

The effect of platinum distribution in monolithic catalysts on the oxidation of CO and hydrocarbons

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Abstract

Monolithic Pt/ γ -Al₂O₃ catalysts were prepared by depositing of the platinum phase, either homogeneously or heterogeneously (i.e., local high platinum concentration), in the washcoat. The influence of the platinum distribution on the ignition and extinction processes for oxidation of CO, propene, and propane, respectively, was investigated by both temperature-programmed and oxygen step-response flow-reactor experiments. In addition, in situ XANES spectroscopy was used to follow changes in the chemical state of platinum during propane oxidation. For samples with heterogeneous platinum distribution, the results show an improved low-temperature activity for CO oxidation, whereas no clear improvement is observed for oxidation of propene or propane. Comparison of the results for CO and hydrocarbon oxidation shows that the improved activity cannot be explained by thermal effects. Moreover, calculations indicate that the enhanced activity for CO oxidation can be due to mass-transfer phenomena. This could not be confirmed by our experiments, however. Instead, the improved activity for CO oxidation can be due to varying platinum particle size between the samples. Furthermore, the oxidation of propane is shown to be highly influenced by the oxygen concentration, showing an activity maximum for gas compositions close to the stoichiometric. High oxygen levels result most probably in a predominantly oxygen-covered surface, which inhibits the reaction and, as supported by the in situ XANES experiments, passivates the surface by forming platinum oxide.

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1. Introduction

To meet current emission standards for vehicles, efficient catalytic converters for the complete oxidation of carbon monoxide (CO) and hydrocarbons (HC) are required. Catalytic oxidation is also important for the removal of volatile

organic compounds in waste gas streams from stationary sources. In common for these applications is the need for improved low-temperature activity to reduce, for example, cold-start emissions from vehicles [1,2] and energy consumption in industrial processes [3]. Moreover, this need is also emphasised by the trend towards more efficient lean-burn [4] and HCCI [5] engines, which, especially at low loads, produce raw emissions that are too cold to be efficiently converted in the present exhaust abatement systems.

With the goal of enhancing low-temperature catalytic activity, one may choose from different strategies [6], like controlled changes of the exhaust gas composition by, for

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example, periodic operation, addition of make-up gases or trapping hydrocarbons and water in zeolites, or heat management, with the use of, for example, electrically heated or close-coupled catalysts. Alternative catalyst solutions involve new material combinations, but must also solve the problem of how to distribute the active phase in the support to govern the reaction kinetics by influencing mass and heat transfer.

In a previous study [7] it was shown that the distribution of the active phase, platinum, can affect the low-temperature activity for CO oxidation. With a new preparation method, the platinum was deposited heterogeneously, concentrated locally in the alumina support, instead of homogeneously in the washcoat. The idea behind heterogeneous distribution is to better utilise the generated reaction heat and thereby improve the low-temperature activity for exothermic reactions in such samples. However, even though these samples showed an enhanced activity for CO oxidation, calculations suggested that the improved activity is probably not due to thermal effects occurring in the catalyst. Instead the origin of the enhanced activity was discussed in terms of mass transfer and structure effects. Mass transfer effects seemed to be the most probable reason for the improved activity, although this was not unambiguously established. Thus, in the present paper we continue the previous investigation of the improved CO oxidation activity for these catalysts, which in the following will be referred to as *the distribution effect*. We also complement the previous study by including other exothermic reactions, such as oxidation of hydrocarbons.

The objective of the present investigation is to better understand the origin of the distribution effect and to reveal whether this effect is specific for CO oxidation or if the new preparation method is also beneficial for complete oxidation of propene and propane. This is accomplished by a study of the ignition and extinction processes by both temperature-programmed (TP) and oxygen step-response (SR) flow-reactor experiments. Moreover, in situ XANES spectroscopy is used to follow changes in the chemical state of platinum during propane oxidation.

2. Experimental

2.1. Catalyst preparation and characterisation

Three monolithic Pt/ γ -Al₂O₃ samples (cordierite substrate with *l*: 20 mm, \varnothing : 14 mm and 400 cps) were prepared: one with the platinum homogeneously distributed in the alumina washcoat (Pt/100% Al₂O₃), one with the platinum distributed in only 10% of the alumina washcoat (Pt/10% Al₂O₃) (i.e., 90% of the washcoat is platinum-free), and one with platinum deposited on only 1% of the total alumina washcoat (Pt/1% Al₂O₃). For more details about the preparation procedure, see Arnby et al. [7]. For each monolith, a constant amount of washcoat (0.25–0.26 g) and platinum (0.50–0.52 mg, corresponding to 0.2 wt%) was used. The

Table 1
Basic characteristics of the catalysts

	Catalyst		
	Pt/ 100% Al ₂ O ₃	Pt/ 10% Al ₂ O ₃	Pt/ 1% Al ₂ O ₃
Amount Pt covered Al ₂ O ₃ (%)	100	10	1
Amount applied washcoat (g)	0.26	0.26	0.25
Pt content (mg)	0.52	0.52	0.50
Amount adsorbed CO (μ mol)	1.03–1.07	0.81–0.85	0.36–0.38
Dispersion ^a (%)	56	44	21
Pt surface area ^b (dm ²)	7.2	5.7	2.5
Average Pt particle diameter ^c (nm)	2.0	2.6	5.6
BET area (m ² /g washcoat)	160	163	163
Average pore diameter (Å)	69	68	69

^a Assuming Pt:CO stoichiometry of 1:0.7 [8].

^b Assuming 0.08 nm²/Pt atom [9].

^c Assuming spherical particles [9].

characteristic data for the different samples are summarised in Table 1. We prepared a Pt/zeolite Y sample containing 3 wt% Pt by impregnating NH₄-Y (Ultra-stable Zeolite Y, Katalistiks) with Pt(NH₃)₄(OH)₂ (Johnson Matthey) at room temperature for 12 h. The sample was then filtrated, washed with distilled water, freeze-dried with liquid nitrogen, freeze-dried, and finally calcined in air at 550 °C for 3 h.

