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Silica and boron nitride supported molybdenum and vanadium oxide catalysts for propane oxidation

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Abstract

A range of silica supported molybdenum catalysts and ranges of vanadium catalysts supported on silica and boron nitride have been prepared, characterised and tested for propane oxidation. The silica supported molybdenum catalysts demonstrated appreciable activity for propane total oxidation to carbon oxides, with trace acrolein in some cases. The silica supported vanadium catalysts were also active for propane oxidation, and although the major oxidation product was CO_2, higher selectivity to acrolein was observed when compared to the silica supported molybdenum catalysts. The use of boron nitride as support significantly increased the selectivity towards acrolein. The boron nitride support has a low surface area (SA) ($7\,m^2\,g^{-1}$) and it is also hydrophobic. Temperature programmed reduction showed that the vanadium species supported on boron nitride were chemically different from those supported on silica and it is envisaged that this in combination with the characteristics of the boron nitride support are important for the improved acrolein selectivity.

Keywords: Propane oxidation; Silica; Boron nitride; Molybdenum; Vanadium

1. Introduction

The identification of improved catalysts showing high activity and selectivity for the effective transformation of short chain alkanes to higher value products is a major challenge. There are many potential routes for upgrading alkanes, amongst which one of the most attractive is direct gas phase catalytic selective oxidation. The major products from current industrial oxidation processes are alkenes, alcohols, aldehydes, anhydrides and acids. Up to now, the only three industrial processes in operation or close to operation using short chain alkane feedstocks are *n*-butane oxidation to maleic anhydride on VPO catalysts, propane/butane aromatisation (Cyclar process) on Ga-MFI zeolite and propane ammoxidation on $VSbO/Al_2O_3$. Recently, many reports and patents have dealt with propane oxidation to acrylic acid on MoNbSb(Te)VO catalysts, but such a process is very far from commercialisation.

Generally, the oxidation of short chain alkanes requires a relatively high temperature in order to activate the alkane, but unselective gas phase homogeneous reactions can then predominate and the partial oxidation products can be destroyed. Against this background, there remains a drive to study new catalysts and to determine the influence of gas phase reactions and surface reactions in an attempt to promote more selective surface chemistry.

One of the most difficult alkanes partial oxidation reactions is the selective oxidation of methane to methanol. Many different catalysts have been studied, however, two of the most widely study to and successful are molybdenum and a vanadium oxide supported on silica [1]. In this study molybdenum and a vanadium oxide catalysts supported on silica

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have been prepared with varying loadings and the catalysts tested for their efficacy in propane oxidation. The studies have been extended by preparing a range of vanadium oxide catalysts supported on boron nitride. Boron nitride was selected as it is recognised as an inert material and it is also hydrophobic, and of both these properties maybe beneficial for potential alkanes selective oxidation catalysts.

2. Experimental

2.1. Catalyst preparation

A range of molybdenum and vanadium silica supported catalysts were prepared using an incipient wetness impregnation method. Fumed silica (BDH Cab-O-Sil M5, SA $= 194\,m^2\,g^{-1}$) was impregnated with a solution ($4.2\,ml\,{g_{silica}}^{-1}$) containing the appropriate concentration of ammonium metavandadate and ammonium hetpamolybdate. The resulting materials were dried in an oven at 100 °C for 16 h and calcined at 700 °C for 4 h in static air.

The boron nitride supported catalyst was also prepared using an impregnation technique. The boron nitride support (Strem, SA $= 7\,m^2\,g^{-1}$) wads impregnated by a solution of vanadyl acetylacetonate dissolved in methanol ($3.0\,ml\,{g_{BN}}^{-1}$). This material was dried at 100 °C for 16 h and calcined at 700 °C for 4 h in static air. A summary of the catalysts prepared and the BET surface areas (SA) are presented in Table 1.

2.2. Catalyst testing

Catalyst performance was evaluated in a fixed bed stainless steel microreactor using molecular oxygen as oxidant. Gas flow rates were regulated electronically using thermal mass flow controllers, helium was used as a diluent and the reaction gas had the ratio $C_3H_8/O_2/He = 2/1/7$. Catalysts were pelleted to a uniform particle size range of 250–600 μm. The catalyst bed was packed to a constant volume and was supported between plugs of silica wool in a 1/2 in. o.d. stainless steel reactor tube. A gas hourly space velocity of $2400\,h^{-1}$ was used and reaction temperatures were determined by a thermocouple placed in the centre of the catalyst bed. Analysis was performed on-line using a Varian 3800 GC with a 2 m packed molecular sieve 13X and a 2 m packed Poropak Q column. The columns were valved in a series/by-pass configuration with a thermal conductivity detector (TCD) and flame ionisation detector (FID) in series. Propane conversion was calculated by the difference between inlet and outlet concentration and selectivities determined by the proportion of products after correction for the carbon number of the products. Carbon balances were in the range 98–102% for all reactions.

