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On the rehydration of vanadyl pyrophosphate to vanadyl hydrogenphosphate hemihydrate

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Vanadyl pyrophosphate-based VPO catalysts for butane oxidation to maleic anhydride can be completely rehydrated in the solid phase into their vanadyl hydrogenphosphate hemihydrate precursors which again can be transformed into vanadyl pyrophosphate thus enabling a reuse of spent catalysts.

Vanadyl pyrophosphate, $(VO)_2P_2O_7$ (VPP) is well known to be the active and selective component of VPO catalysts in the partial oxidation and ammoxidation of hydrocarbons. Owing to its unique catalytic properties it plays a significant role especially in the oxidation of *n*-butane to maleic anhydride (MA).[1]

VPP is formed by dehydration of vanadyl hydrogenphosphate hemihydrate, $VOHPO_4{\cdot}0.5H_2O$, (VHP) in a topotactic reaction at temperatures above 638 K according to eqn. (1):[2]

$$2\ VOHPO_4{\cdot}0.5H_2O \rightarrow (VO)_2P_2O_7 + 2\ H_2O \qquad (1)$$

Well crystallized VPP catalysts obtained by calcination at high temperatures (*e.g.* above 900 K) or after an equilibration procedure in a chemical reactor for hundreds of hours time on stream are described to be comparatively resistent against overoxidation.[3] In this state they are insoluble in boiling water and even poorly soluble in concentrated hydrochloric acid. No rehydration reaction of VPP has been mentioned until now. Experience shows that also the presence of large amounts of water vapour in the feed and effluent gases of oxidation reactions passing through the VPP catalyst bed does not lead to any detectable hydration of VPP resulting only in a loss of phosphorus[4] and influencing recrystallization processes in the catalyst particles.[5]

Therefore, it was surprising that in a well crystallized VPP sample having been kept for some years at room temperature in a laboratory atmosphere (with a typical moisture content of 2–3% water vapour) a small amount of VHP was detected by X-ray diffraction (XRD). This observation led us to study the behaviour of VPP at higher water vapour pressure to elucidate the rehydration process of this compound and to find a new advantageous route to regenerate spent catalysts. Therefore, we studied sequences of the hydrothermal transformation of VPP into VHP and of the reconversion of these VHP samples into VPP by calcination. Furthermore, the influence of these procedures was investigated on the catalytic properties of the VPP materials obtained.

The VPP samples applied in this study were prepared as follows: the precursor VHP A1 was synthesized after stepwise addition of V_2O_5 into a hot solution of oxalic acid in dilute phosphoric acid by evaporation to dryness. The precursor VHP B1 was prepared by reaction of V_2O_5 with an ethanolic solution of oxalic acid in phosphoric acid. The P : V ratio of both VHP compounds was 1 : 1. The precursors were pelletized, crushed, sieved (1.25–2.5 mm) and transformed into VPP A1 and VPP B1, respectively, in a N_2 stream at 770 K for 2 h. For deactivation and 'deselectivation' a sample of VHP A1 was calcined at 923 K for 6 h and then for 5 h at 1123 K yielding VPP C1. Renewed transformations of the obtained VPP A1, VPP B1 and VPP C1 samples led to the precursor samples VHP A2, VHP B2 and VHP C2, respectively, which were calcined again as described above forming the samples VPP A2, VPP B2 and VPP C2.

The rehydration experiments were performed as follows: The VPP A,B,C samples were placed together with water in an ampoule (molar ratio VPP : H_2O = 1 : 2.5) and heated at 393–413 K for 24 h. The hydration reaction led to VHP according to eqn. (2).

$$(VO)_2P_2O_7 + 2\ H_2O \rightarrow 2\ VOHPO_4{\cdot}0.5H_2O \qquad (2)$$

This change was evident by a change of colour to blue for the VHP A samples (broad distribution of particle sizes, average particle size: 6.2 μm) and to greenish for the VHP B samples (narrow distribution of particle sizes, average particle size: 1.7 μm). Another possibility to introduce water into VPP is its reaction with water-rich vanadyl hydrogenphosphate hydrates, *e.g.* according to eqn. (3).

$$3\ (VO)_2P_2O_7 + 2\ VOHPO_4{\cdot}4H_2O \rightarrow 8\ VOHPO_4{\cdot}0.5H_2O + H_2O \qquad (3)$$

Excess water was then removed from the samples by drying of the obtained solids at 400 K.

