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The Production of Methacrylic Acid by the Vapor-Phase Aldol Condensation over V-Si-P Ternary Oxide Catalyst

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The vapor-phase aldol condensation of propionic acid with formaldehyde was performed over a V-Si-P ternary oxide catalyst of atomic ratio of 1 : 2 : 2.2. The one-pass yield of methacrylic acid was 55 mol% on the charged formaldehyde basis at the propionic acid/formaldehyde molar ratio of 2. The maximum yield of methacrylic acid remained unchanged with the variation in temperature and the dilution of reactants, but it increased with the propionic acid/formaldehyde ratio; the yield reached 82 mol% at the propionic acid/formaldehyde ratio of 6. The effects of reaction variables such as temperature, concentrations of propionic acid, formaldehyde, water vapor, methacrylic acid, and oxygen, and propionic acid/formaldehyde ratio were examined.

Methacrylic acid (MAA), a raw material of the so-called organic glass, is currently produced by a two step oxidation of isobutene. On the other hand, attempts have been made to form MAA by means of a vapor-phase aldol condensation of propionic acid (PA) with formaldehyde (HCHO) over acidic oxide catalysts.[1-3)]

$$CH_3CH_2COOH + HCHO \longrightarrow CH_2{=}C(CH_3)COOH + H_2O$$

It should be noted that the one-pass yield of MAA did not exceed 39 mol% at the PA/HCHO molar ratio of 2, while acrylic acid was obtained with a high yield of 96 to 98 mol% by the reaction of acetic acid with HCHO.[3-5)] This suggests that the formation of MAA is more difficult than that of acrylic acid, similarly to the case of the partial oxidation of unsaturated aldehydes.

It was recently found that the combination of divanadium (IV) dioxide pyrophosphate [$V_2O_2(P_2O_7)$] with silica gel in the presence of a small amount of phosphoric acid brings about an improved catalytic formation of MAA. In this study, the catalytic performance of the V-Si-P ternary oxide with an atomic ratio of 1 : 2 : 2.2 was investigated.

Experimental

Catalyst. The catalyst used in this study is the V-Si-P ternary oxide with the atomic ratio of 1 : 2 : 2.2 and was prepared as follows. To about 100 ml of hot water containing about 20 ml of lactic acid, 29.5 g of NH_4VO_3 was dissolved, yielding a blue solution of VO^{2+}. Then, 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. Excess water was then evaporated with stirring in hot air current. The cake obtained 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 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 21.3 $m^2 g^{-1}$ and the average oxidation numbers of vanadium ions in the catalyst,[6,7)] was ca. 4.0.

Reaction Procedures. The reaction of PA with HCHO was carried out by a continuous-flow system. Trioxane [$(HCHO)_3$] was used as the source of HCHO. Unless otherwise indicated, the feed rates of PA, HCHO, and nitrogen were 30, 15, and 350 mmol h^{-1}, respectively; the composition was 7.6, 3.8, and 88.6 mol%. Other procedures were the same as those described in the previous studies.[2,3,5)] The contact time was defined as (volume of catalyst)/(flow rate of gaseous feed). The packing density of catalyst was ca. 0.5 g ml^{-1}. The yield (mol%) was defined as 100×(moles of product)/(moles of HCHO fed).

Results

Effect of Temperature. The reaction was conducted by changing both the amount of catalyst and the reaction temperature from 280 to 360 °C. The main products were MAA, propylene, CO_2, and a small amount of CO. The yield of MAA on basis of charged HCHO at five temperatures are shown in Fig. 1 as a function of the contact time.

The yield of MAA increased with the contact time, passed through a broad maximum, and then decreased

