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Journal of Catalysis 221 (2004) 252-261

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Investigation of Pt/γ -Al₂O₃ catalysts with locally high Pt concentrations for oxidation of CO at low temperatures

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Received 22 May 2003; revised 18 August 2003; accepted 22 August 2003

Abstract

A new method for preparing supported catalysts, in which Pt was distributed in locally high concentrations on the γ -Al₂O₃ support, was studied. These catalysts were compared with a conventionally prepared Pt/ γ -Al₂O₃ catalyst in which Pt was deposited evenly on the support. The object was to ascertain whether it is possible to prepare catalysts that retain heat released from exothermic reactions to a higher extent and thereby become more low-temperature active than a conventionally prepared catalyst. A significant improvement of the activity was observed for the catalysts prepared with locally high Pt concentrations when CO (1%, 1000 and 100 ppm) was oxidized at a constant O₂ concentration (10%). The improved activity is discussed in terms of heat transfer, mass transfer, and structure sensitivity. Differences in heat transfer appear to be the least probable reason for the enhanced activity for the catalysts with locally higher Pt concentrations, whereas structural effects also seem to be an unlikely explanation. Differences in mass transfer seem, however, to be a more likely reason for the improved activity.

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Keywords: Catalytic activity; CO oxidation; Low temperature; Platinum; Alumina; Mass transport; Heat transport; Structure sensitivity

1. Introduction

The development of low-temperature active catalysts is important for applications such as catalytic combustion of VOC (volatile organic compounds) and abatement of vehicle exhausts. The usage of such catalysts will in these applications reduce both emissions of harmful compounds and costs for external heating of the feed gas (generally required for VOC combustion). To obtain high activity at low temperatures, it is essential to optimize the effects from heat and mass transfer in the catalyst. For reactions which are structure sensitive it is also important to optimize the size of the active sites.

Heat released from chemical reactions on the surface of a catalyst is removed from the active sites to the surrounding support material and the gas phase by convection, conduc-

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tion, and radiation. Even if the heat is rapidly removed from the active sites, large temperature gradients between the active sites and the support material can arise which affect the catalytic activity. The topic of such temperature gradients was first discussed by Damköhler [1], and since that several theoretical [2–7] and experimental [8–16] studies have been contradictory. Early theoretical studies [3–6] report instantaneous temperature rises in crystallites in the order of several hundred degrees Celsius, lasting up to 10^{-10} s. Instead of considering the transient gradients, Holstein and Boudart [7] calculated the constant temperature gradients between the active metal and the support at steady state, $(T_{metal} - T_{support})/T_{support}$, during exothermic reactions to be less than 0.03%.

Large temperature gradients between active sites and support material may result in hot active sites, but to experimentally verify the existence of such hot sites is a difficult task. In 1973, Mark and Low [9] used IR radiometry to measure temperature changes when prereduced Ni/SiO₂ was oxidized. The authors did not find any emission gradients and concluded that the Ni crystallites and the silica support had

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the same temperature during the oxidation. However, Kember and Sheppard [10] reported a temperature difference of 190°C between the metal and the support material when CO was oxidized over Pd/SiO₂. They measured the Pd crystallite temperature using IR spectroscopy and the support temperature with a thermocouple. Sharma et al. [14] argued, however, that the support temperature reported by Kember and Sheppard was incorrectly measured, which resulted in too high temperature gradients between the Pd crystallites and the silica support. For CO oxidation over Pt/SiO2, studied in situ by FTIR absorption spectroscopy, Sharma et al. [14] reported quite small temperature gradients, e.g., at a gas-phase temperature of 200 °C the support and crystallite temperature was 210 and 235 °C, respectively. Matyi et al. [12] reported temperature gradients in the same range for the reaction between H₂ and CO (Fischer-Tropsch synthesis) over Fe/SiO₂. Using Mössbauer spectroscopy they found temperature gradients of 13 and 19°C between the metal and the support at gas-phase temperatures of 275 and 300 °C, respectively. Further, Frost et al. [15] used neutron resonance radiography to study possible microscopic temperature inhomogeneities within a Pt/Sm₂O₃ catalyst used for CO hydrogenation. The authors did, however, not find any significant temperature gradients between Pt and Sm₂O₃ under the experimental conditions used. Clearly it is an experimental challenge to measure whether the heat released from exothermic reactions can give rise to sufficiently large temperature gradients between the metal and the support to significantly increase the reaction rate over a catalyst.

For a given catalyst material at fixed bulk concentrations of the reactants, the reaction rate can vary due to local variations in concentrations at the catalyst surface. Mass transfer limitations locally decrease the concentration of the reactant resulting in concentration gradients which affect the corresponding reaction rate. This is most interesting for reactions with negative reaction orders since the reaction rate increases with decreasing concentration. The oxidation of CO on Pt is especially interesting since it is highly exothermic and has negative reaction order with respect to CO concentration, due to self-poisoning of the active sites by CO at low temperatures.

