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Induced low temperature catalytic ignition by transient changes in the gas composition

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Abstract

The effect of gas composition changes on the low temperature activity for supported platinum model catalysts has been studied. By introducing well-controlled periodic O_2 pulses to a simple diluted gas mixture of CO and O_2, a substantial improvement of the low temperature oxidation activity was observed. The reason for low activity on noble metals at low temperatures is often attributed to self-poisoning by CO. The improved catalytic performance observed is proposed to origin from the transients causing a surface reactant composition that is favourable for the reaction rate, i.e. lower degree of self-poisoning. This was also confirmed by in situ Fourier transform infrared (FT-IR) spectroscopy in combination with mass spectrometry (MS) measurements, which gave evidence for the existence of a strong interplay between the gas phase concentration and the adsorbate composition for these catalysts.

Keywords: Platinum; Carbon monoxide; Catalytic oxidation; Low temperature activity; Self-poisoning; Cold start emissions; Periodic pulsing; Transient changes; In situ FT-IR; DRIFT

1. Introduction

The major part of the total emissions from cars with stoichiometric engines equipped with catalytic three-way converters is released during the first minute of driving [1,2]. This is due to the fact that the catalyst is inactive at low temperatures which in turn may be caused by self-poisoning of different compounds on the catalyst surface [3]. Over the years, several different solutions like placing the converter closer to the engine [4] or using an electrically heated metal monolith with low thermal mass [5] have been proposed. These two actions result in shorter heat-up time. The use of a hydrocarbon trap, which stores the hydrocarbons during the heat-up time have also been suggested as a way to minimise the emissions during the cold start period [6].

Another possible technique, previously investigated by Skoglundh et al. [7], applies the use of fast switching between different gas compositions. It was found that the presence of transients shifted the conversion starts of CO, NO and propene as well as the light-off temperatures towards lower temperatures both for a commercial and for a $Pt/CoO_x/Al_2O_3$ model catalyst.

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Further studies based on this transient technique also suggested that the improved low temperature activity origins from the transients causing an adsorbate composition favourable for the reaction rate [8].

The objective of this study is to gain a deeper understanding of the involved underlying mechanisms during low temperature catalytic ignition induced by transient changes in the gas composition. To mimic the behaviour of a cold start, CO oxidation on supported platinum is chosen as a model system due to the strong self-poisoning by CO at low temperatures. Additionally, the few gas components (CO, O_2 and CO_2) involved makes analysis of the result fairly simple and straightforward. Different continuous flow reactor experiments during transient conditions were performed in order to study the light-off process of a monolith sample. Combined in situ Fourier transform infrared (FT-IR) spectroscopy used for surface analysis, and mass spectroscopy (MS) for detection of the product stream, were used to study both light-off and extinction of CO oxidation over powder catalysts.

2. Experimental procedure

2.1. Catalyst preparation

A monolith sample of cordierite, 15 mm long and 12 mm in diameter, was cut out from a commercial honeycomb structure of cordierite with 64 square channels/cm^2. The monolith was then repeatedly impregnated with γ-Al_2O_3 as the support material and then with H_2PtCl_6 as a precursor for the active material, see previous papers for details [9,10]. The Al_2O_3 and Pt content are 200 and 20 mg, respectively, which corresponds to 330 g Pt/ft^3. The Pt dispersion was 11%, measured with CO-TPD [10] with the assumption that 0.7 CO molecules adsorb per surface Pt [11]. The BET surface area was measured to be 27.5 m^2. For the FT-IR study, powder samples of Pt/γ-Al_2O_3 (3% Pt by weight) and Pt/SiO_2 (1% Pt by weight) were prepared by the impregnation technique previously described by Axelsson et al. [12]. The support materials were dispersed in distilled water under continuous stirring and the pH was adjusted to 10.5 by ammonia addition. A dilute solution of $Pt(NH_3)_4(OH)_2$ was then added to each of the support slurries, which subsequently were stirred for 20 min. The samples were then freeze-dried and finally calcined in air at 600 °C for 1.5 h.

