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The oxidative destruction of hydrocarbon volatile organic compounds using palladium–vanadia–titania catalysts

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A range of titania supported palladium catalysts modified by the addition of vanadium have been prepared and tested for the total oxidation of short chain hydrocarbons. The addition of vanadium promoted the rates of oxidation at lower temperatures. Vanadium loadings between 0.5 and 3.0 wt.% were investigated and the most active catalyst was 0.5% Pd1.5% V/ TiO_2. The addition of vanadium decreased the palladium dispersion, but temperature programmed reduction studies showed that the combination of palladium with vanadium dramatically increased the ease of catalyst reduction. It is proposed that the increased catalyst activity is related to the modified redox properties of the catalysts.

KEY WORDS: VOCs; hydrocarbons; catalytic oxidation; palladium; vanadium; titania.

1. Introduction

In recent years environmental legislation has imposed increasingly stringent targets for permitted levels of atmospheric emission. The emission of Volatile Organic Compounds (VOCs) have received particular attention as they have been established with the increase in photochemical smog [1], depletion of atmospheric ozone [2] and the production of ground-level ozone [3]. VOCs are a wide ranging class of chemicals, and currently over 300 compounds are classed as VOCs by the US EPA. Although the scale of their discharge is not known it was estimated that at least 20.3 million tons were released from the US alone in 2000 [4]. VOC emissions have decreased by about 40% over the last 20 years but further reductions are still required. Similarly in Europe the Gothenburg Protocol adopted by the 15 EU member states in 1999 requires a 40% reduction in VOC emissions by 2010. In view of the scale of the problem presented to the chemical and processing industries the major challenge they face is to reduce the emission of pollution without stifling economic growth.

Many different technologies have been developed for VOC abatement, but one of the most versatile is catalytic oxidation to carbon dioxide. Catalytic oxidation offers the advantage that VOCs can be removed from aerial effluents to very low levels. More importantly, in contrast to thermal incineration, the lower temperatures used result in a more economical process, and the potential for the production of toxic by-products such as dioxins and NO_X are significantly reduced. Generally, noble metal catalysts, such as Pt and Pd dispersed on a high area metal oxide, are the commercial catalysts of choice due to their high intrinsic oxidation activity. Studies of catalytic VOC oxidation have shown that short chain hydrocarbons are amongst the most difficult to destroy [5]. These VOCs are also potent greenhouse gases and the development of more efficient catalysts for their effective abatement is a major research aim. In this work results showing that palladium supported on vanadium modified titania catalysts have improved oxidation activity for short chain alkanes at lower temperatures are presented.

2. Experimental

The catalysts were prepared by dissolving $PdCl_2$ (0.169 g, Aldrich 99%) in 100 ml of deionised water. The solution was heated to 80 °C and stirred continuously. An approprate quantity of ammonium metavanadate (Aldrich 99 + %) and oxalic acid (1.59 g, Aldrich 99 + %) were added to the solution of $PdCl_2$. Titanium oxide (19.60 g, Degussa P25. $SA_{BET} = 50\ m^2\ g^{-1}$) was added to the heated solution and stirred at 80 °C to form a paste. The resulting paste was dried at 110 °C for 16 h. The catalyst contained 0.5 wt% Pd and V in the range 0.5–3.0 wt%. A similar method was used to prepare TIO_2 based materials without vanadium and without palladium. Final catalysts were prepared by calcination in static air at 550 °C for 6 h.

Catalyst activity was determined using a fixed bed laboratory micro reactor. Catalysts were tested in powdered form using a 0.25"O.D. stainless steel reactor tube. The reaction feed consisted of 5000 vppm hydrocarbon in air. A total flow rate of 50 mL min^{-1} was used and catalysts were packed to a constant volume to give a gas hourly space velocity of 45000 h^{-1} for all studies. Analysis was performed by an on-line gas chromato-

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graph with thermal conductivity and flame ionisation detectors. Catalytic activity was measured over the range 100–550 °C and temperatures were measured by a thermocouple placed in the catalyst bed. Conversion data were calculated by the difference between inlet and outlet concentrations and all carbon balances were in the range $100 \pm 10\%$.

