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Calorimetric measurements of the acidity of supported vanadium oxides prepared by ALE and impregnation

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Abstract

The surface acidic properties of supported vanadium oxide catalysts prepared by atomic layer epitaxy (ALE) and for comparison by a conventional incipient wetness impregnation were investigated by adsorption microcalorimetry, using ammonia as probe molecule. The acidic characteristics were strongly affected by the preparation method and the oxide supports. When using γ-Al_2O_3 and TiO_2 as supports, the acidic character of supported vanadium catalysts always decreased compared to vanadia-free supports, whereas on weakly acidic SiO_2, new acidic centres were created when depositing V_2O_5. The same types of acidic sites, Lewis and Brönsted, were present in all the catalysts, but those prepared by ALE showed stronger acidity. The ALE samples were more easily reduced by H_2 thermo-programmed reduction and were twice as active as the impregnated samples in propane dehydrogenation to propene.

Keywords: Supported vanadium oxide; Adsorption calorimetry; ALE; Acidity

1. Introduction

Vanadium oxide based catalysts are used in many oxidation processes such as the selective oxidation of methanol or toluene [1,2] or the oxidative dehydrogenation of alkanes [3–6], but also in the selective catalytic reduction of NO by ammonia [7,8]. A number of investigations have been devoted to the characterisation of vanadium pentoxide spread over the surface of oxide supports [9–12]. However, few papers are reporting the characterisation of vanadia/metal oxide catalysts prepared by a gas-phase method [13–16]. Materials of this class are of growing interest in a wide range of practical applications.

The aim of these methods is that the supported oxides do not form three-dimensional crystal phases, but rather a patchy or continuous ''monolayer'' covering the support. Among these methods, a sophisticated gas-phase deposition method, atomic layer epitaxy (ALE), was first introduced for thin film growth [17] and later expanded to tailored catalyst preparation [18–20]. This technique closely linked to grafting and chemical vapour deposition (CVD) is based on a systematic use of surface saturation through chemisorption and, it is thus, providing the means for adsorption control in catalyst processing [19]. More detailed articles concerning the theory of ALE and its use in the preparation of catalysts can be found in the literature [17–21]. In the present contribution, atomic layer epitaxy (ALE) and for comparison a conventional impregnation method were applied to prepare supported vanadium oxide catalysts.

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As the vanadium dispersion depends on the nature of the oxide support, the influence of both the preparation method and acidic character of the support on the dispersion, acidic properties and catalytic properties of the samples was studied. Silica, γ-alumina and titania have been used as supports, since they possess different acid–base character. The surface acidity was determined by ammonia adsorption microcalorimetry which gives the number and strength of surface acid sites. To ensure that in the case of supported catalysts, the compounds to be reduced are present on the surface or are potentially available to the surface, temperature-programmed reduction (TPR) has been used to investigate the reducibility of the catalysts. Differences in the catalytic behaviour were studied in the reaction of propane dehydrogenation to propene at 500°C.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation by ALE

A vanadium oxide layer was deposited by the reaction of a precursor with the surface hydroxyl groups of the support. The supports (SiO_2, aerosil 200 and γ-Al_2O_3, oxid C from Degussa) were pretreated in air for 16 h at 250°C. The pre-heating treatment was continued at 250°C in a fixed-bed flow-type reactor [18] (Microchemistry Ltd.), in nitrogen flow for 5 h (pressure of 1–3 kPa). The solid precursor, vanadyl acetylacetonate $VO(C_5H_7O_2)_2$, was vaporised at 170°C and transported, in nitrogen, downwards through the bed of support. The VO-$(acac)_2$-support reaction was carried out at 180°C for 10 h followed by nitrogen purge for 2 h at the reaction temperature. For the removal of the ligand residues in the samples, an air treatment was effected at 350°C for 6 h.

2.1.2. Preparation by impregnation

The supports (SiO_2, aerosil 200; γ-Al_2O_3, oxid C; and TiO_2, P25, 75% anatase from Degussa) were impregnated to incipient wetness with ammonium metavanadate (NH_4VO_3 from Strem Chemicals, 99% purity) aqueous solutions. After drying for 16 h at 110°C, the solids were calcined in air flow at 500°C for 12 h.