Since the reactivity for structure-sensitive reactions depends on the shape and size of active sites, the catalytic performance can be improved by optimizing these forms. Even for a thoroughly studied reaction such as CO oxidation over supported noble metal, there is no consensus whether it is structure insensitive or the activity increases with increasing size of the active sites [17,18]. A study by McCarthy et al. [19] showed that CO oxidation over Pt/ α -Al₂O₃ can be structure sensitive depending on the CO concentration. More recently, Zafiris and Gorte studied the same system as above [20] but observed that the activity increased with increasing Pt crystallite size irrespective of the CO concentration and suggested that this is because CO desorbs more easily from large Pt crystallites.

In this investigation we have studied a new method for preparing supported catalysts. The object was to ascertain whether it is possible to prepare catalysts that locally, around the active sites, retain heat released from exothermic reactions to a higher extent than a conventionally prepared catalyst. Using the new preparation method, the active phase, platinum, was deposited on a small part (1, respectively 10%) of the available γ -Al₂O₃ support while the major part of the support material was left unimpregnated. The catalysts prepared using this method were compared with a conventionally prepared Pt/γ -Al₂O₃ catalyst in which platinum was deposited on the entire part (100%) of the alumina support. If the heat released from the exothermic reaction between CO and O₂ was isolated in the close vicinity of the active sites, the reaction rate would self-accelerate at lower temperatures over the catalysts with local Pt concentration compared to the conventional catalyst with evenly distributed platinum.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by depositing three different wash coats on separate monolithic substrates. Each wash coat contained boehmite, γ -Al₂O₃, and Pt.

2.1.1. Boehmite sol (A)

The boehmite sol was prepared by adding 30 g of boehmite powder (Dispersal S, Condea Chemie) to a solution containing 16.2 g 1 M HNO₃ and 154 g distilled water under moderate stirring. The dispersed powder was stirred for at least 30 min in order to obtain a stable boehmite sol without aggregated particles.

2.1.2. Wash coat with uniform Pt density, conventional catalyst— $Pt/100\% Al_2O_3$ (B)

A 64.0 g γ -Al₂O₃ powder (Puralox S Ba 70, Condea Chemie) was added to 100 g distilled water under continuous stirring. The pH was adjusted to 1.9 by adding nitric acid before impregnation with 1.035 g 0.8 M platinum(II) nitrate solution (Hereaus) diluted with distilled water to 10 g. The impregnated powder was dried at 100 °C for 15 h and calcined at 500 °C in air for 1 h. The resulting surface concentration of Pt on this powder was about 0.0754 µmol/m² γ -Al₂O₃. The Pt/ γ -Al₂O₃ powder and boehmite sol, prepared according to Section 2.1.1. were added to a mixture of 199 g ethanol and 30 g 1 M nitric acid. The slurry (Pt/ γ -Al₂O₃, ethanol, nitric acid, and boehmite sol) was finally ball-milled at a constant rate of 50–70 rpm for 10–24 h.

2.1.3. Wash coat with medium local Pt density—Pt/10% Al₂O₃ (C)

A portion, 10 wt% (6.4 g), of the total amount of γ -Al₂O₃ powder intended for use in the preparation of the alumina slurry was added to 50 g distilled water under continuous

Table 1
Sample data

	Catalyst		
	Pt/100% Al2O3	Pt/10% Al ₂ O ₃	Pt/1% Al2O3
Amount applied wash coat (g)	0.15	0.20	0.30
Pt content (mg)	0.30	0.39	0.59
Amount Pt-coated Al_2O_3 (%)	100	10	1
Amount adsorbed CO (µmol)	$0.52^{a} (0.54)^{b}$	$0.58^{a} (0.58)^{b}$	0.55 ^a (0.51) ^b
Dispersion ^c (%)	$48^{a} (50)^{b}$	$41^{a} (41)^{b}$	$26^{a} (24)^{b}$
Pt surface area ^d (dm^2)	$3.6^{a}(3.7)^{b}$	$4.0^{a} (4.0)^{b}$	$3.8^{a}(3.5)^{b}$
Mean Pt crystallite diameter ^e (nm)	2.3	2.7	4.5
Mean support particle radius ^f (µm)	1.25	1.25	1.25
S_{BET} (m ² /g wash coat)	151	152	162

^a Before activity study.

^b After activity study.

^c Assuming Pt:CO stoichiometry of 1:0.7 [23].

^d Assuming $0.08 \text{ nm}^2/\text{Pt}$ atom [24].

^e Assuming spherical particles [24].

^f Estimation from SEM studies.

stirring. The pH was adjusted to 1.9 by adding nitric acid before impregnation with an aqueous platinum(II) nitrate solution, dried, and calcined, as described in Section 2.1.2. The resulting surface concentration of Pt on this powder was about 0.754 μ mol/m² γ -Al₂O₃. The Pt/ γ -Al₂O₃ powder, the remaining γ -Al₂O₃ powder (90 wt% of the total amount of γ -Al₂O₃), and the boehmite sol (A) were mixed in the same proportions and with the same compounds as described in Section 2.1.2. and the resulting slurry was finally ball-milled according to the procedure in Section 2.1.2.

