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Vapor-Phase Reaction of Methanol with Methyl Acetate and Acetic Acid in the Presence of Oxygen

MAMORU AI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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Vapor-phase reactions of methanol with methyl acetate and acetic acid in the presence of gaseous oxygen were studied using a binary phosphate catalyst with a V/Ti/P atomic ratio of 1/2/5.2. In the presence of gaseous oxygen, methyl acetate itself undergoes hydrolysis to methanol and acetic acid, then the produced methanol is oxidized promptly to formaldehyde, and finally the formaldehyde reacts with acetic acid and methyl acetate. The yields of acrylic acid and methyl acrylate attained 21 and 13 mol%, respectively, at 330°C with SV = ca. 310 h^{-1}. In the presence of an excess of oxygen, the sum of the yields of acrylic acid and methyl acrylate was almost the same, whether one of the reactants was formaldehyde or methanol, and whether methanol was fed in with methyl acetate or acetic acid. It was found that the oxidation of methanol and the esterification–hydrolysis proceed much more promptly than the aldol condensations. In the reaction of methanol with acetic acid at 350°C with a feed rate of $CH_3COOH/CH_3OH/O_2/N_2$ = 19/38/25/350 mmol/h (SV = ca. 340 h^{-1}), the yields of acrylic acid and methyl acrylate attained 42 and 13 mol% (based on the charged acetic acid), respectively, and the selectivity of acetic acid to the condensation products was about 73 mol%.

INTRODUCTION

Acrylic acid and methyl acrylate are widely used in the manufacture of various resins and polymers. Acrylic acid is currently produced by a two-step oxidation of propylene. On the other hand, attempts have also been made to form acrylic acid by means of a vapor-phase aldol condensation of formaldehyde (HCHO) with acetic acid,

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

As regards the catalysts, both acidic and basic compounds have been claimed in patents to be useful, for example, alkali and alkaline earth metal hydroxides or oxides (*1–3*), alkali and alkaline earth metal phosphates (*4*), V–P oxides prepared in an organic medium (*5*), and multicomponent oxides containing phosphorus (*6*). In addition to the patent information, only a few scientific reports (*7, 8*) have been published. Recently, $(VO)_2P_2O_7$–TiP_2O_7 binary pyrophosphates have been found to be effective as catalysts for this reaction (*9*).

It is known that methyl acrylate is obtained by a vapor-phase aldol condensation of HCHO with methyl acetate over the same catalysts as those used in the reaction of HCHO with acetic acid,

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

On the other hand, Fernholz and Wunder (*10*) have disclosed the preparation of methyl acrylate by oxidation of methanol to HCHO and subsequent condensation of methyl acetate with the produced HCHO in a single stage using TiO_2–V_2O_5–H_3PO_4 catalysts. Interestingly, Niizuma *et al.* (*11*) have claimed that acrylic acid but not methyl acrylate is obtained in the reaction of methyl acetate in the presence of gaseous oxygen over TiO_2–P_2O_5-based catalysts.

In this study, we investigated the reactions of methanol with methyl acetate and

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acetic acid in the presence of gaseous oxygen using a binary phosphate catalyst.

EXPERIMENTAL

Catalyst

The catalyst used in this study was a binary phosphate with a V/Ti/P atomic ratio of 1/2/5.2; the amount of phosphorus was slightly in excess with respect to $(VO)_2P_2O_7$–$4TiP_2O_7$ (V/Ti/P = 1/2/5.0). It was prepared as follows. A fine powder of V–P oxide (P/V atomic ratio = 1.1) prepared in an organic medium according to the method of Katsumoto and Marquis (*12*) was kneaded with ethylene glycol. The paste thus obtained was then mixed with a paste-like titanium hydroxide gel prepared by hydrating $TiCl_4$ with ammonia in an aqueous medium, then washing about 10 times with water by decantation, and filtering. The mixture was stirred to achieve complete mixing and then the required amount of 85% H_3PO_4 was added to the mixture. Excess water was evaporated off with vigorous stirring by means of hot air current, yielding a gray cake. The obtained cake was evaporated again in an oven at 150°C for 6 h and at 200°C for 6 h. The resulting solid was first calcined at 300°C for 6 h in a stream of air; then it was broken up and sieved to an 8- to 20 mesh size. Finally, it was calcined again at 450°C for 6 h in a stream of air.

