

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 cpsi) 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-

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