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The Production of Methacrylic Acid by the Vapor-Phase Aldol Condensation of Propionic Acid with Formaldehyde

V_2O_5–P_2O_5 catalysts, which perform well in the oxidation of *n*-butane to maleic anhydride, also perform well in the vapor-phase aldol condensation of acetic acid and propionic acid (PA) with formaldehyde (HCHO) to form acrylic acid and methacrylic acid (MAA), respectively (*1–4*):

$$RCH_2COOH + HCHO \rightarrow$$
$$CH_2 = CRCOOH + H_2O \quad (R = \mathrm{H\ or\ } CH_3).$$

It should be noted that acrylic acid is obtained in a high yield (96 to 98 mol%, based on the charged HCHO), while the yield of MAA does not exceed 39 mol%, with a PA/HCHO molar ratio of 2 (*3, 4*). This suggests that the formation of MAA is more difficult than that of acrylic acid, much as in the case of the partial oxidation of unsaturated aldehydes.

In this study, for the purpose of discovering more effective catalysts for the production of MAA, the V_2O_5–P_2O_5 system was modified by adding a third component. The catalytic performance was then examined.

The V_2O_5–P_2O_5 catalyst (V/P atomic ratio 1/1.1) was prepared according to patented procedures (*5*). The V/*M*/P ternary oxides (*M* was the third component) were prepared in the presence of an organic solvent (lactic acid) to produce a large surface area (*6–8*). For example, the V/Si/P = 1/2/2.2 catalyst was prepared as follows. NH_4VO_3 (29.5 g) was dissolved in hot water (ca. 100 ml) containing about 20 ml of lactic acid, yielding a blue solution of VO^{2+}, and 63.5 g of 85% H_3PO_4 was dissolved in water (ca. 100 ml). The two solutions were added to 150 g of colloidal silica "Snowtex O" (Nissan Chem. Ind.) containing 20% SiO_2 in water. Excess water was evaporated by stirring in a hot-air current. The cake so obtained was dried again by gradually raising the temperature from 50 to 200°C in an oven for 6 h. The resulting solid was broken up and sieved to a 8- to 20-mesh size. It was calcined finally at 450°C for 6 h in a stream of air. The procedures for the V/Ti/P catalysts were also described in a previous study (*9*). As the starting materials for the other third components, we used $SnCl_2 \cdot 2H_2O$ for SnO_2, $FeCl_3 \cdot 6H_2O$ for Fe_2O_3, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ for NiO, $Co(CH_3COO)_2 \cdot 4H_2O$ for Co_3O_4, $Mn(CH_3COO)_2 \cdot 4H_2O$ for MnO_2, $SbCl_5$ for Sb_2O_5, and $ZrO_2Cl_2 \cdot 8H_2O$ for ZrO_2.

Reaction of PA with HCHO was carried out with a continuous-flow system. Trioxane [$(HCHO)_3$] was used as the source of HCHO. Unless otherwise indicated, the feed rates were PA/HCHO/nitrogen = 30/15/350 mmol/h; the composition was 7.6/3.8/88.6 mol%. Other procedures were as described in previous studies (*2–4*).

Performance of the V/Ti/P oxides. The study was begun with the V/Ti/P ternary oxide catalysts, since they had shown an improved performance in the formation of acrylic acid (4, 7.8). First, the effect of the phosphorus content was studied using a series of V/Ti/P = 1/2/*x*, where *x* was varied from 4 to 8 ($x = 5$ corresponds to stoichiometry $(VO)_2P_2O_7 + 4TiP_2O_7$). The main products were MAA, propylene, and CO_2, with a small amount of CO. Formation of propane, ethylene, and ethane was not detected. As the temperature was raised, the yield of MAA increased, passed through a broad maximum, and then decreased gradually. The maximum yields of MAA obtained with 20-g portions of each catalyst

