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RESEARCH NOTE

New Insights into the Nature of the Active Phase of VPO Catalysts—A Quantitative Static LEIS Study

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The atomic composition of the outermost atomic layer of equilibrated VPO catalysts was studied with low-energy ion scattering. Using external reference samples, absolute numbers for the atomic densities of both P and V could be determined. VPO catalysts prepared in either aqueous or organic media showed large amounts of carbonaceous surface species. From catalysts prepared in an aqueous medium the carbonaceous species could be removed using a mild oxidation treatment without significantly changing the average valence of the vanadium atoms in the catalyst as evidenced from XPS. After this cleaning treatment the surface concentration of vanadium (atoms/cm^2) agrees well with that expected for a vanadyl pyrophosphate structure. However, the surface phosphorus concentration is twice as high as that in vanadyl pyrophosphate, leading to a surface P/V ratio of 2.0 ± 0.2. This shows that VPO catalysts may be terminated by a distorted vanadyl pyrophosphate structure, where the excess amount of phosphorus is positioned between the vanadyl units and the phosphate groups. The catalyst surface is also compared to $VOPO_4$ phases. A significant contribution of a phase such as α_{II}-$VOPO_4$ could explain the observed surface P/V ratio of 2.0. © 2000 Academic Press

Key Words: **butane oxidation; maleic anhydride; VPO catalysts; P/V ratio; LEIS; ISS; XPS; surface characterization.**

INTRODUCTION

Vanadium phosphorus oxide (VPO) catalysts are commercially applied for the selective oxidation of *n*-butane to maleic anhydride. Maleic anhydride and its derivatives, maleic acid and fumaric acid, are produced with an annual worldwide capacity of almost 1×10^6 tons (1, 2). The average annual demand growth is estimated to be about 4% (3). These numbers together with the fact that the current yield to maleic anhydride of an equilibrated catalyst amounts to about 58% indicate that improvement of the process is of great economic and environmental interest. These improvements require a thorough knowledge of the catalytic and structural properties of the active V–P–O phase. The bulk of VPO catalysts is assumed to consist of vanadyl pyrophosphate, $(VO)_2P_2O_7$, which has a stochiometric P/V ratio of 1. It is generally mentioned in the literature, however, that a prerequisite for optimum catalytic performance of VPO catalysts is the addition of an overstoichiometric amount of phosphate during the preparation. The best catalytic performance has been reported for catalysts of a preparative P/V ratio of 1.1 (2). Assuming that the bulk indeed consists of stoichiometric vanadyl pyrophosphate, the excess phosphate must either be present at the surface or be poorly bound to the surface and removed during the synthesis procedure. To investigate the catalyst surface, several groups have employed XPS. However, univocal results have not been obtained (4–14). Generally, the experimental P/V ratio ranges from 1.5 to 3, which is much higher than the stoichiometric bulk value of vanadyl phosphates, i.e., 1.0.

Coulston and co-workers have calculated the dependency of the P/V ratio on the morphology of vanadyl pyrophosphate (14). Their results indicate that exposure of different crystallographic planes of vanadyl pyrophosphate will result in maximum P/V ratios: 1.015 (021 plane), 0.986 (001 plane), 1.098 (100 plane, phosphate termination), and 1.136 (100 plane, pyrophosphate termination) (14). These numbers indicate that only a limited amount of excess phosphate can be bound at the surface of vanadyl pyrophosphate.

Delichere *et al.* have argued that the high experimental P/V ratios are the result of vanadium vacancies in the (amorphous) surface layers of vanadyl pyrophosphate (13). For this reason, they proposed a model in which the

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composition of the VPO catalysts is described by the general formula $[(V^{IV}_{(1-5x)}V^{V}_{4x}\Diamond_x)O]_2P_2O_7$. In this formula $\Diamond$ is a vanadium vacancy. Nevertheless, this is not sufficient to explain the experimental P/V ratios of 1.5–3, and other effects have to be taken into account as well.

More phosphate could be present at the surface when different surface VPO phases are formed. Morishige *et al.* proposed that the high experimentally observed P/V ratio is the result of the presence of an amorphous metaphosphate phase on the surface (10). $VO(PO_3)_2$ would be formed upon thermal pretreatment of $VO(H_2PO_4)_2$, present in the $VO(HPO_4)\cdot 0.5H_2O$ precursor as a contaminant (7, 10). Sananes and co-workers have shown that this poorly active $VO(PO_3)_2$ phase has a surface P/V ratio of 4.0, which is much higher than the generally observed values for vanadium pyrophosphates (15, 16).

