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Oxidation of O-Xylene on Potassium Vanadates

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Potassium vanadates, $K_2O \cdot 3V_2O_5$, $K_2O \cdot 4V_2O_5$, $K_2O \cdot 5V_2O_5$, and $K_2O \cdot 5V_2O_5 \cdot V_2O_4$, have been studied as catalysts for *o*-xylene oxidation in the temperature range 350–450°C. The product distribution with these catalysts is similar to that with vanadia catalysts with the exception of $K_2O \cdot 3V_2O_5$ which is the least active of all the vanadates. In an *o*-xylene–air mixture the vanadates decompose to Pourchard's ψ-phase (a nonstoichiometric compound of $3 \leqslant V/K \leqslant 4$ and V^{4+} content up to $\sim$10 at %) with production of V_6O_{13}. Under the same treatment in the reaction medium pure V_6O_{13} is oxidized into V_2O_5. Thus the presence of potassium vanadates stabilizes the lower vanadium oxide. The gas–solid phase equilibria in the studied systems are discussed. V_6O_{13} is considered to be the surface active phase of these catalysts, the ψ-phase playing the role of a "buffer" in providing a relatively large amount of V_6O_{13} and protecting it from oxidation to V_2O_5.

Potassium is known in the literature as a modifying agent added to catalysts based on vanadium pentoxide for oxidation of both inorganic (e.g., SO_2) and organic (naphthalene or *o*-xylene) compounds. However, the mechanism of its modifying action has not so far been explained. At a higher concentration of this addition, introduced most often in the form of sulfates, the formation of compounds of the vanadate type reported in Refs. (*1–4*) cannot be excluded. At lower concentrations of potassium the effect may consist in lowering the V=O bond strength (*5*), the latter factor determining the activity of the catalysts, or in affecting the acidity of the surface (*6*) and in this way influencing the selectivity of the oxidation of hydrocarbons. Studies on the properties of vanadia–titania catalysts with addition of $KHSO_4$ for oxidation of *o*-xylene to phthalic anhydride carried out by XPS and bulk chemical analysis have shown that during preparation of the catalysts the surface becomes enriched in potassium, whereas sulfur is almost completely lost from the sample at temperatures about 500°C (*7*). Moreover, visual observations of the processes of formation of V–Ti–K–S–O catalysts in the stages of mixing of the initial reagents ($KHSO_4$ and NH_4VO_3 in suspension) revealed changes of color which could be ascribed to formation of the compound of the formula $K_3H_4V_5O_{16}$. This last compound may undergo dehydration during the calcination and eventually may react with an excess of V_2O_5 forming potassium vanadates (*8*). In view of these results it seemed of interest to investigate the catalytic properties of various potassium vanadates in the oxidation of *o*-xylene bearing in mind the possibility of their being the surface active phases in the catalytic systems used in this reaction.

In this work several potassium vanadates of different V/K ratios and of different de-

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grees of reduction have been synthesized and their activity in *o*-xylene oxidation has been studied in the temperature range 350–450°C. For comparison a preparation containing TiO_2 and prepared in the manner ensuring formation of the potassium vanadate has been included in the investigations.

