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The development of supported vanadia catalysts for the combined catalytic removal of the oxides of nitrogen and of chlorinated hydrocarbons from flue gases

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Abstract

Supported vanadia catalysts are commercially used to remove the oxides of nitrogen contained in oxygen-containing flue gases by selective catalytic reduction (SCR) using ammonia as reductant. This paper examines the possibility of using the same catalysts for the complete oxidation of chlorinated hydrocarbons (ethyl chloride or chlorobenzene) in the presence of NO and ammonia. It is shown that vanadia supported on an alumina-modified zirconia is capable of giving 100% conversion of the chlorinated molecules while giving also 100% conversion of the NO over a relatively wide range of temperature (593–683 K). This material also shows a resistance to poisoning by HCl but it is slowly poisoned by SO_2 if present. The addition of tungsten oxide to the formulation has no significant effect on the catalytic behaviour towards NO and ethyl chloride but it improves the resistance to SO_2.

Keywords: Vanadia; Chlorinated hydrocarbons; Selective catalytic reduction

1. Introduction

The removal of nitrogen oxides from oxygen-containing flue gases emitted from power stations is usually carried out using ammonia as reductant with a catalyst comprising of vanadia supported on titania [1]. Commercial catalysts frequently contain tungsten oxide as this improves the resistance of the catalyst to sulphur poisoning. Such catalysts have also been used for the control of NO_x emissions from waste incinerators. The presence of chlorinated hydrocarbons (including dioxins and difurans) and also the oxides of nitrogen in incinerator emissions have slowed down the introduction of incineration methods. The main contributory sources of the dioxins in the flue gases are: (i) trace amounts of these molecules present in the waste which are not fully oxidised in the combustion chamber; and (ii) the formation of these molecules from precursors such as chlorinated phenols and polychlorinated biphenyls during the incineration process [2,3].

Dioxins are generally considered to be extremely hazardous to man. Long-term low-level exposure to dioxins has been shown to cause Hodgkin's disease, soft tissue sarcoma, cancer (liver, stomach and nasal), diabetes and chloracne [4,5]. In 1994, the European Union introduced legislation to limit the emissions of dioxins from incinerators and, as a result, new incinerators will have to be fitted with a system

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capable of lowering dioxin emissions in their flue gases.

There is some indication in the literature that SCR catalysts containing vanadia supported on titania are also able to oxidise chlorinated hydrocarbons and dioxin-like molecules to carbon dioxide, water and hydrochloric acid in the presence of nitrogen oxides and ammonia [6,7] and that they might therefore be suitable for the control of NO_x and chlorinated hydrocarbons in incinerator flue gases. We report here a study of the use of a range of vanadia-containing catalysts for the simultaneous reduction of NO and the oxidation of ethyl chloride or chlorobenzene. We compare the behaviour of materials supported on different oxides and show that an alumina-promoted zirconia gives the optimum behaviour for the removal of both NO and chlorinated molecule. We also report results of experiments in which HCl or SO_2 were added to the feed, showing that the addition of tungsten oxide to the vanadia–zirconia–alumina formulation assists the resistance of the catalyst to SO_2.

2. Experimental

2.1. Catalyst preparation

A range of catalysts with low loadings of vanadia were prepared by impregnation of a series of supports (see Table 1) with appropriate amounts of ammonium metavanadate dissolved in oxalic acid to give catalysts containing the desired weight percentages of vanadia [8]. The supports were first calcined in air at 773 K for four hours. After impregnation, the samples were vacuum-dried at 353 K, then dried further in air at 393 K overnight and finally calcined at 773 K in air for 4 h. The commercial deNO_x catalyst was calcined in air for 4 h at 500°C. The calcined catalysts were pressed for one minute at 10 bar and sieved to particle size 212–500 μm.

The ammonium metavanadate was supplied by Aldrich. The doped zirconias were obtained from M.E.L. Chemicals. The sample of monoclinic zirconia was obtained from Gimex. The titania used was Degussa P25.

2.2. Catalyst characterisation

2.2.1. Surface area measurement

The specific surface areas, S_{BET}, and pore size distributions were determined from nitrogen physisorption measurements at 78 K, using a Micromeritics Gemini 2370. All the samples were first degassed at a pressure of 70 mTorr at 473 K. The surface areas determined are shown in Table 1.

