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Superior catalytic behaviour of Pt-doped Pd catalysts in the complete oxidation of methane at low temperature

G. Lapisardi [a], L. Urfels [a], P. Gélin [a,*], M. Primet [a], A. Kaddouri [a],
E. Garbowski [a], S. Toppi [b], E. Tena [b]

[a] *Laboratoire d'Application de la Chimie à l'Environnement, UMR CNRS 5634 Université Claude Bernard Lyon 1,*
Bat. Chevreul, 69622 Villeurbanne Cedex, France

[b] *Gaz de France, Direction de la Recherche, DEG/PCCMF, 361, avenue du Président Wilson,*
P.O. Box 33, 93211 St-Denis La Plaine Cedex, France

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Abstract

The catalytic combustion of methane at low temperature under lean conditions was investigated over bimetallic palladium-platinum catalysts supported on alumina. Pd-Pt catalysts with constant 2 wt.% metal loading and varying compositions in Pt and Pd were prepared by successive impregnations of the metal salts. The catalysts were characterised by powder X-ray diffraction, transmission electron microscopy/electron dispersion X-ray spectroscopy (TEM/EDX), volumetry of H_2 chemisorption, FTIR study of CO adsorption and temperature-programmed oxidation (TPO). In the absence of water added to the feed, the methane conversion over Pd-rich bimetallic catalysts (Pt/Pt + Pd molar ratios less than 0.3) was found to be the same as that of the reference Pd/Al_2O_3 catalyst. Interestingly, under wet conditions, these bimetallic catalysts exhibited an improved performance with respect to Pd/Al_2O_3. This effect was found to be maintained upon mild steam ageing. An interaction between both metals was suggested to explain the enhanced activity of bimetallic catalysts. This was confirmed by TPO experiments indicating that formation and decomposition of PdO is affected upon Pt addition even for very low amounts of Pt. The adsorption of CO on reduced catalysts studied by FTIR revealed new types of adsorbed CO species, suggesting again an interaction between two metals.

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Keywords: Methane oxidation; Catalytic combustion; Palladium; Platinum; Al_2O_3; Catalytic activity; TPO; FTIR; CO adsorption

1. Introduction

Methane emissions abatement from lean-burn natural gas fuelled vehicles (NGV) and co-generation engines require the use of specific catalysts able to oxidise low concentrations of methane at lowest temperatures under strongly oxidising conditions. These catalysts must also resist to higher temperatures (550–600 °C) as well as the presence of water vapour (10–15 vol.%), carbon dioxide (15 vol.%) and traces of SO_x (about 1 ppm). Pd-based catalysts are the most active in the oxidation of methane under these conditions but the presence of high concentrations of water vapour strongly inhibits the activity and also might cause irreversible deactivation [1–3]. Moreover, sulphur compounds induce a strong deactivation of Pd catalysts by formation of stable inactive Pd sulphates [4,5].

A few studies on bimetallic Pt-Pd catalysts were reported and they suggested some improvement of the catalytic behaviour of Pd catalysts with respect to monometallic ones [6–12]: absence of deactivation with time on stream and improved catalytic activity possibly attributed to Pd–Pt interactions. The improvement of the catalytic activity over bimetallic catalysts is still of debate and it might be not maintained after long term use of the catalyst because of metals segregation.

The present work aims at investigating the catalytic properties of γ-Al_2O_3-supported bimetallic Pt-Pd catalysts in the combustion of methane under lean conditions at low temperatures. Pd-Pt catalysts with constant *ca.* 2 wt.% metal loading and varying atomic compositions in Pt and Pd were prepared and studied. The catalysts were characterised by physicochemical techniques (X-ray diffraction, H_2 chemisorption, FTIR study of CO

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* Corresponding author. Tel.: +33 472 43 11 48; fax: +33 472 44 81 14.
E-mail address: Patrick.Gelin@univ-lyon1.fr (P. Gélin).

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adsorption and temperature-programmed oxidation). The catalytic activity was measured in the presence and the absence of 10% water vapour added to the feed. The influence of mild steam ageing (10 vol.% H_2O, 600 °C for 22 h) on the catalysts properties was also addressed. The improved performance of some bimetallic systems with respect to reference Pd/Al_2O_3 is discussed on the basis of physicochemical data.