In accordance with the previous study [7], the platinum dispersion and surface area of the samples were calculated from the amount of adsorbed CO, determined by CO chemisorption measurements, assuming that 0.7 CO molecule adsorbs on each Pt surface atom [8] with a surface area of 0.08 nm² [9]. Moreover, we calculated the mean platinum particle diameter, assuming spherical particles, according to the method of Anderson and Pratt [9]. The specific surface area and the average pore diameter of the washcoat were determined by nitrogen adsorption according to the BET method (Micromeritics ASAP 2010 instrument). The determination of the BET surface area was based on six measurements at relative pressures of N₂ in the range of 0.03–0.20. The cross-sectional area used for the nitrogen adsorbate was 0.162 nm².

2.2. Flow reactor experiments

The influence of the platinum distribution in the washcoat on the ignition and extinction processes for oxidation of CO, propene, and propane, respectively, was studied by both TP experiments with a constant gas composition and oxygen SR experiments at constant temperature. The catalytic performance was compared for constant amounts of platinum and washcoat material for each sample, while the number of active sites (Pt surface area) varied between the three samples. The experiments were carried out at atmospheric pressure in a continuous gas flow reactor consisting of a quartz tube positioned horizontally in a cylindrical furnace, as described previously [7]. The temperatures were measured with two thermocouples, one located about 10 mm in front of the cat-

Table 2
Summary of experiments. In Figs. 1–5 Pt/100% Al₂O₃, Pt/10% Al₂O₃ and Pt/1% Al₂O₃ were used. In Fig. 6 the Pt/zeolite Y sample was used

Figure	Gas composition ^a				Temperature (°C)	Flow (ml/min)	Space velocity (h ⁻¹)
	CO (ppm)	Propene (ppm)	Propane (ppm)	Oxygen (%)			
1	1000	–	–	10	30–205 ^b	2000	39,000
2	1000	–	–	1–10 ^c	150	2000	39,000
3	–	1000	–	10	30–420 ^b	2000	39,000
4	–	–	1000	10	30–420 ^b	2000	39,000
5	–	–	1000	0–10 ^d	350	2000	39,000
6	–	–	1000	0–20 ^e	175	50	35,000

^a Nitrogen used as balance gas.

^b Temperature ramps: 5 °C/min.

^c Oxygen steps: 1, 1.5, 2, 3, 4, 5, 7.5 and 10% O₂.

^d Oxygen steps: 0, 0.05, 0.1, 0.3, 0.5, 0.8, 1.5, 3 and 10% O₂.

^e Oxygen steps: 0, 0.5, 1, 2, 4, 8, 16 and 20% O₂.

alyst and the other in one of the monolith channels close to the catalyst front. The product gases were analysed on-line with respect to CO and CO₂ with IR instruments (UNOR 6N Maihak), and the total hydrocarbon content with a FID (VE 5 FID, JUM Engineering). In all experiments a total flow of 2000 ml/min, corresponding to a space velocity of 39,000 h⁻¹, was used. See Table 2 for a summary of the experiments.

2.2.1. Temperature-programmed experiments

In the TP experiments, a reaction mixture consisting of 10 vol% O₂ and 1000 vol-ppm of CO, propene, or propane was fed to the reactor (N₂ as balance). We studied the ignition process by ramping the temperature by 5 °C/min, from room temperature to a maximum temperature of 205 °C in the case of CO and 420 °C in the case of propene and propane. The maximum temperature was maintained for 15 min before we initiated the extinction process by ramping to room temperature again. Since the cooling was performed without additional equipment, this ramping was somewhat slower than 5 °C/min, about 4 °C/min. Before each experiment the sample was reduced in 4 vol% H₂ for 15 min and oxidised in 10 vol% O₂ for 15 min at 400 °C, and then cooled in N₂ to room temperature. The sample was then exposed to the reaction mixture and the experiment started. In the following, vol% and vol-ppm are denoted by % and ppm, respectively.

2.2.2. Oxygen step-response experiments

In the case of CO oxidation, 1000 ppm CO was introduced at a constant inlet gas temperature of 150 °C while the O₂ concentration was first increased (ignition) stepwise, by 1, 1.5, 2, 3, 4, 5, 7.5, and 10% (20 min at each composition) and then decreased (extinction) correspondingly to 1% again. For propane oxidation, 1000 ppm propane was fed into the reactor at a constant inlet gas temperature of 350 °C, and the O₂ concentration was first increased stepwise by 0, 0.05, 0.1, 0.3, 0.5, 0.8, 1.5, 3, and 10% (20 min at each composition) and then correspondingly decreased to 0%. Each

sample was pretreated in 10% O₂ for 10 min, followed by 4% H₂ for 20 min at 400 °C, before cooling in N₂ to the relevant temperature. Before the experiment was started, the reduced surface was covered by CO or propene, with the introduction of the reactant to the sample in an oxygen-free environment.

2.3. In situ XANES spectroscopy

In situ XANES spectroscopy measurements were performed at beamline ID24 at ESRF in Grenoble, France, on a pressed powder sample of Pt/zeolite Y. Pt L_{III}-edge spectra were collected in transmission mode with a Si(111) polychromator crystal, and the oxidation of 1000 ppm propane was studied in an oxygen step-response experiment at 175 °C with a Balzers Prisma mass spectrometer. The oxygen levels were changed stepwise every 60 s: first increased and then decreased in the interval of 0–20% O₂.

