The Effects of the Reaction Variables on the Yields of Acrylic Acid and Methyl Acrylate in the Reaction of Acetic Acid with Methanol in the Presence of Oxygen

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The effects of the reaction variables on the yields of the aldol condensation products, i.e., acrylic acid and methyl acrylate, in the reaction of acetic acid with methanol in the presence of gaseous oxygen was studied using a V–Ti–P ternary oxide catalyst with an atomic ratio of 1:2:6, respectively. The best catalyst performance was obtained with an oxygen/methanol molar ratio of between 0.5 to 0.75. The yield of acrylic acid decreased with increasing the methanol concentration, while that of methyl acrylate increased; the sum of the two yields increased with methanol concentration above 360 °C. The feed rate did not have much effect on the yield, except at high conversions. Better catalytic performance was observed with longer contact times at lower temperatures than with shorter contact times at higher temperatures.

It is well-known that acetic acid and methanol react over solid-acid catalysts to form methyl acetate by esterification. Recently, it has also been reported that acrylic acid and methyl acrylate are obtained with a high selectivity by vapor phase aldol condensation of formaldehyde (HCHO) with acetic acid and methyl acetate, respectively, over vanadium phosphate and vanadium–titanium binary phosphate; V–P binary and V–Ti–P ternary oxide, catalysts.[1–4] When a mixture of acetic acid and methanol is passed over these catalysts in the presence of gaseous oxygen, a part of methanol is oxidized to HCHO which subsequently reacts with acetic acid and methyl acetate to form acrylic acid and methyl acrylate, respectively.[5,6] The reaction involves the following oxidation, condensation, and esterification.[6]

$$CH_3OH + 0.5\,O_2 \longrightarrow HCHO + H_2O$$

$$CH_3COOH + HCHO \longrightarrow CH_2{=}CHCOOH + H_2O$$

$$CH_3COOCH_3 + HCHO \longrightarrow CH_2{=}CHCOOCH_3 + H_2O$$

$$CH_3COOH + CH_3OH \rightleftarrows CH_3COOCH_3 + H_2O$$

$$CH_2{=}CHCOOH + CH_3OH \rightleftarrows CH_2{=}CHCOOCH_3 + H_2O$$

In order to improve the yields of the aldol condensation products, i.e., acrylic acid and methyl acrylate, and also for better understanding of this reaction, we investigated the effects of the reaction variables on the yields, since no detailed information about this reaction has yet been reported.

Experimental

Catalyst. The catalyst used in this study was a V–Ti–P ternary oxide catalyst with an atomic ratio of 1:2:6, respectively, and prepared as follows. To 500 ml of chilled water, 0.166 mol (about 20 ml) of $TiCl_4$ was added dropwise. The solution was diluted with ca. 5 l of water, then dilute aqueous ammonia was added giving an precipitate of titanium hydroxide (final pH, 8 to 9). This precipitate was washed with water about 10 times by decantation, and then filtered, yielding a paste-like hydroxide gel. To about 200 ml of water containing 50 ml of lactic acid, 9.7 g of NH_4VO_3 was added. The mixture was warmed slowly, yielding a clear blue solution of VO^{2+}. The titanium hydroxide gel was mixed with 57 g of 85% H_3PO_4 yielding a white sticky syrup. The sticky syrup was mixed with the blue solution of VO^{2+}. Excess water was then evaporated with stirring by hot-air blow, yielding a light blue cake. This cake was dried in an oven for 6 h by gradually heating from 50 to 200 °C. The resulting solid was calcined at 300 °C for 6 h in a stream of air, then ground and sieved to a 8- to 20-mesh size. Finally, it was calcined again at 450 °C for 6 h in a stream of air.

The specific surface area of the catalyst was 36 $m^2\,g^{-1}$ and the average oxidation numbers of vanadium ions in the fresh and used catalyst were 4.1 and 3.8, respectively.

