JOURNAL OF CATALYSIS **120**, 457–464 (1989)

Phase Transformations of Vanadia–Titania Catalysts Induced by Phosphoric Acid Additive

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Received February 2, 1989; revised April 24, 1989

The effect of phosphoric acid addition on the nature of the species present in vanadia–titania catalysts has been studied by ESR, XPS, and TPR. All the results indicate that phosphoric acid reacts not only with the vanadium species deposited on the outer part of the titania support, but also with the surface (and probably with a few subsurface) TiO_2 layers of these particles. The chemical features and the extent of formation of the resulting vanadium and titanium phosphates were found to be strongly influenced by the phosphorus content of the preparations.

INTRODUCTION

The activity patterns of metal oxides for the removal of NO_x emissions from stacks in power and nitric acid plants have attracted the attention of many researchers in recent years. The selective catalytic reduction (SCR) of NO_x with NH_3 seems to be the most reliable process for this purpose (for a review, see Ref. (*1*) and references therein). Although it is expensive due to NH_3 consumption, it has a high removal efficiency (nearly 90%). Most of the catalysts employed in the high-temperature SCR process are based on V_2O_5 as the active component. In the case of power plants, WO_3 is also used in minor amounts, in order to decrease the catalytic activity in the oxidation of SO_2 to SO_3 (*2*, *3*), as the latter gas causes serious corrosion problems in the cold parts of the air preheater. Both active ingredients supported on titania (anatase), to which phosphoric acid was added as a pelletizing agent, were used very recently by Blanco *et al.* (*4*) in the SCR of the NO_x. In spite of the beneficial mechanical strength of the catalyst provided by the phosphorus additive, there is no available information on the chemical transformations induced in the catalyst surface by the presence of phosphorus. The aim of the work reported here is the understanding of the effect of phosphorus on the processes taking place at the catalyst surface during activation.

EXPERIMENTAL

Catalyst preparation. The catalysts consisted of an amorphous hydrated titanium oxide basis (Tioxide; composition by weight: H_2O 56% and SO_4^{2-} 8%) which was impregnated with ammonium metavanadate (Merck) and ammonium paratungstate (Prolabo) aqueous solution to give a final atomic ratio Ti : V : W = 90 : 8 : 2. The dried precursor paste was then mixed, homogenized with aqueous phosphoric acid of varying concentrations (the amount being chosen to achieve a slurry viscosity of 500.000 cp), and then quickly pelletized. Catalyst pellets were then dried at 380 K followed by air-calcination at 773 K. For comparison, a P-containing titania sample (P1′) was prepared similarly and examined. Chemical composition and specific surface areas of these samples are summarized in Table 1.

XRD revealed in all samples anatase as the only TiO_2 form; some titanium phos-

0021-9517/89 $3.00

TABLE 1

Composition, Surface Area, and Reducibility Parameters

Catalysts	Composition[a]			Surface area (m²/g)	Reducibility parameters	
	V	W	P		T_0 (K)	T_{max} (K)
P0	4.6	4.4	—	64 ± 3	560 ± 5	682 ± 3
P1	3.4	3.2	12.3	12.7 ± 0.7	693 ± 5	753 ± 2
P2	3.2	3.0	14.7	7.7 ± 0.6	596 ± 5	752 ± 2
P1′	—	—	13.1	9.2 ± 0.7	647 ± 5	721 ± 3

[a] Weight percentage of the corresponding element. Estimate error is below 1.5%.

phate peaks (β-Ti$(HPO_4)_2$ phase) were also observed in samples P1 and P2. As to the V component, V_2O_5 was detected only in sample P0; a definitive vanadium phosphate (β-$VOPO_4$ phase) was found only in sample P2. No other Ti- or V-related phases were observed in these XRD patterns.

