Development of Fluidized-Bed Catalyst for Partial Oxidation of *n*-Butane

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Optimization experiments were carried out for preparation of a catalyst precursor. Results show that the acid concentration and reaction temperature in precursor preparation exhibit strong effects on the catalyst behavior. For the catalysts prepared at higher concentrations of acid, the quantity of the V^{4+} phase $(VO)_2P_2O_7$ is large, and the n-butane conversions are all quite high. When decreasing the acid concentration in precursor preparation, the relative amount of the V^{5+} phase δ-$VOPO_4$ and the n-butane conversion increase continuously; at the same time, the selectivity to maleic anhydride increases at the beginning, and then decreases after reaching a maximum value. The catalyst prepared at an acid concentration of 102.3% gave a maximum yield of maleic anhydride of 48.10% at an inlet n-butane concentration of 4.0% and a space velocity of 500 h^{-1}. The fine particle catalyst in this study offers great flexibility of operation.

Introduction

VPO based catalysts are known to be efficient in selective oxidation of *n*-butane to maleic anhydride (MA) (Centi et al., 1988) and are employed industrially for this reaction in processes developed by several companies (Cavani and Trifiro, 1995). The selective oxidation of C_4 fractions has been reviewed by Hodnett (1985) and Centi et al. (1988). Certain factors affect the selectivity toward MA such as the method of preparation of VPO catalyst, phosphorus/vanadium (P/V) atomic ratio of the catalyst, temperature, and atmosphere of calcination of the catalyst.

The nature of the phases present in the catalyst strongly affects the catalyst behavior in *n*-butane oxidation, and this effect has been studied by several authors. The contemporaneous presence of oxidized $V^{V}PO$ and reduced $V^{IV}PO$ phases are cited as a necessary condition to have an active and selective catalyst (Busca et al., 1986; Harrouch Batis et al., 1991; Zhang-Lin et al., 1994). The $V^{V}PO$ and $V^{IV}PO$ phases exhibit structural similarities that allow, under reaction conditions, easy redox cycles between different oxidation states of vanadium (Ben Abdelouahab et al., 1992; Bordes, 1993).

Although there are many publications on the topic of chemistry of VPO catalysts, there is very little information regarding the optimization of the variables together to obtain the maximum yield of MA. The purpose of the present study is to investigate experimentally the technology of catalyst preparation, and then to develop a fluidized-bed catalyst having a higher yield of MA under industrial conditions of approximately 4% *n*-butane concentration.

Experimental Studies

Catalyst preparation

The V_2O_5 (0.048 kg) was suspended in a definite volume of *n*-butanol and was heated to 60°C while stirring. A proper amount of *o*-H_3PO_4 at a predetermined concentration was then added ($P/V = 1.2$). At a concentration above 85%, the *o*-H_3PO_4 was made of *o*-H_3PO_4 at a concentration of 85% and P_2O_5. The mixture was heated and refluxed with constant stirring at a predetermined temperature for 7–11 h. After being cooled to 60°C, the slurry was filtered and then dried at 120°C for 12 h. Thus, the catalyst precursor was obtained.

The precursor (0.070 kg) and a proper amount of silica (Si/V atomic radio = 0.1) were suspended in 0.280 dm^3 of H_2O. The suspension was heated and refluxed for 12 h under constant stirring, and then spray dried. The resulting material was calcined in N_2 at 693 K for 4 h. The brown fluidized-bed catalyst was provided for testing.

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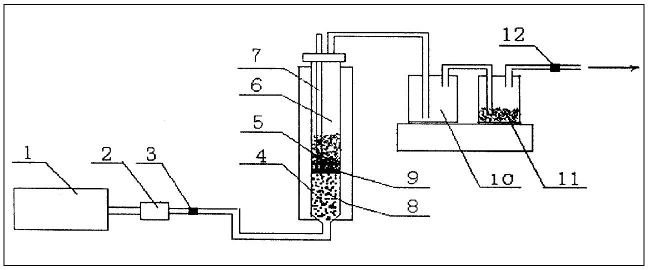

Figure 1. Catalyst test equipment.

(1) feedstock gas mixer; (2) mass flowmeter of inlet gases; (3) sampling point of feedstock gases; (4) feedstock gas preheater; (5) catalyst; (6) fluidized-bed reactor; (7) thermocouple; (8) sintering glass; (9) electrothermal mantle of reactor; (10) maleic anhydride gatherer; (11) sweep gas scrubber; (12) sampling point of sweep gases.

