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Reaction of Methyl Propionate with Methylal over V-Si-P Ternary Oxide Catalysts

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Synopsis. The vapor-phase aldol condensation of methyl propionate with formaldehyde was performed using methylal as the source of formaldehyde. The main products were methyl methacrylate and methacrylic acid. The one-pass yield of methyl methacryalte plus methacrylic acid on methylal basis reached 53 mol% at a methyl propionate/methylal molar ratio of 2 over the V-Si-P oxide with an atomic ratio of 1 : 16 : 3.2.

It was recently found that combination of vanadium(IV) dioxide pyrophosphate [$V_2O_2(P_2O_7)$] with silica gel in the presence of a small amount of phosphoric acid [H_3PO_4] brings about an improved catalytic performance in the vapor-phase aldol condensation of propionic acid (PA) with formaldehyde (HCHO) to form methacrylic acid (MAA):[1,2]

$$CH_3CH_2OOH + HCHO \rightarrow CH_2{=}C(CH_3)COOH + H_2O.$$

As the source of HCHO, formalin, i.e., aqueous solution of HCHO, is a familiar and convenient compound. However, this reaction is markedly retarded by water vapor present in the feed.[3,4] Therefore, the reaction has been studied mainly using trioxane [$(HCHO)_3$].[1–5]

Similarly to PA, methyl propionate (MP) reacts with HCHO to form methyl methacrylate (MMA):[3–5]

$$CH_3CH_2COOCH_3 + HCHO \rightarrow CH_2{=}C(CH_3)COOCH_3 + H_2O.$$

In this study, methylal (dimethoxymethane, formaldehyde dimethyl acetal) [$CH_2(OCH_3)_2$] was used as the source of HCHO and the reaction of MP with methylal was investigated.

Experimental

Catalysts. The catalysts used in this study are a V-P oxide of atomic ratio 1 : 1.06 and V-Si-P ternary oxides. The V-P oxide was the same as that used in a previous study;[3] it was prepared according to patented procedures[6] and consisted of divanadium(IV) dioxide pyrophosphate.[7] Its specific surface area was 23 $m^2 g^{-1}$.

The V-Si-P oxides were prepared in the presence of lactic acid according to a principle reported.[8] For example, the V-Si-P oxide with an atomic ratio of 1 : 8 : 2.8 was prepared as follows. NH_4VO_3 (23.4 g) was dissolved in ca. 100 ml of hot water containing 20 ml of lactic acid, and 64.4 g of 85% H_3PO_4 was dissolved separately in ca. 100 ml of water. The two solutions were added to 480 g of colloidal silica "Snowtex O" (Nissan Chem. Ind.) containing 20% SiO_2. Excess water was evaporated with stirring in a hot air current. The obtained cake was dried in an oven for 6 h by gradual heating from 50 to 200 °C. The resulting solid was ground and sieved to get the 8 to 20 mesh size portion. It was finally calcined at 450 °C for 6 h in a stream of air. The specific surface area was 57 $m^2 g^{-1}$ and the average oxidation number of vanadium ions in the catalyst[9,10] was about 4.

Reaction Procedures. The reaction of MP with methylal was conducted with a continuous-flow system. The procedures were the same as those used in the previous studies.[1–4] Unless otherwise indicated, the feed rates of MP, methylal, and nitrogen were 27.4, 13.7, and 350 mmol h^{-1}, respectively.

The yield in mol% is defined as 100 (moles of product)/(moles of methylal fed). The selectivity of methylal to the condensation products, S_M, is defined as 100 (moles of MMA+MAA)/(moles of methylal consumed) and the selectivity of MP to the condensation products, S_P, defined as 100 (moles of MMA+MAA)/(moles of MP consumed).

Results and Discussion

Performance of P/V=1.06 Oxide Catalyst. A mixture of MP, methylal, and nitrogen was passed over the V-P oxide with the atomic ratio of 1 : 1.06 at 320 °C. The main products were MMA, MAA, PA, HCHO, methanol, and dimethyl ether, with small amounts of propylene and CO_2 accompanied. The amount of unreacted methylal was negligibly small at a contact time of 5 s, which indicates that methylal is rapidly decomposed to HCHO and methanol under the conditions used. The results are shown in Fig. 1. The yields of MMA, MAA, and MMA+MAA reached 25.5, 6.5, and 32.0 mol%, respectively.

