JOURNAL OF CATALYSIS **107**, 201–208 (1987)

Vapor-Phase Aldol Condensation of Formaldehyde with Acetic Acid on V_2O_5–P_2O_5 Catalysts

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Received February 4, 1987; revised April 15, 1987

V_2O_5–P_2O_5 binary oxides with P/V atomic ratios from 1.06 to 1.2 were found to be effective as catalysts for the aldol-type condensation of formaldehyde (HCHO) with acetic acid to form acrylic acid. As the source of HCHO, 37% formalin or trioxane was employed. In the case of trioxane, the yield of acrylic acid attained about 98 mol%, based on the charged HCHO with the acetic acid/HCHO molar ratio of 2.5. On the other hand, in the case of formalin, the yield attained about 75 mol%, and methyl acetate and methyl acrylate were also formed by the esterification of the acids with methanol present in the formalin. The main side-reaction is the decomposition of acetic acid to form acetone and CO_2. This side-reaction is greatly accelerated over acrylic acid formation by an elevation of the temperature. The rates of both reactions were found to be inhibited by water vapor. The reactions of HCHO with derivatives of acetic acid, such as methyl acetate and acetaldehyde, were also studied.

INTRODUCTION

Acrylic acid is currently produced by a two-step oxidation of propylene; this process has already been studied relatively well. On the other hand, attempts have also been made to form acrylic acid by means of a vapor-phase aldol-type condensation between formaldehyde (HCHO) and acetic acid:

$$\mathrm{HCHO} + \mathrm{CH_3COOH} \rightarrow \mathrm{CH_2(OH)CH_2COOH} \rightarrow \mathrm{CH_2{=}HCOOH} + \mathrm{H_2O}.$$

This reaction is attractive in view of the utilization of C_1 chemical resources, too.

Vitcha and Sims (*1*) reported that basic oxide catalysts, such as calcium Decalso, a synthetic sodium aluminosilicate cation-exchanged with calcium chloride, are effective as catalysts for this reaction, while acidic oxide catalysts are not suitable. They showed selectivities to acrylic acid from 80 to 100 mol% (based on the charged HCHO), with HCHO conversions from 50 to 60%.

As for the condensation of HCHO with propionic acid or methyl propionate to form methacrylic acid or methyl methacrylate, basic oxide catalysts, such as KOH, CsOH, and Rb_2CO_3, supported on silica gel have been claimed in patents (*2*, *3*) to be useful.

On the other hand, Albanesi and Moggi (*4*) reported that supported Nb_2O_5, Ta_2O_5, and WO_3, which are not basic oxides, are effective as catalysts for the reaction of HCHO with methyl propionate to form methyl methacrylate.

Recently, we found that V_2O_5–P_2O_5 catalysts, which exhibit excellent performance in the oxidation of *n*-butane to maleic anhydride, also perform well in the aldol condensation of HCHO with acetone to form methyl vinyl ketone (*5*). It is interesting to note that the V_2O_5–P_2O_5 binary oxides possessing an enhanced acidic property and, at the same time, a certain basic property (*6*) are effective in promoting the aldol-type condensation reactions.

In this study, we investigated the catalytic behavior of V_2O_5–P_2O_5 oxides in the aldol-type condensation of HCHO with acetic acid and its derivatives.

0021-9517/87 $3.00

EXPERIMENTAL

Catalysts

The V_2O_5–P_2O_5 catalysts with P/V = 0.9 to 2.0 and the V_2O_5–P_2O_5–M_nO_m ternary oxides, where M_nO_m = Nb_2O_5, Co_3O_4, TeO_2, and ZrO_2, are the same as those used in a previous study (*7*). They were prepared according to patented procedures (*8, 9*). Unless otherwise indicated, the catalyst was the V_2O_5–P_2O_5 (P/V = 1.06). The surface area was 23 m^2/g and the packing density was about 0.67 g/cm^3.