Catalyst test

The catalyst performance and fluidization properties were tested in a laboratory-scale fluidized bed with a diameter of 0.025 m and a reactor length of 0.600 m (Figure 1). The reactor was built with hard glass, and the gas distributor consisted of sintering glass. Heating tape and high-temperature insulation material were used in such a way that it was possible to observe the fluidization behavior. A thermocouple for the indication and control of axial temperature was inserted in a longitudinal tube ($\phi 3$ mm).

The feedstock and noncondensable effluent gases were analyzed by an on-line gas chromatograph system. The condensable products were analyzed by volumetric titration. The catalytic test conditions were as follows: reaction temperature: 410°C–430°C: space velocity: 500 h^{-1}–550 h^{-1}; feedstock: 4.0% (vol.) butane in air.

Characterization of the catalyst

The average oxidation state of vanadium (AV) was determined by a redox procedure as reported by Nakamura et al. (1974).

The specific surface area was measured by low-temperature nitrogen adsorption according to the BET method. The particle-size distribution of the catalyst was measured by the screen analysis.

The fluidized-bed catalyst was tested for 12 h; then, XRD powder patterns were recorded with a Rigaku D/max-B diffractometer using Cu K_a radiation.

Results and Discussion

Optimization of catalyst preparation

Optimal reaction time, reaction temperature, suitable solvent/solute (vol./wt.) ratio, and the concentration of orthophosphoric acid added during preparation of the catalyst precursor were investigated using the orthogonal statistical experiment method (Liu, 1997). The factors and their levels in preparation of the catalyst precursor are shown in Table 1.

This study has been carried out to determine the effects of different factors in precursor preparation on the behavior of the catalyst. The responses are conversion C of n-butane, selectivity S to MA, and yield Y of MA. Results of the orthogonal statistical experiments are listed in Table 2. Results of extreme difference (D_e) analysis for the catalyst evaluation are listed in Table 3.

The results of extreme difference analysis have led to the conclusion that acid concentration and reaction temperature exhibit strong effects on all three evaluation targets of conversion of n-butane, selectivity to MA, and yield of MA. It exhibits the strongest effects on the evaluation targets, especially for the acid concentration. The factors of reaction time and solvent/solute ratio are the two weak ones influencing the behavior of the catalysts.

The acid concentration in precursor preparation is the most important factor influencing the evaluation targets; at the same time, its optimum value changes with temperature. Therefore, the effects of reaction temperature should be studied further. However, the optimum temperature of 110°C

Table 1. Factors in Preparing for the Catalyst Precursor

	Factor			
Level	Reacting Temp. (°C)	Reacting Time (h)	Solvent/Solute Ratio (dm^3/kg)	Conc. of Acid (%)
I	90	7	8.75	103.9
II	100	9	10	104.1
III	110	11	11	104.3

Table 2. Orthogonal Experiment Table $L_9(3^4)$

	Rank No.				Targets for Catalyst Evaluation		
	Reaction Temp. (°)	Reaction Time (h)	Solvent/Solute Ratio (dm^3/kg)	Acid Conc. (%)	C (%)	Y (%)	S (%)
No. of Catal.	1	2	3	4			
1-1	90(I)	7(I)	8.75:1(I)	103.9(I)	52.92	23.08	43.61
1-2	90(I)	9(II)	10:1(II)	104.1(II)	59.49	31.22	52.28
1-3	90(I)	11(III)	11:1(III)	104.3(III)	49.65	20.73	41.73
1-4	100(II)	7(I)	10:1(II)	104.3(III)	50.92	22.41	44.05
1-5	100(II)	9(II)	11:1(III)	103.9(I)	58.21	26.75	45.95
1-6	100(II)	11(III)	8.75:1(I)	104.1(II)	61.88	33.92	54.82
1-7	110(III)	7(I)	11:1(III)	104.1(II)	63.18	36.87	58.36
1-8	110(III)	9(II)	8.75:1(I)	104.3(III)	56.93	25.47	44.74
1-9	110(III)	11(III)	10:1(II)	103.9(I)	62.13	29.01	46.69

is the highest level of this factor in orthogonal experiments. The experiment of precursor preparation should be performed at a higher temperature. The normal boiling point of the reaction solution in preparation is 110°C, so the experiment should be carried out in an elevated pressure reactor. The solvent/solute ratio and the reaction time exhibit a small effect on the yield of MA, but the solvent recovery and economic benefit should be taken into account. Thus, the solvent/solute ratio and reaction time are determined to be 10 and 9 h, respectively.