The quantitative XPS analysis (4–14) makes use of the photoionization cross sections, which have been calculated for a very large number of metal oxides by Scofield (17). These values have proven, however, to be inadequate for the analysis of VPO XPS data (12–14). Therefore, several authors determined experimental sensitivity factors for vanadium and phosphorus using VPO glasses (12, 18–20). For these compounds, it is assumed that the surface P/V ratio is the same as that of the bulk. With this approach, experimental surface P/V ratios of 1.1 to 1.4 were determined for bulk VPO catalysts (12, 18–20). Since the surface P/V ratio of VPO glasses may also be the result of phosphorus segregation from the bulk, the assumption that the surface P/V ratio is equal to the bulk P/V ratio is not obvious for these materials.

To overcome this problem, Coulston *et al.* have used five organometallic complexes containing vanadium and phosphorus atoms as standard materials (14). Phosphorus segregation is not expected in these clusters; however, it has not been proven that the ligands are stable under UHV conditions. Nevertheless, an experimental P/V ratio of 1.1 was found for a bulk VPO catalyst with 10% excess phosphorus (14). This amount is in agreement with the predictions of Coulston *et al.*, based on a model of phosphate groups terminating the vanadyl pyrophosphate surfaces (14).

Since the surface P/V ratios that have been determined with XPS are neither univocal nor selectively dealing with the outermost surface layer, we have applied static low-energy ion scattering (LEIS) to establish the surface composition of bulk VPO catalysts. In contrast to XPS, which has a penetration depth of typically 10 monolayers, LEIS is a technique that selectively probes the outermost atomic layer of a (catalyst) surface. This offers the opportunity to study the surface P/V ratio VPO catalysts more precisely than with XPS, which averages out the surface and subsurface composition of the samples.

Three earlier LEIS studies of VPO catalysts have been reported (12, 13, 49). Using LEIS, Richter *et al.* determined a surface P/V ratio of ∼2–3 (12, 49). However, their quantification is based on comparison with VPO glasses and therefore may have been distorted because of possible phosphorus segregation in these glasses, as mentioned above. Moreover, a very high ion current has been applied in this study (2700 nA/cm^2); hence, the catalyst surface may have been damaged. Preferential sputtering can change the surface composition.

A second LEIS study of VPO catalysts has been reported by Delichere *et al.*, who found a surface P/V ratio of 2.4 (13). However, they suggested this value could be an overestimation since carbon, which they observed with XPS, may have preferentially masked vanadium. Indeed, we also found large amounts of carbon deposits on the VPO catalysts. Using a mild oxidation treatment in air, without significantly changing the average valence, we were able to remove the carbonaceous species from VPO catalysts prepared in an aqueous medium. A comparison of contaminated and cleaned VPO showed that carbon is indeed preferentially masking vanadium. Therefore, carbon has to be removed before the intrinsic surface can be analyzed. In Eindhoven, the ERISS analyzer is used, which is orders of magnitude more sensitive than conventional LEIS equipment. Hence, we could perform our analyses in a static mode, thus without damaging the surface. In addition, we applied calibration of the elemental sensitivity for both phosphorus and vanadium against external reference samples. This allowed a quantitative analysis of the surface of a cleaned VPO catalyst and determination of the surface P/V ratio.

METHODS

Catalyst Preparation

Bulk VPO was prepared in a mixture of organic solvents following a procedure described by Katsumoto *et al.* (21). V_2O_5 (15 g) was reduced for 16 h at 393 K in 60 ml of 1 : 1 (v/v) *i*-butanol/cyclohexanol mixture. After the mixture was cooled to room temperature, 21 g of 85% *o*-H_3PO_4 in 30 ml of *i*-butanol was added to the dark green suspension, resulting in a P/V ratio of 1.1. After this mixture was refluxed for 6 h, a blue/green suspension was obtained, which was filtered and dried in a nitrogen flow for 12 h at 398 K.

In another method the bulk VPO was prepared in an aqueous medium following a procedure described by Centi *et al.* (22). After reduction of 15 g of V_2O_5 for 16 h in boiling concentrated HCl (37%), 85% *o*-H_3PO_4 was added to the dark blue V(IV) solution until a P/V ratio of 1.1 was established. After 2 more hours of refluxing, the solution was concentrated by evaporation of the water. A blue, viscous syrup was obtained, which was dried in a nitrogen flow for 10 h at 393 K.

XRD showed that both preparation methods resulted in the formation of the same hemihydrate precursor phase.

Finally, the VPO catalysts were obtained by thermal pretreatment of the hemihydrate phase in a microreactor (50 ml/min N_2, 723 K, 16 h). All catalysts were tested and equilibrated in the *n*-butane oxidation reaction for more than 100 h. They will be referred to as VPO-org and VPO-aq for the first and second of the above-mentioned preparation methods, respectively. Both VPO-org and VPO-aq show a selectivity of about 60% toward maleic anhydride over a broad conversion range. However, VPO-org is more active than VPO-aq (45% versus 17% respectively at 723 K (37). The difference in conversion can be explained by the difference in specific surface area. The specific surface area (BET method) was determined to be 9 m^2/g for VPO-org and 3 m^2/g for VPO-aq, respectively (37).