Techniques. ESR spectra were obtained with a Bruker ER 200D spectrometer operating in the *X*-band. All spectra were recorded at 77 K. A Mn : MgO standard ($g_{eff} = 2.0066$) was used to calibrate the magnetic field/frequency ratio. Samples of ca. 50 mg were placed inside a quartz probe cell assembled with greaseless stopcocks, and pretreated under vacuum or H_2 at temperatures ranging between 295 and 773 K. Temperature-programmed reduction experiments were carried out gravimetrically with a Cahn RG microbalance, working with a sensitivity of 1 μg. Samples of ca. 40 mg were heated in He flow (80 $cm^3\ min^{-1}$) at a rate of 4 K min^{-1} up to 673 K, this temperature being then maintained for half an hour. After cooling in He flow to 393 K, the flow was switched to H_2 and then the sample weight change was recorded as a function of temperature. When the maximum temperature (783–793 K) was reached, the samples were kept isothermally for half an hour.

XP spectra were acquired with a Leybold Heraeus LHS 10 spectrometer working in the (ΔE = constant) mode at a pass energy of 20 eV. The spectrometer was provided with a hemispherical electron analyzer and a Mg X-ray source (Mg Kα = 1253.6 eV). The samples were mounted on a long rod placed inside an introduction chamber and outgassed up to ca. 10^{-5} Torr for 0.5 h before the samples were moved into the turbopumped analysis chamber. The pressure in this chamber was maintained below 4×10^{-9} Torr during data acquisition. A 20-eV energy region of the photoelectrons of interest at the pass energy selected was chosen as a compromise, enabling acceptable energy resolution to be obtained within reasonable data acquisition time. Each spectral region was signal-averaged to a number of scans to provide a good signal-to-noise ratio. Although surface charging was observed on all samples, accurate binding energies (BE) were determined by charge referencing to the adventitious C1*s* line, arising from contamination in the initial outgassing step, at 284.6 eV.

RESULTS

ESR Data

The effect of heat treatments in the temperature range 295–773 K, in the presence of H_2, has been studied by ESR on the three vanadium-containing catalysts and two other samples without vanadium, i.e., the TiO_2 precursor paste and phosphoric acid-treated TiO_2 (P1′), that are used as reference samples.

The hydrated TiO_2 sample did not show Ti^{3+} signals even after reduction treatments at 773 K. The P1′ sample reduced at 473 K presented an axial signal with $g_\perp = 1.950$, $g_\parallel = 1.874$, and $\langle g \rangle = 1.925$. These *g* values are slightly lower than those expected for Ti^{3+} ions in TiO_2 (*5*) and closer to those observed in titanium phosphate phases (*6*). After outgassing at 295 K, the spectrum of sample P0 (Fig. 1a) shows a broad signal *A* (ΔH = 360 G) centered at $g = 1.960$, overlapping two signals of lower intensity which show a partially resolved eight-line hyperfine structure (hfs) assignable to interaction with the magnetic V nuclei ($I = 7/2$). The

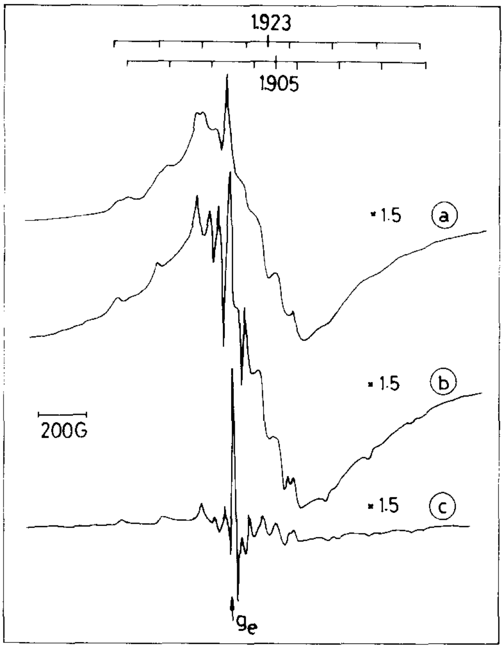

FIG. 1. ESR spectra of phosphorus-free (P0) sample subjected to various pretreatments: (a) outgassing at 295 K; (b) H_2 reduction at 573 K; (c) H_2 reduction at 673 K followed by gas-phase removal at the same temperature.

parameters of these two signals ($g_{\|_1}$ = 1.923, $A_{\|_1}$ = 184 G; $g_{\|_2}$ = 1.905, $A_{\|_2}$ = 180 G; perpendicular components not well resolved in both cases) are more appropriate to vanadyl groups than to V^{4+} ions, which usually show smaller hyperfine splitting constants (hfsc) (7). Therefore they indicate the presence, in small amounts, of two types of isolated VO^{2+} groups with two different coordination spheres. None of these signals are affected by adsorption of gaseous O_2 ($P_{O_2} > 5$ Torr) at 77 K, indicating that these paramagnetic species are not located at the sample surface.

