Catalysis Letters Vol. 110, Nos. 1–2, August 2006 (© 2006)
DOI: 10.1007/s10562-006-0094-y

Naphthalene oxidation over vanadium-modified Pt catalysts supported on γ-Al_2O_3

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Received 4 April 2006; accepted 11 April 2006

Alumina-supported platinum catalysts modified by vanadium were synthesised and tested for the complete oxidation of naphthalene. The catalysts were characterised by BET, pulsed CO chemisorption, powder X-ray diffraction, laser Raman spectroscopy and temperature-programmed reduction. Whilst BET and CO chemisorption results showed that the addition of vanadium modified both the textural properties of the support and the distribution of Pt, XRD and TPR data suggested the presence of V_2O_5 on catalysts with higher V loadings. TPR data showed that the concentration of V_2O_5 and possibly some other vanadium species increased as the V loading increased. Only 0.5%V was found to promote the activity of the 0.5%Pt/γ-Al_2O_3 catalyst. The activity enhancement has been related to the presence of a more easily reducible vanadium species coupled with the enhanced number of surface Pt sites. On the other hand, the reduced activity demonstrated by catalysts with higher vanadium content (1 – 12%) has been attributed to the presence of crystalline V_2O_5.

KEY WORDS: catalytic oxidation; VOCs; PAHs; vanadium; platinum.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, phenanthrene, and pyrene constitute a ubiquitous class of atmospheric pollutants released during the combustion of organic matter, such as diesel, gasoline, biomass, coal and wood [1–4]. Therefore, the release of PAHs to the atmosphere is widespread and takes place on a large scale, and they have now been identified as posing serious environmental and health risks. In response, there has been increasing regional enforcement of environmental legislation which in turn has led to ever more stringent targets for the release of PAHs to the atmosphere.

A range of technologies have been developed for the abatement of Volatile Organic Compounds (VOCs), like PAHs. Catalytic oxidation to more environmentally benign CO_2 and H_2O appears to be one of the most cost-effective as it requires lower combustion temperatures and ensures higher total oxidation selectivity compared with the alternative thermal incineration. There have been relatively few studies in the literature concentrating on the catalytic oxidation of PAHs. The oxidation of naphthalene, a model PAH, and naphthalene-containing mixtures has been attempted over metal oxide and metal-supported catalysts [5–12]. A review of these studies reveals that Pt/γ-Al_2O_3 is so far amongst the best catalysts reported for naphthalene total oxidation. In the present work we have demonstrated that the activity of Pt/γ-Al_2O_3 catalysts for naphthalene oxidation can be promoted by the addition of vanadium, when added by co-impregnation with platinum to the γ-Al_2O_3 support.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by dissolving a known amount of hydrogen hexachloroplatinate (IV) hydrate (Aldrich, 99.9%) in 100 ml of deionised water. The solution was heated to 80 °C and stirred continuously. An appropriate amount of ammonium metavanadate (Aldrich 99+ %) and oxalic acid (1.59 g, Aldrich 99+ %) were added to the solution of the salt. Aluminium oxide (10 g, Aldrich 99+ %) was then added to the heated solution and stirred at 80 °C to form a paste. This was then dried at 110 °C for 16 h. The catalysts had a Pt loading of 0.5 wt% and V loading in the range 0.5–12 wt%. A similar method was used to prepare Pt-alumina catalysts without vanadium. The catalysts were finally calcined in static air at 550 °C for 6 h. The complete range of catalysts prepared is detailed in table 1.

2.2. Catalyst characterization

The surface areas of catalysts were determined by multi point N_2 adsorption at 77 K using the BET technique. Pulsed CO chemisorption at 35 °C using an

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Ar flow of 20 ml min^{-1} and pulses of 0.2 ml of 10% CO in Ar, were used to determine the CO uptake. All samples were treated under flowing hydrogen (50 ml min^{-1}) and flushed by Ar (20 ml min^{-1}) for 60 min prior to the determination of CO uptake.

Powder X-ray diffraction was used to identify the crystalline phases present in the catalysts. An Enraf Nonius PSD120 diffractometer with monochromatic Cu Kα source operated at 1.2 kW (40 keV and 30 mA) was used. The experimental patterns were calibrated against a silicon standard and by matching experimental patterns to the JCPDS powder diffraction file; the phases present in the catalysts were identified.