Sample Pretreatment

Before analysis the VPO powders were pressed (312 MPa) into stainless steel cups. Measurements comparing powders to pressed powders showed no influence of pressing on the surface composition.

In the UHV chamber of the ERISS LEIS setup samples can be heated *in situ* up to 1250 K, and the temperatures higher than 430 K can be measured within 3 K accuracy with an Impac IP 120 pyrometer. A loadlock allows treatments of samples in various gases up to 1 bar at temperatures between room temperature and 773 K without exposure to air. In the loadlock a chromel/alumel-couple is used to measure the temperature of the sample. After the treatment(s) is (are) carried out, the samples are evacuated and inserted in the UHV where LEIS can be applied.

LEIS

LEIS has been used to characterize the surface composition of the catalysts. In LEIS a beam of monoenergetic noble gas ions is scattered by atoms of the target surface (23, 24). According to the laws of conservation of energy and momentum, the energy of the backscattered ions is characteristic for the mass of the atoms from which they scattered. Hence, the energy spectrum of the backscattered ions can be interpreted as the mass spectrum of the surface atoms. The information depth of LEIS is limited to one monolayer since ions penetrating the outermost layer will be almost all neutralized and therefore not detected. As a consequence of the ion bombardment, atoms are sputtered from the surface. This allows for the determination of the in-depth distribution of the atoms by measuring during prolonged sputtering. However, intrinsic information on the outermost surface layer should be obtained before sputtering has damaged this layer, thus using a low dose.

The LEIS experiments were carried out in the ERISS setup (energy-resolved ion-scattering spectrometer). This ultrahigh vacuum setup has a base pressure in the low 10^{-10} mbar range, which increases to 10^{-9}–10^{-8} mbar during LEIS experiments due to noble gas influx. It is equipped with an ion source (Leybold-type IQE-12/38) and an electrostatic analyzer. The primary ions are mass selected, focused, and directed perpendicular to the target. Ions scattered over 145° are accepted by the analyzer. The analyzer is a double-toroidal electrostatic analyzer, similar to that of the EARISS setup, which has been described in more detail elsewhere (25–27). This analyzer makes very efficient use of the backscattered particles by measuring simultaneously a considerable part of the energy spectrum of the backscattered particles and 320° of the azimuthal range. In addition, the sample manipulator can be scanned under the ion beam during measurements, effectively increasing the beam spot and thus reducing the ion dose even more. The EARISS-type analyzer together with scanning measurements allow us to perform static LEIS, i.e., with negligible damage. Measurements can be carried out using only 10^{13}–10^{14} ions/cm^2 while typically a ^{3}He dose of 10^{16} ions/cm^2 is required to remove one monolayer. Because ^{3}He has the lowest sputter rate, we have used 3 keV of ^{3}He for this study. To prevent charging of insulating samples, such as VPO, low-energetic electrons (10 eV) can be flooded from all azimuths over the sample during measurements.

Calibration

Since in LEIS the scattering events can be considered as binary collisions between the impinging ions and the target surface atoms, LEIS data are generally independent of the chemical environment of the scattering element (no matrix effects). This allows calibration of the sensitivity for a certain element against external reference samples with a well-known surface atomic density.

The sensitivity for V was calibrated against a high-purity polycrystalline vanadium metal sample. The bulk of this vanadium sample was very pure since it was grown via the zone-melting method. Moreover, it was annealed at 1850 K for 2 h to remove contamination. Then, the sample was inserted into the UHV of the ERISS and sputter-cleaned at room temperature. The signal obtained upon sputter cleaning was used as the reference signal. Measurement of the complete LEIS spectrum proved the vanadium surface was indeed clean. Assuming an atomic radius of 0.135 nm (35) and exposure of the most densely packed surface plane (36), the measured vanadium signal should represent 1.43×10^{15} atoms/cm^2. However, from experience with tungsten we know the signal drops to 75% upon sputter cleaning due to sputter-induced roughness. Therefore, the V signal is assumed to correspond to $0.75 \times (1.43 \times 10^{15})$ atoms/cm^2; see Table 1.

In the case of P we could not use the pure element for calibration because it is not stable in vacuum. The well-defined GaP(110) surface, on the other hand, is stable in vacuum and is restored upon heating to 873 K (28, 29). In

TABLE 1

Absolute Atomic Densities (in 10^{15} atoms/cm^2) in the Outermost Atomic Layer for VPO-aq and Reference Samples

	V poly-crystalline	V_2O_5	GaP (110)	Equilibrated VPO-aq after transport through air	Equilibrated VPO-aq cleaned
P	—	—	0.476	0.029	0.17
V	1.09	0.19	—	0.0099	0.086
P/V	—	—	—	2.9 ± 0.2	2.0 ± 0.2

Note. All data were obtained with a ^{3}He dose of 0.1×10^{15} ions/cm^2. VPO-aq was cleaned with a 1-h oxidation treatment in 200 mbar O_2 at 573 K.

