Title: TAP analysis of single and double peak responses during CO oxidation over Pt

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Abstract

Critical phenomena in heterogeneous catalysis have attracted a considerable interest throughout history due to their intriguing dynamical complexity. The coordinated interplay of various phenomena, such as surface interactions, nonlinear reaction mechanisms and the transport of energy and mass, determine the likelihood of dynamic patterns in certain catalytic systems. In this work, pulse experiments performed with a Temporary Analysis of Products (TAP) reactor showcase the complex dynamic behavior of CO oxidation over a Pt catalyst and exhibit its dependence on the pulsed CO/O_2 ratio and the local bed temperature. Pulse responses exhibit a dynamic transition between two critical values of the reaction rate for feed mixtures richer in O_2 due to the controlled interactions of the adsorbed species on the surface of the catalyst.

Keywords: Transient kinetics, pulse experiment, dynamic transition, critical phenomena

1. Introduction

The kinetics of CO oxidation on Pt are generally considered to follow a Langmuir-Hinshelwood mechanism [1], where CO and O_2 are adsorbed from the gas phase onto the surface of the catalyst. Generally, adsorption/desorption processes of CO and O_2 over Pt are considered complex multi-step processes. However, in typical models of the Ideal Adsorbed Layer (IAL), a single active site is sufficient for a CO molecule to adsorb, whereas O_2 requires a pair of sites to dissociate and thus form the adsorbed oxygen species in two separate steps [2]. The adsorbed species can then react to produce CO_2, which rapidly desorbs from the surface [1]. Following the product formation step, the previously occupied active sites become available for reactants to adsorb. Since reactivity depends on the presence of adsorbed CO and oxygen on the surface, their respective coverages greatly affects the reaction rate and the apparent catalyst activity. The differences between the adsorption of CO and O_2 creates a competitive dynamic for available sites. Since CO is able to adsorb freely on a single site, extensive CO coverages can form dense layers that hinder O_2 dissociation due to limited available site pairs [3, 4]. In contrast, adsorbed oxygen allows the adsorption of CO, even for a surface saturated with oxygen atoms [5]. Both CO and O_2 can form non-uniform distributions on the surface of the catalyst consisting of segregated domains or islands [6-8]. CO oxidation is thereby limited to the reaction between the adsorbed CO and oxygen species present on the boundaries of their respective surface islands [9].

Critical phenomena for CO oxidation on Pt can arise as a result of the interplay between adsorption/desorption processes and the interaction of surface species. The reaction rate can change dynamically depending on the surface coverage of the adsorbed species and the partial pressures of CO and O_2 in the gas phase. For surfaces predominantly covered with oxygen, the reaction rate increases proportionally with respect to the partial pressure of CO, reaching a region once a sufficient CO coverage is reached. Beyond this point, adsorbed CO starts to impede the adsorption of O_2 and the reaction rate is consequently diminished [8, 10]. These underlying complexities of the reaction mechanism can be a factor that favors critical phenomena, such as the occurrence of multiple steady states [11-14]. Under certain conditions, special dynamic

behaviors such as oscillations can appear around the maximum reaction rate of the system, which is achieved during the dynamical transitions between high and low reactivity regimes [15]. Feedback mechanisms that cause periodic transitions of reactivity can involve various types of dynamically complex surface phenomena, such as adsorbate induced reconstructions of the Pt surface [5, 16, 17], the appearance of subsurface oxygen phases [18, 19] or the formation of non-uniform spatiotemporal patterns of CO and oxygen islands on the catalyst surface [20-23]. The objective of this work is to analyze the dynamic kinetics of CO oxidation over a Pt catalyst under transient reaction conditions. For this purpose, pulse experiments with a Temporal Analysis of Products (TAP) reactor are performed under different CO/O_2 mixtures and various temperature conditions to observe their influence on the temporal evolution of the pulse responses.

2. Materials and methods

2.1. Catalyst synthesis and support preparation

The synthesis methodology followed the approach presented in the work of Ramachandran *et al*. [24]. The catalyst consists of Pt nanoparticles (NPs) supported on non-porous quartz particles via Atomic Layer Deposition (ALD). NPs were deposited at 200°C by cyclically alternating the exposure of quartz particles to the pulses of (methylcyclopentadienyl)trimethylplatinum ($MeCpPtMe_3$) vapor and ozone (O_3) gas. The $MeCpPtMe_3$ precursor was heated to 30°C and the delivery line to 60°C. $MeCpPtMe_3$ was pulsed into the reaction chamber using Ar as a carrier gas. Both ALD half cycles were performed in a static way: the precursor/reactant was pulsed for 10 sec reaching a pressure of 1 mbar after which the valves to the pumping system were kept closed and the quartz particles were exposed to the gas for an additional 20 sec, resulting in a total exposure of 30 sec. In between two pulses the chamber was evacuated. This process was conducted for 100 cycles, to assure the deposition of sufficient Pt on the surface of the non-porous particles. The deposited layer was then treated under a Temperature Programmed Reduction (TPR) with H_2.

2.2. Setup description and reactor configurations

CO oxidation experiments with the ALD Pt catalyst were performed in a TAP-3E reactor system previously detailed by Gleaves *et al.* [25-27]. Four main sections comprise the setup: a pulse valve manifold, a microreactor, a high vacuum analysis chamber and a computer system for control and data acquisition (seeFigure 1A). The manifold contains two high speed electromechanical pulse valves, each with its own separate gas feed line for testing different gas mixtures, and couples directly to the microreactor inlet. The valves' opening time can be tuned within a microsecond resolution from the main computer for precisely adjusting the gas pulse intensity and defining the transport conditions within the microreactor bed. The manifold also offers the option of continuous flow experiments at higher pressures (up to 2 bar) through the use of a needle valve connection. When coupled, the manifold forms a sealed connection with the microreactor, thus ensuring a separation between the high vacuum conditions inside the reactor and the outside atmosphere. The microreactor consists of a quartz tube with a length of (44.6 ± 0.1) mm and a diameter of (4,0 ± 0.1) mm housed in a stainless steel enclosure. A metallic heating wire is wrapped around the quartz tube and a thermocouple is placed at the center of the reactor bed for correctly measuring and controlling the bed temperature during experiments. An Eurotherm controller is responsible of regulating the bed temperature with a PID algorithm and a Mastech DC Power Supply that feeds the heating element. The analysis chamber is equipped with an Extrel Quadrupole Mass Spectrometer (QMS) located just beneath the microreactor outlet for sampling the pulse response of the gas components. High vacuum conditions in the order of 10^{-7} torr are achieved in the chamber during experiments due to the combined work of a Varian turbomolecular pump and a water cooled diffusion pump.

Reactor bed configurations were prepared in accordance with the Thin-Zone TAP reactor (TZTR) model proposed by Shekhtman [28]. This model consists of a thin catalyst layer placed at the center of the reactor between two large beds of inert particles. The TZTR configuration is often employed during pulse experiments due to a series of advantages, such as the minimization of concentration and temperature gradients across the catalytic layer, the mathematical separation of transport and reaction and the option of determining kinetic parameters with moment calculations. An example of this configuration is presented in Figure 1B. The catalytic layer for all

experiments was prepared by separately weighing and posteriorly placing (10.7 ± 0.1) mg of the Pt catalyst between two large inert zones filled with quartz particles with an average diameter smaller than 250 µm, thus forming a thin zone of (0.8 ± 0.1) mm in length. This active layer was put in direct contact with the reactor's thermocouple for an adequate measurement and control of the reaction temperature during experiments. Before experiments, the reactor was heated up to 500°C for 20-30 min for preactivation. Pulse reduction experiments with a H_2/Ar mixture at such temperatures did not show any significant water formation before or after CO oxidation experiments.

