EFFECT OF THE METHOD OF SYNTHESIS, FORMING, AND ACTIVATION ON THE CATALYTIC ACTIVITY OF VANADIUM–PHOSPHORUS CATALYSTS

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Methods where vanadium in the precursor is reduced to V^{4+} in solution are well suited to the synthesis of vanadium–phosphorus catalysts because the high temperatures (500 to 800 °C) required to transform the precursor to the active catalyst are thus avoided, which is desirable from the chemical as well as structuro-physical aspects. The way of forming and activating the catalyst, i.e. the temperature regime of the treatment and the kind of the gas atmosphere, were found to affect appreciably the catalyst activity in the partial oxidation of butane to maleic anhydride. Forming procedures resulting in sufficiently fine crystals and optimized lattice defects are suitable. The application of synthesis, forming and activation procedures exhibiting a low tendency to form, in the catalyst phase composition, condensed phosphates such as $VO(PO_3)_2$ or even $V(PO_3)_3$ is also beneficial to the catalytic activity. The catalytic properties of the vanadium–phosphorus catalyst which was prepared in concentrated HCl were improved considerably by doping the lattice with modifying metal cations.

Active and selective vanadium and phosphorus based catalysts are indispensable for an efficient process of partial oxidation of the C_4 hydrocarbon fraction, particularly of the rather low-reactive butane[1,2]. As a prerequisite for an efficient preparation of such catalysts, the effect of the chemical and physical (structural) factors on the activity and selectivity of the vanadium–phosphorus catalysts in the reaction of partial oxidation of butane to maleic anhydride must be known and optimized[3 – 5].

The activity of a vanadium–phosphorus catalyst is affected by the kind of the precursor formed during the synthesis[6,7] and by the way of its forming and activation[8,9]. Doping with modifying cations also results in changes in the catalyst phase composition and structure characteristics[8,9]. It is reasonable to expect that such changes in the chemical and structural nature will ultimately manifest themselves in the activity and selectivity of the unmodified as well as modified vanadium–phosphorus catalysts. This problem is the subject of the present work.

EXPERIMENTAL

Precursors and catalysts were prepared by two procedures: *A*: By dissolving V_2O_5 in boiling HCl under reflux and reacting it with the calculated amount of H_3PO_4 (ref.[7]), followed by the forming and activation of the precursor either first in an inert gas (nitrogen) and then in the reaction mixture of 1 – 1.4% (v/v) butane in air (procedure *A*-1), or directly in the reaction mixture[8] (procedure *A*-2).

B: By dissolving V_2O_5 in an excess of boiling H_3PO_4 and washing the excess H_3PO_4 off, followed by reduction of the dry product with SO_2 at temperatures up to 750 – 800 °C and activation[9] in the reaction mixture at temperatures up to 500 °C.

The chemical analysis procedure has been reported[9]. All chemicals were of reagent grade purity, gaseous SO_2 was pure.

The catalyst activity, expressed in terms of the starting reaction rate, was measured in an integral flow reactor comprising a quartz or glass tube 70 cm x 7 mm i.d. The central part of the tube was packed alternately with the catalyst and with crushed silica (for a better dissipation of heat). The upper part of the reactor accommodated a 15 – 20 cm layer of crushed silica for preheating the reaction mixture. The total catalyst volume was 4 cm^3, its grain size was 0.63 to 1 mm. The reactor was heated by means of a controllable resistance furnace of a special design ensuring a constant temperature along the entire catalyst bed[10]. It was verified that the catalytic activity data were not distorted by macrophysical factors (ref.[11]).

Analysis of the reaction products as well as of the starting reaction mixture was accomplished on two CHROM 4 chromatographs (Laboratorní přístroje, Praha), one equipped with a flame ionization detector and the other equipped with a katharometer. Butane, ethylene and CO_2 were quantitated based on the peak heights whereas maleic anhydride, CO, acrylic acid, acetic acid and acrolein were quantitated based on their peak areas (ref.[12]). The relative precision of measurement in the mass balance of the components was ± 2% to ± 4% (the lower precision concerns the low-content components). It should be noted that for the catalysts working in the steady regime, the amounts of acrylic and acetic acids, acrolein, and ethylene were negligible in the overall balance.