Table 1
Summary of catalysts prepared and BET surface areas

Catalyst	BET SA ($m^2\,g^{-1}$)
2.5 wt.% Mo/SiO_2	168
3.5 wt.% Mo/SiO_2	161
5 wt.% Mo/SiO_2	109
6.9 wt.% Mo/SiO_2	49
10 wt.% Mo/SiO_2	45
15 wt.% Mo/SiO_2	35
2.5 wt.% V/SiO_2	163
3.5 wt.% V/SiO_2	156
5 wt.% V/SiO_2	118
7 wt.% V/SiO_2	49
10 wt.% V/SiO_2	35
15 wt.% V/SiO_2	32
SiO_2	194
7 wt.% V/BN	6
21 wt.% V/BN	6
35 wt.% V/BN	5
BN	7

2.3. Catalyst characterisation

Catalyst surface areas were measured by the BET method, using a Micromeritics ASAP 2010 apparatus. Prior to surface area determination catalysts were degassed at 75 °C for 6 h. Measurements were carried out at 77 K using multiple point high purity nitrogen adsorption.

Powder X-ray diffraction was performed using an Enraf Nonius FR590 diffractometer with a Cu source operated at 30 mA and 40 kV. A Ge(1 1 1) monochromator was used to select Cu Kα X-rays. The powdered samples were compressed into an aluminium sample holder, which was rotated during data collection to compensate for any ordering of crystallite orientation which may occur during sample packing. Data were calibrated against a silicon standard and phase identification was performed by matching the experimental pattern against standard entries in the JCPDS powder diffraction file.

The apparatus used for these experiments was a TPR/TPO/TPD Micromeritics Autochem 2910 equipped with a TCD detector. The reducing gas used in all experiments was 10% H_2 in Ar, with a flow rate of 50 ml min^{-1}. The temperature range explored was from room temperature to 1000 °C. The heating rate was maintained at 10 °C min^{-1} for all samples whilst the sample mass was varied depending on the sample under study. Details of specific conditions are given with the TPR profiles and sample masses were in the range 25–200 mg.

3. Results and discussion

3.1. Silica supported molybdenum catalysts

The oxidation a propane over selected Mo silica supported catalysts are shown in Fig. 1. A range of activity was exhibited and this was dependent on Mo loading. The 5 wt.% catalyst was the most active, showing appreciable propane conversion above 150 °C, whilst above 275 °C conversion did not significantly increase further. Propane conversion increased rapidly above 225 °C for the 6 wt.% catalyst and this was by far the most active catalyst at 400 °C. The catalysts with the lowest and highest Mo loadings of 3.5 and 10 wt.% showed similar activity. Initial activity was observed around 275 °C and this increased to ca. 10% at 550 °C. It is difficult to normalise the rates of propane conversion in terms of surface area as silica alone showed low activity and the surface area measurements do not discriminate between inactive silica and the active supported phase. However, the 6 wt.% catalyst, which was the most active at 400 °C, was prepared because this loading is the theoretical monolayer and hence the potential for a highly dispersed molybdenum phase is greatest. Blank data from an empty reactor tube showed low activity throughout the temperature range when compared to propane conversion over the catalysts.

The major reaction product with all the Mo based catalysts was CO_2. Other minor products were also detected with some catalysts, selectivity to these products is shown at 10% propane conversion (Fig. 2). The 6 wt.% catalyst showed 100% selectivity towards CO_2. This catalyst has an Mo loading close to the theoretical monolayer. Similar high total oxidation activity has also been observed with ZrO_2 catalysts containing Mo close to monolayer coverage [2]. From in situ Raman studies of Mo/ZrO_2 it has been postulated that Mo spreads over the support under reaction conditions and maximum Mo dispersion is achieved at theoretical monolayer coverage. The same type of