Performance of V-Si-P=1 : 8 : 2.8 Oxide Catalyst. The reaction was conducted at 320 °C with the V-Si-P

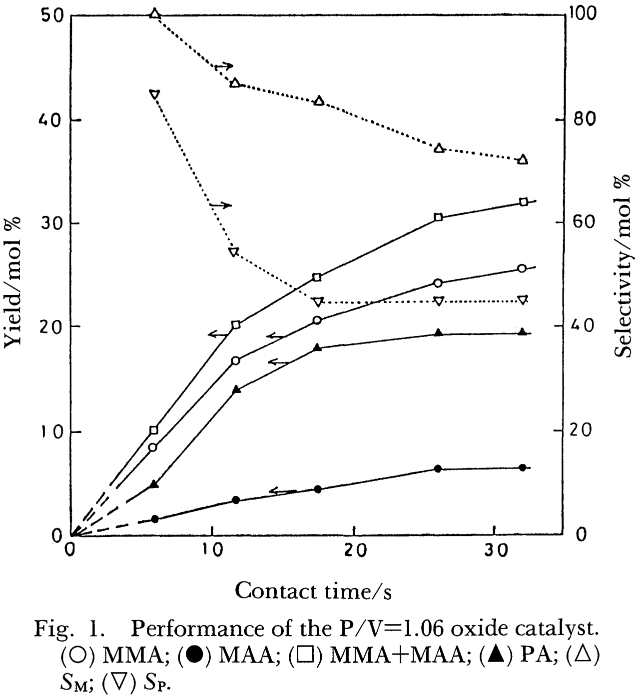

Fig. 1. Performance of the P/V=1.06 oxide catalyst. (○) MMA; (●) MAA; (□) MMA+MAA; (▲) PA; (△) S_M; (▽) S_P.

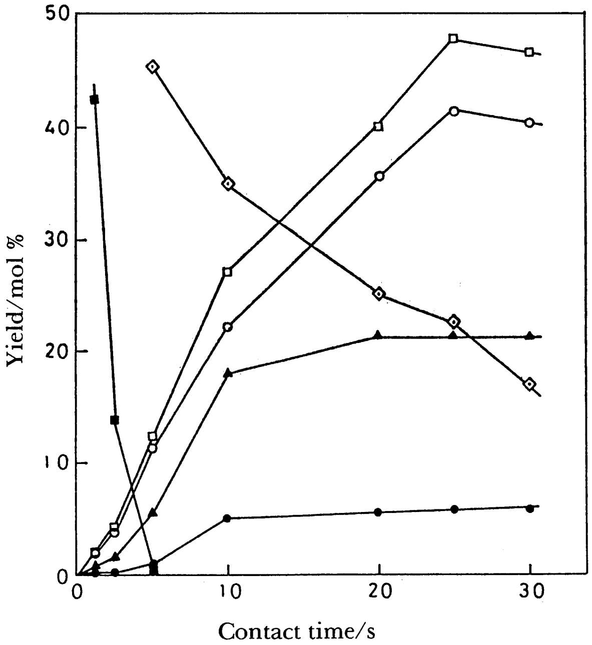

Fig. 2. Performance of the V/Si/P=1 : 8 : 2.8 oxide catalyst. (○) MMA; (●) MAA; (□) MMA+MAA; (▲) PA; (■) methylal; (◇) [HCHO]×0.5.

oxide of atomic ratio 1 : 8 : 2.8. The results are shown in Fig. 2. The rates of formation of MMA and MAA increased as the amount of methylal decreased, and methylal was consumed completely at a contact time of 5 s. The yields of MMA, MAA, and MMA+MAA reached 42, 6, and 48 mol%, respectively. It is clear that the V-Si-P ternary oxide is more effective as catalyst for this reaction much as it is when trioxane is used as the source of HCHO.[1,2]

Effect of V-Si-P Composition. Three oxides, different in composition, having V-Si-P atomic ratios 1 : 2 : 2.2, 1 : 8 : 2.8, and 1 : 16 : 3.2, were examined as catalysts, the P/V ratios were chosen which might give the highest yields of MAA in the condensation of PA with trioxane.[1,11] The results at 320 °C are shown in Fig. 3, together with those obtained with the P/V=1.06 oxide. The yield of MMA+MAA reached 53 mol% at an MP/methylal molar ratio of 2 over the V-Si-P=1 : 16 : 3.2 oxide.

