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Surface characteristics and activity in selective oxidation of *o*-xylene of supported V_2O_5 catalysts prepared by standard impregnation and atomic layer deposition

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Abstract

Alumina-, silica-, and titania-supported vanadium oxide systems with V_2O_5 loadings ranging from 3 to 12 wt.%, corresponding to 0.02–0.09 V/(Al,Si,Ti) atomic ratios, were prepared by atomic layer deposition (ALD) and compared with the corresponding impregnated catalysts. The surface acidic properties of the supports and catalysts were investigated using ammonia adsorption microcalorimetry to determine the number and strength of the surface acid sites. Deposition of V_2O_5 on alumina and titania supports gave rise to catalysts with lower amounts of acid sites than the respective supports, while for the samples prepared on silica, an increase of the number of acid sites was observed after V_2O_5 deposition. As a common trend, the surface acid strength was greater for the ALD catalysts than for the impregnated ones, suggesting a stronger interaction of the VO species with the support centers, which act as electron attractor centers creating Lewis-like vanadium species. Redox cycles were performed, involving temperature programmed reduction (TPR) analyses separated by an oxidation treatment (TPO). The results evidenced the good reversibility of the redox behavior of the vanadium centers in every case, while significant differences were observed when comparing the temperatures of reduction (T_{max}). Lower T_{max} values were observed for the better dispersed vanadia catalysts. After reduction, the V centers had a final formal average oxidation state corresponding to +3 or less (+2.5 to +2). The reactivity of the vanadia systems was examined by measuring their performance for the oxidation of *o*-xylene to phthalic anhydride. Activity tests indicated the superior selectivity of the V_2O_5 systems based on the more acidic supports (Al_2O_3 and TiO_2). The nature of the support governed the activity, and the more concentrated catalysts gave rise to improved selectivity to phthalic anhydride.

Keywords: Vanadium/alumina/silica/titania catalysts; *o*-Xylene partial oxidation; Selective catalytic oxidation; Adsorption calorimetry; Acidity; Redox properties

1. Introduction

Supported vanadia systems are of widespread use as heterogeneous catalysts in a great variety of selective oxidation/reduction reactions [1–4]. It is now accepted that the nature of the oxide carrier affects both the redox properties and dispersion of the vanadia active phase besides the catalytic activity [5–7]. Among supported vanadia catalysts, V_2O_5/TiO_2 systems are the most commonly used, extensively employed in environmental catalysis for the selective catalytic reduction of NO_x and for oxidation and ammoxidation reactions [8,9]. The unique remarkable crystallographic fit between the (0 1 0) plane of V_2O_5 and the (0 1 0) and (0 0 1) planes of anatase TiO_2 could justify the high activity of the V_2O_5/TiO_2 system [10].

In addition to the nature of the support, the preparation method used to synthesize supported vanadia catalysts affects the structure of the active phase. Vanadia catalysts have been prepared by conventional impregnation, adsorption from solution (grafting), co-precipitation, and chemical vapour deposition [11]. Highly dispersed isolated vanadium oxide species (monovanadate) anchored to the oxide carrier by strong interaction or monolayer crystalline V_2O_5 phases

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(polyvanadate) [12] can be stabilized at the oxide surface, depending on the preparation method and on the vanadia loading on the oxide carrier. The V_2O_5 "theoretical" monolayer coverage of a support may be estimated from crystallographic assumptions with a series of simplifications. Assuming close packing and dimensions of 0.66 nm for monovanadate and 0.38 nm for polyvanadate, the "theoretical" monolayer coverage corresponds to 0.35 and 1.05 wt.% V_2O_5, respectively, for 10 m^2/g of support surface area [12].

The usefulness of the atomic layer deposition (ALD) method for nanotechnology applications and the merits of the method for the manufacturing of future generation catalysts have been recently discussed in the literature [13,14]. The method consists in a gas phase preparation based on surface-saturating precursor adsorption on the support, thus allowing a high dispersion of the deposited species on the finished catalyst. The surface characteristics of vanadia-based catalysts prepared by the ALD method have been presented in the recent literature [14]. In the present contribution, a series of ALD-prepared catalysts and conventional impregnated systems on three different supports (Al_2O_3, SiO_2, and TiO_2) have been studied comparatively. Several important properties of the surfaces were taken into account, in particular the acidity and reducibility. It is known that catalytic activity in selective oxidation of hydrocarbons can be related to the cooperative action of an oxidizing and an acidic function [15,16]. As concerns catalytic activity, the selective oxidation of *o*-xylene to phthalic anhydride has been chosen as test reaction. The oxidation of *o*-xylene is a well studied reaction for which several kinetic studies have been performed and many reaction mechanisms have been proposed [4,17,18]. The reaction takes place through a Mars-van Krevelen mechanism, involving a reduction-oxidation cycle of the vanadia active centers through consecutive steps starting with the adsorption of the reactant molecules. In this perspective, the determination of the redox properties of the vanadium centers, as carried out in the present study, becomes a topic of renewed importance.

