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CALORIMETRIC STUDY OF METHANE INTERACTION WITH SUPPORTED Pd CATALYSTS

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Abstract

As supported palladium oxide catalysts present the best performances in methane combustion in lean conditions, microcalorimetric studies of the interaction between methane and palladium oxide or metallic palladium supported on Al_2O_3, ZrO_2 and BN have been performed at 673 K. At this temperature methane reduced the palladium oxide, and the heat of reduction of palladium oxide was shown to depend on the dispersion and on the support. The lowest heats of reduction corresponded to the highest rates of methane combustion. Moreover methane reforming occurred on metallic palladium, producing hydrogen, and again methane decomposition was shown to depend on the support.

Keywords: calorimetry, methane combustion, methane decomposition, supported palladium catalysts

Introduction

The use of methane, the main component of natural gas (90–95%) [1], as source of energy is acquiring more and more importance, not only from an economic point of view (the reserves of natural gas are larger than those of petroleum) but also for environmental reasons.

Methane is considered the best candidate as a source of hydrogen for fuel cells due to its highest H/C ratio among all hydrocarbons. The current fuel cell systems require a CO-free hydrogen feed, so direct decomposition of methane to hydrogen instead of a conventional process such as stream reforming followed by CO removal has been suggested as a good solution [2–4].

In combustion, methane has the advantage over other fuels that it burns more cleanly, emitting less pollutants and less CO_2 for a given amount of energy produced. However methane itself is considered to have a large contribution to the greenhouse effect, much more than CO_2 [1] so the emissions of unburned methane present in exhaust gases must be avoided. Catalytic combustion of unburned methane present in exhaust gases has been found to be the best solution to achieve this goal. Different catalysts, supported noble metals, metal oxides, mixed oxides, perovskites, have been studied [5, 6],

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but under the conditions present in the exhaust gases, i.e. low temperature and oxygen-rich environment, supported palladium seems to present the best properties [7].

Alumina has been the most studied support, due to its high performance, high surface area and low cost [8]. Palladium catalysts supported on ZrO_2 seem to present better conversion and higher stability than those supported on alumina [9]. Methane combustion is a highly exothermic reaction, producing spots of high temperature which can affect the properties and performance of the catalyst. The above described supports (Al_2O_3, ZrO_2) and other oxides used as supports such as SnO_2, TiO_2, SiO_2, are thermal isolator materials that cannot spread the heat released in the reaction. The use of ceramic compounds with a higher thermal conductivity such as SiC, Si_3N_4 or BN [10–12] could increase the stability of the catalysts.

There is some controversy about the active phase of palladium in methane combustion [13]. It is now generally accepted that metallic palladium is inactive [14], and that palladium oxide (the stable phase in an oxygen-rich environment at the temperature found in the exhaust gases [15]) is the active phase, although some authors claim the necessity of the presence of both phases Pd^0/PdO_x [13]. Recent studies seem to confirm that the Mars-van Krevelen (redox) mechanism plays a role in methane combustion [5]. According to this mechanism a reduction of PdO by methane takes place, followed by reoxidation by oxygen.

The aim of this work was to study by means of microcalorimetry the interaction of methane with supported palladium oxide on the two most used supports, Al_2O_3 and ZrO_2 and a non-oxide ceramic support, boron nitride (BN), in order to see the influence of the support on the active phase. The catalytic test of methane combustion has been performed at the same temperature as the calorimetric experiments in order to establish a relation between catalytic activity and methane-PdO interaction. Interactions between methane and supported metallic palladium at mild temperature have been also investigated, to study the effect of the support in the ability of palladium to decompose methane.

Experimental

All the catalysts have been prepared by impregnation using the appropriate amounts of $Pd(NO_3)_2$ hydrate from Strem Chemicals (41.9 mass% Pd). The supports used were either commercial, γ-Al_2O_3 (Oxid C) and ZrO_2 (VP) from Degussa or synthesised such as BN [12]. The samples have been named respectively Pd/Al_2O_3, Pd/ZrO_2 and Pd/BN. After drying overnight at 393 K the samples were calcined in oxygen flow at 773 K for 12 h, cooled down in N_2 flow, and reduced in hydrogen flow for 4 h at 573 K.