Reaction Procedures. The reaction of acetic acid and methanol was carried out with a continuous-flow system. The reactor was made of a steel tube of 50 cm long and 1.8 cm i.d. which was placed vertically and immersed in a lead bath. The amount of catalyst used was fixed at 20 g. A mixture of nitrogen and oxygen was fed in from the top of the reactor. The feed rate of nitrogen was fixed at 140 ml (at 20 °C) min^{-1} (ca. 350 mmol h^{-1}). A mixture of acetic acid and methanol was introduced into the preheating section of the reactor by means of a syringe pump. Unless otherwise indicated, the feed rates of acetic acid, methanol, oxygen, and nitrogen were 25, 50, 25, 350 mmol h^{-1}; the space velocity (SV) was about 300 h^{-1}. The procedures for product recovery and analysis were the same as those described previously.[6]

The yield (mol%) was defined as 100× (moles of product)/(moles of acetic acid fed). The selectivity of acetic acid to the condensation products was defined as 100× (yields of acrylic acid+methyl acrylate)/(conversion of acetic acid−yield of methyl acetate), since the previous study[6] showed that the esterification of acetic acid with methanol was sufficiently rapid and, as a result, methyl acetate was

almost in an equilibrium with acetic acid and methanol.

Results and Discussion

Performance of V-Ti-P Oxide Catalyst. The reaction was conducted at a temperature from 320 to 400 °C. The main products were acrylic acid, methyl acrylate, methyl acetate, and HCHO. The yields of these products and unreacted acetic acid and the selectivity of acetic acid to the aldol condensation products are shown in Fig. 1.

The yields of acrylic acid and methyl acrylate attained 45 and 20 mol%, respectively, with the selectivity of 89 mol% at 390 °C. The selectivity was held almost 100 mol% until the sum of the yields attained 35 mol%. However, with further increae in the yields at higher temperatures, the selectivity fell markedly.

Effect of Oxygen Concentration. The reaction was conducted by fixing the feed rates of acetic acid, methanol, and nitrogen at 25, 50, and 350 mmol h^{-1}, respectively, while changing the oxygen/methanol molar ratio from 0.30 to 1.0. The yields of acrylic acid and methyl acrylate obtained at 335, 345, 355, 365, and 375 °C are shown in Fig. 2. As the oxygen concentration increased, the yield of acrylic acid increased until it reached about 50 mol%. The formation of methyl acrylate decreased with oxygen

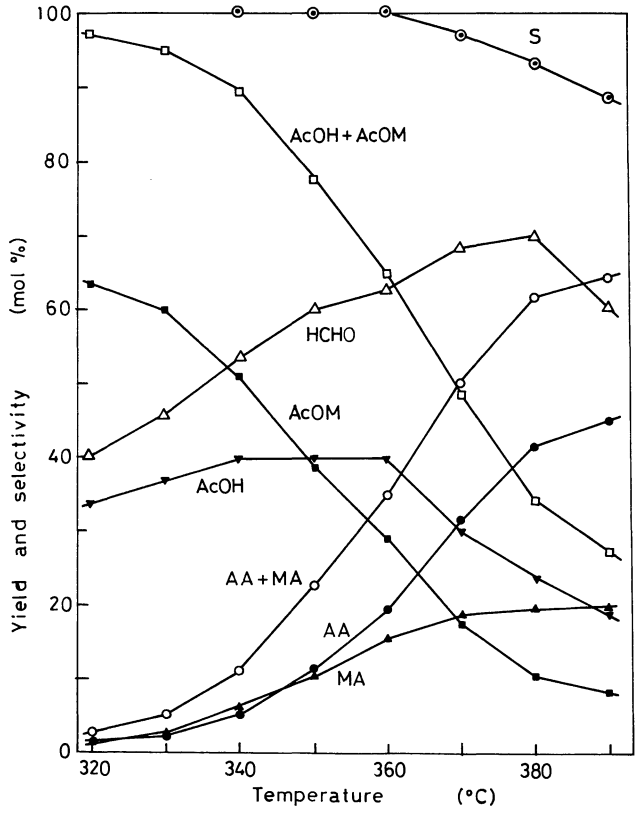

Fig. 1. Performance of the V/Ti/P=1/2/6.0 oxide catalyst. (●) AA, acrylic acid; (▲) MA, methyl acrylate; (○) AA+MA, acrylic acid plus methyl acrylate; (▼) AcOH, acetic acid; (■) AcOM, methyl acetate; (□) AcOH+AcOM, acetic acid plus methyl acetate; (△), HCHO, formaldehyde; (⊙) S, selectivity of acetic acid to acrylic acid plus methyl acrylate.

