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Determination of the Active Surface Area of Vanadia by Electrophoretic Migration and XPS Measurements

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Electrophoresis migration and X-ray photoelectron spectroscopy techniques were applied to measure the active surface area of vanadia in titania- and alumina-supported vanadium oxide catalysts. For V-oxide contents ranging between 0 and 2.3 × 10^{14} cm^{-2} for Al_2O_3 and 0 and 7.2 × 10^{14} cm^{-2} for TiO_2, it was found that V-oxide has a very high degree of dispersion mainly as monolayer. The V 2*p*/T 2*p* and V 2*p*/Al 2*p* intensity ratios, taken from the XPS spectra, increase monotonically with the V content. However, for V/TiO_2 catalysts the straight line declines for V contents above 4.9 × 10^{14} cm^{-2}, thus indicating the end of the first vanadium layer. For the V/Al_2O_3 catalyst series both apparent surface coverage and V 2*p*/Al 2*p* intensity ratio steadily increase with V content, indicating that in all these preparations, even with the highest V content, the V-layered structures do not fully cover the surface of the carrier.

INTRODUCTION

Vanadium oxides form a group of industrially important catalysts for selective oxidations (*1–3*). In these processes, bulk oxides can generally not be used because of their lack of thermal and mechanical strength. However, the stability of the catalysts may be greatly enhanced when the active phase is incorporated on a support (Al_2O_3, TiO_2, SiO_2). The most efficient utilization of any supported catalyst depends on the dispersion of the active phase on the surface of the support. This dispersion is often controlled, among other factors, by the nature of the support, presence of impurities, and the extent of loading.

It is well known that vanadium oxide may remain as a highly dispersed monolayer (*4, 5*), although the presence of very small crystallites cannot be fully excluded (*6*). Much research activity has been devoted to understanding the properties of V-oxide monolayer catalysts (*4*), as well as the role of V=O bonds (*7, 8*) in the catalytic activity of these catalysts. Apparently, no effort has been made to estimate the active surface area of the active ingredient of the supported catalysts. Very recently, Fierro *et al.* (*6*) and Nag *et al.* (*9*) have applied the low-temperature oxygen chemisorption (LTOC) method (developed by Parekh and Weller (*10*) for estimating the active surface area of supported Mo-oxide catalysts) for calculating the active surface area of V-oxide in silica- and alumina-supported V-oxide catalysts, respectively. In these chemisorption studies it was found that O_2 is not a selective probe molecule for the reduced vanadium ions. This finding is in agreement with the data reported by Khalif *et al.* (*11*), who observed several V centers on the surface of a vanadia–silica catalyst, viz, V^{3+}_{3V} and V^{4+}_{Ta} (which adsorb O_2 without activation energy) and V^{4+}_{3V} (which requires a significant activation energy to oxidize to V^{5+}_{OH}).

The purpose of the present work has been to determine the active surface area of V-oxide on Al_2O_3 and TiO_2 supports by means of fast methods, viz, electrophoretic migration rate and X-ray photoelectron spectroscopy (XPS) measurements. This could permit us to establish dispersion–selectivity–activity correlations for layered

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catalysts by investigating catalytic behaviors in various oxidation reactions.

EXPERIMENTAL

Preparation of catalysts. A series of alumina-supported vanadium catalysts was prepared by "wet" impregnations (excess of solution) of a Girdler T-126 γ-Al_2O_3 (S_{BET} = 188 m^2 g^{-1}, pore volume = 0.39 cm^3 g^{-1}, ground and sieved to 0.42–0.53 mm) with an ammonium vanadyl oxalate complex, AVO = $(NH_4)_2[VO(C_2O_4)_2] \cdot H_2O$, solution. The concentrations of the solutions were selected in order to achieve V loadings ranging between 0 and 2.3 × 10^{14} molecules V_2O_5 cm^{-2} of support. Details of preparation of this complex have been given elsewhere (*6*). The impregnated samples were dried at 343 and 27 K N m^{-2} and then kept at 383 K for 16 h. Finally, they were calcined at 773 K in a forced flow of air for 4 h.

