

On Oxygen Chemisorption for Characterization of Silica-Supported Vanadium Oxide Catalysts

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Oxygen chemisorption experiments on prereduced silica-supported vanadia catalysts have been performed in order to determine the optimum conditions for measuring the relative dispersion of vanadium oxide on the silica substrate. By following the extent of vanadia reduction microgravimetrically, it is shown that an appropriate prereduction of the catalyst at 823 K under hydrogen is fundamental in obtaining a reproducible well-defined stoichiometrically reduced vanadium oxide system (V^{3+}). At 643 K the reduction process is very much slower and requires very long times in order to approach a plateau. Measurement of the binding energies of the $V2p_{3/2}$ core level spectra indicates that high-temperature oxygen chemisorption (643 K) results in a reoxidation of the prereduced vanadium oxide species within crystallites leading to an overestimation of the number of exposed vanadium sites. Chemisorption at low temperatures (298 or 195 K) does not affect the stoichiometrically reduced vanadium oxide species within crystallites, thus allowing the number of exposed surface vanadium sites to be measured. © 1997 Academic Press

INTRODUCTION

Vanadia oxide catalysts constitute a class of industrially important catalysts for the selective oxidation and ammoxidation of light hydrocarbons (1, 2), oxidation of methanol to formaldehyde (3, 4), oxidation of sulfur dioxide (1, 5, 6), and the selective reduction of nitrogen oxides with ammonia (7–9). Understanding of the catalyst behavior requires an appropriate evaluation of the exposed vanadium sites. In general, knowledge of the apparent surface area of a transition metal oxide in a supported catalyst by chemisorption of oxygen has proved useful for several systems (10). As originally developed, the method based on oxygen chemisorption has involved a preliminary reduction in hydrogen at elevated temperatures followed by oxygen chemisorption at an appropriately low temperature. This procedure referred

to as low-temperature oxygen chemisorption has been employed with chromia catalysts for about 40 years and with molybdena catalysts for about 15 years. A review summarizes the low-temperature oxygen chemisorption for chromia and molybdena up to 1983 (10).

The philosophy underlying the low-temperature oxygen chemisorption methodology is as follows: (i) Since the higher valent transition metal oxides do not chemisorb oxygen in a stoichiometric manner, hydrogen prereduction is conducted under conditions such that the metal ion ends up in a reproducible and well-defined lower valent state. Standardized conditions (temperature, time) for this reduction should be chosen only after the extent of reduction has been quantitatively monitored in preliminary studies on the system of interest. Bulk reduction, as well as reduction of surface ions, of transition metal oxides may occur in this step and should be known. (ii) Although bulk reduction may have occurred, the purpose of oxygen chemisorption is to measure only the transition metal ions in the surface. The chemisorption temperature recommended for a standardized low-temperature oxygen chemisorption test procedure is chosen, therefore, to be low enough to preclude reoxidation of bulk phase material. Since the standardized test conditions are arbitrary, one reasonable demand is that the measured chemisorption value should be relatively insensitive to small variations in adsorption temperature.

Recently, a significant change in procedure has been recommended for silica-supported vanadia catalysts (11), and for silica-supported molybdenum oxide catalysts (12), namely high-temperature oxygen chemisorption. The high-temperature oxygen chemisorption is characterized by a prereduction of the materials at a lower temperatures than in low-temperature oxygen chemisorption methodology (13–15) to prevent overreduction of the materials. In addition, the oxygen chemisorption is performed at the same elevated temperature used for the prereduction of the material (640 K) as previous studies indicate that oxygen chemisorption is temperature activated (16) and underestimation of the exposed vanadium sites is prevented.

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However, for a given catalyst there are important differences in the measurement of the extent of oxygen chemisorption using both methodologies. The present work addresses the origins of these differences.