X-ray diffraction analysis showed that the catalyst is amorphous. The specific surface area measured by the BET method using nitrogen at −196°C was 23.8 m^2/g. The average oxidation numbers of vanadium ions in the fresh catalyst and in that used for vapor-phase aldol condensation of HCHO with acetic acid in a nitrogen atmosphere were 4.32 and 3.86, respectively.

Reaction Procedures

The reactions were carried out with a continuous-flow system. The reactor was made of a steel tube, 50 cm long and 1.8 cm i.d., mounted vertically and immersed in a lead bath. The amount of catalyst used was 20 g. Nitrogen or a mixture of nitrogen and oxygen was fed in from the top of the reactor with a fixed rate of 140 ml (at 20°C)/min (ca. 350 mmol/h) and liquid reactants were introduced into the preheating section of the reactor by means of a micro-liquid-feeder.

The effluent gas from the reactor was led into four chilled water-scrubbers to recover the water-soluble compounds. After 1 h time-on-stream, the contents of the water-scrubbers were collected (120 ml). The products were analyzed by gas chromatographs; a 1-m column of molecular sieve 13X for CO; a 6-m column of propylene carbonate for CO_2; a 2-m column of PEG 20 *M* at 100°C for aldehydes, ethers, esters, and alcohols; and a 1-m column of SP-1200 + H_3PO_4 at 100°C for acids. HCHO was analyzed by iodometry.

RESULTS

Reaction of Methyl Acetate with HCHO in the Absence of Oxygen

As a source of HCHO, trioxane was employed. A mixture of methyl acetate and trioxane was introduced, together with the nitrogen carrier gas, into the reactor packed with a 20-g portion of the catalyst. The feed rate was $CH_3COOCH_3/HCHO/N_2 = 24/24/350$ mmol/h (SV = ca. 320 h^{-1}).

The main products obtained at a temperature from 280 to 360°C were methyl acrylate, acrylic acid, acetic acid, methanol, dimethyl ether, and carbon oxides. The yield is defined as 100 · (moles of product or unreacted reactant)/(moles of methyl acetate fed in). The yields of these products and unreacted reactants are shown in Fig. 1.

The yields of methyl acrylate and acrylic acid attained 35 and 14 mol%, respectively, at 330°C. The sum of the yields of methyl acrylate, acrylic acid, and acetic acid was approximately in accord with the consumption of methyl acetate, indicating that the loss of methyl acetate is small under these reaction conditions. However, with a fur-

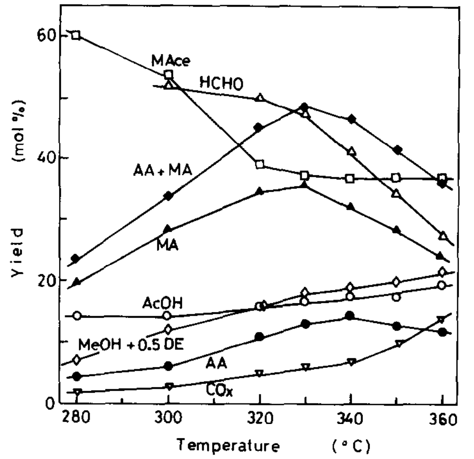


FIG. 1. Reaction of methyl acetate with HCHO in the absence of oxygen. (□) MAce, methyl acetate; (△) HCHO, formaldehyde; (●) AA, acrylic acid; (▲) MA, methyl acrylate; (♦) AA + MA, acrylic acid plus methyl acrylate; (○) AcOH, acetic acid; (◇) MeOH + 0.5 De, methanol plus 0.5 dimethyl ether; (▽) CO_x, carbon oxides.

ther elevation of the temperature, the yields of methyl acetate and acrylic acid fell.