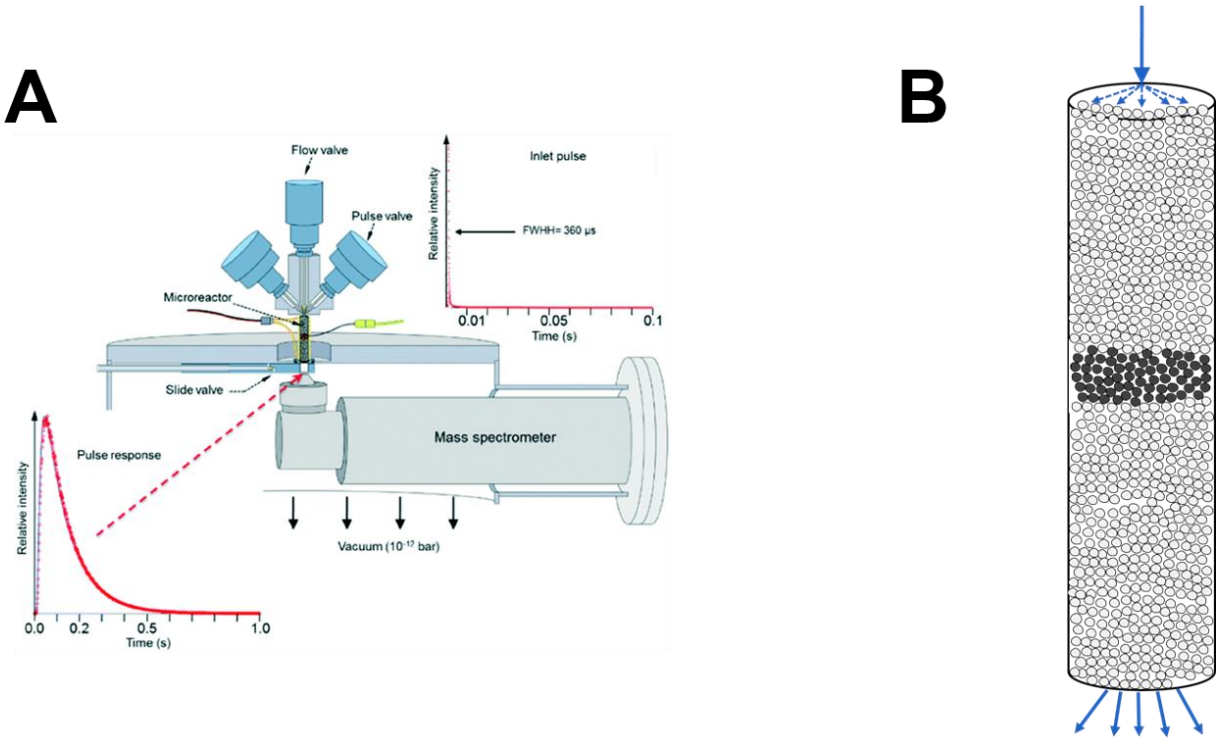

Figure 1 (**A**) General schematic of the TAP-3E reactor system (**B**) Graphical representation of the Thin-Zone TAP reactor (TZTR) configuration. Dark gray particles represent the thin layer formed by catalytic particles, whereas light gray particles indicate the large inert zones comprised by non-active quartz particles

2.3. Pulse experiments with multiple CO/O_2 ratios and variable temperatures

In order to observe the influence of the pulsed CO/O_2 ratio on the reaction's dynamic response, different reactant gas mixtures were prepared separately for each set of experiments. CO (99,997%), O_2 (≥ 99,995%) and Ar (≥ 99,999 %) were mixed in a gas

preparation tank, with the latter serving as an inert standard for all experiments. The proportion between CO and O_2 was adjusted by controlling their respective partial pressures during the mixing stage. These were determined from the observed pressure differences in the tank's manometer when filling up the tank with each gas. Experiments were conducted with the following CO/O_2 gas ratios: 1:1, 1:2, 2:1 and 3:1. The amount of pulsed molecules for CO and O_2 ranged in the order of 10^{15}-10^{16} molecules, in accordance to the proportions dictated by the CO/O_2 ratios in the feed mixtures.

Different temperature conditions were evaluated for each set of reactant gas ratios. At first, pulse experiments were carried out at a stable temperature of 300°C. Afterwards, pulse experiments were performed under an increasing temperature ramp with a rate of 5°C/min, from 300°C to 450°C. Subsequently, another series of pulse experiments were then conducted at a controlled 450°C. Lastly, experiments were then carried out under a temperature ramp descending from 450°C to 300°C with a cooling rate of 5°C/min. Sufficient time was allocated during the temperature ramp experiments for collecting data during the ramp and after temperature stabilized at its final value. For each experiment, the total number of pulses was 800, the width of each pulse 150 μs and the data collection time per pulse was set to 4 sec, with a millisecond sampling resolution. The MS was configured to track the 28, 32, 40 and 44 AMUs in order to respectively analyze CO, O_2, Ar and CO_2. Different signal gains were employed for each set of feed mixtures to account for the impact of gas composition on signal intensity. Separate experiments with CO_2 and Ar were done to evaluate the fragmentation of CO_2 and its contribution to the 28 AMU signal.

2.4. TAP Data Correction and Analysis

A baseline correction procedure was applied to all raw pulse data collected from CO oxidation experiments in order to eliminate possible offsets in the voltage signals generated by the QMS. Such shifts tend to be uniform and can raise or lower the pulse signals [29]. A simple vertical shift in the other direction is sufficient to translate the baseline of the signal as close as possible to zero. This correction procedure was developed in MATLAB and involves the adjustment of each pulse by subtracting the average value of its baseline before the pulse is injected to the reactor. Such values

represent the baseline response of the QMS and therefore correspond to the reference values assigned by the baseline correction subroutine. Following this process, pulse data was also averaged by taking the mean of the collected pulse responses at the outlet of the reactor. This data shows of the average time evolution of the flowrate of a given chemical species at the outlet of the microreactor.

3. Results

3.1. Pulse experiments with 1:1 and 1:2 CO/O_2 feed ratios

The average pulse responses for all species in an experiment with a 1:1 CO/O_2 mixture at 300°C are presented in Figure 2A, where the responses of CO and O_2 exhibit a more drastic decay after their peak compared to the Ar response. CO oxidation at these conditions is evident from the clear CO_2 signal that appears during the collection time. Nevertheless, the CO_2 response in Figure 2A exhibits an exceptionally characteristic shape. This signal initially rises as it normally would in the case of product formation, forming a small peak. However the curve does not fully decay after this point, but rather decays slightly before forming a plateau with a 1 sec duration, forms a second peak and then slowly decays to its baseline. Moreover, the CO and O_2 signals also display a remarkable change in their curvature during this phenomenon, with a noticeable descent taking place at the same time the second CO_2 peak appears. These traits can be observed with more detail in Figure 2B.

The temperature evolution of the CO_2 response provides a more complete view of the double peak phenomenon. Figure 3A displays the CO_2 responses under a temperature ramp of 5°C/min, from 300°C to 450°C. It can be observed during the pulse profile that the timing of the second CO_2 peak changes consistently with incremental temperature values. As temperature rises with the ramp, the duration of the plateau between both CO_2 peaks is gradually shortened. At approximately 360°C and above, the double peaks the in CO_2 responses start to seemingly merge with each other, until a single and fully developed peak is consistently achieved at temperatures beyond 380°C. This behavior at higher temperatures can be further observed in the average pulse responses at 450°C shown in Figure 3B, where a single and fully developed CO_2 pulse exhibits a

decay similar to the Ar signal. Furthermore, reactant signals do not display any inconsistent changes in their shape unlike their respective counterparts at 300°C. The system also produces a consistent CO_2 response for the temperature ramp from 450°C to 300°C, with the unified CO_2 peak reducing its intensity before splitting again in a double peak response at lower temperatures, similar to the pattern observed in Figure 3A.

