Deactivation of Pt/Al₂O₃ during propane oxidation at low temperatures: kinetic regimes and platinum oxide formation

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Abstract

The kinetics of propane oxidation over Pt/Al₂O₃ are investigated in this work as a function of O₂/C₃H₈ ratio in the 150-300 °C temperature range. At high O₂/C₃H₈ ratios, the platinum nanoparticles are saturated with oxygen and the reaction rate is zero-order with respect to the oxygen partial pressures in this regime. As the oxygen coverage decreases with decreasing O₂/C₃H₈ ratio, the reaction rate increases and the reaction order changes from zero-order to negative-order in the oxygen partial pressure. The reaction rate is controlled to a large extent by the oxygen coverage on the platinum nanoparticles. However, at lower temperatures and higher oxygen pressures there is a slow deactivation of the catalyst that cannot be explained by a slow change in the oxygen coverage. Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) of adsorbed CO was performed to track the evolution of the nanoparticle structure over the course of the propane oxidation reaction and to determine whether the slow deactivation

was caused by reconstruction of the platinum nanoparticles. We found that the platinum nanoparticles are significantly reconstructed during the course of the reaction, including the formation of a platinum oxide (PtO) which has a characteristic CO-DRIFTS band at 2123 cm^{-1} . The extent of PtO formation decreases with increasing temperature and, as a result, deactivation of the catalyst is less severe at higher temperatures. Unexpectedly, increasing the oxygen partial pressure resulted in less PtO formation. We believe that a different platinum oxide phase (e.g. PtO₂ or Pt₃O₄) is formed at higher oxygen pressures, which is reduced to metallic platinum during CO exposure at 25 °C, and therefore is not detectable by CO-DRIFTS. These results are unique because they show how the nanoparticle structure evolves over many hours of propane oxidation, and how the temperature and oxygen pressure influence the reconstruction of the nanoparticles, which has implications for a wide range of reactions not limited to propane oxidation.

Keywords: kinetic regimes, oxidation, platinum oxide, infrared spectroscopy

1. Introduction

Due to the vast number of possible elementary reaction steps in alkane oxidation reactions, even for the simplest alkanes methane [1] and ethane [2], reaction rate equations are often simplified to include only the most kinetically-relevant step. For alkane oxidation over a typical oxidation catalyst such as platinum, several different kinetic regimes can exist in which the kinetically-relevant step and the rate equations are different in each regime. These kinetic regimes have been investigated recently for methane [3] and ethane [4] oxidation over Pt/Al₂O₃. It was shown that there are three distinct kinetic regimes for oxidation of both methane and ethane over platinum clusters in the 450-640 °C temperature range. The reaction order with respect to the oxygen partial pressure was different in each regime, and the transition between regimes was related to changes in the chemisorbed oxygen (O*) coverage. At high O₂/alkane ratios, C-H bond activation on the oxygen-saturated platinum surface is the kinetically-relevant step, and the reaction rate is zero-order with respect to the oxygen partial pressure. As bare platinum sites (*) are exposed by decreasing the O₂/alkane ratio, C-H bond activation at O*-* site pairs is the kinetically-relevant step, and the reaction rate is negative-order with respect to the oxygen partial pressure. At low O₂/alkane ratios, O₂ dissociation on the bare platinum surface is the kinetically-relevant step and the reaction rate is first-order in the oxygen partial pressure. The similarities between the kinetic regimes of methane and ethane oxidation suggest that similar reaction pathways may exist for the oxidation of larger alkanes such as propane.

There are discrepancies in the literature regarding the kinetics of propane oxidation which might be related to different kinetic regimes analogous to those of methane and ethane oxidation. It is generally agreed that the rate of propane oxidation over platinum is first-order with respect to the propane partial pressure [5-8]. However, the propane oxidation rate has been reported as

both zero-order [5-10] and negative-order [6-8] with respect to the oxygen partial pressure. It is probable that these discrepancies in the oxygen reaction order are a result of different kinetic regimes, similar to those of methane and ethane, in which the reaction order depends on the chemisorbed oxygen coverage. A thorough characterization of the kinetic regimes of propane oxidation is needed to determine whether the different oxygen reaction orders are due to different kinetic regimes.

Repulsive interactions between oxygen atoms destabilize chemisorbed oxygen at high coverages, and another oxygen species, platinum oxide, becomes more thermodynamically favorable than chemisorbed oxygen [11-19]. It is widely accepted that platinum oxide formation has a significant impact on the catalytic activity of platinum for many different reactions, including oxidation of CO [20], NO [21], methane [22], methanol [23], and propane [24-29]. In a series of articles investigating the effects of the platinum dispersion [25], the support [24, 25, 27], and metal additives [26, 27] on the propane combustion activity of platinum, a group of researchers discovered a strong correlation between the oxidation state of platinum and its catalytic activity: reduced platinum was more active than oxidized platinum. Other studies [28, 29] have corroborated these findings and have found that platinum oxide is significantly less active for propane oxidation than metallic platinum. However, there are still many aspects of platinum oxide formation—including the structure of platinum oxides, the kinetics and mechanisms of oxide formation and reduction, and the catalytic activity of platinum oxides—which remain poorly understood.

In this work, the kinetics of propane oxidation over Pt/Al₂O₃ are investigated as a function of O₂/C₃H₈ ratio in the 150-300 °C temperature range. We show that there are distinct regimes in the reaction rate that are dictated by the chemisorbed oxygen coverage on the

platinum nanoparticles. However, there is a slow deactivation of the catalyst at lower temperatures and higher O_2/C_3H_8 ratios which is not likely due to a slow change in the chemisorbed oxygen coverage. DRIFTS of adsorbed CO was used to investigate the evolution of the platinum nanoparticle structure over the course of the propane oxidation reaction. We found that there is significant reconstruction of the platinum nanoparticles during the reaction, including the formation of platinum oxides, which could explain the slow deactivation of the catalyst. These results indicate that the kinetics of propane oxidation are controlled to a large extent by the chemisorbed oxygen coverage at higher temperatures. At lower temperatures, however, the rate of propane oxidation is governed by more than simply the chemisorbed oxygen coverage and the slow formation of platinum oxides significantly influences the reaction rate.

2. Experimental

2.1 Catalyst preparation and characterization

The Pt/ Al_2O_3 catalyst used in this work was prepared by incipient wetness impregnation of $\gamma-Al_2O_3$ (Davicat AL 2100, Davison Catalysts) with Pt(IV) nitrate solution (Pt 15% w/w, Alfa Aesar), followed by calcination in air at 700 °C for 16 hours. The Pt concentration in the prepared Pt/ Al_2O_3 catalyst was 16.5% of the total weight of the catalyst, measured by inductively coupled plasma atomic emission spectrometry at Galbraith Laboratories, Inc. The deposition of Pt nanoparticles on Al_2O_3 was examined using transmission electron microscopy (Figure S1 in Supporting Information). The dimensions of more than 200 Pt nanoparticles were measured using TEM images and the average diameter of the Pt nanoparticles is 18 nm (Figure S2 in Supporting Information). The as-prepared Pt/ Al_2O_3 (16.5 wt% Pt) was diluted with Al_2O_3 that was pre-calcined at 700 °C for 16 hours to give a Pt loading of 2%.