Butane, maleic anhydride and other flammable components were separated in a glass column 1.2 m long, packed with Porapak Q (0.146 – 0.175 mm grain size, or 80 – 100 mesh). The thermostat temperature was 190 °C, nitrogen flow rate was 0.66 $cm^3\ s^{-1}$. The first column of the chromatograph equipped with a katharometer was 2.5 m long, packed with Porapak R (0.175 – 0.246 mm grain size, or 60 – 80 mesh) and accommodated in a thermostat at 50 °C; CO_2 was separated in it from the remaining components. In the second column, which was packed with 5A molecular sieve 0.175 – 0.246 mm grain size, CO was separated from the remaining components. Hydrogen at a flow rate of 0.66 $cm^3\ s^{-1}$ served as the carrier gas. Samples were injected by means of six-way two-position valves through a capillary whose volume was precisely known (1.5 and 3 cm^3). The valves as well as all tube (stainless steel) joints were heated at 170 °C in a metal box to prevent any reaction product from condensing.

The specific surface area of the catalyst was determined chromatographically based on the thermal desorption of argon (about 13% (v/v) argon in a mixture with helium). The katharometer response (area drawn by the recorder) was calibrated by using Al_2O_3 and TiO_2 standards whose surface area had been determined by the BET method.

The catalytic reaction rate was calculated from the starting linear segments of the butane conversion curves (not farther than to 25%) and from the maleic anhydride yield in dependence on the time of contact according to the relation

$$r = K(1/\tau)(C_0/m\,s)X\,, \qquad (1)$$

where K is a factor converting the reaction mixture volume to normal conditions, C_0 is the starting concentration of butane, m is the catalyst weight in the reactor, s is the catalyst specific surface area, and X is the degree of butane conversion or the maleic anhydride yield expressed as the fraction with respect to total butane in the mixture. The productivity of maleic anhydride, which is a quantity important in practice, was calculated as

$$\pi_{MA} = K(v/V_k)C_0 Y M_{MA}, \qquad (2)$$

where K and C_0 are as above, v is the mixture flow rare, V_k is the catalyst volume, Y is the maleic anhydride yield (butane fraction converted to maleic anhydride) and M_{MA} is the maleic anhydride molar mass. The v/V_k ratio corresponds to the value of $1/\tau$.

RESULTS AND DISCUSSION

Two preparation procedures were used with the aim to assess the effect of the method of synthesis on the catalytic properties of the vanadium–phosphorus catalysts. In the one procedure (*A*), the precursor was vanadyl hydrogen phosphate[7], where vanadium occurs in oxidation state IV (refs[7,8]). In the other procedure (*B*), vanadium in the precursor was present in oxidation state V (refs[6,9]), and the reduction proceeded in the solid phase at high temperatures[9]. The widths, appearance and intensities of the diffraction lines as well as the IR spectra revealed[8,9] that in comparison with the catalysts prepared by procedure *B*, those prepared by procedure *A* consist of smaller crystals whose size is less uniform and structure order is less perfect, hence, their lattice defectiveness is higher. Although the catalysts prepared by procedure *B* also contain $(VO)_2P_2O_7$, β-$VOPO_4$ and $(VO)_2P_4O_{12}$, they exhibit a higher tendency to involve more condensed phosphates[9] such as α-$VO(PO_3)_2$ or even $V(PO_3)_3$. As has been demonstrated in ref.[13], phases of more condensed phosphates are less active in the reaction of partial oxidation of butane to maleic anhydride.

Thus, the above experimental findings indicate that the specific features of the synthesis methods affect the catalytic activity of stabilized vanadium–phosphorus contacts.

The rates of butane conversion (r_c) and the rates of maleic anhydride formation (r_{MA}) for the catalysts prepared by the two methods are compared in Table I. In method *A*, the effect of the forming and activation procedures (*A*-1 and *A*-2 – see Experimental) was also examined.

Although for unmodified catalysts the differences in activity are low, the sample prepared by method *B* exhibits a lower rate of formation of maleic anhydride and hence, a lower selectivity. Direct forming and activation in the reaction mixture (method *A*-2) appears more favourable with regard to the appreciably higher selectivity and reaction rate. For the modified catalysts, the effect of the methods of synthesis, forming and activation on the catalytic parameters is considerably higher. While method *A*-1 brought about a slight improvement of the catalytic parameters, method *A*-2 led to a considerable improvement; the specific surface area was considerably higher than that of the unmodified samples. The modified catalysts prepared by method *B* exhibited a sufficient activity for the conversion of butane but a low rate of formation of maleic anhydride and a low selectivity. They also possess low surface areas.

The catalytic activity as reported above can be accounted for in the following manner. Samples prepared by method *A* and differing in the way of forming and activation[8] exhibit different defectiveness of their lattices. The optimum lattice defectiveness for the given reaction is better approached by catalysts prepared by procedure[8] *A*-2. The results are consistent with the well-known fact that partial oxidation of butane is a structure-sensitive reaction[14]. Changes in the structure deviations and in the lattice defects are inferred based on analysis of the width and shape of the catalyst diffraction lines[8,9].