EXPERIMENTAL

Synthesis of the vanadates and their characteristics. Potassium vanadates $K_2O \cdot 3V_2O_5$ (KV–3), $K_2O \cdot 4V_2O_5$ (KV–4), and $K_2O \cdot 5V_2O_5$ (KV–5) were prepared by the solid state reaction between $KHCO_3$ and V_2O_5 which occurs on heating the mixtures of the reactants of the appropriate V/K ratio for 20 hr at 450°C (KV–3 and KV–4) or 480°C (KV–5). The X-ray diagrams of samples of KV–3 and KV–4 were consistent with the literature data (*9*, *10*) whereas that obtained for the KV–5 sample (see Table 1) was different from the data reported by Pourchard (*10*). Unlike the brown color reported previously (*10*), catalyst KV–5 had a black color. The vanadate $K_2O \cdot 5V_2O_5 \cdot V_2O_4$ (KV–6) (*11*) was obtained by the solid state reaction between KV–5 and V_2O_4 on heating in an evacuated quartz ampule for 20 hr at 480°C. Preparations KV–P and KV–PT were obtained by adding dropwise the solution of $KHSO_4$ to a solution of NH_4VO_3 at 90°C (KV–P) or to a suspension of TiO_2 (anatase) in NH_4VO_3 solution (KV–PT). The precipitate was mixed at this temperature, filtered, and washed with water until free of sulfate ions, then dried for 5 hr at 120°C and annealed at 480°C for 5 hr. An X-ray diagram of KV–P showed the presence of $K_2O \cdot 5V_2O_5$ (*10*) and some weak nonidentified diffraction lines. Preparation KV–PT containing 79 wt% TiO_2 showed the presence of the anatase modification of TiO_2 and some very weak diffraction lines of potassium vanadate.

TABLE 1

X-Ray Data for Potassium Vanadate of V/K Ratio of 5 KV–5

d(Å)	I[a]	d(Å)	I[a]
6.60	s	2.73	m
6.00	ms	2.61	vw
5.88	m	2.54	vw
3.40	vw	2.38	vw
3.23	m	2.01	m
3.17	s	1.97	w
2.81	s		

[a] s, strong; m, medium; w, weak; vw, very weak.

As shown below the potassium vanadates decompose in the reaction medium of *o*-xylene/air into V_6O_{13} and the reduced vanadate (the so-called phase ψ) described in detail by Pourchard (*10*). Phase ψ is a nonstoichiometric phase contained in a triangular diagram of K_2O–V_2O_5–V_2O_4 between the lines corresponding to the compositions:

$$K_2V_8O_{21-x} \text{ with } 0.05 < x < 0.33; \quad V^{4+} \text{ content: } 1.25\text{–}8.27 \text{ mole\%} \tag{1}$$

and

$$K_2V_6O_{16-x} \text{ with } 0.1 < x < 0.25; \quad V^{4+} \text{ content: } 3.33\text{–}8.34 \text{ mole\%}. \tag{2}$$

In view of this decomposition the studies also comprised pure oxide V_6O_{13} and the two preparations of phase ψ corresponding to the reduced forms of KV–3 and KV–4 and characterized by compositions with the value of x at its upper limit, $K_2V_6O_{15.75}$ (ψ–3) and $K_2V_8O_{20.67}$ (ψ–4). The preparations of these compounds were obtained by a solid state reaction in sealed evacuated quartz ampules between V_2O_5 and V_2O_4 for 10 hr at 500°C (V_6O_{13}), $3K_2O \cdot 5V_2O_5$, V_2O_5, and V_2O_4 (ψ–3), and KV–3, V_2O_5, and V_2O_4 (ψ–4), the latter two phases being synthesized at 550°C for 10 hr. All three preparations had X-Ray patterns in keeping with the literature data.

X-Ray diagrams of the samples under study were recorded on a Rigaku–Denki model DF–3 diffractometer, using CoKα radiation.

TABLE 2

Characteristics of Potassium Vanadates, Fresh and after Reaction in o-Xylene/Air Mixture[a]