Reaction Procedures

The reactions were carried out with a continuous-flow system at atmospheric pressure. 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. Nitrogen was fed in from the top of the reactor with a fixed rate of 140 ml (at 20°C)/min (ca. 0.35 mol/h) as the carrier or the diluent, and a mixture of either 37% formalin or trioxane, $(HCHO)_3$, with acetic acid, methyl acetate, or acetaldehyde was introduced into a preheating section of the reactor by means of a micro-liquid-feeder. Space velocity, expressed as the gaseous volume at room temperature and atmospheric pressure of the total feed per unit hour per unit volume of the catalyst, was about 330 h^{-1} (in the case of the P/V = 1.06 catalyst).

The effluent gas from the reactor was led into two chilled water-scrubbers to recover the water-soluble compounds. At the end of 1 h, the contents of the water-scrubbers were collected (120 ml). The products were analyzed by gas chromatographs: a 1-m column of molecular sieve 13× for CO; a 6-m column of propylene carbonate for CO_2; a 2-m column of PEG 20M at 100°C for aldehydes, esters, and alcohols; and a 1-m column of SP-1200 + H_3PO_4 at 100°C for acids. HCHO was analyzed by the iodometry or the sodium sulfite method (*10*).

RESULTS

Reaction of Formalin with Acetic Acid

As a source of HCHO, formalin, a 37% aqueous solution of HCHO containing about 8% of methanol, was employed. A mixture of acetic acid and formalin in a volumetric ratio of 2 : 1 was introduced, together with the nitrogen carrier gas, into a reactor packed with a 2- to 40-g portion of the V_2O_5–P_2O_5 (P/V = 1.06) catalyst. The feed rate was $CH_3COOH/HCHO/CH_3OH/H_2O/N_2$ = 30.6/12.2/2.2/26.8/350 m mol/h; the composition was 7.26/2.85/0.52/6.35/83.02 mol%.

The main products obtained at a temperature from 300 to 375°C were acrylic acid, carbon oxides, acetone, methyl acetate, and methyl acrylate. The formation of propionic acid, methyl propionate, methyl formate, and acetaldehyde was also detected, but their amounts were negligibly small. Figure 1 shows the yields of the main products (based on the charged HCHO) obtained with a 20-g portion of catalyst (SV = 340 h^{-1}).

The effects of the temperature and the contact time on the yield of acrylic acid were studied by changing both the temperature and the amount of catalyst used (Fig. 2). The yield attains about 75 mol%. The apparent activation energy for the forma-

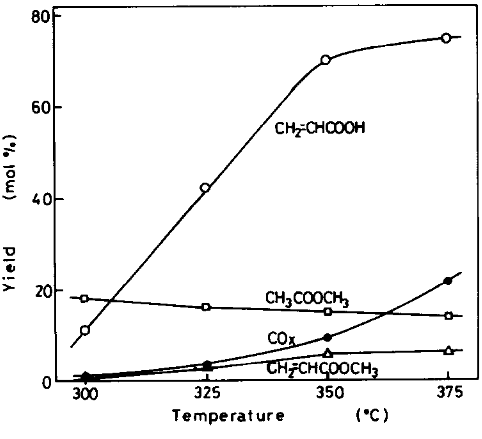

FIG. 1. Reaction of formalin with acetic acid on the V_2O_5–P_2O_5 (P/V = 1.06) catalyst.

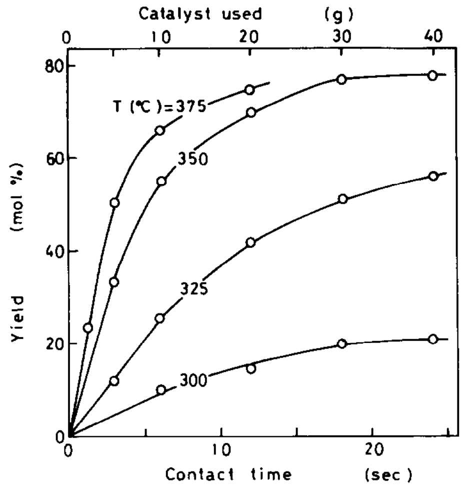

FIG. 2. Effects of the temperature and the contact time on the yield of acrylic acid in the reaction of formalin with acetic acid.

tion of acrylic acid was calculated to be about 25 kcal/mol.