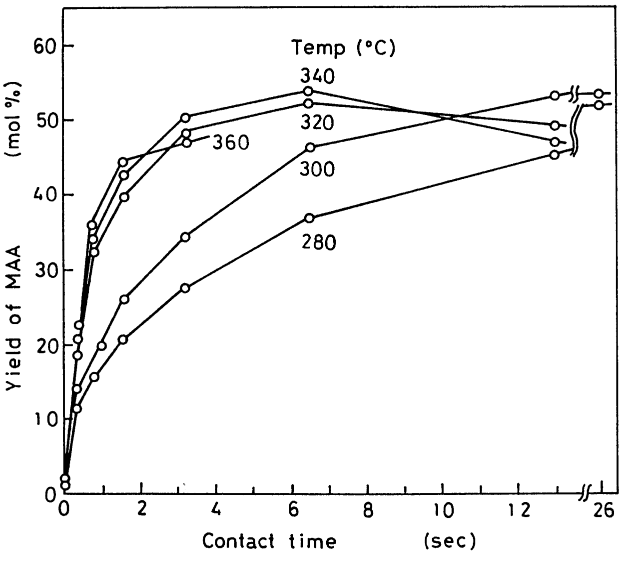

Fig. 1. Effect of the temperature on the yield of MAA.

gradually. The maximum yield of MAA was in the range of 52 to 55 mol% and remained almost unchanged with the change of temperature.

Propylene and CO_2 were the main by-products of the same order of amount. The yields of propylene on the basis of charged HCHO at five temperatures are shown in Fig. 2 as a function of the yield of MAA. The yield of propylene increased markedly with temperature, indicating that the side-reaction is greatly accelerated at elevated temperatures.

Effect of Propionic Acid Concentration. The reaction was conducted at 300 °C by fixing the feed rates of HCHO and nitrogen at 15 and 350 mmol h^{-1}, respectively, while changing the feed rate of PA. The yields of MAA obtained at four different PA/HCHO molar ratios are shown in Fig. 3 as a function of the contact time. The initial rate of MAA formation was almost independent of the PA concentration in the range 3.8 to 22.8, whereas the maximum yield of MAA increased with the PA concentration; the yield reached 82 mol% on basis of charged HCHO at a PA/HCHO molar ratio of 6.

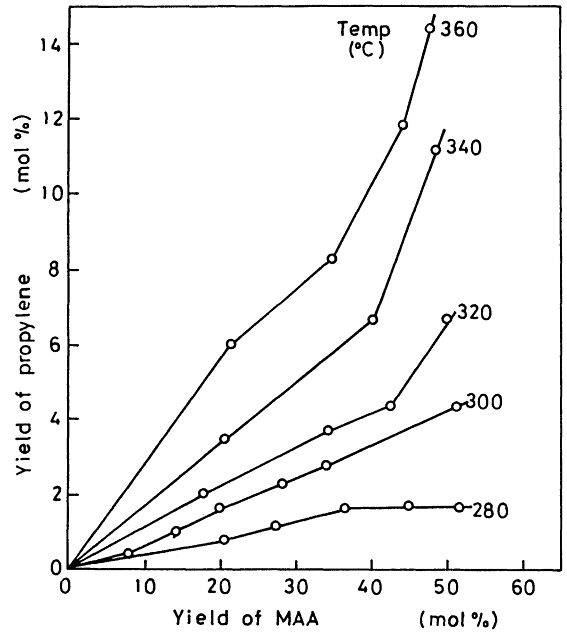

Fig. 2. Effect of the temperature on the yield of propylene.

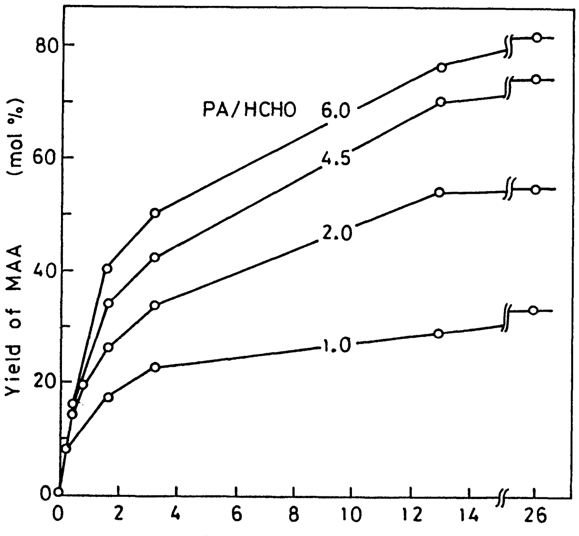

Fig. 3. Effect of the PA/HCHO molar ratio on the yield of MAA. Temperature=300 °C; feed rate of HCHO/nitrogen=15/350 mmol h^{-1}.