Titania-supported vanadium catalysts with similar V-oxide contents (0–2.3 × 10^{14} molecules V_2O_5 cm^{-2}) were prepared following the same method and procedure as for the vanadia–alumina catalysts. In this case, a Degussa TiO_2 (70% anatase) with S_{BET} = 59 m^2 g^{-1} was used as support. Specific surface areas of the catalysts were calculated by the BET method from the gravimetric N_2 isotherms at −196°C, using a value of 0.164 nm^2 for the cross section of N_2.

Experimental methods. Zeta potential (ZP) measurements were carried out in a Zeta-meter Zm-77, using 200 mg of 2-μm hydrated sample particles ultrasonically dispersed in 200 ml of 10^{-3} *M* KCl solution as reported before (*12, 13*). The pH values were adjusted with either 10^{-3} *M* HCl or KOH solutions. Both electrophoretic migration rate and zeta potential are related by the well-known Smoluchowski equation.

XPS spectra were acquired with a Vacuum Generators ESCA 3 spectrometer equipped with a Tracor Northern TN-1710 signal-averager which allowed improvement of the signal-to-noise ratio. The spectrometer was equipped with a magnesium anode (Mg$K\alpha$ = 1253 GeV), operated at 14 kV and 20 mA. The analysis energy was fixed at 100 eV. The residual pressure inside the analysis chamber was better than 1.3 × 10^{-6} N m^{-2}. The powdered samples were pressed (4 × 10^7 N m^{-2}) and then the dust was mounted on holders fixed on a long rod which allowed fast entry into the analysis chamber. C 1*s*, O 1*s*, Al 2*p* (or Ti 2*p*), V 2*p*, and C 1*s* signals were recorded for each catalyst. All binding energies (BE) were referred to the C 1*s* line at 285.0 eV. The $I_{V\,2p}/I_{Al\,2p}$ or $I_{V\,2p}/I_{Ti\,2p}$ ratio was taken as a measure of the vanadium dispersion on Al_2O_3 and TiO_3, respectively.

RESULTS AND DISCUSSION

Electrophoretic Migration

Figures 1 and 2 show the zeta potential vs pH curves of some V_2O_5/TiO_2 and V_2O_5/γ-Al_2O_3 catalysts, respectively. The isoelectric point (IEP) of the V_2O_5 (IEP = 1.40 pH) and the TiO_2 (IEP = 6.30 pH), shown in Fig. 1, are in agreement with the previously reported values of 1.0–2.5 for V_2O_5 (*14*) and 7.2 for TiO_2 (*15*). The IEP of this γ-Al_2O_3

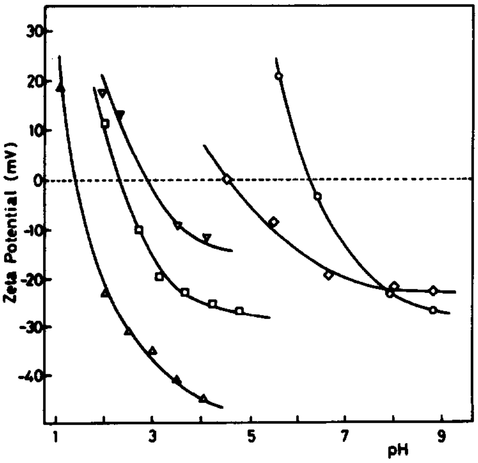

FIG. 1. Zeta potential (mV) at 23°C as a function of pH of the suspension media of V/TiO_2 catalysts with different V content. △, Pure V_2O_5; □, Ti-4; ▽, Ti-2; ◇, Ti-1; and ○, TiO_2.

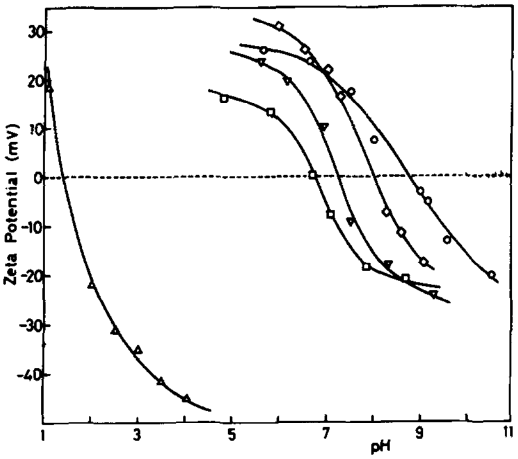

FIG. 2. Zeta potential (mV) at 23°C as a function of pH of the suspension media of V/Al_2O_3 catalysts with different V content. △, Pure V_2O_5; □, Al-8; ▽, Al-5; ◇, Al-2; and ○, Al_2O_3.