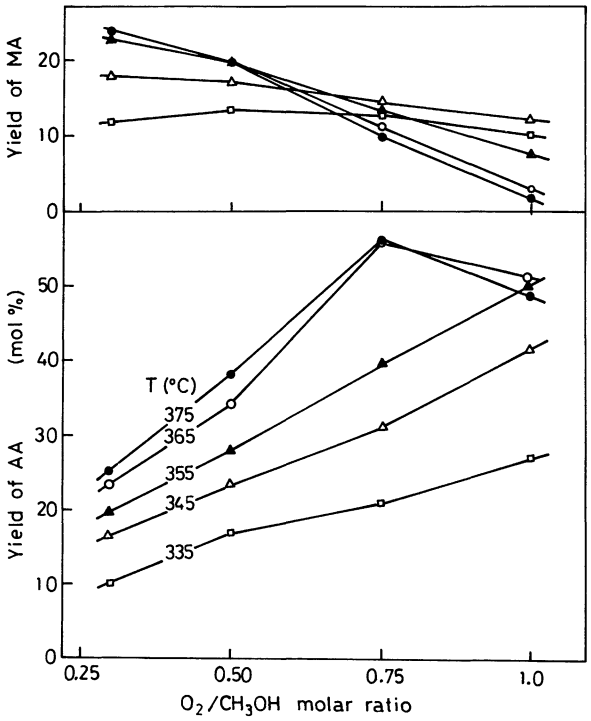

Fig. 2. Effect of the oxygen concentration on the yields of acrylic acid and methyl acrylate. Abbreviations are the same as those for Fig. 1.

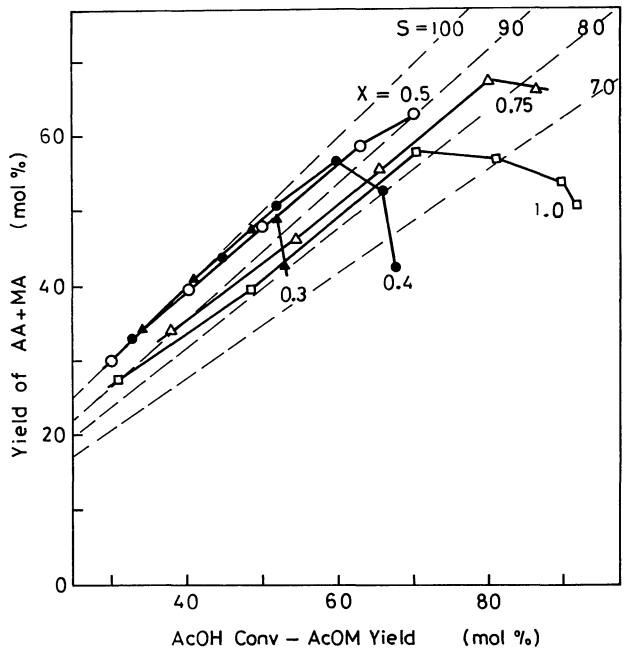

Fig. 3. Effect of the oxygen concentration on the selectivity. X=oxygen/methanol molar ratio. Abbreviations are the same as those for Fig. 1.

concentration, and the extent of the decrease became greater at higher temperatures. These findings indicate that the methyl acrylate formed initially is hydrolyzed to acrylic acid and methanol as the extent of methanol consumption increases.

The sum of yields of acrylic acid and methyl acylate obtained with different oxygen/methanol ratios is plotted as a function of [(conversion of acetic acid)−(yield of methyl acetate)] in Fig. 3. The extent of reaction was varied by changing the temperature from 300 to 380 °C. The selectivity of acetic acid to the aldol condensation products is given as the slope. When the oxygen/methanol ratio was lower than 0.5, the selectivity was about 95 mol% at a low extent of the reaction. However, at a higher extent of the reaction, the yield fell markedly due to lack of HCHO. On the other hand, when the oxygen/methanol ratio was more than 0.75, the selectivity decreased, suggesting that the consecutive oxidation of the acrylic acid once formed was promoted by oxygen. The highest yield of the aldol condensation products was thus obtained with an oxygen/methanol ratio of 0.75.

Effect of Methanol Concentration. The reaction was conducted by fixing the feed rates of acetic acid, oxygen, and nitrogen at 25, 25, and 350 mmol h^{-1}, respectively, while changing the methanol/acetic acid molar ratio from 1.07 to 2.74. The yields of acrylic acid and methyl acrylate obtained at different reaction temperatures from 320 to 380 °C are shown in Fig. 4. The sums of the two yields are also shown in Fig. 5.