EXPERIMENTAL

Catalyst Preparation

A commercial silica (Aerosil 200, Degussa), particle size 12 nm, BET area 200 m² g⁻¹, and composition SiO₂ > 98.3%, Al₂O₃ = 1.3%, Fe₂O₃ < 0.01%, and Na₂O approximately 0.05% was used as support. This was impregnated with an aqueous solution of ammonium metavanadate (NH₄VO₃, Merck reagent grade) in appropriate amounts to give surface concentrations in the range 0.3–3.0 vanadium atoms per square nanometer of the silica surface (V/nm²). The excess water was removed in a rotary evaporator at 343 K under reduced pressure. The impregnates were then dried at 383 K for 12 h and subsequently calcined in air in two steps: 623 K for 2 h and 923 K for 5 h. Prior to chemisorption tests the catalysts were pelleted and sieved in the mesh range below 0.42 mm. The samples will be referred to as *x*V/nm², where *x* denotes the surface concentration of vanadium atoms. A high-purity V₂O₅ sample (Spex quality) was used as a standard for photoelectron spectroscopy measurements.

Experimental Techniques

Catalyst reducibility was calculated from the kinetic reduction isotherms performed using a Cahn 2000 microbalance operating with a sensitivity of 10 μg. Catalyst samples (approximately 80 mg) were firstly heated at 4 K min⁻¹ to 823 or 643 K in a flow (60 cm³ min⁻¹) of helium (99.997% vol) before measuring the kinetic reduction curves in a flow (60 cm³ min⁻¹) of H₂ (99.995% vol) at the same temperatures. Weight changes as a function of time were collected automatically by a microprocessor.

Photoelectron spectra were acquired with an ESCALAB 200R spectrometer equipped with a hemispherical electron analyzer and MgKα 120-W X-ray source. A PDP 11/04 computer from Digital Equipment Co. was used for collecting and analyzing the spectra. The powder samples were pressed into small aluminium cylinders and then mounted on a sample rod placed in a pretreatment chamber and outgassed at room temperature for 1 h. Then they were reduced in 400 Torr (1 Torr = 133.33 N/m²) hydrogen at 823 or 643 K for 2 h prior to being moved into the analysis chamber. After analysis, the samples were moved to the pretreatment chamber and exposed to 10 Torr oxygen at 297 or 643 K for 0.5 h. The pressure in the ion-pumped analysis chamber was below 3 × 10⁻⁹ Torr during data acquisition. The spectra were collected for 20 to 90 min, depending on the peak intensities, at a pass energy of 10 eV

(1 eV = 1.602 × 10⁻¹⁹ J) which is typical of high-resolution conditions. The intensities were estimated by calculating the integral of each peak after smoothing and subtraction of the “S-shaped” background and fitting the experimental curve to a combination of Gaussian and Lorentzian lines of variable proportion (G/L = 10–35%). All binding energies (BE) were referenced to the adventitious C1s line at 284.9 eV. This reference gave BE values within an accuracy of ±0.2 eV.

Chemisorption measurements were performed in a Micromeritics Pulse Chemisorb 2700 apparatus. Catalyst samples of 200–400 mg were dried at 323 K in helium (30 cm³/min) (99.999% vol) and then reduced at either 823 or 643 K under 30 cm³/min hydrogen (99.998% vol) for periods of 1 to 4 h. They were subsequently cooled to 643, 298, or 195 K in a flow of He (30 cm³/min). Oxygen chemisorption was performed by dosing 50-μl pulses of oxygen (99.998% vol) and determining the amount of consumed oxygen by a thermal conductivity detector. A second series of experiments indicated that the participation of physically adsorbed oxygen during the chemisorption test at 195 K was negligible.