Signal *A*, broad and with a *g* value far from g_e, must be due to transition metal cations affected by magnetic interactions. Since this signal can be observed at 295 K, which is not the case for Ti^{3+} signals in TiO_2 (5), it can be assigned to vanadium(IV) ions; the broadness of the signal and the lack of resolved hfs indicate that these ions experience strong magnetic dipolar interactions, suggesting an assignation to agglomerates of a vanadium oxide phase. According to its intensity, this signal must represent most of the reduced ions detected by ESR in this sample.

When the catalyst is heated under H_2 at increasing temperatures, an increase in the intensity of the three ESR signals is initially observed, but for a reduction temperature of 573 K, signal *A* decreases, allowing a better resolution of signals 1 and 2 (Fig. 1b). At 673 K, signal *A* disappears, the intensity of the other signals decreases (Fig. 1c) and a sharp signal is observed at $g \simeq g_e$, probably due to electrons trapped in oxygen vacancies. After treatment at 773 K only this last signal, with low intensity, is detected.

The spectrum of sample P1 after outgassing at 295 K (Fig. 2a) does not show signal *A*, but a new signal 3 is observed ($g_{\|_3} \simeq$ 1.921, $A_{\|}$ = 206 G, and perpendicular components not resolved) due to VO^{2+} ions, together with two signals 1′ and 2′ with parameters similar to those of 1 and 2. The hfsc of signal 3 is higher than those observed for VO^{2+} in vanadia–titania catalysts and similar to these observed for VO^{2+} in vanadium phosphate compounds (8). These vanadyl groups are less affected by the reduction treatment than those of sample P0, and after heating under H_2 at 773 K their signals are still detected, although with low intensity (Fig. 2b). An additional axial signal with $g_{\perp}$ = 1.948, $g_{\|}$ = 1.870 is also shown by spectrum 2b; it is similar to the signal observed in sample P1′ and, therefore, can be assigned to Ti^{3+} ions in a titanium phosphate phase.

The spectra obtained for sample P2 after the different reduction treatments show a behavior relatively similar to that of sample P1. However, the contribution of signal 3 in the initial sample (outgassed at 295 K, Fig. 2c) is larger, and after reduction at 773 K the VO^{2+} signals have practically disappeared, while the Ti^{3+} signal is more marked (Fig. 2d).

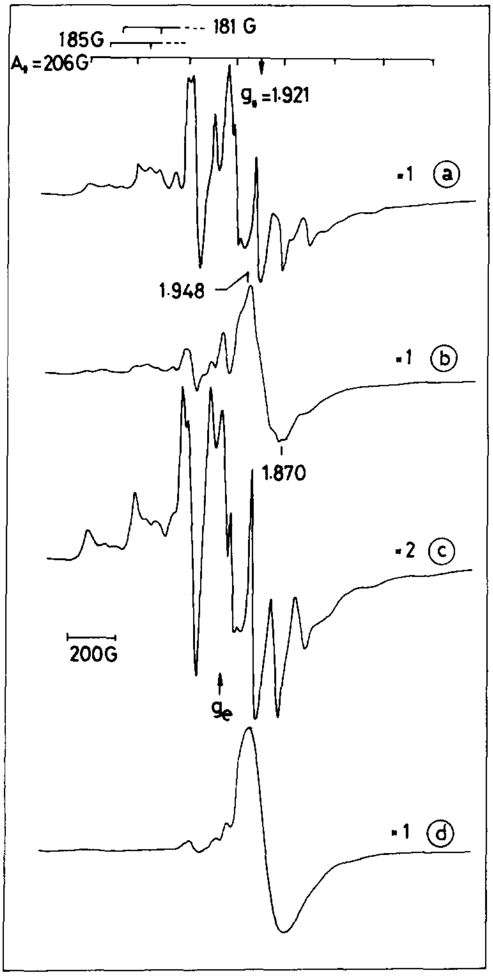

FIG. 2. ESR spectra of phosphorus-containing samples subjected to various pretreatments: (a) P1 outgassed at 295 K; (b) P1 reduced at 773 K; (c) P2 outgassed at 295 K; (d) P2 reduced at 773 K.