2.2 Instrumentation

All experiments were performed in a Harrick Praying MantisTM High Temperature Reaction Chamber. The reaction chamber was placed inside of a Praying MantisTM Diffuse Reflectance Accessory (Harrick Scientific Products, Inc.) in the sample compartment of a Bruker Vertex 70 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector. The sample cup of the reaction chamber was filled with approximately 25 mg of the 2%Pt/Al₂O₃ catalyst for each experiment. A Fischer Scientific Isotemp 3016 water chiller was used to cool the reaction chamber. Mass flow controllers (MKS Instruments 1179A Mass-Flo®) were used to regulate the flow rates of feed gases to the high temperature reaction chamber. The product gas exiting the catalyst bed was analyzed by an Agilent 3000A Micro gas chromatograph (GC) and an Agilent Technologies 5973 Mass Selective Detector. The GC columns were molecular sieve, Plot U, alumina, and OV-1.

2.3 Catalyst pre-treatment

The catalysts were pre-treated using the following sequence of steps: (1) heat the catalyst from 25 °C to 600 °C at a heating rate of 25 °C/min while flowing 3 mL/min O₂ (Airgas, 99.999%) and 80 mL/min Ar (Airgas, 99.999%) over the catalyst; (2) hold the catalyst at 600 °C for 10 minutes while flowing 3 mL/min O₂ and 80 mL/min Ar over the catalyst; (3) purge the reaction chamber with 80 mL/min Ar; (4) flow 50 mL/min 4.45%H₂/balance N₂ (Air Products) over the catalyst at 600 °C for 40 minutes; (5) cool the catalyst to 250 °C while flowing 50 mL/min 4.45%H₂/balance N₂; (6) purge the reaction chamber with 80 mL/min Ar and then cool to 25 °C. Following pre-treatment, the catalyst was heated to the temperature of the reaction while flowing 80 mL/min Ar through the reaction chamber.

2.4 Propane oxidation experiments

Propane oxidation experiments were performed isothermally at atmospheric pressure with both variable O₂/C₃H₈ ratio, to investigate the kinetic regimes, and with constant O₂/C₃H₈ ratio, to investigate the transient deactivation of the catalyst. The propane flow rate (0.6 mL/min) and the total flow rate (80.4 mL/min) were held constant during all propane oxidation experiments. Propane was fed to the reactor by flowing 15.0 mL/min of a (4.0±0.1)% propane in Ar balance gas mixture (Airgas), giving a propane flow rate of 0.6 mL/min. Propane oxidation experiments with variable O₂/C₃H₈ ratio began by flowing 0.5 mL/min O₂ (Airgas, 99.999%) and 64.9 mL/min of Ar (Airgas, 99.999%) at the reaction temperature. After 5 minutes of O₂ pre-exposure, 15.0 mL/min of the 4% propane in Ar gas mixture was introduced to the reaction chamber. Once a steady-state CO₂ production rate was achieved, measured by GC analysis of the product gas, the O₂ flow rate was increased by 0.5 mL/min and the Ar flow rate was decreased by 0.5 mL/min to maintain a constant flow rate. The O₂ flow rate was increased step-wise up to a maximum flow rate of 60 mL/min, resulting in a wide range of O₂/C₃H₈ ratios from 0.8 to 100. Once the maximum O₂/C₃H₈ ratio was reached, the O₂/C₃H₈ ratio was decreased step-wise in a similar fashion to determine whether there was a hysteresis in the propane oxidation rate. During propane oxidation experiments with a constant O₂/C₃H₈ ratio, two different O₂/C₃H₈ ratios (5 and 20) were used at 200, 250, and 300 °C. Following 8 minutes of O₂/Ar pre-exposure, 15.0 mL/min of the 4% propane in Ar gas mixture was introduced to the reaction chamber and the product gases were analyzed continuously for 8 hours.

The specific CO₂ production rate (TOF) was calculated using the following equation [22]:

$$TOF = \frac{C_{CO_2} \cdot F_{total} \cdot M_{Pt}}{w_{cat} \cdot D \cdot L \cdot 22400}$$

where C_{CO_2} represents the **fraction** of CO_2 in the product gas measured by GC, F_{total} represents the total flow rate of the feed gas (**1.34 mL/s**), M_{Pt} represents the molecular mass of Pt (195.09 g/mol), w_{cat} represents the weight of the catalyst (~0.025 g), D represents the dispersion of Pt estimated below, L represents the Pt loading (0.02), and 22400 (mL/mol) is the factor for converting mL of gas to moles. The dispersion (D) was calculated assuming the Pt particles are spherical according to the following equation [22]:

$$D = \frac{6 \cdot V_{atom}}{A_{atom} \cdot d_{particle}} = 0.06$$

where V_{atom} represents the atomic volume (0.0151 nm³), A_{atom} represents the surface area of one Pt atom (0.08 nm²), and $d_{particle}$ represents the average particle size measured by TEM (18 nm).

2.5 DRIFTS of adsorbed CO on Pt/Al₂O₃

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed CO was used to monitor the evolution of the platinum nanoparticles resulting from propane oxidation at elevated temperatures. Each DRIFTS spectrum was collected at 25 °C with a spectral resolution of 2 cm⁻¹ and 128 scans per spectrum. Following catalyst pre-treatment, the catalyst was cooled to 25 °C and a background spectrum was collected while flowing 50 mL/min of Ar. A 10%CO in Ar gas mixture (Airgas) was then introduced to the reactor with a flow rate of 50 mL/min to saturate the platinum surface with CO. After 10 minutes of CO exposure, the reaction chamber was purged with 50 mL/min of Ar and DRIFTS spectra were collected during the Ar purge until no more gas-phase CO was detected in the DRIFTS spectra (~15 minutes). The catalyst was then heated to the reaction temperature and propane oxidation over the catalyst was performed for 5 minutes in a manner similar to that described in the previous section. In order to quench the deactivated state of the catalyst, the catalyst was quickly (~20 minutes) cooled from

the reaction temperature to 25 °C while flowing the feed gas mixture until the catalyst reached 75 °C. At 75 °C, the flow of 4%propane/Ar to the reactor was stopped and at 50 °C the flow of O₂ to the reactor was stopped. Cooling from 50 °C to 25 °C was done while flowing 50 mL/min Ar. DRIFTS of adsorbed CO was then performed in a similar manner to that performed on the freshly pre-treated catalyst. We found that the CO chemisorption capacity of the platinum was reduced by cooling the catalyst to 50 °C in O₂, but the reconstruction of the catalyst resulting from propane oxidation at elevated temperatures influenced the adsorption of CO on platinum much more significantly. The catalyst was then heated to the reaction temperature and propane oxidation was performed for an additional 15 minutes (for a total of 20 minutes of propane oxidation time) before CO-DRIFTS was performed. For each set of experiments, DRIFTS of adsorbed CO was performed after 5, 20, 120, and 1000 minutes of propane oxidation at elevated temperatures.