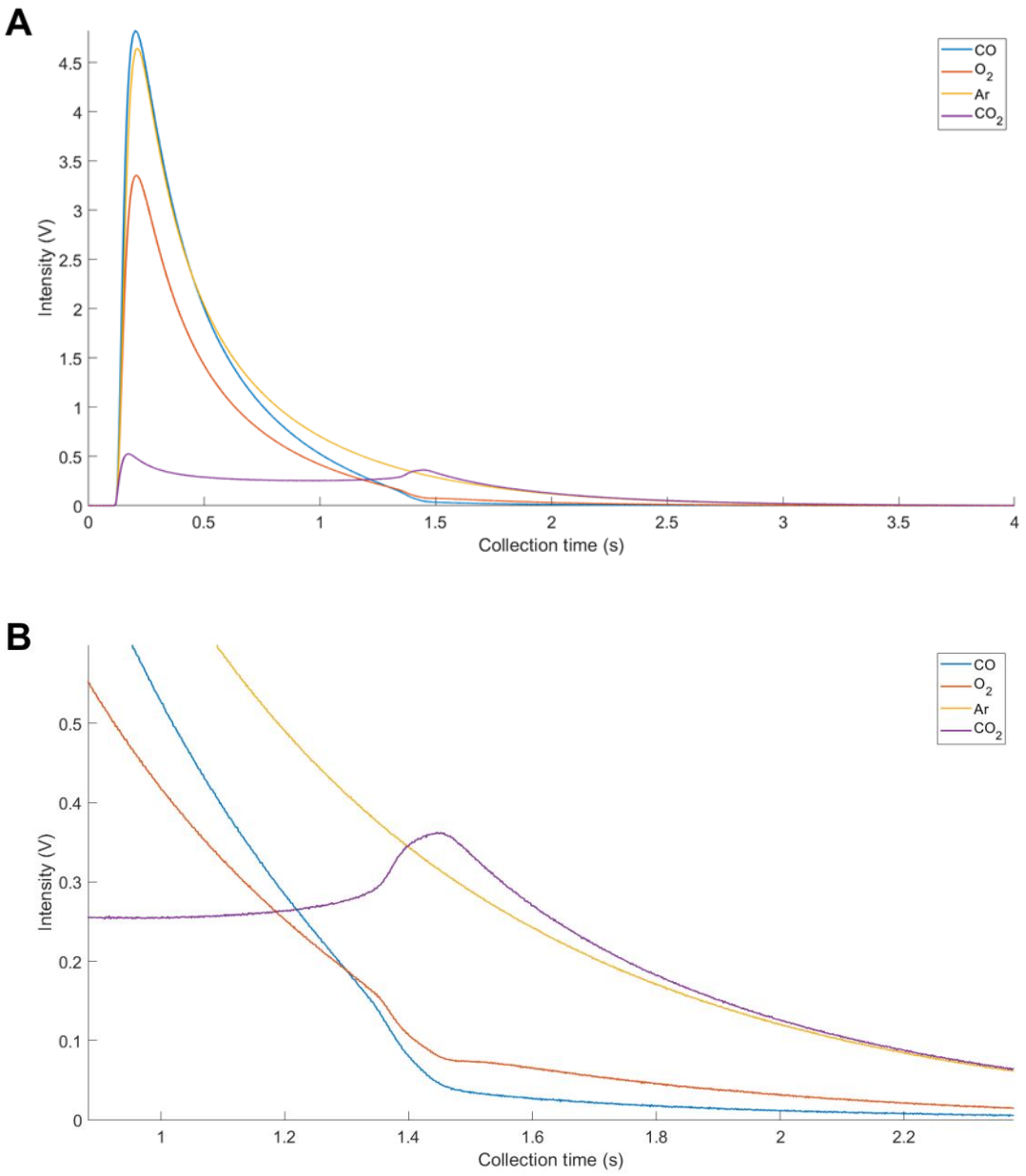

Figure 2. Average responses for a pulse experiment with a 1:1 ratio of CO/O_2. Signal gains $\kappa_{CO} = 8$; $\kappa_{O_2} = 8$; $\kappa_{Ar} = 8$; $\kappa_{CO_2} = 8$. (**A**) Average pulse responses of CO, O_2, Ar and CO_2 at 300°C. (**B**) Detailed view of the double peak phenomenon, showcasing the second CO_2 peak that occurs after the plateau

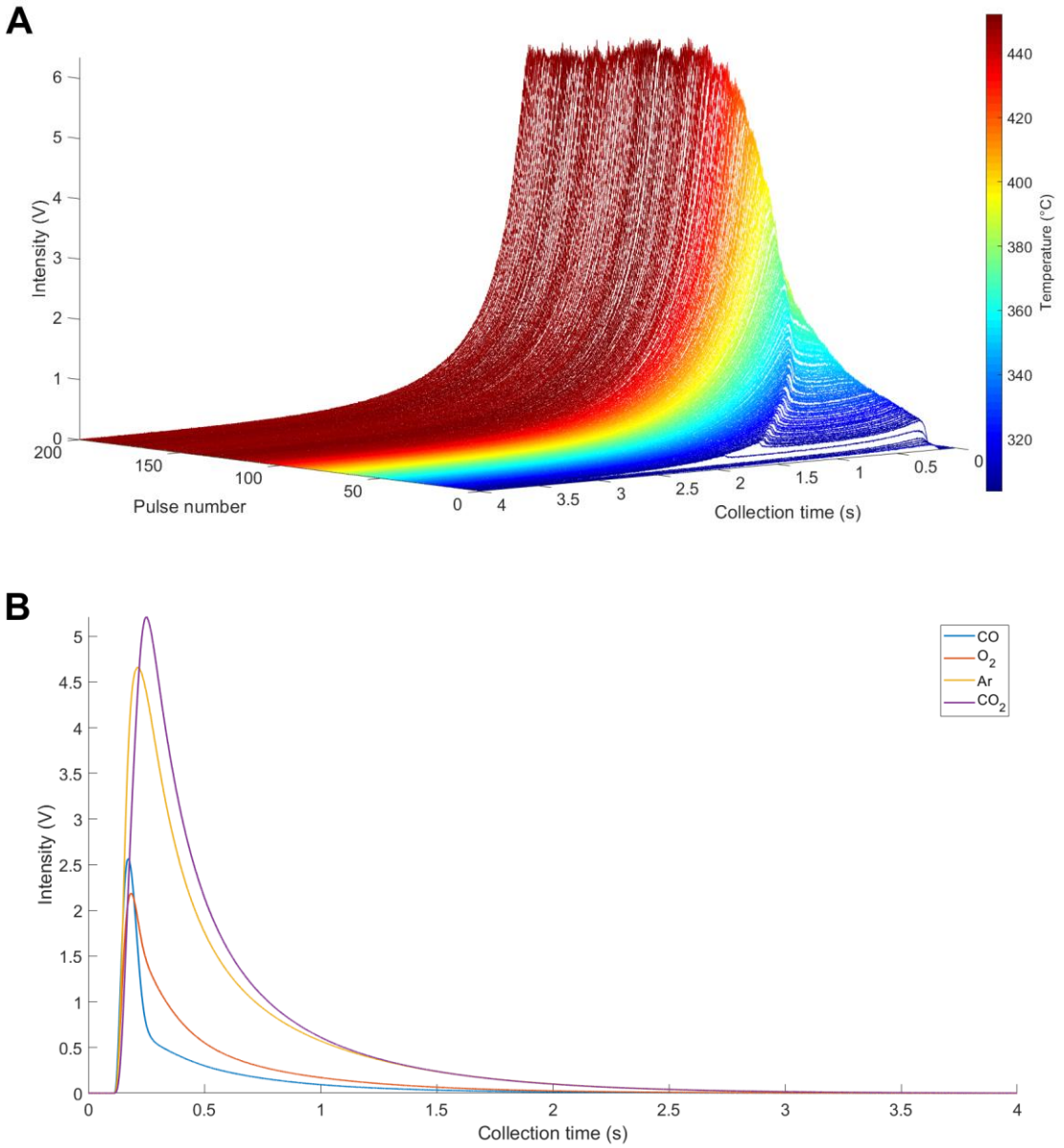

Figure 3. Evolution of the CO_2 pulse response with increasing temperatures under a 1:1 CO/O_2 ratio. (**A**) Pulse responses of CO_2 during an experiment under an increasing temperature ramp from 300°C to 450°C (5°C/min). (**B**) Average pulse responses of CO, O_2, Ar and CO_2 at 450°C. Signal gains $\kappa_{CO} = 8$; $\kappa_{O_2} = 8$; $\kappa_{Ar} = 8$; $\kappa_{CO_2} = 8$

Figure 4A presents the average pulse responses for a 1:2 CO/O_2 ratio at 300°C. It can be seen that the CO_2 signal also exhibits a double peak response, albeit with a smaller peak intensity and a slightly longer plateau. Moreover, with the appearance of the second CO_2 peak, the CO and O_2 responses show a weaker descent in curvature at

300°C compared to the one observed with a 1:1 ratio. These features can be observed with greater detail in Figure 4B. Under the increasing temperature ramp, shown in Figure 5A,the double peak response gradually merges together into a fully developed single peak in a similar manner to the response observed with a 1:1 CO/O_2 ratio. The average pulse responses at 450°C shown in Figure 5B are similar to those observed in Figure 3B as well, presenting a sharp CO and O_2 responses in conjunction with a strong CO_2 signal containing a single peak. The reactant responses display a consistent curvature during the experiment, without any radical and sudden changes. The descending temperature ramp also reproduces the behavior of the CO_2 response displayed in Figure 5A, with the double peak response appearing after the single CO_2 peak splits apart at a low enough temperature.