Experiments of precursor preparation had been performed at different acid concentrations at 110°C and at two elevated temperatures, 125°C and 140°C. The temperature of 125°C was determined to be the optimum one by taking the yield of MA as the evaluation target.

Reaction experiments of precursor preparation at 125°C had been carried out at a pressure of 0.21 MPa to explore the effects of acid concentration on the catalyst behavior. Under the above technological conditions, six catalysts were prepared.

Phase compositions of the precursor and catalyst

Figure 2 shows the X-ray diffraction (XRD) patterns of prepared precursor and catalyst. The positions are the same for the XRD lines for the catalysts prepared at different acid concentrations, with the only difference being between the peak heights. Therefore, the ones shown in Figure 2 are only the XRD patterns of precursor and catalyst, where the average valence state of vanadium is 4.011.

The precursor was found to possess XRD lines at 15.57°, 19.67°, 24.27°, 27.12°, 28.75°, 30.46°, 32.07°, and 33.71°(2θ). These lines were assigned by Guliants et al. (1996) to the vanadyl hydrogen phosphate hemihydrate $VOHPO_4 \cdot 0.5H_2O$. Therefore, the precursor of the catalyst prepared in this study is mainly constituted of $VOHPO_4 \cdot 0.5H_2O$.

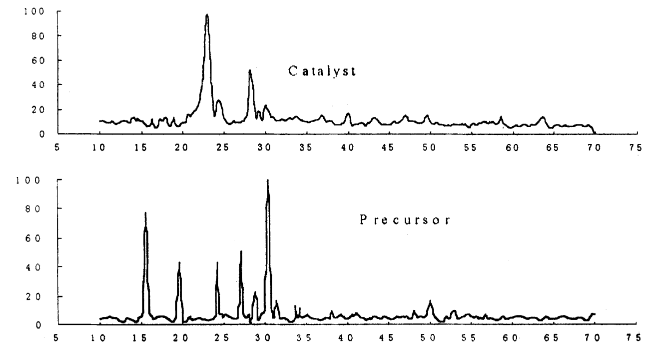

Figure 2. XRD patterns of the precursor and catalyst.

XRD spectra of pure $(VO)_2P_2O_7$ and of the different $VOPO_4$ phases were reported by Ben Abdelouahab et al. (1992). It shows that the XRD lines of the V^{4+} phase $(VO)_2P_2O_7$ and the V^{5+} phase δ-$VOPO_4$ are mainly at 23.005° and 22.080°, 28.550° (2θ), respectively. According to the analysis of XRD patterns, the catalysts prepared may be characterized by the reflections at 23.0°, 24.3°, 28.2°, and 30.0° (2θ). The peak of $(VO)_2P_2O_7$ at 23.0° was the strongest and the peak of δ-$VOPO_4$ at 28.2° was the next strongest. The phases indicated by the two small peaks were possibly other ones of VPO (Z-1, Z-2).

The relative peak heights of the characteristic peaks of the above four phases for the catalysts 2-1–2-6, along with the average valence state (AV) of vanadium in them and the relative peak height ratio of δ-$VOPO_4$ to $(VO)_2P_2O_7$ are given in Table 4.

It can be seen that the phases of the catalysts prepared are mainly constituted of the V^{+4} phase $(VO)_2P_2O_7$ and secondly of the V^{+5} phase δ-$VOPO_4$ from their relative peak heights. The average valence state of vanadium in the two catalysts among six catalysts is less than 4, and the highest average valence state of vanadium in the catalysts is only 4.224. At the same time, the amount of the V^{+5} phase is quite large according to its peak height. Therefore, a definite quantity of the V^{+3} phase must exist in the catalysts.