RESULTS AND DISCUSSION

Catalyst Reducibility

Figure 1 shows the extent of reduction (expressed as O atoms removed per V atom) as a function of catalyst loading and temperature during isothermal reduction of silica-supported vanadium oxide catalysts. The extent of reduction for vanadium oxide is very sensitive to the reduction temperature. The higher temperature results in both faster and more extensive reduction. For all loadings, reduction at 643 K is slow and nonstoichiometric (Fig. 1A). Even for the lowest loading (0.3 V/nm²), the extent of reduction only approaches a plateau of about 0.6 oxygen atoms removed per vanadium atom. Reduction at 823 K (Fig. 1B), by contrast, results in almost stoichiometric reduction of V⁵⁺ to V³⁺ for vanadium catalysts with 0.3 and 0.7 V/nm². Oxygen removal is about 0.89 oxygen atom per vanadium atom for the 0.3 loading, and 0.95 for the 0.7 loading; this is accomplished in the relatively short time of 2 h. For the 3.0 V/nm² sample, where aggregated vanadium oxide species are observed (17), the reducibility decreases (13–15). This is in agreement with previous results which indicate the bulk vanadium oxide species show a much lower reducibility than dispersed surface vanadium oxide species (13–15).

The higher reducibility of dispersed vanadia on silica is connected with its structure. The structural characterization of surface vanadium oxide species on SiO₂ by Das *et al.* (18) revealed that a single Raman band was present at 1037 cm⁻¹, whose position is independent of the vanadium oxide loading, and the isotropic chemical shift in the ⁵¹V MAS-NMR for the surface vanadium oxide species was

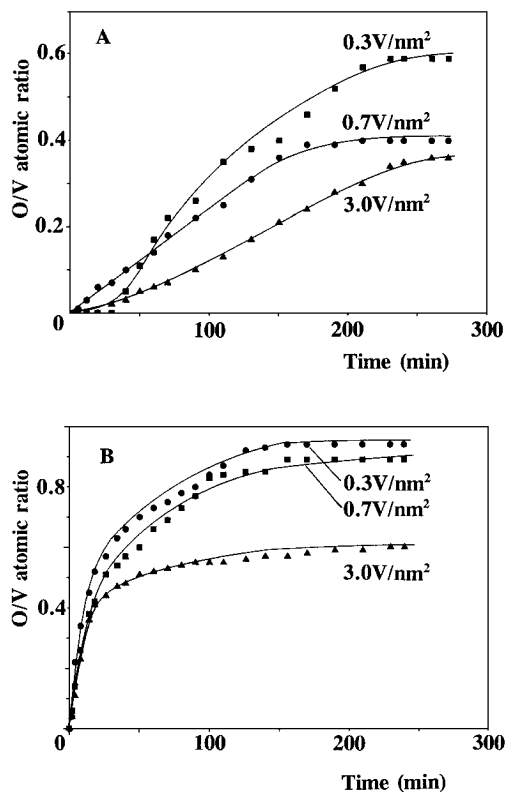


FIG. 1. Kinetic curves of reduction of silica-supported vanadia catalysts under isothermal conditions: (A) 643 K and (B) 823 K. The vanadium contents are indicated on each curve.

at -710 ppm with an axially symmetric line shape. However, they did not observe V–O–V vibrations in the $250\text{--}150\text{ cm}^{-1}$ energy region, suggesting the absence of polymeric structures. The absence of V–O–V bonds was also substantiated by EXAFS/XANES studies where no V–V neighbor was observed less than 0.35 nm (19). Furthermore, the structure of these isolated vanadium oxide species on SiO_2 was determined to be a three-legged isolated $(\text{SiO})_3\text{V}=\text{O}$ unit, and the presence of its single terminal V=O bond was also confirmed by $^{18}\text{O}\text{--}^{16}\text{O}$ exchange experiments (11).

Photoelectron Spectroscopic Analysis

Further insight into the extent of modification of the oxidation state of the vanadium sites may be obtained using X-ray photoelectron spectroscopy. As the binding energies for $\text{V}2p$ and $\text{O}1s$ lay very close together, a careful analysis of the profile of the $\text{V}2p$ energy region is required. Figure 2 displays the $\text{V}2p$ peaks of an unsupported V_2O_5 sample. The splitting of the two $\text{V}2p_{3/2}$ and $\text{V}2p_{1/2}$ peaks is approximately 7.2 eV in agreement with literature reports (20–22). The exact determination of the binding energies and specifically that of the $\text{V}2p_{3/2}$ peak is difficult due to the interfering $\text{O}1s$ satellite component, whose origin lies in the $\text{MgK}\alpha_{3,4}$ line. This interfering peak is present in all the spectra as