Initial preparation						After reaction in o-xylene/air mixture[a]			
Symbol	V/K ratio	Color	Phase composition	V^{4+} content (mole%)	Sp. surface area (m^2/g)	Color	Phase composition	V^{4+} content (mole%)	Reaction time (hr)
KV–3	3	Brick red	$K_2O \cdot 3V_2O_5$	0	0.55	Black (a)	$K_2O \cdot 3V_2O_5(\psi)$[b]	5.9	7
						Red (b)	$K_2O \cdot 3V_2O_5$	0.9	
ψ–3	3	Brown–black	ψ	—	—	Olive–brown	ψ, $K_2O \cdot 3V_2O_5$	4.8	7
KV–4	4	Brown–black	$K_2O \cdot 4V_2O_5$	—	1.5	Dark green	$\psi(V_6O_{13})$	23.7	38
ψ–4	4	Brown–black	ψ	9.4	1.4	Olive–brown	$\psi(V_6O_{13})$ $(K_2O \cdot 3V_2O_5)$	21.8	10
KV–5	5	Red	See text and Table 1	0	0.6	Dark green	ψ, V_6O_{13}	23.0	16
KV–6	6	Black-green	$K_2O \cdot 5V_2O_5 \cdot V_2O_4(\psi)$	21.9	2.5	Black	ψ, V_6O_{13}	24.1	8
KV–P	5.57	Brown–green	$K_2O \cdot 5V_2O_5$	3.2	2.2	Dark green	ψ, $K_2O \cdot 4V_2O_5$	10.3	9
KV–PT	6.14	Beige	TiO_2	3.1	6.9	Light green	$TiO_2(\psi)$	11.2	22
V_6O_{13}		Black	V_6O_{13}	69.1	7.1	Black	$V_2O_5(V_6O_{13})$	10.8	12

[a] Conditions of the reaction: o-xylene concn, 43.5 g/m^3; flow rate, 30 liters/hr; catalyst volume, 4 ml; temperature, 330–450°C.

[b] The parentheses denote a phase with weak reflections in the X-ray diagram of the given sample.

The content of vanadium at oxidation states lower than 5+, and expressed as equivalent concentration of V^{4+}, was determined by a manganometric titration method.

The specific surface areas of the preparations were determined by the BET method from krypton adsorption isotherms at liquid nitrogen temperature.

The characteristics of all preparations synthesized are given in Table 2.

Catalytic activity measurements. The measurements were carried out in a flow reactor. Four milliliters of a sample (grain size 0.5–0.75 mm) diluted with glass of the same grain size (1:1) was used. The concentration of o-xylene in a stream of air was 43.5 g/m^3, and the flow rate of the reaction mixture was 30 liters/hr. The reaction mixture was analyzed by gas chromatography, both liquid and gaseous products being introduced into two gas chromatographs in series by means of six-way valves. The liquid and solid products were analyzed on a 2-m × 4-mm column filled with 10% silicone oil DC 550 on Chromosorb W HMDS programmed from 120 to 210°C at the rate of 24°C/min; the time of initial isothermal analysis at 120°C was 4 min and final isothermal analysis at 210°C was 7 min. The flow rate of the carrier gas (nitrogen) was 50 ml/min.

Analysis of CO and CO_2 was carried out on a 4-m × 4-mm column filled with silica gel supporting Octoil S (Carlo-Erba product) with temperature programming from room temperature to 120°C and a hydrogen carrier gas flow rate of 55 ml/min. Willy Giede GChF 18.3 chromatographs were used for the two types of analyses.

Before the measurements started the catalysts were heated in the reaction mixture at 350°C for 2 to 3 hr. The conversion and distribution of the products were examined at temperatures ranging from 350 to 450°C after attaining the stationary state at each temperature (usually after 30 to 60 min). Sometimes the catalytic experiments were repeated by screening the same temperature range down and up to check the reproducibility of the results. Then the catalysts were cooled down in the reaction mixture and their phase composition and V^{4+} content were again analyzed. The total reaction time is marked in Table 2.

RESULTS AND DISCUSSION

Results of the measurements of catalytic activity for the vanadates studied are given in Tables 3 and 4 in the form of conversion and selectivities at different reaction temperatures. As seen from the tables, the main product of partial oxidation of *o*-xylene on all samples with the exception of KV–3 and ψ–3 is phthalic anhydride. As side products tolualdehyde, maleic anhydride, and phthalide are observed in quantities not exceeding a few percent. In some cases also phthalaldehyde, quinone, and products of dealkylation (benzene, toluene) were registered in very small quantities (1–2%). The selectivities to phthalide decrease with increasing temperature, whereas those to maleic anhydride increase. In all cases the partial oxidation is accompanied by some total combustion to CO and CO_2. The selectivities to various products depend on the vanadate composition and the preparation method.