2.2. Flow reactor measurements

The continuous gas flow reactor used for the measurements, described previously [13], consists of a horizontal quartz tube placed in a divisible tubular furnace. The monolith catalyst was sealed in the middle of the heated zone with quartz wool and the gases were introduced into the reactor via mass flow controllers. The inlet gas and the catalyst wall temperatures were individually measured. The inlet gas temperature was measured at a position 11 mm before the sample and the catalyst temperature was measured in the centre channel at the rear half of the catalyst. The CO and CO_2 outlet concentrations were analysed on-line with IR analysers (Maihak UNOR 6N).

In order to clean the catalyst surface, each measurement series was initiated with a pre-treatment (8.0 vol.% O_2 in N_2 at 500 °C) for about 5 min. The catalyst was then cooled in N_2 to 150 °C.

Two different experiments were performed. In the first one the catalyst was treated with 1.0 vol.% CO in N_2 for 5 min in order to create a CO saturated catalyst surface. After this treatment short 16.0 vol.% O_2 pulses (4 s long, once every minute) were introduced to a 1.0 vol.% CO and 0.6 vol.% O_2 in N_2 gas mixture at an inlet gas temperature of 150 °C. A total gas flow of 800 ml/min (NTP), corresponding to a space velocity of 30 000 h^{-1} was used. In the second experiment the catalyst was treated with 0.5 vol.% CO in N_2 for 10 min followed by a sequence of short 1500 vol. ppm O_2 pulses (4 s long, once every minute) introduced to a 100 vol. ppm CO and 50 vol. ppm O_2 in N_2 gas mixture at an inlet gas temperature of 150 °C. The total gas flow was in this case 1000 ml/min (NTP), corresponding to a space velocity of 37 500 h^{-1}.

2.3. In situ FT-IR measurements

The in situ FT-IR spectroscopy experiments were performed in diffuse reflectance (DRIFT) mode with a BioRad FTS6000 spectrometer equipped with a Harrick DRIFT cell previously described in [14]. The Pt/Al_2O_3 and the Pt/SiO_2 (diluted to 9 wt.% in KBr) powder sample were oxidised in 4.5 vol.% O_2 at 400 °C and in 5.0 vol.% O_2 at 500 °C, respectively, for

5 min. The samples were then cooled in Ar to the relevant temperature to be studied (150 °C for Pt/Al_2O_3 and 170 °C for Pt/SiO_2) and background spectra were collected. Both samples were then saturated with CO in a 500 vol. ppm CO flow.

The Pt/Al_2O_3 sample was exposed to a CO/O_2 mixture where the CO concentration was kept constant at 500 vol. ppm while the O_2 concentration was stepwise increased from 0 via 0.04, 0.10 to 4.5 vol.%. A total gas flow of 200 ml/min (NTP) was used. A single spectrum was recorded for each O_2 concentration.

For the Pt/SiO_2 catalyst an exposure to a CO/O_2 mixture with a 500 vol. ppm CO concentration (constant) and a stepwise changed O_2 concentration from 0 vol.% followed by the sequence 3.0, 6.0, 3.0 and 2.0 vol.% was performed. The total gas flow was in this case 300 ml/min (NTP). A spectrum was collected every 0.135 s during a 6 min period, starting at the gas composition switches, in order to follow the step changes in detail. The reactor outlet stream was in this case monitored by a quadrupole MS following the *m*/*e* signals of 28 (CO) and 32 (O_2).

3. Results

3.1. Flow reactor experiments

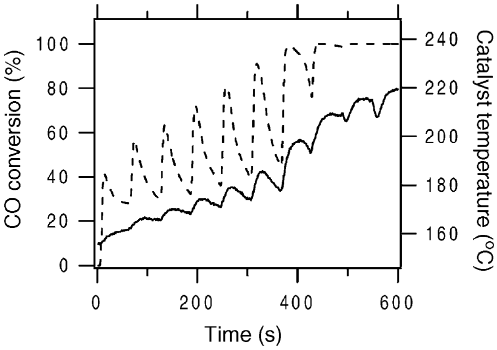

Fig. 1. CO conversion (dashed line) and catalyst temperature (solid line) when 16.0 vol.% O_2 pulses (4 s long, once every minute) were added to a 1.0 vol.% CO and 0.6 vol.% O_2 in N_2 gas mixture at an inlet gas temperature of 150 °C.

