

A CONTRIBUTION TO THE STRUCTURE CHARACTERISTICS AND PHASE COMPOSITION OF VANADIUM-PHOSPHORUS CATALYSTS PREPARED FROM THE $\text{VOPO}_4 \cdot x \text{H}_2\text{O} \cdot y \text{H}_3\text{PO}_4$ PRECURSOR

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Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

Catalysts were prepared from $\text{VOPO}_4 \cdot x \text{H}_2\text{O} \cdot y \text{H}_3\text{PO}_4$ ($x = 0.3 - 2$, $y = 0.2 - 0.85$) by reduction with SO_2 up to a final temperature of $750 - 800^\circ\text{C}$, and activated in a reaction mixture of 1.0 - 1.4% butane in air up to 500°C . The structure characteristics and phase composition of the catalysts were found to be affected by the preparation procedure and heat treatment regime. Their diffraction lines and IR spectra revealed that the catalysts form larger and less defective crystals than catalysts which were obtained from the $\text{VOHPO}_4 \cdot x \text{H}_2\text{O} \cdot y \text{H}_3\text{PO}_4$ precursor and activated in the reaction mixture at temperatures up to 500°C . In the catalysts prepared by the above procedure, the tendency to the formation of phases of higher-condensed phosphates, in particular $\text{VO}(\text{PO}_3)_2$ or even $\text{V}(\text{PO}_3)_3$, increases with increasing $n(\text{P}) : n(\text{V})$ ratio and is then more pronounced than with vanadium-phosphorus catalysts prepared by other procedures. The tendency to the formation of the catalytically less active condensed phosphates is partly suppressed by the embedding of modifying metal cations (Fe or Cu in this case).

Vanadium-phosphorus catalysts are promising contacts for partial oxidation of C_4 hydrocarbons to maleic anhydride¹⁻⁴. If a catalyst of this kind is prepared by a method during which a precursor of the type of $\text{VOPO}_4 \cdot x \text{H}_2\text{O}$ is formed in the first stage⁵, the second stage must include reduction of vanadium(V) in the solid precursor using a reducing gas (SO_2) at a temperature increasing gradually to $750 - 800^\circ\text{C}$ (ref.⁶). This procedure, including the heat treatment regime, differs considerably from the method where the precursor is formed in concentrated HCl and vanadium in the V_2O_5 used for the synthesis is reduced to oxidation state IV in the solution (ref.⁷). In this latter case the precursor is formed and activated in nitrogen atmosphere and in a reaction mixture, or in a reaction mixture solely (1.0 to 1.4 vol.% C_4 hydrocarbon in air), at temperatures which are considerably lower, viz. up to 500°C (refs.^{8,9}). It is reasonable to expect that the different method of synthesis, including the different heat treatment regime and different kind of atmosphere, will bring about some differences in the structure charac-

teristics and phase composition of the active vanadium–phosphorus catalyst at the same $n(\text{P}) : n(\text{V})$ ratio.

The effect of the method of preparation and heat treatment of the catalyst on its lattice defectiveness and phase composition is the subject of this paper, which also deals with the effect of increasing the $n(\text{P}) : n(\text{V})$ ratio and of embedding modifying ingredients on the structure and phase characteristics of the forming V–P–O and V–P–O–M catalyst (M is the embedded modifying metal cation).

EXPERIMENTAL

The vanadium–phosphorus precursor was prepared by dissolving V_2O_5 in excess concentrated H_3PO_4 at elevated temperature⁵. To achieve the desired $n(\text{P}) : n(\text{V})$ ratio, the reaction product – precursor was rinsed with distilled water and acetone; the number of rinsings was chosen based on experience, and the actual $n(\text{P}) : n(\text{V})$ ratio of the dry product was determined by chemical analysis.

The dry precursor was reduced in a stream of SO_2 in a quartz tube accommodated in an electric furnace at temperatures gradually increasing to 750 – 800 °C. The grey-brown product was purified by agitating with concentrated HCl and then with water, and after drying, activated in the reaction mixture for a minimum of 5 h at a temperature up to 500 °C, whereby the properties of the catalyst were stabilized.

For analysis, the catalyst was transferred into solution following fusion with sodium peroxide. Vanadium was determined titrimetrically, phosphorus, gravimetrically¹⁰. All chemicals were of reagent grade purity.

To obtain the modified catalyst, the precursor was mixed with a solution containing the calculated amount of modifier. The modifier salt penetrated into the laminar structure of the catalyst during drying and mixing, and was embedded into the structure during the subsequent heat treatment and formation of the active catalyst.

The instrumentation for obtaining the X-ray diffraction patterns and IR spectra as well as the experimental procedures were as in ref.⁸.

RESULTS AND DISCUSSION

The precursor with the $n(\text{P}) : n(\text{V})$ ratio higher than one contains excess H_3PO_4 so that it is proper to express its composition by the formula $\text{VOPO}_4 \cdot x \text{H}_2\text{O} \cdot y \text{H}_3\text{PO}_4$. The laminar structure of the precursor⁵ can host substances such as water, H_3PO_4 , etc. During the (high-temperature) reduction of the catalyst precursor, the excess H_3PO_4 reacts with the basic component, VOPO_4 . As a result of this interaction and chemical conversion of VOPO_4 during the heat treatment, a multiphase vanadium–phosphorus catalyst emerges.