2. Experimental

2.1. Catalyst

Commercial oxides were used as supports for the preparation of dispersed V_2O_5 catalysts: γ-alumina (Degussa, Oxid C), silica (Crosfield Ltd., EP10), and titania (Degussa, P-25, 75% anatase). The vanadia precursor was $VO(C_5H_7O_2)_2$, vanadyl acetylacetonate, or NH_4VO_3 (Strem Chemicals, purity >99 %) depending on the preparation methodology.

For the ALD preparation, the reactor and the procedure were similar to those described elsewhere [19]. The support oxides were pretreated in air for 16 h at 523 K in a muffle furnace and subsequently in the ALD reactor at the same temperature for 5 h under moderate pressure (1–4 kPa). The $VO(C_5H_7O_2)_2$ precursor was transported in nitrogen flow downward through the heated bed of support kept at 443 K. The chemisorption of $VO(C_5H_7O_2)_2$ was performed at 453 K for 10 h. The solids were subsequently purged under nitrogen flow at 623 K for 6 h and then calcined under oxygen flow at 773 K for 16 h. The ALD catalysts are designated by labels of the form VX-A*n*, in which V indicates vanadium; X = A or S or T the alumina, or silica, or titania support; A the ALD preparation method; and the last figure *n* indicates the wt.% of V_2O_5.

The impregnated vanadia catalysts were prepared by a conventional aqueous-phase method using solutions of NH_4VO_3. The excess water was evaporated, the wet powders were dried for 24 h at 383 K and then calcined under air flow at 773 K for 12 h. The impregnated catalysts are designated by labels of the form VX-I*n*, in which V indicates vanadium; X = A or S or T the alumina, or silica, or titania support, respectively; I the impregnation method; and the last figure *n* indicates the wt.% of V_2O_5.

Mechanical mixtures of each support with V_2O_5 (Carlo Erba, purity >99%) were prepared for some comparative measurements, with a V_2O_5 concentration of 5 wt.%. These are labelled VX-M*n* in which V indicates vanadium; X = A or S or T the alumina, or silica, or titania support; M the mechanical mixture; and the last figure *n* indicates the wt.% of V_2O_5.

2.2. Catalyst characterization

The vanadium contents of the samples prepared by ALD and impregnation were determined by ICP-AES in a Spectroflame-ICP instrument.

The BET surface area, pore volume and diameter of the samples were determined by N_2 adsorption performed at 77 K after heat pretreatment at 623 K under vacuum for 3.5 h.

The calorimetric-volumetric experiments of NH_3 adsorption were performed in a heat flow microcalorimeter (C80 from Setaram) linked to a volumetric apparatus. The samples were activated in air for 12 h and subsequently under vacuum at 673 K. Small pulses of NH_3 (Air Liquide, purity >99%) were sent onto the sample kept at 353 K until an equilibrium pressure of ca. 67 Pa was reached. Then, the samples were outgassed for ca. 30 min at the same temperature and a second NH_3 adsorption was carried out. This procedure permitted the determination of the NH_3 chemisorbed uptake ($V_{NH_3,irr}$). Additional experimental details can be found elsewhere [20].

Redox cycles (TPR1/TPO/TPR2) were realized carrying out three analyses in sequence: a first reduction on the oxidized sample (TPR1), an oxidation (TPO), and a second reduction (TPR2). An automatic apparatus (TPDRO-1100 from Thermofinnigan) with a thermal conductivity detector (TCD) was employed. The powder samples were introduced into a quartz reactor over a porous septum (ca. 8 mm i.d.). The samples were pre-oxidized ($O_2/N_2$20%, v/v) at 623 K for 1 h, and then cooled at 313 K. The TPR1 analysis was carried out using an H_2/Ar mixture (4.98%, v/v, 14 cm^3/min) from 313 to 800 K with a constant heating rate of 8 K/min. The TPO analysis was carried out on the reduced samples (after TPR1) cooled at 313 K in H_2/Ar flow using an O_2/He mixture (5.02%, v/v, 14 cm^3/min) from 313 to 800 K. The oxidized sample was further reduced during the TPR2 analysis, under the same experimental conditions described above. The amount of powder (from 0.05 to 0.1 g) used was adjusted to have a constant amount of V_2O_5 (27 (mol) for all the analyses. According to this methodology previously described [21,22] the values of K (80 s) and P (12 K) parameters were kept constant. TPR peak areas were calibrated employing standard bulk CuO as reference material and pure H_2 injections (Sapio, Italy; purity >99.9999%) [23]. The ratio between the amount of H_2 consumed and the amount of vanadium in the sample gave the reduction extent of the V species $(H_2/V)_{mol}$. From the experimental $(H_2/V)_{mol}$ ratios, the average formal oxidation numbers of the V species after the TPR1 and TPR2 analyses could be calculated [24].