The result from the CO oxidation experiment over the Pt/Al_2O_3 monolith catalyst where short 16.0 vol.% O_2 pulses (4 s long, once every minute) were introduced to a 1.0 vol.% CO and 0.6 vol.% O_2 in N_2 gas mixture at an inlet gas temperature of 150 °C, is displayed in Fig. 1. An increasing CO conversion after each O_2 pulse is clearly seen. After each pulse the conversion decays, but it remains at a higher level than before the pulse. The overall CO conversion increases gradually for each O_2 pulse and after a number of pulses ($t = 400$ s) complete CO conversion is obtained. A second feature observed is that the catalyst temperature shows a more or less pronounced stepwise increase for each O_2 pulse. It decays somewhat between the pulses but an overall temperature increase is obvious and a maximum catalyst temperature of 220 °C is reached at $t = 600$ s.

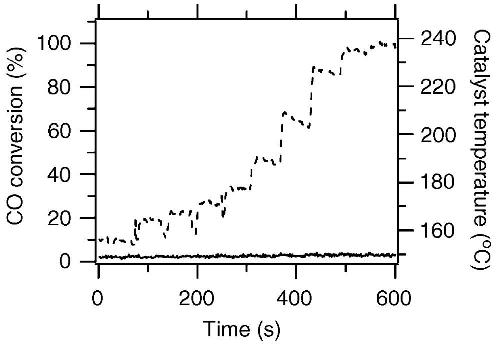

Fig. 2. CO conversion (dashed line) and catalyst temperature (solid line) when 1500 vol. ppm O_2 pulses (4 s long, once every minute) were introduced to a 100 vol. ppm CO and 50 vol. ppm O_2 in N_2 gas mixture at an inlet gas temperature of 150 °C.

Fig. 2 shows CO conversion and the catalyst temperature during the experiment where 1500 vol. ppm

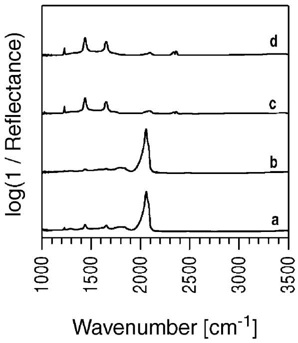

Fig. 3. Evolution of FT-IR spectra of a Pt/Al_2O_3 catalyst during oxidation of 500 ppm CO at 150 °C when adding (a) 0.00 vol.% O_2, (b) 0.04 vol.% O_2, (c) 0.10 vol.% O_2 and (d) 4.50 vol.% O_2.