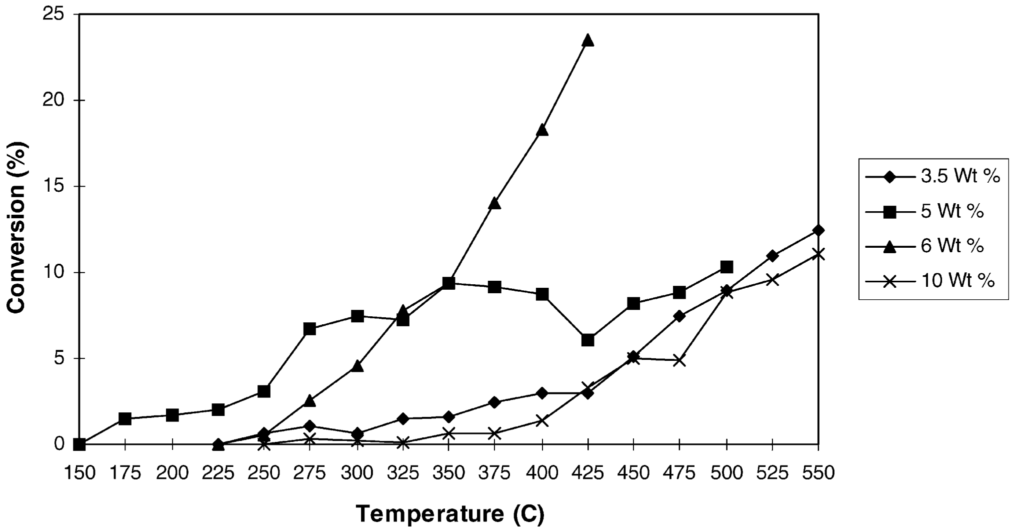

Fig. 1. Activity for propane oxidation over silica supported molybdenum catalysts (GHSV = 2400 h^{-1}, $C_3H_8/O_2/He = 2/1/7$).

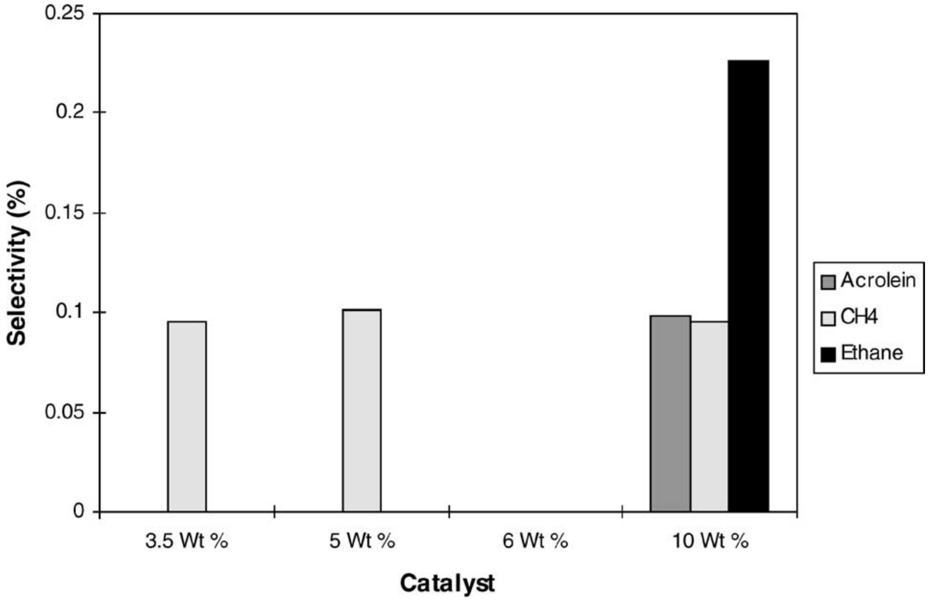

Fig. 2. Selectivity to products other than CO_2 at 10% propane conversion over the silica supported molybdenum catalysts.

highly dispersed Mo phase may be formed on the 6 wt.% Mo/SiO_2 catalysts under reaction conditions and this could account for the high total oxidation activity. Catalysts with a lower Mo loading of 3.5 and 5 wt.% showed trace selectivity towards methane. The 10 wt.% catalyst also showed trace selectivities to methane, ethane and acrolein. However, it must be noted that in all cases the selectivity to products other than CO_2 was very low.

Characterisation of the range of catalysts by powder XRD indicated that crystalline MoO_3 was present in all cases. The diffraction peaks from MoO_3 on the low loading catalysts were relatively broad with low intensity. Increasing the loading resulted in an increase in the intensity and a decrease in peak width. These data indicate a probable increase in the proportion of MoO_3 with a greater crystallite size as the Mo loading was increased. A similar conclusion can also be drawn from laser Raman, as a band at ca. 818 cm^{-1} was present in all the catalysts and an MoO_3 standard and is assigned to a Mo=O vibration in MoO_3 [3]. The catalysts also showed a band at ca. 995 cm^{-1} indicating that the catalysts also had β-silicomolybdic acid on the surface [3].

Under the reaction conditions used in this study the range of silica supported molybdenum catalysts are active for the deep oxidation of propane. It has been recognised that the formation of β-silicomolybdic acid is important for selective methane oxidation [4], whilst silica supported MoO_3 has been implicated in methane deep oxidation [4]. The catalysts prepared in this study are comprised of a combination of dispersed MoO_3 and β-silicomolybdic acid, either of which or the combination are effective for total propane oxidation.

