Preparation, structural properties and catalytic selectivity of sulfate-doped $(VO)_2P_2O_7$ catalysts in the oxidation of *n*-butane

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Sulfate-doped $VOHPO_4{\cdot}0.5H_2O$ precursors with molar ratios of $0 < S : V < 0.1$ were prepared by three different methods and calcined to the respective sulfate-doped $(VO)_2P_2O_7$ catalysts in which the distances of the crystal planes parallel to (200) are enlarged. Sulfate doping influences both the crystal structure and the selectivity to maleic anhydride in the oxidation of *n*-butane. The best catalytic selectivity was achieved for slightly disordered catalysts and moderate lattice distances.

Keywords: sulfate-doped $(VO)_2P_2O_7$ catalysts, crystal structure, ESR, oxidation of *n*-butane, selectivity

1. Introduction

Vanadium phosphates are known to catalyze the selective oxidation of *n*-butane to maleic anhydride (MA). To date, vanadyl pyrophosphate, $(VO)_2P_2O_7$, obtained on dehydrating the precursor $VOHPO_4{\cdot}0.5H_2O$ is the most effective catalyst for this reaction. Therefore, it is widely used in industrial processes and much research work has been done in recent years to investigate the relation between structural properties and catalytic behaviour [1]. In earlier studies it was shown that small amounts of sulfuric acid favour the crystallization of the precursor $VOHPO_4{\cdot}0.5H_2O$ from aqueous solution in high yield [2]. The sulfate is partly incorporated in the crystal lattice of $VOHPO_4{\cdot}0.5H_2O$ probably substituting for HPO_4^{2-} ions and remains to a certain degree also in the final catalyst, $(VO)_2P_2O_7$ [3]. The catalytic activity of such catalysts in the selective oxidation of *n*-butane was found to be higher than without sulfate doping due to a lack of phosphorus at the catalyst surface and, hence, the oxidation of some vanadyl surface layers to V^{5+} [4]. However, the influence of sulfate doping on the MA selectivity is not properly understood so far.

The aim of this work is to study the formation of the precursor $VOHPO_4{\cdot}0.5H_2O$ in the presence of sulfuric and various sulfonic acids and the influence of sulfate incorporation in the crystal lattice of the catalyst $(VO)_2P_2O_7$ on the MA selectivity in the oxidation of *n*-butane.

2. Experimental

Precursor preparation: $VOHPO_4{\cdot}0.5H_2O$ was crystallized from the following aqueous solutions: (i) V_2O_5 in oxalic acid, dilute H_3PO_4 and H_2SO_4 (method A, samples A_1–A_6); (ii) $VOHPO_4{\cdot}4H_2O$ in diluted sulfuric, methanesulfonic or benzenesulfonic acid, respectively (method B, samples B_1–B_3); (iii) γ-$VOHPO_4{\cdot}2H_2O$ (obtained from $VOHPO_4{\cdot}4H_2O$ by treatment with acetic acid at room temperature for 1 day) in diluted sulfuric acid of varying concentration (method C, samples C_1–C_3). The filtered solutions were evaporated at 150°C. The products were washed with diluted HCl, water and acetone and then dried in air.

Catalyst preparation, conditioning and catalytic tests: 7.5 g particles of $VOHPO_4{\cdot}0.5H_2O$ (1.25–2.5 mm) were calcined in a fixed-bed reactor (11 mm i.d.) at 480°C for 4 h in a nitrogen stream. Thereafter, the $(VO)_2P_2O_7$ catalyst formed was conditioned by a short-time high-temperature procedure [5] in a stream of 1.5% butane in air. For the catalytic tests 2.5 g of the respective conditioned catalyst were mixed with 11.5 g of inert α-Al_2O_3 and heated in nitrogen to 420°C. Then the feed (1.5% butane in air) was passed over the sample and the products were analyzed by gas chromatography (butane, MA) and IR photometry (CO, CO_2). Butane conversion degrees between 30 and 100% were adjusted by changing the space velocity. MA selectivities at a conversion degree of 50% were interpolated from the conversion–selectivity plots.

Characterization: The phosphorus and sulfur contents of the precursors and the used catalysts were analyzed by gravimetric methods. The content and average oxidation state of vanadium in the latter were determined by potentiometric titration [6]. Specific surface areas were determined by the one-point BET method.