2.3. Catalytic measurements

Activity tests were carried out in a Pyrex fixed-bed tubular reactor (i.d. 0.7 cm) fitted with an axial thermowell (e.d. 0.4 cm), which permitted measuring the inner temperature of the catalytic bed by means of a thermocouple. The powder catalysts, sieved as 0.125–0.300 mm particles and diluted three times in mass with quartz sand, were held in the middle of the reactor between two portions of glass wool. Liquid *o*-xylene (0.090 mL/h) was fed by means of a perfusion pump and vaporized by mixing with pre-heated air (0.50 mol% *o*-xylene/air). The so obtained feed mixture passed through a second pre-heater before being introduced into the reactor. The reactor and the pre-heaters, for air and for the feed mixture, were heated by an electrical tubular furnace with two different sections kept at independent temperatures, one for the pre-heaters and the other one for the reactor.

The reaction was carried out at atmospheric pressure in the 573–623 K temperature interval at fixed contact time (4.5×10^{-2} g (*o*-xylene) h/NL(air)). The unreacted *o*-xylene and the reaction products were condensed in an ice-bath trap kept at ca. 258 K. The total mass collected for fixed times (usually 45 min) was determined by weighing the trap. The weighted products, after addition of weighted amounts of durene chosen as inner standard and dissolution in methyl ethyl ketone, were analyzed in a FID gas-chromatograph (HP 5890 II), using a Supelco-SPB5 column (30 m long, 0.32 mm i.d.) and He as carrier gas. The steady-state *o*-xylene conversion and selectivity to the main oxygenated reaction products, i.e., phthalic anhydride, *o*-tolualdehyde, and phthalide were calculated in wt.%. These three main products display the same carbon content as *o*-xylene (eight carbon atoms per molecule) therefore conversion and selectivity in terms of carbon content correspond to molar ones. Other products, e.g., maleic anhydride, were ignored because they were present in very small quantities. Carbon balances is a critical issue in hydrocarbon oxidation reactions. More specifically, oxidation of *o*-xylene on oxide catalysts exhibiting both redox and acid functionalities usually leads to carbon deposition and/or formation of heavy condensed products [18].

As expected, important deviations in carbon balances were observed probably due to the formation of non-volatile by-products.

3. Results and discussion

3.1. Catalyst properties

The studied catalysts are presented in Table 1 together with the V_2O_5 loadings expressed as weight percentages and V/(Al,Si,Ti) atomic ratios. Catalysts were prepared with increasing vanadia contents both by ALD (6–12 wt.% and 0.044–0.090 V/Si) and impregnation (6–10 wt.% and

Table 1
Main characteristics of the supported vanadia catalysts

Catalyst	V_2O_5 (wt.%)	V/(Al,Si,Ti) atomic ratio	BET surface area (m^2/g)	d_s (VO_x/nm^2)[a]
Al_2O_3			108	
VA-A4	3.90	0.022	117	2.3
VA-I5	4.93	0.029	111	3.1
SiO_2			301	
VS-A6	6.43	0.044	286	1.6
VS-A9	8.93	0.063	299	2.2
VS-A12	12.30	0.090	293	3.1
VS-I6	6.43	0.044	305	1.5
VS-I10	10.35	0.074	272	2.5
TiO_2			55	
VT-A3	2.86	0.025	48	4.1
VT-I6	6.02	0.055	46	9.2

[a] Surface density.

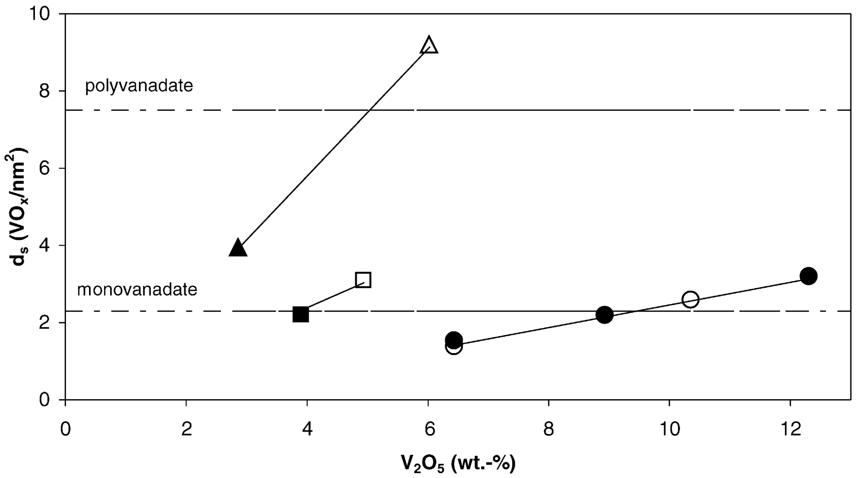

Fig. 1. Loading of the vanadia catalysts on the three supports expressed as surface density (d_s) as a function of V_2O_5 weight content. Squares, alumina support; circles, silica support; and triangles, titania support. Filled symbols, catalysts prepared by ALD; open symbols, catalysts prepared by impregnation.