Table 3. Extreme Difference Analysis for the Catalyst Evaluation

	Reaction Temperature (°C)				Reaction Time (h)			
	I	II	III	D_e	I	II	III	D_e
Y (%)	25.01	28.03	30.45	5.44	27.68	27.81	28.55	0.87
C (%)	54.02	57.00	60.75	6.73	55.67	58.21	57.89	2.54
S (%)	45.87	48.68	49.93	4.06	48.90	47.66	48.82	1.16
	Solvent/Solute (dm^3/kg)				Acid Concentration (%)			
	I	II	III	D_e	I	II	III	D_e
Y (%)	27.49	27.54	28.71	1.22	26.27	34.00	22.87	11.13
C (%)	57.24	57.51	57.01	0.49	57.75	61.52	52.50	9.02
S (%)	44.72	47.67	49.57	4.85	45.42	55.15	43.51	11.64

Table 4. Main Characteristic Peak Heights of the Catalysts

No. of Catal.	2-1	2-2	2-3	2-4	2-5	2-6
Conc. of Acid (%)	102.9	102.6	102.3	102.0	101.7	101.4
AV	3.845	3.921	4.011	4.103	4.187	4.224
$(VO)_2P_2O_7$	98.3	98.6	97.8	97.3	98.1	96.9
δ-$VOPO_4$	47.4	49.2	51.9	53.2	54.4	56.6
Z-1	26.1	26.9	27.4	28.0	28.9	29.6
Z-2	22.1	22.5	22.9	23.6	24.1	25.0
δ-$VOPO_4/(VO)_2P_2O_7$	0.482	0.499	0.531	0.547	0.555	0.584

From the above results, it may be shown that the average valence state of vanadium in the catalysts and the relative peak height ratio of δ-$VOPO_4$ to $(VO)_2P_2O_7$ increase with decreasing acid concentration. The results above show that the concentration of phosphoric acid in precursor preparation remarkably affects the catalyst behavior. Water is a product of oxidation of alcohol to aldehyde. The water in the reaction system increased with decreasing acid concentration. Therefore, the decrease of acid concentration does not favor alcohol oxidation and vanadium reduction. With decreasing acid concentration, the average valence state of vanadium increases and the mass ratio of high valence vanadium phase to low valence vanadium phase also increases.

Reactive properties of the catalysts

The catalysts prepared were evaluated at 420°C, an inlet *n*-butane concentration of 4.0%, and a space velocity of 500 h^{-1}. The evaluation results of and the average valence state (AV) of vanadium in the catalysts, along with the relative peak height ratio of δ-$VOPO_4$ to $(VO)_2P_2O_7$, are listed in Table 5.

It can be seen from Table 5 that, with an increasing average valence state of vanadium in the catalysts, the conversion of *n*-butane increases. At the same time, the selectivity to MA increases, reaches a maximum value, and then progressively decreases. The average valence state of vanadium in the catalyst giving the maximum yield of MA is slightly above 4. The above catalyst behavior may be illustrated by a general scheme for *n*-butane oxidation on VPO catalysts shown as Figure 3, which is similar to the one proposed by Cavani et al. (1984).

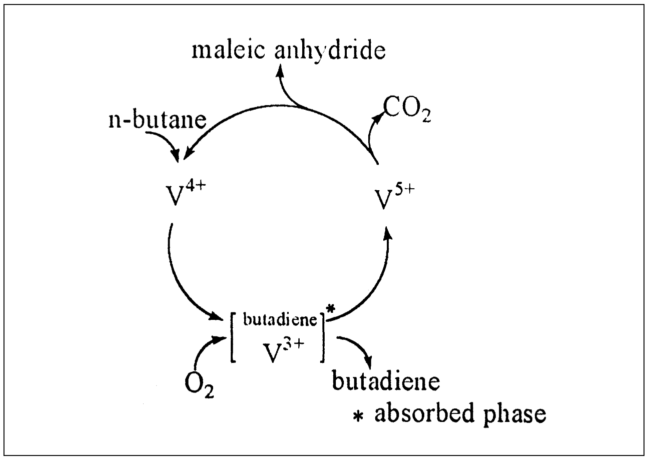

Figure 3. General scheme for *n*-butane oxidation on VPO catalysts.

Some authors (Cavani et al., 1984, 1985) proposed the two different types of reaction going from the alkane or alkene to maleic anhydride: a first step of oxidative dehydrogenation up to adsorbed butadiene, and a second step of further oxidation of this intermediate. The first step was suggested to be controlled by the rate of the V^{+4} reduction to the V^{+3}, and the second step was controlled by the rate of the V^{+5} reduction to the V^{+4}. Thus, the amount of the V^{+4} phase (vanadyl pyrophosphate) determines the dehydrogenation extent of *n*-butane to olefins, and the relative amount of the V^{+5} phase (vanadyl orthophosphate) determines the further oxidation extent of these olefins. The V^{+3} phase is only the transition phase. The concept involving the V^{4+} and V^{5+} sites being active and selective for MA production from butane, as well as the essential participation of the V^{5+} centers in reaction, has been assumed (Hodnett and Delmon, 1984) and confirmed (Contractor et al., 1990).