The concentrations of supported palladium were determined by AES-ICP in a Spectroflame-ICP instrument. Surface areas were determined by the BET method from the adsorption of nitrogen at 77 K. The crystallographic structure was examined by X-ray diffraction in a Bruker (Siemens) D5005 apparatus (CuK_α radiation, 0.154 nm).

The interaction of methane with the different catalysts was studied using a high temperature Tian-Calvet calorimeter (Setaram) coupled with a conventional volumetric apparatus equipped with a Barocel capacitance manometer. The experiments were carried out at 673 K, a typical temperature in exhaust gases. Successive doses of methane of increasing pressure were sent onto the sample until an equilibrium pressure of ≈100 Pa was reached. Then after 1 h of pumping under vacuum a second experiment with methane was carried out on each sample.

The study of the interaction of methane was carried out both on oxidized samples containing palladium oxide and on reduced samples containing palladium in its metallic state. In the experiments performed on the reduced samples, the samples were kept in hydrogen overnight at 673 K and then outgassed at the same temperature during 3 h. In the experiments performed on the oxidized samples, the samples were oxidized in oxygen flow at 773 K 12 h in an independent apparatus and then outgassed at 673 K during 3 h.

The catalytic test was carried out in a conventional continuous flow U shaped reactor at 673 K. A commercial mixture of 1% methane in N_2 (Air Liquide) was mixed with O_2 (Air Liquide) through a Brooks 5850E mass flow controller to obtain a final reaction mixture of 0.95% methane, 4.5% oxygen and a total flow rate of 6.3 L h^{-1}. The composition of the output stream of the reaction was determined using a FID detector (Intersmat IGC 120 FC) equipped with a 2 m length Cabosil column followed by a methanizing column. This assembly allowed us to detect CO, CH_4 and CO_2.

Results and discussion

Table 1 summarizes the BET surface areas and palladium loadings for the studied samples.

Table 1 Physico-chemical characterization of supported palladium samples

Sample	Support	Pd loading/wt%	S_{ext}/m^2 g^{-1}
Pd/Al_2O_3	Al_2O_3	2.07	108
Pd/ZrO_2	ZrO_2	1.99	49
Pd/BN	BN	1.78	26

Calorimetric experiments carried out at lower temperature (473 K) did not show any interaction between methane and supported Pd or PdO catalysts, and no conversion was observed for the catalytic test at this temperature either.

In the experiments performed at 673 K on the samples reduced by H_2 according to the chemical equation

$$H_2+PdO \rightarrow Pd+H_2O \tag{1}$$

the three catalysts presented the same heat flow and pressure evolution profiles, as represented in Fig. 1 for the Pd/Al_2O_3 sample. After a very small initial exothermic peak and pressure drop due to the expansion of methane in the calorimetric cells, an endothermic peak was recorded together with a pressure increase. Similar shapes of the curves were observed for the successive doses. This behaviour can be attributed to methane decomposition following the reaction

$$CH_{4\,g} \rightarrow C + 2H_{2\,g} \tag{2}$$

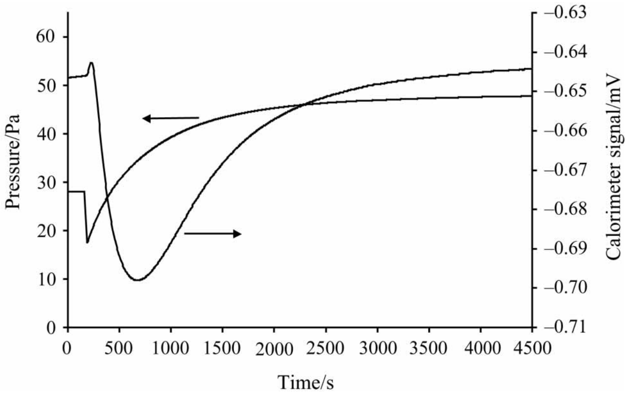

Fig. 1 Pressure and calorimeter signal from methane interaction with the Pd/Al_2O_3 sample at 673 K (after reduction by H_2)

The XRD patterns of the oxidized samples PdO/Al_2O_3 and PdO/BN are presented in Fig. 2, showing that, after calcination at 773 K in oxygen flow, palladium is indeed in the PdO form. The XRD profile for the PdO/ZrO_2 sample is not presented because the zirconia support displays peaks at the same 2θ position as PdO and it was not possible to identify the palladium metallic phase.