3.2. Silica supported vanadium catalysts

The conversion of propane over representative catalysts with varying V wt.% loadings on silica are shown in Fig. 3. In contrast to the behaviour shown by the Mo silica supported catalysts, the vanadium supported catalysts all showed broadly similar activity. Initial activity was observed around 275 °C. At temperatures below 425 °C the lowest loading 3.5 wt.% catalyst demonstrated slightly higher propane oxidation activity. At higher temperatures the 7 wt.% catalyst was marginally more active whilst the highest loading of 10 wt.% was the least active.

As observed for the Mo catalysts, the V catalysts also showed high selectivity towards CO_2. However, the selectivity to other products was higher over the

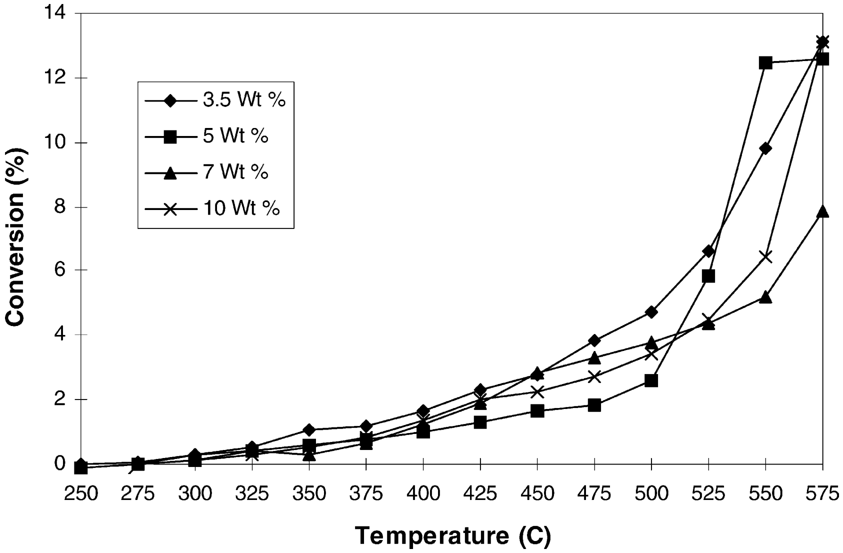

Fig. 3. Activity for propane oxidation over silica supported vanadium catalysts (GHSV = 2400 h^{-1}, $C_3H_8/O_2/He$ = 2/1/7).

catalysts. The selectivity to these other products at 10% propane conversion is shown in Fig. 4. With the 3.5, 5 and 10 wt.% catalysts, acrolein was the most selective product after CO_2. These catalysts also showed low selectivity to other oxygenated products, these were other C_3 compounds with the most abundant being acrylic acid. Selectivity towards methane was also observed. The 7 wt.% catalyst also showed selectivity towards acrolein, but the most abundant product after CO_2 was methane. No other C_3 oxygenated products were observed with the 7 wt.% catalyst.

Below monolayer coverage (ca. 6 wt.%) no crystalline phases were detected by XRD on the silica supported vanadium catalysts. However, once the loading was increased above monolayer coverage crystalline V_2O_5 was detected. Diffraction from the

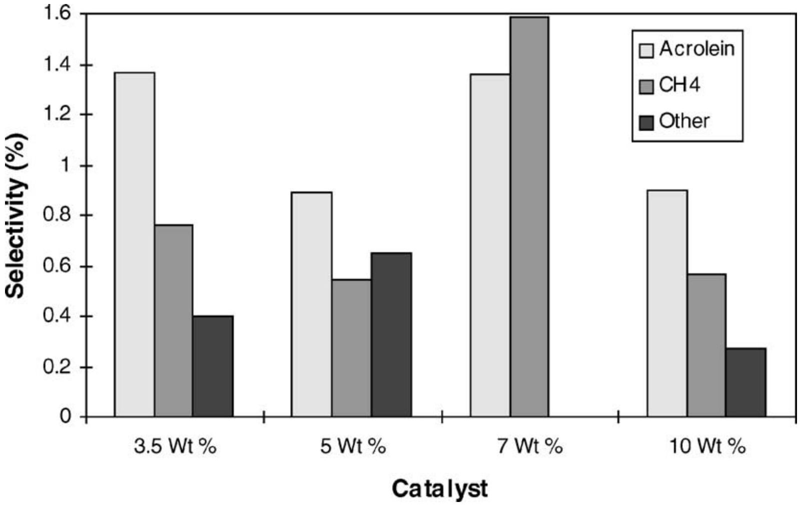

Fig. 4. Selectivity to products other than CO_2 at 10% propane conversion over the silica supported vanadium catalysts.

