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Catalysis Today 78 (2003) 191–196

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Methane oxidation over vanadium-modified Pd/Al_2O_3 catalysts

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Abstract

Three different vanadium-modified Pd/Al_2O_3 catalysts were prepared and tested as catalysts for the deep oxidation of methane. Vanadium was added to the palladium catalyst by incipient wetness of palladium catalyst in order to modify its properties and improve its thermal stability and thioresistance. The behaviour of vanadium-modified catalysts depends on the concentration of this compound, being 0.5 wt.% the optimum amount. However, when strong catalyst poisons are present in the gas (SO_2), these modified catalysts do not show a better performance than unmodified catalyst. Bimetallic catalysts were tested with and without further reduction, being observed that reduced bimetallic catalysts perform worse than the non-reduced ones.

Keywords: Catalytic oxidation; Methane; Vanadium–palladium catalyst

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1. Introduction

Methane abatement in flue gases is one of the most environmental concerns because it is a powerful greenhouse gas, being released in many industrial processes such as coke ovens, farms and biological processes [1]. Thermal incineration (the conventional technique) requires very high temperatures (up to 1000 °C), producing noxious by-products such as NO_x. Catalytic oxidation is the most attractive alternative for the abatement of methane in off-gases. In this operation, lower temperatures are needed, providing lower energy consumption and avoiding the formation of NO_x [2].

Although this technique is widely developed for the abatement of many VOCs (aromatic, oxygenated or paraffinic of medium molecular weight), methane is the most difficult hydrocarbon to oxidise catalytically, requiring higher temperatures than other VOCs [3]. Most studies about catalytic oxidation have been carried out with more reactive VOCs and so the thermal stability of the support does not play any important role.

It is known that supported palladium catalysts are the most active for the total oxidation of methane and there are many studies focusing on the alumina supported ones [4 and references cited therein]. However, alumina supported palladium catalysts are not stable at the temperatures commonly used for methane oxidation (in the range 400–500 °C). Different causes have been proposed in the literature for this behaviour: γ-Al_2O_3 sintering, spinel formation, PdO or Pd sintering or PdO → Pd transformations. All these phenomena are favoured at higher operation temperatures.

By these reasons, two alternatives are suggested in the literature. On the one hand, the use of alternative supports such as zirconia-based supports [5], being considered more stable at higher temperatures but they are not widely used in industrial practice because they are expensive and present lower surface areas. On the other hand, the modification of the catalyst properties (increasing thermal stability) by addition of a promoter

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PII: S0920-5861(02)00329-2

in order to increase the thermal stability is considered as an attractive alternative to enhance the performance of conventional catalysts.

The presence of sulphur compounds in some of these emissions (coke ovens, composting plants, etc.) is also an important problem, since sulphur is a strong catalyst poison, especially with palladium-based catalysts [6].

On the other hand, the modification of the catalysts by adding different promoting agents (usually metals or metal oxides) is widely used in other catalytic processes such as hydrogenations, isomerizations or partial oxidations [7,8]. Although in many cases the mechanisms are not well understood (alloying phenomena and modification of the properties of the support are considered as the most important phenomena), promoted catalysts usually present higher conversions, better selectivities and extended resistance to deactivation. At this point, cerium, lanthanum and zirconium-modified Pd/Al_2O_3 catalysts are reported to present better performance than unmodified Pd/Al_2O_3 catalysts for methane deep oxidation [9]. Although these modified catalysts are often considered to increase selectivity for intermediate products (it is not good for environmental purposes), these authors claim that CO is not found using these modified catalysts. However, to the best of our knowledge there is information about neither the resistance to sulphur poisoning nor the effect of the addition of other metals.

In the literature referred to other catalytic processes, it is reported that vanadium addition to Pd and Pt catalysts can enhance both resistance to thermal deactivation (increasing the stability of the alumina or hindering the coalescence of metal particles) and resistance to poisoning. So, an important increase in the resistance to chlorine poisoning in vanadium-modified catalysts was found by Srinivas et al. [10], whereas Ordóñez et al. [11] showed that vanadium addition to Pt/Al_2O_3 catalysts modify not only the thermal properties but also reactive (acid–base) properties of the catalyst. In the same work it was observed that the oxidation state of vanadium (V or V_2O_5), plays an important role in the modified catalyst properties.