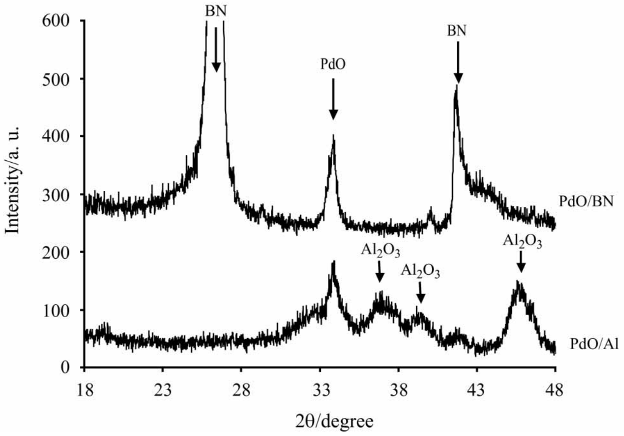

Fig. 2 X-ray diffractograms of oxidized samples PdO/Al_2O_3 and PdO/BN

The interaction of methane with the oxidized samples is completely different from the behavior observed with the reduced samples. The calorimetric and pressure signals corresponding to the interaction between methane and the PdO/BN sample are presented in Fig. 3. For the first dose (Fig. 3a) a broad exothermic peak can be observed, with no increase in the pressure signal. This situation fits well with the following reaction of reduction of palladium oxide by methane:

$$CH_4+4PdO \rightarrow CO_2+2H_2O+4Pd \tag{3}$$

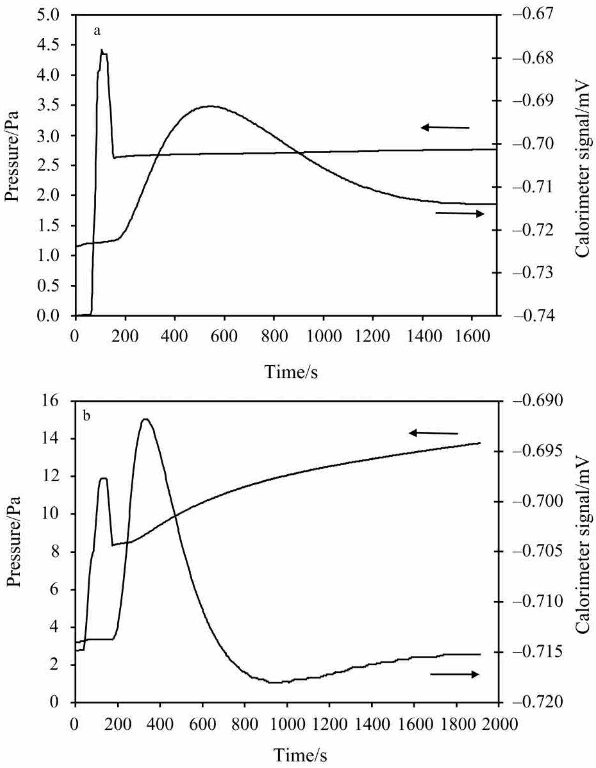

Fig. 3 Pressure and calorimeter signal from methane interaction with the PdO/BN sample at 673 K. a – first dose and b – second dose

The volumetric apparatus is equipped with a U shaped trap maintained at dry ice temperature to retain the produced water, so in the reduction reaction CO_2 is the only molecule that can be detected in gas phase. As one molecule of methane yields one molecule of CO_2, no pressure increase was observed during the reduction and the thermal effect observed gave rise to an exothermic peak. The methane amount used in the first dose (1.83 μmol) was not enough to reduce all the PdO present in the sample (25.7 μmol).

For the second dose (Fig. 3b) an initial exothermic peak was observed, followed by a smaller and wider endothermic peak, and an increase of the pressure was observed. The pressure increase became faster as the reaction progressed. As shown above, this pressure increase cannot be attributed to a reduction reaction, so it should be due to methane decomposition on the newly generated metallic palladium, in the same way as observed in the interaction between methane and the reduced sample. The fact that the pressure increases faster and faster as the reaction advances is due to the amount of metallic palladium capable of decomposing methane, which becomes larger and larger as methane reduces more PdO. Even the hydrogen produced by methane decomposition (reaction (2)) can contribute to reduce palladium oxide, accelerating the generation of metallic palladium and consequently accelerating methane decomposition.

The third dose, not shown, presents the same trend as for the reduced sample, an endothermic peak with an increase of the pressure due to methane decomposition, indicating that no more reduction takes place.