Reaction of Methyl Acetate in the Presence of Oxygen

Methyl acetate was passed over a 20-g portion of the catalyst in the presence of gaseous oxygen. The feed rate was CH_3 $COOCH_3/O_2/N_2$ = 22/15/350 mmol/h (SV = ca. 310 h^{-1}). A marked consumption of methyl acetate was observed at temperatures above 260°C. The main products were acetic acid, acrylic acid, methyl acrylate, HCHO, methanol, dimethyl ether, and carbon oxides. The yield is defined as 100 · (moles of product or unreacted reactant)/(moles of methyl acetate fed in). The yields of these products and unreacted reactant are shown in Fig. 2.

The yields of acrylic acid and methyl acrylate attained 21.5 and 13 mol%, respectively, and the sum was 34.5 mol%. The selectivity of methyl acetate to the condensation products, defined as 100 · (CH_2=CHCOOH + CH_2=$CHCOOCH_3$)/(consumed CH_3COOCH_3 − CH_3COOH), remained almost constant at 58 to 60 mol% in the temperature range 280 to 320°C.

Reaction of Methyl Acetate with HCHO in the Presence of Oxygen

A mixture of methyl acetate and trioxane was passed over a 20-g portion of the catalyst at a temperature from 280 to 350°C in the presence of gaseous oxygen. The feed rate was $CH_3COOCH_3/HCHO/O_2/N_2$ = 27.5/15/15/350 mmol/h (SV = ca. 330 h^{-1}). The yield is defined as 100 · (moles of product or unreacted reactant)/(moles of methyl acetate fed in). The yields of main products and unreacted reactants are shown in Fig. 3.

The yields of acrylic acid and methyl acrylate attained 32 and 22 mol%, respectively, and the sum was 54 mol%. The selectivity of methyl acetate to the condensation products, defined as 100 · (CH_2=CHCOOH + CH_2=$CHCOOCH_3$)/(consumed CH_3COOCH_3 − CH_3COOH), remained almost constant at about 75 mol% at temperatures above 310°C. The formation of methanol and dimethyl ether was small, while that of HCHO remained relatively high, indicating that the methanol produced by the hydrolysis is oxidized promptly to HCHO under these conditions.

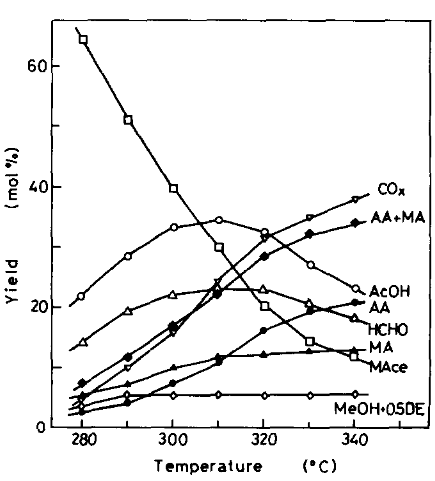


FIG. 2. Reaction of methyl acetate in the presence of oxygen. Symbols are the same as those for Fig. 1.

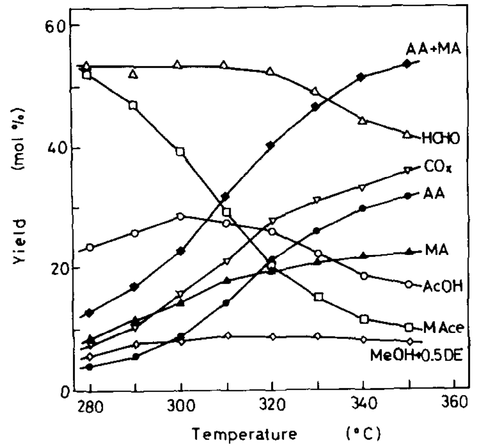


FIG. 3. Reaction of methyl acetate with HCHO in the presence of oxygen. Symbols are the same as those for Fig. 1.