As the methanol concentration increased, the yield of acrylic acid decreased, while that of methyl acrylate varied in a complicated manner. When the methanol concentration was low, the yield of methyl acrylate decreased with an increase in the reaction temperature, but when the methanol concentration was high, the yield increased with the temperature. The sum of the two yields increased as the methanol/acetic acid ratio increased up to 1.8, when the temperature was above 360 °C. The highest yield in the aldol condensation

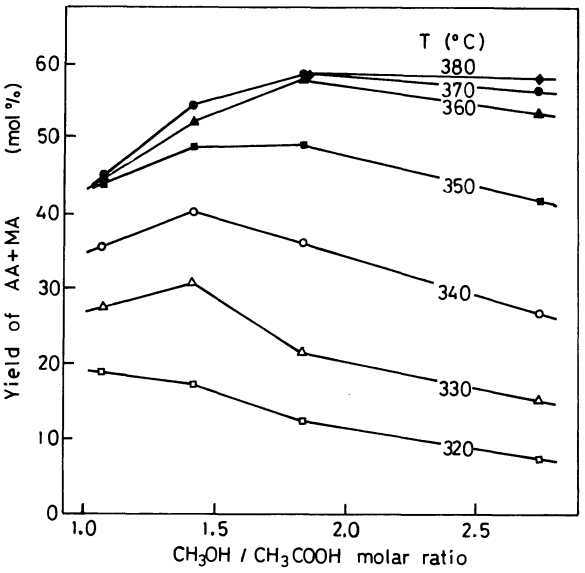

Fig. 5. Effect of the methanol concentration on the sum of yields of acrylic acid and methyl crylate. Abbreviations are the same as those for Fig. 1.

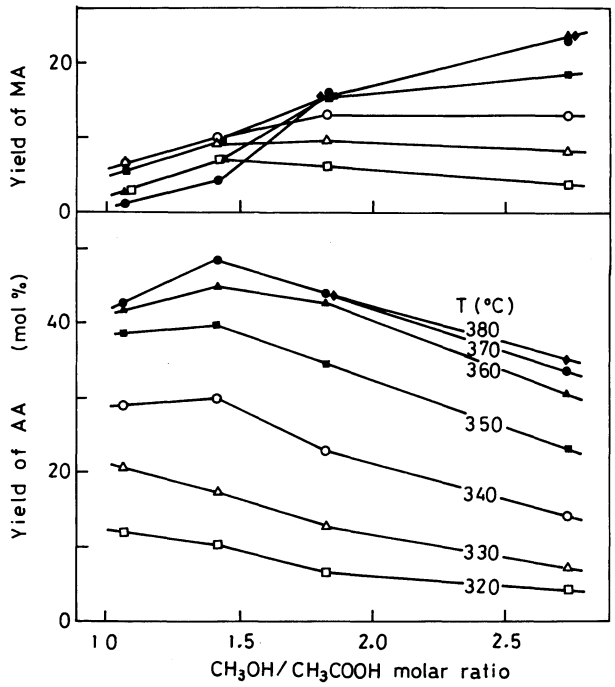

Fig. 4. Effect of the methanol concentration on the yields of acrylic acid and methyl acrylate. Abbreviations are the same at those for Fig. 1.

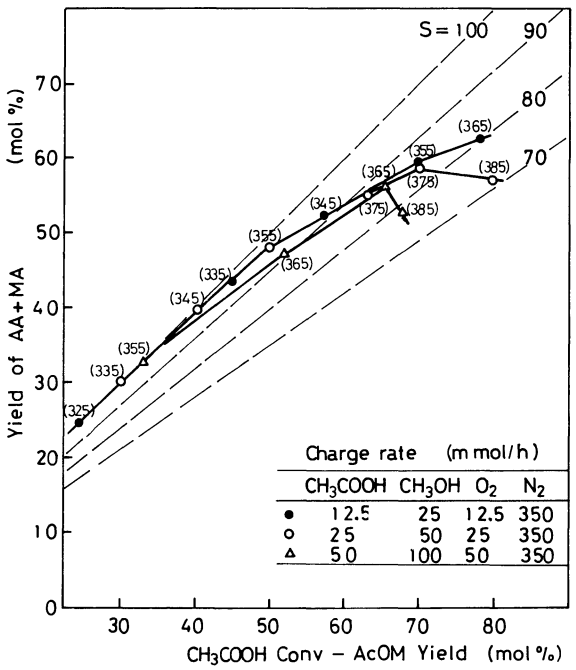

Fig. 6. Effect of the feed rate on the selectivity. The reaction temperatures are shown in parentheses. Abbreviations are the same as those for Fig. 1.