Figure 4 shows the experiments of methane interaction with PdO/Al_2O_3 before (Fig. 4a) and after reduction by CH_4 (Fig. 4b). The calorimetric signal from the first dose presents an initial exothermic peak followed by a small, long-lasting endothermic peak. The amount of CH_4 sent in the first dose (10.37 μmol) is larger than the amount needed to reduce the palladium oxide present on the alumina (35.7 μmol). So it can be concluded that both processes, first PdO reduction and then decomposition of methane on metallic palladium, occur. The following methane doses produced only an endothermic peak and an increase of pressure due to methane decomposition into dihydrogen and carbon.

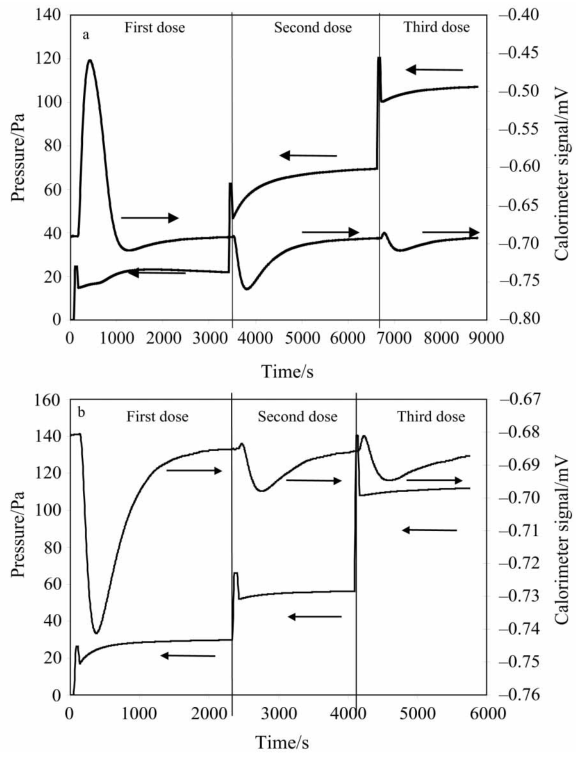

Fig. 4 Pressure and calorimeter signal from methane interaction at 673 K with a – PdO/Al_2O_3 sample and b – after reduction by methane and pumping

The same trend was observed for PdO/ZrO_2. For this sample the amount of methane used in the first dose (1.65 μmol) was smaller than the amount required to reduce completely PdO (7.9 μmol), so only an exothermic peak was observed. The successive doses presented the same trend of endothermic heats due to methane decomposition as in the case of PdO/Al_2O_3.

Once the process completed, and after 30 min of evacuation at the same temperature of 673 K, the experiment was repeated. The three catalysts presented the same trend, shown in Fig. 4b for Pd/Al_2O_3. As it can be seen, the behavior was identical to that found for the sample reduced by hydrogen, endothermic peaks with increasing pressure corresponding to methane decomposition, indicating that palladium was mainly present in the reduced form.

Figure 5 shows the X-ray diffractograms of PdO/Al_2O_3 and PdO/BN after interaction with methane. Only peaks corresponding to the metallic Pd phase are present; no peaks could be attributed to PdO. For the Pd/ZrO_2 sample, the zirconia support presents peaks in the same domain as metallic Pd, which made it impossible to observe the presence of Pd.

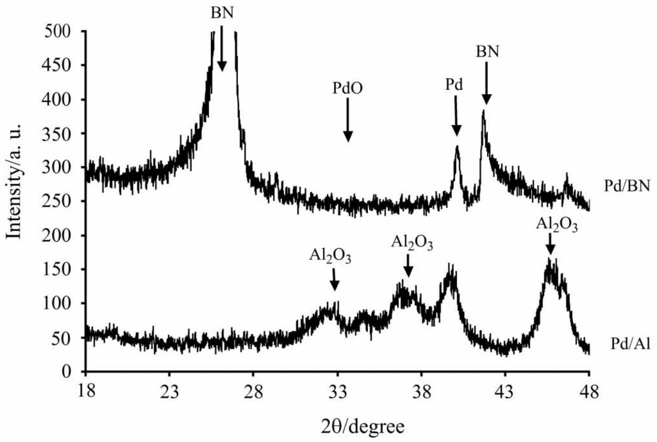

Fig. 5 X-ray diffractograms of PdO/Al_2O_3 and PdO/BN after interaction with methane at 673 K

Table 2 summarizes the heats of reduction of PdO by methane at 673 K for the three samples, calculated from the calorimetric peak generated by the first dose of CH_4.