Catalyst surface areas were determined by multi point N_2 adsorption at 77 K, and data were treated in accordance with the BET method. Palladium dispersion was determined by pulsed CO chemisorption at 35 °C using an Ar flow of 20 mL min^{-1} and pulses of 0.2 mL of 10% CO in Ar. Prior to CO uptake determination all samples were treated under flowing hydrogen (50 mL min^{-1}) and then flushed by Ar (20 mL min^{-1}) for 60 min. In order to calculate the metal dispersion, an adsorption stoichiometry of $Pd/CO = 1$ was assumed. Temperature-programmed reduction was carried out in a Micromeritics Autochem 2910 apparatus equipped with a TCD detector. The reducing gas used was 10% H_2 in Ar, with a flow rate of 50 mL min^{-1}. The temperature range explored was from room temperature to 650 °C using a heating rate of 10 °C min^{-1}.

3. Results and discussion

The oxidation of propane over the $Pd/V/TiO_2$ catalysts with varying vanadium loadings are shown in figure 1. Initial activity was observed at ca. 200 °C with all the catalysts. Propane conversion increased with temperature and approached 100% at 400 °C. The sole reaction product was CO_2, no partially oxidised hydrocarbon products or CO, were observed at any temperature. Variation of the vanadium loading influenced the rate of propane conversion. Comparison of the temperature for 50% conversion (T_{50}) showed that the catalyst with 1.5% vanadium was the most active. The order of activity based on T_{50} was:

$$\begin{aligned} 0.5\%Pd/1.5\%V/TiO_2 &> 0.5\%Pd/3.0\%V/TiO_2 \\ &> 0.5\%Pd/1.0\%V/TiO_2 \\ &> 0.5\%Pd/0.5\%V/TiO_2 \end{aligned}$$

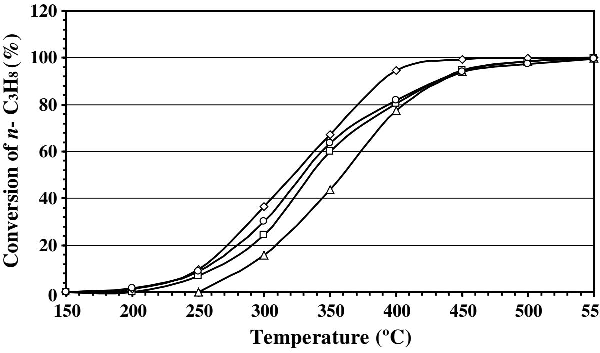

Figure 1. Effect of vanadium loading on propane conversion over 0.5% $Pd/V/TiO_2$ catalysts: (Δ) 0.5% Pd/0.5% V /TiO_2; (□) 0.5% Pd/ 1.0% V/TiO_2; (◇) 0.5% Pd/1.5%V/TiO_2; (○) 0.5% Pd/3.0% V/TiO_2.

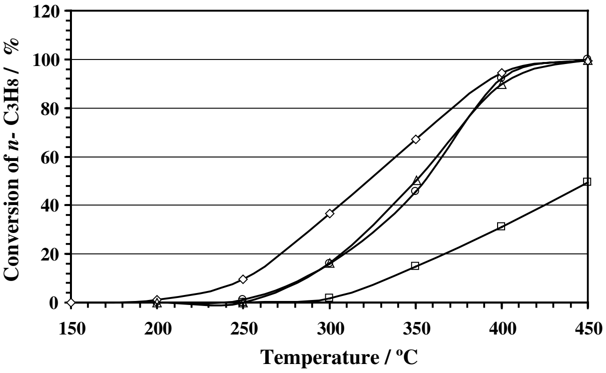

Figure 2. Comparison of propane conversion as a function of temperature: (◇) 0.5% Pd/1.5% V/TiO_2; (○) 0.5% Pd/ TiO_2; (□) 1.5% V/ TiO_2; (Δ) 5% Pd/Al_2O_3.