GaP(110), P atoms in the outermost layer are not shielded since they protrude somewhat from the surface (29). Therefore, the P signal was calibrated against GaP(110). A setup combining low-energy electron diffraction (LEED) and LEIS was used to confirm that sputter/anneal cycles produced a clean GaP(110) surface. This setup was described in detail by Cortenraad *et al.* (30). After several sputter cycles followed by 7 min of annealing at 873 K, a sharp 1 × 1 LEED pattern, characteristic for GaP(110), was obtained. *In situ* LEIS measurements proved the surface to be clean. Subsequently, we used the same treatment in ERISS and measured the LEIS signal of GaP(110) for calibration of the elemental sensitivity for P. Using a unit mesh of 5.405 × 3.864 Å, we calculated a phosphorus density of 4.76×10^{14} atoms/cm^2 for the GaP(110) surface (29).

In addition to polycrystalline vanadium and GaP(110), we used V_2O_5 powder as a reference for the oxidic shielding. The vanadyl groups in vanadyl pyrophosphate and V_2O_5 have a similar structure (31, 39). In both cases the vanadium atoms are octahedrally surrounded by oxygen. The oxygen atoms therefore partly mask vanadium atoms. Comparison of the vanadium signal in VPO to that in V_2O_5 makes it possible to determine whether the vanadium signal is consistent with a vanadyl pyrophosphate structure. The V_2O_5 powder was pressed in a stainless steel cup (312 MPa). To dehydrate and clean the surface, the V_2O_5 was oxidized (10 min, 200 mbar O_2 at 773 K) prior to LEIS analysis. The specific surface area of the V_2O_5 powder was 20 m^2/g; hence, the difference in surface roughness compared to VPO can be neglected.

To analyze the LEIS spectra, we have used a linear background subtraction and simply integrated the peak content. For each element, the energy range that was used in the integration was kept constant for all spectra.

XPS

XPS spectra were obtained with a VG Clam 2 spectrometer equipped with a Mg $K\alpha$ source and a hemispherical analyzer connected to a single-channel detector. Measurements were performed at 20-eV pass energy. The background pressure during data acquisition was kept below 10^{-8} mbar. The samples were crushed and mounted on an iron stub carrying an indium film.

The average valence of the vanadium in the catalyst can be calculated from XPS measurements according to the empirical formula reported by Coulston *et al.* (14):

$$AV = 13.82 - 0.68 \cdot \left[O(1s)\text{–}V(2p_{3/2})\right]. \qquad [1]$$

In this formula, $O(1s)$ and $V(2p_{3/2})$ are the absolute values of the electron binding energies. A difference of 0.1 eV in the peak positions already results in a difference in the AV values of 0.07. In general, the resolution of an XPS spectrometer amounts to 0.25 eV and, hence, the uncertainty in the AV is ±0.2.

RESULTS

LEIS Analysis VPO

LEIS measurements of equilibrated VPO-org and VPO-aq catalysts, which were transported through air after catalytic tests, show upon a ^{3}He dose of only 7×10^{13} ions/cm^2 clear surface peaks corresponding to vanadium, phosphorus, and oxygen; see filled circles in Fig. 1. This proves all

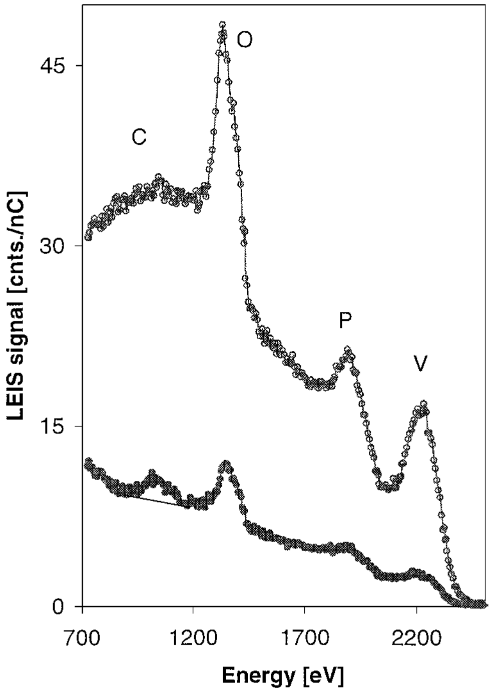

FIG. 1. LEIS spectra of VPO-aq (dose: 1×10^{14} ions/cm^2, 3 keV of ^{3}He). Comparison of VPO-aq before cleaning (filled circles) and after 1 h, 200 mbar O_2 at 573 K (open circles) shows both V, P, and O are present in the outermost atomic layer of VPO. Due to the removal of carbonaceous compounds, the V, P, and O contributions dramatically increase upon cleaning.

three elements are present in the outermost surface of VPO. Moreover, a carbon peak can be seen; since the sensitivity of LEIS decreases with decreasing mass, this peak corresponds to a surface that is for more than 80% covered by carbon, as described below. Carbon might preferentially mask either vanadium or phosphorus and has to be removed to measure the intrinsic surface P/V ratio.