3. Results

3.1. Catalyst characterisation

The amount of adsorbed CO is given in Table 1 as an interval, since the CO chemisorption measurements were carried out twice for each sample, and the corresponding platinum dispersion, surface area, and particle size are calculated from the average value from the two measurements. The highest Pt dispersion, about 56%, was obtained for the Pt/100% Al₂O₃ sample, whereas the Pt/10% Al₂O₃ and Pt/1% Al₂O₃ samples had significantly lower Pt dispersions, about 44 and 21%, respectively. The variation in Pt dispersion originates from the different platinum distributions in the samples. For the Pt/1% Al₂O₃ catalyst, the platinum concentration is 20 wt% locally (0.50 mg Pt deposited on 1% of the total alumina content), which should be compared with the Pt/100% Al₂O₃ sample with 0.52 mg Pt deposited on the entire alumina content; hence in the latter case the Pt can be dispersed more easily. The higher the Pt dispersion is, the smaller the Pt particles become, and consequently, the Pt/100% Al₂O₃ sample has the smallest Pt particles, about 2.0 nm, and the Pt/1% Al₂O₃ catalyst has the largest particles, about 5.6 nm. Although the total platinum content is equal for the three catalysts, the Pt/100% Al₂O₃ sample possesses the highest platinum surface area, about three times higher compared with the Pt/1% Al₂O₃ catalyst. According to the BET measurements, the surface area of the washcoat is similar for the three samples, between 160 and 163 m²/g washcoat, and the average pore diameter is also similar, 68–69 Å.

3.2. CO oxidation

The results from the TP ignition–extinction experiments for the CO oxidation are shown in Fig. 1. The figure dis-

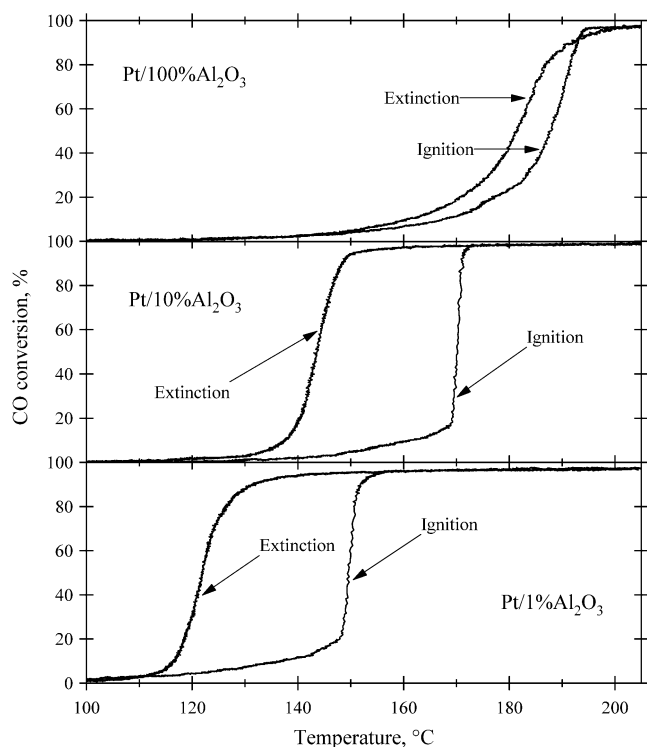


Fig. 1. CO conversion versus inlet gas temperature during TP experiments at 5 °C/min. A total flow rate of 2000 ml/min consisted of 1000 ppm CO and 10% O₂ in N₂ was passed over Pt/100% Al₂O₃, Pt/10% Al₂O₃ and Pt/1% Al₂O₃.

plays the CO conversion versus the inlet temperature for the three different catalysts, Pt/100% Al₂O₃ (top), Pt/10% Al₂O₃ (middle), and Pt/1% Al₂O₃ (bottom). The Pt/1% Al₂O₃ and Pt/10% Al₂O₃ samples show typical light-off profiles for CO oxidation [10], that is, a rapid transition from low to high CO conversion in a narrow temperature interval of about 5 °C. For the Pt/100% Al₂O₃ catalyst, however, the CO conversion profile appears to be smoother, and the transition from low to high CO conversion occurs in a broader temperature interval of about 40 °C. From the ignition experiments a clear trend in light-off temperature (here denoted by T_{50} and defined as the temperature at which 50% CO conversion is achieved [11]) is observed for the three catalysts. In the case of the Pt/1% Al₂O₃ catalyst, the T_{50} is 159 °C, whereas for the Pt/10% Al₂O₃ and Pt/100% Al₂O₃ samples the T_{50} is 170 and 188 °C, respectively, indicating a higher activity for catalysts with heterogeneous distribution of platinum in the washcoat. The results from the extinction experiments are similar to those from the ignition experiments. The CO conversion for the Pt/1% Al₂O₃ and Pt/10% Al₂O₃ catalysts drops rapidly during the ramping towards room temperature, whereas the extinction of the reaction for Pt/100% Al₂O₃ is somewhat slower and smoother. The trend in the extinction temperature (defined analogously to light-off temperature) is also similar to the ignition experiments. For the Pt/100% Al₂O₃ catalyst the extinction temperature is 181 °C, whereas for the Pt/10% Al₂O₃ and Pt/1% Al₂O₃ samples the extinction temperatures are 144 and 122 °C, re-