3. Results and Discussion

3.1 Kinetic regimes of propane oxidation over Pt/Al₂O₃

The kinetic regimes of propane oxidation over Pt/Al₂O₃ were investigated in the 150-300 °C temperature range by flowing propane, oxygen and argon to a Pt/Al₂O₃ catalyst bed held at constant temperature while measuring the CO₂ concentration in the product gas with a gas chromatograph. The oxygen flow rate in the feed gas was increased step-wise, starting from fuel-rich conditions (O₂/C₃H₈ = 0.8) up to fuel-lean conditions (O₂/C₃H₈ > 20) while the propane flow rate and the total flow rate were held constant. A steady-state reaction rate was established for 20 minutes before the oxygen flow rate was increased during each step-increase.

Figure 1 shows the influence of the O₂/C₃H₈ ratio on the CO₂ production rate over Pt/Al₂O₃ at (a) 200 °C, (b) 250 °C, and (c) 300 °C. For all reaction temperatures and O₂/C₃H₈

ratios, CO_2 and H_2O were the only products detected. At all three temperatures, the CO_2 production rate increases with increasing $\text{O}_2/\text{C}_3\text{H}_8$ ratio, indicating a positive reaction order with respect to the oxygen partial pressure, until the CO_2 production rate reaches a maximum at $\text{O}_2/\text{C}_3\text{H}_8 \sim 4$. After the maximum CO_2 production is reached, the CO_2 production rate decreases with increasing $\text{O}_2/\text{C}_3\text{H}_8$ ratio at all three temperatures, which indicates a change in the kinetic regime from positive-order with respect to the oxygen partial pressure to negative-order. At 250 °C and 300 °C a steady-state CO_2 production rate is reached almost immediately after each step-increase in the oxygen flowrate. However, at 200 °C and for $\text{O}_2/\text{C}_3\text{H}_8$ greater than 4, the time to reach steady state is approximately 100 minutes, which indicates that the catalyst slowly deactivates at these conditions. The slow deactivation of the catalyst will be discussed in more detail in section 3.2.

Figure 1. CO_2 production rate (left axis) and $\text{O}_2/\text{C}_3\text{H}_8$ feed gas ratio (right axis) versus time during propane oxidation over $\text{Pt}/\text{Al}_2\text{O}_3$ at (a) 200 °C, (b) 250 °C, (c) 300 °C. The oxygen flow rate in the feed gas was increased once the CO_2 production rate reached a steady-state, while the propane and total flow rates were held constant. Slow deactivation of the catalyst was observed at 200 °C and $\text{O}_2/\text{C}_3\text{H}_8$ greater than 4.

The steady-state CO_2 production rates from Figure 1 are plotted as a function of the $\text{O}_2/\text{C}_3\text{H}_8$ ratio in Figure 2(a), and Figure 2(b) shows an expanded view of the CO_2 production rates at low $\text{O}_2/\text{C}_3\text{H}_8$ ratios. Also shown in Figure 2(a) and 2(b) are the steady-state CO_2 production rates measure at 150 °C. The dependence of the steady-state CO_2 production rate on

the O_2/C_3H_8 ratio and temperature clearly shows three distinct regimes. At low O_2/C_3H_8 ratios (Regime 1), the CO_2 production rate increases linearly with increasing O_2/C_3H_8 ratio and is independent of temperature. At intermediate O_2/C_3H_8 ratios (Regime 2), the CO_2 production rate decreases with increasing O_2/C_3H_8 ratio and is strongly dependent on the temperature. At high O_2/C_3H_8 ratios (Regime 3), the CO_2 production rate is also dependent on the temperature but does not change significantly with increasing O_2/C_3H_8 ratio.

Figure 2. Steady-state CO_2 production rate versus O_2/C_3H_8 ratio in the feed gas at 150 °C, 200 °C, 250 °C, and 300 °C, showing the (a) entire range of O_2/C_3H_8 ratios and (b) a close-up of low O_2/C_3H_8 ratios. Three distinct regimes for propane oxidation are clear. At low O_2/C_3H_8 ratios, the CO_2 production rate is limited by the rate of oxygen transport to the catalyst surface. At intermediate O_2/C_3H_8 ratios (Regime 2), the CO_2 production rate is negative order with respect to the O_2 partial pressure. At high O_2/C_3H_8 ratios (Regime 3), the CO_2 production rate is nearly independent of O_2 partial pressure.

In Regime 1, the CO_2 production rate increases with increasing O_2/C_3H_8 ratio and is independent of temperature, which indicates that the rate-relevant step in this regime is first-order with respect to the oxygen partial pressure and is non-activated. These observations suggest that the rate-relevant step in Regime 1 is either (1) diffusion of O_2 through the gas-phase to the catalyst surface, or (2) dissociation of O_2 on Pt, which previous studies of O_2 dissociation on Pt [30, 31] have shown is not hindered by large activation barriers. Spectroscopic cells such as the one used in this study are excellent for spectroscopic characterization of the catalyst, but

are not ideal for performing kinetic measurements [32]. The catalyst bed is surrounded by a large dead volume and diffusion of the reactants to the catalyst surface may limit the rate of propane oxidation. Several diagnostic tests were performed to determine whether the propane oxidation rates in Regime 1 are limited by the rate of O_2 transport to the catalyst surface. A detailed discussion of these results is given in section S.2 of the Supporting Information. Briefly, we found diluting the 2%Pt/ Al_2O_3 catalyst down to 1%Pt loading did not reduce the propane conversion, which indicates that the rate of propane oxidation in Regime 1 is limited by the rate of oxygen transport to the catalyst surface. Therefore, the propane oxidation rates measured in Regime 1 do not reveal any information about the inherent activity of the catalyst, except that the surface reaction rate is greater than the rate of oxygen transport to the surface.

In Regimes 2 and 3, the trends in the CO_2 production rate with increasing O_2/C_3H_8 ratio and temperature are not fully consistent with transport-limited processes. First, there is a strong temperature-dependence in the CO_2 production rate, and second, the rate is negative-order (Regime 2) and zero-order (Regime 3) with respect to the oxygen partial pressure. Diagnostic testing of mass and heat transport corruptions (section S.2 in Supporting Information) indicates that the propane oxidation rates in Regimes 2 and 3 are not entirely free from mass and heat transport effects. However, the propane oxidation rates in Regimes 2 and 3 are not limited by the rate of O_2 transport to the catalyst surface, and the measured reaction rates are related to the inherent activity of the catalyst. Therefore, the propane oxidation rates in Regimes 2 and 3 can be used to explain trends in the activity of the catalyst with changing reaction conditions (time, temperature, O_2/C_3H_8), but kinetic parameters such as activation barriers cannot be accurately extracted from the data.