0.044–0.074 V/Si) only over the silica support. On alumina and titania, only one vanadia loading was considered for each preparation. Due to the importance of the presence of a V_2O_5 monolayer for the obtention of an active catalyst, the vanadia surface density (d_s expressed in VO_x/nm^2) was calculated. The d_s values could be compared with the "theoretical" monolayer values of 2.3 and 7.5 VO_x/nm^2 for the monovanadate and polyvanadate species, respectively [12]. The BET surface areas of the catalysts and their calculated d_s values are also presented in Table 1. These data show that V_2O_5 deposition did not induce any remarkable decrease in the surface areas of the supported catalysts compared with the surface areas of alumina, silica, and titania. Fig. 1 shows the relationship between the surface density and the weight loading of V_2O_5 on the three series of catalysts. Due to the small value of the surface area of titania (55 m^2/g), a low V_2O_5 loading was sufficient to attain the value of the "theoretical" monolayer coverage for polyvanadate (for the impregnated catalyst VT-I6). The series of catalysts prepared on the alumina and silica supports, which offer a large surface area for the V_2O_5 deposition, and the low loading catalyst prepared by ALD on titania, have all surface densities around the "theoretical" monolayer coverage for monovanadate. It can be estimated that all the prepared catalysts contain from 0.5 to 1.7 times the "theoretical" monolayer coverage for monovanadate, except the VT-I6 sample.

Among the surface properties of vanadia catalyts of some importance for their catalytic activity in selective oxidation reactions, acidity is one of the most significant. The protonic acidity of the support is not desired as it leads to side reactions such as polymerization or cracking of the organic molecules at high temperatures and coking. The complete coverage of the support by V_2O_5 phase might give rise to Lewis-like vanadium centers which are characterized by a lower acid strength than the acid centers of the oxide support. The acidity measurements were performed by means of NH_3 adsorption experiments monitored by microcalorimetry coupled to volumetry. Table 2 summarizes the main results obtained and Figs. 2–4 show the plots of the differential heats of NH_3 adsorption as a function of NH_3 coverage for the series of alumina, silica, and titania catalysts and the respective supports. On the alumina and titania supports, the main trends observed were a remarkable decrease of the number of acid sites (both the total population, $V_{NH_3,tot}$, and that of strong sites, $V_{NH_3,irr}$) of the vanadia catalysts, together with a decrease of the total acid strength compared with the acidic properties of alumina and titania. On the contrary, due to the neutral behavior of the silica surface, the acidity of the V_2O_5 phase deposited on silica was much more apparent. Both the number and strength of the acid sites of the silica-supported catalysts increased as the vanadia loading increased, independently of the preparation method. Comparing catalysts at similar V_2O_5 loadings prepared by ALD and impregnation (VS-A6 with VS-I6 and

Table 2
Catalyst acidity evaluated by calorimetric/volumetric measurements of NH_3 adsorption

Catalyst	$V_{NH_3,tot}$[a] (μmol/m^2)	$V_{NH_3,irr}$[b] (μmol/m^2)	Q_{int}[c] (J/m^2)
Al_2O_3	2.486	1.476	0.309
VA-A4	2.185	1.228	0.229
VA-I5	2.182	1.171	0.205
SiO_2	0.220	0.092	0.003
VS-A6	0.735	0.094	0.057
VS-A9	0.923	0.120	0.074
VS-A12	1.295	0.175	0.107
VS-I6	0.456	0.068	0.031
VS-I10	0.632	0.137	0.044
TiO_2	5.126	3.120	0.530
VT-A3	3.593	2.275	0.343
VT-I6	4.061	2.422	0.347

[a] Adsorbed amount under an equilibrium pressure of 27 Pa.

[b] Irreversibly adsorbed volume at 27 Pa (number of strong sites).

[c] Integral heat of adsorption at 27 Pa.