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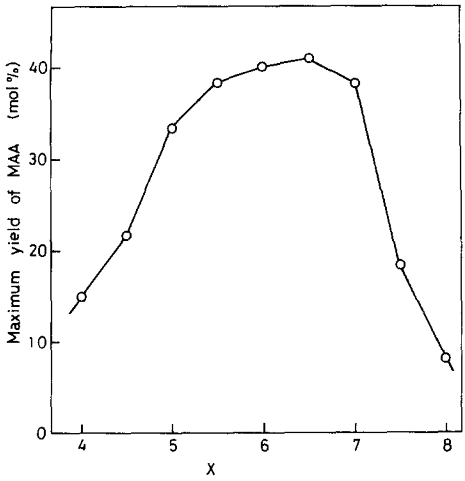

FIG. 1. Effect of phosphorus content on the maximum yield of MAA. Catalyst: V/Ti/P; atomic ratio 1/2/x.

TABLE 1

Performances of the V/M/P Ternary Oxide Catalysts[a]

Catalyst[b]	Atomic ratio	T (°C)	Y_{MAA} (mol%)	Catalyst[b]	Atomic ratio	T (°C)	Y_{MAA} (mol%)
V/P	1/1.1	310	37	V/Sn/P	1/2/3.3	310	26
		330	38	V/Fe/P	1/2/4.4	250	10
V/Sb/P	1/2/1.2	340	3			290	19
V/Si/P	1/2/2.2	310	45	V/Ni/P	1/2/3.3	280	26
		330	51			300	27
V/Zr/P	1/2/5.5	270	26	V/Co/P	1/2/3.3	310	14
		290	28			330	16
V/Ti/P	1/2/5.5	290	36	V/Mn/P	1/2/3.3	320	14
	1/2/6.5	260	39				
		310	41				

Note. T, temperature; Y_{MAA}, yield of MAA.

[a] Amount of catalyst used, 20 g; feed, PA/HCHO/N_2, 30/15/350 mmol/h.

[b] Composition: $[V + 1.1P] + 2[M^{n+} + 0.55P] = V + 2M^{n+} + 1.1(n + 1)P$, except for M = Sb and Si.

(contact time ca. 15) at a temperature from 270 to 330°C are shown in Fig. 1. A 41 mol% yield of MAA, based on the charged HCHO, was obtained with $x = 6.5$.

Then, the effect of the V/Ti ratio was studied using a series of $[(Ti + 2.15P) + y(V + 1.2P)]$ catalysts, where y was varied from 0.1 to 1.5. The maximum yield of MAA obtained with 20-g portions of each catalyst at a temperature from 270 to 330°C, increased with y in the range 0.1 to 0.5, while it leveled off at 38 mol% in the range of $y > 0.5$. It is concluded that the yield of MAA is improved only a little (from 38 to 41 mol%) by the combination of titanium phosphate with V–P oxide.

Performance of various V–P-based ternary oxides. In order to explore more effective catalysts for the production of MAA, various third components were combined with V–P oxide and the catalytic performance was then tested. The yields of MAA obtained with 20-g portions of each ternary oxide are listed in Table 1. The addition of silicon phosphate enhances markedly the yield of MAA, but the other phosphates, except for titanium phosphate, do not improve the yield.

Effect of the V/Si/P composition. The effect of the composition of the V/Si/P oxide catalyst was studied by changing both the silicon and phosphorus contents. The maximum yields of MAA obtained with 20-g portions of four series of catalysts at a temperature 270 to 330°C are shown in Fig. 2 as a function of the content of phosphorus, x. There exists an optimal content of phos-

