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The Vapor-Phase Preparation of V-P-O Catalysts Effective for Butane Oxidation to Maleic Anhydride

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Synopsis. Almost pure α-$VOPO_4 \cdot 2H_2O$ powder was obtained by a vapor-phase reaction between $POCl_3$, $VOCl_3$, and water at about 763K in the presence of oxygen. Although α-$VOPO_4 \cdot 2H_2O$ changed into α- and β-$VOPO_4$ in the calcination in N_2, it was transformed into $(VO)_2P_2O_7$ and a small amount of β-$VOPO_4$ by in situ activation at 733 K at the heating rate of 10 K min^{-1} in a C_4H_{10}-O_2-N_2 stream, the resulting catalysts effected the selective oxidation of butane to maleic anhydride comparable to pure $(VO)_2P_2O_7$.

The production of maleic anhydride (MA) has been achieved practically by the oxidation of benzene and butenes (1-butene, *cis*-2-butene, *trans*-2-butene), MA production by the oxidation of butane has, however, been magnified since it has distinct economical merit.

V-P-O catalysts have been claimed to be effective for the oxidation of butane[1] and there are many studies on the catalysis of the V-P-O system from the viewpoint of the active phases for the reaction,[2] the role of a small excess of phosphorus in catalysts,[3,4] the differences in composition between bulk and surface,[5] the reaction path[6] and so on.

There also are much patent literature concerning the preparation method of the selective catalysts.[7] The preparation methods published so far can be classified into two large categories. One is the method using V_2O_5 as a starting material and the other is the method using organic or inorganic vanadium compounds. Each category can be further subdivided into many groups in terms of the reducing agents. Common to all is the use of a liquid reaction medium.

In this paper, the authors deal with a new vapor-phase preparation of V-P-O catalysts effective for MA synthesis from butane using vanadium chloride oxide and phosphoryl chloride as the starting materials.

First, the reaction conditions suitable for the preparation of powders containing V and P were explored extensively. The following conclusions were abstracted from the experiments.

(1) N_2 is suitable for the carrier gas of both $VOCl_3$ and $POCl_3$ vapor.

(2) $VOCl_3$ and $POCl_3$ should be mixed in a vapor phase at the place just before the entrance of a reactor.

(3) O_2 is favorable for the carrier gas of water vapor.

(4) The collector of the powders formed should be kept at about 420 K to prevent the condensation of the hydrochloric and phosphorus containing acids formed.

An improved apparatus for the catalyst preparation is shown in Fig. 1. The length of the reactor used here was about 15 cm which was sufficient to form oxide powders. The optimum flow rates of the introducing gases were dependent on the length and diameter of the reactor. The adoption of 1±0.2 as the flow rate ratio, $F_{(O_2+H_2O)}/F_{(N_2)}$, and 9—10 as the linear velocity ratio, $L_{(O_2+H_2O)}/L_{(N_2)}$, maintained the powder formation for at least 17 h.

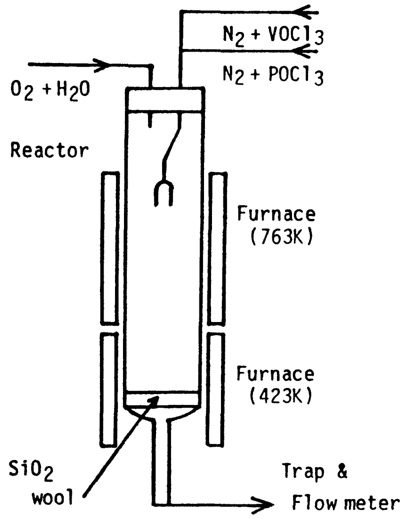

Fig. 1. Schematic diagram of the apparatus for powder preparation.

All of the vanadium atoms fed is seemed to be incorporated into the powders since no vanadium oxide was recovered from the effluent gas, however, phosphorus compounds were partly passed through the reactor and were recovered in a trap with a NaOH aqueous solution in most of the experiments. 0.06—0.15 g of the powders were formed per hour in each experiment.

The powders formed in this manner were subjected to XRD measurement and the results are summarized in Table 1. The mixture of α-$VOPO_4$ and V_2O_5 was obtained when the $POCl_3/VOCl_3$ ratio of the reactant gas was lower than unity (Run 1), on the contrary, a large $POCl_3/VOCl_3$ ratio gave the peaks assigned to $(VO)_2P_2O_7$, though the intensities were small. It is of interest that $(VO)_2P_2O_7$ with V(IV) ions was formed when an excess amount of $POCl_3$ was supplied.