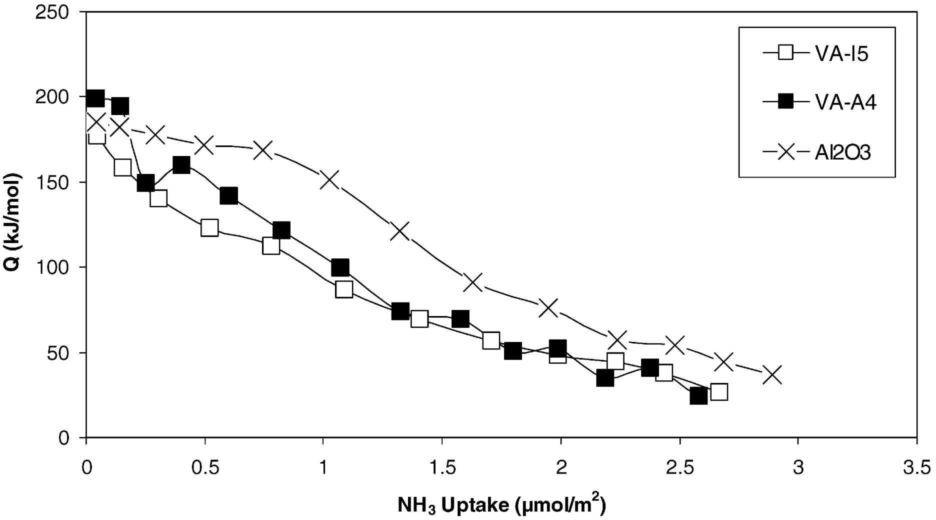

Fig. 2. Differential heats of ammonia adsorption over the alumina support and the corresponding vanadia catalysts prepared by ALD (filled symbols) and impregnation (open symbols).

VS-A12 with VS-I10), it appears that the ALD preparation yields a V_2O_5 phase characterized by a higher number of acid sites and a stronger surface acidity than the preparation by impregnation. This indicates a better dispersion of the vanadia centers and a stronger interaction with the support that leads to Lewis-like vanadium centers of higher acidity.

Redox cycles consisting of temperature-programmed reduction (TPR) and reoxidation (TPO) are an effective technique to get information on the reducibility of oxide phases. In the present work, all the catalysts were analyzed by performing two successive TPR analyses (TPR1 and TPR2) with a TPO run in between, with the aim to study the redox character of the vanadium centers. The temperatures of the maxima (T_{max}) of the reduction peaks in the first and second analyses are reported in Table 3 together with the quantitative results of hydrogen consumption calculated in terms of H_2/V molar ratio. From the H_2/V ratios, the final formal average oxidation states of the V centers after the TPR1 and TPR2 analyses were computed and are listed in the last two columns of Table 3. In addition to the ALD and impregnated catalysts, mechanical mixtures of V_2O_5 with the alumina, silica, and titania supports (VA-M5, VS-M5, and VT-M5) were prepared in order to make useful comparisons with the supported V_2O_5 phases.

The TPR profiles for the samples show only one prominent maximum, independently of the preparation and the vanadia loading, with the exception of VT-I6 due to the high number of monovanadate layers or the presence of polyvanadate. The appearance of single peaks during TPR analyses for the vanadia-supported catalysts is in good agreement with the literature [25,26] which reports that only one single reduction peak is obtained, if less than four

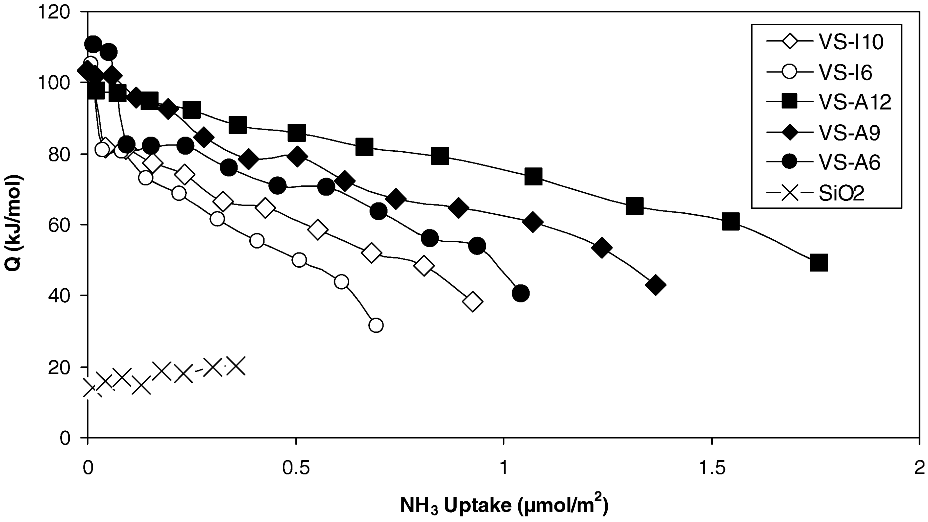

Fig. 3. Differential heats of ammonia adsorption over the silica support and the corresponding vanadia catalysts prepared by ALD (filled symbols) and impregnation (open symbols).