2.1.4. Wash coat with high local Pt density—Pt/1% Al₂O₃ (D)

A small portion, 1 wt% (0.64 g), of the total amount of γ -Al₂O₃ powder intended for use in the preparation of the alumina slurry was added to 40 g distilled water under continuous stirring. The slurry was impregnated with an aqueous platinum(II) nitrate solution, dried, and calcined using the same method as described in Section 2.1.2. The resulting surface concentration of Pt on this powder was about 7.54 µmol/m² γ -Al₂O₃. The Pt/ γ -Al₂O₃ powder, the remaining γ -Al₂O₃ powder (99 wt% of the total amount of γ -Al₂O₃), and the boehmite sol (A) were mixed and finally ball-milled according to the procedure described in Section 2.1.3.

2.1.5. Preparation of monolith catalysts—Pt/1% Al₂O₃, Pt/10% Al₂O₃, and Pt/100% Al₂O₃ (E)

Small samples (23 mm long and 13 mm in diameter) of washed and dried monolithic cordierite with a cell density of 400 CPSI (cells per square inch) were used as framework for the wash coats. The wash coat was uniformly applied onto the monolith sample by immersing the monolith in one of the three catalyst slurries prepared according to (B), (C), or (D). After each immersion, the slurry in the monolith channels was removed by gently blowing with pressurized air. The wet monolith sample was dried in hot air (300 °C) and weighed. This stepwise procedure was repeated until the desired amount of wash coat was applied on each monolith sample (Table 1). The wash-coated monoliths were finally calcined in air at 500 °C for 1 h in order to fixate the wash coat on the monolith framework. During the calcination, the boehmite binder particles were dehydrated and transformed into γ -Al₂O₃.

The catalysts slurries (B)–(D) had the same Pt content (0.2 wt% based on the dry wash coat). The difference between the slurries was that Pt was deposited on either 100% (B), 10% (C), or 1% (D) of the total alumina content, and these proportions did not change during the ball milling, since both Pt/Al₂O₃ and Al₂O₃ particles were affected to same extent by the grinding. The amount of applied wash coat differed in an inverse proportion to the Pt dispersions, resulting in constant Pt surface area (measured with CO chemisorption) for all catalysts prepared. Basic characteristics of the catalysts are given in Table 1. Moreover, three additional catalysts were prepared in similar procedures as above but with constant Pt loading instead of constant Pt surface area.

2.2. Catalyst characterization

The dispersion and surface area of Pt for the catalysts were measured with CO chemisorption [21]. The chemisorption measurements were performed in a continuous flow reactor system described elsewhere [22]. The Pt dispersion was measured for each catalyst twice (first as fresh samples and secondly after the activity tests). The experiments were performed by first prereducing the catalyst in 10% H₂ at 400 °C for 30 min. The catalyst was then cooled to 0 °C in N₂ and was kept at this temperature during the entire experiment. After about 10 min, the catalyst was instantly exposed to 50 ppm CO in N₂, while measuring the outgoing concentration of CO. During this step, CO was chemisorbed on the surface Pt atoms. When the outlet concentration reached

Table 2	
Summary of experiments	

Figure	Catalyst	Gas composition ^a		Temperature ^b	Flow	Space velocity
		CO (vol ppm)	O ₂ (vol %)	(°C)	(ml/min)	(h^{-1})
1	Pt/100% Al2O3	10,000	10	50-280	1000	17,000
	Pt/10% Al2O3	10,000	10	50-280	1000	17,000
	Pt/1% Al ₂ O ₃	10,000	10	50-270	1000	17,000
2	Pt/100% Al2O3	1000	10	50-220	1000	17,000
	Pt/10% Al2O3	1000	10	70–220	1000	17,000
	Pt/1% Al ₂ O ₃	1000	10	60–210	1000	17,000
3	Pt/100% Al2O3	100	10	40-170	1000	17,000
	Pt/10% Al ₂ O ₃	100	10	40-190	1000	17,000
	Pt/1% Al ₂ O ₃	100	10	50-170	1000	17,000

^a N₂ as balance.

^b Heating and cooling ramp at 5 °C/min.

the inlet CO concentration, the catalyst was saturated with CO and the reactor was flushed with pure N_2 whereby nonchemisorbed CO desorbed from the sample. Then once again, the catalyst was exposed to 50 ppm CO in N_2 . Subtracting the CO responses from the two experiments gives an area correlating with the amount of chemisorbed CO on Pt. The Pt dispersion and the corresponding Pt surface area of the catalysts were calculated from the amount of chemisorbed CO divided by the total Pt content, using a stoichiometric factor of 0.7 adsorbed CO molecules per Pt surface atom for dispersion [23] and a surface area of 0.08 nm² per Pt atom [24].