2.2. Catalyst characterisation

The vanadium concentration of each sample was determined by ICP atomic emission spectroscopy in a Spectroflame-ICP instrument. The specific surface area of the catalysts was calculated by the BET method from the N_2 adsorption–desorption isotherms recorded at −196°C. The catalysts were also characterised by X-ray diffraction, electron paramagnetic resonance (EPR), X-ray photoelectronic spectroscopy (XPS), and ^{51}V nuclear magnetic resonance (NMR) in order to identify the main vanadium species. H_2-TPR experiments were performed to study the reducibility of the active species. Samples of ∼100 mg were first treated in air flow at 450°C for 1 h. After cooling, the samples were subsequently contacted with an H_2/Ar mixture (H_2/Ar volume ratio of 1% and a total flow of 1.3 l/h) and heated to a final temperature of 820°C at a rate of 5°C/min. The hydrogen consumption was monitored using a TCD.

The microcalorimetric studies of ammonia adsorption were performed at 80°C in a heat flow calorimeter (C80 from Setaram) linked to a conventional volumetric apparatus. Before each experiment, the samples were heated under air flow at 400°C and then outgassed during 2 h at the same temperature. The differential heats of adsorption were measured as a function of coverage by repeatedly sending small amounts of gas onto the catalyst until an equilibrium pressure of about 66 Pa was reached [22]. The nature of the acid sites was examined by infrared spectroscopy of pyridine adsorption.

2.3. Catalytic tests

The catalytic tests were performed in a tubular quartz flow microreactor using a catalyst charge of 0.5 g. The catalysts were used without dilution and supported by quartz wool. The catalysts were activated by heating at 400°C under air flow overnight and then flushed with nitrogen for 30 min before reaction. The gas feed was C_3H_8:N_2 = 1:4 with a total flow rate of 2.5 l/h. The catalysis runs were performed in the range 400–600°C. Between two successive runs, the sample was flushed with air for 15 min. The reaction products were analysed in an FID chromatographic system with a packed column (unibead 3S).

Table 1
Characteristics of supports and supported vanadium oxide catalysts[a]

Catalyst	V_2O_5 (wt.%)	Surface area (m^2/g)	TPR results		
			T_{onset}[b] (°C)	T_M[c] (°C)	mol H_2/mol V
γ-Al_2O_3	–	108	–	–	–
I-VA	4.4	112	400	568	0.55
A-VA	3.3	117	390	526	0.39
SiO_2	–	208	–	–	–
I-VS	5.0	190	554	642	0.84
A-VS	6.0	201	540	617	0.71
TiO_2	–	55	–	–	–
I-VT	6.0	46	380	514	0.53

[a] I: impregnation; A: ALE.
[b] Onset temperature of reduction.
[c] Temperature of the maximum hydrogen consumption.

3. Results and discussion

The physicochemical properties of the supports and vanadium oxide catalysts are listed in Table 1 which gives the V_2O_5 content (wt.%) for each sample, the BET surface area, and the TPR results of supported vanadium catalysts.

The amount of vanadia needed to form a monolayer is somewhat arbitrary. However, assuming 2.4 V_2O_5 molecule/nm^2 as the monolayer capacity [23], this implies a vanadia loading of ca. 8, 14.5 and 4 wt.% V_2O_5 to form a complete monolayer on alumina, silica, and titania, respectively. If truly monolayered, the samples chosen for study would span the range from 40 to 50% of a monolayer (for the samples on alumina and silica) up to a full V_2O_5 monolayer for the sample on titania.

The XRD spectra of all samples did not show any peak characteristic of V_2O_5 crystallites, thus, arguing for a good dispersion of the active phase on the supports. The oxidation degree and the surface structure of the vanadium layer, as examined by XPS, EPR and ^{51}V NMR, were more determined by the nature of the support than by the preparation method. In all the catalysts studied, tetrahedrally coordinated V^{5+} were the main vanadium species. Consequently, the differences in their catalytic properties can be explained by the influence of the acid character (favouring a high dispersion) of the supports and/or the catalysts on the conversion and selectivity.