Table 2
Summary of laser Raman spectroscopy of silica supported vanadium catalysts and comparison with V_2O_5

Catalyst	Raman bands (cm^{-1})
2.5 wt.% V/SiO_2	n.a.
3.5 wt.% V/SiO_2	n.a.
5 wt.% V/SiO_2	995, 698
6 wt.% V/SiO_2	995, 698
7 wt.% V/SiO_2	995, 698, 515
10 wt.% V/SiO_2	994, 698, 533, 406, 284
15 wt.% V/SiO_2	987, 698, 524, 404, 284
V_2O_5	985, 700, 526, 405, 283

V_2O_5 phase became more predominant as the loading was increased. Laser Raman spectroscopy of the catalysts showed a high background due to fluorescence in the laser source, but broad Raman bands were detectable (Table 2). With vanadium loadings less than 5 wt.% it was not possible to observe any Raman features. Between 5 and 10 wt.% loading Raman bands characteristic of V_2O_5 were observed. The catalysts in this range of loading demonstrated a band at ca. 995 cm^{-1} and this was shifted in frequency compared to 985 cm^{-1} for the V_2O_5 standard. This shift in frequency is consistent with the interaction of the vanadium oxide with the silica support. The 15 wt.% catalyst showed a Raman spectrum identical to bulk V_2O_5 and it is evident that the interaction between the vanadium oxide and silica is diminished at the higher loadings.

The temperature of programmed reduction profiles for selected silica supported vanadium catalysts are shown in Fig. 5. The 10 wt.% catalyst had an extremely broad reduction peak with a maximum in the region of 500 °C. Decreasing the vanadium loading did not significantly alter the temperature of the reduction peak maxima, but it did result in a narrowing of the reduction feature and similar results have been observed previously [5]. These data indicate that the type of vanadium species on the 5–15 wt.% catalysts were not significantly different, and this is consistent with the XRD and laser Raman spectroscopy data. Interesting TPR results were observed for the catalyst with a 3.5 wt.% loading. The same characteristic broad peak was observed around 515 °C, however, a narrow reproducible reduction feature was observed at 225 °C. The observation of this lower temperature reduction peak is significant as the 3.5 wt.% catalyst showed the greatest propane conversion over the range of the lower temperatures investigated.

3.3. Boron nitride supported vanadium catalysts

A series of vanadium catalysts supported on boron nitride were prepared and tested for propane oxidation.

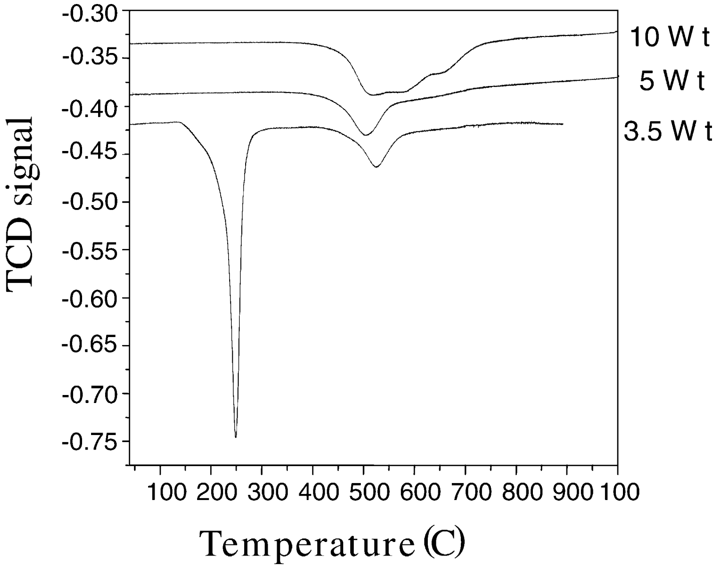

Fig. 5. Temperature programme reduction profiles of the boron nitride supported catalysts (10% H_2/Ar, 10 °C min^{-1}).