A Renishaw system – 1000 dispersive laser Raman microscope was used for recording of Raman spectra. The excitation source used was an Ar ion laser (514.5 nm) operated at a power of 20 mW. The laser was focused on powdered samples placed on the microscope slide to produce a spot size of ca. 3 μm in diameter. A backscattering geometry with an angle of 180 ° between illuminating and collected radiation was used for data collection.

TPR data were collected using a Micromeritics Autochem 2910 with a TCD detector. In all experiments, 10% H_2 in Ar, at a constant flow rate of 50 ml min^{-1}, was used as reducing gas. A temperature range from room temperature to 650 °C was employed and a constant heating rate of 10 °C min^{-1} was used. The sample mass was varied depending on the sample under investigation.

2.3. Catalytic activity

Catalyst activity for naphthalene oxidation was determined using a fixed bed laboratory micro reactor. Catalysts were tested in powdered form using a 1/4 o.d. stainless steel reactor tube. The reaction feed consisted of 100 vppm naphthalene 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 45,000 h^{-1} for all studies. Analysis was performed by an on-line gas chromatograph with thermal conductivity and flame ionisation detectors. Catalytic activity was measured over the temperature range 100–300 °C in incremental steps, and temperatures were measured by a thermocouple placed in the catalyst bed. Data were obtained at each temperature after a stabilization time. Three analyses were made at each temperature to ensure that steady state data were collected. The reaction temperature was increased and the same procedure followed to determine each data point.

3. Results and discussion

Table 1 shows the BET surface areas, CO uptake and phases identified for synthesised catalysts. The BET results show that all catalysts had surface areas slightly lower than the alumina support. There was a general decrease in surface area with increase in catalyst loading. This could be attributed to the filling of pores of the support by the V and Pt species. Table 1 also shows that CO uptake for catalysts with 0.5–6%V loading decreased with increasing V loading. This can be interpreted as a decrease in the number of surface Pt sites with increasing V loading, since CO uptake is proportional to the amount of surface Pt atoms. These data imply that the addition of vanadium to the Pt/γ-Al_2O_3 catalyst modified the Pt dispersion on the support. 0.5%V yielded the maximum CO uptake whilst the catalyst without vanadium showed the lowest CO uptake. BET and CO chemisorption results therefore suggest that the addition of vanadium modified both the textural properties of the support and the distribution of surface Pt.

The results of XRD analyses are summarised in table 1 and figure 1. These results reveal that except for the catalyst with 12% V, diffraction peaks seen in patterns of all other catalysts were representative of γ-Al_2O_3. The additional peaks observed in the patterns of catalysts with 12% V were from V_2O_5, which probably resulted from the dispersion of large crystallites of V_2O_5on the surface of the γ-Al_2O_3 support. The absence of diffraction from Pt or V containing phases in catalysts with lower loadings can be attributed to a combination of the low concentration and phases that are not detectable by diffraction due to their relatively high dispersion.

Raman spectra recorded for the catalysts are shown in Figure 2. It can be observed that except for the catalyst with 12% V loading which had an intense band centred at 1000 cm^{-1}, spectra of all other catalysts were similar, showing no distinctive Raman bands. The Raman band at 1000 cm^{-1} observed for the catalyst with 12 %V, is identified as the Raman band (centred at 997 cm^{-1}) which has been assigned to crystalline V_2O_5 in Pd/V/TiO_2 catalysts with high vanadium loading [13–17]. The identification of V_2O_5 in this catalyst is

Table 1
Chemical composition, BET surface area and CO uptake of synthesised catalysts

Catalysts	BET surface area/m^{2}g^{-1}	CO uptake/μ molCO g^{-1}	Identified phases
γ-Al_2O_3	194	–	γ-Al_2O_3
0.5%Pt/γ-Al_2O_3	169	5.3	γ-Al_2O_3
0.5%Pt/0.5%V/γ-Al_2O_3	180	17	γ-Al_2O_3
0.5%Pt/1%V/γ-Al_2O_3	185	11	γ-Al_2O_3
0.5%Pt/3%V/γ-Al_2O_3	169	9.4	γ-Al_2O_3
0.5%Pt/6%V/γ-Al_2O_3	164	6.0	γ-Al_2O_3
0.5%Pt/12%V/γ-Al_2O_3	149	4.9	γ-Al_2O_3, V2O5 (Scherbinaite, syn)