Due to these properties of vanadium, this compound could be a good promoter to enhance the stability of the palladium catalysts and increase their thioresistance. This last aspect is also of great practical importance, since the use of palladium catalysts is hindered by the poisonous effect of sulphur compounds, often present in off-gases.

In the present work, the effect of the addition of different concentrations of vanadium to a home-made Pd/Al_2O_3 catalyst has been studied for the oxidation of methane in air, alone and in the presence of SO_2.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst support used in this work is γ-Al_2O_3, supplied by BASF. Its surface area, measured by nitrogen physisorption method in a Micromeritics ASAP 2000 apparatus, is $228.8\,m^2\,g^{-1}$.

Palladium catalyst was prepared by incipient wetness, using an aqueous solution of $Pd(NO_3)_2$ (Fluka) as precursor in order to get 1 wt.% of palladium. The catalyst so prepared was dried overnight at 100 °C after impregnation and then calcined in air at 550 °C for 2 h.

Vanadium was added to the palladium catalyst, also by incipient wetness, using an aqueous solution of ammonium metavanadate as precursor. Three different concentrations of vanadium have been tested (0.1, 0.5 and 1 wt.%). These modified catalysts were also dried and calcined. Final concentration of V and Pd in the catalysts was checked using ICP analysis.

Temperature programmed reduction analyses were carried out using a Micromeritics TPD/TPR 2900 Analyzer apparatus, operating at room pressure. The reactor was a quartz glass vertical tube and the catalyst sample (0.02 g) was kept in position by plugs of quartz wool. This reactor was placed inside an electric furnace, temperature being measured by a PID controller (Eurotherm). The gas flow rate was controlled by rotameters and the gas leaving the reactor was analysed by a TCD detector. The carrier gas used consists of a mixture of hydrogen (5%) and nitrogen with a flow rate of 50 ml/min. The temperature was increased from room temperature to 900 °C with a ramping temperature rate of 10 °C/min. The hydrogen consumed was detected by the TCD.

2.2. Reaction studies

Experiments were carried out in a laboratory fixed-bed catalytic reactor, which is a stainless steel tube of

400 mm length and 9 mm internal diameter. The reactor was loaded with 0.06 g of catalyst, mixed with 1 g of inert pyrex glass, and placed in the middle section of the reactor. Its top part was filled with additional packing material. The reactor was placed inside an electric furnace, temperature being controlled by a PID controller (Honeywell) connected to a thermocouple situated inside the reactor, that monitored the reaction temperature. The system was provided with five additional thermocouples that measured the reactor wall temperature at different positions.

The reactor feed consists of methane (5000 ppm V) into a N-50 synthetic air (Air Liquid). For studying poisonous effect of sulphur compounds, SO_2 was added to the feed (40 ppm V). Both methane and sulphur concentrations are typical values in off-gases, as coke oven or composting facilities emissions. Gas flow rate (1 L/min (at s.t.p.)) was controlled by a mass flow controller (Brooks 5850 TR), and the exhaust gas was analysed by gas chromatography (Hewlett Packard HP 5890 Series II). Partial oxidation products, such as CO, have not been detected in any experiment.

3. Results and discussion

3.1. Fresh catalyst characterization

The fresh vanadium-modified and unmodified catalysts were characterized by temperature programmed reduction analyses. A characteristic profile of a supported palladium catalyst shows a negative peak at low temperature (∼75 °C), corresponding to a release of chemisorbed hydrogen (β-PdH phase), followed by two positive peaks (hydrogen consumption), the first of them closed to the release and the other one at 200–300 °C [12].

As it can be observed in Fig. 1, no differences were detected among the samples in the negative peak. Concerning to the second peak, in these catalysts is very small due to the low metal load and the high dispersion. In contrast, the third peak is observed in the unmodified catalyst and in the catalyst modified with the lower amount of vanadium, whereas in the case of higher amounts of vanadium, this peak is not observed.

This result suggests that the addition of vanadium-modified the redox properties of the palladium, varying the mechanism for the reduction of palladium oxide. So, the apparent absence of reduction peaks in the catalysts doped with 1% of vanadium is tentatively explained by the existence of different species that are progressively reduced, being this signal too low to be observed.