2.2.2. Metal contents of the catalysts

The metal contents of the samples, after dissolution in HF, were determined using a Varian

Table 1
Metal contents and BET specific surface areas of the supports and calcined catalysts

Support	Theor. vanadia content (wt%)	Meas. vanadia content (wt%)	BET surface areas of supports ($m^2\ g^{-1}$)	BET surface areas of calcined catalysts ($m^2\ g^{-1}$)	Fractional coverages by vanadia (%)[a]
TiO_2 (Degussa)	4	3.9	47	34	57
ZrO_2 (Gimex)	4	3.8	51	50	51
γ-Al_2O_3	4	4.0	121	82	22
ZrO_2–Al_2O_3	4	3.8	106	72	25
ZrO_2–SiO_2	4	3.7	37	22	68
ZrO_2–La_2O_3	4	3.9	48	32	56
TiO_2 (comm.)	–	6.2	–	35	–

[a] The theoretical fractional coverage is based on the assumption that 0.145 wt% of vanadia covers 1 m^2 of support [9].

Spectra A-40 atomic absorption spectrophotometer; see Table 1.

2.2.3. Temperature programmed reduction (TPR) measurements

The TPR behaviour of the samples was measured by monitoring hydrogen consumption while increasing the temperature of the sample at a constant rate. A gas flow of 20 cm^2 min^{-1} of 5% H_2 in N_2 was passed over 20 mg of catalyst held between quartz wool plugs in a quartz reactor tube of 6 mm i.d. The reactor tube was heated in a Stanford Redcroft furnace from 373 to 923 K with a heating rate of 10°C min^{-1}. A thermal conductivity detector was used to measure the consumption of hydrogen.

2.3. Catalytic measurements

The catalytic measurements were carried out using a conventional fixed-bed micro-reactor system. The reactor was a quartz tube of 6 mm i.d. with a thermocouple placed at the end of the catalyst bed. The reactor wall and the quartz wool used to support the catalyst were inert to the reactant mixture under all the reaction conditions examined.

The activities of 200 mg samples of the catalysts were determined by carrying out isothermal tests over the range of temperature from 413 to 773 K, the temperature being increased in steps of 20 K, dwelling for 30 min at each step. The reaction test mixture used to determine the deNO_x activity contained 1000 ppm of each of nitric oxide and ammonia and 3% by volume of oxygen. A gas flow containing 700 ppm of ethyl chloride was used as the test mixture to examine the oxidation of this molecule; in one set of experiments, chlorobenzene oxidation was tested by introducing 700 ppm of this molecule from a saturator. A flow of argon of 2 cm^3 min^{-1} was added to both reaction streams to act as an internal standard and the total flow rate was increased to 100 cm^3 min^{-1} using helium, this giving a residence time over the catalyst bed of the order 0.2 s or a G.H.S.V. of the order 19000 h^{-1}. The gases were used as mixtures containing 1% nitric oxide, 1% ammonia and 0.7% ethyl chloride, all in helium, supplied by B.O.C. Ltd. Each of the gas flows was controlled by a Brooks mass flow controller (model 5850B).

The effect on the catalyst of the addition of water, HCl or SO_2 to the feed was analyzed at 613 K using 60 mg of catalyst and a total gas flow of 100 cm^3 min^{-1}. The water was added to the feed at 341 K via a syringe pump and the stainless steel interconnecting tubing was heated to 343 K to prevent water condensation.

All the experiments described above were carried out for 120 h; the compositions of the flows used are shown in Table 2.