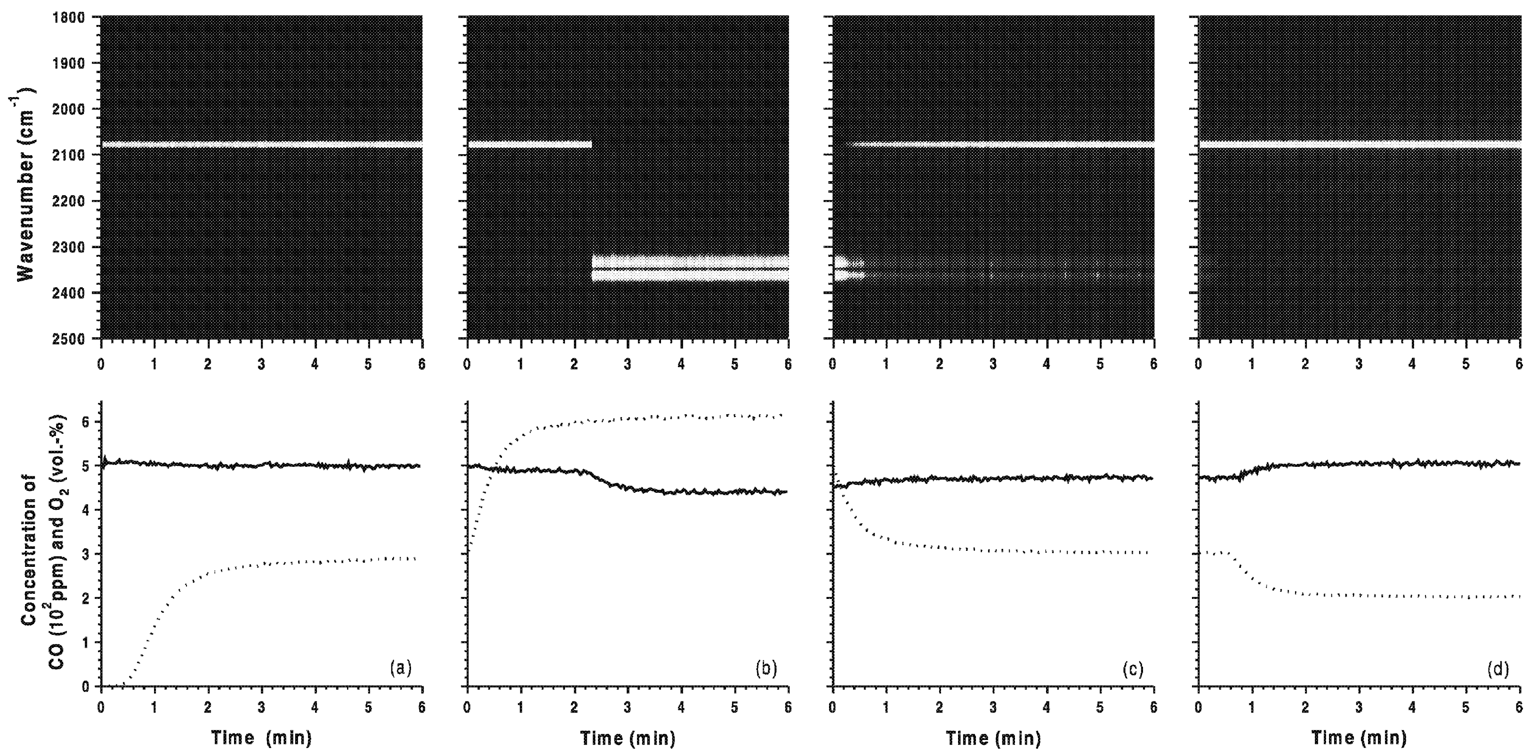

Fig. 4. FT-IR spectra (above, bright areas corresponds to high intensity) and reactor outlet concentrations (below, calculated from MS signals where CO = solid line and O_2 = dashed line) as a function of time for oxidation of 500 ppm CO at 170 °C over a Pt/SiO_2 powder catalyst. The O_2 concentration was stepwise changed according to (a) 3.0 vol.% O_2, (b) 6.0 vol.% O_2, (c) 3.0 vol.% O_2 and (d) 2.0 vol.% O_2.

O_2 pulses (4 s long, once every minute) were added to a 100 vol. ppm CO and 50 vol. ppm O_2 in N_2 gas mixture at an inlet gas temperature of 150 °C. For each and every O_2 pulse the CO conversion increases in an almost stepwise manner. As in the above case, the CO conversion decays somewhat between the pulses. However, similarly to the previous experiment showed in Fig. 1, the overall conversion increases and at $t =$ 550 s a full CO conversion is reached. Contrary to the foregoing experiment with higher concentrations (Fig. 1) the catalyst temperature is about 150 °C and constant throughout the experiment.

3.2. In situ FT-IR and mass spectroscopy experiments

Fig. 3 displays the FT-IR spectra collected during oxidation of 500 vol. ppm CO over Pt/Al_2O_3 at 150 °C with a stepwise increase of the O_2 concentration. Spectrum a is recorded when exposing the sample to CO in Ar only. A large CO on Pt [15] peak positioned at 2056 cm^{-1} and three small peaks in the 1000–1700 cm^{-1} region, probably connected to surface carbonates on Al_2O_3 [16], are observed. After introducing 0.04 vol.% O_2 to the system no pronounced difference is observed (spectrum b). When the O_2 concentration is increased to 0.10 and 4.5 vol.%, spectrum c and d, respectively, the peak at 2056 cm^{-1} declines while the peaks at 1000–1700 cm^{-1} evolve. A very new small peak at 2350 cm^{-1}, corresponding to gaseous CO_2 (CO(g)), occurs for these gas compositions.