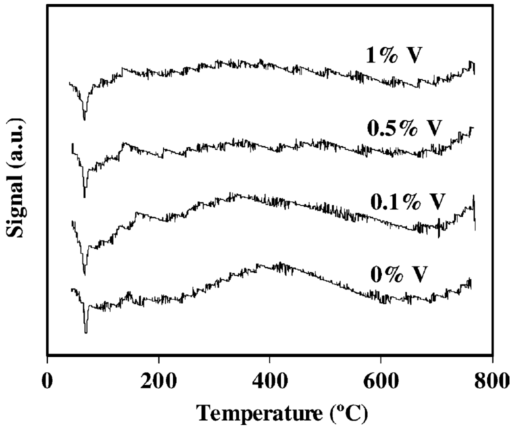

Fig. 1. TPR profiles of vanadium-modified and unmodified catalysts.

Regarding to reduction of vanadium, it was not observed any peak associated to this reaction. This aspect is in a good agreement with the literature. So, Kapteijn et al. [13] state that for temperatures below 600 °C, this reduction is not thermodynamically favoured.

Fresh catalysts were also characterized using XRD, no crystallographic changes in the γ-alumina being observed in these catalysts. Palladium and vanadium phases were not observed because of their low concentration in the solids.

Concerning to the surface area, the addition of vanadium does not lead to noticeable changes in surface area. In all the cases (palladium and vanadium–palladium catalysts), surface areas are around 220 $m^2 g^{-1}$.

3.2. Activity tests

The presence of homogeneous oxidation of methane was discarded at the reaction conditions, being the methane conversions attained negligible up to 600 °C. On the other hand, the activity of the support and supported vanadium catalysts was also negligible at reaction conditions. This result is in a good agreement with the low catalytic activity of vanadium for deep oxidation reaction reported in the literature.

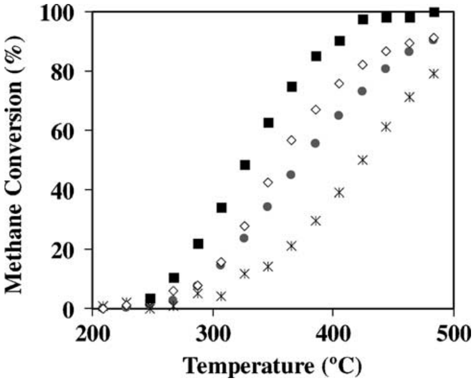

Fig. 2. Light-off curves for the oxidation of 5000 ppm V of methane over non-reduced catalyst: (◇) 0% V; (✱) 0.1% V; (■) 0.5% V; (●) 1% V.

In the first experiments catalysts were used without reduction. In previous works of our research group, it was found that Pd catalysts without further reduction perform better (considering both activity and catalyst stability) than reduced catalysts [14].

In order to test the performance of vanadium-modified catalysts, light-off curves were recorded at the above-mentioned conditions after 16 h on stream at 450 °C. For this purpose, temperature was increased from 150 to 550 °C with a ramping temperature rate of 2 °C/min. The light-off curves were carried out with methane (5000 ppm).

Conversions attained for 1% Pd and three different vanadium-modified catalysts (containing 0.1, 0.5 and 1% V) were shown in Fig. 2. In order to quantificate the activity, the kinetic controlled region of the light-off curves (up to 40%) was fit using a pseudo-first order model. Although it is accepted that the best kinetic mechanisms to model the oxidation of methane over palladium catalysts are Mars–Van Krevelen ones, pseudo-first order models could be enough accurate and suitable for comparing the activities of different catalysts. So, according to this model, considering zero order for the oxygen due to its high concentration, and considering Arrhenius dependence for kinetic constant, the equations will be the following:

$$-r_{\mathrm{CH}_4} = kP_{\mathrm{CH}_4} \qquad (1)$$

$$k = k_0 \exp\left\{\frac{-E_a}{RT}\right\} \qquad (2)$$

Table 1
Summary of catalyst parameters

Catalyst	T_{50} (°C)	k (s^{-1}) at 450 °C	E_a (kJ mol^{-1})
0% V	362	1872	60.8
0.1% V	410	68	62.3
0.5% V	335	1333	68.3
0.5% V (reduced)	466	124	84.6
1% V	381	132	57.7

where $-r$ is the rate of methane conversion, P the partial pressure of methane, k the kinetic constant, R the gas constant, T the temperature, and k_0 and E_a are the pre-exponential factor and activation energy, respectively. The values of these kinetic parameters (considering integral reactor), as well as the T_{50} (temperature needed to reach 50% conversion) are shown in Table 1.