The reactor effluent was continuously monitored by a Hewlett Packard Mass Selective Detector (HP5971A) in Single Ion Monitoring Mode. The gases monitored were nitric oxide, nitrous oxide, nitrogen dioxide, nitrogen, oxygen, carbon dioxide, carbon monoxide, ethyl

Table 2
Feed gas compositions for the catalyst testing

	Gas flows for deNO_x	Gas flows with H_2O in feed	Gas flows with HCl in feed	Gas flows with SO_2 in feed
Nitric oxide	1000 ppm	1000 ppm	1000 ppm	1000 ppm
Ammonia	1000 ppm	1000 ppm	1000 ppm	1000 ppm
Argon	2.0 vol.%	2.0 vol.%	2.0 vol.%	2.0 vol.%
Oxygen	3.0 vol.%	3.0 vol.%	3.0 vol.%	3.0 vol.%
Water	–	2.0 vol.%	2.0 vol.%	–
Hydrochloric acid	–	–	1200 ppm	–
Sulphur dioxide	–	–	–	5000 ppm
Helium	Balance	Balance	Balance	Balance

chloride, hydrochloric acid, chlorine and chlorobenzene. The data were collected and further processed using a Dell 486P/33 computer.

3. Results and discussion

The results of the analyses of the catalysts prepared and tested in this work are shown in Table 1 which also shows data for a commercial catalyst (TiO_2(comm.)) which also contained WO_3. In all but one of the laboratory-prepared catalysts, the measured vanadia contents were slightly lower than those intended but the difference was relatively insignificant. The commercial catalyst contained 50% more vanadia than did the laboratory-prepared samples. Table 1 also shows the surface areas of the various materials before and after the incorporation of the vanadia. In all cases apart from the Gimex ZrO_2, the area after inclusion of the vanadia was significantly lower than that of the fresh support, possibly because the vanadia had blocked micropores in the support or had encouraged sintering of the smaller pores. The various zirconia supports tested were chosen from a range of samples designed to show whether or not the additions to the zirconia had any significant influence on the catalytic properties of the resultant materials; these were compared with the more conventional supports, titania and alumina. The addition of a small amount of alumina (10%) to zirconia gave a large increase in the surface area, the area of the doped sample being about twice that of the commercial monoclinic zirconia sample (Gimex). In contrast, the addition of silica or lanthana did not give any increase in the surface area of the support and, in the former case, there was a significant decrease in area. Table 1 gives the approximate surface coverages of the supports, the figures being based on the assumption [9] that 1 m^2 of surface requires 0.145 wt% V_2O_5 to give full coverage. The surface areas of the clean supports were used in the calculation so no equivalent figure is given for the commercial sample; based on the surface areas of the final catalysts, it would seem that the surface coverage of the commercial sample is closer to a complete monolayer than is the case for the other samples.

Fig. 1 gives results obtained using the commercial deNO_x catalyst, showing the conversions of NO and ethyl chloride as a function of temperature in an experiment in which both were present in the reaction mixture. Complete reduction of the nitric oxide was obtained between 473 and 553 K but complete oxidation of ethyl chloride (giving water, carbon dioxide and HCl) was not achieved until about 573 K. The production of nitrous oxide was observed at temperatures above 553 K (right-hand scale). As the nitrous oxide is probably formed by the direct oxidation of the ammonia or by a combination of the ammonia with an NO molecule [10], there is less ammonia available for the conversion of the NO and the conversion of the latter therefore falls. We conclude that there is not a sufficiently wide temperature window of operation for the commercial catalyst in which complete conversion of both the nitrogen oxides and the ethyl chloride occurs. The subsequent work was therefore carried out in an attempt to find a material which would give a wider temperature window of operation for the complete removal of both types of molecule.

Previous work has shown that zirconia can be an effective support for selective de-NOx cata-

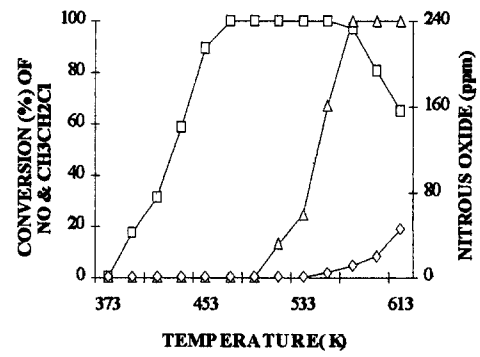

Fig. 1. Combined reduction of nitric oxide and oxidation of chlorinated hydrocarbon over the commercial catalyst (V_2O_5–WO_3/TiO_2): □ nitric oxide, Δ ethyl chloride, ◇ nitrous oxide.