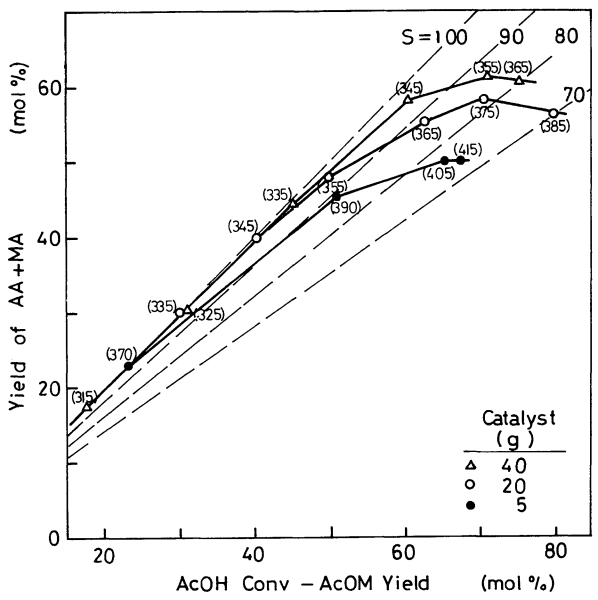

Fig. 7. Effect of the cintact time on the selectivity. The reaction temperatures are shown in parentheses. Abbreviations are the same as those for Fig. 1.

products was obtained with a molar ratio of around 2. Thus, it appears that the aldol condensation of acetic acid with HCHO is retarded by methanol, and that the methyl acrylate formed initially is hydrolyzed to acrylic acid and methanol as both the extent of the reaction and the consumption of methanol become greater.

Effect of Feed Rate. The reaction was conducted at a fixed acetic acid/methanol/oxygen molar ratio of 1/2/1, while changing the feed rate. The sum of the yields of acrylic acid and methyl acrylate obtained at a temperature from 325 to 405 °C are plotted as a function of [(conversion of acetic acid)−(yield of methyl acetate)] in Fig. 6. The feed rate did not have much effect on the yield when the extent of the reaction was not high; the sum of the two yields was below 60 mol%. However, when the extent of the reaction as higher, the yield decreased as the feed rate increased.

Effect of Contact Time. The effect of the contact time was studied by changing the amount of catalyst used from 5 to 40 g, while the other conditions were fixed as those described under Experimental. The sum of the two yields obtained at temperatures from 315 to 515 °C are shown in Fig. 7. The catalytic performance obtained with a long contact time at a low temperature was better than that obtained at a short contact time at a high temperature. Possibly, the consecutive oxidation of the acrylic acid formed is enhanced at high temperatures.

Conclusion

(1) Over a V–Ti–P ternary oxide catalyst with an atomic ratio of 1:2:6, the yields of acrylic acid and methyl acrylate attain 45 and 20 mol%, respectively, with a selectivity of 89 mol% based on acetic acid. The selectivity is almost 100 mol% provided the sum of the two yields does not exceed 35 mol%.

(2) At a low conversion, the main products are methyl acetate and HCHO. As the reaction proceeds and as methanol is consumed, both methyl acetate and methyl acrylate formed are hydrolyzed to the corresponding acids and methanol.

(3) The best catalytic performance is obtained with an oxygen/mthanol molar ratio between 0.5 and 0.75, and the yield of acrylic acid relative to that of methyl acrylate increases with an increase in the oxygen concentration.

(4) As the methanol concentration increases, the yield of acrylic acid decreases, while that of methyl acrylate increases. The sum of the two yields decreases with the methanol concentrtion at low temperatures (below 320 °C), but it increase at higher temperatures above 360 °C.

(5) The effect of the feed rate on the yield is small except at high conversion of acetic acid.

(6) A better catalytic performance is observed with a long contact time at a low temperature than with a short contact time at a high temperature.

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