Chemical characteristics and crystallographic aspects of the vanadyl phosphate catalyst prepared in the medium of hydrochloric acid

M. BRUTOVSKÝ and †Š. GEREJ

Department of Physical and Analytical Chemistry, Faculty of Natural Sciences,
P. J. Šafárik University, CS-041 54 Košice

An active catalyst of partial oxidation of the C_4 fraction of hydrocarbons to maleic anhydride arises by forming and activating the precursor of the vanadyl phosphate catalyst, in our case vanadyl hydrogen phosphate. This catalyst crystallizes in the rhombic system, the volume of unit cell being by about 30 % smaller than that one of vanadyl hydrogen phosphate. From the chemical point of view, the known phase of vanadyl diphosphate, *i.e.* $(VO)_2P_2O_7$ is the basic component. The analysis of infrared spectra of the catalyst indicates the presence of a new phase, cyclic vanadyl tetraphosphate $(VO)_2P_4O_{12}$ as well. The method of formation and activation affects chemical and structural characteristics of the resulting stabilized V—P—O catalyst at equal composition expressed by the ratio $n(P):n(V)$.

В результате формирования и активирования прекурсора ванадие-во-фосфорного катализатора, в данном случае кислого фосфата вана-дила, образуется активный катализатор парциального окисления фракции C_4 углеводородов в малеиновый ангидрид. Этот катализатор кристаллизует в ромбической сингонии с объемом элементарной ячей-ки приблизительно на 30 % меньшим, чем у кислого фосфата ванади-ла. С химической точки зрения основным компонентом является из-вестная фаза дифосфата ванадила $(VO)_2P_2O_7$. Анализ ИК-спектров ката-лизатора свидетельствует также о присутствии новой фазы, цикличес-кого тетрафосфата ванадила $(VO)_2P_4O_{12}$. Способ формирования и ак-тивирования влияет на химические и структурные характеристики ко-нечного стабилизированного V—P—O катализатора при его постоян-ном составе, выражаемом соотношением $n(P):n(V)$.

The vanadyl phosphate catalysts have been given attention by professional public as prospective catalysts of partial oxidation of C_4 hydrocarbons including less reactive butane. Their use paves the way for elimination of expensive, scarce, and carcinogenic benzene from the production of maleic anhydride. The C_4 fraction of hydrocarbons, which is a by-product of petrochemical industry is an economically more profitable raw material for that purpose. Maleic anhydride is used for production of some plastics and chemicals [1].

The methods of preparation of the active vanadyl phosphate catalyst may be, according to our view, in principle divided into two groups: A — vanadium as the basic component of catalyst is already present in oxidation state IV in solution [2, 3]; B — vanadium is present in oxidation state V in the precursor and its reduction takes place in the solid phase at increased temperature [4, 5].

The chemical character of the phases originating in different ways of preparation and the structural characteristics of the V—P—O and V—P—O—M catalysts (M is a modifying cation bound in the catalyst) have not yet been elucidated in a satisfactory manner in literature [2, 6—10]. A lot of confusion and contradiction appears in the literature as pointed out in paper [6]. According to our view, this situation is due to the fact that the chemical composition and relative proportion of phases as well as the structural characteristics are dependent not only on the ratio $n(P):n(V)$ in catalyst but also on the method of synthesis and subsequent preparation of an active catalyst (formation and activation) [10, 11].

Experimental

In this study catalysts were prepared by a method belonging to group A, as characterized in the introduction. Dried vanadyl hydrogen phosphate $VOHPO_4 \cdot xH_2O \cdot yH_3PO_4$ was the starting precursor for preparation of the vanadyl phosphate catalyst [12]. The crushed precursor is processed at gradually increasing temperature (to 500 °C at most) either at first in an inert gas with succeeding activation in the working reaction mixture (1—1.4 vol. % of n-butane in air) or is immediately processed in the reaction mixture. In both cases, a vanadyl phosphate catalyst of greenish-grey or even brownish-black colour with stabilized properties arises after being formed and activated at least for 5 h. The ratio of components in the catalyst was $n(P):n(V) = 1.2$, while it was valid $n(M):n(V) = 0.14$ for the modified catalyst. Before analysis the catalyst was transferred into solution and the content of V(IV) and V(V) was determined by the method described in [2]. In our samples stabilized in reaction the content of V(IV) varied between 83 % and 87 %, while the content of V(V) was within the range 13 %—17 %. Phosphorus was determined gravimetrically in the form of $Mg_2P_2O_7$ and no loss of it was found for the activated catalyst.

The instruments used for obtaining X-ray diffractograms and infrared spectra of the samples as well as the experimental methods were the same as described in paper [12].