The X-ray diffraction patterns (Table I) and IR spectra (Fig. 1) give evidence that in the applied method of synthesis and activation of the vanadium–phosphorus catalyst employed in this work, also, the basic phase of the catalyst with $n(\text{P}) : n(\text{V}) = 1.2$ is vanadyl diphosphate, which crystallizes in the rhombic system^{6,9,11}. The catalyst also includes other phases such as $\beta\text{-VOPO}_4$ (refs^{11–14}), vanadyl metaphosphate $\alpha\text{-VO}(\text{PO}_3)_2$ (refs^{12,15}) and vanadyl cyclotetraphosphate $(\text{VO})_2\text{P}_4\text{O}_{12}$ (refs^{9,16}).

As mentioned, the method for the preparation of the active catalyst differs substantially from that used in ref.⁹. For instance, some of the otherwise weak lines are more marked. All diffraction lines are appreciably sharper and the relative intensity of the basic lines is 2 to 3 orders higher than for catalysts prepared in HCl and treated directly with the reaction mixture up to 500 °C. Also, the half line width of the most intense diffraction lines is lower for the catalysts prepared within the present work. The lines are smooth, free of overlap. All this indicates that the preparation method used gives rise to crystals which are on average larger in size and exhibit lower energy strains and defects in the lattice than the catalysts prepared by the method⁹. It is reasonable to expect that the differences in the crystallographic characteristics will also be associated with differences in the catalytic activity of the vanadium-phosphorus catalysts during partial oxidation of C₄ hydrocarbons to maleic anhydride.

The phase contents of the catalyst vary with changing $n(\text{P}) : n(\text{V})$ ratio, as can be deduced from the changes in the relative intensities of the diffraction lines (Table I) and of the IR absorption bands (Fig. 1). For catalysts with $n(\text{P}) : n(\text{V}) > 1.2$, the relative intensities of lines corresponding to crystalline $(\text{VO})_2\text{P}_2\text{O}_7$ and $\beta\text{-VOPO}_4$ decrease while new lines appear and the relative intensities of lines belonging to $\alpha\text{-VO}(\text{PO}_3)_2$ increase. The cyclic $(\text{VO})_2\text{P}_4\text{O}_{12}$ is probably present in a lower quantity in the catalyst and/or occurs in the amorphous state (its presence is revealed by IR spectra). Hence, the catalyst is a multiphase crystalline material. Table I demonstrates that although some diffraction lines overlap, within the entire set of diffraction maxima the phases can be discriminated reliably. Diffraction line overlap, though, can aggravate the reading of changes in their relative intensities if one, belonging to $(\text{VO})_2\text{P}_2\text{O}_7$, decreases while the other, belonging to $\text{VO}(\text{PO}_3)_2$, increases.

The infrared spectra (Fig. 1) supplement and corroborate information derived from the X-ray diffraction patterns. Band assignment^{11,16,17} confirms the above chemical phase composition. Additional analysis based on band intensity and shape considerations was as in ref.⁹. As compared with the catalyst examined in ref.⁹, the catalyst

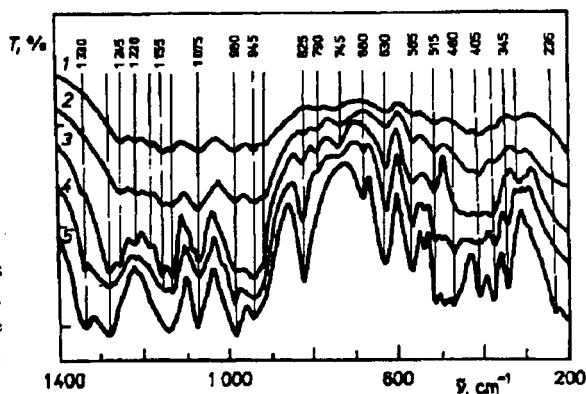


FIG. 1
Infrared spectra of vanadium-phosphorus catalysts prepared from $\text{VOPO}_4 \cdot x\text{H}_2\text{O} \cdot y\text{H}_3\text{PO}_4$ precursor; $n(\text{P}) : n(\text{V})$: 1 1.2 (Fe modifier), 2 1.2 (Cu modifier), 3 1.2, 4 1.37, 5 1.85

with $n(\text{P}) : n(\text{V}) = 1.2$ prepared in this work (Fig. 1, curve 3), exhibits bands which are better resolved, narrower and more intense. This confirms the conclusion that the catalyst is composed of crystals that are on average larger in size and less defective.