lysts [11]. A zirconia-supported material, as well as a range of doped zirconia-supported materials (see Table 1) in which alumina, silica or lanthana were added to the zirconia prior to incorporation of the vanadia, were therefore examined. Figs. 2 and 3 show the results obtained for the reduction of nitric oxide and for the oxidation of ethyl chloride respectively over catalyst materials consisting of 4% vanadia supported on an undoped zirconia and on the doped zirconia supports; in contrast to the conditions used for the experiment of Fig. 1, these experiments were carried out using separate gas mixtures. The vanadia/zirconia (monoclinic) sample achieved 100% conversion of the nitric oxide between 523 and 553 K (Fig. 2); above this upper temperature, the selectivity again fell off due to the formation of nitrous oxide. With this material, 100% conversion of the ethyl chloride (giving only CO_2, water and HCl) was not obtained until above about 653 K (Fig. 3). Similarly, the vanadia/zirconia–silica sample gave 100% conversion of the nitric oxide between 573 and 623 K; however, with this material, 100% conversion of the ethyl chloride was not observed until temperatures greater than 653 K. Hence, neither of these materials gave any improvement over the commercial catalyst. Samples of vanadia supported on both zirconia–lanthana and zirconia–alumina both showed significantly improved activities for the

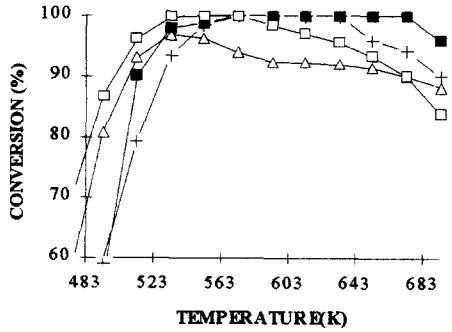

Fig. 2. Reduction of nitric oxide over vanadia supported on zirconia stabilised with additives: + 4% V_2O_5/ZrO_2-SiO_2, ■ 4% $V_2O_5/ZrO_2-Al_2O_3$, □ 4% V_2O_5/ZrO_2, Δ 4% $V_2O_5/ZrO_2-La_2O_3$.

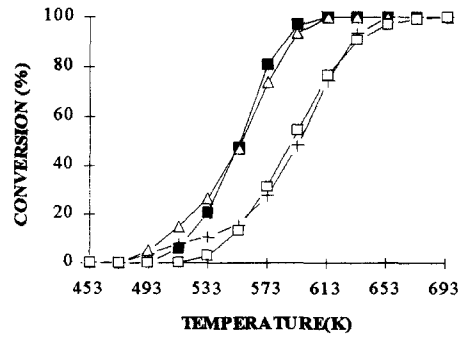

Fig. 3. Oxidation of ethyl chloride over vanadia supported on zirconia stabilised with additives: + 4% V_2O_5/ZrO_2-SiO_2, □ 4% V_2O_5/ZrO_2, ■ 4% $V_2O_5/ZrO_2-Al_2O_3$, Δ 4% $V_2O_5/ZrO_2-La_2O_3$.

oxidation of ethyl chloride, 100% conversion of ethyl chloride being obtained at temperatures above about 593 K. However, the sample consisting of vanadia on zirconia–lanthana did not give complete conversion of nitric oxide at any temperature, the highest conversion observed being 94% at 533 K. The vanadia/zirconia–alumina sample gave 100% conversion of nitric oxide over a temperature range of 533 K to 673 K. Hence, there was a window of more than 80 K, 593–673 K, over which this material gave 100% conversion of both molecules.

Figs. 4 and 5 give results equivalent to those given in Figs. 2 and 3 for samples consisting of 4 wt% vanadia supported on alumina and on titania and also show again for comparison purposes the data for the zirconia and alumina-doped samples discussed above. The

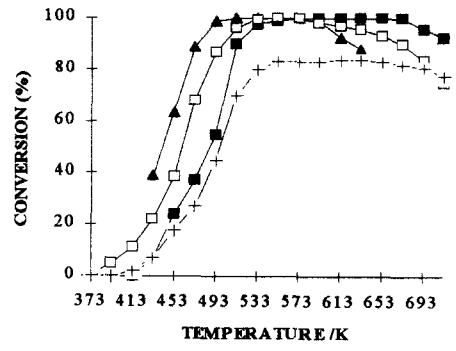

Fig. 4. Reduction of nitric oxide over 4 wt% V_2O_5 supported on undoped material. ▲ Vanadia/titania, ■ vanadia/zirconia–alumina, □ vanadia/zirconia, + vanadia/alumina.