The yields of propylene obtained at four different PA/HCHO molar ratios are shown in Fig. 4 as a function of the yield of MAA. The yield of propylene decreased clearly with the increase in PA concentration.

The yields of MAA are plotted as a function of the overall conversion of HCHO in Fig. 5. The selectivity of HCHO to MAA, defined as 100×(yield of MAA)/(conversion of HCHO), is given from the slope through the origine. The selectivity increased with

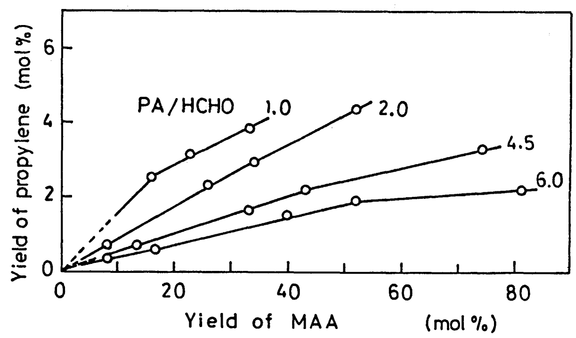

Fig. 4. Effect of the PA/HCHO molar ratio on yield of propylene. Conditions are the same as those for Fig. 3.

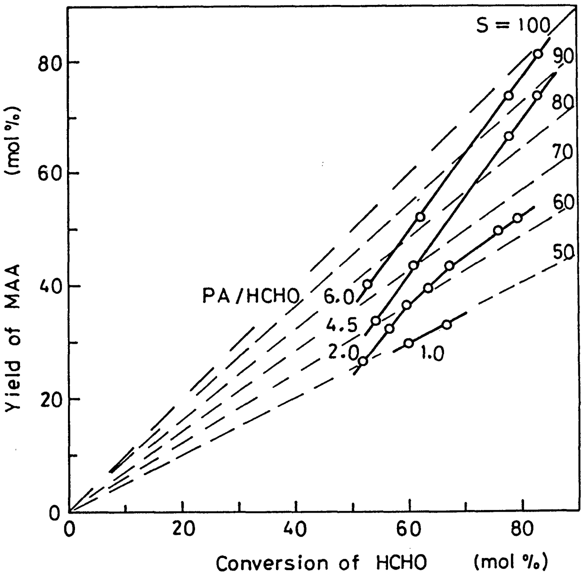

Fig. 5. Yield of MAA as a function of the conversion of HCHO. Conditions are the same as those for Fig. 3. S=selectivity (mol%).

the increase in PA concentration.

Effect of HCHO Concentration. The reaction was conducted with a fixed PA concentration of 7.6 mol% using a 2.5 g portion of catalyst (contact time=1.6 s), while the initial concentration of HCHO changed from 1.0 to 3.8 mol%. The rate of MAA formation obtained at a low HCHO conversion is plotted in Fig. 6 as a function of the HCHO concentration. The rate increased steadily with the HCHO concentration in the range 1.0 to 3.8 mol%.

Effect of Reaction Dilution. The effect of dilution of reactants was examined by changing the concentrations of the two reactants and temperature at the fixed PA/HCHO molar ratio of 2 and using a 20 g portion of catalyst. The maximum yield of MAA remained unchanged with the variation in concentration.

Effect of Water Vapor. The reaction was conducted in the presence of water vapor at 300 °C. The yield of MAA at the contact time of 2 s is plotted in Fig. 7 as a function of the H_2O/HCHO molar ratio. The reaction was retarded by water vapor. It was also found that the yield of MAA does not exceed 45 mol% at the PA/HCHO molar ratio of 2 and H_2O/HCHO molar ratio of ca. 3.

Effect of Methacrylic Acid. The reaction was conducted in the presence of MAA at 300 °C. Figure 8 shows the yield of MAA obtained at the contact time of 2 s as a function of the MAA/HCHO molar ratio. The reaction was retarded also by MAA.

Stability and Regeneration of Catalytic Activity. The stability of catalytic activity was checked at 300 °C using a 20 g portion of catalyst (contact time=ca. 15 s) at the feed rate of PA : HCHO : nitrogen=67.5 : 15 : 350 mmol h^{-1}. The change in the yield of MAA is shown in Fig. 9 as a function of the elapsed time-on-stream (open symbols with solid line). The activity was relatively stable at temperatures about 300 °C.