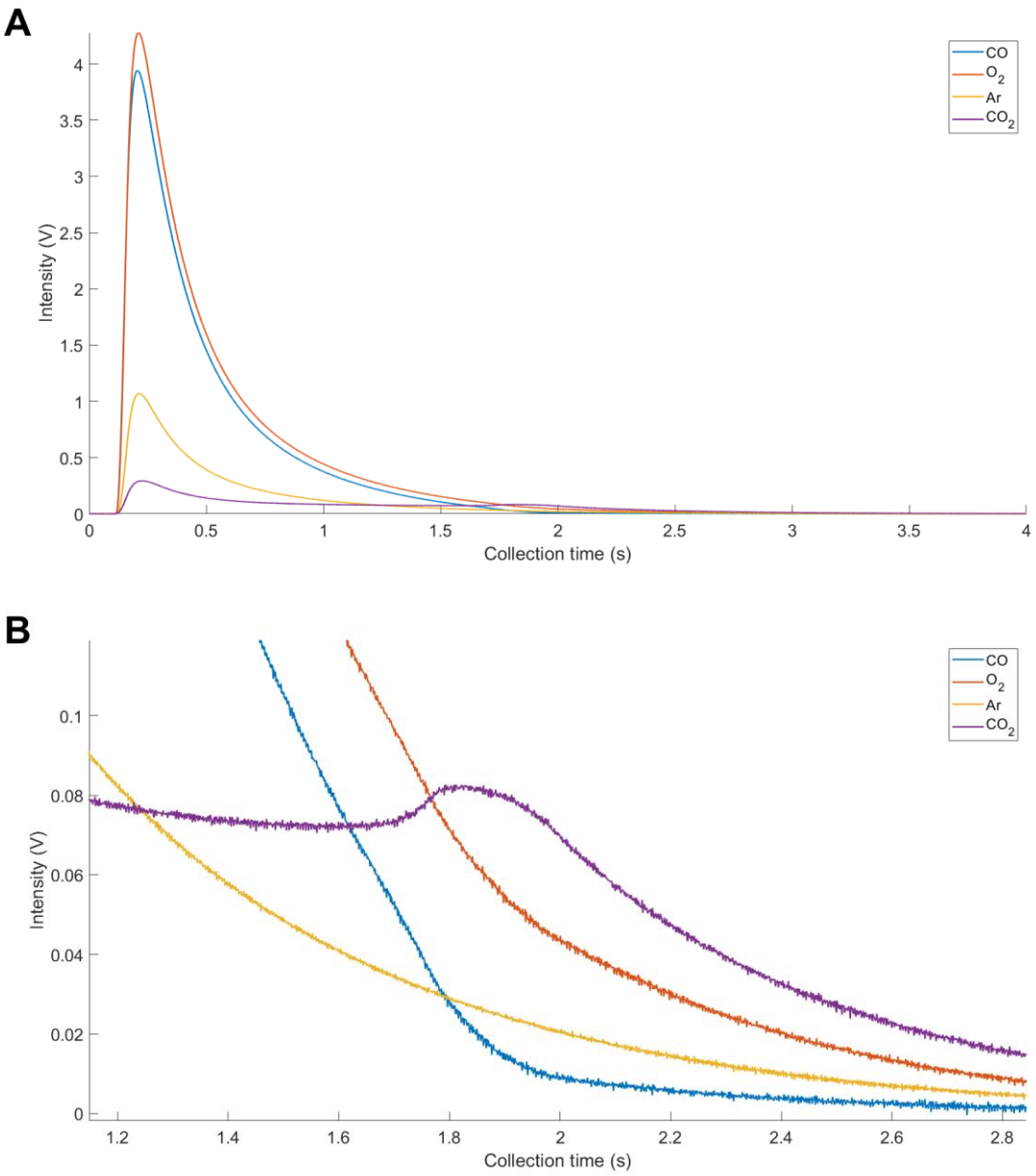

Figure 4. Average responses for a pulse experiment with a 1:2 ratio of CO/O_2 at 300°C. Signal gains $\kappa_{CO} = 8$; $\kappa_{O_2} = 8$; $\kappa_{Ar} = 7$; $\kappa_{CO_2} = 8$. (**A**) Average pulse responses of CO, O_2, Ar and CO_2. (**B**) Detailed view of the double peak phenomenon, showcasing the small second CO_2 peak that occurs after the plateau

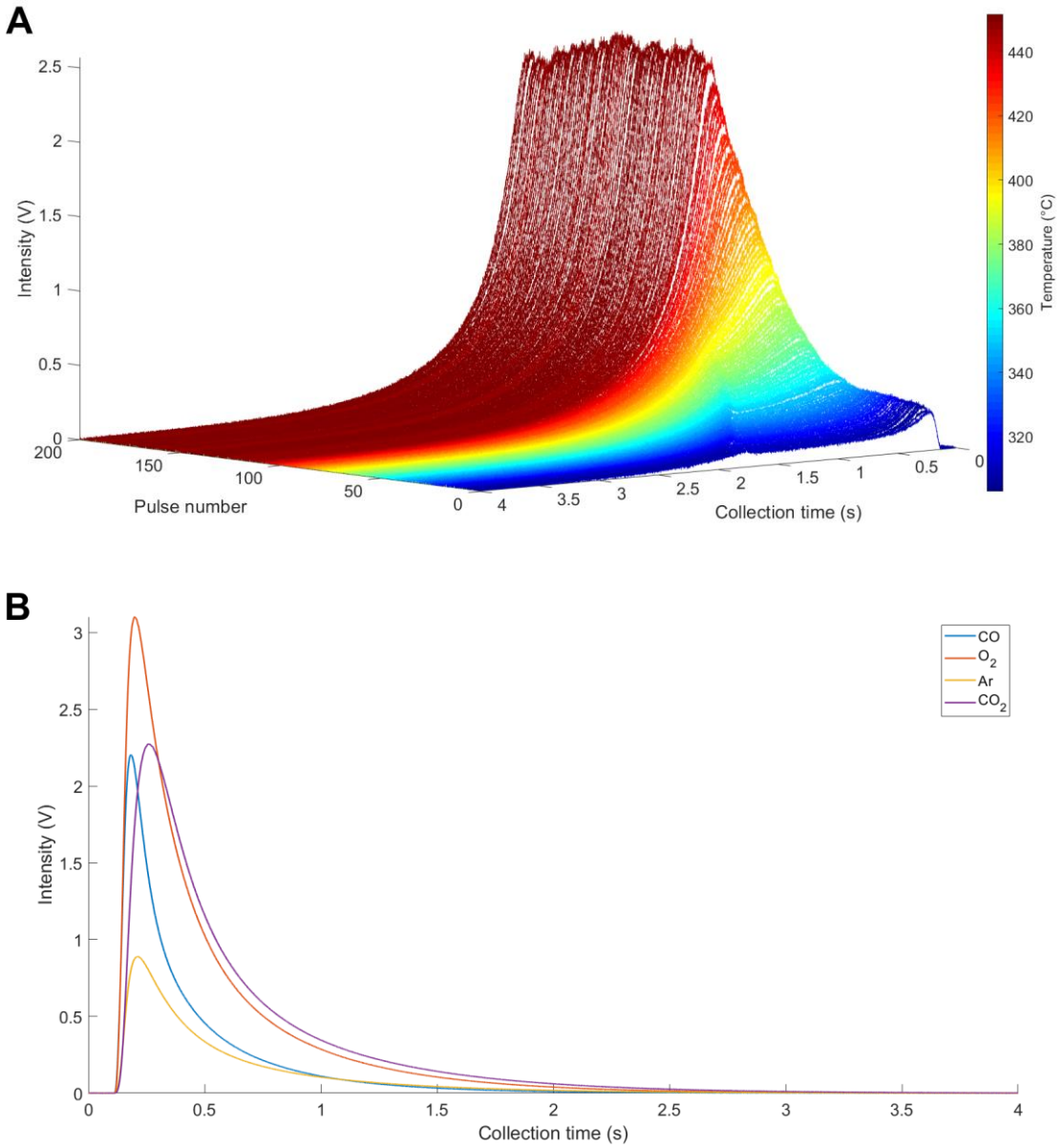

Figure 5. Evolution of the CO_2 pulse response with increasing temperature under a 1:2 CO/O_2 ratio. (**A**) Pulse responses of CO_2 during an experiment under an increasing temperature ramp from 300°C to 450°C (5°C/min). (**B**) Average pulse responses of CO, O_2, Ar and CO_2 at 450°C. Signal gains $\kappa_{CO} = 8$; $\kappa_{O_2} = 8$; $\kappa_{Ar} = 7$; $\kappa_{CO_2} = 8$

3.2. Pulse experiments with 2:1 and 3:1 CO/O_2 feed ratios

The average pulse responses for a 3:1 CO/O_2 feed ratio at 300°C are shown in Figure 6A, where the CO_2 response exhibits a weak signal intensity. Most importantly,

the shape of the CO_2 signal displayed in Figure 6B does not present a double peak or a plateau, but its tail end is rather characterized by a slow and almost linear decay. Similar pulse responses can be observed for a 2:1 CO/O_2 ratio (see Supplementary Information). Additionally, the curvature of the CO and O_2 pulse responses lacks any abrupt changes, unlike the sharp descents in their respective signals observed with 1:1 and 1:2 CO/O_2 gas ratios at the time of the second CO_2 peak.