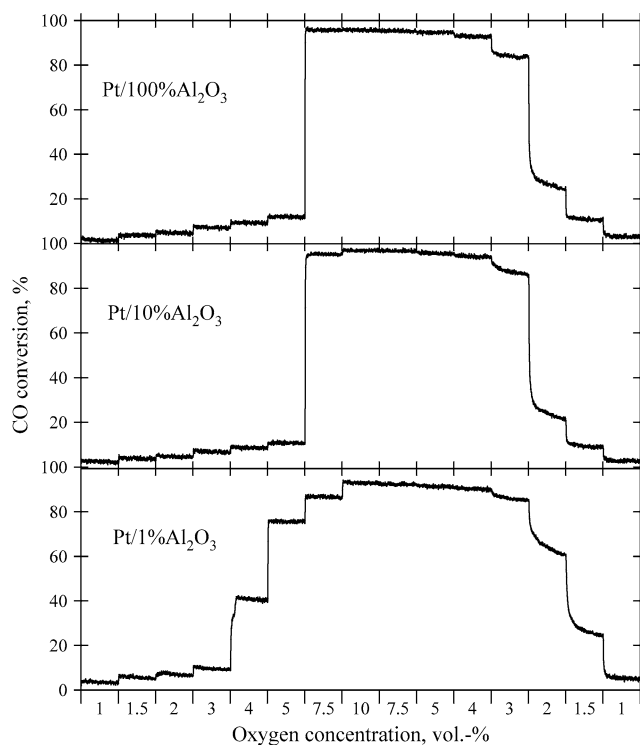


Fig. 2. The oxidation of 1000 ppm CO plotted against the O₂ concentration during oxygen SR experiments. The oxygen concentration is shifted in steps lasting 20 min each, in the interval of 1–10% O₂. A total flow rate of 2000 ml/min is passed over Pt/100% Al₂O₃, Pt/10% Al₂O₃ and Pt/1% Al₂O₃ using N₂ as balance gas at a constant temperature of 150 °C.

spectively. Moreover, an ignition–extinction hysteresis is observed for all samples in this study. This hysteresis is due to both kinetics and heat effects occurring in the catalysts [7,12,13]. The most obvious hysteresis is seen for the Pt/1% Al₂O₃ and the Pt/10% Al₂O₃ samples, whereas for the Pt/100% Al₂O₃ catalyst only a small difference between the ignition and extinction processes can be seen.

The results from the oxygen SR experiments for a constant inlet gas temperature of 150 °C are presented in Fig. 2. As seen, steady-state conversion of CO is reached rather rapidly for all catalysts as the O₂ concentration is increased. However, it takes a longer time for the CO oxidation to reach steady-state conversion when the oxygen concentration is decreased, especially in the regime of 20–70% conversion. The Pt/100% Al₂O₃ and Pt/10% Al₂O₃ samples show almost equal CO conversion for the different oxygen concentrations. A distinct light-off for 7.5% O₂ and a clear extinction for 2% O₂ can be seen for both catalysts. However, the result for the Pt/1% Al₂O₃ catalyst differs compared with the results from the other two samples. The Pt/1% Al₂O₃ sample is active in a wider oxygen interval, and, in contrast to the previous catalysts, no distinct light-off can be observed. Instead the conversion increases more or less stepwise as the oxygen concentration is changed by 4, 5, 7.5, and 10%. In the extinction process for the Pt/1% Al₂O₃ sample, no such distinct oxygen concentration-dependent drop in CO conversion can be seen, as in the case of the Pt/100% Al₂O₃

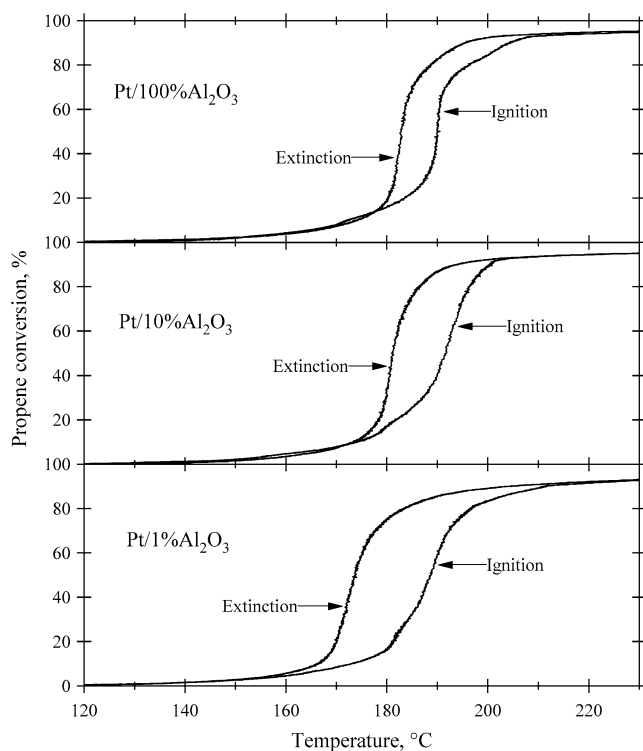


Fig. 3. Propane conversion versus inlet gas temperature during TP experiments at 5 °C/min. A total flow rate of 2000 ml/min consisted of 1000 ppm C₃H₆ and 10% O₂ in N₂ was passed over Pt/100% Al₂O₃, Pt/10% Al₂O₃ and Pt/1% Al₂O₃.

and Pt/10% Al₂O₃ samples. Instead, the CO conversion decreases stepwise as the oxygen concentration is decreased. Furthermore, a hysteresis in CO conversion is seen for all catalysts, as the extinction processes occur at lower oxygen concentrations compared with the corresponding ignition processes.

3.3. Propane oxidation

The results from the TP ignition–extinction experiments for propane oxidation are shown in Fig. 3. As in the case of CO oxidation, an ignition–extinction hysteresis is seen. However, the differences between the samples are minor, indicating that the platinum distribution in the catalyst has less effect on this reaction. The light-off temperature is close to 190 °C for all catalysts, whereas the extinction temperature is slightly above 180 °C for the Pt/100% Al₂O₃ and Pt/10% Al₂O₃ samples, and about 174 °C for the Pt/1% Al₂O₃ catalyst. Since propane oxidation is highly exothermic and, over platinum-based catalysts, can suffer from self-poisoning by propene [14,15], rather rapid light-off and extinction (transitions from low to high propane conversion and vice versa) processes are observed.