A slightly decreasing value of the specific surface area can be observed for samples prepared by impregnation on silica (referred as I-VS in Table 1) and titania (I-VT). The reducibility was measured by monitoring H_2 consumption while increasing the temperature of the sample at a constant rate. In this way, one or more reduction peaks occur at different temperatures and the reduction profile can be obtained [24]. In all cases, the TPR profiles of our catalysts exhibited only one prominent maximum. The onset temperature, T_{onset}, and the temperature of the maximum hydrogen consumption, T_M, are listed in Table 1. In all cases the amount of hydrogen consumed during the TPR experiment was <1.0 mol H_2/mol vanadium (Table 1). No reduction peak was observed for the bare supports except for TiO_2 which showed a small one with temperature of maximum around 660°C. Since the temperature at which the maximum hydrogen consumption is observed depends on the V content and probably on the dispersion, the reducibility of the catalysts can be better reflected by the onset temperature [24]. According to the results shown in Table 1, it can be seen that T_{onset} increases in the same order as T_M which allows a meaningful comparison of the samples. As observed by H_2-TPR, the ALE catalysts were found to be highly dispersed and more easily reduced compared to the corresponding impregnated catalysts. The reducibility of the catalysts decreased in the sequence I-VT > A-VA > I-VA > A-VS > I-VS.

The acidity as determined by adsorption calorimetry, expressed in terms of initial heats of adsorption (noted Q_{init}) and amounts of ammonia adsorbed under an equilibrium pressure of 27 Pa, is shown in Table 2.

The heat of adsorption is a quantitative measure of the strength of the interaction and the variation of the differential heat with coverage reflects the presence of heterogeneity, with the surface made up of sites of more than one kind. The differential heats of ammonia adsorption versus uptake (expressed in μmol NH_3/g_{cat}) for the alumina support and the corresponding supported V_2O_5 catalysts (I-VA and A-VA) are shown in Fig. 1. The bare support displays a curve with the occurrence of a plateau of heats around 180 kJ/mol. As coverage was increased, the heat of adsorption decreased, reaching ca 40 kJ/mol at full coverage.

The heats of adsorption of ammonia on supported vanadia samples were much less than those on alumina

Table 2
Surface acidity and catalytic properties of supports and supported vanadium oxide catalysts[a]

Catalyst	Acidity			$V_{propene}$ at 500°C (mmol/h g_{cat})
	Ammonia uptake (μmol NH_3/g_{cat})		Q_{init} (kJ/mol)	
	a	*b*		
γ-Al_2O_3	269	220	185	0.34
I-VA	244	156	177	0.60
A-VA	256	179	199	1.13
SiO_2	37	0	31	0
I-VS	131	94	104	1.68
A-VS	212	241	132	2.94
TiO_2	282	214	165	0.88
I-VT	187	105	151	2.50

[a] I: Impregnation; A: ALE; *a*: adsorbed amount under an equilibrium pressure of 27 Pa; *b*: number of sites with heat evolved >70 kJ/mol.

except for a greater initial heat value of the A-VA sample. The initial Q_{diff} value on A-VA was 200 kJ/mol, decreasing continuously to 50 kJ/mol at an uptake of ca. 250 μmol NH_3/g of catalyst. The sample prepared by impregnation (I-VA) displayed even lower heats of adsorption versus coverage than the A-VA sample, which shows a more evident heterogeneity. However, the total numbers of sites which adsorb ammonia at an equilibrium pressure of 27 Pa do not differ by more than 10% between the support and the supported catalysts (see Table 2).

Fig. 2 shows the differential heats of ammonia adsorption versus coverage on the silica support and supported vanadium oxide samples. In comparison with the bare support, which shows only reversible adsorption, the impregnated (I-VS) and ALE (A-VS) samples were much more acidic. Moreover, an important distinction can been seen between the plot for A-VS and that for I-VS. The initial values were around 135 and 105 kJ/mol, respectively (Table 2).