Since the V_2O_5–P_2O_5 oxides possess a redox property, it is predictable that the catalyst tends to suffer from its reduction by the reactants during the condensation reaction. Therefore, the stability of the catalytic activity was examined. The change in the yield of acrylic acid is shown in Fig. 3 as a function of the elapsed time of the reaction (open symbols with solid lines). The activity is relatively stable at temperatures below 350°C, but with a further elevation of the temperature it gradually falls with the time.

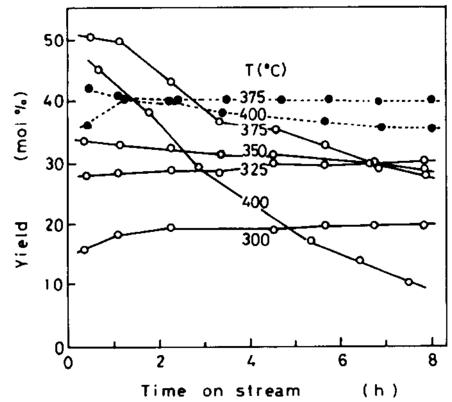

FIG. 3. Stability of the catalytic activity for acrylic acid formation in the reaction of formalin with acetic acid. Amount of catalyst used: 300°C, 30 g; 325°C, 20 g; 350°C, 5 g; 375°C, 5 g; 400°C, 3 g. Open symbols with solid lines, without oxygen; blocked symbols with dotted lines, with 2.2 vol% oxygen.

In order to reoxidize the reduced catalyst and to avoid the deactivation, a small amount (about 2.2 vol%) of oxygen was added to the nitrogen carrier gas. The results are also shown in Fig. 3 (blocked symbols with dotted lines). The stability is markedly improved by the addition of oxygen.

However, the addition of oxygen induces a marked formation of carbon oxides, principally, CO_2. The yields of acrylic acid and carbon oxides obtained with a 10-g portion of catalyst are compared in Fig. 4.

Next, the effects of the reaction variables on the rate of acrylic acid formation were studied. First, the reaction was performed by changing the initial concentration of acetic acid from 1.5 to 11.0 mol%, while keeping the HCHO concentration fixed at 2.85 mol%. Figure 5 shows the yield of acrylic acid (based on the charged HCHO) obtained with a 20-g portion of the catalyst at 325°C as a function of the acetic acid

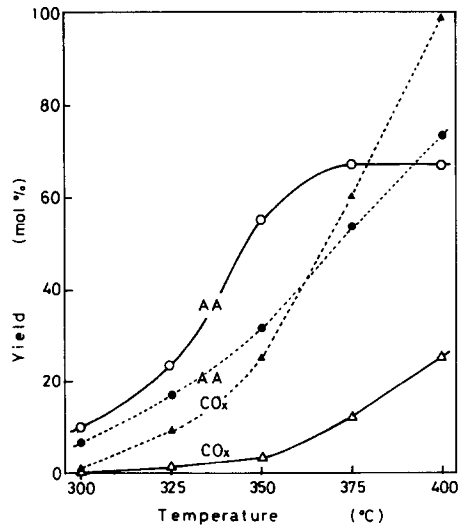

FIG. 4. Effect of the oxygen added on the yields of acrylic acid and carbon oxides. Open symbols with solid lines, without oxygen; blocked symbols with dotted lines, with 2.2 vol% oxygen. AA = acrylic acid. SV = 680 h^{-1}.