XPS Data

X-ray photoelectron spectra of V2*p* and Ti2*p* levels for samples P0, P1, and P2 are shown in Figs. 3A and 3B, respectively. The BE of the most intense $V2p_{3/2}$ and $Ti2p_{3/2}$ peaks for these samples and also for several reference compounds are summarized in Table 2. As can be observed in Fig. 3A, the line profile of the V2*p* spectrum is rather complex because an O1*s* satellite interfering peak, arising from the Mg $K\alpha_{3,4}$ line in the excitation source (no monochromator was used), is placed in between the V2*p* doublet. Owing to this, the precise determination of BE of the $V2p_{1/2}$ peak is difficult; consequently only the most intense $V2p_{3/2}$ level will be analysed. An examination of spectra a–c in Fig. 3A reveals that important changes occur both in BE and line shape of the $V2p_{3/2}$ peak when phosphorus is added to the base vanadium–titanium oxide catalyst precursor. While the $V2p_{3/2}$ line at BE = 517.0 eV is intense and not too large (FWHM = 2.19 eV) in sample P0, it appears with two components at 517.2 and 516.2 eV in sample P1 and with only one component at 517.3 eV (but somewhat broadened, FWHM = 2.72 eV) in sample P2. On the other hand, some differences in the Ti2*p* peaks (Fig. 3B) are also observed. Although the BE for the most intense $Ti2p_{3/2}$ peak is essentially independent of the presence of P (Table 2, Fig. 3B), the FWHM of this peak depends markedly on the P content; the minimum FWHM of 1.45 eV for the P-free preparation contrasts with those of 2.36 and 2.14 eV found for samples P1 and P2, respectively.

To estimate the abundance of the P, V, and Ti atoms at the catalyst surface, V/Ti and P/V atomic ratios have been calculated. For this calculation, integrated intensities of the P2*p*, $V2p_{3/2}$ and $Ti2p_{3/2}$ peaks averaged for the number of scans and corrected for the published sensitivity factors for these levels (*9*) have been used. The P-free sample (P0) shows a very high V/Ti ratio

TABLE 2

XPS Data of Several V-Containing Catalysts

Catalyst	$Ti2p_{3/2}$ (eV)	$V2p_{3/2}$ (eV)	V/Ti[a]	P/V[a]
P0	458.5 (1.45)[b]	517.0 (2.19)[b]	0.279	0.00
P1	458.6 (2.36)[b]	517.2 516.2	0.031	138
P2	458.6 (2.14)[b]	517.3 (2.72)[b]	0.062	56
α-$VOPO_4$[c]	—	516.6 (1.8)[b]	—	—
$(VO)_2P_2O_7$[c]	—	515.6 (1.8)[b]	—	—
V_2O_5	—	517.4	—	—

Note. Estimate error for BEs and FWHMs is ±0.1 eV. Estimate error for atomic ratios is ±10%.

[a] Surface atomic ratios.

[b] FWHM in eV.

[c] Taken from Ref. (*13*).