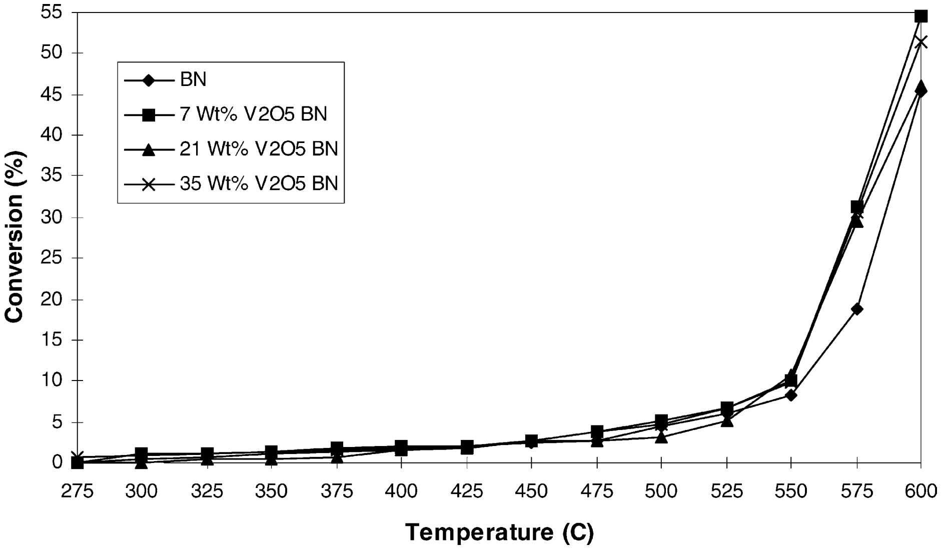

Fig. 6. Activity for propane oxidation over born nitride supported vanadium catalysts (GHSV = 2400 h^{-1}, $C_3H_8/O_2/He = 2/1/7$).

Boron nitride has not been studied extensively as a support, however, there are recent literature reports with Pt supported catalysts [6], The activity of boron nitride supported vanadium catalysts are shown in Fig. 6. The boron nitride supported catalysts and boron nitride showed broadly similar activity. Near complete oxygen conversion was observed over the silica supported catalysts at 575 °C and propane conversion was limited to <20%. With the boron nitride catalysts are a oxygen conversion was a lower and significantly higher conversions were observed at 600 °C. Across the entire temperature range born nitride supported vanadium catalysts showed higher conversion when compared to boron nitride alone, although this

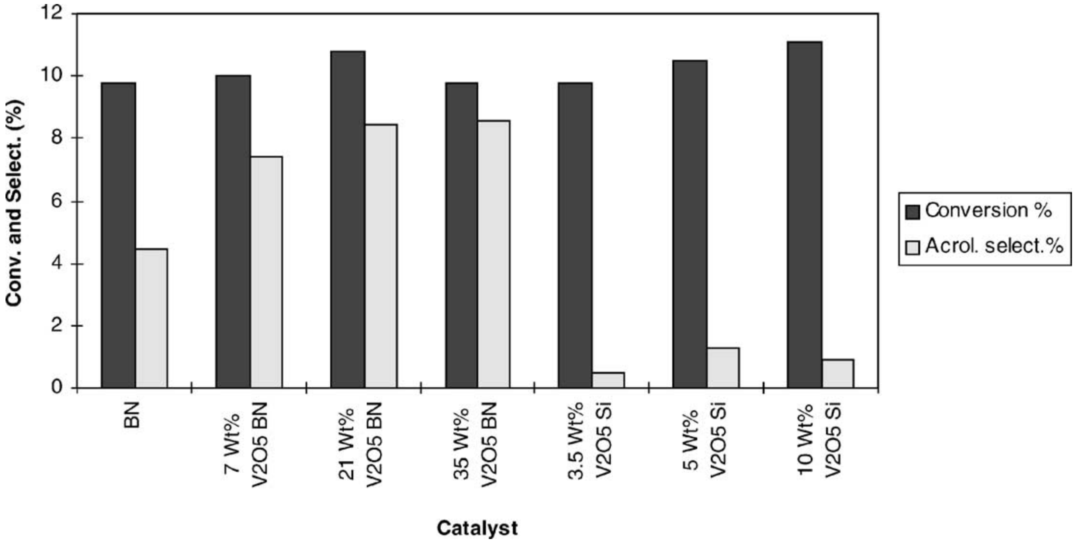

Fig. 7. Selectivity to products other than CO_2 at 10% propane conversion over the boron nitride supported vanadium catalysts.