The differences in the activities of catalysts with different metal ions embedded in the lattices are, naturally, due to their different chemical nature, as corroborated by refs[4,15]. It is assumed that the different chemical nature of the metal ions can affect the important surface (as well as bulk) characteristics of the catalysts.

Catalyst samples prepared by method *B* exhibit larger crystals with fewer defects[9], but this on its own cannot fully account for the substantially poorer catalytic properties demonstrated in Table I. Apparently, the quality of the active centres changes to some extent, because the rate of butane conversion is high whereas the rate of formation of maleic anhydride is low, which implies a very low selectivity. We assume that during the high-temperature treatment, the microadditions brought about formation of microcrystals or even of an amorphous layer of their oxides. Furthermore, it is characteristic of method *B* that a higher tendency appears to form more condensed phosphates

TABLE I

Effect of the method of synthesis, forming and activation of vanadium–phosphorus catalysts ($n(P) : n(V) = 1.2$) on their activity and selectivity in the reaction of partial oxidation of butane to maleic anhydride

Modifier $n(M) : n(V) = 0.14 - 0.18$	Method[a]	s [b]	$r_c \cdot 10^8$ [c]	$r_{MA} \cdot 10^8$ [c]	Selectivity, %
None	*A*-1	2.4	13.0	6.0	46
	A-2	2.4	12.0	6.8	57
	B	2.3	12.0	4.8	40
Cu	*A*-1	5.1	12.0	6.0	50
	A-2	4.8	18.8	11.5	61
	B	1.1	15.5	3.1	20
Fe	*A*-1	5.3	13.0	6.7	52
	A-2	5.8	20.0	12.2	61
	B	2.0	15.2	3.5	23

[a] Synthesis and forming method; [b] specific surface area in $m^2\ g^{-1}$; [c] in $mol\ s^{-1}\ m^{-2}$.

having a phase composition such as $VO(PO_3)_2$ or even $V(PO_3)_3$ (ref.[9]). These phases are catalytically less active in the reaction under study.

Similar conclusions were derived from the practically important catalytic parameters given in Table II. Modified catalysts prepared by method *A* and formed and activated directly in the mixture (procedure *A*-2) are more suitable, bringing about a higher reaction rate and the highest selectivity of all the catalysts examined. With respect to the important parameter of productivity of maleic anhydride, the higher specific surface area of the catalysts is also beneficial.

In conclusion, the results of this study in conjunction with the previous work[7 – 9] give evidence that active and selective unmodified as well as modified vanadium–phosphorus catalyst can be better prepared by methods where vanadium is converted to V^{4+} in the solution, because the high temperatures of vanadium reduction are thus avoided.

TABLE II
Effect of the method of synthesis, forming and activation of vanadium–phosphorus catalysts ($n(P) : n(V) = 1.2$) on the maleic anhydride yield X (mole %) and productivity π_{MA} (g h^{-1} dm^{-3})

Modifier $n(M):n(V)$ = = 0.14 – 0.18	Method[a]	Degree of conversion, mole %	X	π_{MA}
None	*A*-1	75	31.5	10.5
		90	30.1	6.4
	A-2	75	35.5	11.1
		90	34.0	6.7
	B	75	30.4	15.3
		90	28.3	11.2
Cu	*A*-1	75	45.5	53.3
		90	51.0	41.6
	A-2	75	46.1	75.1
		90	55.1	57.4
	B	75	12.8	8.3
		90	9.0	3.5
Fe	*A*-1	75	45.6	58.8
		90	51.2	44.6
	A-2	75	47.2	98.3
		90	55.5	69.4
	B	75	13.4	10.9
		90	9.8	4.5

[a] Synthesis and forming method.

Introduction of modifying cations into the vanadium–phosphorus catalyst matrix (method *A*) largely brings about improvement of the catalytic parameters[4]. With respect to the reaction examined, the application of conditions for the preparation of the catalysts and for their forming and activation such as give rise to fine crystalline and samples with adequate defects is convenient. It is, however, noteworthy that samples with very fine crystals or amorphous samples, with a high lattice defectiveness, exhibit a low selectivity at a sufficiently high rate of butane conversion (unpublished results). Convenient are such methods of synthesis and treatment of vanadium–phosphorus catalysts as do not result in condensed phosphates of the $VO(PO_3)_2$ and $V(PO_3)_3$ type which are low active in the reaction in question.

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