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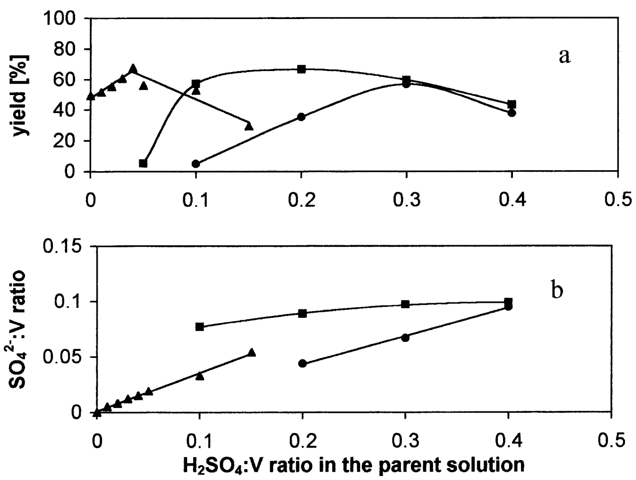

Figure 1. Yields of $VOHPO_4{\cdot}0.5H_2O$ (a) and SO_4^{2-} : V molar ratio in the crystals (b) as a function of the H_2SO_4 : V ratio in the parent solution, method A (▲), B (●), C (■).

The XRD powder patterns were obtained with a transmission powder diffractometer and a Guinier-de Wolff camera using Cu K_α radiation. ESR spectra were recorded at room temperature using the cw-spectrometer ESR 300 in X-band (Zentrum für Wissenschaftlichen Gerätebau, Berlin).

3. Results and discussion

3.1. Preparation of $VOHPO_4{\cdot}0.5H_2O$

The yields of $VOHPO_4{\cdot}0.5H_2O$ depend on both the amounts of sulfuric acid added and on the preparation procedure. When V_2O_5 is used as a starting material (method A) the yield passes a maximum at small dopant concentrations (figure 1a). During the crystallization a certain amount of sulfate is incorporated into the lattice of $VOHPO_4{\cdot}0.5H_2O$ which is proportional to the S : V molar ratio in the parent solution (figure 1b). However, since the yield of $VOHPO_4{\cdot}0.5H_2O$ is negligible when the S : V ratio in the solution is higher than 0.2 only products with low sulfate contents ($0 < S : V < 0.05$) can be obtained by this preparation procedure.

When the vanadyl hydrogenphosphates $VOHPO_4{\cdot}4H_2O$ (method B) and γ-$VOHPO_4{\cdot}2H_2O$ (method C) are used as starting materials higher amounts of sulfate up to a molar ratio of $S : V \approx 0.1$ can be incorporated in $VOHPO_4{\cdot}0.5H_2O$ (figure 1b) while the yields reach values between 50 and 60% comparable to those of method A. However, small S : V ratios cannot be obtained by these methods because the yield is very poor when the SO_4^{2-} : V ratio in the parent solution is lower than 0.1 (figure 1a). Despite small differences especially for low dopant concentrations the results of the methods B and C are rather similar leading to higher doped precursors. A possible reason might be that structural elements of the vanadyl hydrogenphosphates remain in the parent solutions which facilitate the crystallization of $VOHPO_4{\cdot}0.5H_2O$ even in the presence of higher H_2SO_4 concentrations.

Methanesulfonic and benzenesulfonic acid also favour the crystallization of $VOHPO_4{\cdot}0.5H_2O$ and even higher yields as with H_2SO_4 can be obtained (table 1). However, while about 10% of the HPO_4^{2-} ions can be substituted by SO_4^{2-} using H_2SO_4 as a doping agent (figure 1b) $CH_3SO_3^-$ is inserted only to a small extent and $C_6H_5SO_3^-$ not at all probably due to charge differences and steric reasons. The $VOHPO_4{\cdot}0.5H_2O$ crystals obtained in the presence of methanesulfonic or benzenesulfonic acid are much smaller than those from H_2SO_4-containing solutions. This indicates that the sulfonic acids favour not only the nucleation of $VOHPO_4{\cdot}0.5H_2O$ but also the rate of crystal growth.