has been reported in previous studies (*12*). The IEP of V_2O_5/TiO_2 or $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts decreases with the increase of the vanadium content. This behavior must be explained as a consequence of the increase of the TiO_2 or $\gamma\text{-}Al_2O_3$ surface fraction covered by any phase with an IEP lower than that of TiO_2 or $\gamma\text{-}Al_2O_3$. As was mentioned, the vanadium oxide can remain as a monolayer (*4, 5*) or as small crystallites (*6*) of V_2O_5. In any case, the TiO_2 or $\gamma\text{-}Al_2O_3$ surface must be covered by a phase that, as in our early experiments with other supported oxides (*12*), must have an IEP similar to that of the unsupported V_2O_5. Thus, an increase of the TiO_2 or $\gamma\text{-}Al_2O_3$ surface fraction covered by V_2O_5 explains the decrease of the IEP of the V_2O_5/TiO_2 or $V_2O_5/\gamma\text{-}Al_2O_3$ catalysts.

The change of the IEP with the increase of the vanadium content is, however, significantly higher at a low vanadium content than at a high content. Table 1 shows that the difference between the IEP of the Ti-0 and Ti-1 (ΔIEP) is 1.8 pH units, while between Ti-5 and Ti-6 this difference is only 0.25 pH unit.

The gradual decrease of the influence of the vanadium charge on the IEP of the supported V_2O_5 is higher in the TiO_2 than in the $\gamma\text{-}Al_2O_3$ series. The decrease must be explained in both supports as a consequence of the V_2O_5 multilayer formation (*7*) which seems to be more important in $\gamma\text{-}Al_2O_3$ than in the TiO_2 support (*8*).

Coverage

The fractional surface areas covered by V_2O_5, also called apparent surface coverage (ASC), were calculated using (*3*)

$$\mathrm{ASC} = \frac{M_s^{-1}(\mathrm{IEP_s} - \mathrm{IEP_c}) \times 100}{(M_M^{-1} - M_s^{-1})(\mathrm{IEP_c} - \mathrm{IEP_s}) + M_M^{-1}(\mathrm{IEP_s} - \mathrm{IEP_M})}, \quad (1)$$

where the molecular weights of the supports were $M_s = 101$ g mol^{-1} and $M_s = 80$ g mol^{-1} for $\gamma\text{-}Al_2O_3$ and TiO_2, respectively. The molecular weight of the supported phase M_M was assumed as 182 g mol^{-1} which corresponds to the molecular weight of the V_2O_5. The isoelectric points of the support, IEP_s, and of the catalysts, IEP_c, are given in Table 1. The IEP of supported phase, IEP_M, was assumed as 1.40 pH which corresponds to the isoelectric point of the V_2O_5. The assumptions in the M_M

TABLE 1

Metal Content, Isoelectric Point (IEP), Apparent Surface Coverage (ASC), Surface Area (BET), and V_2O_5 Surface Area (*S*)

Sample	10^{-14} molecules V_2O_5 cm^{-2}	IEP (pH)	ASC (%)	BET (m^2 g^{-1})	*S* (m^2 g^{-1})
Al-0	—	8.80	—	188	—
Al-1	0.11	8.25	13	180	23
Al-2	0.21	8.00	18	182	33
Al-3	0.32	7.64	26	179	46
Al-4	0.41	7.40	29	179	52
Al-5	0.83	7.20	33	175	58
Al-6	1.23	7.05	36	180	65
Al-7	1.66	6.95	37	171	63
Al-8	2.29	6.80	40	177	71
V_2O_5[a]	—	1.40	—	—	—
Ti-0	—	6.30	—	59	—
Ti-1	0.57	4.50	57	55	31
Ti-2	1.1	2.85	84	57	48
Ti-3	1.7	2.55	88	57	50
Ti-4	2.5	2.30	91	56	51
Ti-5	4.8	2.20	92	56	52
Ti-6	7.2	1.95	95	58	55

[a] Unsupported V_2O_5.

and IEP_M lead to inexact ASC values. This lack of exactness is, according to previous studies, not very important.