The dependence of the CO₂ production rate on the O₂/C₃H₈ ratio in Regimes 2 and 3 is similar to that observed for methane [3] and ethane [4] oxidation over platinum. By analogy to the kinetic regimes of ethane oxygen over platinum [4], the kinetically-relevant step in Regime 2 is likely C-H bond activation at O*-O* surface site pairs, where O* is a chemisorbed oxygen site and * is a vacant surface site. At much higher O₂/C₃H₈ ratios (Regime 3), the CO₂ production rate is nearly independent of the O₂ partial pressure. In Regime 3, the surface is saturated with chemisorbed oxygen atoms, and the kinetically-relevant step is likely C-H bond activation at O*-O* surface site pairs according to Garcia-Dieguez et al. [4]. The transition between Regime 2 and 3 occurs at higher O₂/C₃H₈ ratio with increasing temperature because the oxygen coverage decreases with increasing temperature and therefore, a higher O₂/C₃H₈ ratio is required to saturate the surface with oxygen atoms. At 150 °C, the platinum surface is saturated with oxygen at very low O₂/C₃H₈ ratios resulting in a transition to Regime 3 at very low O₂/C₃H₈ ratios.

A small but significant hysteresis in the CO₂ production rate was observed, which is shown in Figure 3. In Regime 3 (high O₂/C₃H₈), there is no significant difference in the CO₂ production rate when increasing or decreasing the O₂/C₃H₈ ratio. At intermediate O₂/C₃H₈ ratios (Regime 2), however, the CO₂ production rate is significantly lower when decreasing the O₂/C₃H₈ ratio after increasing the O₂/C₃H₈ ratio. This effect increases with decreasing temperature in the 300 to 150 °C range. Figure 3(b) and 3(c) display the hysteresis at 200 °C and 150 °C, respectively, more clearly. In Regime 3, the difference in the CO₂ production rate while increasing O₂/C₃H₈ and decreasing O₂/C₃H₈ is not significantly different from the error in the measured CO₂ production rate, which is less than 5%. At 150 °C and O₂/C₃H₈ equal to 1.7 (Figure 3(c)), on the other hand, the CO₂ production rate while decreasing the O₂/C₃H₈ ratio is ~50% of the rate while increasing the O₂/C₃H₈ ratio. These results indicate that the catalyst is

modified while increasing the O_2/C_3H_8 ratio, and the modification of the catalyst is more significant at lower temperatures. A similar hysteresis was observed by Pakharukov et al. [22] during methane oxidation over Pt/Al_2O_3 . The lower activity observed while decreasing the oxygen pressure was correlated to a decrease in the electron density of the platinum particles, which was caused by either an increase in the O/Pt surface ratio or the formation of a two-dimensional platinum oxide. The slow deactivation of the catalyst at 200 °C, shown in Figure 1(a), may be the cause of the hysteresis.

Figure 3. (a) Steady-state CO_2 production rate versus O_2/C_3H_8 ratio in the feed gas at 150 °C, 200 °C, 250 °C, and 300 °C. Filled symbols correspond to CO_2 production rates measured while increasing the O_2/C_3H_8 ratio and open symbols correspond to CO_2 production rates measured while decreasing the O_2/C_3H_8 ratio. There is a significant hysteresis in the CO_2 production rate at lower temperatures. Expanded views of the hysteresis at 200 °C and 150 °C are shown in (b) and (c), respectively.

The kinetic Regimes 2 and 3 observed for propane oxidation over Pt/Al_2O_3 in the 200-300 °C temperature range are mostly similar to those observed for methane [3] and ethane [4] oxidation over Pt/Al_2O_3 in the 450-640 °C temperature range. According to Garcia-Dieguez et al. [4], the transitions between regimes are dictated by changes in the oxygen coverage. However, the slow deactivation of the platinum catalyst at 200 °C, displayed in Figure 1(a), cannot be simply due to a slow change in the oxygen coverage, which should reach steady-state

coverage in a much shorter time scale. Further, the hysteresis observed in Figure 3 suggests that the rate of propane oxidation is dictated by more than the chemisorbed oxygen coverage, particularly at lower temperatures. In the following section we examine the deactivation of Pt/Al₂O₃ in more detail.

3.2 Transient deactivation of Pt/Al₂O₃

In the previous section, we showed that there are at least two distinct kinetic regimes related to the inherent activity of Pt/Al₂O₃ during propane oxidation in the 150-300 °C temperature range. The rate of propane oxidation is strongly influenced by the oxygen coverage. However, slow deactivation of the catalyst was observed at 200 °C which cannot be explained by a slow change in the chemisorbed oxygen coverage. In this section, we show which reaction conditions result in deactivation of Pt/Al₂O₃ in order to better understand the deactivation mechanism.

Deactivation of Pt/Al₂O₃ was investigated by monitoring the propane oxidation rate for 400 minutes at constant temperature and O₂/C₃H₈ ratio. Figure 4 shows the CO₂ production rate over Pt/Al₂O₃ at 200 °C, 250 °C, and 300 °C with O₂/C₃H₈ equal to (a) 5 and (b) 20. The rate of propane oxidation is not limited by the rate of oxygen transport in any of these reaction conditions and, therefore, the reaction rates are related to the activity of the catalyst. Significant deactivation of the catalyst was observed in three out of the six reaction conditions: at 200 °C with O₂/C₃H₈ equal to 5 and 20, and at 250 °C with O₂/C₃H₈ equal to 20. No significant deactivation was observed at 300 °C. At 200 °C and with O₂/C₃H₈ equal to 5, the CO₂ production rate decreased to ~50% of its initial value during the first 100 minutes of propane oxidation. Increasing the O₂/C₃H₈ ratio to 20 at 200 °C resulted in a more significant

deactivation of the catalyst in a shorter time; about 80% of the catalyst activity was lost within 30 minutes of the start of propane oxidation. At 250 °C and $O_2/C_3H_8 = 20$, the catalyst lost ~40% of its activity during the first 40 minutes of the reaction. These results show that lower temperatures and higher O_2/C_3H_8 lead to more significant deactivation of the catalyst. It is therefore not surprising that Garcia-Dieguez et al. [4] did not observe any slow deactivation of Pt/ Al_2O_3 during ethane and methane oxidation in the 450-640 °C temperature range.

Figure 4. CO_2 production rate versus propane oxidation time at 200 °C, 250 °C, and 300 °C with O_2/C_3H_8 equal to (a) 5 and (b) 20. Catalyst deactivation is more severe at lower temperatures and higher O_2/C_3H_8 ratios.