TABLE I
X-Ray data of vanadium-phosphorus catalysts prepared from $\text{VOPO}_4 \cdot x \text{H}_2\text{O} \cdot y \text{H}_3\text{PO}_4$ precursor

d , nm	I/I_0^a			Assignment ^b	
	1.20	1.37	1.85	phase	$(\text{VO})_2\text{P}_2\text{O}_7$ hkl
62.81	0.10	0.08	0.05	B	0 2 1
57.91	0.11	0.05	0.05	E	
56.44	0.12	0.09	0.07	A	1 1 1
52.16			0.07	E	
50.11			0.05	E	
47.96	0.16	0.16	0.13	B	0 0 2
39.69	0.15	0.25	0.45	D	
38.67	1.00	0.94	0.83	A	2 0 0
36.48	0.05	0.40	0.70	C	
34.53	0.05	0.06	0.07	E	
32.90	0.06	0.15	0.21	D	
32.20	0.06	0.11	0.25	D	
31.43	0.83	0.72	0.11	A	0 1 3 0 4 2
30.79	0.06	0.15	0.38	C	
29.84	0.47	0.42		B	0 2 3
29.16	0.08	0.25	0.41	C	
26.55	0.16	0.14	0.08	B	2 3 2
26.29		0.17	0.25	C	
25.29		0.07	0.12	C	
24.40	0.18	0.17	0.14	B	2 1 3 2 4 2
23.88		0.10	0.13	C	
23.64	0.06	0.13	0.14	B	2 2 3
21.88		0.06	0.07	C	
20.87	0.24	0.13	0.07	A	3 3 2 0 6 3
20.23		0.09	0.13	C	
19.89	0.05	0.10	0.22	C	
19.33	0.13	0.12	0.18	C	
18.95			0.15	C	
18.81	0.05	0.09	0.12	C	
18.41	0.13	0.12	0.11	B	2 6 3

^a At different $n(\text{P}) : n(\text{V})$ ratio; ^b A $(\text{VO})_2\text{P}_2\text{O}_7$ (refs^{9,11}), B $(\text{VO})_2\text{P}_2\text{O}_7$ and $\beta\text{-VOPO}_4$ (refs^{11,14}), C $\alpha\text{-VO}(\text{PO}_3)_2$ (ref.¹⁵), D probably $\beta\text{-VO}(\text{PO}_3)_2$ (ref.¹¹), E unidentified phase.

Furthermore, the spectrum displays absorption bands at 1 330, 1 275 and 825 cm^{-1} , characteristic of vanadyl metaphosphate^{11,18}. Comparison of the spectrum with spectra of catalysts of the same composition and prepared in the same manner, containing, however, modifying ingredients (Fig. 1, curves 1, 2), demonstrates that the presence of a modifier partly hinders the formation of higher-condensed phosphates such as $\text{VO}(\text{PO}_3)_2$.

Comparing qualitatively the IR spectra of catalysts with different $n(\text{P}) : n(\text{V})$ ratios (curves 3, 4, 5 in Fig. 1), the intensity of the absorption bands at 1 330, 1 275, 825, 680, 630, 565, 540, 460, 405, 375 and 345 cm^{-1} is seen to increase with increasing $n(\text{P}) : n(\text{V})$ ratio, whereas the opposite is true of the bands at 1 245, 1 220, 1 185, 1 155, 1 135, 790, 745, 435 and 325 cm^{-1} . At $n(\text{P}) : n(\text{V}) = 1.85$ the bands at 1 190, 1 155 and 1 135 cm^{-1} are absent altogether whereas a broad band appears at 1 145 cm^{-1} . These facts indicate that the amounts of the basic phases, viz. $(\text{VO})_2\text{P}_2\text{O}_7$ and $\beta\text{-VOPO}_4$, decrease with increasing $n(\text{P}) : n(\text{V})$ ratio. The bands at 1 245, 1 220, 790 and 745 cm^{-1} , attributed by us to vanadyl cyclotetraphosphate^{9,16}, vanish as well. On the other hand, the proportion of the $\alpha\text{-VO}(\text{PO}_3)_2$ phase increases with increasing $n(\text{P}) : n(\text{V})$ ratio. The tendency to formation of higher-condensed phosphates in the preparation procedure presented is higher than in the method⁹. This is apparently associated with the higher heat treatment temperature during the catalyst reduction in the SO_2 stream.

In conclusion, reduction of $\text{VOPO}_4 \cdot x \text{H}_2\text{O} \cdot y \text{H}_3\text{PO}_4$ at temperatures up to 800 °C gives rise to a multiphase crystalline catalyst. The $\alpha\text{-VO}(\text{PO}_3)_2$ content increases with increasing $n(\text{P}) : n(\text{V})$ ratio faster than in some other preparation procedures; at the same time, the basic phase contents decrease. As compared to vanadium-phosphorus catalysts prepared by dissolution of V_2O_5 in hydrochloric acid in the presence of calculated amount of H_3PO_4 , where the heat treatment temperature does not exceed 500 °C, the catalysts prepared by the present procedure consist of crystals which are on average larger in size and whose lattice is less strained and less defective. Modifiers embedded in the catalyst (Fe or Cu in this case) hinder to an extent the formation of higher-condensed, catalytically less active phosphates such as $\text{VO}(\text{PO}_3)_2$. It is reasonable to expect that the differences in the lattice defectiveness of the catalysts as well as in their phase composition will affect their activity and selectivity in partial oxidation of C_4 hydrocarbons.

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