

# Oxidation behaviour and catalytic properties of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts in the total oxidation of methane

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## Abstract

A series of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with a wide range of mean Pd particle sizes (ca. 2–30 nm in diameter) was prepared by using various precursors (H<sub>2</sub>PdCl<sub>4</sub>, Pd(NO<sub>3</sub>)<sub>2</sub> and Pd(AcAc)<sub>2</sub>) and pre-treatments. The mean particle size of reduced samples was determined by H<sub>2</sub> chemisorption. The catalytic activity in methane oxidation under lean burn conditions was measured. The oxidation of reduced samples was studied at 300 °C. The extent of oxidation was found to decrease with increasing mean particle size. While small particles (<5 nm) oxidised very rapidly, the oxidation of large particles (ca. >15 nm) proceeded via a two-step process, being first fast and then slow. The decomposition of oxide species was studied by temperature-programmed experiments under vacuum. Two distinct oxidised species with different stability were evidenced depending on the particle size. Oxidised species in larger particles were found of lower stability than in smaller ones. A correlation between the existence of distinct types of oxide species and catalytic properties in methane oxidation was discussed.

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## 1. Introduction

Pd/Al<sub>2</sub>O<sub>3</sub> catalysts are well known to be the most active catalysts in the complete oxidation of methane. This is the reason why they are currently used in the abatement of methane emissions from natural gas combustion devices such as the catalytic treatment of emissions from lean burn natural gas fuelled heavy-duty vehicles. Under lean burn conditions (excess of oxygen), it is admitted that PdO is formed and represents the active phase for methane oxidation. However, the question of the dependence of the catalytic activity in methane oxidation as a function of the particle size is still of debate in spite of the huge amount of data published so far in the open literature on these catalysts [1–3].

The purpose of the present study was to prepare Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with mean Pd particle sizes varying in a broad range by using varying Pd precursors and pre-treatments (including

ageing under reactants and mild steam ageing). The catalytic activity of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts in the complete oxidation of methane was measured in the presence of a lean CH<sub>4</sub>:O<sub>2</sub> mixture. The oxidation of the reduced catalysts in O<sub>2</sub> was studied at room temperature and at 300 °C. Oxide species were characterised by temperature-programmed desorption (TPD) experiments, showing the existence of distinct types of oxide species. Attempts to correlate the catalytic activity and the presence of varying oxide species are made.

## 2. Experimental

Alumina-supported Pd catalysts were prepared by impregnation of γ-Al<sub>2</sub>O<sub>3</sub> (Rhône Poulenc SPH569 screened to 80–120 μm, 136 m<sup>2</sup>/g, pore volume of 2.83 cm<sup>3</sup>/g, Cl content less than 0.015 wt%) with aqueous solutions of H<sub>2</sub>PdCl<sub>4</sub> [4] or Pd(NO<sub>3</sub>)<sub>2</sub>. Pd(AcAc)<sub>2</sub> was also used as a precursor, the solvent being toluene. After solvent evaporation, the catalysts were dried overnight at 120 °C, grinded, calcined in air at 500 °C for 4 h and reduced in H<sub>2</sub> from 25 °C up to 300 °C for 2 h. Steam-aged catalysts were obtained by treatment at 650 °C during 24 h

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in 10 vol.% O<sub>2</sub>–10 vol.% H<sub>2</sub>O–N<sub>2</sub>. Reactant-aged catalysts were obtained after CH<sub>4</sub>–O<sub>2</sub> reaction at 600 °C for 12 h. Only catalysts with low Cl amount were considered for the study since it is well known that Cl strongly inhibits methane oxidation [1] (the fresh catalyst prepared from H<sub>2</sub>PdCl<sub>4</sub> was thus discarded).