The mean platinum crystallite diameter was calculated assuming spherical crystallites according to Anderson and Pratt [24],

$$d_{\rm Pt} = 6V_{\rm Pt}/A_{\rm Pt},\tag{1}$$

where V_{Pt} is the total platinum volume, obtained by dividing the platinum mass with its density, while A_{Pt} is the platinum surface area determined by CO chemisorption.

The specific surface area and the mean pore diameter of the wash coats were determined (with an accuracy of $\pm 1\%$) by nitrogen adsorption after the activity experiments according to the BET method using an ASAP 2010 instrument (Micromeritics). The BET surface area determinations were based on six measurements at relative pressures of N₂ in the range of 0.03–0.20. The used cross-sectional area of the nitrogen adsorbate was 0.162 nm².

2.3. Activity studies

The influence of the different platinum distributions on the oxidation of CO was studied using constant gas compositions under temperature ramps at atmospheric pressure. The experiments were performed in the reactor described above. For the activity tests the catalytic performance of each catalyst was compared per the same unit of surface area of platinum metal $(3.6-4.0 \text{ dm}^2)$. The gases (CO, O₂, and N₂ as balance) were introduced into the reactor via mass flow controllers (Bronkorst Hi-Tec). Temperatures were measured with two thermocouples, which were located 11 mm in front of the catalyst and in one of the monolith channels close to the catalyst front. The product gases were continuously analyzed with respect to CO and CO_2 with IR instruments (UNOR 6N Maihak).

The light-off and extinction processes for CO oxidation, using constant O_2 concentration (10%) and varying the CO concentration (1%, 1000 and 100 ppm), were studied by first increasing the reactor inlet temperature at a constant rate of 5 °C/min and then quenching the reaction by constant cooling at 5 °C/min. The three catalysts were initially reduced in 10% hydrogen at 400 °C for 15 min, followed by oxidation in 10% oxygen at 400 °C for 15 min. All experiments are summarized in Table 2.

3. Results

3.1. Catalyst characterization

The platinum dispersion, the platinum surface area, the mean platinum crystallite size, and the BET area of the catalysts are given in Table 1. The dispersions for the fresh and used catalysts do not differ significantly, indicating that the catalysts did not sinter during the activity studies. The Pt/100% Al₂O₃ catalyst shows the highest Pt dispersion (49%), while the dispersion is 41% for Pt/10% Al₂O₃ and 25% for Pt/1% Al₂O₃. The corresponding platinum surface areas are rather constant for the catalysts (3.6 dm² for Pt/100% Al₂O₃, 4.0 dm² for Pt/10% Al₂O₃, and 3.6 dm² for Pt/1% Al₂O₃, with an error range of \pm 0.2 dm²). CO chemisorption studies for both empty reactor and for unimpregnated alumina support showed no significant CO uptake, which strongly indicates that CO only chemisorbs on platinum during the experimental conditions used.

The average diameter of the Pt crystallites calculated from the CO chemisorption data is 2.3, 2.7, and 4.5 nm for Pt/100% Al_2O_3 , Pt/10% Al_2O_3 , and Pt/1% Al_2O_3 , respectively. While preparing the catalysts, the platinum was impregnated on the wash coat before the wash coat was de-



Fig. 1. Conversion of CO versus inlet gas temperature during oxidation of 1% CO in 10% O₂ over Pt/ γ -Al₂O₃. Diamonds (100%); Pt/10% Al₂O₃, triangles (10%); Pt/10% Al₂O₃, and squares (1%); Pt/1% Al₂O₃. Open symbols, heating ramps (5 °C/min); and filled symbols, cooling ramps (5 °C/min).

posited on the monolith. This preparation technique may trap some of the platinum in pores inaccessible to the reactants. Platinum trapping could be avoided by first depositing the wash coat on the monolith, and then impregnating the stabilized wash coat with the Pt precursor. When considering this trapping effect the actual Pt crystallite size could be somewhat smaller than calculated for the catalysts.

The BET surface areas of the three wash coats are similar (S_{BET} , 150–162 m²/g stabilized wash coat; mean pore diameter, 75 Å).

3.2. Oxidation of 1% CO

Fig. 1 shows oxidation of 1% CO over Pt/100% Al₂O₃, Pt/10% Al₂O₃, and Pt/1% Al₂O₃ with 10% O₂ during heating and cooling ramps. The graph displays the effect of the inlet temperature on the CO conversion. The conversion follows a typical light-off process for CO oxidation over platinum which can be divided in three different activity regions. At low temperatures, the reaction is self-inhibited by a high CO coverage on the active sites [25] and the conversion is thus very low. At higher temperatures, the CO conversion is high and the surface coverage of CO is low. In this region the reaction rate is limited by the transport of reactants to the active sites of the catalyst. In the intermediate light-off region, during the heating ramp, the reaction is autocatalyzed by the evolved reaction heat which results in a rapid increase from low to high conversion. While cooling the inlet gas, the reaction proceeds from the region with high conversion to the region with low conversion. In the intermediate extinction interval, the reaction rate decreases fast. The extinction from high to low conversion is somewhat less rapid than the lightoff process.