2. Experimental

2.1. Catalysts preparation

Pd (2.2 wt.%) (respectively, Pt, 1.92 wt.%) catalysts were prepared by impregnation of crushed γ-Al_2O_3 (Rhodia SPH 569, 136 $m^2\,g^{-1}$, screened to less than 80 μm) with $Pd(NH_3)_4(NO_3)_2$ (respectively, $Pt(NH_3)_4(NO_3)_2$) aqueous solution, the suspension being maintained under stirring at 50 °C for 1 h. After complete removal of water by evaporation under reduced pressure, the catalysts were dried overnight in air at 120 °C and calcined in air at 500 °C for 4 h.

Bimetallic Pd-Pt catalysts with a constant total metal loading of *ca.* 2 wt.% and varying Pt loadings were prepared by successive impregnations of Al_2O_3 first with $Pd(NH_3)_4(NO_3)_2$ and then with $Pt(NH_3)_4(NO_3)_2$. An intermediate treatment in O_2 at 500 °C followed by reduction in H_2 at 300 °C was carried out before the second impregnation. Samples were finally calcined in air at 500 °C. Table 1 reports the composition of various catalysts as determined by chemical analysis. It must be noticed that for the Pt-rich bimetallic catalyst, the Pt solution was impregnated first.

2.2. Catalytic activity studies

Catalytic tests were carried out using a U-shaped quartz reactor operating at atmospheric pressure with 200 mg catalyst. The standard test stream contained 2000 vol. ppm CH_4 and 5 vol.% O_2 (helium balance). The total flow rate was 6.5 L h^{-1} (GHSV 20,000 h^{-1}). For experiments under wet conditions, 10 vol.% water vapour were added to the standard feed by injection of liquid water using a syringe at a controlled rate.

Prior to catalytic testing, the catalysts were treated in O_2 at 500 °C (in 5 vol.% O_2–He at 600 °C for aged samples) for 1 h and in He during cooling to 150 °C. During catalytic testing, the reaction temperature was varied from 150 up to 600 °C by steps of 50 °C (heating rate of 1 °C min^{-1}) with 1 h temperature hold between each heating ramp step.

Table 1
Main characteristics of catalysts: metal loading, molar Pd and Pt fractions and metal dispersion

	Total metal loading (wt.%)	H_2 chemisorption		CO chemisorption
		Surface atoms number M_s (μmol g^{-1})	Dispersion (%)	CO/M_s
Pd	2.20	31	15	0.67
$Pd_{0.93}Pt_{0.07}$	2.12	25	13	0.76
$Pd_{0.65}Pt_{0.35}$	2.02	33	22	0.81
$Pd_{0.55}Pt_{0.45}$	1.84	33	27	0.81
$Pd_{0.06}Pt_{0.94}$	1.99	35	32	0.83
Pt	1.92	36	37	0.94

The CH_4 and CO_2 concentrations at the outlet of the reactor were determined using a Hewlett-Packard MTI M200 microchromatograph equipped with two TCD detection units (Poraplot-U and Molecular Sieve A).

2.3. Catalysts characterisation

XRD patterns were obtained using Cu Kα radiation on a Philips PW1710 diffractometer.

The catalysts dispersion and metal surface area was derived from the measurement of the uptake of H_2 chemisorbed at room temperature following the method described by Benson and Boudart [13]. Experimental conditions were reported elsewhere [5]. For calculations of dispersion, the atomic ratio H_{ads}/M_s was assumed to be equal to unity, M_s being a surface metal atom.

CO adsorption on reduced catalysts was studied by FTIR spectroscopy to probe the surface of metal particles. Samples were pressed into thin wafers (30 mg), introduced in an IR cell for treatment under vacuum at 400 °C for 2 h, in 100 Torr H_2 at 300 °C for 12 h and under vacuum at 400 °C. CO (10 Torr) was then admitted into the cell at room temperature, contacted for a few minutes and desorbed at room temperature for 1/2 h. All IR spectra were recorded with a Nicolet Magna 550 (resolution 4 cm^{-1}, 32 scans).