no monochromator was used to filter the X-ray exciting source. Additionally, the resolution of the $\text{V}2p_{1/2}$ peak is much poorer than that of the $\text{V}2p_{3/2}$ peak. This can be significantly complex for supported vanadium oxide species with low vanadium loading. In such cases, the $\text{V}2p_{1/2}$ peak can be completely masked by a more intense $\text{O}1s$ satellite line contribution. Consequently, only the $\text{V}2p_{3/2}$ peak is considered in calculations, even after background removal and peak deconvolution procedures.

The $\text{V}2p_{3/2}$ core-level spectra of vanadium catalysts with 0.7 and 3.0 V/nm^2 , subjected to different pretreatments and oxygen chemisorption tests, are displayed in Figs. 3A and 3B, respectively. For the sake of clarity, vertical bars corresponding to the BE values characteristic of V^{5+} , V^{4+} , and V^{3+} in the $\text{V}2p_{3/2}$ energy region are included in these figures. The reference used for the BE of $\text{V}2p_{3/2}$ core electrons in V^{5+} ions was a high purity V_2O_5 sample (Spex), whereas the BE values for V_2O_4 and V_2O_3 were taken from literature (23). The BE of vanadium peaks and the relative XPS V/Si intensity ratios are summarized in Table 1. Reduction of 0.7 V/nm^2 sample within the pretreatment chamber of the spectrometer for 1 h under hydrogen at 823 K (Fig. 3A, spectrum a) yields a mixture of 22% V^{3+} and 78% V^{4+} . The reduction of the same catalyst at 643 K (Fig. 3A, spectrum d) is much less pronounced as illustrated by the observation of only 57% V^{4+} and 43% V^{5+} , with no V^{3+} being detected after this treatment (Table 1). The observation of a less well reduced vanadium oxide species in 3.0 V/nm^2 sample following treatment at 643 K is consistent with microgravimetric measurements.

Exposure of 0.7 V/nm^2 sample prereduced at 823 K to 10 Torr oxygen at 298 K for 30 min (Fig. 3A, spectrum b) does not significantly change the V^{3+} and V^{4+} percentages. A similar trend is observed for the same sample prereduced

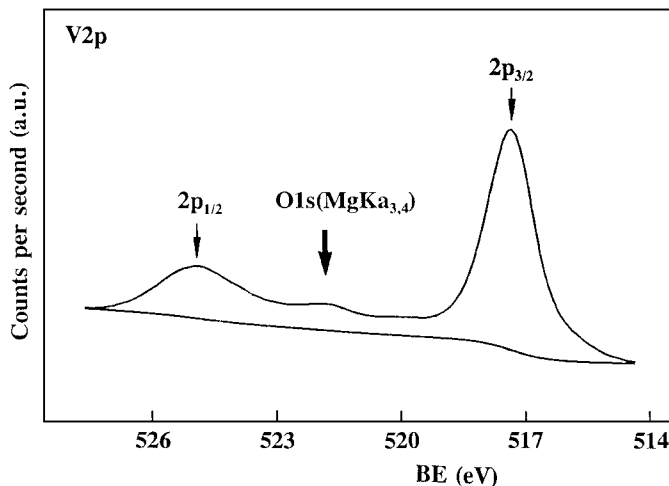


FIG. 2. $\text{V}2p$ core level spectrum of unsupported V_2O_5 (Spex quality) oxide. The contribution of $\text{O}1s$ satellite line ($\text{MgK}\alpha_{3,4}$) to the whole spectrum is clearly seen once the S-shaped background is subtracted.