Reaction of Methyl Acetate with Methanol in the Presence of Oxygen

An equimolar mixture of methyl acetate and methanol was passed over a 20-g portion of the catalyst at a temperature from 300 to 370°C in the presence of gaseous oxygen. The feed rate was $CH_3COOCH_3/CH_3OH/O_2/N_2$ = 22/22/10/350 mmol/h (SV = ca. 330 h^{-1}). The yield is defined as 100 · (moles of product or unreacted reactant)/(moles of methyl acetate fed in). The yields are shown in Fig. 4.

The yields of methanol plus ether remained relatively high (30 to 36 mol%), while that of HCHO decreased markedly as the reaction proceeded. The sum of the yields of acrylic acid and methyl acrylate did not exceed 35 mol%. The results suggest that the amount of oxygen is not sufficient.

Therefore, the reaction was carried out again using a larger amount of oxygen. The feed rate was $CH_3COOCH_3/CH_3OH/O_2/N_2$ = 22/22/25/350 mmol/h. The results are shown in Fig. 5.

The results indicate that the presence of an excess of oxygen induces a marked increase in the formation of acrylic acid. Moreover, the yield of HCHO remained relatively high (70 to 80 mol%), while that of methanol plus ether was much lower.

It should also be noted that in the presence of an excess of oxygen, the performance is almost the same whether one of the reactants is HCHO or methanol (Figs. 3 and 5).

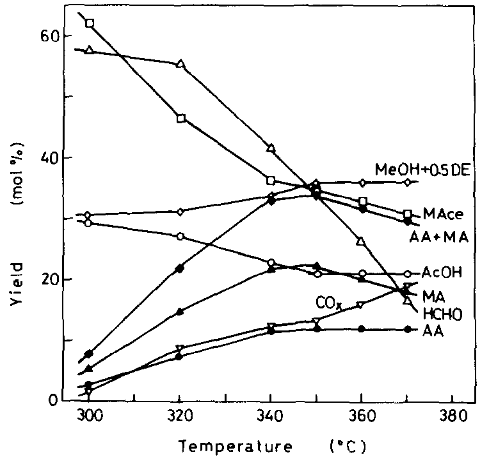


FIG. 4. Reaction of methyl acetate with methanol in the presence of oxygen. The feed rate is $CH_3COOCH_3/CH_3OH/O_2/N_2$ = 22/22/10/350 mmol/h. Symbols are the same as those for Fig. 1.

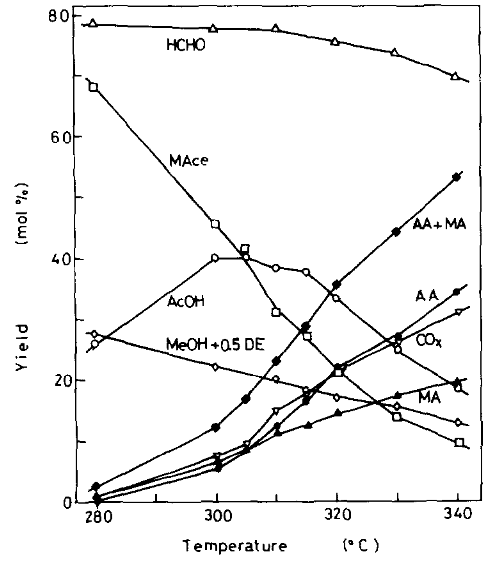


FIG. 5. Reaction of methyl acetate with methanol in the presence of oxygen. The feed rate is $CH_3COOCH_3/CH_3OH/O_2/N_2$ = 22/22/25/350 mmol/h. Symbols are the same as those for Fig. 1.