Catalysts were characterised by BET area measurements, atomic absorption analysis and volumetric measurements of hydrogen chemisorption. Hydrogen chemisorption on reduced catalysts was performed at 25 °C after reduction at 300 °C overnight and treatment under vacuum at 300 °C. The metal dispersion was derived from the H<sub>2</sub> uptake [5]. H<sub>ads</sub>/Pd<sub>s</sub> and O<sub>ads</sub>/Pd<sub>s</sub> equal to unity were assumed. Mean particle diameters (in nm) were related to dispersion values by using the formula  $\frac{6 \times C_a \times M \times 10^9}{\rho \times D \times N_a}$ , with C<sub>a</sub> (concentration of surface metal atoms) = 1.27 × 10<sup>19</sup> atoms/m<sup>2</sup> [6], M being the Pd atomic mass, ρ (Pd volumic mass) = 12.02 × 10<sup>6</sup> g/m<sup>3</sup> [6], D being the metal dispersion and N<sub>a</sub> the Avogadro number.

The total oxidation of methane was performed with 200 mg of catalyst in a U-shaped quartz reactor operating in a steady-state plug flow mode. The reaction mixture contained 1% CH<sub>4</sub> and 4% O<sub>2</sub> (N<sub>2</sub> as carrier gas) at a total flow rate of (108 cm<sup>3</sup> STP/min) (GHSV 15,000/h). Catalysts were activated in situ in H<sub>2</sub> at 300 °C, purged for 1 h at 300 °C with N<sub>2</sub> and cooled down to 150 °C before being contacted with the reaction feed. The catalytic activity expressed in mol CH<sub>4</sub> converted per surface metal atom and per hour or TOF was calculated at 260 °C so that differential conditions were fulfilled.

The effluent gases were analysed using a gas chromatograph equipped with a flame ionisation detector (FID) and packed with a Carbosieve SII column. Carbon dioxide was quantitatively hydrogenated over a Ni/MgO catalyst to methane for further detection by FID.

The adsorption and desorption of O<sub>2</sub> was studied by using a Balzers QMA 125 quadrupole mass spectrometer (MS). The samples (~50 mg) were treated at atmospheric pressure in O<sub>2</sub> at 500 °C for 2 h, purged in He at 300 °C for 1 h, reduced in H<sub>2</sub> at 300 °C for 1 h and finally purged for 1 h at 300 °C in He or cooled down to 25 °C. The O<sub>2</sub> adsorption was performed in 1.03% O<sub>2</sub>–He (20 cm<sup>3</sup> STP/min) at 300 °C (or alternatively at 30 °C). The O<sub>2</sub> concentration was monitored as a function of time and the oxygen uptakes evaluated. Blank experiments (without any catalyst) exhibited no O<sub>2</sub> desorption. Tempera-

ture-programmed desorption experiments were performed under vacuum at a heating rate of 20 °C/min from 30 up to 950 °C. Calibration was made after each TPD experiment by introducing known volumes of O<sub>2</sub> into the system through a leak valve. The linearity of the MS response with the O<sub>2</sub> quantity introduced into the chamber was systematically checked. O<sub>2</sub> uptakes and desorbed amounts measured by this procedure were found in good agreement (within 5% error margin), which made the method reliable.

### 3. Results

Table 1 shows the main characteristics of reduced Pd/Al<sub>2</sub>O<sub>3</sub> samples (precursor used, Pd content, mean Pd particle size determined from H<sub>2</sub> chemisorption) and reaction rates in methane oxidation at 260 °C. In the reduced state, highest Pd dispersions were obtained by using Pd(AcAc)<sub>2</sub> as a precursor. Pd sintering occurs upon mild steam ageing (650 °C) irrespective of the precursor used and the initial dispersion. Interestingly this has no effect on the catalytic activity of the catalyst prepared from Pd(AcAc)<sub>2</sub>, while this induces a sharp decrease of the catalytic activity of the other catalysts. The catalyst prepared from Pd(AcAc)<sub>2</sub> is the most active and the most resistant to ageing of the series. It would thus be more suitable for NGV application.