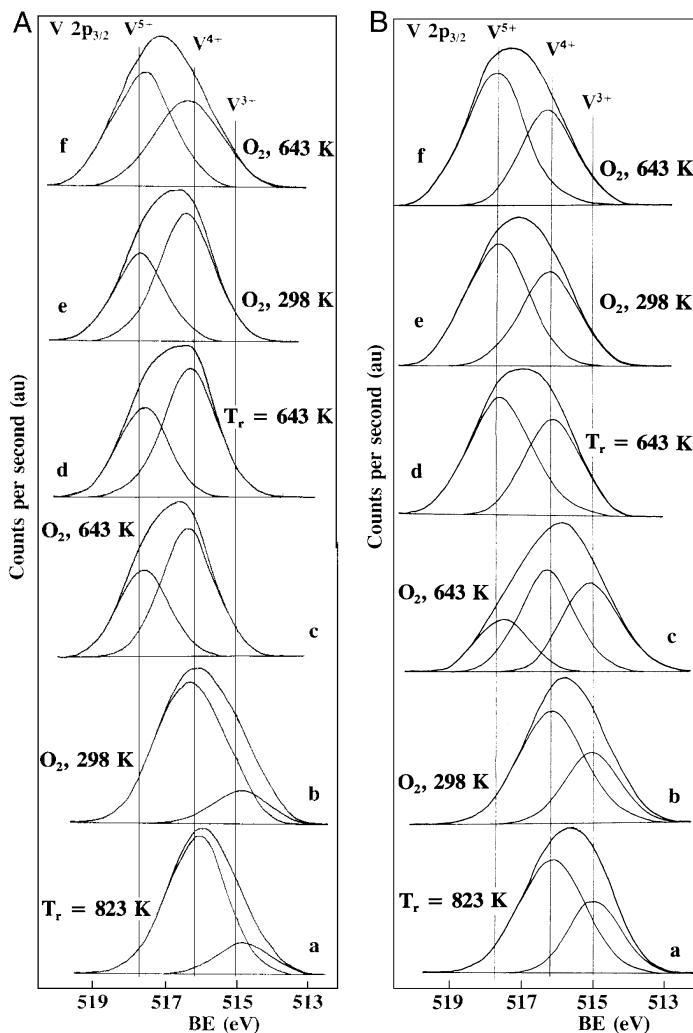


FIG. 3. $V 2p_{3/2}$ core level spectra after background subtraction of the catalysts 0.7 V/nm^2 (A) and 3.0 V/nm^2 (B) subjected to different pretreatments: (a) reduction in hydrogen at 823 K for 1 h followed by outgassing for 10 min at the same temperature; (b) after pretreatment (a), the sample was exposed to 10 Torr O_2 at 298 K for 0.5 h; (c) after pretreatment (a), the sample was cooled to 643 K and then exposed to 10 Torr O_2 at this temperature for 0.5 h; (d) reduction in hydrogen at 643 K for 1 h followed by outgassing for 10 min at the same temperature; (e) after pretreatment (d), the sample was exposed to 10 Torr O_2 at 298 K for 0.5 h; (f) after pretreatment (a), the sample was exposed to 10 Torr O_2 at 643 K for 0.5 h.

at 643 K and exposed to 10 Torr oxygen at 298 K (Fig. 3A, spectrum e). Different behavior, however, is observed when the 0.7 V/nm^2 sample prereduced at 823 and 643 K is exposed to the same pressure of oxygen for the same length of time at 643 K (Fig. 3A, spectra c and f, respectively). While the sample 0.7 V/nm^2 prereduced at 823 K (22% V^{3+} and 78% V^{4+}) becomes strongly oxidized during the chemisorption test at 643 K (48% V^{4+} and 42% V^{5+}) (Fig. 3A, spectrum c), only a slight oxidation seems to occur for the sample prereduced at 643 K and exposed to oxygen at the same temperature (Fig. 3A, spectrum f). In this latter case, V^{4+} and V^{5+} were the only vanadium species present, and the proportion of 55% V^{4+} and 45% V^{5+} in the reduced catalyst changed to 48% V^{4+} and 52% V^{5+} after exposure to oxygen at 643 K.