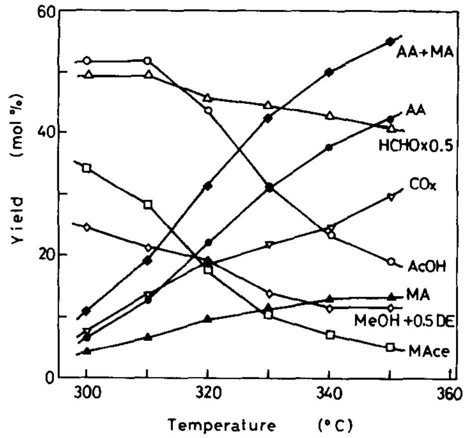


FIG. 6. Reaction of acetic acid with methanol in the presence of oxygen. The feed rate is $CH_3COOH/CH_3OH/O_2/N_2$ = 19/38/25/350 mmol/h. Symbols are the same as those for Fig. 1.

Reaction of Acetic Acid with Methanol in the Presence of Oxygen

A mixture of acetic acid and methanol with a CH_3COOH/CH_3OH molar ratio of 1/2 was passed over a 20-g portion of the catalyst at a temperature from 300 to 350°C. The feed rate was $CH_3COOH/CH_3OH/O_2/N_2$ = 19/38/25/350 mmol/h (SV = ca. 340 h^{-1}). The yield is defined as 100 · (moles of product or unreacted reactant)/(moles of acetic acid fed in). The results are shown in Fig. 6.

The yields of acrylic acid and methyl acrylate attained 42 and 13 mol%, respectively, and the sum was 55 mol%. The selectivity of acetic acid to the condensation products, defined as 100 · ($CH_2{=}CHCOOH + CH_2{=}CHCOOCH_3$)/(consumed $CH_3COOH - CH_3COOCH_3$), was about 74 mol% at temperatures above 320°C.

The sums of the yields of acrylic acid and methyl acrylate were almost the same whether methanol was fed in with methyl acetate or with acetic acid, although the yield of acrylic acid in the reaction with acetic acid was a little higher than that in the reaction with methyl acetate (Figs. 5 and 6).

The reaction was also performed using a smaller amount of oxygen; the feed rate was $CH_3COOH/CH_3OH/O_2/N_2$ = 19/38/10/350 mmol/h. The results are shown in Fig. 7. The amount of unreacted methanol and the formation of methyl acetate were larger, but the yield of acrylic acid was markedly lower. Furthermore, the yield of HCHO decreased as the reaction proceeded. The results also indicate that the presence of an excess of oxygen is required to achieve a good performance in the reaction of acetic acid with methanol.

DISCUSSION

The results obtained in this study show that the V–Ti binary phosphate with a V/Ti/P atomic ratio of 1/2/5.2 is effective as a catalyst for the reactions of methanol with methyl acetate and with acetic acid in the presence of oxygen. The sum of the yields of acrylic acid and methyl acrylate attained 54 mol% based on the charged

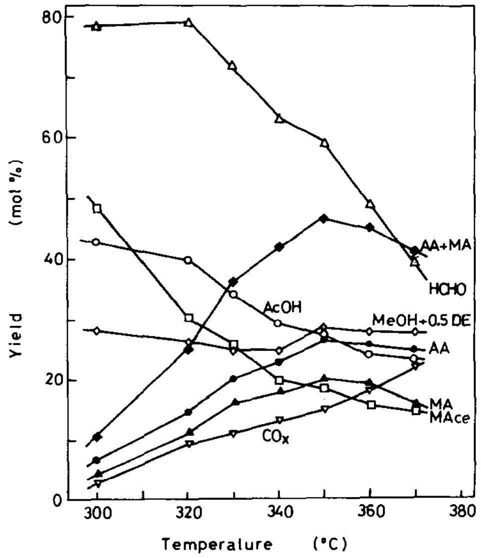


FIG. 7. Reaction of acetic acid with methanol in the presence of oxygen. The feed rate is $CH_3COOH/CH_3OH/O_2/N_2$ = 19/38/10/350 mmol/h. Symbols are the same as those for Fig. 1.