The catalyst deactivated during the reaction was regenerated completely by a heat-treatment at about 350 °C for 2 h in a stream of air.

In order to reoxidize the catalyst and, as a result, to avoid the deactivation, a small amount of oxygen was added into the feed. The feed rate of PA : HCHO : oxygen : nitrogen was 67.5 : 15 : 6 : 350

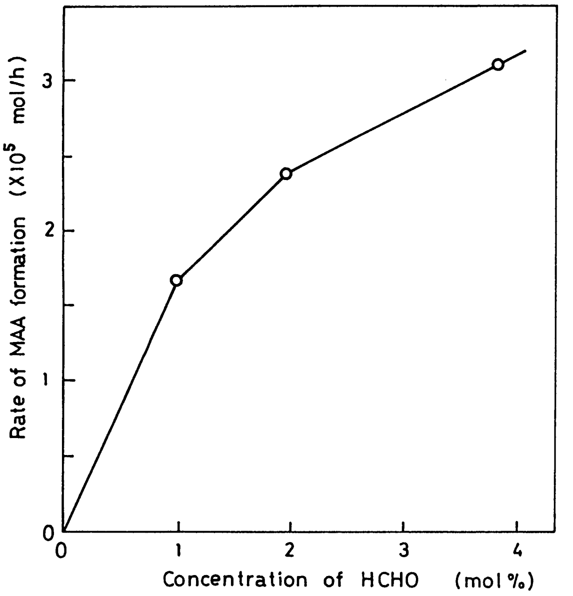

Fig. 6. Effect of the HCHO concentration on the rate of MAA formation. Temperature=300 °C; PA concentration=7.6 mol%.

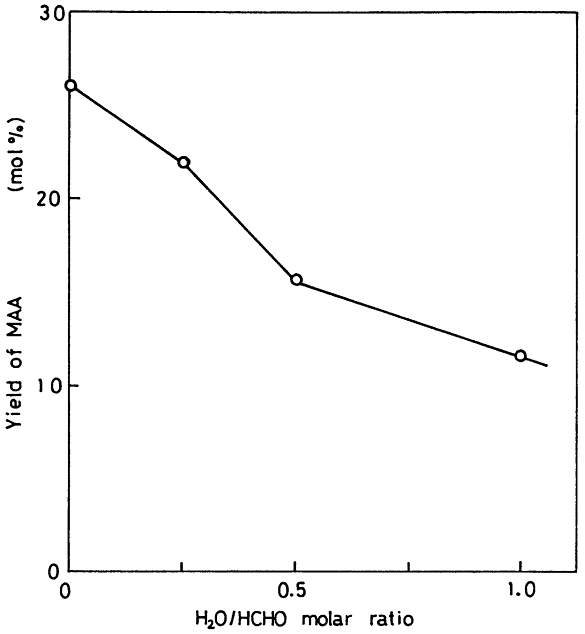

Fig. 7. Effect of the water vapor present in the feed on the yield of MAA. Temperature=300 °C; contact time=2 s.

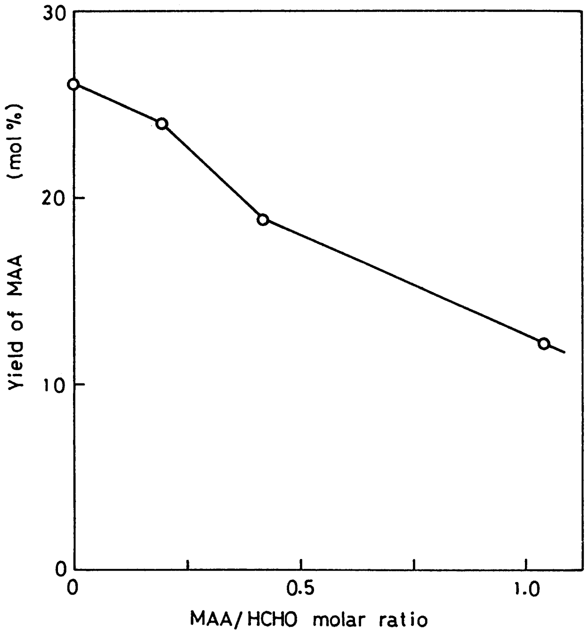

Fig. 8. Effect of the MAA present in the feed on the yield of MAA. Temperature=300 °C; contact time=2 s.