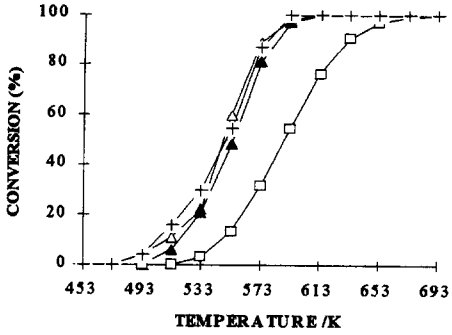

Fig. 5. Oxidation of ethyl chloride over 4 wt% V_2O_5 supported on undoped material. Δ Vanadia/titania, □ vanadia/zirconia, ▲ vanadia/zirconia–alumina, + vanadia/alumina.

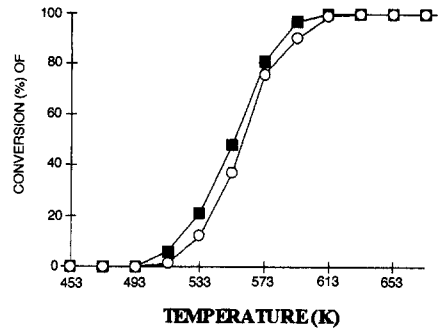

Fig. 7. Comparison of oxidation of ethyl chloride and chlorobenzene over 4 wt% vanadia on zirconia–alumina: ■ ethyl chloride, ○ chlorobenzene.

vanadia/titania sample gave 100% conversion of nitric oxide between 393 and 513 K while 100% conversion of ethyl chloride was only observed at temperatures in excess of 573 K. The vanadia/alumina sample did not give 100% conversion of nitric oxide at any temperature, the highest conversion observed being 82%; with this sample, 100% conversion of ethyl chloride was achieved at 593 K.

Fig. 6 shows the results obtained for the vanadia/zirconia–alumina sample using a mixture of NO, ammonia and ethyl chloride. It can be seen that the results were very similar to those shown above for the separate reaction mixtures. It can therefore be concluded that the presence of the NO and ethyl chloride in the same reaction mixture had little or no effect on the separate reactions.

Fig. 7 compares results for the oxidation of ethyl chloride with those for the oxidation of chlorobenzene over the vanadia/zirconia–alumina material. It can be seen that the oxidation behaviour of both materials was very similar. There was no evidence in the latter case of the production of anything other than CO_2, water and HCl. We can therefore conclude that the catalyst supported on zirconia–alumina is capable of oxidising a range of chlorinated hydrocarbons at the same time as performing the selective reduction of NO.

Since flue gases in typical incineration plants contain relatively high partial pressures of water, experiments were carried out to see if water had any significant effect on the deNO$_x$ reaction. Fig. 8 shows the influence of water on the temperature dependence of the conversion of nitric oxide. The activity was significantly re-

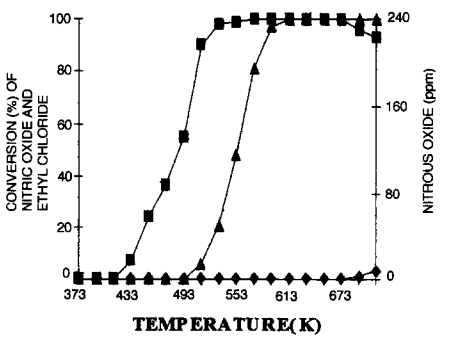

Fig. 6. Combined reduction of nitric oxide and oxidation of ethyl chloride over 4 wt% vanadia on zirconia–alumina: ▲ ethyl chloride, ■ nitric oxide, ◆ nitrous oxide.