The vanadates of the smallest vanadium content KV-3 and its reduced form ψ–3 show the lowest activities among the studied vanadates with tolualdehyde as the predominant product.

The activities of the samples of KV–4, KV–5, and KV–6, richer in vanadium, are

TABLE 3

Activity of Potassium Vanadates in Oxidation of *o*-Xylene

Preparation (initial state)	Reaction temp. (°C)	Conversion *o*-xylene (%)	Selectivity, percentage to[a]				
			PA	TA	Ft	MA	CO_2 + CO
KV–3	380	4	1	40	Trace	—	32
	400	7	2	43	1	—	24
	420	9	22	37	5.5		32
ψ–3	390	20.0	16.5	26.5	2.5	—	52.5
	410	21.0	15.5	26.2	3.8	—	51.5
	430	24.0	13.7	32.1	6.2	—	45.8
	450	27.1	17.1	30.3	9.2	—	41.5
KV–4	370	60.2	66.1	9.5	3.6	2.8	18.3
	390	70.2	61.1	6.8	2.4	3.7	25.9
	410	78.4	54.6	5.0	2.0	4.8	31.1
	430	82.1	47.3	4.4	1.2	4.8	35.8
ψ–4	370	46.0	59.7	17.6	5.6	1.1	14.5
	390	65.2	57.0	12.4	3.3	2.1	23.8
	410	70.0	57.1	10.0	2.3	2.5	26.8
	430	74.1	58.7	8.7	2.1	4.0	26.0
KV–5	350	25.0	51.0	22.0	3.2	Trace	23.6
	390	45.0	52.0	10.0	2.0	1.0	34.6
	430	86.0	60.3	3.6	2.4	1.2	32.5
	450	91.8	57.1	3.5	2.2	1.1	35.9
KV–6	330	23.5	14.5	33.2	12.8	—	28.9
	340	26.5	22.3	29.6	13.5	—	30.0
	350	66.5	32.3	15.9	9.4	Trace	37.6
	360	99.0	45.6	1.4	0.3	2.0	49.4

[a] PA, phthalic anhydride; TA, tolualdehyde; Pt, phthalide; MA, maleic anhydride.

TABLE 4

Activity of Catalysts in the K–V–Ti–O System for Oxidation of *o*-Xylene

Initial preparation	Reaction temperature (°C)	Conversion *o*-xylene (%)	Selectivity, percentage to[a]				
			PA	TA	Ft	MA	$CO_2 + CO$
KV–P	350	38.0	28.1	32.6	12.8	Trace	22.1
	370	68.5	37.6	20.8	13.4	2.0	21.5
	390	92.4	54.0	7.8	7.1	2.5	21.0
	410	98.0	64.2	2.5	4.0	6.1	23.2
KV–PT	320	20	38.3	17.8	18.7	Trace	25.2
	350	97	76.7	0.8	3.0	1.0	17.4
	380	~100	72.0	Trace	1.0	2.5	24.2
V_6O_{13}	350	44.2	28.9	11.7	10.4	1.1	32.4
	370	62.7	45.4	6.7	9.0	3.1	32.8
	390	99.0	53.7	1.4	4.0	6.2	34.6
V_2O_5–TiO_2 industrial catalyst	355	39.3	56.2	8.9	11.5	Trace	23.3
	390	94.1	77.9	1.5	3.2	0.0	14.9

[a] PA, phthalic anhydride; TA, tolualdehyde; Ft, phthalide; MA, maleic anhydride.

considerably higher. The selectivities (at similar conversion values) to partial oxidation products and to CO_2 for the vanadates KV–4, ψ–4, and KV–5 are similar, which is understandable in view of the similar phase composition and similar degree of reduction of the samples after conditioning in the reaction medium (cf. Table 2) and further discussion concerning decomposition of potassium vanadates. Less understandable, in view of these facts, is the low activity to partial oxidation products and the high activity to CO_2 of the vanadate KV–6 next in the series, which at the same time is active already at low temperatures. Explanation of this fact requires further studies.