The heat versus coverage curves for bare titania and the corresponding impregnated sample (I-VT) are included for the comparison in Fig. 3. At low coverage (<50 μmol/g) the profiles of the two curves are similar; beyond this value, the I-VT sample displays a much less acidic behaviour than titania. In the same calorimetric conditions, an initial heat of ammonia adsorption of about 70 kJ/mol was found for a sample of bulk

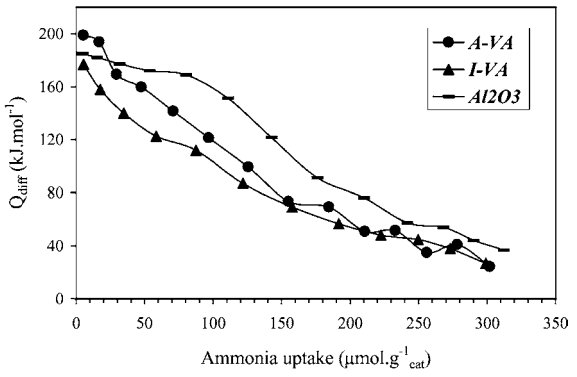

Fig. 1. Differential heat of adsorption of ammonia on γ-Al_2O_3 and alumina-supported V_2O_5 catalysts as a function of amount adsorbed (in μmol/g_{cat}).

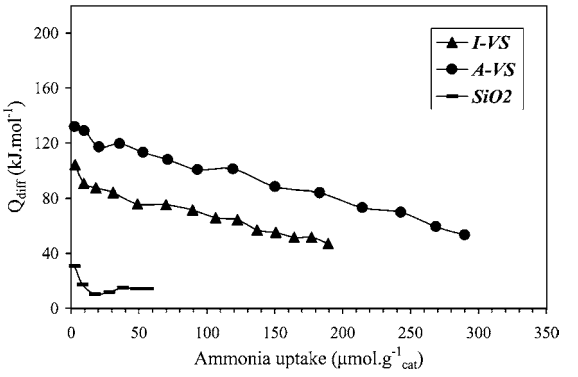

Fig. 2. Differential heat of adsorption of ammonia on SiO_2 and silica-supported V_2O_5 catalysts as a function of amount adsorbed (in μmol/g_{cat}).

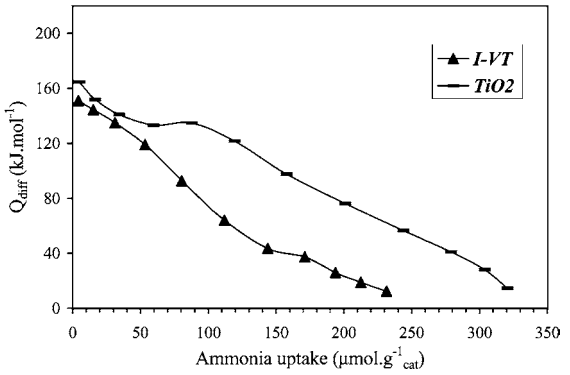

Fig. 3. Differential heat of adsorption of ammonia on TiO_2 and titania-supported V_2O_5 catalysts as a function of amount adsorbed (in $\mu mol/g_{cat}$).

V_2O_5 ($S = 12.8\ m^2/g$) [25], but the low surface area can be a source of incertitude.

In order to facilitate comparison between the samples, uptakes of ammonia can be expressed in terms of the number of acid sites which give rise to a differential heat of NH_3 adsorption higher than 70 kJ/mol. This value can be taken as an estimate of the number of sites which adsorb irreversibly ammonia (see Table 2).

From these values, while the NH_3 uptake on I-VA was 156 μmol/g, the uptake on A-VA was about 15% greater with 179 μmol/g. On silica, the uptake increased from 94 μmol/g on I-VS to 241 μmol/g on A-VS, which means an increase close to 70%. All these features of the adsorption imply that at