The factors affecting the amount of the V^{4+} phase are: (i) the initial quantity of the V^{4+} phase; (ii) the consumed quantity of the V^{4+} phase converting to the V^{3+} phase in dehydrogenation of *n*-butane; and (iii) the increased quantity of the V^{4+} phase resulting from the V^{5+} phase reduction in further oxidation of olefins. At the same time, the factors affecting the relative amount of the V^{5+} phase are: (i) the initial quantity of the V^{5+} phase; (ii) the consumed quantity of the V^{5+} phase converting to the V^{4+} phase in further oxidation of olefins; and (iii) the increased quantity of the V^{5+} resulting from the V^{3+} phase oxidation. The interconverting of various phases in the catalyst under reactant atmosphere is a function of the reducing or oxidizing properties of the reactants, the time onstream, and the reaction temperature. If the above conditions are all kept constant, the initial quantity of one phase will become a determining factor affecting its amount.

The effects are shown in Figure 4 of the relative peak height ratio of the V^{+5} phase (vanadyl orthophosphate) to the V^{+4} phase (vanadyl pyrophosphate) on the *n*-butane conversion and the selectivity to MA.

Since each catalyst has been prepared at a higher concentration of the acid, the initial amount of the V^{4+} phase $(VO)_2P_2O_7$ is quite large. Therefore, the dehydrogenation of *n*-butane on the V^{4+} phase surface can proceed sufficiently, and the *n*-butane conversions are all quite high (larger than 70.0%) for the catalysts prepared. By increasing the relative peak height ratio of δ-$VOPO_4$ to $(VO)_2P_2O_7$, the relative amount of the V^{5+} phase $VOPO_4$ increases. The increase of the V^{5+} phase favors the oxidation of the intermediate olefins, the selectivity to MA increases, and the V^{4+} phase resulting from the V^{5+} phase reduction increases as well. The increase of the V^{4+} phase favors the dehydrogenation of *n*-butane; thus, the *n*-butane conversion still increases. However, when the relative amount of the V^{5+} phase reaches

Table 5. Catalysts Prepared at Different Acid Concentration at 125°C

No. of Catal.	2-1	2-2	2-3	2-4	2-5	2-6
Conc. of Acid (%)	102.9	102.6	102.3	102.0	101.7	101.4
AV	3.845	3.921	4.011	4.103	4.187	4.224
δ-$VOPO_4/(VO)_2P_2O_7$	0.482	0.499	0.531	0.547	0.555	0.584
C (%)	70.28	73.07	75.04	77.91	79.93	82.85
S (%)	61.55	62.99	64.41	58.55	51.30	45.00
Y (%)	43.26	46.03	48.10	45.62	41.00	37.28

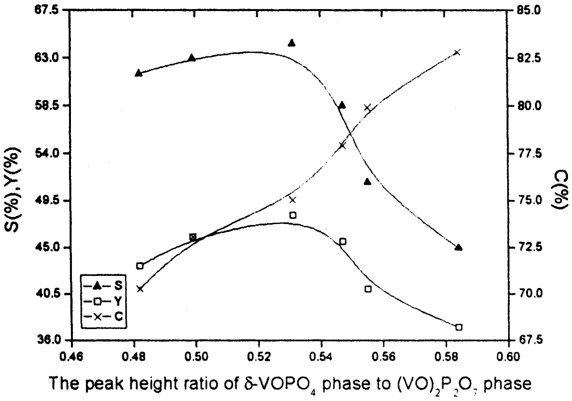

Figure 4. Effects of the peak height ratio on the catalyst behavior.

a given quantity, the oxidation of olefins proceeds further to carbon oxides. After the overoxidation of olefins takes place, when the relative amount of the V^{5+} phase increases, the n-butane conversion still remains to increase, while the selectivity to MA decreases.

Figure 4 shows that, after the maximum selectivity is attained, the decrease in selectivity exceeds the increase in conversion; since $Y = C \times S$, the maximum yield therefore is at the maximum point of selectivity for the catalysts prepared. The optimum acid concentration is the optimum one at which the catalyst was prepared to give the maximum yield of MA.