Preparation of the vanadate by the "wet" method (KV–P) yields a sample which shows lower selectivity to CO_2 as compared with the samples of similar V/K ratio obtained by solid state reaction. Deposition of the vanadate on TiO_2 as carrier considerably improves the selectivity to phthalic anhydride, giving a catalyst with parameters close to those observed for the active mass of the industrial catalysts (cf. Table 4). The preparation of pure vanadium oxide V_6O_{13}, oxidized in the reaction medium to a large extent to V_2O_5, shows selectivity values close to that of the sample richest in vanadium, namely, KV–6, being less selective to phthalic anhydride than the samples of KV–5 and KV–4.

Table 2 shows the change in the phase composition and V^{4+} content of the studied vanadates after the sequence of the catalytic experiments in *o*-xylene/air mixture in the temperature range 350 to 450°C. As seen from Table 2, potassium vanadates are not stable in the reaction medium, decomposing with reduction.

The sample of KV–3 after reaction was composed of two types of grains: red, containing unreacted vanadate KV–3, and black (turning green on grinding), containing phase ψ in addition to unreacted KV–3. On the other hand the sample ψ–3 has been partly reoxidized to KV–3 in the reaction mixture. Thus the solid state reaction proceeding in these two samples may be described by the equation:

$$K_2O\cdot 3V_2O_5 \rightleftharpoons K_2V_6O_{16-x} + \frac{x}{2}O_2(3.3\text{–}8.3\%\ V^{4+}) \quad (3)$$

The values given in the parentheses correspond to the values of V^{4+} content in mole% for lower and higher limit of x.

The samples of KV–4, ψ–4, KV–5, and KV–6 after catalytic reaction show the presence of phase ψ and V_6O_{13}. It may thus be concluded that phase ψ identified by the X-ray method must contain less vanadium than each of the fresh samples. The reaction of decomposition of potassium vanadates can therefore be described as follows:

$$K_2O\cdot 4V_2O_5 = K_2V_6O_{16-x} + \tfrac{1}{3}V_6O_{13} + \left(\frac{1}{3} + \frac{x}{2}\right)O_2(19.1\text{–}22.8\%\ V^{4+}) \quad (4)$$

$$K_2V_8O_{21-x} = K_2V_6O_{16-x} + \tfrac{1}{3}V_6O_{13} + \tfrac{1}{3}O_2(19.1\text{–}22.8\%\ V^{4+}) \quad (5)$$

$$K_2O\cdot 5V_2O_5 = K_2V_8O_{21-x} + \tfrac{1}{3}V_6O_{13} + \left(\frac{1}{3} + \frac{x}{2}\right)O_2(14.3\text{–}20\%\ V^{4+}) \quad (6a)$$

or

$$K_2O\cdot 5V_2O_5 = K_2V_6O_{16-x} + \tfrac{2}{3}V_6O_{13} + \left(\frac{2}{3} + \frac{x}{2}\right)O_2(28.7\text{–}31\%\ V^{4+}) \quad (6b)$$

$$K_2O\cdot 5V_2O_5\cdot V_2O_4 = K_2V_8O_{21-x} + \tfrac{2}{3}V_6O_{13} + \left(\frac{1}{6} + \frac{x}{2}\right)O_2(23\text{–}27.7\%\ V^{4+}) \quad (7a)$$

or

$$K_2O\cdot 5V_2O_5\cdot V_2O_4 = K_2V_6O_{16-x} + V_6O_{13} + \left(\frac{1}{2} + \frac{x}{2}\right)O_2(35\text{–}37.5\%\ V^{4+}) \quad (7b)$$

Comparing the above equations with the experimental values of V^{4+} concentration, one can conclude that after catalytic reactions all preparations contain V_6O_{13} and, with the exception of KV–6, phase ψ of composition close to that of ψ–3.