The ASC values for both supported V_2O_5 catalyst series are plotted in Fig. 3 versus the surface concentration of V_2O_5. Figure 3 shows that in the range studied the ASC values are clearly higher in the vanadium supported on TiO_2 than on γ-Al_2O_3. This behavior agrees with previous studies. van Hengstum *et al.* (*5*) reported that, in samples prepared by batch absorption of vanadia on TiO_2 and Al_2O_3, the maximum metal content absorbed was, respectively, 1.75 and 1.32 g of vanadia per 100 grams of support. Taking into account that the TiO_2 and the Al_2O_3 used by van Hengstum had, respectively, 50 and 90 $m^2 g^{-1}$, we can calculate a maximum vanadia charge per surface unit equal to 2.07×10^{14} molecules V_2O_5 cm^{-2} on TiO_2 and 0.86×10^{14} molecules V_2O_5 cm^{-2} on γ-Al_2O_3. Figure 3 shows that in the samples supported on TiO_2 and Al_2O_3 the ASC increases rapidly until $\sim 1 \times 10^{14}$ and ~ 0.5 molecules V_2O_5 cm^{-2}, respectively. From these values the ASC values reach a plateau due probably to the formation of multilayers of V_2O_5. It is remarkable, moreover, that multilayer on Al_2O_3 appears before the first theoretical monolayer is completed, while on TiO_2 it appears after ~90% of the surface is covered by V_2O_5. This is in agreement with the studies of Inomata *et al.* (*8*, *16*), from which it follows that the selective exposition of the (010) face on TiO_2 carrier leads to a high spread of the V_2O_5 (~90% of the theoretical monolayer (*8*)). On the contrary, on Al_2O_3 there is a diversity of exposed faces (*16*); therefore, the multilayer should appear before the theoretical monolayer is completed.

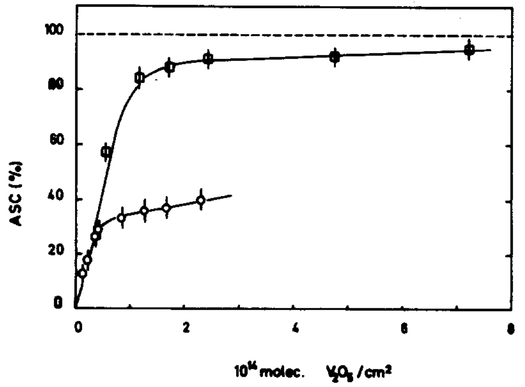

FIG. 3. Influence of the V content on the apparent surface coverage (ASC) as calculated by Eq. (1). □, V/TiO_2; ○, V/Al_2O_3 catalyst series.

On the other hand, however, assuming that the cross-sectional area for a molecule of supported V_2O_5 is 0.201 mm^2, which is actually the area of a molecule of V_2O_5 in a lamella of the three-dimensional V_2O_5 crystal (*17*), a monolayer of vanadium oxide completely covering the surface of the carrier should need 4.98×10^{14} molecules V_2O_5 cm^{-2}. Table 1, however, shows results that are in disagreement with this prediction; i.e., the sample Ti-1 has 0.57×10^{14} molecules V_2O_5 cm^{-2}. Therefore, it should not have an ASC higher than 11%; however, it has an ASC = 57%. Although the Ti-1 is the sample that is least within this prediction, it is clear that, except for samples Al-1, Ti-5, and Ti-6, all of the samples shown in Table 1 actually have ASC values higher than the maximum predicted from the value 0.201 nm^2 for the cross-sectional area of a molecule of supported V_2O_5. The reason for this behavior is indeed unknown. The differences between the theoretical and the experimental ASC values are too high to be attributed to the assumption made in the molecular weight or in the isoelectric point of the supported phase. Neither may be attributed to differences in the hydration grade between the supported and unsupported V_2O_5, because all the samples were hydrated at the same time. Neither may the disagreement be attributed to some heterogeneous distribution of the V_2O_5 along the particle, because, although the original particle size was 0.42–0.53 mm, it is difficult to understand that each powdered particle (~2 μm) can have a heterogeneous distribution of the V_2O_5 charge. A particle with an original size of ~0.45 nm with a heterogeneous distribution of the charge should lead to a group of powdered particles with different zeta potentials.