Surface contamination can be removed either by sputtering or by exposing the surface to a cleaning treatment. Since the surface composition may change due to preferential sputtering, a cleaning treatment is preferred. Of course, one has to be aware of the fact that the surface may also be changed during a cleaning treatment. Therefore, the catalyst was at first only heated in He up to 573 K; however, this treatment did not remove the carbonaceous species. This is in agreement with Delichere *et al.*, reporting no significant changes in catalytic activity of VPO upon heating (13). Because thermal treatment failed in removing carbonaceous species, the catalysts were heated in oxygen (1 h in 200 mbar O_2 at 573 K). This temperature was chosen to stay below 623 K, where XRD measurements indicated a phase transition for VPO in air (33). Because of the mild treatment and the small amount of catalyst (typically 10^{-2} g/sample), heat effects are not expected to play an important role. To check experimentally whether the oxidation treatment did not change the oxidation state of the catalyst, its average valence (AV) was determined before and after the treatment. Using XPS, we found for equilibrated VPO-org and VPO-aq catalysts, which were transported through air after catalytic tests, values ranging from 4.0 ± 0.2 to 4.1 ± 0.2, respectively. This is in agreement with the literature where AV values of 4.02 to 4.3 have been reported for VPO catalysts (34). Upon oxidation treatment in 200 mbar O_2 at 573 K, we measured an AV of 4.3 ± 0.2. Hence, the differences in AV are within the experimental error of the XPS measurements. The average valence state of the surface vanadium atoms is not significantly changed upon the oxidation treatment.

The LEIS spectrum, indicated by the open circles in Fig. 1, shows no more carbonaceous species are detected on VPO-aq catalysts after an oxidation treatment in 200 mbar O_2 at 573 K for 1 h. LEIS spectra of VPO-org catalysts, on the other hand, still show an unknown amount of carbon on the surface upon this treatment. Since carbon could only be removed from the VPO-aq catalyst, we continued our study with this catalyst.

Figure 1 shows LEIS spectra of VPO-aq before (filled circles) and after (open circles) cleaning. From this figure it can be seen that the V, P, and O signals strongly increased upon the cleaning treatment. However, the vanadium signal increased most dramatically.

Removal of carbonaceous species resulting in a recovery of active sites might explain the beneficial effects of a mild oxidation treatment on the catalytic properties of VPO catalysts as reported by Contractor *et al.* (44). They observed enhanced activity and surface area without loss of selectivity upon calcination of VPO. Calcination is patented for both regeneration and activation of VPO catalysts for pressure, temperature, and contact time ranges comprising the conditions used in this study (44, 46). Table 1 shows that only 15% of the vanadium and phosphorus atomic sites is visible to LEIS before cleaning. Because the data in this table have been collected with a ^{3}He dose of only 1×10^{14} ions/cm^2, they selectively represent the outermost atomic layer. The atomic densities of the powder samples have been corrected for their surface roughness compared to those of the flat polycrystalline V and GaP(110) reference samples as explained before. Because VPO is a powder, part of the LEIS signal is lost due to physical screening. Recent measurements comparing a flat quartz sample to silica powders with specific surface areas ranging from 50 to 380 m^2/g show that the LEIS signal ratio of the quartz and the pressed powders is 1 : 0.77. There is no difference in the LEIS signal for pressed powders with different specific surface areas ranging from 50 to 380 m^2/g (32). Both P and V are calibrated against a flat reference sample; hence, the surface roughness correction factor (1.3) is equal for P and V. As a consequence, the determination of the P/V ratio is not influenced. Because the VPO-aq samples have a specific surface area of 3 m^2/g, the surface roughness correction factor is equal for different catalyst samples; hence, differences in P and V atomic densities between different catalyst samples are not affected as well.

When the data are corrected for differences in surface roughness, the intrinsic phosphorus surface density in VPO-aq is 1.7×10^{14} atoms/cm^2 and for vanadium 0.86×10^{14} atoms/cm^2, which gives a surface P/V ratio of 2.0 ± 0.2. Upon an oxidation treatment in 200 mbar O_2 at 573 K, the phosphorus and vanadium signal increased six- and ninefold, respectively. The relative increase for vanadium is higher than that for phosphorus, which shows that carbon preferentially masks vanadium, as suggested by Delichere *et al.* (13). Therefore, determination of the surface P/V ratio on a contaminated catalyst yields a too high value. The surface P/V of our contaminated VPO-aq catalyst was 2.9 ± 0.2. Carbon deposits, preferentially masking vanadium, explain this high P/V ratio.