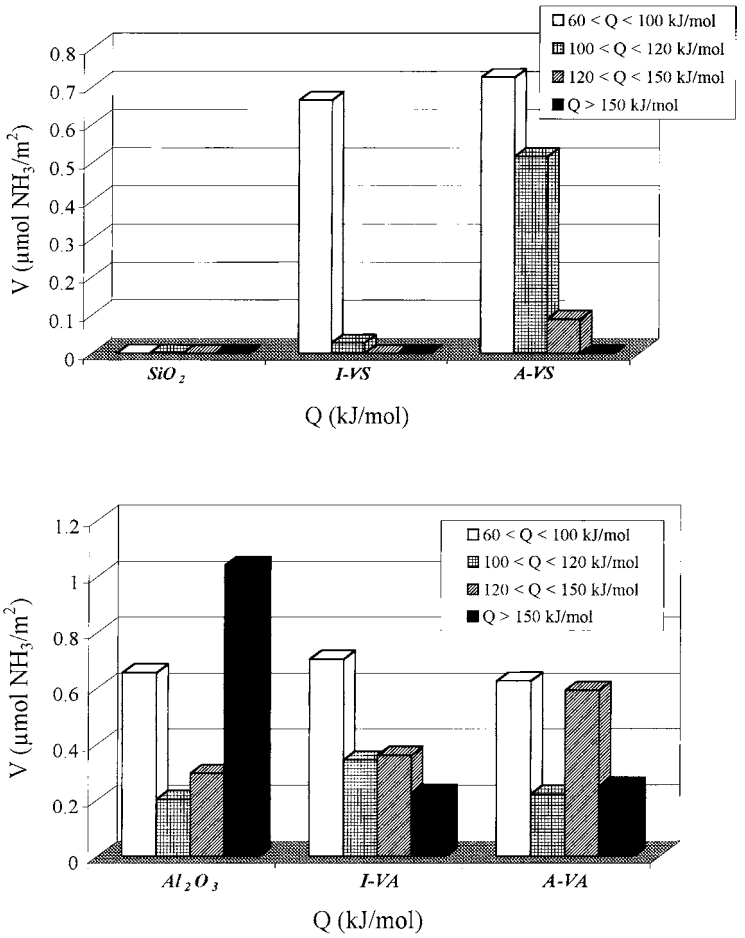

Fig. 4. Acidity spectra of the catalysts.

similar vanadia loading the dispersion is better on the ALE samples.

To summarise, the measurements of ammonia adsorption microcalorimetry showed that the acidic characteristics were strongly affected by the preparation method and the oxide support. The number and the strength of the surface acid sites formed increased remarkably by depositing V_2O_5 on silica by ALE. Also the creation of a large proportion of strong sites ($Q > 100$ kJ/mol) was observed for the ALE catalysts. This can be observed on Fig. 4 which gives the acid site strength distributions of the catalysts, calculated from the differential heats of NH_3 adsorption plotted in Figs. 1 and 2. This figure gives the number of sites on which the evolved heat belongs to a given interval. The total number of acidic sites varied only slightly by depositing V_2O_5 on alumina. However, while the number of very strong acid sites ($Q > 150$ kJ/mol) decreased in particular by impregnation and to a lesser extent by ALE, the number of medium strength acidic sites (100 kJ/mol $< Q <$ 150 kJ/mol) increased significantly (Fig. 4). Loading of V_2O_5 on titania by impregnation markedly decreased the number of acid sites of medium and weak strength.

The same types of acid sites, Lewis and Brönsted, were evidenced by FT-IR after pyridine adsorption, in all the catalysts, but those prepared by ALE showed stronger Lewis acidity [26]. This suggests that vanadium ions act as Lewis acidic sites, in agreement with previously reported work [23].

The activity in propane catalytic dehydrogenation over the supports and supported V_2O_5 catalysts was investigated and the results at 500°C are given in Table 2 in terms of propene formation. The activity is greatly increased by adding V_2O_5 on a support. It is worthnoting that the ALE samples were twice as active as the impregnated samples, which underlines the importance of a high dispersion on the support. From these results, it can be concluded that the catalytic activity per gram of catalyst decreases in the order A-VS > I-VT > I-VS > A-VA > I-VA. A different trend is obtained when specific activities (calculated per square meter of surface area) are considered: I-VT > A-VS > A-VA > I-VS > I-VA. However, because the catalysts have different vanadium contents, their catalytic activities per mol of vanadium decrease in the following trend: A-VS > I-VT > A-VA > I-VS > I-VA. In any case, it can be shown that the activity of the ALE samples is superior to that of the corresponding impregnated samples. For a given support the most acidic sample (the ALE catalyst) is always the most active.

4. Conclusion

The calorimetric studies have revealed the possible difference of structures and surface acidities between the impregnated and ALE catalysts, confirmed by the different catalytic activities. The acid–base properties of the supports deeply influence those of supported catalysts. The superior activity of vanadium-supported catalysts prepared by ALE compared to the impregnated ones may be the result of a high dispersion of the active species and stabilisation of the dispersed phase by the host oxide.

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