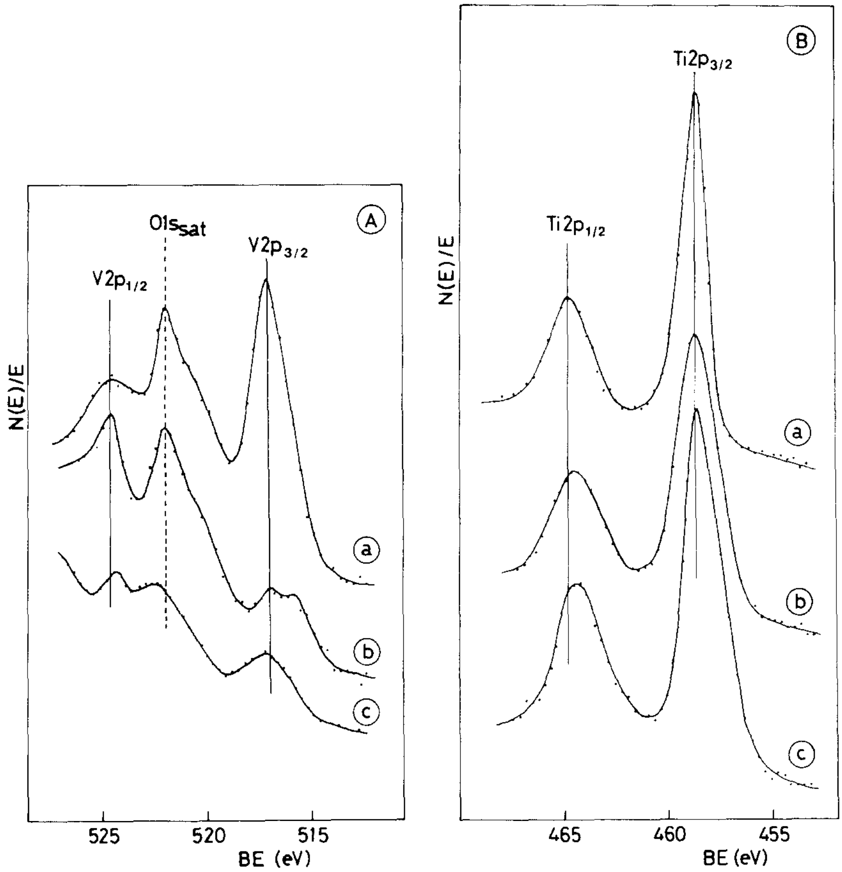

FIG. 3. XP spectra of V2*p* (A) and Ti2*p* (B) levels of different catalysts: (a) phosphorus-free (P0) sample; (b), P1 sample; (c) P2 sample.

but declines by about one order of magnitude in the P1 sample, increasing again in sample P2. In addition, sample P1 shows a very high P/V ratio, which decreases by a factor higher than 2 in the sample P2. The results clearly indicate that phosphorus added to the vanadium–titanium oxide impregnate is mostly concentrated in the outer part of the particles, thus decreasing the exposure of the vanadium ions.

Temperature-Programmed Reduction

Hydrogen reduction profiles of the catalysts are shown in Fig. 4. As can be observed, there are marked differences in both the extent of reduction and the shape of these profiles. In order to compare the reducibility of the samples, the onset temperature of H_2 reduction (T_0) and the temperature for the maximum reduction rate (T_{max}) are summarized in Table 1. The phosphorus-free sample (P0) shows the lowest T_0 and T_{max} values and reaches in the last TPR stages an almost constant weight which roughly corresponds to that expected for a quantitative reduction of the V^{5+} ions to V^{3+}. For sample P1 T_0 is 693 K, decreasing to 593 K for the sample richer in phosphorus (P2). Although P1 attains a T_{max} value close to that of P2 the extent of reduction becomes more important for the P2 sample. Since these samples still present a certain rate of reduction at 783–793 K, they were kept under isothermal conditions for half an hour. The respective kinetic curves for P1 and P2 catalysts in that stage of re-

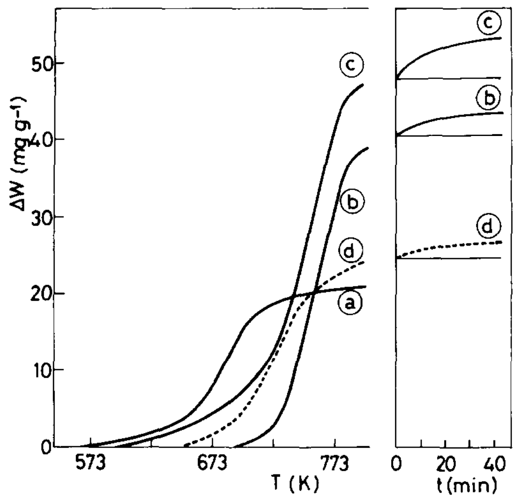

FIG. 4. H_2 reduction profiles of several PVTi catalysts: (a) phosphorus-free (P0) sample; (b) P1 sample; (c) P2 sample; (d) vanadium-free (P1′) sample.