For the heating ramps the light-off temperatures, T_{50} (temperature at 50% conversion), are rather constant, 232, 237, and 228 °C for Pt/100% Al₂O₃, Pt/10% Al₂O₃, and

Pt/1% Al₂O₃, respectively. For all catalysts a pronounced hysteresis between the light-off and extinction temperature regions is observed. For the cooling ramp (extinction) the activity of the different catalysts differs markedly. The Pt/1% Al₂O₃ catalyst has highest low-temperature activity, while the conventional catalyst, Pt/100% Al₂O₃, has the lowest activity. The T_{50} 's for extinction are 177 °C for Pt/100% Al₂O₃, 165 °C for Pt/10% Al₂O₃, and 144 °C for Pt/1% Al₂O₃. The values for T_{50} are summarized in Table 3.

3.3. Oxidation of 1000 ppm CO

The oxidation of 1000 ppm CO with 10% O₂ over the three catalysts is shown in Fig. 2, and the corresponding light-off and extinction temperatures are summarized in Table 3. The conventional catalyst, Pt/100% Al₂O₃, reaches T_{50} at the highest temperature, both for light-off (183 °C) and extinction (166 °C). On the contrary, the lowest T_{50} 's are observed for the Pt/1% Al₂O₃ catalyst ($T_{50,light-off}$ 164 °C, $T_{50,extinction}$ 127 °C). The Pt/10% Al₂O₃ sample shows an intermediate activity in comparison to the other two catalysts, with $T_{50,light-off}$ at 177 °C and $T_{50,extinction}$ at 151 °C. The appearances of the CO conversion profiles are similar to those for 1% CO in 10% O₂ as described above.

3.4. Oxidation of 100 ppm CO

Fig. 3 shows the oxidation of 100 ppm CO with 10% O_2 over the three catalysts and the T_{50} values during the temperature ramp experiments are presented in Table 3. The CO conversion profiles resemble the corresponding profiles for 1000 ppm and 1% CO with sharp light-off and extinction intervals; see above. Even with this rather low CO concentration, a marked hysteresis between the light-off and extinction processes is seen. The hysteresis is most pronounced for the

Table 3
Temperatures for 50% conversion (T_{50}) for light-off and extinction experiments

Figure	Experiment	Catalyst			
		Pt/100% Al ₂ O ₃	Pt/10% Al2O3	Pt/1% Al ₂ O ₃	
1	1% CO				
	T_{50} light-off (°C)	232	237	228	
	T_{50} extinction (°C)	177	165	144	
2	1000 ppm CO				
	T_{50} light-off (°C)	183	177	164	
	T_{50} extinction (°C)	166	151	127	
3	100 ppm CO				
	T_{50} light-off (°C)	126	113	102	
	T_{50} extinction (°C)	117	94	72	



Fig. 2. Conversion of CO versus inlet gas temperature during oxidation of 1000 ppm CO in 10% O_2 over Pt/γ -Al₂ O_3 . Diamonds (100%), Pt/100% Al₂ O_3 ; triangles (10%), Pt/10% Al₂ O_3 ; and squares (1%), Pt/1% Al₂ O_3 . Open symbols, heating ramps (5 °C/min); and filled symbols, cooling ramps (5 °C/min).



Fig. 3. Conversion of CO versus inlet gas temperature during oxidation of 100 ppm CO in 10% O₂ over Pt/γ -Al₂O₃. Diamonds (100%), Pt/100% Al₂O₃; triangles (10%), Pt/10% Al₂O₃; and squares (1%), Pt/1% Al₂O₃. Open symbols, heating ramps (5 °C/min); and filled symbols, cooling ramps (5 °C/min).

Pt/1% Al₂O₃ catalyst. The low-temperature activity is highest for Pt/1% Al₂O₃ and lowest for Pt/100% Al₂O₃. The $T_{50,light-off}$ is 126 °C for Pt/100% Al₂O₃, 113 °C for Pt/10% Al₂O₃, and 102 °C for Pt/1% Al₂O₃. The corresponding $T_{50,extinction}$ is 117 °C for Pt/100% Al₂O₃, 94 °C for Pt/10% Al₂O₃, and 72 °C for the Pt/1% Al₂O₃ sample.

4. Discussion

The results from the CO oxidation experiments for the three catalysts with Pt deposited with different local concentrations on the available alumina support are presented in Figs. 1-3. The graphs show clearly that there are significant differences in activity between the catalysts. The catalyst with Pt deposited on only 1% of the total amount of alumina support, Pt/1% Al₂O₃, shows the highest low-temperature activity for both heating and cooling ramps. The conventional catalyst, with Pt deposited on the entire amount of alumina support, Pt/100% Al₂O₃, has the lowest activity, while the catalyst with Pt deposited on 10% of the alumina support, Pt/10% Al₂O₃, shows intermediate activity for CO oxidation. The hysteresis, the difference between the light-off and extinction temperatures, is smallest for Pt/100% Al₂O₃, increases for Pt/10% Al₂O₃, and is highest for Pt/1% Al₂O₃. Complementary to the experiments in this study, three additional catalysts were prepared with constant Pt loading and tested by oxidizing 0.2% CO in air. This test also showed that the catalyst prepared with high local Pt density had the highest activity, while the conventionally prepared catalyst had the lowest activity for CO oxidation.