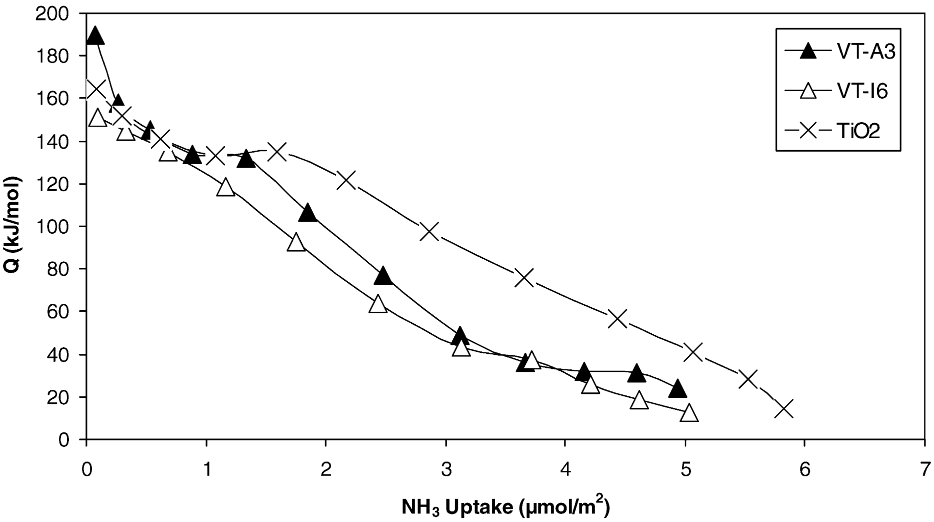

Fig. 4. Differential heats of ammonia adsorption over the titania support and the corresponding vanadia catalysts prepared by ALD (filled symbols) and impregnation (open symbols).

layers of vanadium oxide are deposited on the support. The T_{max} temperatures are dependent on the support (Table 3); the lowest T_{max} values were obtained for the vanadia-titania catalysts, and the highest ones for the silica catalysts. The temperatures of the reduction maxima are indicative of how easy it is to remove oxygen from the vanadia phase; consequently it is reasonable to expect the oxidation activity to be inversely related to the T_{max} temperatures. The differences between the values of T_{max} agree with the well-known superior activity of the vanadia-titania systems in oxidation reactions. The lower T_{max} temperatures of the titania and alumina supported catalysts also indicate a stronger interaction of V_2O_5 with these two supports (the most acidic ones), confirming a better dispersion of the vanadia phase compared to silica. In any case, independently of the support nature, all the vanadia catalysts were reduced at much lower temperatures than the mechanical mixtures (VA-M5, VS-M5, and VT-M5) due to an efficient dispersion of the V_2O_5 phase by the support. As reported in the literature [12], monomeric vanadia species are more easily reduced by hydrogen than the polymeric and bulk V_2O_5 phases. Comparing for each support the ALD and impregnated systems, a better dispersion of the vanadium oxide deposited by ALD is clearly evidenced from the lower T_{max} temperatures of the ALD catalysts compared to those prepared by impregnation (for the silica systems the comparison has to be done for similar V_2O_5 loadings).

Table 3
Experimental results of TPR analyses

Catalyst	T_{max} (K)		H_2/V (molar ratio)		V^{X+a}	
	TPR1	TPR2	TPR1	TPR2	TPR1	TPR2
VA-A4	770	774	1.27	1.33	2.5	2.3
VA-I5	785	783	1.21	1.18	2.6	2.6
VA-M5	970	776	1.30	1.51	2.4	2.0
VS-A6	845	846	1.15	1.16	2.7	2.7
VS-A9	863	873	1.66	1.76	1.7	1.5
VS-A12	866	873	1.29	1.33	2.4	2.4
VS-I6	909	869	1.48	1.51	2.0	2.0
VS-I10	863	876	1.10	1.15	2.8	2.7
VS-M5	931/953	864/932	1.45	1.53	2.1	1.9
VT-A3	738	715	1.24	0.91	2.5	3.2
VT-I6	752/759	811/1025	1.05	0.67	2.9	3.7
VT-M5	929	879	1.49	1.05	2.0	2.9

[a] Final average formal oxidation state of vanadium after TPR analysis.