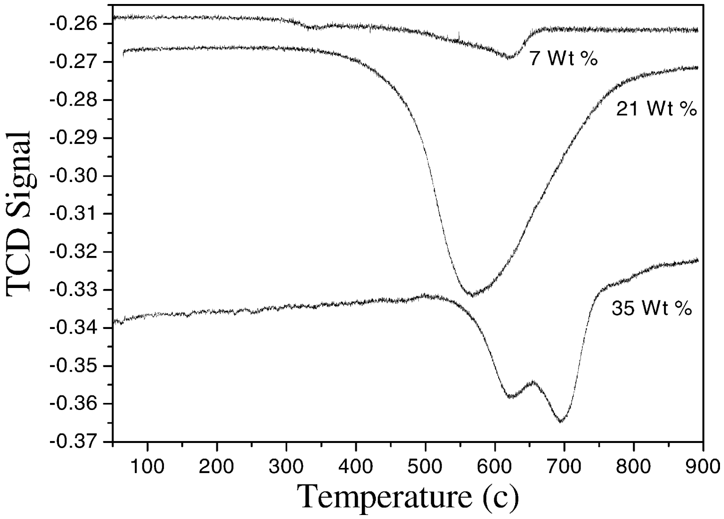

Fig. 8. Temperature programme reduction profiles of the boron nitride supported catalysts (10% H_2/Ar, 10 °C min^{-1}).

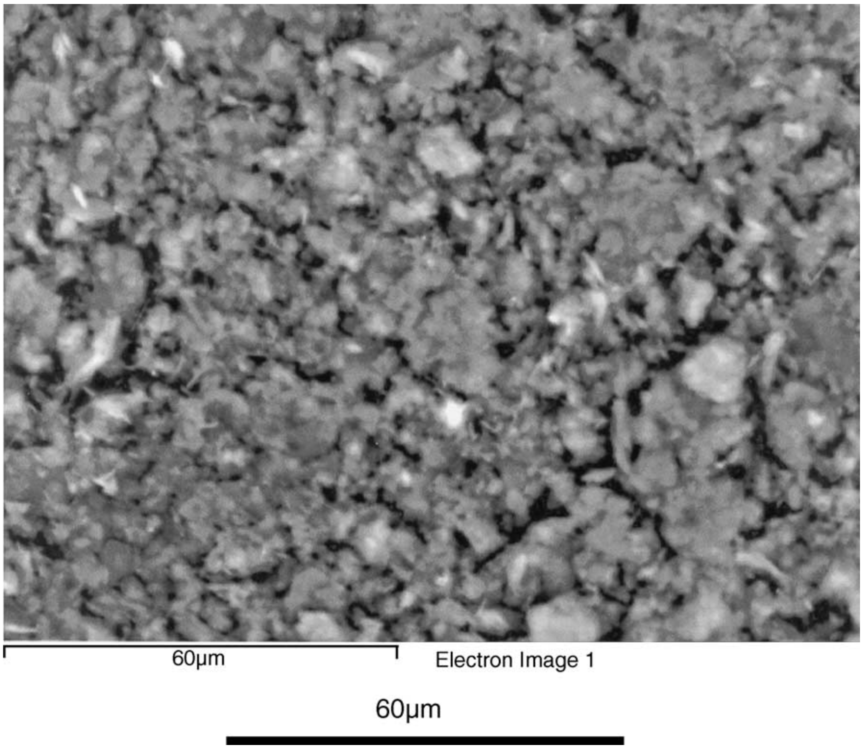

Fig. 9. SEM image of 35 wt.% vanadium supported on boron nitride.

increase was marginal. The similarities between the activities suggest that homogeneous gas phase reactions are important for propane oxidation, but initial activity was observed at 300–325 °C, much lower temperatures than observed for the blank reaction in an empty tube. These observations indicate that there is also a significant contribution from surface catalysed reactions from the boron nitride and the supported catalysts.

The major products from propane oxidation using the boron nitride catalysts were CO_2 and acrolein. Carbon-dioxide was the most abundant oxidation product, a comparison of the selectivity towards acrylic that approximately 10% conversion is shown in Fig. 7. It is clear that the selectivity towards acrolein is appreciably greater over the boron nitride based catalysts when compared to the silica systems. Boron nitride shows selectivity towards acrolein, and this is increased by the addition of vanadium. At 10% propane conversion selectivity towards acrolein was in the region of 8% for catalysts with vanadium loadings of 21 and 35%.

Powder X-ray diffraction studies of the boron nitride supported catalysts only indicated diffraction from the highly crystalline boron nitride phase. Laser Raman spectroscopy was also little help in characterising these catalysts as it was not possible to obtain any information using the argon ion laser source. The temperature programmed reduction profiles for the boron nitride supported catalysts are shown in Fig. 8. The reduction behaviour of the 7 and 21 wt.% catalysts were similar, both exhibited a broad reduction peak at 600 and 575 °C, respectively. The reduction profile of the 35 wt.% catalyst was different, as reduction was observed at higher temperature, with two reduction peaks at 620 and 700 °C. This may indicate that the higher loading catalyst contained two types of vanadium species, whilst the lower loadings contain only one. The reduction peak at 620 °C for the high loading catalyst may well correspond to the single reduction peak observed for the lower loading catalysts.