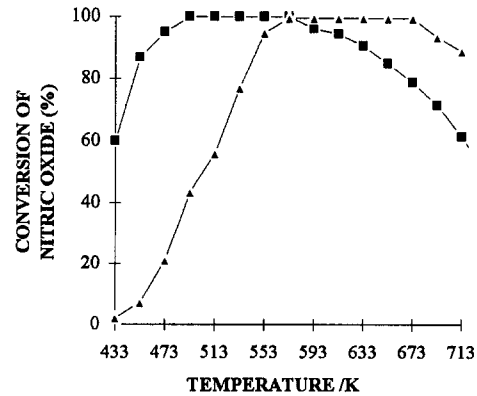

Fig. 8. Influence of water on the conversion of nitric oxide over 7% $V_2O_5/ZrO_2–Al_2O_3$: ■, 0% water; ▲, 4.5% water.

duced on the addition of 4.5 vol.% water to the feed. However, the selectivity to nitrogen at temperatures greater than 573 K was improved as no nitrous oxide was observed at temperatures below 693 K in the presence of 4.5 vol.% of water.

Fig. 9 shows the NO conversion of the vanadia/zirconia–alumina catalyst as a function of time in various atmospheres at 613 K. The activity was highest for the atmosphere containing only ammonia and NO but it dropped off steadily with time; however, when the catalyst was heated briefly in He to 723 K and then returned to the original temperature, the initial activity was regained. The activity then dropped off again over a period of some 10 h and remained constant at the lower level for some 60 h. The original activity was restored by the treatment in He at the higher temperature.

The stability of the catalyst was also tested with 2% water and with 2% water and 1200 ppm hydrochloric acid added to the feed. In both cases, the activity was lower than in the situation without additives, in agreement with the results of Fig. 8. It is interesting to note that the initial drop of activity was somewhat smaller than in the absence of water and that there was little loss of activity after the first three hours. We can conclude that the loss of activity noted in the experiments without the addition of water

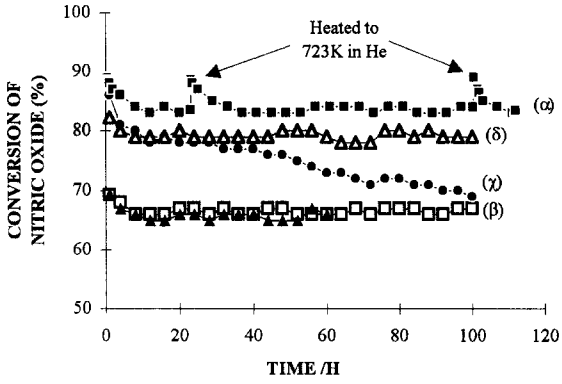

Fig. 9. Stability plots for 6 wt.% $V_2O_5/ZrO_2-Al_2O_3$ with poisons added to feed. ■, water = 0%; □, water = 2%; ▲, water = 2%, HCl = 1200 ppm; ●, SO_2 = 5000 ppm; △, SO_2 = 5000 ppm with 4% WO_3 added to the catalyst.

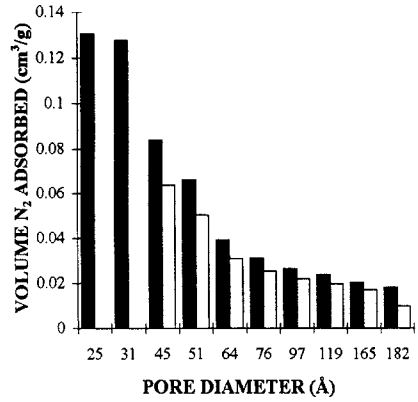

Fig. 10. Pore volume distribution of 6 wt.% vanadia/zirconia–alumina. ■, before sulphur dioxide treatment; □, after sulphur dioxide treatment.

was probably due to the gradual adsorption on the active sites of the catalyst of the water produced in the selective reduction reaction. In the presence of added water, the activity was lowered much further but the effect of the accumulation of the product water was then less significant. The results reported here are in agreement with data on the effect of water published in the literature [11–14].