Moreover, it is remarkable that this disagreement is not actually a surprise, because something similar was previously reported for $MoO_3/\gamma\text{-}Al_2O_3$ systems (*18, 19*). Moreover, in these (*18, 19*), disagreement was established using both the electrophoretic method (*18*) and selective oxygen chemisorption (*19*). Finally, we should consider that the electrophoretic method may not be sufficiently precise to study quantitative parameters of samples with a very low surface concentration of the active phase. If this is true, then from the electrophoretic data we can infer only that the V_2O_5 coverage on the TiO_2 is clearly higher than on Al_2O_3, which seems to be due to the previously mentioned selective exposition of the (010) face on TiO_2 carrier.

The overall surface areas of the active phase shown in Fig. 4 were calculated by multiplying the ASC values by the S_{BET} surface area of each catalyst. From this figure it is clear that the dispersion of the vanadia is similar in both supports if the exposition of the (010) face is high enough, as should occur at low levels of the active phase. At high vanadia charges, practically all the TiO_2 surface is covered by the first monolayer of V_2O_5; therefore, the dispersion decreases. On the contrary, on Al_2O_3 the dispersion can even increase because ~60% of the surface is not covered; therefore, there should still be (010) exposed faces.

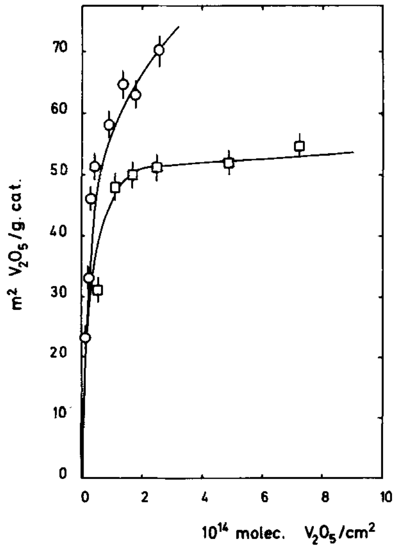

FIG. 4. Overall surface area of vanadia as a function of the vanadium oxide content. □, V/TiO_2; ○, V/Al_2O_3 catalyst series.

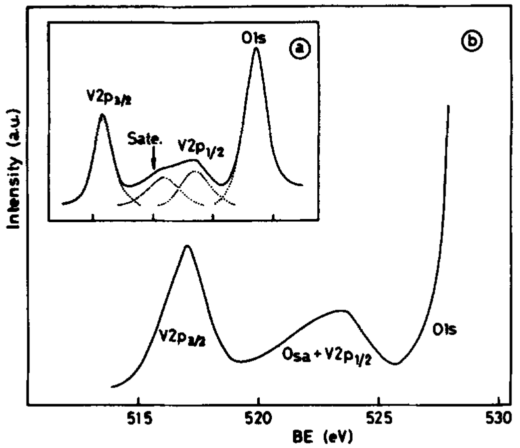

FIG. 5. (a) X-Ray photoelectron spectrum of unsupported V_2O_5. Dotted lines correspond to peak synthesis. (b) X-Ray photoelectron spectrum of 12.8% V_2O_5/TiO_2 catalyst (accumulation number is four times greater than in case (a)).

Relative Dispersion by XPS

The relative coverage of both TiO_2 and Al_2O_3 carriers was determined by XPS measurements. In this respect, the intensity of the signal corresponding to V $2p$ level of vanadium was measured and compared either with the Ti $2p$ or with the Al $2p$ signal intensities. The V $2p$/Ti $2p$ and V $2p$/Al $2p$ ratios were taken as a measure of the relative dispersion of vanadium in these supports.

As occurs for al the $3d$ transition metals, the V $2p_{3/2}$ level is the most intense peak of vanadium in its XPS spectrum; however, a precise determination of the binding energy is difficult because of the O $1s$ satellite-interfering peak, whose origin lies in the $MgK\alpha_{3,4}$ transition (Figs. 5a and b and Table 2). For this reason, background subtraction and smoothing computing programs were applied to take these signals

TABLE 2

V $2p_{3/2}$ Electron Binding Energy and Half-Width for Various Samples

Sample	V $2p_{3/2}$ (eV)	LWHM (eV)	Ref.
V_2O_5	516.7	1.7	(*22*)
V_6O_{13}	516.3	—	(*23*)
α-$VOPO_4$	516.6	1.8	(*24*)
V-SiO_4	516.8	2.5	(*20*)
V-TiO_2	517.0	2.4	This work
V-Al_2O_3	517.1	2.5	This work

apart. Because of its better resolution only the V $2p_{3/2}$ peak was considered in the calculations, even after peak deconvolution. Contamination by carbon (mainly from the oil of diffusion pumps) during time of data acquisition was not important even after recording the V 2*p* peak; the C 1*s* signal was a little less intense than at the beginning of the analysis.