3.4. Propane oxidation

The TP experiments for propane oxidation are presented in Fig. 4. In comparison with CO and propene oxidation, ox-

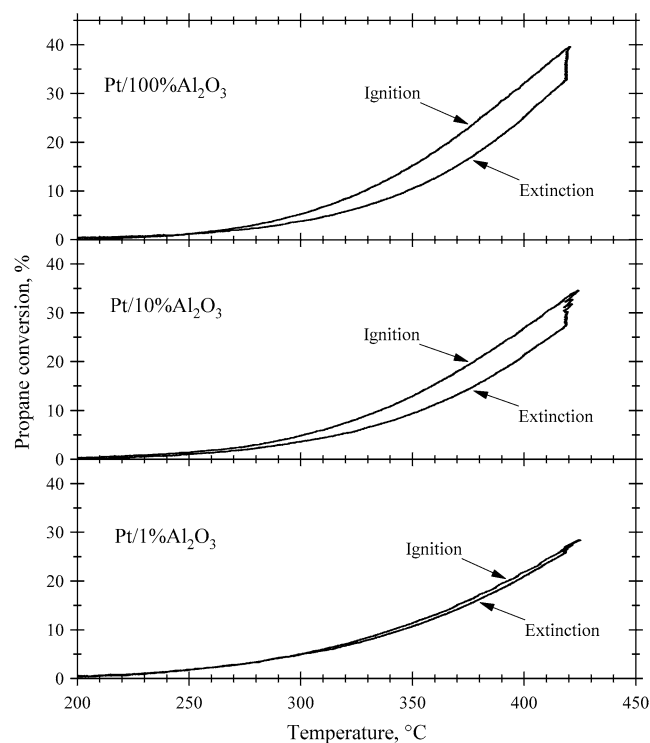


Fig. 4. Propane conversion versus inlet gas temperature during TP experiments at 5 °C/min. The temperature was kept constant at 420 °C for 15 min between the heating and cooling ramps. A total flow rate of 2000 ml/min consisted of 1000 ppm C₃H₈ and 10% O₂ in N₂ was passed over Pt/100% Al₂O₃, Pt/10% Al₂O₃ and Pt/1% Al₂O₃.

idation of propane shows considerably slower ignition and extinction processes, which occur in a rather broad temperature interval. The propane conversion increases slowly as the temperature is increased and decays slowly as the temperature is decreased. A maximum conversion is seen for all samples at the top temperature, that is, at 420 °C, and the Pt/100% Al₂O₃ catalyst is generally the most active sample, showing a maximum propane conversion of about 40%, whereas the Pt/1% Al₂O₃ sample is the least active catalyst, showing maximum propane conversion of about 29%. During the 20-min period at 420 °C, a decrease in propane conversion is seen for all samples. For the Pt/100% Al₂O₃ and Pt/10% Al₂O₃ catalysts (the samples with highest activity) the respective drop in conversion is more pronounced compared with the Pt/1% Al₂O₃ sample. However, after about 20 min, the propane conversion is similar for all three catalysts.

The results from the SR experiments for propane oxidation where the oxygen concentration is changed stepwise at a constant temperature of 350 °C are shown in Fig. 5. The experiments are carried out in two sequences, in which the oxygen concentration is first increased to 10% and then decreased back to zero with the same oxygen levels. Generally the reaction reaches steady state rapidly. However, at some oxygen steps there is a slow gradual decrease or increase in conversion with time. If we consider first the results for the Pt/1% Al₂O₃ sample, a maximum in activity is observed

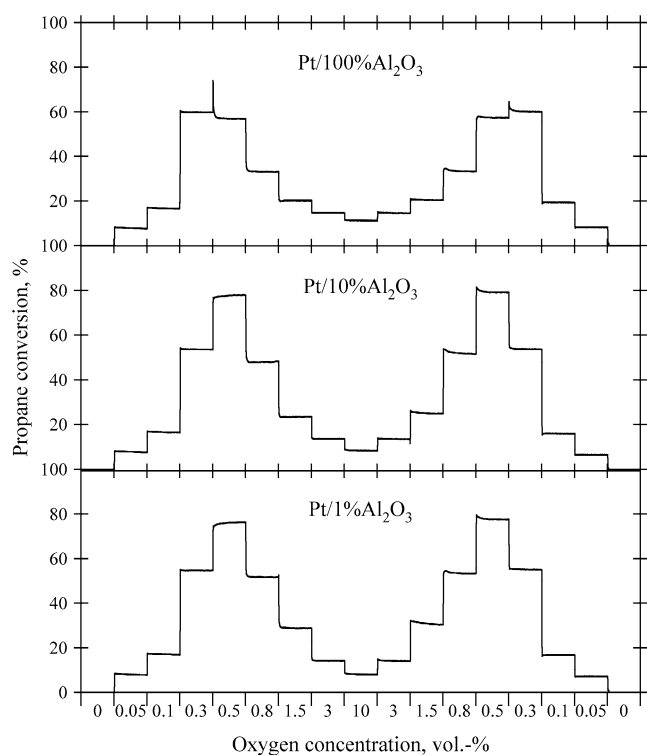


Fig. 5. The oxidation of 1000 ppm propane plotted against the O_2 concentration during oxygen SR experiments. The oxygen concentration is shifted in steps lasting 20 min each, in the interval of 0–10% O_2 . The stoichiometric amount of oxygen is 0.5%. A total flow rate of 2000 ml/min is passed over Pt/100% Al_2O_3 , Pt/10% Al_2O_3 and Pt/1% Al_2O_3 using N_2 as balance gas at a constant temperature of 350 °C.