Fluidizing properties of the catalysts

The particle-size distribution was measured by the screen analysis for the silica supported catalyst prepared at the optimum acid concentration. The results are listed in Table 6.

The mean diameter of the catalyst particles is

$$\bar{d}_p = \frac{1}{\sum_i \frac{x_i}{d_{pi}}} = 75.21\ \mu m$$

The density ρ_s and surface area S_B of the catalyst in this study were measured to be 964.1 kg/m^3 and 42,440 m^2/kg, respectively. The computed viscosity μ and density ρ_g of the gas at reactive temperature were 3.2×10^{-5}Pa·s and 0.5135 kg/m^3, respectively.

Geldart (1973) came up with four kinds of particle behavior from the smallest to the largest particles by using the particle diameter and the density difference between solid and gas. In light of the Geldart figure for particle classification, the catalyst of the fine particle bed in this study belongs to the particle of group A. The catalyst fluidizes easily, with smooth fluidization at low gas velocities and controlled bubbling with small bubbles at higher gas velocities.

To avoid or reduce carryover of particles from the fluidized bed, the gas velocity should be maintained between the minimum fluidizing velocity u_{mf} and the terminal velocity u_t. In calculating u_{mf}, the mean diameter for the size distribution actually present in the bed may be used, whereas the smallest size of particles present in appreciable quantities in the bed should be used for u_t (Kunii and Levenspiel, 1991). For the catalyst particles in this study, the mean diameter of the particles and the smallest size of particles are taken as 75.21 μm and 55 μm, respectively. Under the operating conditions in this study, the Reynolds number Re_p is smaller than 0.4, thus the formulas of u_{mf} and u_t (Kunii and Levenspiel, 1991) are

$$u_{mf} = \frac{d_p^2(\rho_s - \rho_g)g}{1{,}650\mu} = 1.012 \times 10^{-3}\ \mathrm{m/s}$$

and

$$u_t = \frac{d_p^2(\rho_s - \rho_g)g}{18\mu} = 0.04963\ \mathrm{m/s}$$

The ratio u_t/u_{mf} of 49.04 indicates a larger flexibility of the operation in the nonentrained regime. Fluidized beds can in fact be made to operate at velocities well beyond the terminal velocity of all particles without excessive carryover of particles. This is possible because a large fraction of the gas flows through the bed as high-speed gas bubbles, bypassing most of the bed particles. If cyclone separators are used to return the entrained particles to the bed, even higher gas velocities can be used.

Conclusion

Optimization studies have been performed for preparation of the catalyst precursor, and orthogonal experiments are carried out to determine the effects of different factors in precursor preparation on the behavior of the catalyst. The experiment results show that the concentration of orthophosphoric acid and reaction temperature in precursor preparation exhibit strong effects on the phase composition and reactive properties of the catalysts. The optimum temperature and acid concentration in the catalyst preparation have been determined.

The effects of orthophosphoric acid concentration in precursor preparation on the catalyst behavior at an elevated

Table 6. Particle-Size Distribution of the Catalyst

Dia. (μm)	d_{pi} (μm)	Mass Fract., x_i	Dia. (μm)	d_{pi} (μm)	Mass Fract., x_i
10–40	25	0.097	130–160	145	0.116
40–70	55	0.184	160–190	175	0.076
70–100	85	0.226	190–220	205	0.070
100–130	115	0.192	220–250	235	0.039

temperature of 125°C have been studied. Since each catalyst has been prepared at a higher concentration of the acid, the initial amount of the V^{4+} phase $(VO)_2P_2O_7$ is quite large. A large amount of the V^{4+} phase promotes the dehydrogenation of *n*-butane, and the *n*-butane conversions are all quite high for the catalysts prepared.

While decreasing the acid concentration in precursor preparation, the relative amount of the V^{5+} phase δ-$VOPO_4$ increases progressively. The increase of the V^{5+} phase enhances the oxidation of the intermediate olefins, and then promotes the dehydrogenation of *n*-butane. Thus, the selectivity to MA increases initially, whereas, the *n*-butane conversion continuously increases. When the relative amount of the V^{5+} phase reaches a given quantity, overoxidation takes place, and the selectivity to MA begins to decrease.