Results and discussion

The vanadyl phosphate catalyst prepared by the above-mentioned method is active in the partial oxidation of C_4 hydrocarbons to maleic anhydride [13, 14]. The degree of its activity depends on chemical character of the arising phases [7, 15] and structural characteristics [11].

The investigated catalyst predominantly consists of vanadyl diphosphate $(VO)_2P_2O_7$ which crystallizes in the rhombic system [4]. On the basis of the refined coefficients of the following equation appropriate for our samples

$$\sin^2 \Theta_{hkl} = 0.00993h^2 + 0.00645k^2 + 0.00216l^2 \qquad (1)$$

we calculated the lattice parameters and the volume of unit cell: $a = (7.74 \pm 0.02) \times 10^{-10}$ m, $b = (9.60 \pm 0.02) \times 10^{-10}$ m, $c = (16.59 \pm 0.02) \times \times 10^{-10}$ m, and $V = 1233 \times 10^{-30}$ m^3. It is obvious that the volume of unit cell decreased by about 30 % when compared with the precursor [12]. It results from this fact that the transformation of the precursor into active catalyst is accompanied by total reorganization of the lattice.

In accordance with eqn (1) the diffraction indices were assigned to individual lines on the diffractogram (Fig. 1). The X-ray diffractograms of the samples of catalysts differ from one another according to the method of preparation and the kind of formation and activation. As a matter of fact, the position of intensive lines (Fig. 1) remains preserved, but for instance the samples previously formed in nitrogen atmosphere exhibit the relative intensity of diffraction lines as much as from 1.3 to two times higher, while their width at half-height of diffraction maximum is smaller in comparison with the samples immediately processed by the reaction mixture. On diffractograms of the samples immediately formed and activated in the reaction mixture it may be observed that the
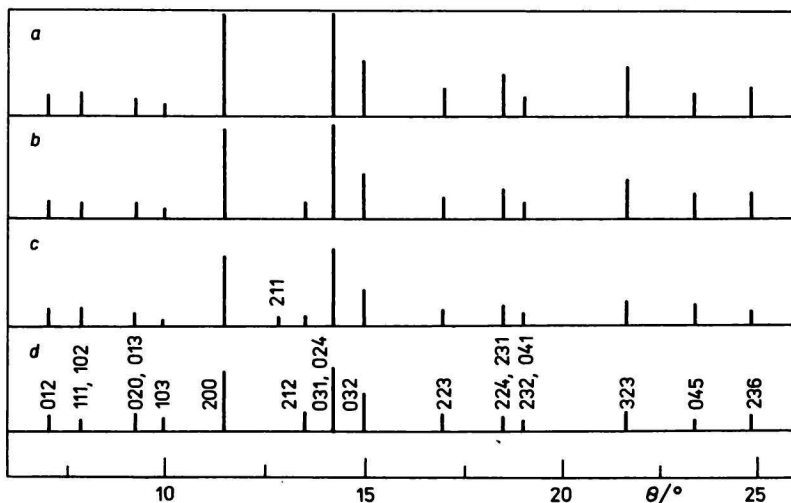

Fig. 1. X-Ray diffractograms of the formed and in reaction mixture activated vanadyl phosphate catalysts, $n(P):n(V) = 1.2$. *a)* and *b)* Formed in nitrogen; *c)* and *d)* processed by reaction mixture; *a)* and *c)* for V—P—O catalyst; *b)* and *d)* for V—P—O—Fe catalyst; $n(Fe):n(V) = 0.14$.

diffraction maxima give indication of splitting, while the number of poorly intensive diffraction lines increases (they are not registered in Fig. 1). Thus we may deduce that the samples processed in the reaction mixture are composed of smaller crystals, are more heterogeneous as regards the size of particles and exhibit a lower degree of order, *i.e.* a greater lattice disturbance. As to this interpretation, there are sometimes objections. But we must take into account that a powdered catalyst containing well developed crystals gives sharp diffraction maxima (narrow-shaped and intensive in relative comparison) whereas only the background is recorded if amorphous samples are used. As for the catalysts immediately processed by the reaction mixture, the observed signs of splitting of lines give evidence of an increased strain in lattice and support the presented interpretation of results.