at the stoichiometric mixture of propane (1000 ppm) and oxygen (0.5%). At 0.5% oxygen, the conversion of propane reaches 78%, for both the stepwise increase and decrease in the oxygen concentration. At less than stoichiometric conditions (oxygen deficit), the conversion of propane is close to complete with respect to the oxygen concentration. For an excess of oxygen the activity decreases with increasing oxygen concentration and a minimum in conversion of 8% is reached at the highest oxygen level. There is no sign of hysteresis in the reaction with regard to the oxygen concentration, the propane conversion for Pt/1% Al_2O_3 is the same at each oxygen level, whether the preceding oxygen concentration is higher or lower. Moreover, the results for the Pt/10% Al_2O_3 and Pt/1% Al_2O_3 samples are almost identical under the experimental conditions. However, the results for Pt/100% Al_2O_3 differ somewhat from the results from the other two samples. Maximum activity is not reached under stoichiometric conditions, but at oxygen deficit. In the 0.3% O_2 step, oxygen is consumed completely, and thereby a conversion of 60% propane is reached. At stoichiometric composition, the conversion decreases to 57%. Just as for the other two catalysts, the additional increase in the oxygen concentration causes a decrease in activity. Even though the Pt/100% Al_2O_3 sample shows the lowest conversion in the regime of 0.5–1.5% O_2 compared with the other two catalysts, this sample actually shows the highest conversion at

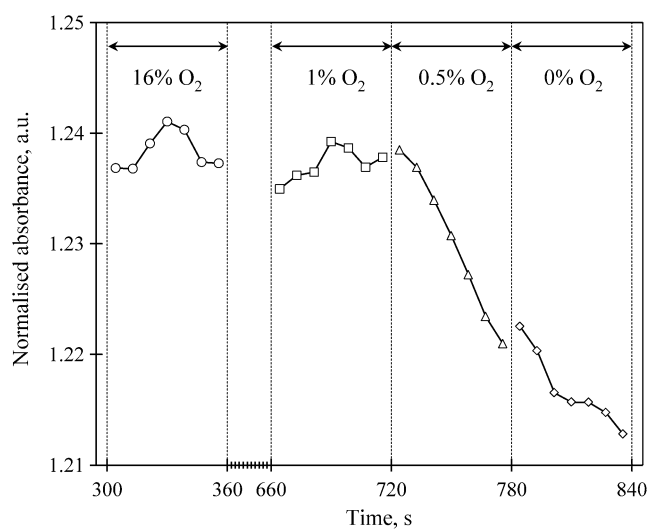


Fig. 6. In situ XANES spectra during propane oxidation; the Pt white line intensity for Pt/zeolite Y as a function of the oxygen concentration. 1000 ppm propane was oxidised in an oxygen SR experiment at 175 °C. Each oxygen concentration was on-stream for 60 s. The oxygen concentration ranged from 0–20%, however, only the most interesting levels are included in the figure. \circ , 16% O_2 ; \square , 1% O_2 ; \triangle , 0.5% O_2 (stoichiometric composition); \diamond , 0% O_2 .

10% O_2 . For Pt/100% Al_2O_3 there are also two spikes in propane conversion. The first and larger one occurs when the oxygen concentration is shifted from 0.3 to 0.5%. The second peak appears in the other sequence when the oxygen level is lowered from 0.5 to 0.3%. The spikes indicate that there is an optimal surface composition of propane and oxygen for O_2 concentrations between 0.3 and 0.5% for the Pt/100% Al_2O_3 sample, causing transient maxima in activity.

3.5. In situ XANES spectroscopy

Fig. 6 shows how the intensity of the white line, the marked adsorption peak at the Pt L_{III} -edge in the XANES spectra, shifts as the oxygen concentration is varied during propane oxidation in oxygen SR experiments. The magnitude of the white line depends on the oxidation state of platinum: high intensity means oxidised platinum, and a lower white line indicates a more reduced state [16,17]. The white line intensity at 1% oxygen (net oxidising conditions) is quite high and rather constant. For the 16% O_2 step, the intensity of the white line is similar to that of the 1% step. All of the other studied oxygen steps (not included in Fig. 6) above stoichiometric conditions had, just as for 1 and 16% O_2 , an average intensity between 1.237 and 1.245. The step of 16% oxygen is shown here since it is the nearest concentration above 10% O_2 , which was used in the other two activity studies for propane (Figs. 4 and 5). At 0.5% oxygen, which corresponds to a stoichiometric gas mixture, there is a constant decrease in the white line with time on stream. This decrease continues as the oxygen is turned off (0% O_2) and does not level off during this last 60-s step. From the activity

data collected during the in situ XANES measurement (not shown), it is observed that the propane oxidation reaches a local maximum in conversion at 0.5% oxygen, which corresponds to the results in Fig. 5, where the activity is also higher under stoichiometric conditions than it is under net oxidising conditions. The results from the in situ XANES study show that the platinum for Pt/zeolite Y changes from an oxidised state to a more reduced and a more active state for propane oxidation, as the oxygen concentration in the gas phase shifts from excess to stoichiometric conditions.

4. Discussion

In the previous study [7] the new preparation method, in which the platinum is locally distributed in small regions of the support, resulted in an improved low-temperature activity for CO oxidation. This enhanced activity for CO oxidation is referred to as the distribution effect. It would be interesting to know whether the distribution effect is general for exothermic reactions, such as propene and propane oxidation, or if the effect is specific for CO oxidation. We therefore start the discussion with a comparison of the results from the oxidation of propene and propane with the corresponding results for the CO oxidation.

In Figs. 1 and 2, the distribution effect is easily observed, since the sample with platinum distributed most heterogeneously, the Pt/1% Al₂O₃ sample, is the most active for CO oxidation, in analogy with previous results [7]. A similar effect is also expected for propene oxidation, since both CO oxidation and propene oxidation are exothermic reactions that under certain conditions suffer from self-poisoning by CO and propene, respectively [14,15,18]. However, no obvious distribution effect could be observed for propene oxidation in Fig. 3, since all three samples showed almost identical activity. Moreover, for propane oxidation, which not is expected to suffer from self-poisoning, no rapid ignition process from low to high conversion is observed during the TP experiments (Fig. 4), in contrast to propene and CO oxidation. Instead, the conversion of propane slowly increases with temperature, reaching only 30–40% at the highest temperature, 420 °C. Contrary to the CO oxidation, neither the ignition nor the extinction process shifts towards lower temperatures for the more heterogeneously distributed catalysts. Consequently, no distribution effect could be observed for propane oxidation.