The yield of MA goes through a maximum value at the optimal acid concentration during the change from high to low acid concentration in precursor preparation. The catalyst prepared at an acid concentration of 102.3% gave the maximum yield of MA of 48.10% at an inlet *n*-butane concentration of 4.0%, and a space velocity of 500 h^{-1}.

The fine particle catalyst in this study belongs to the particle group A. The catalyst fluidizes easily and exhibits a large flexibility of operation.

Literature Cited

Ben Abdelouahab, F., R. Olier, N. Guilhaume, F. Lefebvre, and J. C. Volta, "A Study by in situ Laser Raman Spectroscopy of VPO Catalysts for *n*-butane Oxidation to Maleic Anhydride," *J. Catal.*, **134**, 151 (1992).

Bordes, E., "Nature of the Active and Selective Sites in Vanadyl Pyrophosphate, Catalyst of Oxidation of *n*-Butane, Butane and Pentane to Maleic Anhydride," *Catal. Today*, **16**, 27 (1993).

Busca, G., F. Cavani, G. Centi, and F. Trifiro, "Nature and Mechanism of Formation of Vanadyl Pyrophosphate: Active Phase in *n*-butane Selective Oxidation," *J. Catal.*, **99**, 400 (1986).

Cavani, F., G. Centi, I. Manenti, A. Riva, and F. Trifiro, "Catalytic-Oxidation of C-4 Fraction on Vanadium-Phosphorus Oxides," ACS Meeting, published by American Chemical Society, Washington, DC (1984).

Cavani, F., G. Centi, F. Trifiro, and A. Vaccarri, *In Adsorption and Catalysis on Oxide Surfaces*, M. Che and G. C. Bond, eds., Elsevier, Amsterdam (1985).

Cavani, F., and F. Trifiro, *Preparation of Catalysts VI*, G. Poncelet, J. Martens, B. Delmon, P. A. Jacobs, and P. Grange, eds., Elsevier, Amsterdam (1995).

Centi, G., F. Trifiro, J. R. Ebner, and V. M. Franchetti, "Mechanistic Aspects of Maleic Anhydride Synthesis from C_4 Hydrocarbons over VPO Catalyst," *Chem. Rev.*, **88**, 55 (1988).

Contractor, R., J. Ebner, and M. J. Mummey, "New Development in Selective Oxidation," *Stud. Surf. Sci. Catal.*, **55**, 553 (1990).

Geldart, D., "Types of Gas Fluidisation," *Powder Technol.*, **7**, 285 (1973).

Guliants, V. V., J. B. Benziger, S. Sundaresan, I. E. Wachs, J.-M. Jehng, and J. E. Roberts, "The Effect of the Phase Composition of Model VPO Catalysts for Partial Oxidation of *n*-Butane," *Catal. Today*, **28**, 275 (1996).

Harrouch Batis, N., H. Batis, A. Ghorbel, J. C. Vedrine, and J. C. Volta, "Synthesis and Characterization of New VPO Catalysts for Partial *n*-Butane Oxidation to Maleic Anhydride," *J. Catal.*, **128**, 248 (1991).

Hodnett, B. K., "V-P-O Catalyst for the Selective Oxidation of C_4 Hydrocarbons to Maleic Anhydride," *Catal. Rev. Sci. Eng.*, **27**, 373 (1985).

Hodnett, B. K., and B. Delmon, "Influence of Reductive Pretreatments on the Activity and Selectivity of Vanadium-Phosphorus Oxide Catalysts for *n*-Butane Partial Oxidation," *Ind. Eng. Chem. Fundam.*, **23**, 465 (1984).

Kunii, D., and O. Levenspiel, *Fluidization Engineering*, 2nd ed., Butterworth-Heineman, Boston (1991).

Liu changqing, *Measuring Technology and Experimental Methods* (in Chinese), Publishing House of Chinese University of Mining Industry, Xuzhou (1997).

Nakamura, M., K. Kawai, and Y. Fujiwara, "The Structure and Activity of Vanadyl Phosphate Catalysts," *J. Catal.*, **34**, 345 (1974).

Zhang-Lin, Y., M. Forissier, R. P. Sneeden, J. C. Vedrine, and J. C. Volta, "On the Mechanism of *n*-Butane Oxidation to Maleic Anhydride on VPO Catalysts I. A Kinetic Study on a VPO Catalyst as Compared to VPO Reference Phases," *J. Catal.*, **145**, 256 (1994).

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