3.2. Catalyst characterization

After the catalytic test the S : V and P : V ratios, the BET surfaces, and the vanadium oxidation states were determined (table 2). The S : V ratios of the used catalysts are much smaller than those of the precursors. This is caused by a loss of SO_2 during the calcination process, as confirmed by mass spectrometry. The P : V ratio decreases with increasing S : V ratio indicating that the HPO_4^{2-} groups in the precursor are partially replaced by SO_4^{2-} groups [3]. The surface areas depend on the method of catalyst precursor preparation. Method A provides catalysts with small surfaces (3–6 m^2/g) whereas slightly higher ones (7–11 m^2/g) are obtained employing methods B and C. The reason may be the dif-

Table 1
Yield and S : V molar ratio of $VOHPO_4{\cdot}0.5H_2O$ samples prepared after methods A and B using different doping agents

Method	Molar ratio doping agent : V	H_2SO_4		CH_3SO_3H		$C_6H_5SO_3H$	
		yield (%)	S : V	yield (%)	S : V	yield (%)	S : V
A	0.3 : 1	13.4	–	63.1	0.018	60.2	0
B	0.01 : 0.1	5.1	–	32.6	0.045	54.1	0
B	0.03 : 0.1	56.9	0.076	83.2	0.025	81.4	0
B	0.05 : 0.1	28.2	0.096	68.1	0.022	75.0	0

Table 2

Composition, specific surface area, S_{BET} and mean vanadium valence state of catalysts obtained from precursors synthesized by methods A, B or C

Catalyst	Doping agent	S : V precursor	S : V catalyst	P : V catalyst	S_{BET} (m^2/g)	V valence catalyst
A_1	none	0	0	1.055	4.4	4.009
A_2	H_2SO_4	0.004	–	1.045	3.1	4.017
A_3	H_2SO_4	0.008	–	1.05	3.8	4.003
A_4	H_2SO_4	0.012	–	1.047	5.8	4.010
A_5	H_2SO_4	0.033	0.027	1.036	6.2	4.019
A_6	H_2SO_4	0.054	0.040	1.029	5.4	4.027
B_1	H_2SO_4	0.069	0.038	0.967	9.2	4.032
B_2	CH_3SO_3H	0.025	0.000	0.997	7.2	3.986
B_3	$C_6H_5SO_3H$	0	0.000	0.995	10.6	4.006
C_1	H_2SO_4	0.048	0.031	0.940	9.5	4.026
C_2	H_2SO_4	0.057	0.043	0.954	10.6	4.039
C_3	H_2SO_4	0.103	0.068	0.914	7.9	4.057

ferent size of the crystals obtained by the respective precursor preparation methods and the structural disorder in the lattice of the catalysts prepared after method B. The mean vanadium valence state increases slightly with rising SO_4^{2-} content. This is in agreement with previous investigations in which the phosphorus content of the catalyst surface was found to be lowered leading to the oxidation of some vanadyl surface layers to V^{5+} [4].

In the XRD powder patterns of the used catalysts the positions of the (200) reflections are shifted to lower d-values as the amount of SO_4^{2-} incorporated in the crystal lattice increases, i.e. the distances between the layers parallel to the (200) crystal planes are expanded up to 1%. It is clear that the layer expansion caused by the sulfate incorporation cannot exceed a certain level without destruction of the crystal lattice. Accordingly, the (200) distance plotted as a function of the S : V molar ratio reaches a limit at about 3.902 Å (figure 2). This means that the distances between the vanadyl ions forming ladder-like double chains in the structure of $(VO)_2P_2O_7$ [7] are enlarged, too, since these chains run perpendicular to the (200) crystal faces. In addition to the peak shift, the (200) reflections of catalysts obtained after method B in the presence of sulfonic acids are strongly broadened. Similar effects are also observed for catalysts prepared in alcoholic medium where certain amounts of alcohol are intercalated in the precursor lattice leading to samples of low crystallinity with a lot of lattice defects [1,8]. The sulfonic acids seem to influence the crystal structure in a manner comparable to that of alcohols leading to stacking faults and dislocations, too, although they are incorporated into the crystal lattice only in very small amounts or not at all (table 1).