duction are shown on the right-hand side of Fig. 4. The marked increase in the extent of reduction in the phosphorus-containing samples with respect to the phosphorus-free preparation suggests that a new phase containing both phosphorus and titania would be responsible for such a reduction increase. To support this working hypothesis, the reduction profile of the P1′ catalyst is also included in Fig. 3 (dashed line). Note that T_0 and T_{max} values for this preparation are lower than those of its vanadium-containing counterpart P1 and also that the extent of reduction at 773 K implies that the titania component in the catalyst reaches an average composition of $TiO_{1.81}$, the O loss being much higher than in the typical reduction to $TiO_{1.997}$ found on a phosphorus-free titania sample (ca. 96% anatase) subjected to the same reduction treatment (*10*).

DISCUSSION

Most of the ESR signals detected in these polycrystalline samples, which are observed even after calcination at 823 K, are due to V^{4+} ions stabilized probably by oxygen vacancies or other defects in the bulk of the compounds forming the sample. Each one of these signals indicates a specific environment of the vanadium ions and therefore can be related to the presence of a particular phase that provides such a coordination sphere. In this way we can use these paramagnetic centers as spin labels indicating the presence of the corresponding phases and use them to analyze the composition of the sample.

The absence of Ti^{3+} signals in the ESR spectra of the TiO_2 paste reduced above 573 K, in contrast with their observed presence in pure anatase (without SO_4^{2-}) reduced under the same conditions (*5*), indicates that this additional component of the sample is stabilizing the TiO_2 against reduction. Sulphate ions are indeed known stabilizing agents for TiO_2 (*11*). The phosphoric acid treatment affects significantly the reducibility of the TiO_2 paste, as indicated by the detection of Ti^{3+} signals after reducing this sample at $T \geq 473$ K. This is probably due to the formation of some type of titanium phosphate compound (the crystalline $Ti(HPO_4)_2$ phase detected by XRD and/or any other amorphous phosphate phase that may have been formed), as indicated also by the parameters of the Ti^{3+} signal.

The VO^{2+} ESR signals detected for the P*x* catalysts in the initial state (without further treatments after calcination in air) correspond to relatively small amounts of vanadium; their stability in the presence of atmospheric oxygen shows that these ions are not exposed at the catalyst surface. In addition to that, the absence of a marked intensity maximum in the VO^{2+} signals along the reduction sequence in H_2 up to 773 K and their disappearance at high reduction temperature indicate that such species are not stabilized easily on the surface of the catalysts, but rather the $V^{5+} \rightarrow V^{3+}$ reduction process is favored. In the case of the P0 sample, the TPR results show that the total weight loss corresponds closely to the amount expected for the quantitative reduction of V^{5+} (assuming that no VO^{2+} is initially present) to V^{3+} and that this loss takes place under H_2 at temperatures above 560 K, when the observed drop in the intensity of the VO^{2+} signals indicates the formation of V^{3+}, this species being the only vanadium ions remaining at 773 K. ESR shows also that the agglomerated vanadium oxide phase producing signal *A* (which is absent in P1 and P2 samples) is easiest to reduce; this evidences its easy accessibility to the gas atmosphere. The absence of Ti^{3+} signals in the spectra of P0 sample reduced above 573 K confirms the stability of the titanium(IV) ions when these catalysts are not treated with phosphoric acid and are stabilized by sulphate ions.