The oxidation of the reduced Pd/Al<sub>2</sub>O<sub>3</sub> catalysts in a 1.03% O<sub>2</sub>–He flow at 300 °C was studied (Fig. 1). For all samples, the O<sub>2</sub> adsorption proceeded immediately after the sample was contacted with O<sub>2</sub>, which produced a sharp negative peak. For steam-aged Pd–AcAc-2, reduced Pd–NO<sub>3</sub>-2 and steam-aged Pd–Cl-2 samples, a second distinct adsorption peak was clearly distinguished, which corresponded to a slower O<sub>2</sub> adsorption process. This slow phenomenon occurred for samples of mean Pd particle size higher than ca. 11 nm. In addition, it could be observed that the larger the mean particle diameter, the slower the oxidation rate.

The amounts of O<sub>2</sub> adsorbed during the oxidation at 300 °C at different stages of the process were calculated from these experiments (Table 1). The data clearly indicated that the amount of oxygen adsorbed per gram of palladium at the equilibrium decreased with Pd dispersion. Considering that Pd particles progressively oxidise into PdO, small particles (reduced Pd–AcAc-1, 2.2 nm) are fully and rapidly oxidised

Table 1

Main characteristics of Pd/Al<sub>2</sub>O<sub>3</sub> samples (precursors, Pd content and Pd mean particle size), reaction rates in methane oxidation at 260 °C and percentage of oxidation into PdO upon reaction of reduced samples with 1% O<sub>2</sub>–He at 300 °C

Sample	Precursor	Pd (wt%)	Mean diameter (nm)	Rate at 260 °C (mol/h mol/Pd)	Oxidation (%)
Pd–AcAc-1 reduced	Pd(AcAc) <sub>2</sub>	0.94	2.2	5.7	88
Pd–AcAc-2 reduced	Pd(AcAc) <sub>2</sub>	1.93	3.7	5.1	82
Pd–AcAc-2 reactant-aged	Pd(AcAc) <sub>2</sub>	1.93	6.4	5.2	
Pd–AcAc-2 steam-aged	Pd(AcAc) <sub>2</sub>	1.93	11.2	5.8	70
Pd–NO <sub>3</sub> -2 reduced	Pd(NO <sub>3</sub> ) <sub>2</sub>	1.94	12.4	5.1	49
Pd–NO <sub>3</sub> -2 reactant-aged	Pd(NO <sub>3</sub> ) <sub>2</sub>	1.94	12.4	5.3	
Pd–NO <sub>3</sub> -2 steam-aged	Pd(NO <sub>3</sub> ) <sub>2</sub>	1.94	17	2.8	52
Pd–Cl-2 reactant aged	H <sub>2</sub> PdCl <sub>4</sub>	2.20	14	3.3	
Pd–Cl-2 steam-aged	H <sub>2</sub> PdCl <sub>4</sub>	2.20	32	1.4	35