There are many possible causes of the catalyst deactivation, including sintering of the Pt particles, oxidation of platinum, and the accumulation of poisoning species [33]. Surface species were monitored by DRIFTS in real-time during all of the propane oxidation experiments displayed in Figure 4 to determine whether the accumulation of carbonaceous surface species is responsible for deactivating the catalyst, which is the subject of a future publication. Briefly, we found that there are several different surface species that grow primarily on the Al_2O_3 support during propane oxidation. Their composition and coverage depends on both the reaction temperature and the O_2/C_3H_8 ratio. However, there is no strong correlation between the growth of these surface species and catalyst deactivation. Therefore, we believe that some mechanism

other than the growth of carbonaceous species is responsible for deactivating the catalyst. In the next section, we investigate the evolution of the platinum nanoparticle structure during the propane oxidation reaction by DRIFTS of adsorbed CO to determine whether reconstruction of the platinum nanoparticles is responsible for deactivating the catalyst.

3.3 DRIFTS of adsorbed CO

DRIFTS of adsorbed CO is a powerful technique for characterizing the structure of the platinum nanoparticles because the vibrational frequency of CO is very sensitive to the structure of the adsorption site. In this section, we investigate the evolution of the platinum nanoparticles during the propane oxidation reaction using DRIFTS of adsorbed CO. Specifically, the effect of reaction temperature and O_2/C_3H_8 ratio on the evolution of the platinum structure is investigated in order to determine whether deactivation of the catalyst is due to reconstruction of the platinum nanoparticles. As a baseline for comparison, DRIFTS of adsorbed CO was performed first on the freshly prepared Pt/ Al_2O_3 catalyst at 25 °C. The catalyst was then heated to the reaction temperature and propane oxidation was performed. After 5 minutes of propane oxidation, the catalyst was cooled to 25 °C for CO-DRIFTS analysis. DRIFTS of adsorbed CO was performed following propane oxidation at elevated temperature for 5, 20, 120, and 1000 minutes.

Figure 5(a) shows the CO-DRIFTS spectra collected from the freshly reduced catalyst, and after 5, 20, 120, and 1000 minutes of propane oxidation at 200 °C and O_2/C_3H_8 equal to 5. This condition resulted in slow deactivation of the catalyst shown in Figure 4(a). The spectrum of CO adsorbed on the clean Pt/ Al_2O_3 catalyst, which has one main feature centered at $\sim 2096\text{ cm}^{-1}$, is characteristic of CO adsorbed on relatively large ($\sim 18\text{ nm}$) platinum nanoparticles that are composed primarily of (111) facets [34]. After 5 minutes of propane oxidation at 200 °C, the CO adsorption capacity of the platinum nanoparticles is significantly reduced and the CO

absorption band is shifted by 2 cm^{-1} to lower wavenumber. With increasing reaction time, the main feature continues to decrease in intensity and shifts to lower wavenumber. After 1000 minutes of propane oxidation, the main feature is shifted by 6 cm^{-1} to lower wavenumber relative to the clean catalyst. The shift in the CO absorption band to lower wavenumber is not consistent with sintering of the platinum nanoparticles, which would result in a shift to higher wavenumbers [35]. Therefore, sintering of the platinum nanoparticles can be ruled out as the mechanism responsible for deactivating the catalyst. Starting from about 20 minutes of propane oxidation time, a new feature centered at 2123 cm^{-1} appears and continues to grow with increasing propane oxidation time up to 1000 minutes. This band has been observed in many studies [20, 36-45] of CO adsorption on platinum and is associated with CO adsorbed on, or near, oxidized platinum sites. These results indicate that the platinum nanoparticles are significantly reconstructed during the course of the propane oxidation reaction at $200\text{ }^{\circ}\text{C}$ and $\text{O}_2/\text{C}_3\text{H}_8$ equal to 5, including the formation of platinum oxide, which could explain the slow deactivation of the catalyst displayed in Figure 4(a).

Figure 5. DRIFTS of adsorbed CO on Pt/Al₂O₃ after propane oxidation at (a) $200\text{ }^{\circ}\text{C}$, (b) $250\text{ }^{\circ}\text{C}$, and (c) $300\text{ }^{\circ}\text{C}$, each with $\text{O}_2/\text{C}_3\text{H}_8$ equal to 5. DRIFTS of adsorbed CO was performed at $25\text{ }^{\circ}\text{C}$ first on the freshly prepared catalysts (clean) and then following propane oxidation for 5, 20, 120, and 1000 minutes. Each spectrum was collected after saturating the catalyst with CO at $25\text{ }^{\circ}\text{C}$ and then purging the reaction chamber with Ar.

At 250 °C and 300 °C, the evolution of the platinum nanoparticle structure is significantly different from that at 200 °C. Figures 5(b) and 5(c) show the CO-DRIFTS spectra collected following propane oxidation over Pt/Al₂O₃ at 250 °C and 300 °C, respectively, each with an O₂/C₃H₈ equal to 5. Similar to the behavior observed at 200 °C, the CO adsorption capacity of the platinum nanoparticles is significantly reduced after only 5 minutes of propane oxidation at 250 °C and 300 °C, and the CO-DRIFTS peak shifts by $\sim 3\text{ cm}^{-1}$ to lower wavenumber relative to CO adsorbed on the clean platinum particles. In contrast to the behavior at 200 °C, however, the main CO absorption band at 2093 cm^{-1} does not continue to shift to lower wavenumber with increasing propane oxidation time beyond 5 minutes. There is evidence of platinum surface oxidation given by the band at 2123 cm^{-1} that grows with increasing propane oxidation time, both at 250 °C and 300 °C. However, the intensity of the band at 2123 cm^{-1} is much less than that at 200 °C and becomes weaker with increasing temperature, which indicates that the extent of platinum oxidation decreases with increasing temperature in the 200-300 °C range.

Figure 6 shows a comparison of the CO-DRIFTS spectra collected after 1000 minutes of propane oxidation at 200, 250, and 300 °C. There are clearly several trends in the CO-DRIFTS spectra with decreasing temperature: the main absorption band decreases in intensity and shifts to lower wavenumber, and the intensity of the band at 2123 cm^{-1} , which is associated with CO adsorbed on oxidized platinum, increases with decreasing temperature. These trends indicate that the coverage of platinum oxide increases at the expense of metallic (111) facets on the platinum nanoparticles with increasing temperature. The increasing extent of platinum oxidation with decreasing temperature in the 200-300 °C range is not surprising. Bashlakov et al. [46] showed that the maximum uptake of oxygen on Pt(111) occurred around 500 K (227 °C), and

decreased with increasing temperature up to 800 K. This trend of increasing extent of oxidation with decreasing temperature is consistent with our hypothesis that platinum oxide formation is responsible for deactivating the catalyst: slow deactivation of platinum (Figure 4) is only observed at lower temperatures and higher O_2/C_3H_8 ratios.

Figure 6. Comparison of CO-DRIFTS spectra collected after 1000 minutes of propane oxidation at 200 °C, 250 °C, and 300 °C with O_2/C_3H_8 equal to 5. With increasing temperature, the main absorption band near 2094 cm^{-1} decreases in intensity and shifts to lower wavenumber. The small band at 2123 cm^{-1} , which is associated with CO on platinum oxide, decreases with increasing temperature. The extent of platinum oxidation increases with decreasing temperature, which could explain the slow deactivation of the catalyst observed at 200 °C, but not at 250 °C or 300 °C.