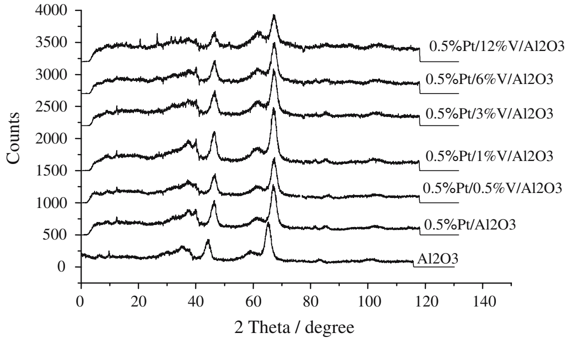

Figure 1. Powder X-ray diffraction patterns of Al_2O_3, Pt/Al_2O_3 and $Pt/V/Al_2O_3$ catalysts.

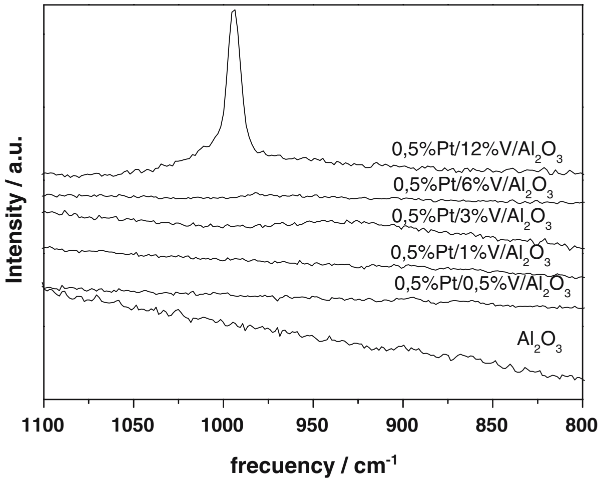

Figure 2. Raman spectra for Al_2O_3 and $Pt/V/Al_2O_3$ catalysts.

consistent with the XRD data. Although no Raman bands corresponding to V-species were observed for Pt catalysts with 0.5–6% V, it is likely that they contained lower concentrations of one or more of the three vanadium species reported in the literature [13] (i.e. isolated tetra coordinated vanadium species, polymeric vanadium species or crystalline V_2O_5). There is a degree of fluorescence experienced when using alumina with an Ar ion laser, and hence identification of weak Raman features is hindered.

TPR profiles for $Pt/V/\gamma\text{-}Al_2O_3$ catalysts (figure 3a) show an increase in the intensity of reduction peaks with increasing vanadium loading. This suggests an increase in the concentration of reducible V-species as the V loading was increased. The absence of major reduction peaks common to both catalysts with and without vanadium suggests that all reduction peaks observed for V-containing catalysts correspond to the reduction of vanadium species. Catalysts with 6 and 12% V both showed two well defined peaks at 150 and 250 °C (figure 3a) whereas the 3% V catalyst only showed a single smaller peak (at 225 °C) which closely matched the most intense peaks for catalysts with 6 and 12% V. The fact that XRD and Raman results for the catalyst with 12% V mainly showed the presence of crystalline V_2O_5 suggests that V_2O_5 was the predominant vanadium species in this catalyst. As such, the TPR peak (between 200 and 300 °C) common to catalysts with 3–12% V can be attributed to the reduction of V_2O_5. The assignment of the reduction peak at 150 °C is not clear. However, it probably corresponds to highly dispersed vanadium species [17–21]. Close examination of the low loading 0.5% V catalyst (figure 3b) showed the presence of a reduction peak at 175 °C which probably corresponds to either (isolated tetra coordinated vanadium species or polymeric vanadium species. From the size of this reduction peak, it is clear that the corresponding vanadium species was only present in low concentration.

