similar rate to gas-phase $^{13}\text{CO}_2$ (Fig. 9a). Unlike what was observed for 0Na:Pt/Al₂O₃ and 12Na:Pt/Al₂O₃ samples during isotopic transient analysis, the bridge bonded and low frequency linear ^{13}CO surface species appear to exchange much faster than the gas-phase $^{13}\text{CO}_2$ product for 30Na:Pt/Al₂O₃. This phenomenon is due to the strong re-adsorption of $^{13}\text{CO}_{2(\text{g})}$ by the catalyst surface, which leads to a longer breakthrough time for the $^{13}\text{CO}_2$ product as detected in the MS. However, the simulated $^{13}\text{CO}_{2(\text{g})}$ response in Fig. 9a shows good agreement between the rate of formation of linear ^{13}CO influenced by Na and bridge bonded ^{13}CO with the isotopically-labeled CO₂ product, thereby indicating that these adsorbed CO species are likely to be involved in the dominant reaction pathway.

Upon further investigation of CO₂ re-adsorption through a ¹²CO₂/¹³CO₂ isotope exchange, it became clear that the surface formates are spectator species for this catalyst as well because of the evolution of ν(¹³C-H) and ν_{as}(O¹³CO) bands along with ¹³CO_{2(g)}. Again, as with 12Na:Pt/Al₂O₃, no adsorbed ¹³CO surface species were detected during re-adsorption of ¹³CO_{2(g)}. These results confirmed that formate species are spectators for WGS (6.8% CO, 11% H₂O, 37.5% H₂, 8.6% CO₂) on Na-Pt/Al₂O₃, while the adsorbed CO species are precursors to the reactive intermediates. Furthermore, by examining only the time evolution of IR-active species with product formation during the ¹²CO/¹³CO isotope exchange alone, one does not take into account the effect of CO₂ re-adsorption by alkali-doped metal oxide supports, such as Na-Al₂O₃, which can lead to false conclusions based on apparent correlations. Although the combined *operando* IR and transient studies with ¹²CO/¹³CO and ¹²CO₂/¹³CO₂ isotope switches show that WGS on Pt/Al₂O₃ and Na-Pt/Al₂O₃ does not appear to proceed through a formate-driven mechanism, there is not sufficient evidence in the present study to differentiate between a red-ox mechanism and an associative mechanism involving a carboxyl intermediate.

The correlation between IR band areas for linear CO on Pt near Na and multiply-bonded CO on Pt with the WGS TOF (Fig. 4) along with transient evolution of these ¹³C-labeled surface species during isotope switching suggests that the composition of the active carbon pool shifts from primarily linear CO on Na-free Pt/Al₂O₃ to predominantly multiply-bonded (1700 – 1800 cm⁻¹) and low frequency linear CO species (1965 – 1972 cm⁻¹) on Na-Pt/Al₂O₃. The shift to low frequency and multiply-bonded CO entities is due to the presence of Na, which modifies the local electronic properties of Pt in the region surrounding the alkali metal and increases the back-bonding from the Pt surface to CO. These findings are also supported by the observed changes in singleton CO frequencies.

5. Conclusions

Steady-state kinetic data for 0.82 wt.% Pt/Al₂O₃ and Na-Pt/Al₂O₃ catalysts obtained from the *operando* IR cell were comparable to results from the laboratory differential PFR, which showed that the highest level of WGS promotion occurred on 30Na:Pt/Al₂O₃ at 250 °C with a TOF per total surface Pt of 0.35 s⁻¹ compared to 0.43 × 10⁻² s⁻¹ for Pt/Al₂O₃ at 250 °C. The addition of Na to Pt/Al₂O₃ perturbs the adsorption of CO from primarily linear species to low

frequency linear and multiply-bonded CO on sites near Na, which correlate with an increase in the WGS TOF when normalized by the number of exposed surface Pt atoms. Analysis of adsorbed CO on Pt from TPD experiments and $^{12}\text{CO}/^{13}\text{CO}$ isotope switches revealed that CO is more strongly bound on Na-Pt/ Al_2O_3 and that the C-O vibrational frequency decreases due to increased back-bonding by Pt that is influenced by the presence of Na. However, when normalized by the number of actual CO active sites that participate during the reaction, the intrinsic TOFs (TOF') per operating site are more closely comparable for Na-free and Na-promoted Pt/ Al_2O_3 .

Time-resolved IR data obtained during isotopic transient analysis of the carbon pathway via ^{13}CO on Na-promoted and non-promoted Pt/ Al_2O_3 catalysts for WGS showed that adsorbed surface species yield the expected IR red shift, which confirms the complete exchange of non-labeled and isotopically labeled reactants. The exchange of multiply-bonded and low frequency linear ^{13}CO species on similar timescale to gas-phase $^{13}\text{CO}_2$ indicates that these adsorbed CO species are likely intermediates in the WGS reaction pathway. While the transient evolution of formate $\nu(^{13}\text{C-H})$ and $\nu_{as}(\text{O}^{13}\text{CO})$ bands with gas-phase $^{13}\text{CO}_2$ leads one to believe that formates are possible intermediates, analysis of $^{13}\text{CO}_{2(g)}$ re-adsorption data reveals that the appearance of these IR bands are the result of isotopically labeled carbon from gas-phase $^{13}\text{CO}_2$ rather than WGS.

Transient kinetic analysis of ^{13}CO intermediates during WGS shows that on the Na-free catalyst, the coverage of active, carbon-containing intermediates occupies less than 1% of the Pt surface. Upon Na addition to 20:1 Na:Pt, the coverage of these active CO intermediates increases to nearly 100% of the exposed Pt surface on the sample. The combined results from *operando* IR and isotopic transient experiments indicate that the enhancement of the WGS rate by Na on Pt/ Al_2O_3 is driven by the creation of new active sites, which are formed from Na in contact with metallic Pt nanoparticles. We postulate that these sites enable water activation and increase the availability of surface hydroxyls so that nearly all of the CO on the Pt surface is able to react during WGS, as shown by the N_C values reported in Table 2.

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Isotopic Transient Studies of Sodium Promotion of Pt/Al₂O₃ for the Water-Gas Shift Reaction

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Graphical Abstract

The addition of Na to Pt/Al₂O₃ promotes the water-gas shift (WGS) turnover frequency (TOF) up to 100x by modifying the local electronic properties of Pt and creating new H₂O activation sites such that all of the CO on the Pt surface participates in the reaction.

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