Effect of Temperature. The reaction was conducted by changing contact time and temperature. The apparent activation energy was calculated to be 34 kcal mol^{-1}. Both the selectivities, S_M and S_P fell with rising temperature, similarly to the case of the reaction of PA with trioxane.[2]

Effect of Methyl Propionate Concentration. The reaction was conducted at 320 °C by changing the feed rate of MP; the feed rates of methylal and nitrogen were fixed at ca. 14 and 350 mmol h^{-1}, respectively. The initial rate of formation of MMA+MAA was almost independent of the MP concentration, while the maximum yield increased with the MP concentration, similarly to the case of the reaction of PA with trioxane.[2] The yield of MMA+MAA reached 70 mol% at an MP/methylal molar ratio of 4.

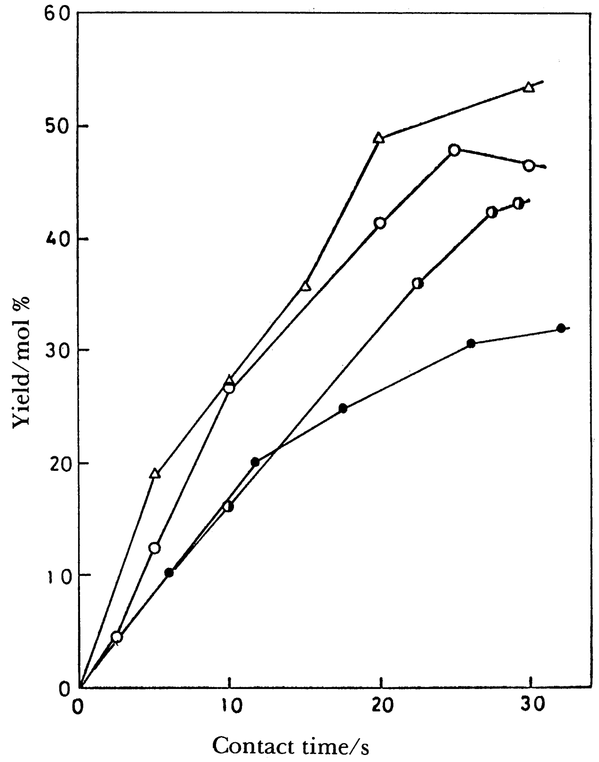

Fig. 3. Effect of the V-Si-P composition on the yield of MMA+MAA. V-Si-P atomic ratio: (○) 1 : 2 : 2.2; (○) 1 : 8 : 2.8; (△) 1 : 16 : 3.2; (●) P/V=1.06.

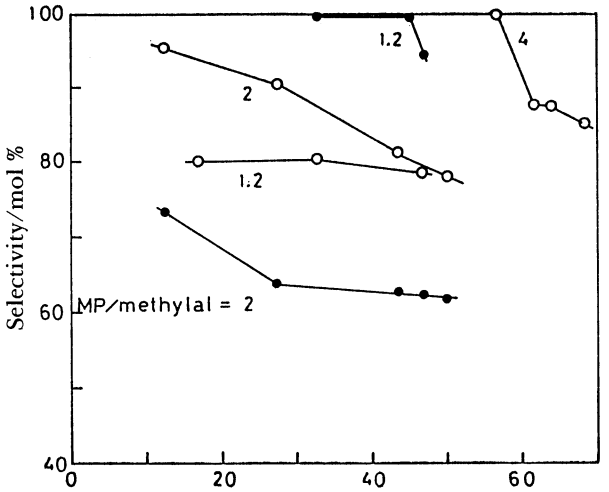

Fig. 4. Effect of the MP/methylal molar ratio on the selectivity to MMA+MAA. (○) on methylal basis; (●) on MP basis. Catalyst: V-Si-P=1 : 8 : 2.8 oxide.

The selectivities, S_M and S_P are plotted in Fig. 4 as a function of the yield of MMA+MAA. The selectivity on methylal basis, S_M, increased with the increase in the MP/methylal molar ratio, while the selectivity on MP basis, S_P, decreased.