According to TPR experiments, VPO reduction in 100 mbar H_2 starts at temperatures higher than 623 K (37). Since we wanted to clean the VPO without reducing it, VPO-aq has been treated in hydrogen (1 h, 200 mbar H_2 at 573 K). Upon this treatment a low atomic density of P and V is found. This can be partly explained by hydrogen adsorbed on the catalyst during the reductive treatment. The adsorbed hydrogen may shield the V and/or P in the catalyst. Upon a ^{3}He dose of 1–1.5 × 10^{15} ions/cm^2, the P and V atomic density are 52 and 36% of those in the cleaned sample. At such doses hydrogen is largely sputtered away since it has typically a 10–50 times higher sputter rate than other elements (38). At low doses, when hydrogen still partly covers the catalyst, a P/V ratio of 3.6 ± 0.2 was found. Upon a ^{3}He dose of 1.5×10^{15} ions/cm^2, the P/V ratio decreased to 2.6 ± 0.2. Probably a considerable part of the catalyst surface is still covered with contamination upon our reduction treatment. When VPO-aq is reduced upon calcination, initially about 70% of the atomic density is found. Again, the P and V atomic densities increase upon low dose, which indicates hydrogen coverage. Upon removal of hydrogen by sputtering, the atomic densities and P/V ratio tend to those of catalysts that were only calcined. The observed surface composition is thus similar upon our calcining treatment (1 h, 200 mbar O_2 at 573 K) and upon this treatment followed by a reductive treatment (1 h, 200 mbar H_2 at 573 K). This indicates the treatments have no strong influence on the surface composition.

Surface Structure of VPO

The vanadyl groups in vanadyl pyrophosphate and V_2O_5 have similar primary structures. Both in vanadyl pyrophosphate and V_2O_5 the vanadium is octahedrally surrounded by oxygen atoms (31, 39). The nearest neighbour oxygen atoms partly shield vanadium atoms. For instance, 50% of the surface vanadyl groups is terminated by oxygen atoms (trans configuration of the vanadyl dimers). Therefore, vanadium atoms in these groups are neither accessible for catalysis nor visible to LEIS. Because of the similar nearest neighbours, a comparison of the vanadium signal in VPO to that in V_2O_5 makes it possible to determine whether the vanadium signal is consistent with a vanadyl pyrophosphate structure. Using lattice parameters of V_2O_5, we calculated a total vanadium atomic density of 9.8×10^{14} atoms/cm^2 in V_2O_5 for the *c* plane (110) (31). Single-crystal data of vanadyl pyrophosphate give a vanadium atomic density of 4.6×10^{14} atoms/cm^2 for the *c* plane (110) (39). Since the nearest neighbours and therefore the chemical accessibility and the visibility for LEIS of the vanadium atoms are similar in vanadyl pyrophosphate and V_2O_5, the vanadium signal of vanadyl pyrophosphate should correspond to 47% of that in V_2O_5, thus assuming that phosphates do not shield the vanadium because they are not nearest neighbours.

The vanadium signal of VPO-aq (after 1 h in 200 mbar O_2 at 573 K) equaled 44% of that in V_2O_5 (see also Fig. 2); hence, assuming a vanadyl pyrophosphate structure, we miss 3% of the vanadium atoms in the outermost layer. This could be explained by vacancies, as suggested by Delichere *et al.* (13). Since the amount of missing vanadium atoms is small, they could also be shielded by strongly bound carbonaceous species, which are not removed from VPO-aq during the cleaning treatment (200 mbar oxygen at 573 K for 1 h). A third explanation for the missing 3% vanadium atoms is coverage by excess phosphorus.