The comparison of the ESR spectra of the untreated samples (Figs. 1a, 2a, and 2c) indicates that the phosphoric acid treatment induces an increment in the average distances between the vanadium ions (obliteration of signal *A*), due probably to the formation of a vanadium phosphate phase (the existence of which is shown by the presence of vanadyl groups of type 3), simultaneous to the formation of titanium phosphate (indicated by the particular parameters of the Ti^{3+} signal). In the XP spectra taken at the V2*p* level (Fig. 3A), some further differences are observed which also point to a transformation of this kind. The fact that sample P1 shows two $V2p_{3/2}$ peaks at 517.2 and 516.2 eV, the former corresponding to the one observed (at 517.0 eV) in sample P0, indicates that not all the surface vanadium ions are equivalent. In agreement with literature findings, the higher BE $V2p_{3/2}$ peak is assigned to V^{5+} ions (*12*) while that at lower BE is characteristic of VO^{2+} ions as in vanadyl phosphates (*13*). The presence of these two types of vanadium ions, observed indeed in sample P1, cannot however be unambiguously established for sample P2, because in this latter case the $V2p_{3/2}$ peak (Fig. 3A, spectrum c) was very broad and poorly resolved. In addition to this, the incorporation of phosphorus into the raw V–Ti–O catalyst (P0) induces simultaneously noticeable changes in Ti2*p* levels. The very large FWHM values for samples P1 and P2 (Table 2, Fig. 3B) can be taken as conclusive that the surrounding of Ti^{4+} ions was modified by the incorporation of phosphorus into the catalyst. These data therefore support the hypothesis that a mixed phosphate has been formed in these catalysts.

However, the observation in the P-containing samples of VO^{2+} ESR signals 1′ and 2′, similar to those found in sample P0 (although more stable against the reduction treatments) indicates that a TiO_2 phase, with some of these VO^{2+} species on its surface, is still present, probably as TiO_2 nuclei covered by the phosphates, which protect it from an easy reduction. The very high P/V ratio observed for sample P1 and the important decrease of the V/Ti ratio (to values substantially below that corresponding to the chemical composition) when phosphorus is added to the raw V–Ti–O preparation point also to the model of TiO_2 nuclei which retain on their surfaces a very thin layer (probably a monolayer) of vanadia and are covered by a thicker layer of titanium phosphates including a small amount of vanadium dispersed in them.

The TPR curves indicate that the supported vanadium phosphates are more stable against reduction than both the supported vanadium oxide and the titanium phosphate but less stable than the P-free TiO_2, which seems to be stabilized by sulphate ions. In this way T_{max} and T_0 are higher for P1 than for P0 and P1′, but the final weight loss is higher for P1 because of the contribution of both types of phosphates.

It is worth noting that the marked drop in the V/Ti ratio measured by XPS for the phosphorus-containing samples, which indicates a lower amount of vanadium at the surface of these samples, is accompanied only by a small decrease in the catalytic conversion of NO_x (*4*). Considering that vanadium ions form part of the active species for that reaction, this result suggests that, although a smaller number of active centers exist in the phosphorus-containing samples, they are more efficient than those existing in the phosphorus-free vanadia–titania catalysts.

The comparison of TPR data for samples Pl and P2, which show for the latter a larger weight loss upon reduction at 773 K, indicates that the use of more concentrated phosphoric acid in the preparation leads to the transformation of a larger fraction of titania to the phosphate phase; this agrees with the larger surface Ti/P ratio detected by XPS for sample P2. It thus seems likely that a substantially smaller amount of unreacted TiO_2 nuclei remain in this last case so that less vanadium is kept stabilized on them, making possible the detection of a higher V/Ti surface ratio and of a higher proportion of ESR signal *C* corresponding to vanadium in the phosphate phase.

In conclusion the samples of vanadia–titania, which in the absence of phosphorus are formed essentially by nuclei of TiO_2 covered by vanadium oxide, are markedly modified by the phosphoric acid treatment. Although the nuclei are still formed by TiO_2 and some vanadium ions are located on the surface, an external layer of titanium and vanadium phosphates (separated or/and mixed) is produced. The phosphoric acid concentration affects the size of the remaining TiO_2 nuclei and the amount of vanadium dispersed on their surface; for larger concentrations the amount of these phosphates formed on the surface increases.

ACKNOWLEDGMENTS

The authors are indebted to Drs. J. Blanco and P. Avila, J. Martí and C. Barthélemy for supplying the samples and discussing the XRD results prior to their publication (*4*). Valuable discussions with Dr. J. A. Odriozola are also acknowledged. We also thank the Spain-US Joint Committee for financial support.

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