Similar findings can be shown for the 3.0 V/nm^2 sample subjected to the same pretreatments as 0.7 V/nm^2 (Fig. 3B, Table 1). The proportion of reduced vanadium species in the 3.0 V/nm^2 prereduced at 823 K (37% V^{3+} and 63% V^{4+}) (Fig. 3B, spectrum a) does not change upon oxygen adsorption at 298 K (38% V^{3+} and 62% V^{4+}) (Fig. 3B, spectrum b). However, an important fraction of V^{4+} species undergo oxidation upon exposure to oxygen at 643 K (38% V^{3+} , 39% V^{4+} , and 23% V^{5+}) (Fig. 3B, spectrum c). From a comparison of the $V 2p_{3/2}$ spectra for the 0.7 and 3.0 V/nm^2 samples prereduced at 823 K and exposed to oxygen at 643 K it is apparent that V^{3+} species in 3.0 V/nm^2 sample are not oxidized during the oxygen chemisorption test. This may be understood as due to a stabilization of V^{3+} species in subsurface layers of V_2O_3 crystals, with only the exposed

TABLE 1

Binding Energies (eV) and XPS Intensity Ratios of V/SiO₂ Catalysts Subjected to Different Pretreatments

Pretreatment	Si2p	V2p _{3/2}	I _V /I _{Si}
3.0 V/nm ² , reduced at 823 K and outgassed	103.4	515.0 (37) 516.3 (63)	0.088
3.0 V/nm ² , reduced at 823 K and O ₂ adsorption at 298 K	103.4	515.1 (38) 516.3 (62)	0.073
3.0 V/nm ² , reduced at 823 K and O ₂ adsorption at 643 K	103.4	515.1 (38) 516.4 (39) 517.3 (23)	0.075
3.0 V/nm ² , reduced at 643 K and outgassed	103.4	516.2 (45) 517.2 (55)	0.092
3.0 V/nm ² , reduced at 643 K and O ₂ adsorption at 298 K	103.4	516.3 (46) 517.2 (54)	0.090
3.0 V/nm ² , reduced at 643 K and O ₂ adsorption at 643 K	103.4	516.4 (44) 517.3 (56)	0.085
0.7 V/nm ² , reduced at 823 K and outgassed	103.4	515.0 (22) 516.1 (78)	0.068
0.7 V/nm ² , reduced at 823 K and O ₂ adsorption at 298 K	103.4	514.9 (23) 516.2 (77)	0.060
0.7 V/nm ² , reduced at 823 K and O ₂ adsorption at 643 K	103.4	516.3 (58) 517.3 (42)	0.062
0.7 V/nm ² , reduced at 643 K and outgassed	103.4	516.2 (57) 517.3 (43)	0.071
0.7 V/nm ² , reduced at 643 K and O ₂ adsorption at 298 K	103.4	516.3 (55) 517.4 (45)	0.070
0.7 V/nm ² , reduced at 643 K and O ₂ adsorption at 643 K	103.4	516.3 (48) 517.3 (52)	0.075

Note. Values in parentheses correspond to peak percentages.

vanadium ions being susceptible to further oxidation by oxygen. It is also emphasized at this point that, under the conditions of the chemisorption test, thermodynamics favor the complete oxidation of the V₂O₃ crystal but the kinetics seems to be very slow. Accordingly, only the surface, and probably a few near subsurface, layer becomes oxidized. It can be noted that estimated electron mean free path for vanadium oxide is 1.1 nm (24). For the vanadium catalyst with 3.0 V/nm² prereduced at 643 K (Fig. 3B, spectrum d), there is no significant change in the proportion of V⁴⁺ and V⁵⁺ species after exposure to oxygen either at 298 K (Fig. 3B, spectrum e) or at 643 K (Fig. 3B, spectrum f).