The reduction profiles of the TPR1 and TPR2 analyses for the alumina and silica supported catalysts were similar in their shape, as indicated by the T_{max} temperatures of the two successive cycles (Table 3). The titania supported catalysts displayed quite different reduction profiles for the two TPR runs, both in terms of shape and of peak intensity. The redox behavior of the VO centers in strong interaction with the support was not completely reversible throughout the redox cycle. The quantitative results of the TPR analyses, in particular the H_2/V ratios indicated in Table 3, confirm these conclusions. The alumina and silica supported catalysts presented a more reversible behavior of the V_2O_5 phase in a redox cycle than those supported on titania. The reoxidation run (TPO) failed to completely restore the V_2O_5 phase for the fresh catalysts supported on titania, probably due to the strong VO-support interaction with the first vanadia layers or to sintering of the support.

From the experimental H_2/V ratios and making assumptions on the initial and final nature of the vanadia phase before and after reduction, it is possible to estimate the final formal average oxidation state of the V-phase. Assuming the presence of V_2O_5 phase on the fresh and reoxidized catalysts and V_2O_3 or VO phase on the reduced ones, one can expect a H_2/V ratio close to 1.0 or 1.5, respectively. Intermediate H_2/V ratios reflect the presence of a complex situation for the V-phase, i.e., heterogeneity of the vanadium centers in strong or weak interaction with the support. The mechanical

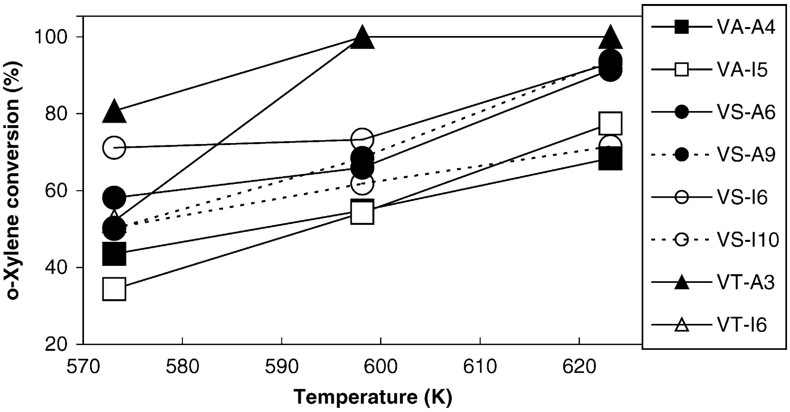

Fig. 5. Total conversion of *o*-xylene over the studied catalysts as a function of reaction temperature.

mixtures of V_2O_5 with alumina and silica showed a H_2/V ratio close to 1.5, while for the corresponding supported catalysts values different from 1.5, in general lower than 1.5, were observed. For these systems, the average oxidation state for the reduced vanadium was around +2.5 to +2.0, indicating a V-phase more reduced than V_2O_3. The reduced titania-supported systems had a V-phase resembling V_2O_3 as indicated by the H_2/V ratio closer to 1 than to 1.5.

3.2. Catalytic oxidation of o-xylene

The selective oxidation of *o*-xylene to phthalic anhydride is a complex reaction that involves the participation of 12 electrons, the abstraction of six hydrogen atoms, and the incorporation of three oxygen atoms in the reactant molecule [4,25]. Intermediate oxygenated products (e.g., *o*-tolualdehyde, phthalide, and maleic anhydride) and deep oxidation products (CO and CO_2) are also formed during the reaction course. The experimental results of *o*-xylene oxidation activity presented here were measured at fixed contact time and variable temperatures, in order to provide a better comparison between catalysts that present different structures, natures, and loadings of vanadia centers.

At almost every temperature investigated, conversion of *o*-xylene followed an order mainly dictated by the support rather than by the vanadia loading; i.e., $TiO_2 > SiO_2 > Al_2O_3$ (Fig. 5). Total *o*-xylene conversions of up to 100, 90, and 70% were attained over the vanadia catalysts supported on titania, silica, and alumina, respectively, at the highest temperature. This behavior does not reflect the ease of reducibility of the V_2O_5 phase determined by TPR analysis, as a better activity for the alumina-supported catalysts would have been expected on the basis of the T_{max} temperatures. However, it has to be considered that when total *o*-xylene conversion is concerned, all the formed products are taken into account, including deep oxidation products (CO and CO_2). The easier reducibility of the V_2O_5 phase on alumina compared to silica would be expected to mainly influence the *o*-xylene oxidation selectivity.