In Fig. 4 the FT-IR spectra and MS signals recorded during the oxidation of 500 vol. ppm CO (stepwise changes of the O_2 concentration) over the Pt/SiO_2 at 170 °C are shown. The upper panels display the evolution of the FT-IR spectra, wavenumber as a function of time (where bright areas correspond to high intensity), and the lower panels show the corresponding reactor outlet concentrations (calculated from the MS response signals) in time.

Fig. 4a shows the FT-IR spectra and the concentrations (during 6 min) after a stepwise change of the O_2 concentration from 0 to 3 vol.%. The step is clearly seen in the figure as the O_2 concentration increases to a new steady-state level in about 3 min. The CO concentration remains however at a constant level 6 min after the change in oxygen concentration. The corresponding FT-IR spectra show a strong CO on Pt band at 2080 cm^{-1} [15] with constant intensity during the period.

For the next stepwise increase of the inlet O_2 concentration (from 3.0 to 6.0 vol.%, Fig. 4b) the O_2 concentration reaches a new level after about 2.0 min. Contrary to the previous oxygen step with constant CO concentration, the CO concentration starts to decay 2.3 min after the change in oxygen concentration. An intense CO on Pt band at 2080 cm^{-1} and two very pale bands around 2350 cm^{-1}, corresponding $CO_2(g)$, are seen in the FT-IR sequence during approximately the first 2 min. Suddenly at $t = 2.3$ min, the CO on Pt band at 2080 cm^{-1} vanish, while the $CO_2(g)$ bands around 2350 cm^{-1} intensifies abruptly.

Part c of Fig. 4 corresponds to a step change from 6.0 to 3.0 vol.% O_2. A slight increase of the CO concentration may be seen during the first 1.5 min. The O_2 concentration decreases during this time. An intense $CO_2(g)$ double band at 2350 cm^{-1} is seen in the FT-IR picture in the beginning of this 6 min period, but after 0.2 min it decays and turns into two pale tracks only. During this time the CO on Pt band at 2080 cm^{-1} evolves again and after 2 min the intensity increases just slowly throughout the experiment.

For the last 6 min (Fig. 4d) the step change from 3.0 to 2.0 vol.% O_2 concentration was performed. The O_2 concentration decays between $t = 0.5$ and 1.5 min, while the CO concentration increases during this time. The intensity of the CO on Pt band at 2080 cm^{-1} increases and the pale $CO_2(g)$ bands around 2350 cm^{-1} vanish totally at $t = 0.4$ min.

4. Discussion

CO oxidation on Pt is usually described to proceed via a Langmuir–Hinshelwood type of mechanism both at ultra-high vacuum (UHV) and at atmospheric pressure [17,18]. At low temperatures CO and O_2 adsorbs reversibly associatively and irreversibly dissociatively, respectively, in a competitive adsorption process [19]. It is also well known that CO may inhibit the oxidation reaction on Pt due to self-poisoning of the active Pt sites at low temperature [20]. Contrary to this no clear evidence for oxygen poisoning is found [10]. During the catalytic ignition (which occurs for oxygen excess conditions due to the large difference in sticking probability between CO and O_2) a first-order kinetic phase transition takes place, described by Zhdanov and Kasemo [21]. Essentially, this means that the kinetics of the system suddenly change as a result of any control parameter passing through a critical point. This corresponds in our study to a transition from a Pt surface predominantly covered by CO (low oxidation activity) into an almost O covered Pt surface (high oxidation activity) as the relative reactant pressure β ($\beta = p_{CO}/(p_{CO} + p_{O_2})$) is changed. Since CO adsorption is favoured compared to O_2 adsorption, the system has a bistable region. In practice this means that ignition occurs for a certain relative reactant ratio β_i. Once the system is ignited all the adsorbing CO molecules immediately react due to the high surface reaction rate to form CO_2. The catalytic extinction, a transition from high (O covered Pt surface) back to low (CO covered Pt surface) oxidation activity therefore occurs at a β value higher than that for the ignition ($\beta_e > \beta_i$). Furthermore, the exothermic CO oxidation reaction generates heat. This leads to an increased catalyst temperature which gives a higher surface reaction rate (and CO desorption rate) producing even more heat. If the heat from the chemical reaction cannot stably dissipate from the system a sudden self-acceleration in the surface reaction rate occurs. This is a critical point, which defines the conditions for a catalytic ignition [22].