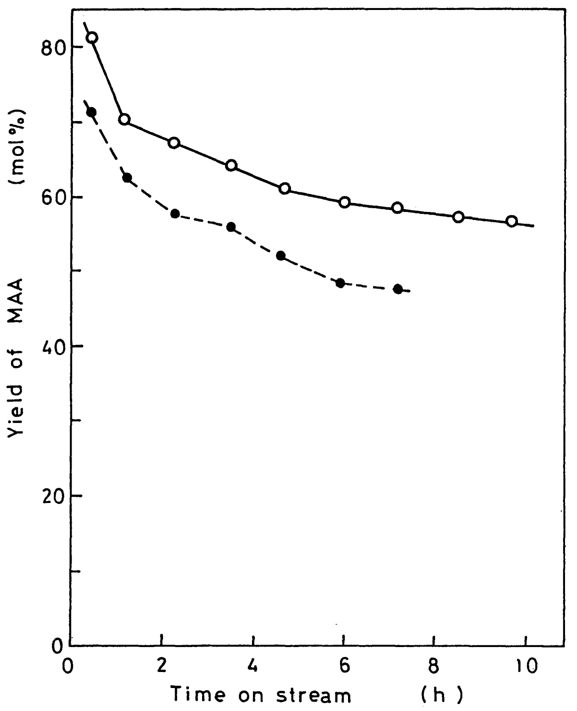

Fig. 9. Stability of catalytic activity. Temperature=300 °C; contact time=15 s; feed rate, PA/HCHO/nitrogen=67.5/15/350 mmol h^{-1} (○); PA/HCHO/oxygen/nitrogen=67.5/15/6/350 mmol h^{-1} (●).

mmol h^{-1} and the amount of catalyst used was 20 g. The results are shown in Fig. 9 (blocked symbols with dashed line). The addition of oxygen did not suppress the deactivation of catalyst, but it caused marked formation of CO_2. Therefore, the addition of oxygen is unsuitable.

Discussion

The fact that the yield of MAA does not exceed a certain level by the increase in the contact time suggests that the reaction is limited by the reaction equilibrium. In order to check the possibility of the reverse reaction, an equimolar mixture of MAA and water was passed over the catalyst at the contact time of 15 s. However, no PA was detected in the product even at 340 °C. This indicates that the reverse reaction does not occur under these conditions and that the yield of MAA is not limited by the reaction equilibrium. Therefore, it is likely that the yield of MAA is limited by retardation with the products such as MAA and water.

PA and MAA are relatively stable over V-P-based oxides under the reaction conditions used; moreover, propylene is not formed by the decomposition of these compounds,[2,8] although isobutyric acid is decomposed to propylene, CO, and water over acidic catalysts.[9] It should be noted that the amounts of propylene and CO_2 are of almost the same order of magnitude. Therefore, it seems that propylene and CO_2 are formed by the decomposition of intermediate compounds formed in the reaction between PA and HCHO. For example:

$$CH_3CH_2COOH + HCHO \longrightarrow [CH_2(OH)CH(CH_3)COOH]$$

$$\longrightarrow \begin{cases} CH_2{=}C(CH_3)COOH + H_2O \\ CH_2{=}CHCH_3 + CO_2 + H_2 \end{cases}$$

As is seen in Fig. 2, the side reaction to form propylene and CO_2 is accelerated greatly over the formation of MAA with an elevation of temperature, suggesting that the activation energy for C-C bond fission is greater than that for dehydration.

It is interesting that the formation of propylene and CO_2 is greatly suppressed by an increase in the concentration of PA relative to that of HCHO (Fig. 4). The sites which serve to promote the C-C bond fission are possibly blocked selectively by PA.

The addition of a small amount of oxygen to the feed served to suppress the catalyst deactivation in the reaction of acetic acid with HCHO.[5] On the other hand, in the reaction of PA with HCHO, the addition of oxygen is not effective. This may be ascribed to the difference in the reactivity between acrylic acid and MAA; oxygen serves to reoxidize the reduced catalyst in the reaction with acetic acid, but oxygen is consumed in oxidizing MAA rather than in reoxidizing the catalyst.

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