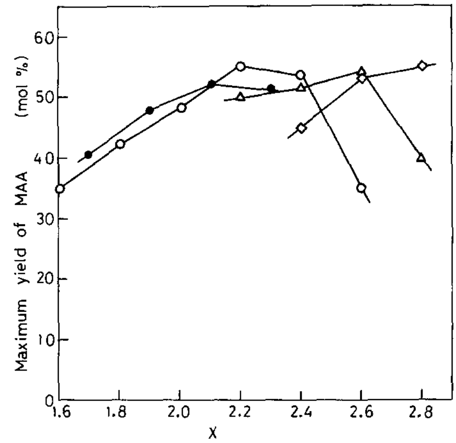

FIG. 2. Effect of the composition of the V/Si/P oxides on the maximum yield of MAA. Catalyst: V/Si/P; atomic ratio (●) 1/1/x; (○) 1/2/x; (△) 1/4/x; (◇) 1/8/x.

phorus which varies depending on the content of silicon. The best results are obtained with the V/Si/P = 1/2/2.2, 1/4/2.6, and 1/8/2.8 catalysts; the yield of MAA attained 55 mol%, based on the charged HCHO, with a PA/HCHO ratio of 2.

Silica-supported V–P oxides have been examined as catalysts for oxidation of butane to maleic anhydride (*10, 11*), although this oxidation is usually conducted with V–P oxides without support. As preliminary experiments, the V/Si/P oxides used in this study were tested also as catalysts for oxidation of butane (*12*). Interestingly, the selectivity to maleic anhydride fell as an increase in the content of silicon, though the oxidation activity remained at almost the same level, much as in the case of the V/Ti/P oxides where the selectivity to maleic anhydride decreased with the content of titanium (*4*). This finding indicates that the catalytic functions required for the condensation reactions are not exactly the same as those for the oxidation of butane.

In view of the results obtained in the previous studies (*2–4, 12*), the catalytic performance of the V–P-based oxides is summarized as follows:

formation of acrylic acid, V/Ti/P > V/P > V/Si/P

formation of MAA, V/Si/P > V/Ti/P > V/P

This difference may be caused mainly by the difference in the reactivity between acrylic acid and MAA, much as in the case of partial oxidations of acrolein and methacrolein. In this respect, the acid–base properties of the catalyst are believed to play an important role in deciding the yield of the condensation products.

An attempt was made to check those properties in order to clarify the catalytic function of the V/Si/P oxides. As a measure of acidic property (*13*), the catalytic activity for dehydration of 2-propanol to propylene was determined under the following conditions: temperature, 140°C; 2-propanol concentration, 1.3 mol% in air; feed rate of air, 400 ml/min; amount of catalyst used, amount corresponding to the surface area of 100 m^2. As a measure of basic property (*13*), the activity for oxydative dehydrogenation of ethanol to acetaldehyde was measured under the following conditions: temperature, 220°C; ethanol concentration, 1.75 mol% in air; feed rate of air, 400 ml/min; amount of catalyst used, amount corresponding to the surface area of 100 m^2.

TABLE 2

Activities for 2-Propanol Dehydration and Ethanol Dehydrogenation, Surface Areas, and Maximum Yields of MAA

Catalyst	Atomic ratio	S (m^2/g)	r_p	r_e	Y_{max} (mol%)
			(mol/h m^2 × 10^5)		
V/P	1/1.1	22.8	4.0	4.4	38
V/Ti/P	1/2/6.5	24.1	5.3	5.6	41
	1/2/7.0	22.4	4.1	4.5	38
V/Si/P	1/2/2.0	30.8	2.4	5.6	48
	1/2/2.2	21.3	4.7	5.6	55

Note. S, surface area; r_p, rate of 2-propanol dehydration; r_e, rate of ethanol dehydrogenation; Y_{max}, maximum yield of MAA with a PA/HCHO molar ratio of 2.

The results obtained for the V/P, V/Ti/P, and V/Si/P oxide catalysts are shown in Table 2, together with the surface area and the maximum yield of MAA in the aldol condensation.

Unfortunately, it seems hard to explain the difference in the yields of MAA with the obtained acid–base properties. Possibly the yield may be governed by a more subtle distinction in the acid–base properties. Thus, more detailed information about strength of acidic and basic sites is required, although it is still hard to actually measure these properties.

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