It is observed that the addition of vanadium has important effects on the catalyst activity. Therefore, the lower amount of vanadium (0.1% V) does not affect the catalyst performance, whereas 1% of V leads to slightly less active catalyst and 0.5% of V lead to the most active catalysts. These results can be explained considering different aspects. On one hand the vanadium oxide could physically cover the active phase. This effect appears to be the dominant at lower vanadium concentrations. As the V concentration increases, the catalysts perform better. This result leads to think into Pd–V interactions or a modification of the support properties.

In order to test the influence of the catalyst reduction in its catalytic properties, experiments with catalyst doped with 0.5% V and reduced at 550 °C have been carried out. As in the case of the non-reduced catalysts, the catalyst was aged according to the above-mentioned procedure used for non-reduced catalysts. Recorded light-off curve (Fig. 3) shows that the reduced catalyst performs worse than the non-reduced catalyst and even worse than the non-modified Pd catalyst. These results suggest that reduced vanadium acts as a poison. Similar behaviour is reported in the literature for Pt catalysts [10].

3.3. Ageing experiments

The study of the ageing of the catalysts is important in order to obtain information about the active

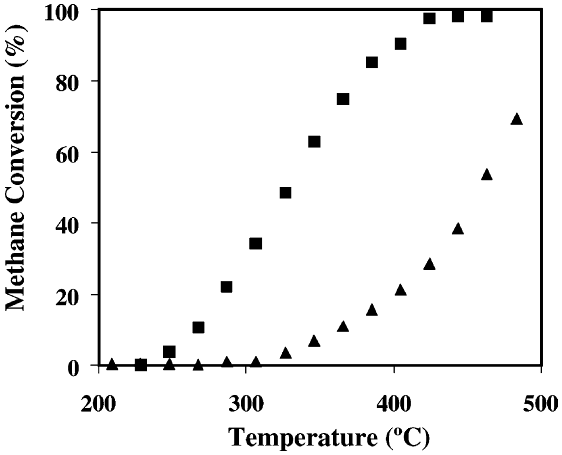

Fig. 3. Light-off curves for the oxidation of 5000 ppm V of methane: (▲) 0.5% V reduced catalyst; (■) 0.5% V non-reduced catalyst.

phase. So, the ageing experiments carried out at 450 °C for 16 h. The operation temperature was chosen because in previous experiments, it was observed that self-deactivation of palladium catalysts is important at these temperatures [14]. The other operation conditions (space time and methane concentration) are mentioned in the previous section. Results obtained for non-reduced catalysts with 0, 0.1, 0.5 and 1% V, as well as for reduced catalysts with 0.5% V are shown in Fig. 4.

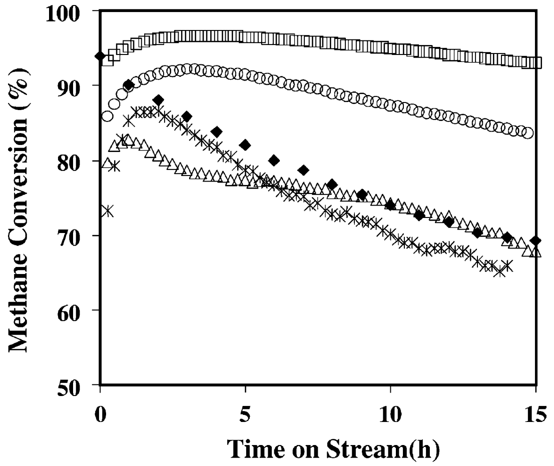

Fig. 4. Evolution of methane conversion with time on stream for the reduced catalyst: (△) 0.5% V and catalysts without reduction: (◆) 0% V; (✳) 0.1% V; (□) 0.5% V; (○) 1% V.