Samples were studied by temperature-programmed oxidation (TPO) in 1 vol.% O_2/He. The experiment was carried out in a U-shaped quartz reactor loaded with 0.1 g catalyst by using a Pfeiffer Omnistar quadrupole mass spectrometer. Prior to the experiment, samples were reduced in H_2 flow at 300 °C and desorbed in He at 50 °C. O_2 consumption and release corresponding to metal oxides formation and decomposition, respectively, were recorded from 50 up to 1000 °C (heating rate of 20 °C min^{-1}).

3. Results

3.1. Characteristics of the catalysts

Main characteristics of the catalysts are reported in Table 1. The number of surface metal atoms is observed to remain fairly constant irrespective of the Pd(Pt) composition. As a consequence, dispersion increases gradually with increasing Pt content. It may be mentioned that the stoichiometry for CO adsorption also varies depending on the Pd(Pt) composition, being much less than unity (0.67) for the monometallic Pd sample, close to unity for the Pt monometallic sample and equal to intermediate values for bimetallic catalysts.

XRD patterns (not shown) revealed the existence of PdO phase only in Pd/Al_2O_3 and $Pd_{0.93}Pt_{0.07}$ samples. For the other samples, no other phase than Al_2O_3 could be detected, which could be related to decreasing Pd content, possibly decreasing size of PdO domains due to Pt mixing with Pd and/or the high dispersion of Pt/PtO_x particles.

3.2. Catalytic activity measurements

The methane conversion over oxidised Pd, Pt and Pd-Pt catalysts plotted as a function of reaction temperature in the standard dry feed is reported in Fig. 1.

Bimetallic catalysts rich in palladium ($Pd_{0.93}Pt_{0.07}$ and $Pd_{0.65}Pt_{0.35}$) are found to be as active as the reference monometallic Pd catalyst in the whole range of temperature. The $Pd_{0.55}Pt_{0.45}$ sample appears to be slightly less active than the former ones. Increasing more Pt content induces further decrease of catalytic performance in methane oxidation. The lowest activity is obtained with the monometallic Pt catalyst. As previously reported [5], Pd/Al_2O_3 does not exhibit any deactivation with time on stream under these experimental conditions and Pd-rich bimetallic catalysts behave similarly to Pd/Al_2O_3. On the contrary, Pt/Al_2O_3 slowly deactivates with time as already reported [5] and adding a low amount of Pd does not change this property.

From these data, we calculated reaction rates at 260 °C expressed in mol CO_2 per hour and per mol metal over various catalysts. It can be found that the rate on monometallic Pd is four times higher than on monometallic Pt, which agrees well with the well-known better performance of Pd compared to Pt. The key point is that, for both Pd-rich bimetallic catalysts ($Pd_{0.93}Pt_{0.07}$ and $Pd_{0.65}Pt_{0.35}$), an enhanced reaction rate at 260 °C was obtained with respect to the reference Pd catalyst: the reaction rate is approximately twice higher. On the contrary the reaction rate over the $Pd_{0.55}Pt_{0.45}$ sample was found to be the same as for the reference Pd catalyst. Finally, reaction rates over $Pd_{0.06}Pt_{0.94}$ and Pt samples were the lowest of the catalysts series.

Adding 10 vol.% H_2O to the reaction feed induces an increase of T_{50} of all catalysts (Fig. 2). This effect is much higher for Pd/Al_2O_3 than for Pt/Al_2O_3. It was attributed to a competition at low temperature between water and methane molecules on the PdO catalytic sites [14–16].

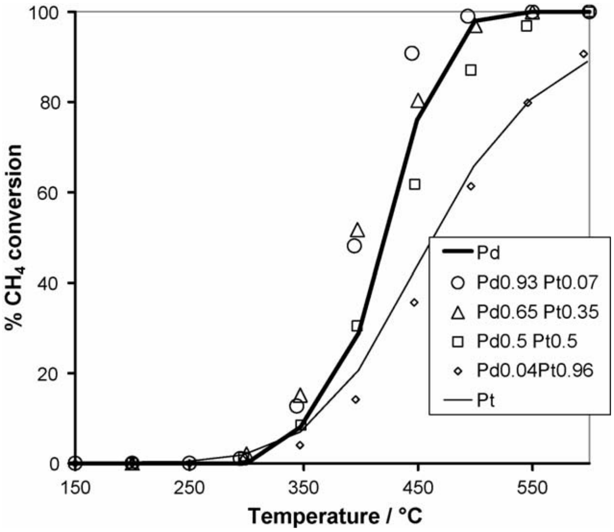

Fig. 2. Methane conversion *vs.* temperature over fresh Pd/Al_2O_3, Pt/Al_2O_3 and bimetallic Pd-Pt/Al_2O_3 catalysts in wet feed. Feed composition: 2000 vol. ppm CH_4, 5 vol.% O_2, 10 vol.% H_2O, He balance; 200 mg catalyst; total flow rate of 6.5 L h^{-1}; GHSV = 20,000 h^{-1}.