In Fig. 5b the XPS spectrum corresponding to the V 2*p* levels of vanadium in the 8.2 × 10^{14} molecules V_2O_5 cm^{-2} on TiO_2 is given. The XPS spectrum of the reference compound, V_2O_5, is also included (Fig. 5a) (for comparative purposes). The most relevant features of these spectra for both catalyst series are as follows: (a) as V-oxide content decreases the intensity of the V $2p_{3/2}$ peak decreases and its linewidth at half-maximum (LWHM) increases; (b) a slightly higher BE (0.4 eV) of the V $2p_{3/2}$ peak was observed for the supported catalysts; and (c) no significant differences in characteristics (a) and (b) were found between titania and alumina.

The BE shift of the V $2p_{3/2}$ level to higher BE values is in agreement with the results obtained on the V/SiO_2 catalysts (*6, 20, 21*). When the BE values of unsupported V_2O_5 and supported catalysts are compared, a small shift (0.4 eV) to higher BE values is observed in the V $2p_{3/2}$ level. The sign of the shift is in agreement with the one observed in the silica-supported vanadium oxide catalyst (*21*), for which a positive shift as high as 1.2 eV was found.

The V 2*p*/Ti 2*p* and V 2*p*/Al 2*p* ratios as a function of the V content are given in Fig. 6. For both series a nearly linear dependence exists between both parameters, except in the low V content region where a deviation appears and corresponds to the ascending branches of the ASC curves presented in Fig. 3. These results seem to indicate a certain proportionality between dispersion and V content in the catalysts. As already stated above, the V dispersion is high enough on both TiO_2 and Al_2O_3 carriers. As can be observed in Fig. 6, for V/TiO_2 catalysts series the V 2*p*/Ti 2*p* increases monotonously with V content up to about 4 × 10^{14} molecular units cm^{-2} and then declines for a higher surface concentration.

The separation from linearity for V-surface concentration above about 4 × 10^{14} molecular units cm^{-2} can be due to the appearance of multilayered V structures. The formation of the multilayers is detected by XPS measurement at higher vanadia content than that by electrophoretic measurement. The difference between these results can be due to the fact that XPS analyses

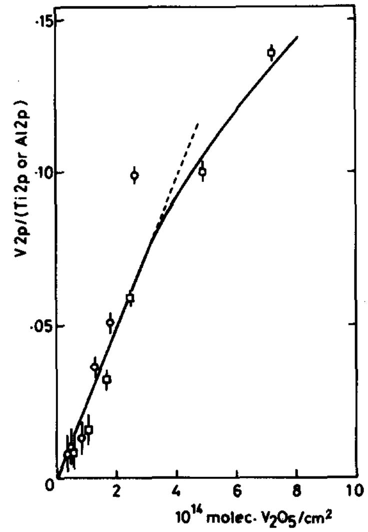

FIG. 6. Dependence of the V content on the V 2*p*/Ti 2*p* (□) and V 2*p*/Al 2*p* (○) normalized integrated intensity ratios, taken from the XPS spectra of both catalyst series.

cover more than one surface layer while the electrophoretic analyses only cover one surface layer. Thus, the ratio V 2*p*/(Ti 2*p* or Al 2*p*) of the sample shown in Scheme 2 would be higher than the ratio in Scheme 1, while the ASC values calculated from the electrophoretic method would be the same for both schemes.

SCHEME 1

SCHEME 2

The above representation together with the electrophoretic migration measurements give us a fairly accurate description of the surface area of the active ingredient as well as what is happening when more V is added to the carrier. Finally, we recall that our main purpose will be to test these catalyst series in the oxidation of butenes and *o*-xylene, and with the active areas define intrinsic activity in order to select the more efficient catalysts. Catalytic activity/selectivity and dispersion trends will also be discussed.

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