Experiments show again that the effect of the vanadium depends on its concentration. In general, it is observed that the addition of vanadium leads to a more stable operation, especially working at 0.5% V. In the case of 1% V, the stability is not so marked as in the case of 0.5% V and the conversion is slightly slower.

Results obtained lead to think that the addition of vanadium becomes catalysts more resistant to deactivation. This behaviour could be tentatively explained considering that vanadium modify the interaction between the active phase (palladium oxide) and the support, avoiding the coalescence of active phase crystallites.

In the case of the catalyst with the highest amount of vanadium, this element present two effects: on one hand vary active phase-support interaction, increasing the catalyst stability, but the poisoning effect of vanadium is also more important, leading to lower conversions. By contrast, lower amounts of vanadium do not provide higher stability to the catalyst. These aspects suggest that there is an optimal amount of vanadium to be added to enhance the properties of the catalyst. Concerning to the reduced catalysts, it performs very similar to the unmodified catalysts, the resistance to deactivation being not increased.

At this point, it is interesting to remark that in previous works with unmodified Pd catalysts [14], it was observed that the difference between the performance of reduced and non-reduced catalysts is not so important as in this case, attaining similar conversion after 10 h on stream. This aspect can be tentatively explained considering that for unmodified palladium catalysts it is assumed that the active phase is a palladium oxide, the reduced palladium being oxidised under the reaction conditions. Results obtained indicate that the addition of vanadium (metal with high chemical affinity for oxygen) hinders this oxidation. This effect is in a good agreement with the conclusion obtained from the TPR experiments.

3.4. Sulphur poisoning

As mentioned in Section 1, vanadium addition is mentioned to increase the resistance of the catalysts to poisoning, although there are no specific references to the effect of vanadium sulphur poisoning in oxidative conditions.

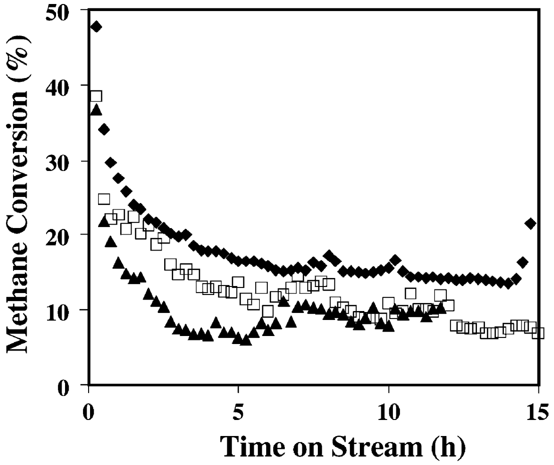

Fig. 5. Evolution of methane conversion with time on stream in presence of 40 ppm V of SO_2 for the reduced catalyst: (▲) 0.5% V and catalysts without reduction: (◆) 0% V; (☐) 0.5% V.

In order to study the poisonous effect of sulphur compounds, SO_2 was added to the feed (40 ppm V). In previous works of our research group, it was found that the effect of SO_2 and H_2S over the combustion of methane over palladium catalyst was equivalent [15]. The experiments were carried out with unmodified Pd/Al_2O_3 catalyst, and catalysts modified with 0.5% vanadium both reduced and non-reduced. Sulphur poisoning studies were carried out in the same conditions that the ageing experiments.

Results obtained (Fig. 5) show that vanadium addition does not enhance the thioresistance of the Pd catalysts. Deactivation curves of the modified catalysts are very similar, or even slightly worst than the attained with the reference Pd/Al_2O_3 catalyst. This result suggests again that the properties of the active phase are not modified by the addition of vanadium.

Concerning to the role of support, in previous works it was observed that the support has a strong influence on the resistance of palladium catalysts to sulphur poisoning [16]. So, supports that not adsorb SO_2 (as SiO_2) lead to total deactivation of the catalysts, whereas deactivation is not so fast when materials with high surface affinity for SO_2 are used as supports. Therefore, results attained shows that the addition of vanadium does not change the adsorption properties of the support.

Acknowledgements

This work has been supported by a grant from the European Community (contract ENV4-CT97-0599) and the Spanish Commission for Science and Technology (contract PPQ2001-3675).

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