The addition of 0.5% V to the $Pt/\gamma\text{-}Al_2O_3$ catalyst promoted the activity for naphthalene total oxidation, whilst, the addition of 1–12% V had a negative effect, suppressing activity (figure 4). Catalysts containing 1–12% V showed light-off temperature (LOT) of 200 °C and T100 of 250–275 °C, whereas, the 0.5% V catalyst showed a relatively lower LOT (175 °C) and T100 (225 °C). It is postulated that the enhanced activity of $0.5\%Pt/0.5\%V/\gamma\text{-}Al_2O_3$ compared to the $Pt/\gamma\text{-}Al_2O_3$ and other $Pt/V/\gamma\text{-}Al_2O_3$ catalysts resulted from two factors. Firstly, the most active catalyst showed a unique vanadium (species that was identified by TPR). Secondly, the Pt dispersion will also have a crucial influence on the catalyst activity. The most active $0.5\%Pt/0.5\%V/\gamma\text{-}Al_2O_3$catalyst had the highest Pt dispersion amongst all catalysts under investigation. The relationship between the number of Pt surface sites exposed and naphthalene oxidation rate is not a simple one. Although the 1–6% V catalysts had higher CO uptake than the catalyst without V they clearly were less active than the $Pt/\gamma\text{-}Al_2O_3$ catalyst. It is evident that the nature of the vanadium species that was present with the Pt particles exerts a major influence over the catalytic activity. Consequently the increased oxidation rate of naphthalene over the catalyst with 0.5% V was due to a combination of the dispersed Pt with the relatively facile reducible vanadium species unique to the catalyst. This combination may promote activity by aiding the activation of oxygen and/or the adsorption of naphthalene. Furthermore, it appears that the presence of relatively large V_2O_5 crystallites was detrimental to naphthalene oxidation; therefore, in order to promote activity the form of the vanadium is critical.

4. Conclusions

The activity of an alumina-supported platinum catalyst for naphthalene total oxidation is promoted by a small amount of vanadium added during the impreg-

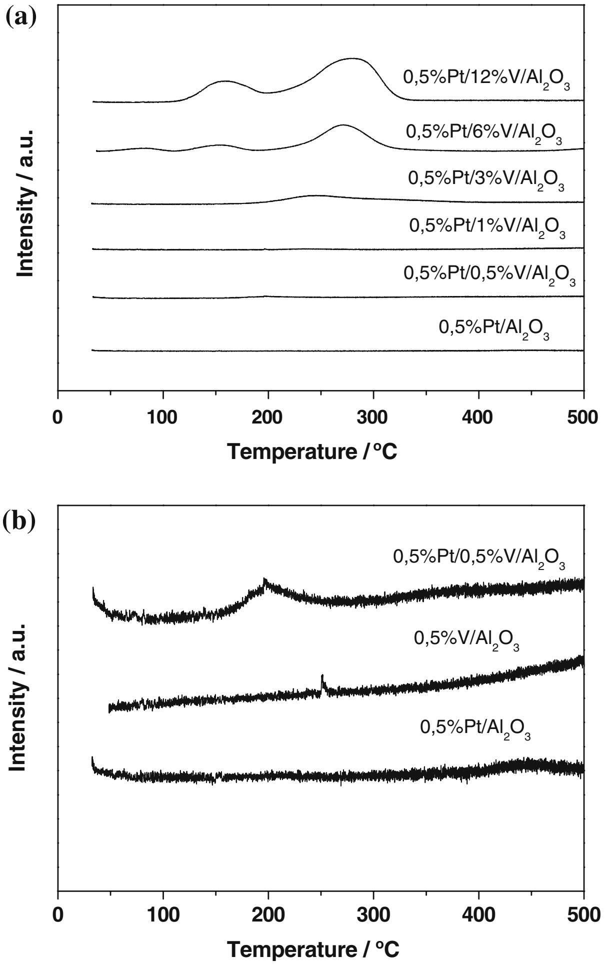

Figure 3. Hydrogen temperature programmed reduction profiles (a) for Pt/Al_2O_3 and $Pt/V/Al_2O_3$ catalysts; (b) for 0.5 %Pt/Al_2O_3, 0.5%V/Al_2O_3,and 0.5% Pt/0.5 %V/Al_2O_3.

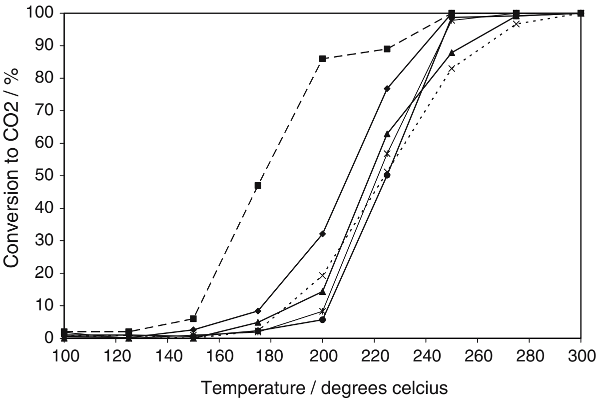

Figure 4. Activity of Pt/Al_2O_3 and $Pt/V/Al_2O_3$ catalysts for naphthalene oxidation: 0.5% Pd/Al_2O_3 0.5%Pd/0.5%V/Al_2O_3 0.5%Pd/1%V/Al_2O_3 0.5%Pd/3%V/Al_2O_3 0.5%Pd/6%V/Al_2O_3 0.5%Pd/12%V/Al_2O_3.