TABLE 1

Comparison of the Performances Obtained with Different Reactants[a]

Reactant feed (mmol/h)	Yields of product[b]				
	MAA	AA	AcOH	HCHO	MeOH + ether
$CH_3COOCH_3/HCHO(24/24)$	34	14	17	(42)	19
$CH_3COOCH_3/O_2(22/15)$	13	21	23	18	5
$CH_3COOCH_3/HCHO/O_2(28/15/15)$	22	29	17	(44)	7
$CH_3COOCH_3/CH_3OH/O_2(22/22/25)$	19	34	18	70	13
$CH_3COOH/CH_3OH/O_2(19/38/25)$	13	38	23	85	11

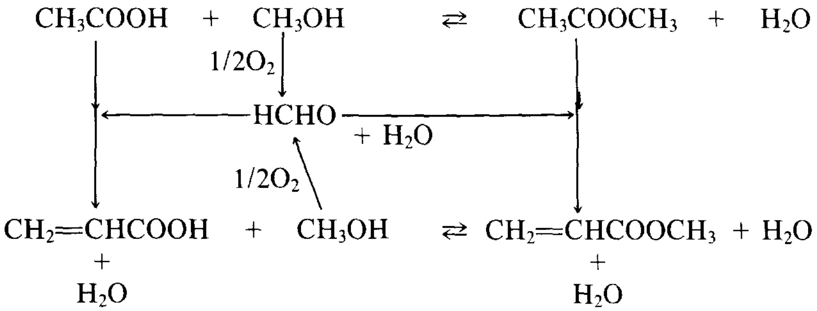
[a] Reaction conditions: $T = 340°C$; SV = 310 to 340 h^{-1}.

[b] Mole percent based on the charged CH_3COOCH_3 or CH_3COOH. MAA, methyl acrylate; AA, acrylic acid; AcOH, acetic acid; MeOH, methanol; ether, dimethyl ether; ( ), unreacted reactant.

methyl acetate or acetic acid, and the selectivity to the condensation products is in the range 74 to 80 mol%.

For the purpose of comparing the performances achieved with five different kinds of reactants, the yields of main products obtained at fixed reaction conditions are listed in Table 1.

It is considered that the reactions proceed through the following pathways,



As may be seen in Fig. 1, in the absence of oxygen, two reactions of methyl acetate, i.e., condensation with HCHO to form methyl acrylate and hydrolysis to form acetic acid and methanol, take place in parallel. It is likely that acrylic acid is formed either by the condensation of acetic acid with HCHO or by the hydrolysis of methyl acrylate, and that dimethyl ether is formed by the dehydration of methanol.

As may be seen in Fig. 2, in the presence of oxygen, the hydrolysis of methyl acetate occurs relatively easily and the produced methanol is oxidized promptly to HCHO.

For comparative purpose, methyl acetate was passed over the same catalyst in the absence of oxygen. Interestingly, the consumption of methyl acetate was small, less than 20%, even at 320°C. Therefore, it may be ensured that the water required to perform the hydrolysis of methyl·acetate is supplied by certain oxidation reactions. Once the hydrolysis occurs, water is also supplied by the condensation reactions with HCHO. Even in the absence of gaseous oxygen, a small amount of oxygen should be supplied by the reduction of the oxide catalyst. This may be the reason why the hydrolysis occurs to a small extent in the absence of gaseous oxygen.

By contrasting Figs. 1 and 3, Figs. 4 and 5, and Figs. 6 and 7, it is evident that the presence of a large amount of oxygen induces a marked increase in the formation of acrylic acid. This may be understood from the view that the presence of a large amount of oxygen promotes the consumption of methanol to form HCHO, which results in an acceleration of the hydrolyses of both methyl acetate and methyl acrylate.

Comparison of the data shown in Figs. 3 and 5 and Figs. 5 and 6 reveals that, in the presence of an excess of oxygen, the sum of the yields of acrylic acid and methyl acrylate is almost the same whether one of the reactants is HCHO or methanol and whether methanol is fed in with methyl acetate or with acetic acid. This may be understood with the view that both the oxidation of methanol and the esterification–hydrolysis are much more rapid than the condensation reactions.

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