The reduction degree of the preparation obtained by the "wet" method, KV–P, and that deposited on TiO_2 (KV–PT) are lower than those of the vanadates of similar V/K ratio but prepared by the solid state reactions. In both cases the presence of phase ψ is confirmed by X-ray analysis. Taking into account the reduction mechanism of all other potassium vanadates and the fact that the V/K ratio in these two preparations exceeds the upper limit of composition of phase ψ, we may conclude that in these samples V_6O_{13} should also be present. Probably it is not detectable by X-ray analysis due to its small amount and poor crystallinity. It is noteworthy that in the presence of reduced potassium vanadates (phase ψ), V_6O_{13} is not oxidized to V_2O_5 whereas in similar reaction conditions pure V_6O_{13} undergoes almost complete oxidation. Thus the presence of potassium vanadates seems to stabilize the lower vanadium oxide. This fact may be explained as follows.

Let us consider two systems, each of them composed of two solid phases and the gas phase:

(a) the pure vanadium oxides system:

$$V_2O_5 + V_6O_{13} + pO_2 = (1 + 3p)V_2O_5 + (1 - p)V_6O_{13} \quad (8)$$

(b) the phase ψ-vanadium oxide system:

$$K_2V_6O_{16-x} + V_6O_{13} + \left(p \pm \frac{\Delta x}{2}\right) O_2 = K_2V_{6+6p}O_{16+15p-x\pm\Delta x} + (1 - p)V_6O_{13} \quad (9)$$

System (a) is univariant since nonstoichiometry of the V_2O_5 phase is negligibly small (*12*) and at constant temperature the equilibrium oxygen pressure is constant. When in conditions of the catalytic reaction oxygen pressure exceeds the equilibrium value, oxidation of V_6O_{13} to V_2O_5 should proceed unless some kinetic factors operate to hinder it. A different situation exists in the case of system (b). Phase ψ is a nonstoichiometric phase and may be considered as the solution of defects in the stoichiometric matrix. The system is thus at least bivariant, the equilibrium oxygen pressure being a function of the concentration of defects, dedescribed by parameters x and p in the formula of phase ψ. Increase of the oxygen pressure in the reaction mixture causes a change of the concentration of defects, resulting in an increase of the equilibrium pressure until it attains the external value. In such conditions V_6O_{13} may remain practically unchanged.

As shown in the present studies potassium vanadates decompose in *o*-xylene/air mixture to V_6O_{13} and the reduced phase of composition close to ψ–3. Direct catalytic test of the sample of phase ψ shows that it has a very low activity and selectivity in oxidation of *o*-xylene to phthalic anhydride. As therefore neither the initial unstable potassium vanadates nor the ψ-phase has been found to be the active component of this type of catalyst, it may be assumed that this role is played by the lower vanadium oxide V_6O_{13}. On the other hand, however, the ψ-phase acts, according to Eq. (9), as a "buffer" providing a relatively large amount of V_6O_{13} and protecting if from oxidation to V_2O_5. Thus the simultaneous presence of V_6O_{13} and the ψ-phase may account for improvement of the catalytic properties of vanadia catalysts by the presence of large amounts of potassium. It cannot be excluded that this factor may be helpful in elucidation of the role of K added in small quantities as a promoting agent, provided that the presence in this case of potassium vanadates on the surface is proved, the more so as the surface of such catalysts is enriched in K (*7*). Further studies are required to reveal the phase composition of vanadia catalysts with small addition of K.

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