Table 2 PdO reduction heats and rate of methane combustion on the supported PdO samples

Sample	PdO reduction heat/ kJ (mol PdO)$^{-1}$	Rate of methane combustion at 673 K/ mol CH_4 (mol Pd)$^{-1}$
Pd/Al_2O_3	70.6	84.3
Pd/ZrO_2	73.3	68.9
Pd/BN	75.2	38.5

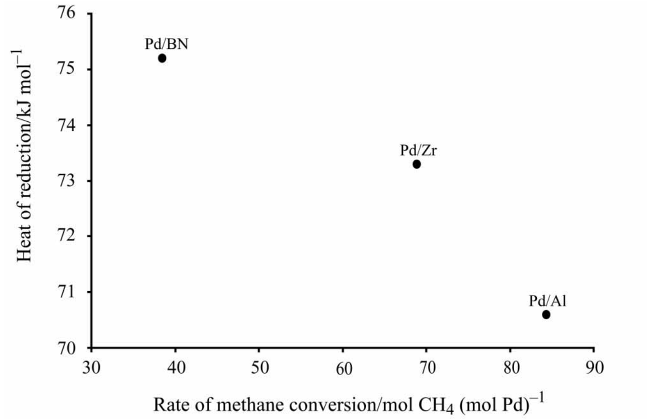

Fig. 6 Relation between the reduction heat of supported palladium oxide and the rate of methane combustion at 673 K

The reduction heats present similar values on the three catalysts, increasing in the order $Pd/Al_2O_3<Pd/ZrO_2<Pd/BN$. The order of activity found in the catalytic combustion of methane for these three samples at the same temperature is the opposite, Pd/Al_2O_3 being the most active of all catalysts. In Fig. 6 the reduction heats of supported palladium are presented *vs.* the rate of methane combustion per mol of palladium at 673 K, showing a quasi-linear relation. This means that, the easier the reduction of palladium oxide, the more active the catalyst, in good agreement with the proposed mechanism for methane combustion [5]. Nevertheless the differences between the reduction heats are not very large. In the XRD spectra (Figs 2 and 5), well-defined peaks are observed for Pd and PdO in spite of the low loading of the catalysts, indicating that the dispersion is not very good. The lower the dispersion, the closer the behaviour of the supported metal or oxide to that of the bulk phase, diminishing the influence of support. We can assume that the heat of PdO reduction increases with the particle size of the palladium crystallites, which itself depends on the interaction between the active phase and the support.

Table 3 Heat and extent of decomposition of methane on the supported palladium samples

Sample	CH_4 decomposition heat/kJ (mol CH_4)$^{-1}$	α^*/%
Pd/Al_2O_3	92	99
Pd/ZrO_2	99	86
Pd/BN	70	24

*Extent of methane decomposition

The experiments of methane interaction with metallic palladium have been used to calculate the heats of methane decomposition and the extent of decomposition (α) of methane at 673 K on palladium over different supports. Table 3 summarizes these values. The heats and extents of decomposition of methane over Pd/Al_2O_3 and Pd/ZrO_2 are very similar, α being bigger for Pd/Al_2O_3. The Pd/BN sample presented a lower extent of decomposition, probably due to the lower surface area of this sample and its lower dispersion taking into account the more inert character of the BN surface compared to alumina or zirconia, and also a lower heat of decomposition.

Conclusions

The interaction of methane with metallic palladium at 673 K gives rise to methane decomposition. The order of activity is Pd/Al_2O_3>Pd/ZrO_2>Pd/BN. The heat of methane decomposition at this temperature is around 95 kJ mol^{-1}.

The interaction of methane with palladium oxide is marked by the reduction of palladium oxide, followed by methane decomposition on the newly created metallic palladium. The reduction heat of palladium oxide is in the order Pd/BN>Pd/ZrO_2>Pd/Al_2O_3, opposed to the rate of methane combustion found at the same temperature. Such a behaviour fits well with the proposed mechanism for methane combustion, which consists of firstly the reduction of palladium oxide by methane and secondly the reoxidation of metallic palladium by oxygen.

* * *

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