Comparison of propane oxidation activity was made between the most active 0.5% Pd/1.5% V/TiO_2 catalyst, Pd/TiO_2 and V/TiO_2 figure 2). Whilst the Pd/TiO_2 catalyst demonstrated propane conversion at 250 °C, the V/TiO_2 catalyst did not show any conversion. Moreover, the conversion over V/TiO_2 did not increase as rapidly with temperature as for the Pd/TiO_2 catalyst. The propane conversion over V/TiO_2 was only 48% at 450 °C. Below 400 °C the $Pd/V/TiO_2$ demonstrated higher propane oxidation rates than Pd/TiO_2, whilst at 400 °C the TiO_2 supported catalyst without vanadium was marginally more active. It was particularly noteworthy that the activity of the $Pd/V/TiO_2$ catalyst was significantly greater than Pd/TiO_2 at the lower temperatures probed.

Alumina supported Pd catalysts are recognised as one of the most active for the deep oxidation of hydrocarbons to CO_2 [6]. Comparison of the activity for propane oxidation with a commercial 5 wt.% Pd/Al_2O_3 catalyst demonstrated that the Pd/1.5% V/TiO_2 catalyst was more active figure 2. The performance of the Pd/1.5% V/TiO_2 and Pd/Al_2O_3 catalysts were similar at 450 °C. However, at temperatures below 450 °C the Pd/1.5% V/TiO_2 catalyst was significantly more active. For example, the titania catalyst produced 10% propane conversion at 250 °C, whilst the alumina system only showed trace conversion. Furthermore, at 300 °C the rate of propane oxidation over Pd/1.5% V/TiO_2 was at least twice that for Pd/Al_2O_3.

Short chain alkanes are common VOCs and their oxidation using the 0.5% Pd/1.5% V/TiO_2 catalyst has been probed table 1. It is recognised that the alkanes are more difficult to oxidise to CO_2 as the carbon number decreases. This trend is reflected by the data, as there was a successive increase in light-off temperature from n-butane to methane. Both catalysts produced CO_2 as

Table 1
Alkane conversion over Pd-based catalysts

Alkane feed	Catalyst	Temperature (°C)							
		200	250	300	350	400	450	500	550
Methane	0.5% $Pd/V/TiO_2$	0	1.0	3.2	7.3	15	31	56	75
	5% Pd/Al_2O_3	0	0	1.0	7.3	54	94	100	100
Ethane	0.5% $Pd/V/TiO_2$	0	4.0	16	35	71	99	100	100
	5% Pd/Al_2O_3	0	0	11	44	88	100	100	100
Propane	0.5% $Pd/V/TiO_2$	0	9.6	37	67	95	99	100	100
	5% Pd/Al_2O_3	0	0	16	50	90	100	100	100
n-Butane	0.5% $Pd/V/TiO_2$	0	11.7	43	75	95	100	100	100
	5% Pd/Al_2O_3	0	0	21	95	99	100	100	100

the only oxidation product. The Pd/1.5% V/TiO_2 catalyst had a lower light-off temperature for *n*-butane, propane, ethane and methane when compared to the Pd/Al_2O_3 catalyst. Moreover, appreciable rates of hydrocarbon oxidation were observed for the alkanes over Pd/1.5% V/TiO_2 at temperatures where the Pd/Al_2O_3 catalyst was inactive. The rate of methane oxidation was greater over Pd/Al_2O_3 than Pd1.5% V/TiO_2 at 400 °C and above. However, the rates were equal at 350 °C, and consistent with the oxidation of C_2–C_4 alkanes, the Pd/1.5% V/TiO_2 catalyst was more active below 350 °C.

Catalyst characterisation results from CO chemisorption to determine the number of surface metal sites, and N_2 BET surface areas are presented in table 2. The addition of vanadium to TiO_2 decreased the Pd dispersion from 34 to 21% when 0.5% vanadium was added. The palladium dispersion was decreased further as the vanadium loading was increased, however, above 1.0% vanadium the palladium dispersion was not significantly reduced. The catalyst surface areas also decreased slightly as the vanadium loading increased. Therefore, it is clear that the addition of vanadium decrease the number of surface Pd sites and the enhancement of rate on the addition of vanadium is due to electronic modification rather than purely physical redistribution of palladium.