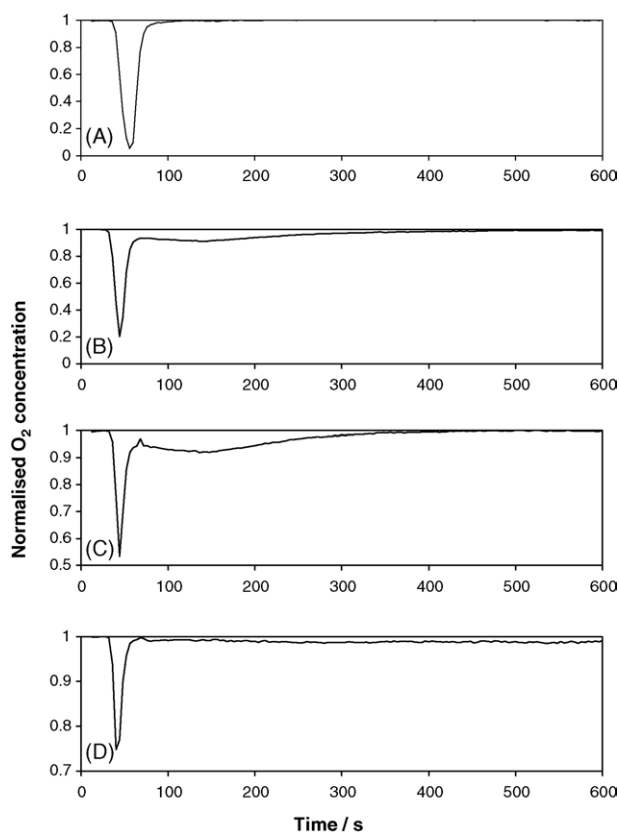


Fig. 1. Variation of the  $O_2$  concentration in 1.03%  $O_2$ -He flow ( $20 \text{ cm}^3 \text{ STP/min}$ ) at  $300^\circ\text{C}$  as a function of time over reduced Pd based catalysts of varying mean particle size: (A) Pd-AcAc-1, reduced (2.2 nm); (B) Pd-AcAc-2, steam-aged (11.2 nm); (C) Pd- $\text{NO}_3$ -2, reduced (12.4 nm); (D) Pd-Cl-2, steam-aged (32 nm).

into PdO while, in the sample with the lowest dispersion (Pd-Cl-2 steam-aged, 32 nm), only 35% of the Pd metal is oxidised into PdO. These results are fully consistent with previous data reported by Hicks et al. [7] showing that large Pd particles supported on alumina are only partially oxidised by  $O_2$  at  $300^\circ\text{C}$ , the Pd metal core of the particle being suggested to remain at the metallic state and be covered by a PdO layer, while small particles oxidise from the surface to the core of the particle, leading to PdO supported on alumina.

After  $O_2$  adsorption, TPD experiments under vacuum were carried out. Fig. 2 shows the TPD profiles following a saturation exposure of oxygen on reduced Pd/ $\text{Al}_2\text{O}_3$  samples at  $30^\circ\text{C}$  and  $300^\circ\text{C}$ , respectively.

The TPD profile of the reduced Pd-AcAc-1 catalyst oxidised at  $300^\circ\text{C}$  exhibits mainly one broad peak centred near  $660^\circ\text{C}$ , which parallels the desorption peak of oxygen chemisorbed at  $30^\circ\text{C}$ . This suggests no major difference of Pd–O bond strength between oxygen bonded to the surface of small metallic Pd particles and subsurface oxygen of fully oxidised small particles.

The TPD profile of the steam-aged Pd-Cl-2 sample (large Pd particles, 32 nm mean diameter) exhibits a narrow and intense peak near  $550^\circ\text{C}$ . A second peak of much lower intensity can be distinguished near  $800^\circ\text{C}$ , which can be unambiguously attributed to oxygen chemisorbed at the surface of metallic

particles. The first peak is tentatively attributed to the progressive decomposition of the palladium oxide layer. This suggests that for large particles, oxygen in PdO is more weakly bonded than oxygen chemisorbed at the surface of the metallic particle. This experiment would also indicate that at PdO decomposition completion, fully reduced metallic particles are covered by a monolayer of chemisorbed oxygen species, which are highly stable [8].

For samples with intermediate mean particle size, two desorption peaks at  $550$  and  $650^\circ\text{C}$  are observed. From the above results, they are attributed to the decomposition of large and small PdO particles respectively. In spite of almost identical mean Pd particle diameters, the lower intensity of the “high temperature” desorption peak for the reduced Pd- $\text{NO}_3$ -2 catalyst compared to steam-aged Pd-AcAc-2 would indicate fewer small particles. TPD experiments would then reflect the distribution of palladium particles between two types, small and large ones. This interpretation agrees with experiments of Marti et al. [9] on PdO/ $\text{ZrO}_2$  samples. Smaller particles were proposed to strongly interact with  $\text{ZrO}_2$ , thus decomposing at higher temperatures than larger ones weakly interacting with the support. As observed in Fig. 2d, the small desorption peak at higher temperatures ( $750$ – $800^\circ\text{C}$ ), which is identical to that observed from oxygen adsorbed at  $30^\circ\text{C}$  on reduced samples, can be attributed to oxygen desorbing from the surface of fully reduced Pd particles.