Interestingly, the catalytic activity of $Pd_{0.93}Pt_{0.07}$, $Pd_{0.65}Pt_{0.35}$ and $Pd_{0.55}Pt_{0.45}$ samples was less affected upon water addition than the reference Pd/Al_2O_3 catalyst: the increase of T_{50} was restricted to 80–85 °C compared to 105 °C for the monometallic Pd catalyst. The two Pd-rich bimetallic samples turned out to be significantly more active than Pd/Al_2O_3 under wet conditions, *i.e.* under realistic experimental conditions.

In order to simulate a long term use of the catalysts, a mild steam ageing (treatment of the oxidised catalysts in a 10 vol.% H_2O–10% O_2–N_2 mixture for 24 h at 600 °C) was performed on all catalysts. No loss of noble metal was observed after this treatment, as revealed by chemical analysis measurements. Interestingly, even after mild ageing treatment, improved

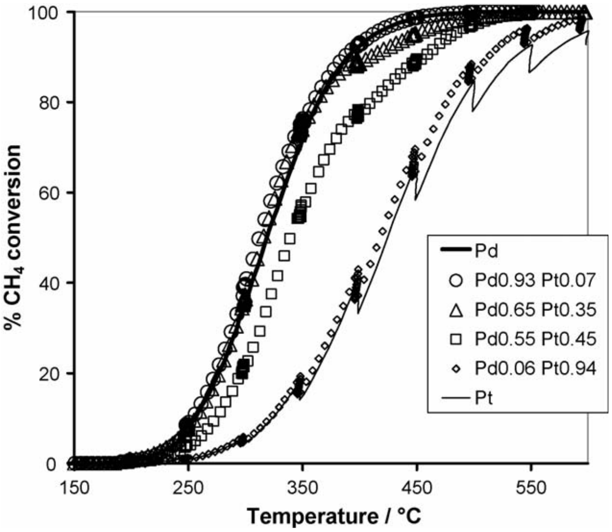

Fig. 1. Methane conversion *vs.* temperature over fresh Pd/Al_2O_3, Pt/Al_2O_3 and bimetallic Pd-Pt/Al_2O_3 catalysts in dry feed. Feed composition: 2000 vol. ppm CH_4, 5 vol.% O_2, He balance; 200 mg catalyst; total flow rate of 6.5 L h^{-1}; GHSV = 20,000 h^{-1}.

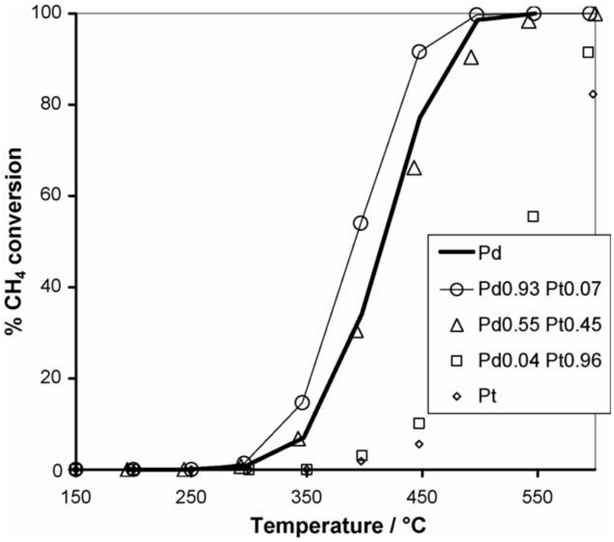

Fig. 3. Methane conversion *vs.* temperature over aged Pd/Al_2O_3, Pt/Al_2O_3 and bimetallic Pd-Pt/Al_2O_3 catalysts in wet feed. Feed composition: 2000 vol. ppm CH_4, 5 vol.% O_2, 10 vol.% H_2O, He balance; 200 mg catalyst; total flow rate of 6.5 L h^{-1}; GHSV = 20,000 h^{-1}.

conversion was still observed over the Pd-rich bimetallic sample ($Pd_{0.93}Pt_{0.07}$) in wet feed compared to the monometallic Pd catalyst, as indicated by a decrease of T_{50} equal to 30 °C (Fig. 3).