Although no distribution effect is seen for the experiments with propane, two other interesting effects are observed. The first effect is the gradual decrease in activity for the Pt/100% Al₂O₃ and Pt/10% Al₂O₃ samples during steady-state conditions at 420 °C in the TP experiments (see Fig. 4). The second noteworthy effect is observed during the oxidation of propane in the SR experiments, where the activity passes through a maximum under stoichiometric or net reducing conditions (see Fig. 5).

It is known that oxygen can inhibit the oxidation of propane over supported platinum catalysts [19,20] because of competition between oxygen and propane adsorption. However, this does not completely explain the gradual drop in activity at 420 °C. At this temperature the platinum particles is likely oxidised [21–24], resulting in a less active catalyst [16,25–27]. Such passivation of the platinum phase is probably an ongoing process throughout the heating ramp and continues for the Pt/100% Al₂O₃ and Pt/10% Al₂O₃ samples during the steady-state conditions at 420 °C. For the Pt/1% Al₂O₃ sample, only a minor decrease in activity was observed while the temperature was kept constant at 420 °C. The Pt/1% Al₂O₃ sample has the largest platinum particles and consequently the lowest Pt surface area. The activity for propane oxidation is thus the lowest for this sample. However, the larger Pt particles are more difficult to oxidise, which might explain the relatively low decrease in activity during the steady-state period at 420 °C.

The second effect concerns the oxidation of propane, which passes an activity maximum for compositions close to stoichiometry. A similar behaviour has previously been reported by Carlsson et al. for Pt/Al₂O₃ catalysts [28]. The authors showed that a maximum in activity for propane oxidation can be observed for both net oxidising and net reducing conditions, depending on the platinum particle size. The maximum in activity was reached at higher oxygen concentrations for samples with larger platinum particles, and for net reducing conditions for samples with smaller platinum particles. The results in the present study correspond with the results presented by Carlsson et al. [28]. The Pt/100% Al₂O₃ sample with the smallest platinum particles (i.e., lowest mean particle size) shows a maximum in propane conversion under net reducing conditions, and the other two samples with larger platinum particles show activity maxima for higher oxygen concentrations. The reason for the optimum in activity for oxygen concentrations close to stoichiometric conditions is most likely due to the inhibition of the oxidation of propane by an excess of oxygen on the platinum surface [20]. At low oxygen concentrations, oxygen is the limiting reactant because of complete consumption of the available oxygen, and thus the reaction is of first order with respect to oxygen. At some point (at about 0.5% O₂ in Fig. 5), the oxygen concentration passes a threshold and oxygen starts to inhibit the reaction. Further increase in the oxygen concentration inhibits the reaction even more. The possibility that the adsorbed oxygen blocks the surface for propane or passivates the active sites by platinum oxide formation can be considered. The results from the in situ XANES measurements (Fig. 6) indicate the latter, since a shift in the oxidation state of platinum towards a more reduced platinum surface is observed when the oxygen concentration is switched from net oxidising to stoichiometric conditions. However, the in situ XANES experiments presented here cannot establish the exact oxidation state of the platinum, but indicate a reduction. The oxidised state has a rather low activity for oxidation of hydrocarbons, whereas

metallic (or partially oxidised) platinum is reported to be more active [26]. Even though the in situ XANES experiment is performed for a platinum sample supported on zeolite Y, a similar change in oxidation state is expected to occur at about stoichiometric gas composition for the three Pt/Al₂O₃ samples used in this study, since the Pt/zeolite Y, just like the three Pt/Al₂O₃ samples, showed a maximum in activity under stoichiometric conditions. The suggestion by Carlsson et al. [28] for why smaller platinum particles reach a maximum in propane conversion at lower oxygen concentrations rather than at larger concentrations involves the formation of platinum oxide. As smaller platinum particles are more readily oxidised than larger ones, a lower oxygen concentration is required to turn samples with small platinum particles into the less active oxidised state.

One of the main objectives of this study is to understand the origin of the distribution effect. As mentioned above, the distribution effect was previously discussed in terms of heat and mass transfer and structure sensitivity [7]. Here we will widen that discussion, and the results from the oxidation of propene and propane in particular will make some aspects clearer.

The original idea behind distributing the active phase heterogeneously with high local platinum concentration was to make more efficient use of the evolved reaction heat by increasing the temperature locally in the washcoat, which would result in an enhanced activity. However, experiments with low CO concentrations accompanied by calculations indicated that the heat effect could not explain the distribution effect [7]. This is further supported by experiments in the present study. The reaction heat for oxidising CO to CO₂ is about 280 kJ/mol. The corresponding value for complete oxidation of propene and propane, respectively, is approximately 2000 kJ/mol. If high temperatures are generated locally in the washcoat during CO oxidation, then, clearly, propene and propane have an even higher potential to generate temperature gradients enhancing the reaction rate. Since the platinum distribution has almost no influence on the activity for oxidation of propene and propane, respectively, heat effects due to the platinum distribution are likely not the origin of the distribution effect.

Heterogeneous catalytic reactions can be controlled by mass transfer. This is normally the case during high conversions, when the surface reaction rate exceeds the diffusion rate (in gas phase or in the porous support) of reactants. In the mass transfer controlled regime, pronounced concentration gradients are developed with lower concentration close to the active phase. Mass transfer limitations will result in a reduced reaction rate for reactions with positive order, and it will enhance the rate of reactions with negative reaction order. Therefore, reactants that can be of both negative (CO and propene) [14,15,18] and positive (propane) [19,20] orders were chosen for this study. If the distribution effect is due to mass transport phenomena, the positive effect observed for CO oxidation is expected also for the oxidation of propene, whereas the opposite effect is expected for propane

oxidation. However, in the TP experiments the samples show similar activity for the propene and propane oxidation, indicating that mass transport phenomena cannot explain the distribution effect.