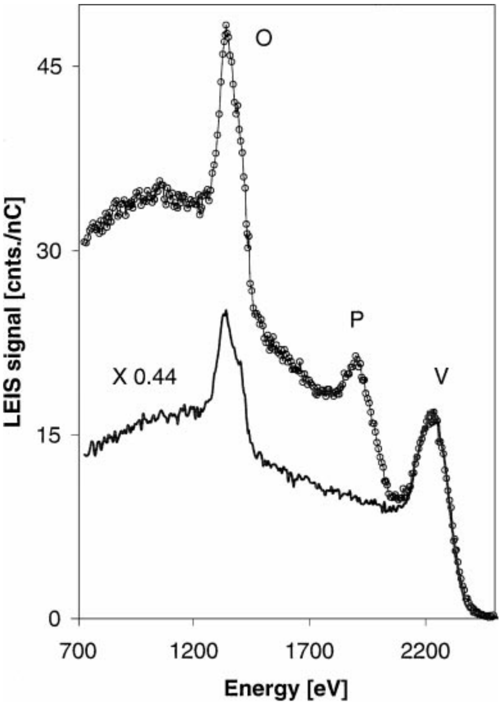

FIG. 2. LEIS spectrum of cleaned VPO-aq (open circles) compared to that of V_2O_5 (solid line). To scale the vanadium signals, the V_2O_5 has been multiplied by 0.44. The vanadium atomic density in V_2O_5 is 9.8×10^{14} ions/cm^2; hence, 44% of this signal corresponds to 4.3×10^{14} ions/cm^2 of octahedral-surrounded V atoms on the catalyst surface.

While the surface concentration of vanadium is in reasonable agreement with that expected for vanadyl pyrophosphate, the situation for phosphorus is completely different. We find 8.9×10^{14} atoms/cm^2 of phosphorus if we assume a similar oxygen shielding for vanadium and phosphorus. The actual oxygen shielding of phosphorus in a vanadyl pyrophosphate structure is expected to be rather higher than lower in comparison to that of vanadium. Since the phosphorus and vanadium atomic densities are equal in vanadyl pyrophosphate, only 4.6×10^{14} atoms/cm^2 of phosphorus are expected. Hence, there is about a factor of 2 more phosphorus than that in the surface of the ideal vanadyl pyrophosphate structure. Both the surface P/V ratio and the phosphorus atomic density thus disagree with a VPO catalyst that is terminated with a vanadyl pyrophosphate structure.

However, one could imagine a vanadyl pyrophosphate structure having an extra amount of phosphates on top. LEIS analysis showed that, in VPO, in comparison to vanadyl pyrophosphate, only 3% of the vanadium atoms exposed to the surface is missing. Hence, the huge excess amount of phosphorus cannot reside on top of vanadium oxide groups, exposing their vanadium atoms to the surface. In that case the phosphorus atoms would shield about all the vanadium atoms. If the extra amount of phosphorus would be on top of other phosphorus atoms, the phosphorus atoms would shield each other. Hence, the high phosphorus atomic density as determined with LEIS cannot be explained by stacking phosphorus on top of phosphorus in the outermost surface layer. Furthermore, oxygen-terminated vanadium oxide and phosphate groups, which are already protruding from the surface, are no likely positions to incorporate the excess amount of phosphorus. Hence, the best places that can account for the excess amount of phosphorus are probably in between the vanadyl octahedrons and phosphate groups. Since this structure is very open, it leaves about 43% of the *c* plane (110) of the vanadyl pyrophosphate structure for the excess amount of phosphorus. The incorporation of extra phosphates in the vacancies would highly distort the vanadyl pyrophosphate structure.

This is in agreement with previous studies that already indicated the vanadyl pyrophosphate structure is not continued at the surface of VPO catalysts (40, 41, 45). In an ESR study Ruitenbeek *et al.* found evidence for the presence of an amorphous VPO phase (40). HREM measurements of Guliants *et al.* showed a 15-Å amorphous overlayer terminating the VPO catalyst surface (41). A distorted vanadyl pyrophosphate structure may correspond to an amorphous signal in ESR and HREM.

The overstoichiometric amount of phosphate used in the catalyst synthesis is enough to cover the catalyst surface without disturbing the bulk vanadyl pyrophosphate structure. The VPO-aq has a specific surface area of 3 m^2/g and, therefore, exposes 1 in 280 atoms to its surface and the VPO-org with a specific surface area of 9 m^2/g exposes 1 in 93 atoms to its surface. Hence, the 10% excess phosphate, used in the catalyst synthesis, would even be enough to form 9 (for the VPO-org) or 28 (for the VPO-aq) monolayers of pure phosphate. In the preceding we explained our LEIS data in terms of a $(VO)_2P_2O_7$ structure with additional phosphate groups. In the literature VPO catalysts are often considered as a mixture of $(VO)_2P_2O_7$ with different $VOPO_4$ phases (47, 48). In regard to the total atomic phosphorus and vanadium atomic densities, the $(VO)_2P_2O_7$ and $VOPO_4$ phases are rather comparable. For instance, slabs of (001) α-$VOPO_4$ and (201) β-$VOPO_4$ phases match closely with (100) $(VO)_2P_2O_7$ and the crystallographic misfits are 2 and 3%, respectively, for α-$VOPO_4$ and β-$VOPO_4$ (47). Any solid mixture obtained at the steady state with stoichiometric composition between VPO_5 and $VPO_{4.5}$ can be pictured. The frameworks of γ-$VOPO_4$ and $(VO)_2P_2O_7$ are made of the same elementary units (pairs of octahedra). Only small displacements of the atoms laying in the (010) γ-$VOPO_4$ are needed to incorporate V^{5+} species in $(VO)_2P_2O_7$ (or the reverse, some V^{4+} in γ-$VOPO_4$) by the local formation of microdomains with the same structural unit (47).