It is obvious that the sample with highest local Pt density, Pt/1% Al₂O₃, shows the highest low-temperature activity. In contrast, the lowest activity for CO oxidation is found for the conventionally prepared sample, Pt/100% Al₂O₃. Since the amount of platinum surface area between the catalysts is constant, the differences in activity for CO oxidation most be due to the deposition and distribution of the platinum in the wash coat. To explain these results, we have considered three effects. One possible explanation is that mass transfer of reactants to the active Pt sites affects the activity. Another is that heat transfer at the active sites in the catalysts differs. Even if it is uncertain whether CO oxidation is a structure-sensitive reaction [17,18], this can also be a possible explanation for the differences in activity since the mean size of the Pt crystallites in the three samples varies.

4.1. Difference in mass transfer

A typical criterion if the catalytic activity is affected by mass transfer of reactants to the active sites of the catalyst is that the net transport effect should alter the true chemical rate by more that 5% [26]. This criterion can be determined calculating the Weisz modulus, $\Phi = \eta \phi^2$ (η is the effectiveness factor and ϕ the Thiele modulus), which compares the reaction rate versus the diffusion of the reactants. For mesoporous catalysts rapid reactions such as CO oxidation can be diffusion limited in a single pore [27] due to slow diffusion. Mass transfer limitations will reduce the reaction rate for reactions with positive order while it will increase the rate of reactions with negative reaction order. The kinetics for CO oxidation over Pt can be divided in two regimes since it is self-inhibited [28]: at high CO concentrations the reaction order is negative (-0.62), while at low concentrations it follows first-order reaction. The breakpoint between these two regions is when the partial pressure of CO is about 13 Pa [28]. Other studies [19,29] have shown that this breakpoint is not fixed, but varies with temperature. According to Weisz and Prater [30], mass transfer will affect a first-order reaction for Weisz-modulus values equal or higher than one. Reactions with negative reaction orders are influenced by mass transfer at $\Phi \ge |n|^{-1}$ [31].

For spherical Pt/Al_2O_3 particles is the Weisz modulus given by

$$\Phi = \frac{r_{\rm p}^2 r_{\rm v}}{D_{\rm eff} c_{\rm wc}},\tag{2}$$

where r_p is the radius for the Pt/Al₂O₃ particles, D_{eff} the effective diffusion of CO, c_{wc} the concentration of CO in the wash coat, and r_v is the reaction rate per active catalyst volume. Expressing as usual $D_{\rm eff}$ via the bulk [32] and Knudsen diffusion coefficient [33] and using $r_{\rm p} = 1.25 \ \mu {\rm m}$ (estimation using scanning electron microscopy), at 50% conversion we have $\Phi = 0.12$ (Pt/1% Al₂O₃), $\Phi = 17 \times 10^{-3}$ (Pt/10% Al₂O₃), and $\Phi = 2.4 \times 10^{-3}$ (Pt/100% Al₂O₃). None of these values are close to the regime where mass transport limitations affect the reaction rate (at $\Phi \sim 0.6$ or higher). The figures used for the calculation were bulk temperature, 500 K; pore diameter, 75 Å; and total flow rate, 1.67×10^{-5} m³/s. The active catalyst volume was obtained by multiplying the wash-coat mass (see Table 1) with the fraction which was Pt-impregnated, divided by the density $(1500 \text{ kg/m}^3).$

When considering the entire wash coat, instead of one Pt/Al_2O_3 particle, mass transfer limitations could affect the reaction rate due to a long diffusion distance from the bulk phase to the catalyst surface. The Weisz modulus for a planar layer (wash coat) with the depth, δ_{wc} , is expressed as

$$\Phi_{\rm wc} = \frac{\delta_{\rm wc}^2 r_{\rm wc}}{D_{\rm eff} c_{\rm wc}},\tag{3}$$

where r_{wc} is the reaction rate for all the wash-coat material, irrespective if Pt is locally distributed or not. Using the same figures as above results in $\Phi_{wc} = 0.60$ (catalyst Pt/1% Al₂O₃), $\Phi_{wc} = 0.38$ (Pt/10% Al₂O₃), and $\Phi_{wc} =$ 0.31 (Pt/100% Al₂O₃). These results, where the entire wash coat is regarded, indicate that the experiments performed in this study are close to being mass transfer limited at 50% conversion. As the Weisz modulus increases with increasing conversion, mass transfer most probably does affect the activity for CO oxidation at higher conversions, especially during the beginning of the extinction region. In correspondence with Zhdanov and Kasemo [27] diffusion limitation will provide a higher reaction rate for CO oxidation because the self-inhibition regime will be postponed. On the contrary, at low conversions, such as during the start of the light-off region it seems unlikely that mass transfer influences the reaction. This can explain why the differences in activity between the catalysts are larger for the extinctions compared to the light-off processes.