In summary, H₂-reduction at 823 K of the vanadium catalysts with 0.7 and 3.0 V/nm² produces both V³⁺ and V⁴⁺ species, which do not undergo significant reoxidation upon exposure to oxygen at low temperature (298 K) and only oxygen chemisorption appears to take place. Reoxidation of the vanadium sites is minimal, if at all, for the vanadia-silica samples reduced at lower temperature (643 K). The vanadia-silica samples prereduced at 823 and 643 K become oxidized to a greater extent upon exposure to oxygen at higher temperatures (643 K).

The comparison of XPS V/Si intensity ratios (Table 1, last column) for the 0.7 and 3.0 V/nm² samples also provides some clues on the changes of vanadium oxide dis-

persion. Although for a given catalyst (0.7 or 3.0 V/nm²) the V/Si varies to a certain extent with the pretreatments, this allows to compare V/Si intensity ratios for the 0.7 and 3.0 V/nm² catalysts. On average, the V/Si intensity ratio for the 0.7 V/nm² catalyst is approximately 0.070, but this ratio only increases by about 23% for the 3.0 V/nm² sample containing more than three times V loading. This result clearly emphasizes the decay of vanadia dispersion of xV catalysts in the region of high vanadium oxide content.

Oxygen Chemisorption

Photoelectron spectroscopy provides a good insight into the nature of the different prereduced surface vanadium sites. These differences may be expected to affect the extent of oxygen consumption in the chemisorption experiments. Oxygen consumption, expressed as the O/V ratio, is presented in Figs. 4 and 5 under several experimental conditions, as a function of surface vanadium loading.

The extent of oxygen chemisorption at 195 and 298 K does not appear to be significantly affected by the length of the reduction period at 823 K (Fig. 4). There is an initial increase in the O/V ratio up to surface vanadium loadings close to 1.0 V/nm², followed by a progressive decrease at higher vanadium contents. For the catalysts with vanadia concentrations higher than 1 V/nm², the decay of the O/V ratio indicates agglomeration of vanadium oxide entities into well-defined crystalline vanadium oxide (15, 17, 18). Larger vanadia crystals present at higher vanadium loadings have a well-defined structure that decreases the probability of defects in the vanadia lattice, thus preventing additional chemisorption of oxygen at 195 and 298 K leading to constant values at higher loadings.

No significant differences are observed between chemisorption experiments at 195 and 298 K (low-temperature oxygen chemisorption experiments) (Figs. 5A

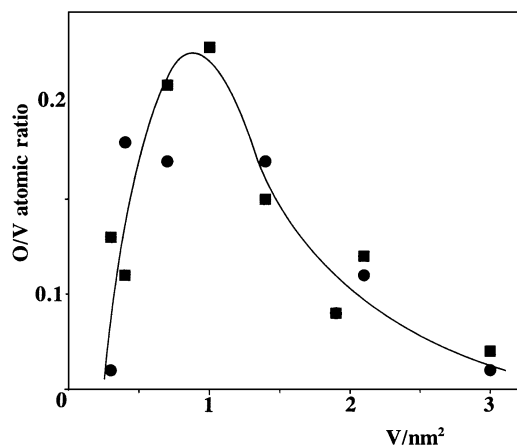


FIG. 4. Extent of oxygen chemisorption at 298 K on H₂-prereduced samples as a function of the vanadium surface concentration for catalysts prereduced for 1 h (circles), and for 4 h (squares).