In the present study there is another argument, which concerns the diffusivity, implying that mass transfer limitations are not causing the distribution effect. Because of the rather small pores in the samples (~7 nm in mean diameter), the diffusion (D) is controlled by Knudsen diffusion, which is proportional to the square root of the temperature divided by the molecular mass, $D \propto \sqrt{T/M}$. When the oxidation of CO is compared with the oxidation of propene, the latter reaction becomes mass transfer limited at lower conversions because of the slower diffusion rate of propene compared with CO. As a rough estimate, the propene oxidation should enter the mass transfer limited regime at about a 4–10% lower conversion compared with the CO oxidation, for the conditions used in the TP experiments. If the distribution effect observed for CO oxidation is due to mass transfer limitations, then the same effect should be observed for propene; however, this was not the case.

In the previous study [7], calculations were performed to establish whether the CO oxidation was affected by mass transfer limitations by determining the Weisz modulus. The calculations indicated that the reaction enters the mass transfer limited regime at high conversions (above 50%); hence the extinction process might be affected by mass transfer limitations, whereas the ignition process is likely not. Moreover, the calculations showed that the Pt/1% Al₂O₃ sample is the catalyst in which mass transfer limitations affect the oxidation of CO the most. This is in agreement with the experimental results, where Pt/1% Al₂O₃ generally is the sample with the highest low-temperature activity during both the extinction and ignition processes. However, the calculations were performed on the basis of a constant reaction rate in the entire volume of the catalyst, although it is known that, for example, the ignition process for the oxidation of CO can occur locally in the rear part of Pt/Al₂O₃ monoliths [13]. This indicates that the calculations in [7] should be performed for only a minor part of the catalyst volume, instead of the entire volume. That the ignition proceeds only in a minor part of the catalyst volume means that the CO oxidation enters the mass transfer limited regime at an overall lower conversion compared with the calculations performed in [7]. Thus it is possible that the ignition process is affected by mass transfer limitations even at low conversions, especially for the samples with heterogeneous platinum distribution. Although the results from the calculations show that the distribution effect can be a mass transfer effect, there are experimental results contradicting this statement, since no distribution effect is observed for the oxidation of propene.

For so-called structure-sensitive reactions, the particle size of the active material can have a significant effect on the catalytic performance. This can be of importance for the interpretation of the results, since the three samples used in this study not only possess different platinum distribution,

they also have different average particle sizes, which is seen as varying platinum dispersions. The low-dispersion sample (Pt/1% Al₂O₃) consists of larger platinum particles (with a mean diameter of 5.6 nm), and the high-dispersion catalyst (Pt/100% Al₂O₃) consists of smaller particles (2.0 nm in average diameter). The platinum particle size effect on oxidation reactions such as those for CO and different kinds of hydrocarbons has been summarised in various reports [29–35]. For propane oxidation Marécot et al. [29] showed an optimum in activity for samples with intermediate platinum dispersion (20%) and that smaller platinum particles are more active for propene oxidation than larger ones. The other investigations [30–35] almost exclusively report that the oxidation reactions are either structure insensitive or that larger platinum particles are more active than smaller ones. For example, in one of the more recent studies in this area [30], Zafiris and Gorte show a much higher turnover frequency for CO oxidation over 14-nm platinum particles than over 1.7-nm particles. They suggest that the oxidation is controlled by CO desorption and that CO more easily desorbs from larger particles. In a recent work by Vaccaro et al. [31] three other suggestions for why larger platinum particles are more active than smaller ones in oxidation reactions are summarised: (i) the binding energy for oxygen is decreased for larger particles, resulting in an improved activity; (ii) variations in activity are observed for different crystal planes where larger particles expose more favourable crystal plane distributions compared with smaller particles; (iii) larger particles remain metallic and more active in oxidising environments, whereas oxygen binds with an ionic character to smaller particles, making them inactive. The results from the experiments with CO oxidation in the present study follow the trend that larger platinum particles are more active than smaller ones, since Pt/1% Al₂O₃ is the most active and Pt/100% Al₂O₃ is the least active sample. This indicates that the distribution effect can be a particle size effect. With this, the results from propene and propane oxidation suggest that the particle size dependency for these reactions must be considerably lower than for CO oxidation under the experimental conditions used. To confirm the hypothesis of structure sensitivity, further work is required.

5. Conclusions

Three Pt/ γ -Al₂O₃ catalysts were prepared with constant platinum and alumina loadings; the platinum was distributed either homogeneously in the washcoat or heterogeneously with high local platinum density in the washcoat. In accordance with previous results, the samples with a heterogeneous platinum distribution showed an improved activity for CO oxidation. This distribution effect was established to be CO specific, since no obvious distribution effect was observed for propene or propane oxidation.

Since the mean platinum particle size varies between the catalysts, as does the local loading of platinum in the wash-

coat, we discuss the distribution effect in terms of particle size effect and heat and mass transfer. The distribution effect was found to not be caused by heat transfer. Although calculations indicate that the distribution effect can be a mass transfer effect, this could not be confirmed by our experiments. Instead, the distribution effect can be due to surface kinetics. It is possible that the difference in platinum particle size between the samples influences the activity for the oxidation of CO and thereby causes the distribution effect.

Two interesting effects were observed during the oxidation of propane. First, the activity decreased with time during steady-state conditions at 420 °C. This passivation of the catalysts is probably caused by oxidation of the platinum particles. Second, the activity decreased with increasing oxygen concentrations under net oxidising conditions. Supported by in situ XANES analysis, this effect is most likely due to oxidation of the platinum surface to a less active state and/or inhibition of the reaction by adsorbed oxygen species that suppress propane adsorption.

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