Temperature programmed reduction profiles for the titania supported catalysts are shown in figure 3. T PR profiles Of V/TiO_2 (not shown) produced three reduction features at 350–360 °C, 390 °C and 420–430 °C, and these features can be related to the reduction of vanadium species described in the literature. TPR profiles of $Pd/V/TiO_2$ catalysts were significantly different from V/TiO_2. TPR data for the catalysts containing palladium showed two or/three poorly defined reduction peaks between 50 and 125 °C. These features contrasted with the maxima at 350–430 °C observed for Pd-free catalysts. The assignment of these peaks is not clear, but they can be related to a partial reduction of VO_x species in close contact with the palladium [7] and/or to the presence of highly dispersed bulk palladium oxide [8]. The hydrogen consumption for the low temperature reduction peak in the 0.5% Pd/1.5% V/TiO_2 and 0.5% Pd/3.0% V/TiO_2 were 313 and 563 μmol H_2 g_{cat}^{-1}, respectively. These values were considerably higher than the amount corresponding to the complete reduction of palladium oxide (47 μmol H_2 g_{cat}^{-1}). Moreover, the high temperature reduction peaks observed with V/TiO_2 were not present when palladium was present. These results suggest that vanadium oxide reduction also took place in the temperature range 50–125 °C. Therefore, it can be concluded that the reducibility of vanadium sites were

Table 2
Palladium dispersion and catalyst surface areas

Catalyst	BET surface area (m^2 g^{-1})	Pd dispersion (%)
0.5% Pd/TiO_2	50	34
0.5% Pd/0.5%V/TiO_2	47	21
0.5% Pd/1.0%V/TiO_2	47	14
0.5% Pd/1.5%V/TiO_2	45	13
0.5% Pd/3.0%V/TiO_2	39	9
5% Pd/Al_2O_3	130	5

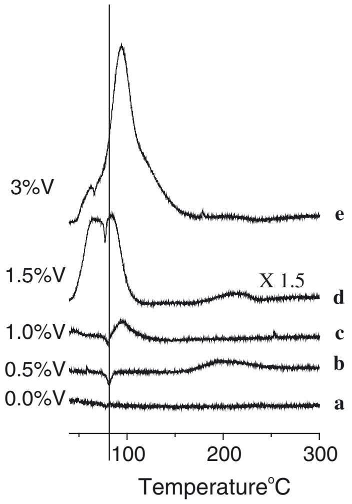

Figure 3. Temperature reduction profiles titania supported palladium catalysts modified with varying vanadium loadings (50 ml min^{-1} 10% H_2 in Ar, 10 °C min^{-1}): (a) 0.5%Pd/TiO_2; (b) 0.5%Pd/0.5%V/TiO_2; (c) 0.5%Pd/1.0%V/TiO_2; (d) 0.5%Pd/1.5%V/TiO_2; (e) 0.5%Pd/3.0% V/TiO_2.

dramatically enhanced for Pd/V/TiO$_2$ catalysts when compared to V/TiO$_2$ catalysts. Interestingly, the optimum vanadium loading for catalyst activity was 1.5% and this coincided with the lowest reduction temperature of all the Pd/V/TiO$_2$ catalysts.

The TPR profile of Pd/TiO$_2$ is reported in figure 3(a). TPR data showed a very small negative peak at 80 °C which has been attributed to the release of hydrogen from the decomposition of palladium hydride species [9]. TPR profiles have been carried out from 30 °C and usually the main reduction peak of palladium, corresponding to $1.5H_2 + Pd^sO \rightarrow Pd^sH + H_2O$ and $(1 + 1/2x)H_2 + Pd^bO \rightarrow Pd^bH_x + H_2O$ transitions, are at subambient temperatures [10] and therefore have not been recorded. It is also apparent that the reduction of palladium around 80 °C is more intense in the Pd/V/TiO$_2$ catalysts than in the Pd/TiO$_2$ catalyst. It is known that the intensity of this peak is lower in samples with a high dispersion of palladium on the support surface [7]. This is in agreement with the data from table 2 since the palladium dispersion of the 0.5% Pd/TiO$_2$ catalyst is considerably higher than that of the 0.5% Pd/V/TiO$_2$ catalysts. It is also observed that the temperature at which this negative peak appears decreases when V-loading increases.