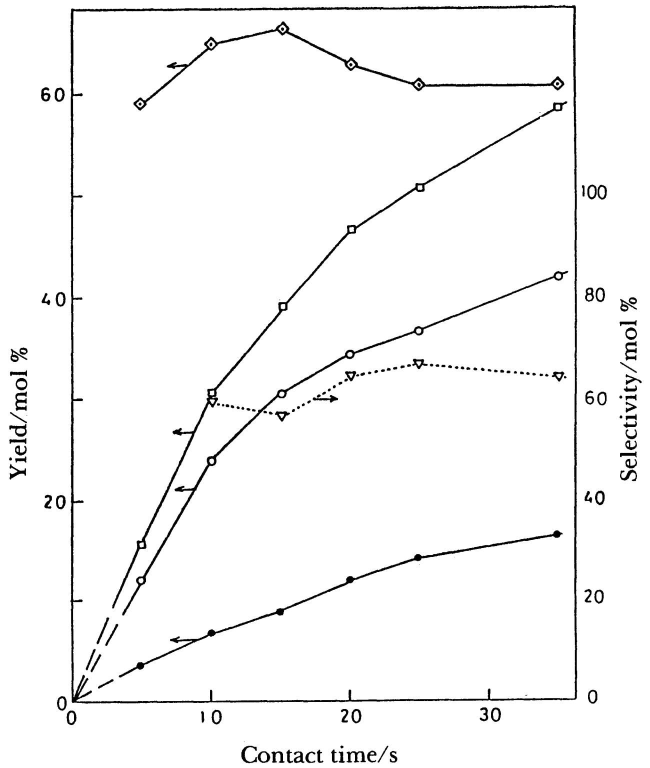

Fig. 5. Performance obtained in the presence of oxygen. (○) MMA; (●) MAA; (□) MMA+MAA; (◇) [HCHO]×0.5; (▽) selectivity on MP basis. Catalyst: V–Si–P=1 : 8 : 2.8 oxide.

Effect of Reactant Dilution. The effect of the dilution of reactants was examined at a fixed MP/methylal molar ratio of 2 and 320 °C by changing concentrations of the two reactants and contact time. The yield of MMA+MAA increased as the concentrations decreased.

Effect of Oxygen. The reaction was conducted at 320 °C in the presence of oxygen; the feed rates of MP, methylal oxygen, and nitrogen were 27.4, 13.7, 12.5, and 350 mmol h^{-1}, respectively. The yields of MMA, MAA, MMA+MAA, and HCHO and the selectivity on MP basis are plotted in Fig. 5 as a function of contact time. The yield of MAA increased with the addition of oxygen and so that, the yield of MMA+MAA increased from 48 to 58 mol%. It should be noted that the formation of HCHO was faster than in the absence of oxygen (Fig. 2). This may be understood from the fact that the methanol formed by the decomposition of methylal is oxidized to HCHO with oxygen over the catalyst.[12)]

References

1) M. Ai, *J. Catal.*, **124**, 293 (1990).

2) M. Ai, *Bull. Chem. Soc. Jpn.*, **63**, 1217 (1990).

3) M. Ai, *Appl. Catal.*, **36**, 221 (1988).

4) M. Ai, Proc. 9th Intern. Congr. Catal., Calgary, 1988, Vol. 4, p. 1562.

5) G. Albanesi and P. Moggi, *Appl. Catal.*, **6**, 293 (1983).

6) K. Katsumoto and D. M. Marquis, U. S. Patent 4132670 (1979); *Chem. Abstr.*, **90**, 110667p (1979).

7) E. Bordes and P. Courtine, *J. Catal.*, **57**, 236 (1979).

8) P. Courty and B. Delmon, *C. R. Acad. Sci. Paris, Ser. C*, **268**, 1795 (1969).

9) M. Nakamura, K. Kawai, and Y. Fujiwara, *J. Catal.*, **34**, 345 (1979).

10) B. K. Hodnett, P. Permanne, and B. Delmon, *Appl. Catal.*, **6**, 231 (1983).

11) M. Ai, Proc. 5th Intern. Symp. Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain-la-Neuve, 1990, p. 453.

12) M. Ai, *Appl Catal.*, **59**, 227 (1990).