It may be concluded that the addition of Pt to Pd has a positive effect on the catalytic activity of Pd in CH_4 oxidation at low temperature in the presence of large amounts of water vapour. Higher conversions can be reached by bimetallic catalysts under wet conditions compared to the monometallic Pd catalyst, which makes Pd-Pt catalysts as potentially superior to monometallic Pd ones in lean-burn NGV CH_4 abatement.

These data strongly suggested the existence of an interaction between Pd and Pt in Pd-rich bimetallic catalysts, this interaction leading to improved catalytic performance of Pd in methane oxidation.

3.3. FTIR study of CO adsorption on reduced catalysts

In order to evidence such interaction, CO was used as a probe molecule to characterise the surface of bimetallic catalysts (Fig. 3). While CO adsorbs mainly linearly on atop surface sites of Pt particles of Pt/Al_2O_3, in agreement with the appearance of one single intense νCO band at *ca.* 2070 cm^{-1}, CO adsorbs both linearly and in bridged form on Pd surface sites of Pd/Al_2O_3 as shown by a weakly intense band at *ca.* 2070 cm^{-1} and multiple broad absorptions below 2000 cm^{-1} [17] (Fig. 4). As expected, decreasing Pt content in bimetallic samples induces a decrease of the band mainly characteristic of CO adsorbed on Pt surface while the absorption characteristic of CO adsorbed on Pd (bands below 2000 cm^{-1}) develop progressively. In addition, two new features may be observed for $Pd_{0.65}Pt_{0.35}$ and $Pd_{0.55}Pt_{0.45}$ samples: a broadening of the band at 2070 cm^{-1} and a new broad band at about 1880 cm^{-1}. These bands can be attributed to linear and bridged CO species, respectively. It is not clear whether these bands could be related to Pt sites, Pd sites or PdPt sites. However this unambiguously indicates the existence of an interaction between Pt and Pd in these samples, which partly affects the adsorption of CO. It is noteworthy mentioning that such interaction could not be evidenced in the $Pd_{0.93}Pt_{0.07}$ sample, likely for sensitivity reasons (the number of perturbed surface sites would be too low).

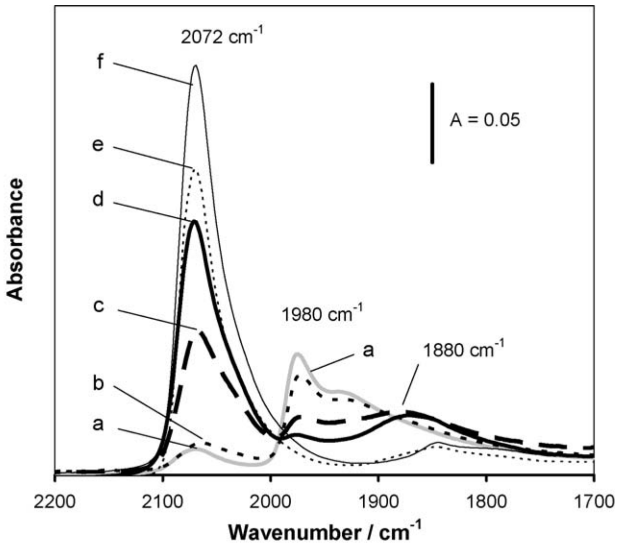

Fig. 4. IR spectra of CO irreversibly adsorbed on Al_2O_3-supported Pd, Pt and Pd-Pt catalysts reduced at 300 °C and desorbed at the same temperature: (a) Pd; (b) $Pd_{0.93}Pt_{0.07}$; (c) $Pd_{0.65}Pt_{0.35}$; (d) $Pd_{0.55}Pt_{0.45}$; (e) $Pd_{0.06}Pt_{0.94}$; (f) Pt.

3.4. Temperature-programmed oxidation

TPO profiles obtained on reduced catalysts are shown in Fig. 5 where O_2 consumption appears as a negative peak and O_2 release as a positive one.