In some of the $VOPO_4$ phases half of the phosphate groups are phosphorus terminated and the other half is oxygen terminated, like in $(VO)_2P_2O_7$. However, in α_{II}-$VOPO_4$ all of the phosphate groups expose their phosphorus atom to the surface. Therefore, the surface P/V ratio of α_{II}-$VOPO_4$ is 2, instead of 1 like in $(VO)_2P_2O_7$. Hence, a significant contribution of a phase such as α_{II}-$VOPO_4$ could explain the surface P/V ratio and the phosphorus atomic density as found in LEIS on the VPO_{aq} catalyst. In regard to the vanadium atoms, the nearest neighbours and the orientation of the vanadium atoms toward the surface are the same in α_{II}-$VOPO_4$ and $(VO)_2P_2O_7$. Hence, the vanadium atomic density in α_{II}-$VOPO_4$ is only 14% higher than that in $(VO)_2P_2O_7$ because the α_{II}-$VOPO_4$ is more closely packed. Moreover, it should be noticed that the AV of the vanadium atoms, as determined with XPS, is in the range 4–4.3, whereas in α_{II}-$VOPO_4$ the AV is 5. Since XPS averages over several atomic layers, it is not to be excluded that part of the outermost surface layer of the catalyst might be α_{II}-$VOPO_4$ alike.

Evidently, there are differently bound phosphates in the VPO catalysts studied. These may have different catalytic activity. Moreover, the required phosphoric acid addition during catalysis may selectively replenish a single type of phosphates.

CONCLUSIONS

Using the LEIS technique, we have found that equilibrated VPO catalysts, prepared in both aqueous and organic media, are largely covered by carbonaceous species upon exposure to air after catalytic tests. Thermal treatment in an inert atmosphere or vacuum up to 573 K does not remove these species. Only upon mild oxidation treatment (200 mbar O_2 at 573 K) are carbon deposits removed from the VPO-aq catalysts. XPS showed this treatment does not significantly change the average valence of the catalyst. After mild oxidation treatment, the average valence of the vanadium in the catalyst was 4.3 ± 0.2. No more carbonaceous species are detected on VPO-aq catalysts upon this treatment. VPO-org catalysts, on the other hand, still contain carbon upon oxidation treatment. VPO catalysts have a platelike morphology; therefore, they can accommodate carbon in the bulk (42, 43). In the VPO-org catalysts, carbon from the organic medium may have been left between these layers during synthesis. During the cleaning treatment this carbon may segregate and replenish the removed carbon at the VPO-org surface.

Upon the cleaning treatment, the total surface atomic densities of P and V increased six- and ninefold, respectively. Since the vanadium atomic density increased most, carbon deposits are thus preferentially shielding surface vanadium atoms. Therefore, this feature can explain the higher surface P/V ratios, which were earlier observed with LEIS (12, 13). The cleaned VPO-aq catalyst exposed 1.7×10^{14} of P atoms/cm^2 and 0.86×10^{14} of V atoms/cm^2, corresponding to a surface P/V ratio of 2.0 ± 0.2. Due to the oxidic environment, phosphorus and vanadium atoms in VPO are partly shielded. The shielding of vanadium atoms in a vanadyl pyrophosphate is similar to that in V_2O_5. A comparison between the vanadium signals of a cleaned VPO-aq catalyst and V_2O_5 showed that only 3% of the vanadium atoms is missing in the outermost surface layer compared to that of a vanadyl pyrophosphate structure. The missing vanadium atoms may be explained by vacancies, shielding due to either remaining contamination or excess phosphorus or simply a different structure. Assuming a similar oxygen shielding of vanadium and phosphorus in a vanadyl pyrophosphate structure, we have found a huge excess of phosphorus. In comparison to a vanadyl pyrophosphate structure the surface P/V ratio of 2.0 ± 0.2 should not be explained in terms of missing vanadium, but in terms of excess phosphorus. The excess amount of phosphorus may be positioned between the vanadyl units and the phosphate groups. This would result in a distorted structure at the surface of a cleaned VPO-aq catalyst that differs from the vanadyl pyrophosphate structure. If the distorted vanadyl pyrophosphate is the actual active phase in the selective oxidation of *n*-butane to maleic anhydride, the excess of phosphate is differently bound to the catalyst and might change under catalytic conditions. It would be worthwhile to investigate whether the phosphoric acid addition during catalysis may selectively replenish a single type of phosphates.

As shown in the previous section, the observed surface P/V ratio of 2.0 can also be explained by a significant contribution of a phase such as α_{II}-$VOPO_4$.

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