The adoption of an intermediate $POCl_3/VOCl_3$ ratio brought about the formation of almost pure α-$VOPO_4 \cdot 2H_2O$ (ASTM Card 27-949) and the reproducibility of the experiments was fairly good (Runs 10—15). The P/V ratios of some of the powders obtained were examined by EPMA and these results are also shown in Table 1. The P/V ratio of the powder formed in Run 1 was 0.34 which is very close to the 0.33 of the $POCl_3/VOCl_3$ ratio of the feed gas. This suggests that all the $POCl_3$ in the feed gas was incorporated into the powder formed.

The ratios of the powders formed in Runs 13 and 15, however, were 1.09 and 1.02 which were coincided the chemical formula of α-$VOPO_4 \cdot 2H_2O$ and the ratio of the former powder was unaltered after having been used for the oxidation of butane for 27 h. It can be inferred from these results that the 2.0—2.5 fold excess of $POCl_3$ to $VOCl_3$ is sufficient to form vanadium phosphate powder with a P/V ratio just exceeding unity. The powders formed in Runs 2, 3, and 6 contained a $(VO)_2P_2O_7$ phase in which vanadium atoms were reduced to V(IV) from the original V(V) of $VOCl_3$. According to Bordes and Courtine,[8] the reduction of α- and β-$VOPO_4$ begins at 920 K even in a N_2 stream. So that it is believed to be difficult for the reduction of V(V) of the powders to take place in the furnace kept at 763K. The Cl/V ratio of some catalysts were also determined by EPMA and were listed in Table 1. The powders formed in Runs 1 and 13 contained a small amount of chlorine, which was the extent of ca. 0.2% of the vanadium atoms but no chlorine was detected from the powder formed in Run 15. Although the chlorine content of the powders of Runs 2, 3, and 6 are not known, it can be inferred that the HCl formed by the hydrolysis of chloride oxides may play a role in the reduction.

The effects of the temperature and the surrounding gas in calcination on the phase of the α-$VOPO_4 \cdot 2H_2O$ were studied in order to obtain the optimum conditions of pretreatment suitable for the preparation of selective butane oxidation catalysts.

The portions of the powder formed in Run 13 were heated to 773 K at the different heating rates such as 2 K min^{-1} and 10 K min^{-1} in a N_2 or C_4H_{10}-O_2-N_2 (1.5, 9.0, and 89.5 vol% respectively) stream, and kept at 773 K for 2 h, and then steeply cooled down to the ambient temperature. The samples calcined in the N_2 stream were changed into α-$VOPO_4$ and β-$VOPO_4$ despite the heating rates in agreement with the results reported by Bordes and Courtine.[8]

The samples calcined in the C_4H_{10}-O_2-N_2 stream gave features different from those in N_2 stream. The XRD spectrum of the sample heated by 10 K min^{-1} consisted of sharp peaks of $(VO)_2P_2O_7$ in addition to weak peaks of β-$VOPO_4$, on the other hand the spectrum obtained at 2 K min^{-1} was mainly composed of β-$VOPO_4$ and α-$VOPO_4$. It can be concluded from these results that in situ pretreatment in the reactant gas mixture of butane oxidation and higher heating rates are favorable to obtain $(VO)_2P_2O_7$ which has been claimed to be the active phase for MA formation.

The results of the butane oxidation over several catalysts prepared by the method mentioned above are shown in Table 2 together with the results over $(VO)_2P_2O_7$ which was prepared from V_2O_5, $NH_2OH \cdot HCl$, and H_3PO_4 by the method described in the literature[2] and over pure V_2O_5 prepared by the thermal decomposition of ammonium metavanadate at 823 K.

Butane was mainly oxidized to carbon oxides over the pure V_2O_5 catalyst and MA was formed with only 13.5% selectivity under the reaction conditions. The MA selectivity reached 58.3% over the $(VO)_2P_2O_7$ catalyst. Although Catalyst 3 showed a considerably high activity, the distribution of products was much similar to that of pure V_2O_5. As shown in Table 1, Catalyst 3 was composed of an amorphous phase and a small amount of $(VO)_2P_2O_7$. The XRD spectrum from Catalyst 3 after the reaction was almost the same as that before pretreatment.