As it was not possible to obtain XRD and laser Raman data on the boron nitride supported catalysts the 35 wt.% catalyst was also investigated by SEM and EDX (Figs. 9 and 10). The catalyst consisted of a single morphology which was angular and blocky in nature with a crystallite size of ca. 6 μm. EDX studies scanning the V Kα_1 emission showed that the

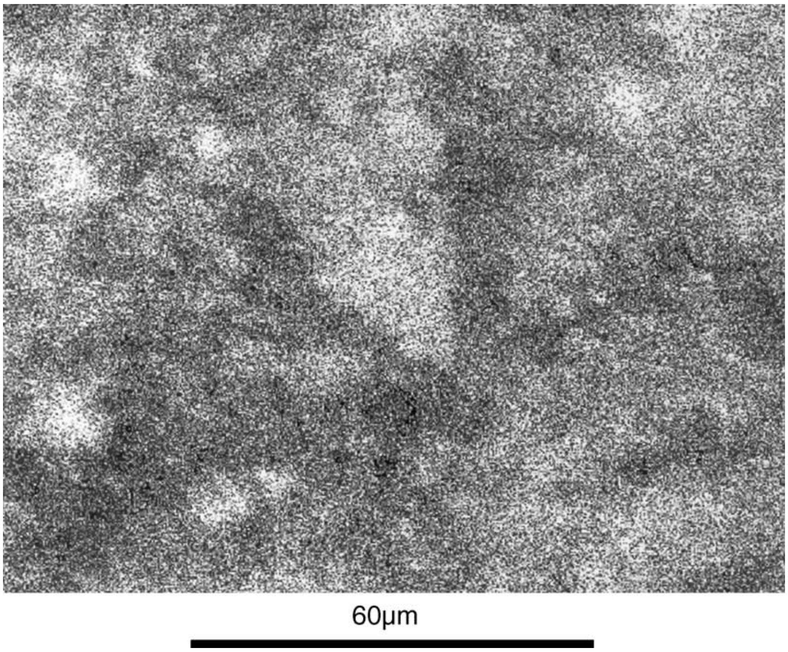

Fig. 10. Energy dispersive X-ray analyst spectrum of V Kα1 emission for 35 wt.% vanadium on boron nitride: light coloured areas are vanadium signal.

vanadium was well dispersed throughout the catalyst and was not present a as large crystallites, this was also confirmed by the powder X-ray diffraction studies.

Although the yields of selective oxidation products where relatively low over the catalysts in this study compared to other systems in the literature, it is clear that the boron nitride supported catalysts are significantly more selective than the silica supported vanadium catalysts. Further work is still needed to establish how this improvement is achieved, however, it is interesting to comment on some important differences between these catalysts in relation to their activity. Firstly, the fumed silica support has a high surface area ($194\,m^2\,g^{-1}$) compared to the boron nitride ($7\,m^2\,g^{-1}$). Furthermore, silica is hydrophilic whilst boron nitride has a hydrophobic surface. Both factors may be important to reduce over oxidation of partially oxidised products such as acrolein to carbon oxides. The combination of the low area and hydrophobic surface of boron nitride could result in a decrease of the adsorption of acrolein and further oxidation on the surface. Consequently, it would be expected that selectivity to partially oxygenated products would be preserved to a greater extent on the hydrophilic support. It is also clear that the vanadium species supported on boron nitride reduce at a much higher temperature than vanadium supported on silica. Thus, the lability of lattice oxygen would be expected to influence product selectivity. The differences observed in the reduction behaviour are most likely associated with the form of the vanadium in the different catalyst systems,V_2O_5 was identified on the silica supported catalysts, whilst at to date it has not been possible to characterise the vanadium species on the boron nitride catalysts. Further microscopy is under way and XPS studies are planned to characterise more fully the vanadium species on these boron nitride based catalysts.

4. Conclusions

A range of molybdenum and vanadium catalysts supported on silica have been prepared, characterised and tested for the oxidation of propane. The silica supported molybdenum catalysts demonstrated appreciable activity for propane total oxidation to carbon oxides, with trace acrolein in some cases. The silica supported vanadium catalysts were also active for propane oxidation, and although the major oxidation product was CO_2, higher selectivity to acrolein was observed when compared to the silica supported molybdenum catalysts. A further series of vanadium catalysts were prepared using a boron nitride support. The use of boron nitride as support significantly increased the selectivity towards acrolein. The boron nitride support has a low surface area ($7\,m^2\,g^{-1}$) and it is also hydrophobic. Temperature programmed reduction showed that the vanadium species supported on boron nitride were chemically different from those supported on silica and it is envisaged that this in combination with the characteristics of the boron nitride support are important for the improved acrolein selectivity.

Acknowledgements

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