The ESR spectra of all $(VO)_2P_2O_7$ catalysts consist of single lines which are narrowed due to spin–spin exchange interactions proceeding between neighbouring VO^{2+} centres along the vanadyl chains. In an earlier work we have already demonstrated that the strength of this exchange and, thus, the line shape depends on the degree of structural disorder caused by the sulfate doping. Increasing lattice distortions led to less efficient exchange interactions, larger line width, and smaller peak-to-peak amplitudes [9]. Similar effects are observed in the ESR spectra of the samples studied in this work (figure 3). As shown recently [10] the quotient of the fourth and the square of the second moment of the ESR signal, $\langle B^4\rangle/\langle B^2\rangle^2$, can be used as a quantitative measure of the exchange efficiency. The stronger the exchange interaction the higher the moment quotient, $\langle B^4\rangle/\langle B^2\rangle^2$. For samples doped with sulfate this value decreases linearly with increasing distance between the layers parallel to the crystal plane (200) as long as the S : V ratio in the precursor does not exceed 0.069 (figure 4, white squares). This is not surprising since the exchange proceeds along chains of VO_6 octahedra per-

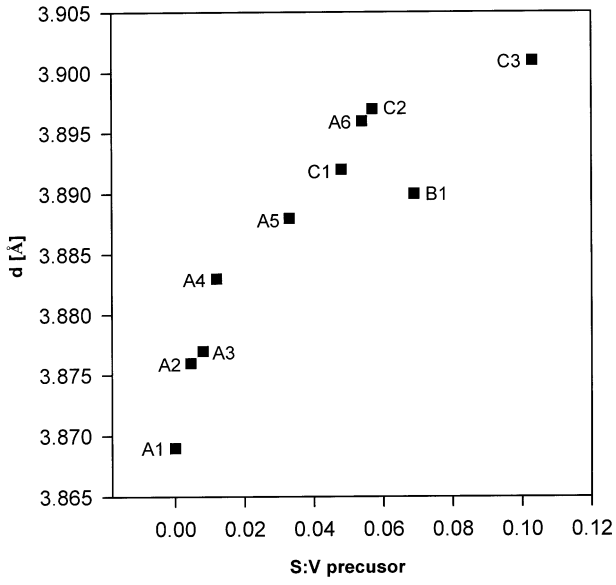

Figure 2. d-values of the (200) plane in the XRD patterns of the used catalysts as a function of the S : V ratio in the precursor.

pendicular to the (200) plane and should be weakened on increasing the vanadyl distance. It is interesting to note that the exchange intensity does not decrease linearly with the S : V ratio (figure 4, black squares). As sulfate is added up to S : V = 0.012 (sample A_4) a rapid decrease of the moment value can be seen which becomes more gradual in the range $0.012 < S : V < 0.069$. At even higher S : V ratios (sample C_3) the exchange efficiency is enhanced markedly again. This effect which is shown impressively also by the ESR spectra (figure 3c) supports pretty well our previous results [9]. It is explained in terms of a clusterlike incorporation of sulfate ions at high S : V ratios rather than a homogeneous one at low sulfate loadings. Thus, lattice distortions are assumed to be restricted to the cluster boundaries and not to occur throughout the whole sample as for homogeneous sulfate distribution at low S : V ratios. Accordingly, the perturbation of spin–spin exchange is minimized. Very weak ESR signals (figure 3b) and small moment values of $\langle B^4\rangle/\langle B^2\rangle^2 = 3.85$ (sample B_2) and $\langle B^4\rangle/\langle B^2\rangle^2 = 3.39$ (sample B_3) are obtained for the catalysts prepared in the presence of sulfonic acids. This agrees with the respective XRD results discussed above and points to the presence of marked lattice distortions.