For Pd/Al_2O_3, a sharp negative peak at *ca.* 350 °C corresponds to the complete oxidation of Pd particles into PdO while the decomposition of PdO occurs at much higher temperatures. The maximum rate is obtained at *ca.* 820 °C under these experimental conditions, while a shoulder at 850 °C corresponds to another type of PdO species, in minor quantity.

For Pt/Al_2O_3, Pt oxides do form also, indicating that Pt particles oxidise too, but the phenomenon occurs in a wider range of temperature compared to Pd. These species decompose more easily than PdO, as indicated by a max rate of O_2 release at 680 °C.

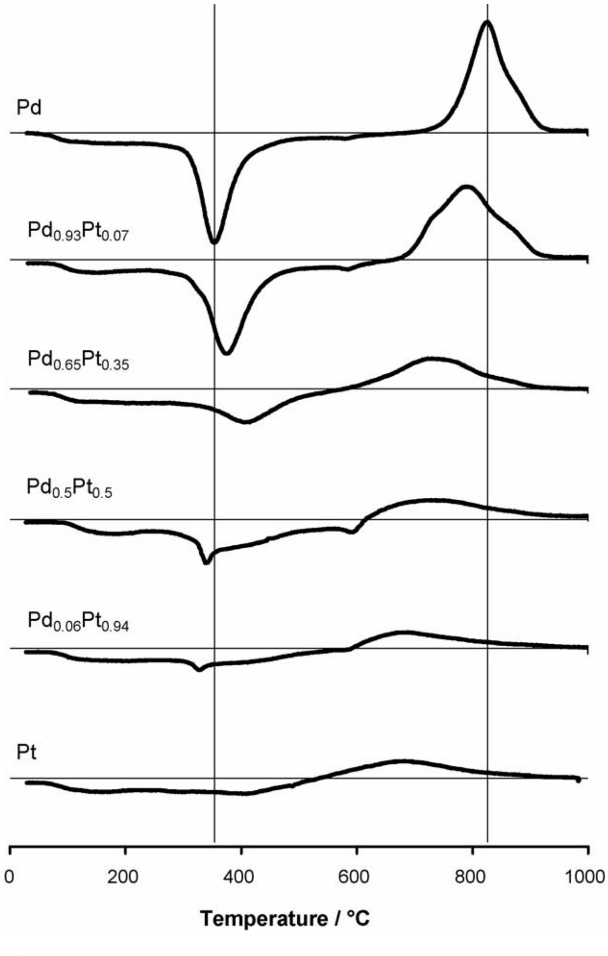

Fig. 5. TPO profiles of the various catalysts 1 vol.% O_2, He balance; flow rate: 20 cm^3 min^{-1}; heating rate of 20 °C min^{-1}; 100 mg catalyst.

Interestingly, the TPO profile of $Pd_{0.93}Pt_{0.07}$ sample is strongly modified with respect to Pd/Al_2O_3. PdO formation occurs in a wider range of temperature at higher temperatures. PdO decomposition is also significantly affected: the maximum rate is shifted at 790 °C and a shoulder at 720 °C is observed. The same observations can be made for $Pd_{0.65}Pt_{0.35}$ confirming the general trend of Pd–O bond weakening upon addition of Pt. This definitely shows that even for very low addition of Pt in bimetallic catalysts, PdO properties are strongly affected. These data are in full agreement with catalytic activity data and confirm that doping of PdO with Pt, even for small Pt content, induces Pd–Pt interactions which lead to improved catalytic properties of PdO in catalytic oxidation of methane.

4. Conclusions

The following conclusions can be drawn:

- The partial substitution of Pd with Pt on Al_2O_3-supported Pd catalysts leads to improved performance in catalytic oxidation of methane under lean-burn conditions, especially in the presence of large amounts of water vapour.
- This positive effect is maintained even after mild steam ageing, which makes these catalysts as potentially more efficient than monometallic Pd catalysts for the abatement of methane in lean-burn NGV exhausts.
- Improved catalytic performance would be due to Pd–Pt interaction.
- Pd–Pt interaction was confirmed by CO adsorption followed by FTIR and TPO experiments.
- The positive effect of Pt on Pd properties is better obtained and maintained with reaction time with low molar Pt/Pd ratios (typically less than 0.5).

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