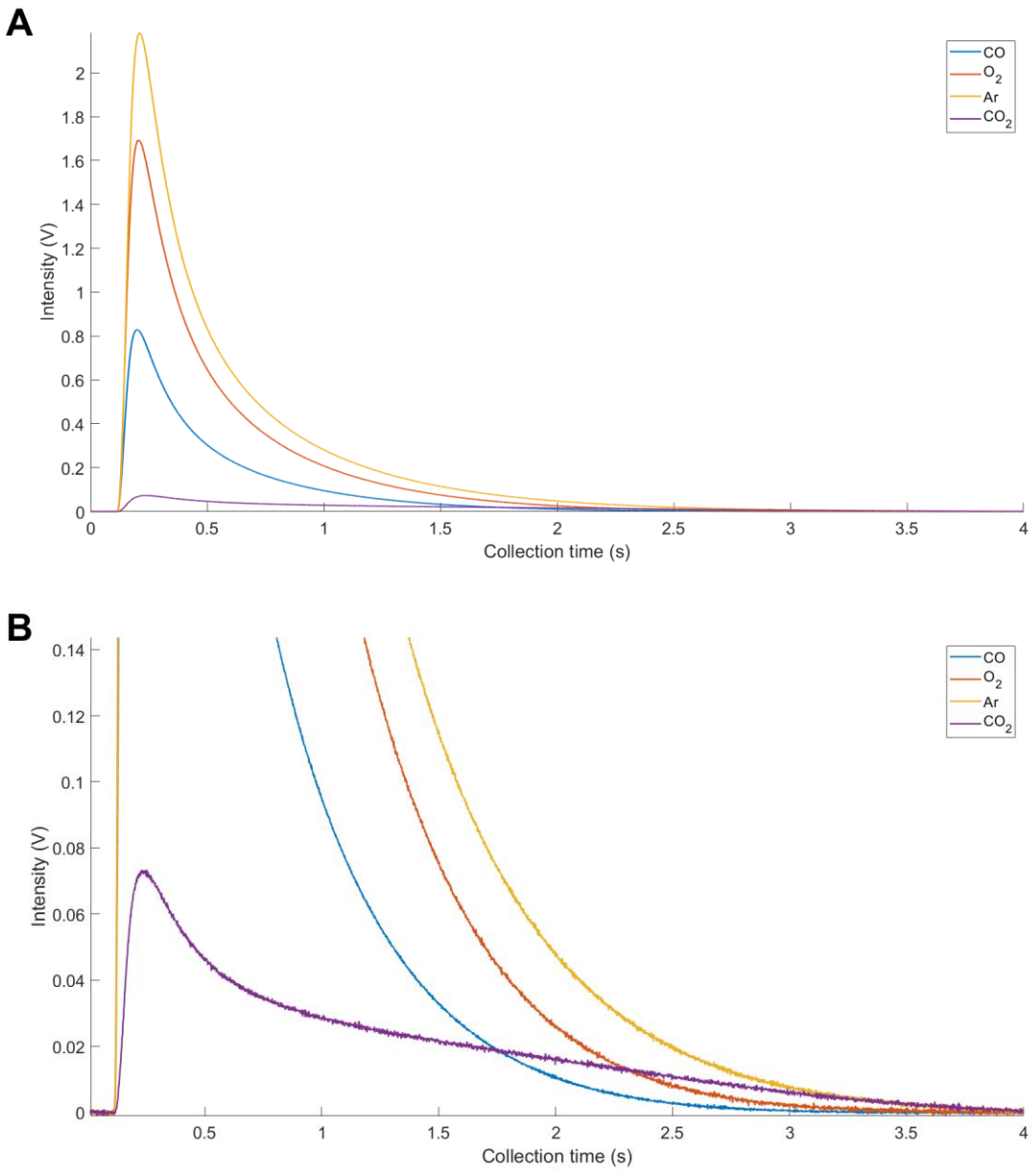

Figure 6. Average responses for a pulse experiment with a 3:1 ratio of CO/O_2 at 300°C. Signal gains $\kappa_{CO} = 7$; $\kappa_{O_2} = 8$; $\kappa_{Ar} = 8$; $\kappa_{CO_2} = 8$. (**A**) Average pulse responses of CO, O_2, Ar and CO_2. (**B**) Detailed view of the CO_2 response

Pulse responses at higher temperatures are also similar for both 2:1 and 3:1 CO/O_2 ratios. Figure 7 displays the CO_2 responses for a feed with a 3:1 CO/O_2 ratio under a temperature ramp from 300°C to 450°C. The slow decaying responses at 300°C start to increase in intensity and exhibit a steeper decay with increasing temperatures. Figure 7B shows that, at 450°C, the CO_2 response is a small and fully developed single pulse,

whereas the CO and O_2 responses showcase a sharp profile similar to those obtained with feed mixtures richer in O_2. Experiments with descending temperature ramps for both 2:1 and 3:1 CO/O_2 ratios produced a trend consistent with the behavior shown in Figure 7A.