The catalytic tests were performed in a tube reactor using 3–10 cm^3 catalyst (granules 1.25–2.5 mm) after conditioning of the fresh VPP samples for 2 h at 750 K in a butane–air mixture (1.5 vol% butane). The maximum MA yields of the VPP samples from the VPP → VHP → VPP sequences were determined at constant space velocities (GHSV = 1000 h^{-1}) adjusting a butane conversion degree of 90% by variation of the reaction temperatures. For sample VPP C1 the space velocity was reduced to 500 h^{-1} to determine the MA yields at similar temperatures relative to VPP C2.

The VPO materials were characterized using XRD, BET and chemical methods.

Fig. 1 shows diffractograms for samples in the VPP B → VHP B → VPP B transformation sequence starting with the fresh sample VHP B1. The diffractogram of VHP B2 shows typical reflections of $VOHPO_4{\cdot}0.5H_2O$,[6] *i.e.* a quantitative conversion of VPP into the VHP precursor took place. This result and the sequence of the other diffractograms in Fig. 1 reveal that the dehydration and rehydration, respectively, of VHP and VPP are reversible over a number of cycles. Preliminary experiments showed that the rates of the conversions depend on the partial pressure of H_2O, the temperature and on the properties of the solids such as their crystallinity and particle size.

The FWHM of the VPP B1–3 reflections (200) decreased from 2θ = 1.13° (VPP B1) to 2θ = 1.07° (VPP B2) and 2θ = 1.02° (VPP B3). This result was mirrored by the decrease of the FWHM of the same reflections from 2θ = 0.305 to 0.231° for the VPP A1–3 samples. Both findings are interpreted to be caused by recrystallization processes occurring especially during the hydration. Simultaneously, the specific surface areas decreased from 1.8 to 1.5, 12.2 to 11.2, 13.9 to 8.8 and 14.5 to 13.0 m^2 g^{-1} for VHP A, B and VPP A, B samples, respectively. This behaviour may also be explained by recrystallization leading to an increase in crystallite sizes. The remarkable increase in the specific surface areas in the conversion of VHP to VPP samples is interpreted in terms of particle size effects.[7]

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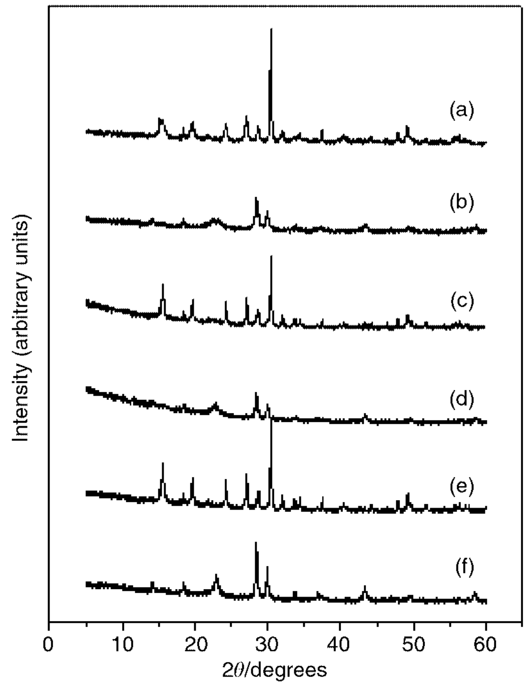

Fig. 1 Diffractograms of VHP B and VPP B samples measured during the transformation VPP B → VHP B → VPP B: (a) VHP B1, (b) VPP B1, (c) VHP B2, (d) VPP B2, (e) VHP B3, (f) VPP B3.

The fact that the colours of the different VHP samples in the sequences A1–3 and B1–3, did not change during the dehydration–rehydration transformations suggest a topotactic nature of this reaction as expected for the mild hydration conditions and the transformation rate.