4.2. Difference in heat transfer

The differences in activity between the catalysts could be due to differences in heat transfer. First we will analyze whether transient temperature gradients between the active sites and the support material could affect the lowtemperature activity for the catalysts. Both Luss [3], and Steinbrüchel and Schmidt [6] report that heat evolved from exothermic catalytic reactions can raise temporarily the temperature of the active sites several hundred degrees Celsius above the temperature of the support material. Luss finds the temporary temperature raise only to last in order of 10^{-13} s before the active site is cooled down. However, Steinbrüchel and Schmidt report longer periods before the temperature declines, up to 10^{-10} s. In our study the number of CO molecules reacted per second and per surface atom of Pt (turnover frequency) is between 0.01 and 10 at complete conversion of CO (depending on the CO concentration in the feed), which is somewhat higher than under typical laboratory conditions [7]. The average time period between two consecutive reactions at one active site is then at maximum 0.1 s, which is a tremendously longer time period than the period for a transient temperature rise according to Steinbrüchel and Schmidt. We conclude that the transient temperature rises is too instantaneous, compared to the turnover frequency, to have a possibility of affecting the low-temperature activity of the catalysts.

Instead of discussing the transient heat effects at one specific active site, heat from exothermic reactions could accumulate in Pt/Al₂O₃ particles causing constant temperature gradients between Pt/Al₂O₃ particles and the surroundings. The generated heat is transferred by conduction to the gas phase and to the surrounding particles in the wash coat. Hot areas may thus occur on the level of an array of alumina particles. However by using a heat transfer model similar to Holstein's and Boudart's [7], we will illustrate an extreme case and calculate the maximum temperature gradient between spherical Pt/Al₂O₃ particles and the unimpregnated alumina support. Even though heat transfer between particles in the wash coat is expected to dominate, the Pt/Al₂O₃ particle in this model is assumed to be isolated from the support material and only adjacent to a stagnant gas phase, see Fig. 4. This condition minimizes heat transfer from the Pt/Al₂O₃ particle and thus overestimates the temperature gradient. The gas bulk and the unimpregnated alumina support are assumed to have equal temperature.



Fig. 4. Model of heat transfer for a spherical Pt/Al_2O_3 particle adjacent to a stagnant gas phase.

For a stagnant gas phase the Nusselt number is 2 (Nu = $2r_ph/\lambda = 2$, where *h* is the heat transfer coefficient and λ the thermal conductivity). The generated heat flux, q_g , and the heat loss from the Pt/Al₂O₃ particle by conduction, q_c , is

$$q_{\rm g} = r \,\Delta H,\tag{4}$$

$$q_{\rm c} = h S_{\rm p} \,\Delta T,\tag{5}$$

where *r* is the reaction rate per Pt/Al₂O₃ particle, ΔH the reaction heat, S_p the area of the particle, and ΔT the temperature gradient between Pt/Al₂O₃ particles and the surroundings. The reaction rate is estimated by dividing the amount of CO reacted per second with the number of Pt/Al₂O₃ particles in the catalyst, n_p (the number of Pt/Al₂O₃ particles is trivial to calculate knowing the particle radius as well as the mass and density of the wash coat). At steady state, the generated heat is equal to the heat loss, resulting in

$$\Delta T = \frac{F_{\rm CO} \operatorname{conv} \Delta H}{4\pi r_{\rm p} n_{\rm p} \lambda},\tag{6}$$

where F_{CO} is the flow rate of CO in the feed and conv the conversion. The highest temperature gradient generated in the experimental study was while oxidizing 1% CO at 100% conversion. Using $F_{\rm CO} = 6.83 \times 10^{-6}$ mol/s, $\Delta H =$ 283 kJ/mol, and $\lambda = 3.86 \times 10^{-2}$ W/mK [34] (dry air at 200 °C) results in $\Delta T = 13 \times 10^{-3}$ °C (for catalyst Pt/1% Al₂O₃), $\Delta T = 2.0 \times 10^{-3} \,^{\circ}\text{C}$ (Pt/10% Al₂O₃) and $\Delta T =$ 0.26×10^{-3} °C (Pt/100% Al₂O₃). For the experiments with lower CO concentrations (1000 and 100 ppm) the corresponding ΔT for each catalyst will be one and two magnitudes lower, respectively. Instead of estimating the temperature rise for a Pt/Al₂O₃ particle, the same model can be used to calculate the temperature rise for a Pt crystallite. Elementary estimates with the parameters corresponding to our system indicate that in this case ΔT is negligibly small $(< 10^{-5} \circ C)$. These calculations clearly show that the reaction heat evolved in our experiments cannot heat Pt/Al₂O₃ particles or Pt crystallites sufficiently enough to produce significant differences in activity between the catalysts.