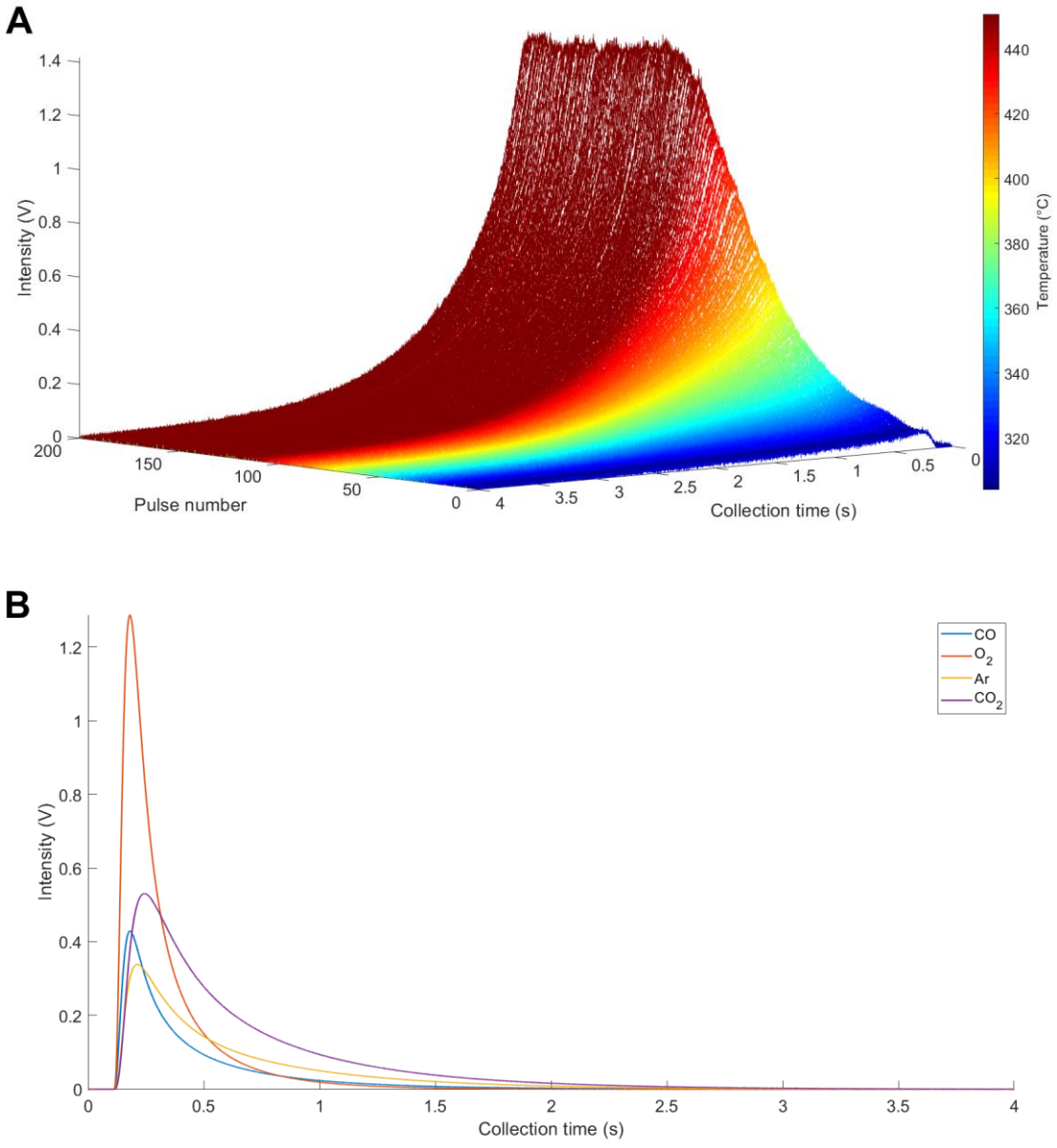

Figure 7. Evolution of the CO_2 pulse response with increasing temperature under a 3:1 CO/O_2 ratio. (**A**) Pulse responses of CO_2 during an experiment under an increasing temperature ramp from 300°C to 450°C (5°C/min). (**B**) Average pulse responses of CO, O_2, Ar and CO_2 at 450°C. Signal gains $\kappa_{CO} = 7$; $\kappa_{O_2} = 8$; $\kappa_{Ar} = 8$; $\kappa_{CO_2} = 8$

4. Discussions

In a TAP experiment, the pulse responses of reactant and product species provide information regarding the surface interactions between multiple adsorbed species on a catalyst's surface. The dynamic nature of the reaction pathway of CO oxidation taking place on the surface of the Pt catalyst can be strongly affected by the ratio of CO and O_2 in the feed. The relative amount of both reactants in the gas phase during each pulse has a direct influence on the total active site coverage of the adsorbed CO and oxygen species, which in turn determines reaction dynamics, surface phenomena and the apparent kinetics. Mechanistic implications of the CO/O_2 ratios in the gas phase can be analyzed by comparing the temporal behavior of pulse responses obtained with different feed mixtures at the same temperature conditions. Since Ar acts an inert standard, the shape of its pulse response solely reflects the influence of transport within the reactor bed. However, the average CO and O_2 responses in Figure 2 through Figure *7* exhibit a more drastic decay after their peak compared to the inert reference for all CO/O_2 ratios at both 300°C and 450°C. This behavior is typically indicative of a process defined by irreversible adsorption and reaction for both CO and O_2 [26].

CO oxidation at 300°C is evident from the clear CO_2 signals that appear during collection times in all experiments, particularly for those with 1:1 and 1:2 CO/O_2 ratios. These responses describe the series of processes involving product formation and desorption from the surface of the catalyst, coupled with diffusion from the active thin zone towards the outlet of the reactor. Nevertheless, CO_2 responses in Figure 2Figure 4 exhibit an exceptionally characteristic shape. The plateau is the most relevant part of this double peak response, because it signifies a steady release of CO_2 at the outlet despite the transient nature of the pulse experiment. This behavior lies in stark contrast with the sustained decay of the Ar response, so it must be necessarily induced by adsorption/reaction phenomena on the surface of the catalyst. Furthermore, the abrupt descents in the curvatures of the CO and O_2 responses take place at the same time the second CO_2 peak appears. This observation further reinforces the hypothesis that the particular behavior of the CO_2 response is directly caused by surface phenomena that affects both reactant responses as well.

A sustained yet slowly decaying product pulse would be possible in the case of reversible adsorption with a slow CO_2 desorption compared to its rate of formation and adsorption on the surface [26]. However, this scenario can be easily discarded given the well-known fast and irreversible nature of CO_2 desorption in the CO oxidation mechanism involving Pt sites [1]. Furthermore, any influence from the support can be neglected due to the lack of significant interactions between CO_2 and the quartz support. This was verified across pulse experiments with CO_2 and a reactor bed comprised of quartz particles similar to those acting as the catalyst's support. Moreover, the shape of the double peak response also provides information that rejects the possibility of a slow CO_2 desorption. Under this condition, the CO_2 signal after the initial peak would feature a broad bump caused by the slow desorption followed by a steady decay that would settle more slowly than the Ar signal. On the other hand, the CO_2 responses shown in Figure 2B andFigure *4*B exhibit a rather sharp second peak, followed by a decay that closely resembles that of the Ar response. This behavior suggests that the second peak is rather caused by an additional surge in CO oxidation instead of a slow CO_2 desorption. An abrupt increase in the rate of reaction would also imply an immediate decrease of the remaining CO and O_2 molecules still inside the reactor. Either due to an increased consumption in the additional formation of CO_2, or because of their adsorption on sites previously occupied by CO and oxygen species consumed in the second surge of activity. Such decreases in the reactant concentrations at the outlet are confirmed by the sudden descents in curvature observed for both the CO and O_2 responses in Figure 2B and Figure *4*B, well synchronized with the second CO_2 peak.

The temperature evolution of the CO_2 responses in Figure 3 and Figure *5* provides a deeper insight on the mechanistic origins of the double peak phenomenon. The CO_2 response that characterizes lower temperatures implies the existence of surface phenomena that limits the interactions between adsorbed CO and oxygen species. The plateau that follows the initial CO_2 peak shows that CO oxidation on the surface of the catalyst is carried out in a controlled manner, regulating the release of CO_2 in such a way that causes a constant response at the outlet despite the decreasing concentrations of CO and O_2 in the gas phase during each pulse. Furthermore, the second peak after the plateau period indicates that the system reaches a critical point of activity resulting in

a surge of CO_2 formation. This is in line with the simultaneous descents in the slopes of the CO and O_2 pulse responses at 300°C, which in turn demonstrate a sudden increase of the adsorption and reaction rates. Overall, these observations suggest a reaction mechanism that dictates an organized surface distribution of the adsorbed species and thus controls the CO_2 formation step.

The existence of a mechanism involving organized storage structures, such as surface islands, [6-8] for CO and O_2 can describe the aforementioned experimental behavior. Separate domains of adsorbed CO and oxygen atoms restrict the oxidation of CO to the boundaries of these islands, consequently limiting the rate of CO_2 formation. As reaction progresses, vacant sites on the islands' peripheries are replenished by either molecules adsorbed from the gas phase, or by the surface diffusion of species already present within the bulk of the islands. Naturally, the gas phase availability of CO and O_2 in the surroundings of the catalyst layer changes during each pulse, first increasing rapidly before decreasing as these molecules are transported across the active zone and exit the reactor. This controlled reaction between adsorbed species describes the initial peak and the plateau in the CO_2 responses at lower temperatures presented in Figure 2Figure 3A,Figure *4*Figure 5A. The plateau section of the double peak responses is a kinetic fingerprint of the structural organization of the adsorbed species. Due to the diminishing gas phase concentrations of CO and O_2, surface diffusion becomes increasingly more relevant in replenishing vacant sites at the boundaries. Consequently, the coverage of the CO and oxygen islands becomes sufficiently reduced at some point, thus breaking the organization that restrains the CO_2 formation rate. This in turn frees sites and allows the remaining CO and O_2 in the gas phase to adsorb and react rapidly. This would explain the second activity peak observed in the CO_2 responses and the sharp descents in the curvature of the CO and O_2 signals of Figure 2B andFigure *4*B.

A reaction mechanism involving CO and oxygen islands can also elucidate the flat profile observed in the double peak response of CO_2 at lower temperatures. The inherently transient nature of the experiment implies time dependent reactant concentrations in the gas phase, which consequently suggest non-steady surface coverages for both reactant domains during the course of the reaction. The initial and

final peaks of the CO_2 signal are an indication that the island mechanism can cause the reaction rate to transition between two critical values depending on the state of the surface islands over the duration of the pulse. The initial rise and peak of the CO_2 response indicates the first critical value of the reaction rate and corresponds to the adsorption of CO and O_2 from the gas phase, initially with a high reactant concentration, before the organization of the adsorbed species into surface islands becomes dominant. As these continue to grow and cover the surface of the catalyst, CO oxidation becomes limited to their boundaries and the reaction rate is consequently restrained. This transition to a “low” activity regime is determined by the dynamic evolution of the CO and oxygen islands, and is characterized by the decay after the initial peak and the posterior formation of the plateau. During this stage, the surface coverages of the adsorbed species may change dynamically due to the interplay between the formation of CO_2 at the islands’ peripheries, the adsorption of reactants from the gas phase and the surface diffusion from to the bulk of the islands towards their boundaries. Surface coverages do not reach critical points during this restrained regime, as evidenced by the sustained behavior of the plateaus observed in the double peak responses. However, as islands begin to reduce and disperse, the reaction rate attains a second critical value after the dynamic surface coverages reach a new critical point. This transition to the high activity regime causes the second CO_2 peak and the abrupt descents of the CO and O_2 signals. In summary, the dynamic evolution of the islands’ surface coverages determine the existence of two critical points for the reaction rate. The first corresponds to the initial organization of the surface islands and the second to their collapse. The transition between these critical points involve a restrained reaction rate due to the organized CO and oxygen domains that limit CO oxidation to their boundaries.