The maximum MA yields of VPP A samples obtained in the course of several transformation sequences and the corresponding catalyst temperatures necessary to adjust a butane conversion degree of 90% demonstrate that the transformations can lead to both a decrease in activity and selectivity of the VPP samples: the MA yields decreased from 52 mol% MA (VPP A1) to 45 mol% MA (VPP A4 sample, obtained after the third transformation sequence) and the temperatures for 90% butane conversion increased from 690 to 707 K. This finding is interpreted to be caused by the recrystallization effect discussed above: from catalytic and EPR experiments using VPP samples of different crystallinity it is known that maximum catalytic performance requires a certain degree of disorder in the VPP lattice.[8] This is supported by recent results which showed that the catalytic performance of well crystallized VPP may be improved by tribomechanical treatment upon milling samples.[9]

Fig. 2 shows the catalytic results of the well crystallized sample VPP C1 (deactivated and 'deselectivated' by prolonged calcination at high temperatures) and of the regenerated sample VPP C2. The figure clearly shows that the transformation led to a marked increase in both the activity and the selectivity of the VPP C2 sample. This result can be explained by the increase in the low surface area from 3.2 m^2 g^{-1} of the deactivated sample to 15.9 m^2 g^{-1} of the regenerated sample and by an increase in

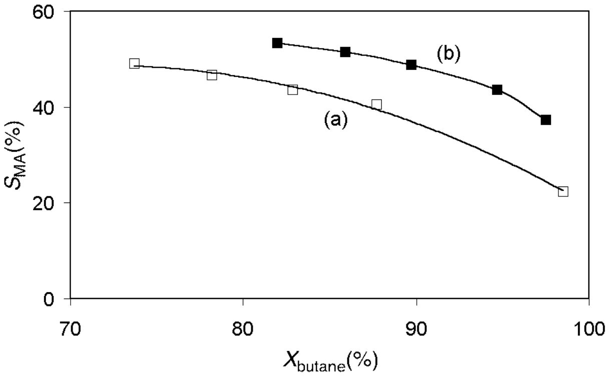

Fig. 2 MA selectivities of samples VPP C1 (a) and VPP C2 (b) as a function of the degree of conversion of butane, GHSV: 500 h^{-1} (VPP C1), 1000 h^{-1} (VPP C2), reaction temperatures: VPP C1: from 716 K ($X_{C_4H_{10}}$ = 73.7%) to 768 K ($X_{C_4H_{10}}$ = 98.5%), VPP C2: from 703 K ($X_{C_4H_{10}}$ = 82%) to 740 K ($X_{C_4H_{10}}$ = 97.5%).

the lattice disorder of the latter due to the transformation procedure.

The presented results illustrate that the described method is suitable for regenerating spent catalysts. Furthermore, as shown by additional experiments, it could open a way to adjust the P : V ratio in regenerated catalysts by adding the desired amount of phosphoric acid to the amount of water necessary for the transformation procedure. The new route presented here avoids chemical conversion of the spent materials by dissolution or other processes followed by separation procedures to recover the vanadium component. It could also be an alternative method of regeneration instead of treatments of catalyst beds with halide containing compounds[10] which can cause difficult technical and environmental problems.

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Notes and references

1 *Catal. Today*, 1987, **1**, 477 (ed. B. K. Hodnett).

2 E. Bordes, J. W. Johnson and P. Courtine, *J. Solid State Chem.*, 1984, **53**, 270; C. C. Torardi and J. C. Calabrese, *Inorg. Chem.*, 1984, **23**, 1308; J. W. Johnson, D. C. Johnston, A. J. Jacobson and J. F. Brody, *J. Am. Chem. Soc.*, 1984, **106**, 8123.

3 *Catal. Today*, 1993, **16**, 1 (ed. G. Centi).

4 B. Kubias, F. Richter, H. Papp, A. Krepel and A. Kretschmer, *Stud. Surf. Sci. Catal.*, 1997, **110**, 461.

5 F. Cavani, A. Colombo, F. Giuntoli, F. Trifiro, P. Vazquez and P. Venturosi, in *Advanced Catalysts and Nanostructured Materials*, ed. W. R. Moser, Academic Press Inc., New York, 1996, p. 43.

6 M. E. Leonowicz, J. W. Johnson, J. F. Brody, H. F. Shannon and J. M. Newsam, *J. Solid State Chem.*, 1985, **56**, 370.

7 N. Duvauchelle, E. Kesteman, F. Oudet and E. Bordes, *J. Solid State Chem.*, 1998, **137**, 311.

8 A. Brückner, B. Kubias, B. Lücke and R. Stößer, *Colloids Surf. A: Physicochem. Eng. Asp.*, 1996, **115**, 179.

9 B. Kubias, M. Fait, M. Estenfelder, H.-J. Eberle, U. Steinike and M. Meisel, Recent Research Poster 054, *12th International Congress on Catalysis, Granada*, July 9–14, 2000, CD-ROM RR054.

10 R. C. Edwards, *US Pat.*, 4861738 , 29.01.88 (Amoco Corp.).