The increased reducibility when the Pd/TiO$_2$ catalysts were modified with vanadium is significant for the promotion of deep oxidation activity. It has been suggested that supported Pd catalysts oxidise hydrocarbons *via* a redox mechanism with the active oxidising species being PdO [11]. Furthermore, the TPR data suggest that oxygen lability for VO$_x$ species are also increased in the presence of palladium. Thus, the lower reduction temperature of Pd/V/TiO$_2$ can help to explain the higher activity of these catalysts at the lower temperatures investigated.

The surface area of the Pd/Al$_2$O$_3$ catalyst was 130 m^2 g^{-1}, with a Pd dispersion of 5%. The Pd dispersion of the Al$_2$O$_3$ supported catalyst was broadly similar to the V/TiO$_2$ supported catalyst. The Pd loading of the Al$_2$O$_3$ supported catalyst was greater than the Pd/V/TiO$_2$ catalysts by an order of magnitude, and consequently the number of surface Pd sites on the alumina based catalyst was significantly greater than the modified titania catalyst. It is therefore apparent that the increased rates of reaction observed with Pd/V/TiO$_2$ compared to Pd/Al$_2$O$_3$ were not a direct function of the number of surface palladium sites. This is consistent with the increase of activity at low temperature due to modification of catalyst reducibility.

Table 3
Comparison of propane conversion in different Pd supported catalysts

Catalyst	GHSV(s^{-1})	T_{10} (°C)	T_{50} (°C)	Reference
5%Pd/MgO	334*	300	425	[12]
5%Pd/ZrO$_2$	334*	300	450	[12]
5%Pd/SiO$_2$	334*	325	375	[12]
5%Pd/SiO$_2$-ZrO$_2$	334*	300	350	[12]
5%Pd/SiO$_2$-Al2O$_3$	67*	325	475	[13]
5%Pd/SO$_4^-$ ZrO$_2$	67*	300	450	[13]
1%Pd/20%Nb$_2$O$_5$/Al$_2$O$_3$	67*	345	400	[13]
1%Pd/CeO$_2$/γ-Al$_2$O$_3$	230	425	485	[14]
1%Pd/γ-Al$_2$O$_3$	37*	350	400	[15]
2%Pd/La Fe$_{0.8}$Co$_{0.2}$O$_3$	14	255	320	[16]
0.05%Pd/γ-Al$_2$O$_3$	23*	330	390	[17]
0.02%Pd/ZrO$_2$	19*	340	510	[17]
0.05%Pd/γ-Al$_2$O$_3$-SO$_4^-$	23*	360	525	[17]
0.02%Pd/ZrO$_2$-SO$_4^-$	10*	420	–	[17]
0.5%Pd/1.5%V/TiO$_2$	13	250	325	This work
0.5%Pd/TiO$_2$	13	300	375	This work

*Estimated density to calculate GHSV was 1.0 g ML^{-1}.

It is interesting to compare the activity of the catalysts in this study with a range of palladium catalysts that are documented in the literature for the deep oxidation of propane table 3. Tt is apparent that catalysts have been tested over a wide range of different conditions. However, comparison of the 0.5% Pd/1.5% V/TiO$_2$ catalyst with others tested under similar conditions showed that the catalyst in this study was more active. In particular the increased activity over 2% Pd/La Fe$_{0.8}$Co$_{0.2}$O$_3$ [16] and 0.02% Pd/ZrO$_2$-SO$_4^-$ [17] was noteworthy. Some of the data in table 3 have been obtained at considerably higher space velocity than those used in this study and it is difficult to compare the data directly. It is clear that the catalysts prepared in the present study show cmparative, and better, activity than many of the other catalysts detailed in the literature. At this stage no attempt has been made to optimise the activity of the catalysts prepared in this study, and it is envisaged that further improvements in activity can be attained.

4. Conclusions

It has been demonstrated that the activity of titania supported palladium catalysts for the deep oxidation of short chain alkanes is increased by modification with vanadium during the impregnation step of catalyst preparation. A vanadium loading of 1.5% with 0.5% palladium was the most active catalyst. The combination of vanadium and palladium increased the ease of catalyst reduction, which can help to explain the promotion of activity. To the best of our knowledge this is the first reported study of a vanadium modified titania supported palladium catalyst for the oxidation of short chain hydrocarbon VOCs. Against this background these systems are now worthy of further investigation to establish their potential as environmental catalysts.

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