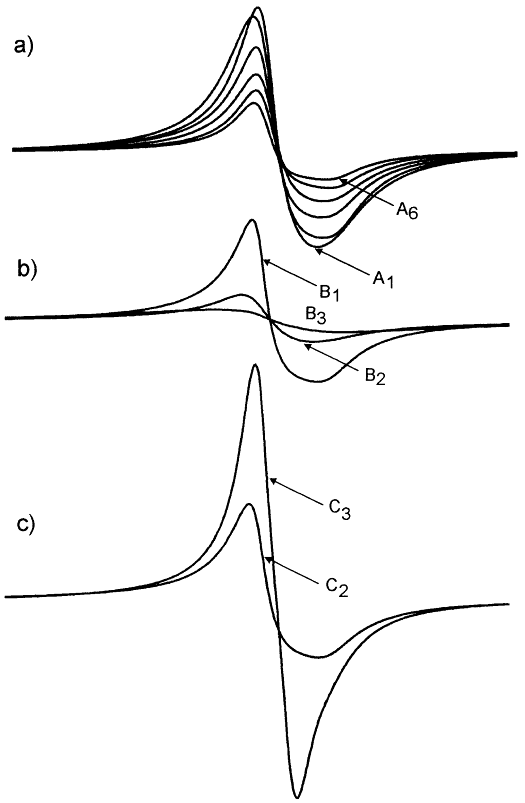

Figure 3. ESR spectra for equal amounts of $(VO)_2P_2O_7$ catalysts obtained from precursors prepared after method A (a), B (b) and C (c) at room temperature, field range: 310–368 mT.

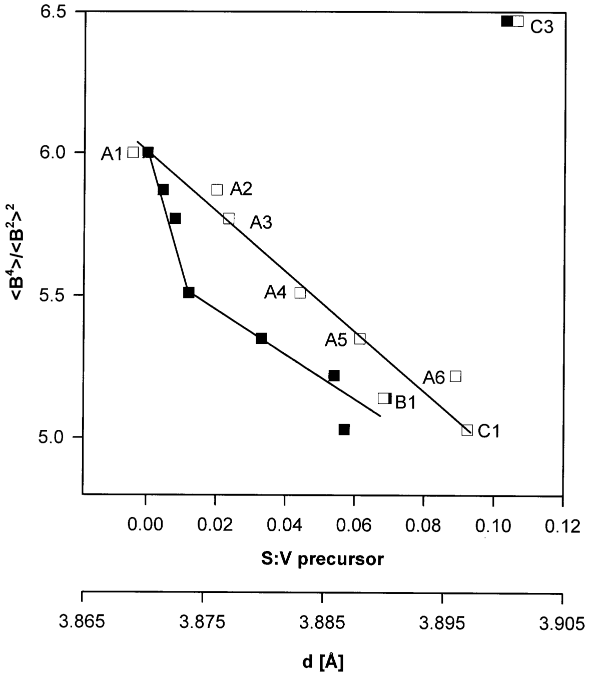

Figure 4. Quotient of the fourth and the square of the second moment of the ESR signals, $\langle B^4\rangle/\langle B^2\rangle^2$ as a function of the d-values (□) and of the $(VO)_2P_2O_7$ catalysts S : V molar ratio in the respective precursors (■).

3.3. Catalytic behaviour in the oxidation of n-butane

As mentioned above the influence of sulfate doping on the catalytic activity has been described recently [4]. In this work, relations between the catalytic selectivity and structural peculiarities caused by sulfate doping are derived. To compare the behaviour of the various catalysts the MA selectivities for a butane conversion degree of 50% were interpolated from the respective selectivity–conversion curves.

Plotting the MA selectivity of the $(VO)_2P_2O_7$ catalysts prepared after method A as a function of the distance between the (200) planes of the crystal structure reveals that maximum selectivities are achieved when these distances are in a medium range taking values around 3.883 Å as it is the case for sample A_4 (figure 5). Since the (200) distances are linearly correlated to the moment values of the ESR signals (figure 4) it follows that high selectivities are obtained when the spin–spin exchange efficiency is in a medium range. In addition to the vanadyl distances reflected by the d-values of the (200) planes the moment values are also influenced by the degree of structural disorder in the crystal lattice. The higher the disorder, the lower the moment value [10]. Very recently we have shown for a series of sulfate-free $(VO)_2P_2O_7$ catalysts that MA selectivities in the oxidation of n-butane are improved when the crystals are disordered to a certain degree. This has been attributed to the high lattice flexibility detected at reaction temperatures and the formation of defect sites which favour the oxygen transport through the lattice and, thus, the conversion of adsorbed nucleophilic and, therefore, less