In addition to the strong influence of the reaction temperature on the extent of platinum oxide formation, the O_2/C_3H_8 ratio has a significant influence on the oxidation behavior of platinum. Figure 7(a) shows the evolution of the platinum nanoparticle structure during propane oxidation over Pt/ Al_2O_3 at 200 °C with O_2/C_3H_8 equal to 20. Similar to the behavior observed with O_2/C_3H_8 equal to 5, the CO chemisorption capacity of platinum is significantly reduced after only 5 minutes of propane oxidation, and the main CO absorption feature is red-shifted by 2

cm^{-1} to 2094 cm^{-1} . In contrast to the trend observed with $\text{O}_2/\text{C}_3\text{H}_8$ equal to 5, however, the main absorption band at 2094 cm^{-1} *increases* in intensity slightly up to 120 minutes of propane oxidation. The main absorption band does not continue to increase in intensity beyond 120 minutes, however, and the intensity is lower after 1000 minutes. A small band at 2123 cm^{-1} appears only after 1000 minutes of propane oxidation, and is significantly smaller than that with $\text{O}_2/\text{C}_3\text{H}_8$ equal to 5. Figure 7(b) shows a comparison of the CO-DRIFTS spectra collected after 1000 minutes of propane oxidation at 200°C with $\text{O}_2/\text{C}_3\text{H}_8$ equal to 5 and 20. One would expect that the extent of platinum oxidation increases with increasing $\text{O}_2/\text{C}_3\text{H}_8$ ratio. However, the intensity of the band at 2123 cm^{-1} , which was previously assigned to CO adsorbed on platinum oxide, decreases when the $\text{O}_2/\text{C}_3\text{H}_8$ ratio is increased from 5 to 20 and the intensity of the band associated with metallic platinum increases. This unexpected result clearly suggests that increasing the $\text{O}_2/\text{C}_3\text{H}_8$ ratio from 5 to 20 changes the oxidation behavior of platinum.

Figure 7. (a) DRIFTS of adsorbed CO on $\text{Pt}/\text{Al}_2\text{O}_3$ after propane oxidation for 5, 20, 120, and 1000 minutes at 200°C with $\text{O}_2/\text{C}_3\text{H}_8$ equal to 20. (b) Comparison of the CO-DRIFTS spectra collected after 1000 minutes of propane oxidation over $\text{Pt}/\text{Al}_2\text{O}_3$ at 200°C with $\text{O}_2/\text{C}_3\text{H}_8$ equal to 5 and 20.

The reduced intensity of the band at 2123 cm^{-1} in Figure 7(b) suggests that increasing the $\text{O}_2/\text{C}_3\text{H}_8$ ratio from 5 to 20 either (1) results in less platinum oxide on the surface or (2) produces a different phase of oxide that is not detectable by DRIFTS of adsorbed CO. There are several theoretical [16, 17] and experimental [11, 18, 19, 47-50] studies which indicate that the extent of platinum oxide formation increases with increasing oxygen coverage. Therefore, it is unlikely that increasing the O_2 partial pressure results in less platinum oxide formation. A more plausible explanation is that increasing the $\text{O}_2/\text{C}_3\text{H}_8$ ratio from 5 to 20 results in the formation of a different oxide phase which interacts differently with CO. This hypothesis is supported by a wide body of literature which indicates that there are many types of platinum oxides that are formed on the surface of platinum nanoparticles during oxidation reactions—including PtO [51, 52], Pt_3O_4 [53, 54], PtO_2 [51, 53-57], and subsurface oxide [14, 16, 46]—and the formation of these oxides depends on a number of factors including the oxygen coverage. For example, it has recently been shown that oxide growth on Pt(111) proceeds through several phase transitions with increasing oxygen coverage [19]. Beyond a critical chemisorbed oxygen coverage of ~ 0.5 ML, a PtO-like surface oxide is formed followed by an α - PtO_2 trilayer structure that is the precursor to bulk oxidation. A theoretical study [54] of oxide growth on Pt single crystal surfaces suggests that α - PtO_2 grows on the Pt(111) surface whereas on the Pt(100) surface, a PtO-like structure is formed at low coverages and a Pt_3O_4 film is favored at high oxygen coverages. Therefore, it is likely that the oxide phase formed with $\text{O}_2/\text{C}_3\text{H}_8$ equal to 5, which has a characteristic CO-DRIFTS band at 2123 cm^{-1} , is different from the oxide phase formed with $\text{O}_2/\text{C}_3\text{H}_8$ equal to 20, which is not detectable by DRIFTS of adsorbed CO at 25°C . The oxide formed with $\text{O}_2/\text{C}_3\text{H}_8$ equal to 20 may not be detectable by DRIFTS of adsorbed CO because either (1) CO does not adsorb on the oxide at 25°C or (2) the oxide is reduced to metallic

platinum during CO exposure. The possibility of these two scenarios is discussed in more detail in the following sections.

3.4 Theoretical calculations of CO adsorption on platinum and platinum-oxide surfaces

The band that we observed at 2123 cm^{-1} has been observed in many other studies [20, 36-45] of CO adsorption on platinum, and has been assigned to CO adsorption on, or near, oxidized platinum sites. However, there are many different platinum-oxide phases (e.g. PtO, Pt₃O₄, PtO₂), and it is not clear which phase is associated with the band at 2123 cm^{-1} . Heyne et al. [41] assigned a band at 2120 cm^{-1} to CO adsorbed on platinum sites with +2 oxidation state (i.e., PtO) based on analogy to Pt(II) carbonyl halogenides. To assign the band at 2123 cm^{-1} to a specific platinum-oxide phase, we carried out theoretical calculations of the stretching frequencies and binding energies of CO adsorbed on platinum and the lowest-energy surfaces of several platinum-oxides (PtO, Pt₃O₄, α -PtO₂, and β -PtO₂). A detailed description of the computational methodologies is given in section S.3 of the Supporting Information. The results are summarized in Table 1.

Table 1. CO vibrational frequencies, binding energies E_{BE} , and C-O bond lengths $R_{\text{C-Pt}}$ on platinum and on platinum-oxide surfaces.

System	$\nu_{\text{CO}}\text{ (cm}^{-1}\text{)}^a$	$E_{\text{BE}}\text{ (eV)}$	$R_{\text{C-Pt}}\text{ (\AA)}$
Pt(111)	2065.2 (2096.0)	-1.65	1.84
Pt(111)-0.25 ML O	2119.1 (2150.7)	-0.01	3.79
Pt(111)-0.50 ML O	2120.1 (2151.7)	-0.02	3.85
Pt(111)-0.75 ML O	2119.0 (2150.6)	-0.01	4.60
Pt(111)-1.00 ML O	2115.9 (2147.5)	-0.01	4.47
PtO(101)	2091.1 (2122.3)	-2.18	1.84
α -PtO ₂ (0001)	2127.3 (2159.0)	-0.01	3.90
β -PtO ₂ (110) ^b	1847.9 (1875.5)	-1.78	2.04
Pt ₃ O ₄ (100)	2089.9 (2121.1)	-0.31	1.93

^a Results in parenthesis are scaled by a factor of 1.015 in order to reproduce the experimental CO-Pt(111) vibrational frequency.