When 5000 ppm of sulphur dioxide was added to the feed (see Fig. 10), the catalyst deactivated steadily as a function of time. However, when a zirconia–alumina supported catalyst containing 4% tungsten oxide in addition to the vanadia was tested, it was found that the initial conversion was similar to that of the catalyst without the tungsten and that the promoted material did not deactivate to any significant extent in the presence of sulphur dioxide. It will be shown elsewhere that small amounts of tungsten oxide had a slight beneficial effect on the activity of the vanadia/zirconia–alumina material for the oxidation of ethyl chloride [15].

Fig. 10 shows pore volume distributions obtained for the 6 wt.% vanadia/zirconia–alumina material before and after the experiment with sulphur dioxide shown in Fig. 9. The fresh material contained a significant proportion of micropores; however, after treatment with sulphur dioxide for 100 h, the smallest pores had completely disappeared and there was a reduc-

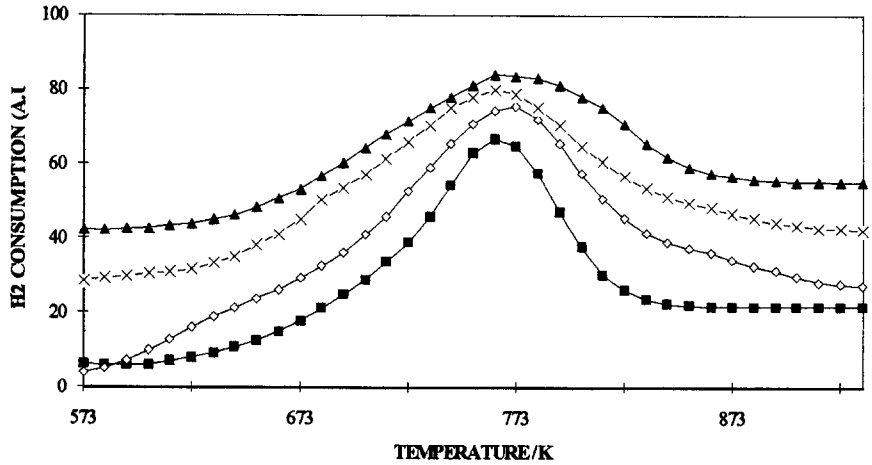

Fig. 11. TPR profile for vanadia supported on: ▲ alumina, ■ titania, ◇ zirconia, and × zirconia–alumina.

tion in the volume of the larger pores. The deactivation of the unpromoted material was therefore probably the consequence of pore blockage by the deposition of ammonium sulphate.

In order to see whether or not the support had any effect on the reduction behaviour of the vanadia added to the catalysts, the TPR data shown in Fig. 11 were obtained. The profiles were all similar, showing one broad peak with the maximum hydrogen consumption at about 773 K. The vanadia species on all the catalysts were therefore very similar in character and there was no evidence for the presence of crystalline vanadia [8]. It therefore appears that the main effect arising from a change in the nature of the support was a consequence of the increase in surface area of the support when the additive was included. As shown in Table 1, the fractional coverage, calculated assuming that all the vanadia was monodispersed on the support surfaces, was lowest (ca. 25%) for the zirconia–alumina material. We shall examine in more detail elsewhere [15] the effect of vanadia loading on these catalysts. It will be shown that higher vanadia loadings give rise to higher proportions of polymeric vanadia species on the surface which tend to favour the formation of nitrous oxide from ammonia and NO [10]. We conclude here that the addition of alumina to the zirconia support stabilised a higher surface area and that the resultant vanadia-containing material had a relatively high concentration of monomeric vanadia species, this favouring selective production of nitrogen over a wider range of temperatures than would be found if polymeric species were present. This enables the material to exhibit the wide temperature window shown in Fig. 10 for the simultaneous removal of NO and ethyl chloride.

4. Conclusion

The addition of small amounts of alumina to zirconia not only improves its mechanical strength and increases its surface area but also improves its selectivity towards nitrogen in the deNO$_x$ reaction at higher temperatures as well as increasing its activity for the oxidation of chlorinated hydrocarbons. This catalyst is stable in the presence of hydrochloric acid and, when promoted by tungsten oxide, shows negligible deactivation in the presence of sulphur dioxide.

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