nation step of catalyst preparation. Whilst the addition of 0.5% V significantly promoted the activity of the Pt-alumina catalyst, higher vanadium loadings had a negative effect, as they suppressed activity. The promotional effect has been attributed to a combination of more facile dispersed reducible vanadium species with dispersed platinum sites. Whereas the presence of crystalline V_2O_5 has been suggested to account for the lower activity observed for catalysts with higher vanadium content.

Acknowledgments

Edwin Ntainjua wishes to thank the School of Chemistry – Cardiff University for his PhD funding. The authors would also like to thank Prof Terence E Warner of The University of Southern Denmark for useful discussions.

References

[1] B.J. Finlayson-Pitts and J.N. Pitts, Jr, Chemistry of the Upper and Lower Atmosphere, (Academic Press, First Edition, 1999) p. 436.

[2] W.O. Siegel, R.H. Herman, B.W. Wenclawiak and B. Luers-jongen, Atmos. Environ. 33 (1999) 797.

[3] H. Li, C.D. Banner, G.G. Mason, R.N. Westerholm and J.J. Rafter, Atmos. Environ. 30 (1996) 35.

[4] U.S E. P. A., Health and Environmental Effects Profile for Naphthalene, EPA/600/x-86/241.

[5] Z. Xiao-Wen, S.-C. Shen, K. Hidajat, S. Kawi, L.E. Yu and Simon K.Y., Catal. Lett. 96 (2004) 87.

[6] Z. Xiao-Wen, S.-C. Shen, L.E. Yu, S. Kawi, K. Hidajat and K.Y. Simon, Appl. Catal. A: General 250 (2003) 341.

[7] A. Kalantar Neyestanaki, L.-E. Lindfors, T. Ollonqvist and J. Vayrynen, Appl. Catal. A: General 196 (2000) 233.

[8] J. Carno, M. Berg and S. Jaras, Fuel 75 (1996) 959.

[9] F. Klingstedt, A. Kalantar Neyestanaki, L.-E. Lindfors, T. Salmi, T. Heikkila and E. Laine, Appl. Catal. A: General 6210 (2002) 1.

[10] M. Ferrandon and E. Bjornbom, J. Catal. 200 (2001) 148.

[11] J.L. Shie, C.Y. Chang, J-H. Chen, W.T., Yi-H. Chen, C. C-S. Chiou and C.-F. Chang, Appl. Catal. B: Environ. 56 (2005) 269.

[12] T. Garcia, B. Solsona and S.H. Taylor, Catal. Lett. 105 (2005) 183.

[13] T. Garcia, B. Solsona, D.M. Murphy, K.L. Antcliff and S.H. Taylor, J. Catal. 229 (2005) 1.

[14] G. Busca, L. Marchetti, G. Centi and F. Trifiro, Langmuir. 2 (1986) 568.

[15] C.B. Rodella, R.W.A. Franco, C.J. Magon, J.P. Donoso, L.A.O. Nunes, M.J. Saeki, M.A. Aegerter, V. Sargentelli and A.O. Florentino, J. Sol Gel, Sci. Technol. 83 (2002) 25.

[16] I.E. Wachs and B.M. Weckhuysen, Appl. Catal. A 157 (1997) 67.

[17] D.A. Bulushev, L. Kiwi-Minsker, F. Rainone and A. Renken, J. Catal. 115 (2002) 205.

[18] H. Berndt, A. Martin, A. Bruckner, E. Schreier, D. Muller, H. Kosslick, G.V. Wolf and B. Lucke, J. Catal. 191 (2000) 284.

[19] B. Solsona, T. Blasco, J.M. Lopez Nieto, M.L. Pena, F. Rey and A. Vidal-Moya, J. Catal. 203 (2001) 443.

[20] J. Santamaria-Gonzalez, J. Luque-Zambrana, J. Merida-Robles, P. Maireles-Torres, E. Rodriguez-Castellon and A. Jimenez-Lopez, Catal. Lett. 68 (2000) 67.

[21] M. Baltes, K. Cassiers, P. Vander Voort, B.M. Weckhuysen, R.A. Schoonheydt and E.F. Vansant, J. Catal. 197 (2001) 160.