^b The CO binding mode is a dual adsorption mode between a neighboring oxygen and platinum site.

CO binds onto a Pt top site on the Pt(111) surface with a calculated binding energy (E_{BE}) of -1.65 eV and a calculated vibrational frequency (ν_{CO}) of 2065.2 cm^{-1} . Taking the experimentally measured CO vibrational frequency of 2096.0 cm^{-1} as our reference, a scaling factor of 1.015 is applied to the calculated vibrational frequency to match the experimentally measured vibrational frequency. This scaling factor, which accounts for discrepancies between the DFT calculations and the experimental conditions, was applied to all the calculated vibrational frequencies. The vibrational frequencies, both with and without scaling, are presented in Table 1.

Before discussing the effect of the oxide phase on the CO stretching mode, it is useful to consider the effect of increasing the oxygen coverage on the Pt(111) surface. Here, the number of oxygen atoms was varied to represent a 0.25 ML, 0.50 ML, 0.75 ML, and 1.00 ML oxygen coverage (as shown in Supporting Information, Figure S6). Table 1 shows that, regardless of coverage, the inclusion of an oxygen adatom(s) results in a repulsive interaction between the adsorbed CO and the platinum surface, which results in the CO being weakly bound to the oxygenated Pt(111) surface. As a consequence, the CO stretching mode is similar to that of the molecular CO stretching mode, allowing us to conclude that the peak observed at 2123 cm^{-1} is not due to the presence of an oxygen covered metallic Pt phase.

Platinum (II) oxide (PtO) is tetragonally structured, with the (101) surface being the lowest energy surface. The PtO(101) surface features a stronger CO binding energy than the Pt(111) surface (-2.18 eV vs. -1.65 eV), which results in a scaled C—O stretching mode of 2122.3 cm^{-1} , in good agreement with the observed band at 2123 cm^{-1} . As the oxygen pressure increases, PtO is further oxidized to platinum (IV) oxide (PtO₂), which features two distinct crystal phases: α -PtO₂ and β -PtO₂. α -PtO₂ features a hexagonal lattice, with the (0001) surface

being energetically preferred. Similar to the oxygenated Pt(111) surfaces, the α -PtO₂(0001) surface does not bind CO, resulting in a C—O stretching mode that is similar to the gas-phase value. β -PtO₂ features a distorted rutile crystal structure wherein the PtO₂ units are rotated around the Pt. Similar to other rutile structured materials, the (110) surface is preferred. In contrast to the α -PtO₂(0001) surface, the β -PtO₂(110) surface binds the adsorbed CO with a binding energy close to value obtained for the Pt(111) surface. The C—O stretching mode is heavily red-shifted to 1875.5 cm⁻¹, with the observed red-shift being due to the carbon atom being associated with a 5-fold coordinated Pt and a bridging oxygen. However, such a dual adsorption mode is not observed in the DRIFTS spectra. For Pt₃O₄, the (100) surface is energetically preferred. Pt₃O₄(100) weakly binds the adsorbed CO (E_{BE} =-0.31 eV) with a C—O stretching mode of 2121.1 cm⁻¹. While the C—O stretching mode is in good agreement with the DRIFTS band at 2123 cm⁻¹, the weak binding energy indicates that CO would not be stable at the temperature of the CO exposure.

The results of our theoretical calculations indicate that the band at 2123 cm⁻¹ is associated with CO adsorbed on PtO, in agreement with the assignment of Heyne [41]. Not only is the calculated CO stretching frequency (2122.3 cm⁻¹) in good agreement with the experimentally observed frequency (2123 cm⁻¹), but the binding energy of CO on the PtO(101) surface (-2.18 eV) is much higher than that on the α -PtO₂(0001) (-0.01 eV), and the Pt₃O₄(100) (-0.31 eV) surfaces. Although the calculated binding energy of CO on β -PtO₂(110) is also relatively high (-1.78 eV), the band at 1875.5 cm⁻¹ which is associated with this phase was not observed experimentally. These results could also help explain why platinum-oxides formed with O₂/C₃H₈ equal to 20 are not detectable by CO-DRIFTS. It is possible that an oxide phase is formed with O₂/C₃H₈ equal to 20, such as α -PtO₂ or Pt₃O₄, but CO does not stick to these phases

at room temperature due to its low binding energy. Another possibility is that the oxide formed with O_2/C_3H_8 equal to 20 is reduced to metallic platinum during CO exposure at 25 °C. This possibility is examined in more detail in the following section.

3.5 Platinum oxide reduction

There are several experimental studies [54, 55, 57-59] which show that surface platinum oxides are easily reduced to metallic platinum by exposure to CO at, or below, room temperature. The structure of this highly reactive oxide has been identified as PtO_2 [55, 57] and Pt_3O_4 [54]. On the contrary, several experimental studies [18, 46, 50, 53, 54, 60] show that platinum oxides are inactive for CO oxidation near room temperature. The structure of the low activity oxides has been identified as PtO_2 [53, 54, 60] and Pt_3O_4 [53], which were also the oxide phases identified as highly reactive. These contradictions regarding the catalytic activity of platinum oxides indicate that there are significant differences in the catalytic activity of platinum oxides, but also that the catalytic activity of platinum oxides is not well understood.

During all CO-DRIFTS experiments, the composition of the gas stream exiting the reaction chamber was analyzed in real time with a mass spectrometer to determine whether any CO_2 was produced during CO exposure of the catalysts at 25 °C. Figure 8 shows the rate of CO_2 production over Pt/Al_2O_3 during CO exposure at 25 °C following propane oxidation at 200 °C with O_2/C_3H_8 equal to 20 (black data points) and 5 (red data points). There is a significant amount of CO_2 production during CO exposure of the Pt/Al_2O_3 catalyst following propane oxidation with O_2/C_3H_8 equal to 20 after (a) 5 minutes, (b) 20 minutes, (c) 120 minutes, and (d) 1000 minutes, and the amount of CO_2 production does not change with increasing propane oxidation time. In contrast, there was no detectable production of CO_2 during CO exposure of the Pt/Al_2O_3 catalyst following propane oxidation with O_2/C_3H_8 equal to 5 after 5 minutes and 20

minutes. After 120 minutes of propane oxidation with O_2/C_3H_8 equal to 5, there is a small amount of CO_2 produced during CO exposure, and the amount of CO_2 produced increases following 1000 minutes of propane oxidation. These observations suggest that an oxide could be formed with O_2/C_3H_8 equal to 20 that is much more reactive towards CO than the oxide that is formed with O_2/C_3H_8 equal to 5 (PtO). It also appears that the low activity oxide phase formed with O_2/C_3H_8 equal to 5 (PtO) is slowly transformed into the higher activity oxide phase with increasing propane oxidation time, resulting in more CO_2 production during CO exposure. Therefore, it is very likely that the oxide formed during propane oxidation with O_2/C_3H_8 equal to 20 is reduced to metallic platinum during CO exposure at 25 °C. The oxide formed during propane oxidation with O_2/C_3H_8 equal to 5 (PtO), on the other hand, is much less reactive towards CO and a band at 2123 cm^{-1} from CO adsorption on PtO is observed.