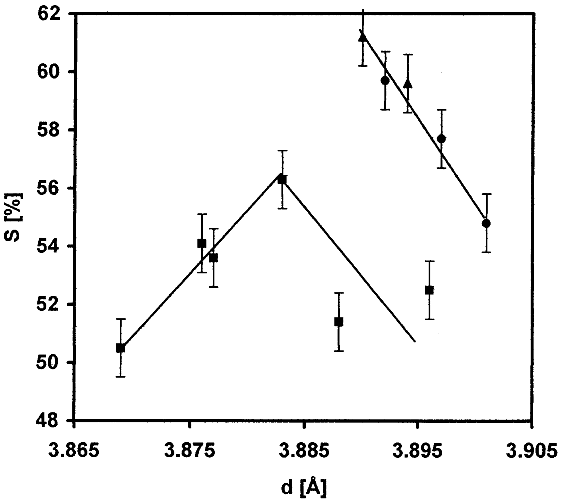

Figure 5. MA selectivity at a butane conversion degree of 50% as a function of the *d*-values of the (200) reflections, precursors prepared by method A (■), B (▲) and C (●).

selective oxygen species into oxide ions [11]. Based on these results the following explanation for the different MA selectivities of the catalysts A_1–A_6 can be given: In samples with very low sulfate contents corresponding to high $\langle B^4\rangle/\langle B^2\rangle^2$ and low *d*-values structural disorder is negligible and the oxygen transport is hindered leading to lower selectivities. At high sulfate contents the spin–spin exchange along the vanadyl chains is distorted due to increasing distances between the (200) planes. However, as we have demonstrated for both the oxidation of *n*-butane [10] and the ammoxidation of toluene as well [12] effective spin–spin exchange pathways in vanadyl phosphate catalysts are essential for fast electron transport from the bulk to the surface and vice versa required for good catalytic performance in redox processes. This condition is obviously not fulfilled when the *d*-values of the (200) planes in the $(VO)_2P_2O_7$ structure exceed a certain level. Therefore, catalysts prepared after method A show best selectivities when the disorder is within an optimum range.

For catalysts prepared after method C the relation between MA selectivity and the (200) distances is similar to that of the samples A_4–A_6. However, only the falling part of the vulcano-curve can be displayed since only sulfate-rich samples were obtained in this way (figure 5). The MA selectivities are slightly higher than for the A-samples although the *d*-values are in the same range. The reason may be that the C-samples can accommodate higher amounts of doping anions without considerable lattice distortion. This becomes obvious also by comparing the ESR signals and corresponding moment values of the samples C_2 and C_3 (figures 3c and 4) and is explained in terms of a cluster-like incorporation of sulfate as discussed above.

The catalysts prepared after method B are among those with the best MA selectivities although at least the samples B_2 and B_3 contain only very few or no sulfate at all. Nevertheless, their structures are highly disordered as can be seen easily from the ESR signals (figure 3b) and the moment values which decrease from 5.14 (B_1) and 3.85 (B_2) to 3.39 (B_3). Like in catalysts obtained from alcoholic medium this disorder probably improves the selectivity due to the beneficial influence on the oxygen transport discussed above. On the other hand it might be possible that crystal faces parallel to (200) assumed to be the selective ones [12] are exposed preferably as it is the case for organically prepared $(VO)_2P_2O_7$, too.

In addition to the reasons discussed so far low selectivities of catalysts with high sulfate contents may also be due to the increased oxidation state of the catalyst surface caused by the loss of phosphorus [4]. It is well known that phosphorus-lean V^{5+} containing phases have a higher oxidation potential than V^{4+} and are therefore more active but less selective.

4. Conclusions

In $(VO)_2P_2O_7$ catalysts doped with sulfate ions in molar ratios of $0 < S : V < 0.1$ the distances between the crystal planes containing the vanadyl ions are enlarged. In addition, structural disorder increases up to a certain limit of the sulfate concentration and decreases again for high sulfate contents probably due to the cluster-like incorporation of the doping ions. For maximum MA selectivities in the oxidation of *n*-butane a certain degree of structural disorder is required but too high distances between the vanadium containing crystal planes must be avoided to support the oxygen and electron transport from the surface to the bulk and vice versa. This is reflected by a vulcano-type curve for the plot of the MA selectivity as a function of the (200) plane distance.

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