The influence of both the vanadia loading and the support nature on catalytic activity is summarized in Fig. 6. At first glance, the impregnated catalysts seem to be more selective

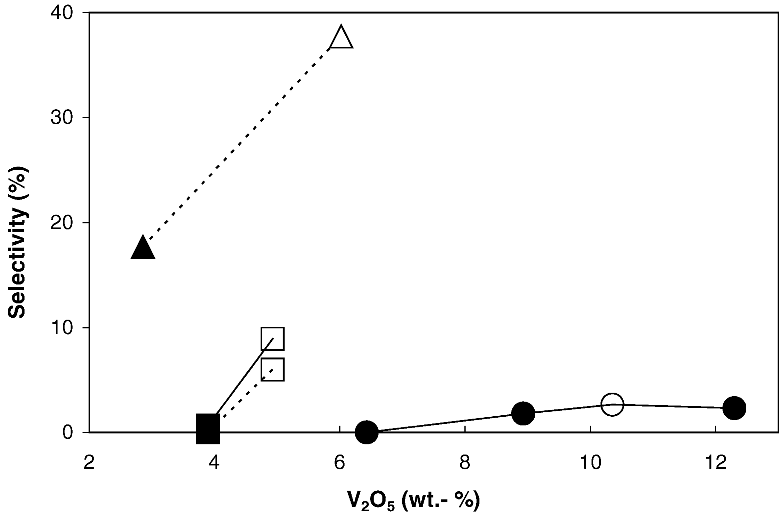

Fig. 6. Selectivity of *o*-xylene oxidation to phthalic anhydride over the ALD (filled symbols) and impregnated (open symbols) catalysts as a function of V_2O_5 loading, at 598 K (dotted lines) or 623 K (solid lines). Squares, alumina support; circles, silica support; and triangles, titania support.

to phthalic anhydride than those prepared by ALD. However, the V_2O_5 loading was in most cases higher for the impregnated than for the ALD catalysts, and therefore the better selectivity of the former may be due to a higher V_2O_5 concentration. The influence of the V_2O_5 loading on the reaction selectivity does not follow a single pattern, but rather depends on the support nature [27]. A small increase of the V_2O_5 concentration on titania- and alumina-based catalysts led to positive effects on the phthalic anhydride selectivity, while a very limited selectivity increase was observed on silica-based catalysts. This confirms the superior activity of the catalysts prepared on the most acidic supports (alumina and titania).

For a given support, the influence of the preparation method on the selectivity can also be observed in Fig. 6. VA-A4 produced only 1% of phthalic anhydride at 623 K, without any formation of phthalide and *o*-tolualdehyde. A better selectivity was observed on VA-I5, which produced from 1 to 9% of phthalic anhydride at reaction temperatures increasing from 573 to 623 K. In the same temperature interval, selectivity to *o*-tolualdehyde decreased from 1 to 0.4%. This behavior agrees with the reaction mechanism which involves consecutive steps for the oxygen insertion in the *o*-xylene molecule [4]. On the silica supported catalysts at low V_2O_5 loading, only very little *o*-tolualdehyde was formed, independently of the preparation method of the catalysts. For higher loading, the sole formation of *o*-tolualdehyde (ca. 1%) was observed at 573 and 598 K. At 623 K, phthalic anhydride was formed with 2–3% selectivity besides *o*-tolualdehyde present in comparable amounts. As expected, activity in terms of phthalic anhydride formation was much higher over the vanadia-titania catalysts (18 and 38% yield on VT-A3 and VT-I6, respectively at 598 K) than over alumina and silica-based catalysts. As *o*-xylene conversion was quantitative at 598 K for both the titania catalysts, the yield values correspond to those of selectivity. At lower temperatures (573 K), the selectivity to phthalic anhydride was 18 and 23% on VT-A3 and VT-I6, respectively. At this temperature, phthalide and *o*-tolualdehyde were formed in similar smaller amounts, globally corresponding to the tenth or the third part of the amount of phthalic anhydride formed on VT-A3 and VT-I6, respectively. This observation also confirms the reaction mechanism of consecutive oxygen insertion in the *o*-xylene molecule.

The main differences found in Fig. 6 are due to the support nature and V_2O_5 loading, but as shown above the preparation method might have an important role too.

At the end, if Fig. 6 was redrawn in terms of surface density instead of V_2O_5 wt.% loading, the higher selectivity of the impregnated catalysts compared to those prepared by ALD (in particular for the catalysts supported on titania) could clearly be attributed to the presence of a monolayer crystalline V_2O_5 phase (polyvanadate) which, due to the heterogeneous character of the impregnated catalysts, could be present in the form of V-patches over the support.

4. Conclusions

The V centers of supported vanadia catalysts exhibit both the redox and the Lewis type acidic properties involved in the general mechanism of selective oxidation reactions. The preparation of catalysts by ALD led to materials with better dispersion of the VO centers on the acidic supports, resulting in better reducibility and stronger acidic character than the conventional impregnated samples. As regards the catalytic activity and selectivity in the studied reaction of selective oxidation of *o*-xylene, they can be attributed to polyvanadate oxide layers rather than to monovanadate layers. The support plays a crucial role in directing the structure of the vanadia layers, and the superior activity of titania as a support oxide for the vanadia phase has been confirmed.

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