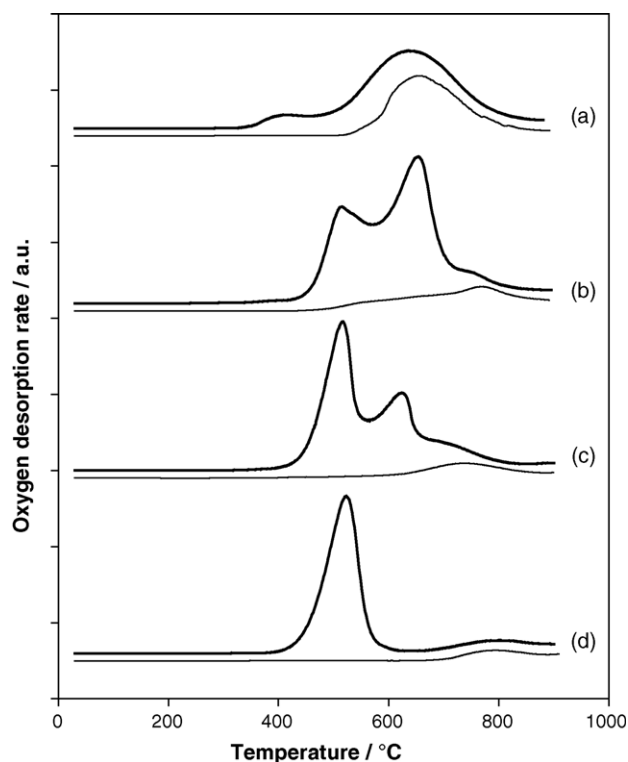


Fig. 2. TPD profiles of oxygen adsorbed at  $300^\circ\text{C}$  on reduced Pd-AcAc-1 (2.2 nm) (a), Pd-AcAc-2, steam-aged (11.2 nm) (b), Pd- $\text{NO}_3$ -2 (12.4 nm) (c) and Pd-Cl-2, steam-aged (32 nm) (d). The thin lines correspond to TPD profiles following saturation exposure of oxygen at  $30^\circ\text{C}$ . The heating rate is  $20^\circ\text{C/min}$ .

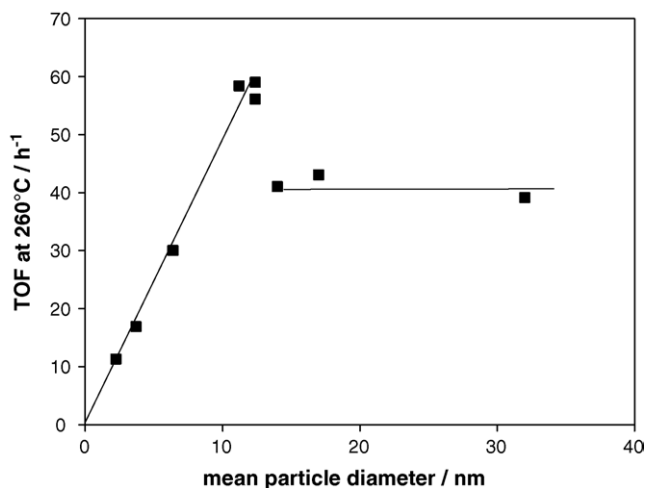


Fig. 3. TOF or activity per surface Pd metal atom mol CO<sub>2</sub>/(surface Pd atom h) at 260 °C of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts vs. mean particle diameter.