These conclusions are not inconsistent with the appearance of infrared spectra (Fig. 2) which is in line with generalized interpretation of the change in intensity and shape of infrared spectra of powdered materials with varying size of crystals [16]. It may be seen that the spectrum of a catalyst formed in an inert gas and subsequently activated in the reaction mixture exhibits distinct absorption bands (Fig. 2, curves *1* and *2*) while the spectrum of a catalyst immediately formed and activated in the reaction mixture (Fig. 2, curves *3* and *4*) is less distinct and has broader absorption bands.
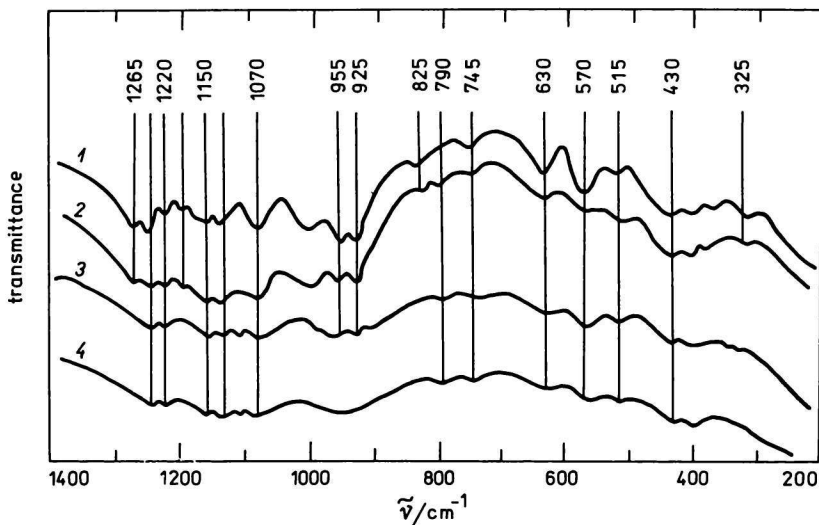

Fig. 2. Infrared spectra of the formed and in reaction mixture activated vanadyl phosphate catalysts, $n(P):n(V) = 1.2$. *1.* and *2.* Formed in nitrogen; *3.* and *4.* processed in reaction mixture; *1.* and *3.* for V—P—O catalyst; *2.* and *4.* for V—P—O—Fe catalyst; $n(Fe):n(V) = 0.14$.

An interesting difference in infrared spectra of the formed and activated catalysts (for $n(P):n(V) < 1.25$) consists in the fact that there are additional bands at $\tilde{v} = 1265 \, \text{cm}^{-1}$ and $\tilde{v} = 825 \, \text{cm}^{-1}$ besides the absorption bands corresponding to the basic phase $(VO)_2P_2O_7$ [8] in the spectrum of a catalyst formed at first in an inert gas (Fig. 2, curves 1 and 2). That evidences that another phase, vanadyl metaphosphate $VO(PO_3)_2$ starts to form because the mentioned absorption bands are characteristic of this compound [17]. A new phase, cyclic vanadyl tetraphosphate $(VO)_2P_4O_{12}$ mentioned in our paper [10] is also present in the investigated catalysts. The existence of this phase in multiphase catalyst is confirmed by synchronous presence of the absorption bands at $\tilde{v}/\text{cm}^{-1}$: 745, 790, 1220, and 1240. A more detailed analysis of bond vibrations in compounds with the cyclic anion $P_4O_{12}^{4-}$ is given in papers [18, 19]. If we take into consideration the data about the linear vanadium(V) tetraphosphate — $(VO)_2P_4O_{13}$ [20] the presence of it in a multiphase V—P—O catalyst must not be ruled out.

An active catalyst must contain a part of vanadium in oxidation state V [2, 6, 21], most likely in the form of $VOPO_4$ [6—8], but its presence in the form of $(VO)_2P_4O_{13}$ cannot be excluded. The presence of these phases in an overlapping infrared spectrum of the catalyst is hard to prove or disprove owing to the fact that the content of these phases is relatively small when compared with the content of the main phase — $(VO)_2P_2O_7$. The fact that the atoms of vanadium(IV) and vanadium(V), and maybe P(V) as well as the oxygen bonded to them participate in formation of the active centres for partial oxidation of C_4 hydrocarbons to maleic anhydride [2, 21, 22] and the presented data enable us to put forward the hypothesis that the dynamically changeable phases $(VO)_2P_4O_{12}$ and $(VO)_2P_4O_{13}$ on the active surface possibly take part in oxidation of C_4 hydrocarbons. It may be that just this dynamic transformation of the mentioned phases brings about the cyclization of one of the surface intermediates which is finally desorbed from the surface of catalyst as maleic anhydride.

After this reasoning, we may conclude in conformity with our experimental material that the kind of starting precursor (e.g. $VOHPO_4 \cdot xH_2O \cdot yH_3PO_4$ [12] or $VOPO_4 \cdot xH_2O \cdot yH_3PO_4$ [4]), the thermal regime of processing of the precursor of V—P—O catalyst, and the selection of gaseous atmosphere for formation and activation of the catalyst play an important role because they produce variations in phase composition and structural characteristics of the arising active vanadyl phosphate catalyst at its equal composition expressed by the ratio $n(P):n(V)$.

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