Interesting to note from the experiments is the hysteresis in temperature between the ignition and extinction processes. For exothermic reactions this phenomenon usually takes place due to the evolved reaction heat. In our experiments the hysteresis is ranging between 55 and 84 °C when oxidizing 1% CO. Surprisingly, for 100 ppm CO the hysteresis is still marked (9–17 °C) and this behavior cannot be explained as a heat effect since the amount of generated heat is insignificant. This hysteresis is probably an effect from the self-inhibition of CO. From the start of the ignition process, the surface is covered by CO preventing the reaction to take off, causing a shift in the light-off to higher temperatures. Since there is no self-inhibition during the extinction, the hysteresis appears as the reaction can proceed at lower temperatures before being quenched.

4.3. Difference in specific activity and structure sensitivity

In this study CO has been oxidized over Pt/γ -Al₂O₃ catalysts. One aspect worth noting for this system is that there is no general agreement whether CO oxidation over noble metals is structure insensitive or the reaction rate increases with increasing noble metal crystallite size [17,18].

Using Pt/α -Al₂O₃ catalysts with crystallite sizes ranging from 2.8 to 100 nm, McCarthy et al. [19] showed that CO oxidation is structure sensitive over Pt/Al_2O_3 at low CO concentrations (< 2000 ppm), while it is structure insensitive at high concentrations (> 1% CO). The authors speculate that PtO forms and the structure sensitivity is because the oxygen in PtO may be more easily extracted from larger crystallites than from smaller ones. These speculations are supported by several studies, reporting that platinum oxide can be formed at adequate temperatures [35–39], that oxygen is more easily reduced from larger PtO crystallites [35,40], and also that reduced Pt is more active for CO oxidation than oxidized platinum [35,41].

Zafiris and Gorte [20] studied CO oxidation over Pt/α -Al₂O₃ for Pt crystallites with average diameters of 14 and 1.7 nm. The authors concluded that CO oxidation is structure sensitive even at high CO concentrations. The result was explained by CO desorption occurring more easily from large Pt crystallites, due to less curvature of the Pt particles, and this desorption controls the oxidation rate since it opens up the surface for O₂ adsorption.

In our study, the Pt/1% Al₂O₃ catalyst with largest Pt crystallites (4.5 nm) showed the highest activity while the Pt/100% Al₂O₃ catalyst with smallest Pt crystallites (2.3 nm) showed the lowest activity. The results from all light-off and quenching experiments, except for the light-off test with 1% CO, seem to be in accordance with the structure sensitivity reasoning in which larger Pt crystallites have higher low-temperature activity for CO oxidation than smaller ones. In the light-off experiment with 1% CO the activity is very similar for all three catalysts. This specific experiment, however, coincides with the results of McCarthy et al. [19] in which the activity is independent of the parti-

cle size at high CO concentrations. Though the results from the activity tests in this investigation can be explained in terms of structure sensitivity, it is still very doubtful. Even if McCarthy and Zafiris insist, there is still a disagreement whether or not CO oxidation over Pt/Al_2O_3 is a structuresensitive reaction. Furthermore, in the experiments reported in the literature the range of crystallite sizes is much wider (from some nm up to 100 nm) compared to the narrow range (2.3–4.5 nm) in our study. It seems unlikely that the relatively small difference in particle size really causes the large difference in activity observed in this investigation. Especially the difference in activity between the Pt/100% Al_2O_3 and the Pt/10% Al_2O_3 catalyst is difficult to describe in terms of structure sensitivity since the estimated crystallite sizes are so similar (2.3 and 2.7 nm, respectively).

5. Concluding remarks

 Pt/γ -Al₂O₃ catalysts prepared with locally higher Pt concentrations in the wash coat showed a considerably higher activity for CO oxidation at low temperatures compared to a conventionally prepared Pt/γ -Al₂O₃ catalyst with homogeneous Pt concentration in the alumina support.

Three reasons for the differences in activity between the catalysts are discussed: differences in mass transfer, differences in heat transfer, and structural differences between the catalysts. Mass transfer limitations were considered both for Pt/Al_2O_3 particles and for the entire wash coat of the catalysts. When considering heat transfer both temporary effects and heat accumulation in the active phase were taken into account. Differences in heat transfer appear to be the least probable reason for the enhanced activity for the catalysts with locally higher Pt concentration, whereas structural effects also seem to be an unlikely explanation. Differences in mass transfer seem, however, to be a more likely reason for the enhanced activity in the wash coat.

To distribute Pt locally in the wash coat may also give positive catalytic consequences in other research areas than low-temperature oxidation of CO. By using a broader approach it could be possible to find the explanation to the improved activity.

Acknowledgments

Prof. Bengt Kasemo, Dr. Erik Fridell, and Dr. Ann Grant are gratefully acknowledged for valuable discussions. This work has been performed within the Competence Centre for Catalysis, which is financially supported by The Swedish Energy Agency and the member companies: AB Volvo, Johnson Matthey-CSD, Perstorp AB, Saab Automobile AB, AVL-MTC AB, Akzo Catalyst, and the Swedish Space Administration.

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