Figure 8. CO_2 production rate during exposure of Pt/Al_2O_3 to CO at 25 °C after propane oxidation with O_2/C_3H_8 equal to 5 (red data points) and 20 (black data points) for (a) 5 min, (b) 20 min, (c) 120 min, and (d) 1000 minutes.

There is a significant amount of CO₂ production during CO exposure to the catalyst following propane oxidation with O₂/C₃H₈ equal to 20 and the amount of CO₂ production does not change with increasing propane oxidation time. In contrast, there is no CO₂ production during CO exposure to the catalyst following propane oxidation with O₂/C₃H₈ equal to 5 until after 120 minutes of propane oxidation. The oxide formed with O₂/C₃H₈ equal to 20 may react with CO at 25 °C, reducing the oxide to metallic platinum and producing CO₂, whereas the oxide produced with O₂/C₃H₈ equal to 5 does not react with CO.

It is clear from our results that PtO, which is the main oxide formed during propane oxidation with O₂/C₃H₈ equal to 5, binds CO strongly and does not react with CO to form CO₂ at 25 °C. As the O₂/C₃H₈ ratio is increased from 5 to 20, we believe that a different oxide phase is formed, such as PtO₂ or Pt₃O₄, which is reduced to metallic platinum during CO exposure and is therefore not detectable by DRIFTS of adsorbed CO. This hypothesis is supported by two studies which showed that PtO is formed on the surfaces of Pt(111) [19] and Pt(100) [54] at low oxygen coverage before transforming into PtO₂ and Pt₃O₄, respectively, with increasing oxygen coverage. Furthermore, there is evidence in the literature [54, 55, 57] that the PtO₂ and Pt₃O₄ phases are easily reduced to metallic platinum during exposure to CO at, or below, room temperature.

It is possible that the hysteresis observed in Figure 3 at lower temperatures (150-200 °C) and intermediate O₂/C₃H₈ ratios ($\sim 4 < \text{O}_2/\text{C}_3\text{H}_8 < \sim 10$) is the result of a significant kinetic barrier hindering the reduction of PtO during decreasing O₂/C₃H₈ ratio. The extent of PtO formation decreases with increasing temperature (see Figure 6), which could explain why no hysteresis is observed at 250 or 300 °C. Therefore, the kinetics of propane oxidation over platinum is most likely controlled by only the chemisorbed oxygen coverage at temperatures greater than ~ 250 °C, as predicted by Garcia-Dieguez et al. [4]. At lower temperatures, however, platinum oxide formation has a significant impact on the catalyst activity. Our results (see Figure 8) suggest that there is a significant kinetic barrier against reduction of PtO, which could explain why the

propane oxidation rate is significantly lower when decreasing the O_2/C_3H_8 ratio than when increasing the O_2/C_3H_8 ratio (see Figures 3(b) and 3(c)); the fraction of PtO is greater when decreasing the O_2/C_3H_8 ratio than when increasing the ratio. At high O_2/C_3H_8 ratios (kinetic Regime 3), another oxide phase such as PtO₂ or Pt₃O₄ is formed which is more easily reduced than PtO (see Figure 8). As a result of the high reducibility of this oxide phase, the coverage of this oxide is the same when increasing and decreasing the O_2/C_3H_8 ratio, and no hysteresis is observed at high O_2/C_3H_8 ratios. Therefore, the hysteresis observed during propane oxidation may be associated with the formation of a specific platinum oxide, PtO, which is not as easily reduced as other platinum oxides that are formed at higher O_2/C_3H_8 ratios.

It is clear from this work that oxide formation has a significant impact on the activity of platinum catalysts, yet there is still much that is not known about platinum oxide formation, including the kinetics and mechanisms of oxide formation and reduction. The present work sheds some new light onto platinum oxide formation and reduction during oxidation of alkanes at low temperatures. Our work suggests that it is likely that more than one phase of oxide can form on the surface of platinum nanoparticles, which can each have a different effect on the activity of the catalyst. This is significant because kinetic models which include the formation of oxides usually include only one type of oxide [61]. Many further theoretical and experimental studies are required to gain a deep understanding of platinum oxide formation, which would have important implications beyond the propane oxidation reaction.

4. Conclusions

In this work, the kinetics of propane oxidation over platinum was evaluated as a function of the O_2/C_3H_8 ratio in the 150-300 °C temperature range. We found that there are distinct regimes in the propane oxidation rate, which are similar to those previously found for methane

and ethane oxidation. At conditions which lead to oxygen-saturate surfaces, such as high oxygen partial pressures or low temperatures, the propane oxidation rate is zero-order with respect to the oxygen partial pressure. As the oxygen coverage decreases with decreasing oxygen partial pressure or increasing temperature, the reaction order with respect to the oxygen partial pressure changes from zero-order to negative-order. These results suggest that the reaction pathways of propane are similar to those of methane and ethane oxidation, which are controlled to a large extent by the chemisorbed oxygen coverage.

At lower temperatures (150-200 °C), there was a hysteresis in the propane oxidation rate during increasing and decreasing the O_2/C_3H_8 ratio. The propane oxidation rate was significantly lower during decreasing the O_2/C_3H_8 ratio after increasing the O_2/C_3H_8 ratio. This suggests that the catalyst is deactivated while increasing the O_2/C_3H_8 ratio, and that there is a significant activation barrier to re-activating the catalyst while decreasing the O_2/C_3H_8 ratio. We observed that the deactivation occurs over hundreds of minutes at lower temperatures and higher O_2/C_3H_8 ratios. This slow deactivation of the catalyst at lower temperatures indicates that the rate of propane oxidation is controlled by more than the chemisorbed oxygen coverage.

DRIFTS of adsorbed CO was used to investigate the evolution of the platinum nanoparticle structure during propane oxidation at elevated temperatures. Under reaction conditions which lead to slow deactivation ($O_2/C_3H_8 = 5$, 200 °C), we found that the platinum nanoparticles are significantly reconstructed during the course of the reaction, including the formation of a platinum oxide (PtO) which has a characteristic CO-DRIFTS band at 2123 cm^{-1} . The extent of PtO formation decreases with increasing temperature and, as a result, deactivation of the catalyst is less severe at higher temperatures. Our results also indicate that a different

oxide phase may be formed at high $\text{O}_2/\text{C}_3\text{H}_8$ ratios, which is more easily reduced to metallic platinum than PtO , but also deactivates the catalyst for propane oxidation.

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