Surface islands and the dynamic transitions between activity regimes also account for the responses obtained during the temperature ramps and at 450°C. The reduced duration of the plateau between peaks and their posterior merging into a single and fully developed pulse can be explained by the increased mobility of the adsorbed CO atoms at higher temperatures [30, 31]. This favored surface diffusion disperses the CO islands and reduces their size, extending their overall reactive boundaries and increasing their interactions with the oxygen islands. Consequently, this improved reactivity translates

into the shorter transitional periods and stronger second peaks observed in Figure 3A. Furthermore, as temperatures continue to rise, CO is able to react with the oxygen at the surface without any significant surface restrictions, thereby generating a single and highly intense CO_2 peak. At 450°C, the sharp CO pulse profiles presented in Figure 3B Figure 5B shows the fast rate of CO adsorption, while the broader O_2 signals suggest an increased desorption step at higher temperatures [1].

The different adsorption mechanisms of CO and O_2 also play a key role in the formation of islands and their overall surface coverage. Due to its dissociative behavior [1, 2], the adsorption of a O_2 molecule requires two free adjacent active sites to form its adsorbed species, in contrast with CO that only requires a single free active site. Therefore, the CO/O_2 ratio in the gas phase possesses a strong influence in the reaction mechanism and its dynamic behavior. Previously, it was found that CO_2 is not formed if a surface saturated with CO is exposed to O_2 [3, 4]. This is a direct consequence of the necessity of vacant adjacent sites for molecular O_2 to adsorb on the surface. On the other hand, CO has been found to adsorb on oxygen covered surfaces [5]. Based on the discussed experimental results with 1:1 and 1:2 CO/O_2 ratios, gas phase mixtures richer in O_2 can result in a high activity and complex dynamic transitions due to the surface island mechanism.

With a 1:2 CO/O_2 ratio in the feed, the surface coverage of oxygen becomes more dominant over the CO islands. CO oxidation takes place on the surface with more limitations due to the smaller amounts of CO. This is evidenced in the smaller peaks and the longer plateau in the CO_2 responses of Figure 4Figure 5A. Additionally, the smaller descents in the slopes of the CO and O_2 further suggests that the second surge in activity is more limited due to the smaller availability of CO in the gas phase. The increased surface mobility of CO at higher temperatures, combined with the larger amount of oxygen covering the surface, results in a quicker vanishing of the plateau compared to the trend presented in Figure 3A.

Due to the increased CO concentration in experiments under 2:1 and 3:1 CO/O_2 ratios, CO can adsorb more easily on the surface of the catalyst, consequently limiting the free surface for O_2 adsorption. This becomes apparent from the average pulse

responses displayed in Figure 6, corresponding to a feed mixture with a 3:1 CO/O_2 ratio at 300°C. The diminished intensity of the CO_2 signal suggests that CO oxidation is more limited compared to feed ratios rich in oxygen. This decreased activity can be directly explained by the excessive CO coverage that that reduces the amount of adsorbed O_2 and thus, diminishes the reaction rate [3, 4]. Another major departure from the responses obtained with feed mixtures richer in O_2 lies in the shape of the CO_2 responses, which do not possess a double peak or a plateau. However, as seen in Figure 6B, the CO_2 signal shows a slow and almost linear decay towards their baselines.

These patterns are also described by the restrained rate of CO oxidation introduced by the surface island mechanism. The separation of the CO and oxygen domains on the surface limits CO_2 formation to their boundaries, which in turn controls the formation and subsequent release of CO_2 in a manner somewhat similar to the trend observed in Figure 2 Figure 4. However, the excessive CO coverage on the catalyst's surface hinders the adsorption of O_2 from the gas phase and limits CO oxidation even further. The increased CO concentration in the gas phase forces the CO_2 response to decay over time as vacant sites are more likely to be occupied by CO. Therefore, CO_2 formation cannot be sustained throughout the duration of the pulse due the limited O_2 adsorption. The absence of a flat response shows that the reaction rate cannot reach a second critical point on a surface predominantly covered with CO. Therefore, the reaction rate reaches a maximum and posteriorly suffers a slow relaxation evidenced by the virtually linear decay of the CO_2 signal displayed in Figure 6B. Additionally, the curvature of the pulse responses for CO and O_2 lacks any abrupt changes, unlike the sharp descents observed with 1:1 and 1:2 CO/O_2 gas ratios at the time of the second CO_2 peak. Such behavior is also indicative of a more controlled CO oxidation rate that decays progressively due to a lack of a sufficient oxygen coverage.

The surface island mechanism is also responsible for the behavior at higher temperatures. Due to the increased surface mobility of CO under such conditions, the CO islands become smaller and more dispersed, which favors the adsorption of oxygen. CO oxidation is thus enhanced since CO and oxygen coverages are better balanced compared to lower temperatures. This explains the larger intensity and steeper decay of the CO_2 responses in Figure 7A, under the increasing temperature ramp, and in Figure

7B at 450°C. Additionally, the sharper profiles of the O_2 responses in Figure 7B confirm that O_2 adsorption is favored at higher temperatures for feed mixtures richer in CO.

5. Conclusions

TAP experiments involving CO oxidation under transient conditions provide information on the reaction mechanism and surface phenomena for a catalyst consisting of Pt NPs deposited on quartz particles via ALD. In particular, the influences of temperature and the proportions of CO and O_2 in the gas phase on the reaction pathway are identified by analyzing the features of the transient responses of CO_2 and both reactants. With CO/O_2 ratios of 1:1 and 1:2, the CO_2 response at 300°C consists of a peculiar double peak curve, with a flat plateau between peaks. This type of response is indicative of a dynamic transition between critical values of the reaction rate introduced by the restrained interactions between segregated islands of adsorbed CO and oxygen on the catalyst's surface. As the boundaries of these domains interact to form CO_2, the interplay between the surface diffusion of reactant species in the islands' bulk and the adsorption of CO and O_2 from the gas phase sustains the reaction rate in a transition period between critical surface coverages of the adsorbed CO and oxygen species. This mechanism explains the temporal evolution of the double peak responses and the abrupt changes in the curvature of the CO and O_2 signals during the formation of the second CO_2 peak. On the other hand, a slow and virtually linear decay was observed for CO_2 responses in pulse experiments with feed mixtures with a richer CO content at 300°C. With 2:1 and 3:1 CO/O_2 ratios, the increased CO coverage hinders the adsorption of O_2 due to the latter's dissociative nature. This consequently limits the surface coverage of the adsorbed oxygen species and diminishes the overall rate of CO oxidation over the duration of the pulse response.

Pulse experiments also detail the dynamic evolution of the kinetics of CO oxidation at higher temperatures. The double peak responses exhibit shorter plateaus with increasing temperatures, until their double peaks merge to form single and intense CO_2 peaks. This behavior can be ascribed to an increased surface mobility of the adsorbed reactant species, which in turns favors the dispersion of the islands and increases their mutual interactions. Therefore, transitions between critical points become more unstable

under higher temperatures due to the less restrained interactions between adsorbed CO and oxygen species on the surface of the catalyst. Dispersion of the islands at higher temperatures is also responsible for improving O_2 adsorption in feed mixtures with higher proportions of CO, thus greatly increasing the rate of CO oxidation.

Author contributions

Conceptualization: JIM, VVG, DC

Data curation: JIM

Formal Analysis: JIM

Methodology: JIM

Software: JIM

Investigation: JIM

Visualization: JIM

Funding acquisition: VVG, DC

Project administration: VVG, DC

Supervision: VVG, DC

Writing – original draft: JIM

Writing – review & editing: JIM, VVG, DC, JD, JM, GY

Declaration of Competing Interest

The authors hereby declare no competing interests.