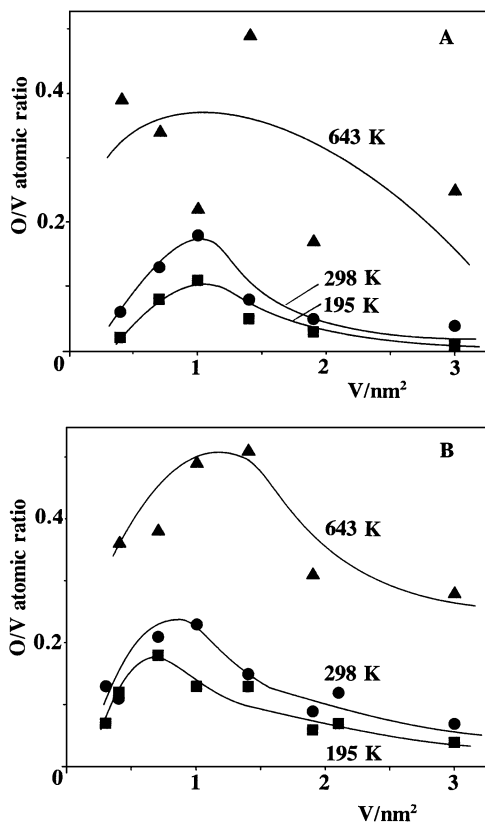


FIG. 5. Extent of oxygen chemisorption on H₂-prereduced samples as a function of the vanadium surface concentration for vanadia catalysts prereduced at (A) 643 K and (B) 823 K for 4 h. The temperatures of the chemisorption test are indicated on each curve.

and 5B). When oxygen is chemisorbed at higher temperatures (643 K) (high-temperature oxygen chemisorption), a significant increase in the O/V ratio is observed. The high O/V ratio observed may be attributed to reoxidation of the reduced vanadium species, as indicated by XPS (Fig. 3A, spectrum f, and Fig. 3B, spectrum f). Comparison of Figs. 5A and 5B also reveals that the prereduction of the silica-supported vanadium oxide species at lower temperatures (643 K) results in a larger scattering of the oxygen chemisorption values, particularly when the temperature of the chemisorption test is 643 K, that is, in a significant decrease in the accuracy of the experimental results. In addition, the consumption of oxygen is higher at low chemisorption temperatures compared to samples prereduced stoichiometrically, as expected from XPS observations (Fig. 3A, spectrum b vs spectrum e).

CONCLUSIONS

Evaluation of the number of exposed vanadium sites in silica-supported vanadium oxide catalysts has been the subject of numerous studies. Unfortunately, important differences in the chemisorption procedures have led different

authors to recommend very different, and in many cases, contradictory procedures for the accurate measurement of vanadium sites exposed on V₂O₅/SiO₂ catalysts. The results presented above reveal that not only the chemisorption conditions but also the prereduction protocol of the materials play a fundamental role in the chemisorption experiments. Vanadium surface coverage is also a critical parameter as it determines whether the vanadium oxide will be present in the form of isolated species, dispersed surface species, or as aggregated bulk crystalline V₂O₅ (17, 18). Prereduction of the surface dispersed vanadium oxide species under hydrogen at 823 K yields well-defined vanadium oxide species stoichiometrically reduced to V³⁺, which are stable to exposure to oxygen at 298 K. Bulk V₂O₅ species show a lower reducibility than surface dispersed vanadium oxide species (13–15, 25). The dispersed surface vanadium oxide when prereduced at a lower temperature (643 K) results in the formation of an ill-defined nonstoichiometric reduced vanadium oxide on silica, which in addition, is more sensitive to the presence of oxygen at low temperature (298 K). This is an additional parameter which is revealed by the experiments of oxygen chemisorption, where lower accuracy and higher amounts of the consumed oxygen at 298 and 195 K are found (Fig. 5). Consequently, the oxygen consumption on nonstoichiometrically reduced vanadium oxide species is not only associated with the chemisorption itself, but also with a partial reoxidation of the vanadium oxide.

When oxygen is chemisorbed at high temperature (643 K), high-temperature oxygen chemisorption, the amount of chemisorbed oxygen increases dramatically. This increase must be associated with a reoxidation of the vanadium species rather than surface chemisorption as indicated by XP spectra. In addition, bulk oxidation is clearly inferred from the almost linear increase in consumed oxygen even at vanadium loadings higher than approximately 1.4 V/nm² where aggregated vanadium oxide species are known to exist (15, 17). XP spectra and chemisorption experiments indicate that at high temperatures the main phenomenon taking place is the reoxidation of the reduced vanadium oxide species. It is worthwhile reiterating that the thermally activated oxygen chemisorption was initially proposed for nonreduced vanadium oxide systems, where reoxidation of the samples is not possible (7).

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