#### 4. Discussion

Attempts have been made in the past to correlate the activity of supported Pd catalysts to the mean particle size, determined by H<sub>2</sub> chemisorption on reduced catalysts [10–15]. No clear relationship could be established. In the case of Pd/ZrO<sub>2</sub> catalysts, Iglesia and co-workers [14] found an approximately linear dependence of the turnover rate versus crystallite size, the turnover at 280 °C (2% CH<sub>4</sub>, 20% O<sub>2</sub> in He) increasing with particles diameter increasing from 3 to 11 nm. However, it is now generally agreed that, under reaction conditions, especially in oxygen-rich atmosphere, reduced palladium particles oxidise into PdO which represents the main active phase. Many studies clearly established the importance of PdO for methane oxidation. Therefore, the number of PdO sites accessible to methane and involved in the reaction might differ significantly from that measured in the reduced metallic state.

Fig. 3 shows the variation of TOF with mean particle size of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts. A nice linear relationship is observed for particles smaller than ca. 12 nm in diameter, similar to that observed for Pd/ZrO<sub>2</sub> catalysts in the same range of particle sizes [14]. The striking feature is that, for particles larger than ca. 15 nm, TOF drops to a lower value (40/h) and remains constant with further increase of the particle size.

These results suggest again classifying Pd particles into two categories, which would exhibit different catalytic properties and could be associated with the two types of palladium oxide species corresponding to the so called ‘small’ and ‘large’ particles. In ‘large’ particles, the catalytic activity would depend essentially on the geometric surface area of PdO/Pd particles size, as determined on reduced catalysts. The constant TOF (activity per surface Pd atom measured from H<sub>2</sub> chemisorption on reduced particles) would be associated with the catalytic property of the surface layer of a PdO film on a Pd metal core. These surface oxide species are thought to be highly reactive towards methane since being of low stability from TPD.

For ‘small’ particles, TOF varies linearly with increasing particle size. According to Fujimoto et al. [14], the methane oxidation turnover rate was thought to depend on the density and stability of oxygen vacancies on the surface of PdO<sub>x</sub> particles. The density of such vacancies would depend on the strength of Pd–O bonds, which is thought to increase with decreasing PdO<sub>x</sub> particle size. Thus the TOF decrease with particle size would be explained by a decreasing number of oxygen vacancies. An alternative explanation could arise from the observation that all samples with ‘small’ oxidised particles exhibit about the same reaction rate. This could be related to a constant number of active sites, which would involve subsurface oxygen atoms participating into the reaction. Similar ideas were developed by Monteiro et al. [16,17] in the study of Pd foils properties in the complete oxidation of methane. The surface measured by O<sub>2</sub> isotopic exchange was shown twice larger than the geometric surface of the Pd foil. The participation of sub layer sites in ‘small’ particles to catalytic activity would then more or less compensate for their higher stability and lower reactivity towards methane compared to oxide species in ‘large’ particles.

#### 5. Conclusions

Pd/Al<sub>2</sub>O<sub>3</sub> catalysts with a wide range of mean particle sizes (determined by H<sub>2</sub> chemisorption) were prepared and studied in the complete oxidation of methane. For particles of size lower than 12 nm, the catalytic activity was constant while for larger particles, it decreased with increasing particle size. To this respect, the catalyst prepared from Pd(AcAc)<sub>2</sub> appeared the most suitable for low temperature applications since even after steam ageing at 650 °C the particle size was kept below 12 nm, which did not affect the catalytic activity.

The oxidation of reduced metal particles was studied at 300 °C. The kinetics and the amount of oxygen adsorbed at 300 °C strongly depended on the mean Pd particle size. While smallest particles (typically ca. <5 nm) were completely oxidised very rapidly, the oxidation of largest particles proceeded via a two-step process, being successively fast and slow. PdO in small particles was found more stable than in large particles. In both cases, the catalytic activity would be related to surface and sub layers of PdO, being thus dependent on the particles oxidation.

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