Catalysts 10 and 13, both derived from α-

Table 1. Preeparation of V-P-O Powders

Run	Reation time/h	Feed rate				$POCl_3/VOCl_3$	Prowders		
		$POCl_3$[a]	N_2[b]	$VOCl_3$[a]	N_2[b]		P/V	Cl/V	Phase[c]
1	50	0.6	29.7	1.83	27.8	0.33	0.34	0.0019	V_2O_5+[α-$VOPO_4$]
2	8	—	36.7	—	17.6	—	—		Amorphous+[$(VO)_2P_2O_7$]
3	8	—	56.0	—	23.8	—	2.32[d]		Amorphous+[$(VO)_2P_2O_7$]
6	17	3.10	35.3	1.96	30.3	1.58	0.50[d]		$(VO)_2P_2O_7$+β-$VOPO_4$
10	17	3.61	39.3	1.38	30.9	2.62	1.18	0	α-$VOPO_4 \cdot 2H_2O$
11	17	3.13	36.6	1.28	32.8	2.45	0.82[d]		α-$VOPO_4 \cdot 2H_2O$
13	17	3.35	37.7	1.42	33.2	2.36	1.09	0.0018	α-$VOPO_4 \cdot 2H_2O$
14	17	—	39.9	—	34.9	—	—		α-$VOPO_4 \cdot 2H_2O$
15	17	5.83	36.9	2.98	33.1	1.96	1.02	0	α-$VOPO_4 \cdot 2H_2O$

a) mmol·h^{-1}. b) cm^3·min^{-1}. c) [ ] means minority. d) Chemical analysis.

Table 2. Oxidation of n-C_4H_{10} over P-V-O Catalysts

Catalyst	$(VO)_2P_2O_7$		V_2O_5	Cat. 3	Cat. 6	Cat. 10	Cat. 13		
Reaction time/h	3	76	27	27	27	27	3	6	27
Conv/%	16.0	15.6	39.8	54.0	18.3	20.6	13.3	13.4	15.3
MA[a]	60.9	58.3	13.5	12.4	52.5	50.0	47.2	47.6	52.9
CH_3COOH	—	—	0.14	0.27	0.94	0.75	—	—	—
$CH_2CHCOOH$	—	—	0.04	0.90	0.38	0.21	—	—	—
CO	33.1	32.9	59.6	54.2	8.82	32.8	36.8	36.5	33.5
CO_2	5.9	8.9	26.3	32.1	36.6	16.3	16.0	15.9	13.6
Others[b]	—	—	0.44	0.06	0.76	—	—	—	—

a) Maleic anhydride. b) C_1—C_3 Alkane, reaction temperature: 733 K, W/F: 0.46 g·s·cm^{-3}, feed gas composition: 1.5 vol% n-C_4H_{10}, 9.0 vol% O_2, 89.5 vol% N_2.

$VOPO_4 \cdot 2H_2O$ showed selectivities as high as that of the $(VO)_2P_2O_7$ catalyst. It can be seen from Table 2 that the activity and selectivity of Catalyst 13 improved with the reaction time. The XRD spectra from Catalysts 10 and 13 after the reaction were composed of many small broad peaks and a half of these peaks could be assigned to those of $(VO)_2P_2O_7$ and α-$VOPO_4$ but the rest could not be assigned. Observations of high base line position and the small broad peaks in all spectra suggested that the catalysts obtained by the gas phase reaction have an abundance of an amorphous solid or a very small crystalline. Since Catalyst 10 overcame the $(VO)_2P_2O_7$ catalyst in the conversion of butane, Catalyst 10 was superior to the $(VO)_2P_2O_7$ catalyst in MA yield.

It is concluded from these results that the vapor phase preparation of α-$VOPO_4 \cdot 2H_2O$ powder is one of the better methods of obtaining precursor of the selective catalysts.

Experimental

The $VOCl_3$ (Wako Pure Chem. 99+%) and $POCl_3$ (Wako Pure Chem., Special Grade) were used for powder preparation without further purification. The determination of the composition of the samples was carried out by means of either of a TN 5500 EPMA system or chemical analysis in conformity with a reference.[9] Reference files of the EPMA system were prepared using K lines from V, GaP, and KCl standards at 25 kV and were checked by analyzing mixtures of V_2O_5 and ammonium dihydrogen phosphate. Catalytic oxidation of butane was carried out using an ordinary flow type reaction system with fixed catalyst bed. The catalysts were in situ pretreated in the stream of a reaction gas mixture at a temperature which was regulated to raise to 773 K at the rate of 10 $K\,min^{-1}$ and then hold at 773 K for 2 h. The MA formed was collected for ca. 1 h after which the concentration of its aqueous solution was analyzed by means of GC (Thermon 1000 column, 423 K) or by titration with a NaOH aqueous solution.

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