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Supplementary Information

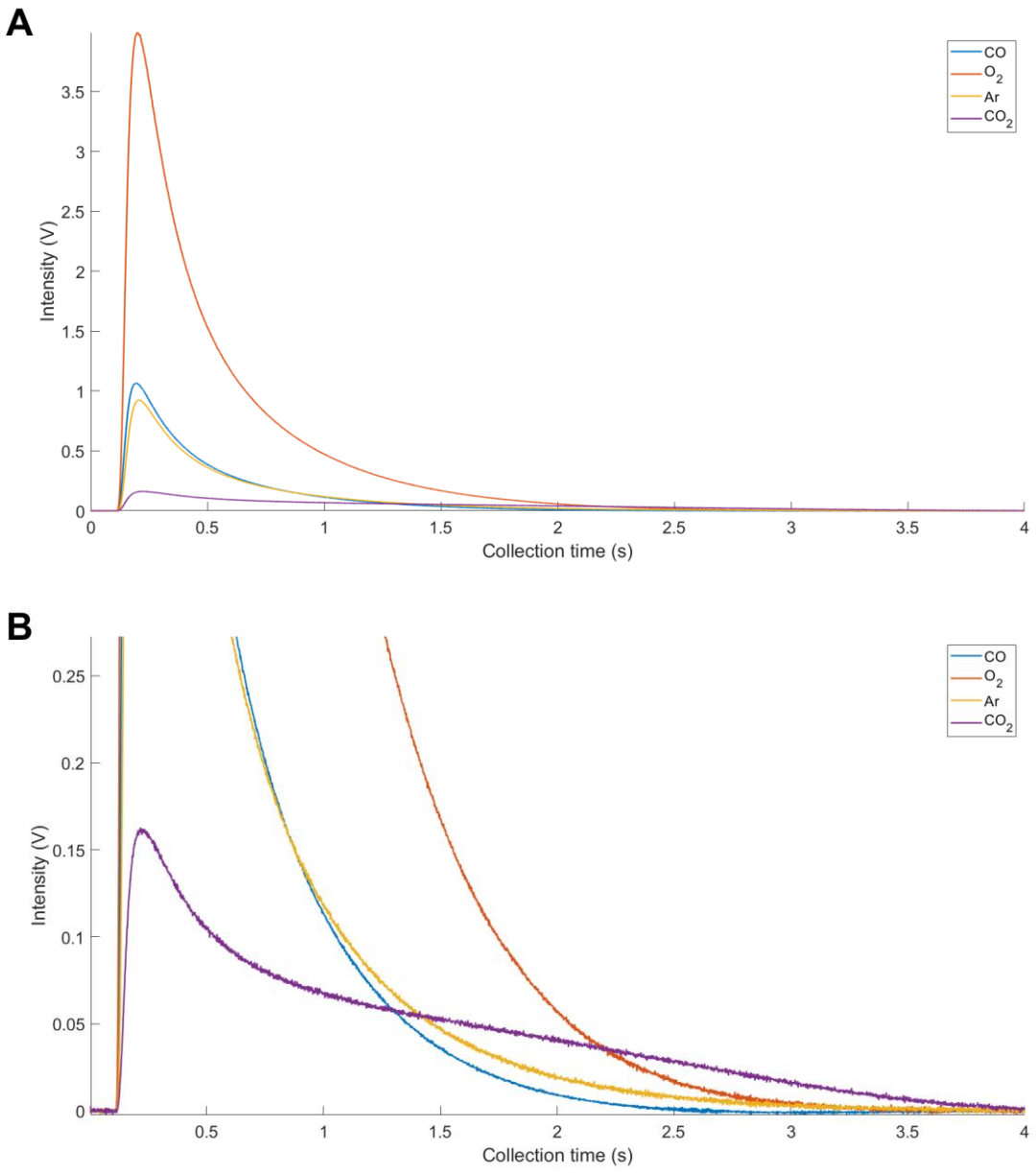

Figure S1. Average responses for a pulse experiment with a 2:1 ratio of CO/O_2 at 300°C. Signal gains $\kappa_{CO} = 7$; $\kappa_{O_2} = 8$; $\kappa_{Ar} = 8$; $\kappa_{CO_2} = 8$. (**A**) Average pulse responses of CO, O_2, Ar and CO_2. (**B**) Detailed view of the CO_2 response.

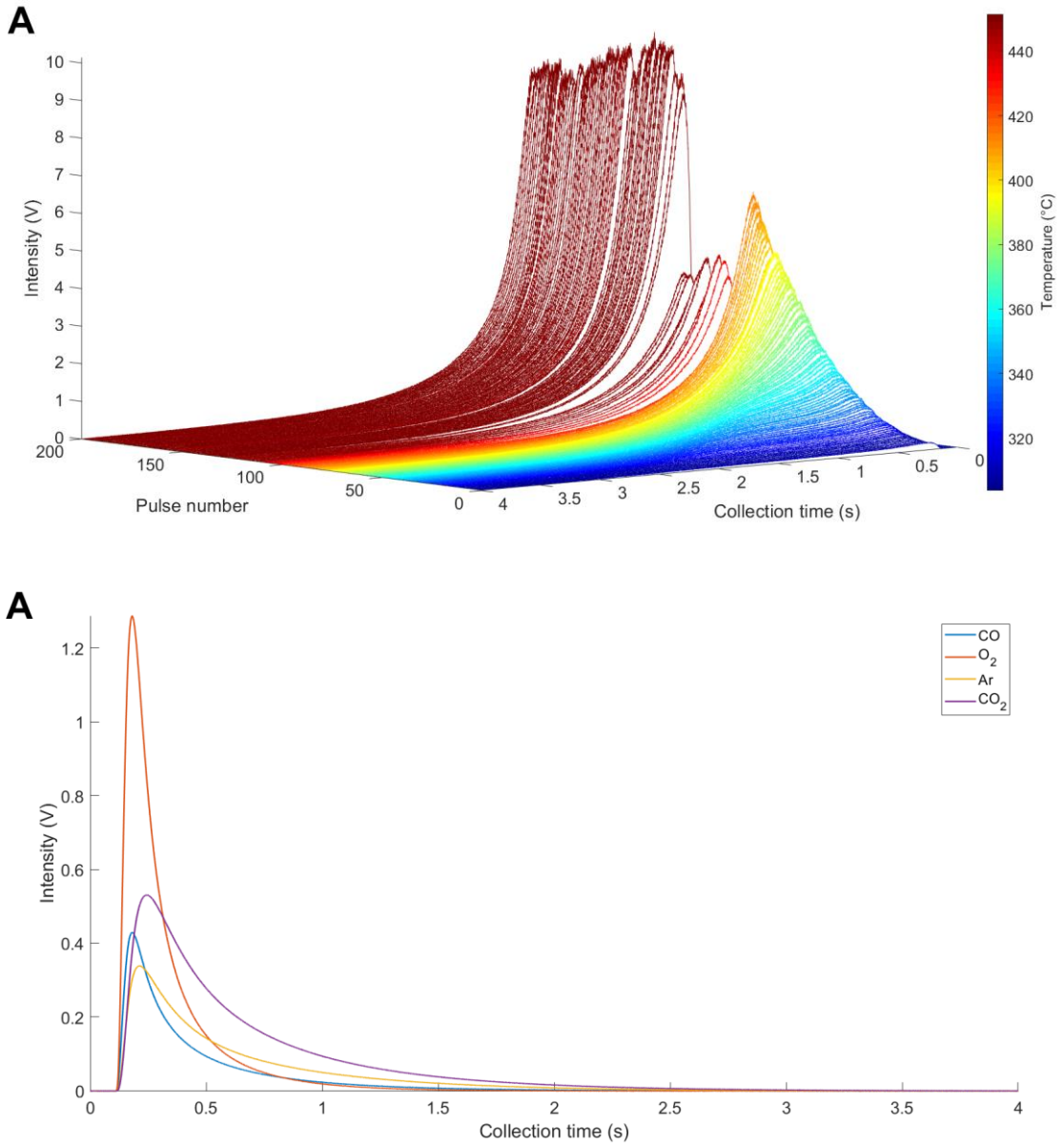

Figure S2. Evolution of the CO_2 pulse response with increasing temperature under a 2:1 CO/O_2 ratio. (**A**) Pulse responses of CO_2 during an experiment under an increasing temperature ramp from 300°C to 450°C (5°C/min). Irregular signal intensities caused by a momentaneous instability in the pulse valve's mechanism. (**B**) Average pulse responses of CO, O_2, Ar and CO_2 at 450°C. Signal gains $\kappa_{CO} = 7$; $\kappa_{O_2} = 8$; $\kappa_{Ar} = 8$; $\kappa_{CO_2} = 7$.