At the start of the first flow reactor oxidation experiment, where 1.0 vol.% CO was introduced (Fig. 1), the reaction rate is very low due to the CO self-poisoning. The oxygen excess during a pulse leads to an increase in the oxygen impingement rate and in the O coverage of the surface. This result in a higher surface reaction rate with the corresponding generation of heat and increase of the temperature, which leads to an increased CO desorption and surface reaction rate. Hence, the system is turned into a regime where the CO oxidation self-accelerates. After an oxygen pulse, due to heat transport limitations, the system slowly turns back into the CO self-poisoned regime and the reaction rate decreases. Continuous pulsing then increases the temperature to a final state where CO self-poisoning is negligible and where complete CO conversion is reached. The average O_2 concentration in Fig. 1 is 1.6 vol.%, which should be compared to the stationary light-off concentration of 8.0 vol.% O_2, described by us in previous work [8], indicating a substantially improved low temperature activity due to O_2 pulsing.

In the second flow reactor measurement (Fig. 2) conversion of 100 vol. ppm CO is achieved. Similar to Fig. 1 the CO oxidation reaction rate is low in the beginning of the experiment due to CO self-poisoning. The oxygen excess during a pulse leads to an increase in the oxygen impingement rate and also in the O coverage, which results in a higher surface reaction rate. However, in this case no measurable increase of the catalyst temperature can be observed due to the low amount of CO (the adiabatic temperature increase is about 1 K in this case). This means that the system is not turned into the regime where it self-accelerates, which is also seen in the shape of the CO conversion curve. If a self-acceleration would have occurred the CO conversion would have had characteristics similar to that in Fig. 1, with large differences in CO conversion between oxygen rich and oxygen deficit conditions, rather than the more or less stepwise CO conversion increase seen in Fig. 2. This experiment reveals that the catalytic activity and implicitly the adsorbate composition are directly affected by manipulations of the gas composition alone (no temperature effects). This is also indicated by the FT-IR measurements (Fig. 3), which shows a vanishing CO on Pt peak, when the gas composition is changed. Moreover, Fig. 3 shows an evolving CO_2(g) peak and three peaks in the 1000–1700 cm^{-1} region, probably corresponding to carbonates on Al_2O_3 acting as spectators, indicating a running CO oxidation reaction. The adsorbate changes are even clearer in Fig. 4 which shows the adsorbate changes on Pt (no carbonates on SiO_2) only as a function of time. At the ignition, a rapid transition from a CO covered to a CO free surface (a quickly vanishing high intensity band at 2080 cm^{-1}) occurs. Once this transition has occurred CO_2 is produced (a highly intense double band around 2350 cm^{-1} and a decay of the CO concentration). Contrary to this rapid adsorbate changes during ignition the transition back to a CO covered surface during extinction occurs more slowly. This asymmetric behaviour was also seen for each and every pulse in Fig. 1 and the reason for this was attributed to heat transport limitations affecting the temperature. In the case of Fig. 4 the CO concentration is low and therefore the contribution of temperature effects is minor. The CO conversion is also low which means that the gas present in reactor volume is not CO deficient. This suggests that some other phenomena, for example noble metal oxide formation may influence the adsorption kinetics [23,24].

5. Conclusions

The experimental results show that transient changes in the gas composition, i.e. O_2 pulsing, can improve the low temperature catalytic activity for CO oxidation on supported platinum catalysts. The improved low temperature activity is caused by the gas phase manipulations, which affect the adsorbate composition on the catalyst, lowering the self-poisoning by CO and hence increase the reaction rate for CO oxidation. Combined in situ FT-IR and mass spectrometry (MS) measurements also support this.

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