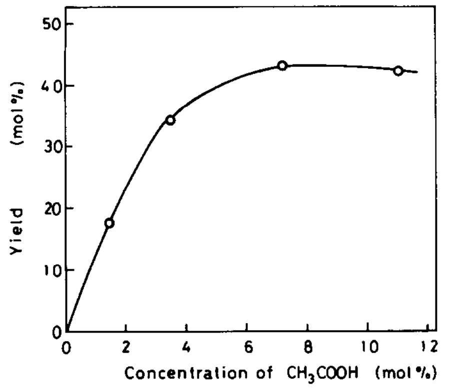

FIG. 5. Effect of the acetic acid concentration on the yield of acrylic acid. Conditions: temperature, 325 °C; HCHO concentration, 2.85 mol%; catalyst, 20 g; SV, 340 h^{-1}.

concentration. The yield increases with the concentration up to about 7 mol%, but it levels off with a further increase in the concentration.

Then, the effect of the HCHO concentrations was studied by changing the initial concentration from 0.86 to 2.85 mol% while keeping the acetic acid concentration fixed at 7.26 mol%, and by using a 5-g portion of the catalyst. Figure 6 shows the rate of acrylic acid formation at 325°C, obtained from the yield held at a low level (less than 20 mol%), as a function of the HCHO concentration. The rate increases with the HCHO concentration up to about 2 mol%, but it levels off with a further increase in the concentration.

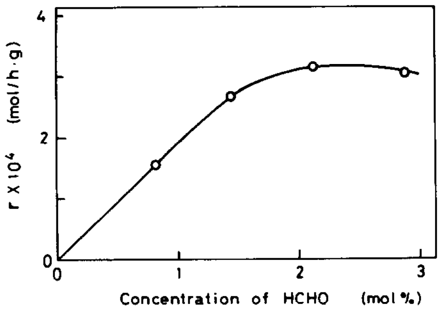

FIG. 6. Effect of the HCHO concentration on the rate of acrylic acid formation. Conditions: temperature, 325°C; acetic acid concentration, 7.26 mol%; catalyst, 5 g; SV, 1360 h^{-1}.

The effect of water vapor was also studied. As a source of HCHO without containing water, trioxane was used. The rate of acrylic acid formation at 325°C obtained with the concentrations of HCHO and acetic acid of 2.85 and 7.26 mol%, respectively, is shown in Fig. 7 as a function of the concentration of water vapor. It is clear that the presence of water vapor decreases the rate markedly.

Reaction of Trioxane with Acetic Acid

The preceding section has revealed that the reaction is hindered by water vapor. Thus, trioxane was used in place of formalin as a source of HCHO. The reaction was conducted with a charge rate of CH_3 $OOH/HCHO/N_2$ = 38.0/17.0/350 m mol/h and a composition of 9.5/4.3/86.2 mol%.

The main products were acrylic acid, carbon oxides, and acetone. The amounts of other products were negligibly small. The yield of acrylic acid was approximately in accord with the consumption of HCHO, as determined by the analysis of the recovered HCHO, though there is some uncertainty in the titration of HCHO for the samples containing a certain amount acetone.

The yields (based on the charged HCHO) of acrylic acid and carbon oxides at differ-

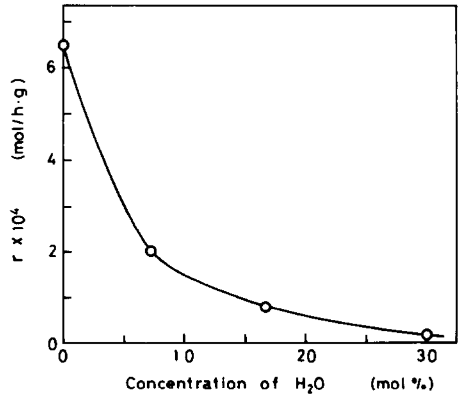

FIG. 7. Effect of the water vapor concentration on the rate of acrylic acid formation. Conditions: temperature, 325°C; HCHO, 2.85 mol%; acetic acid, 7.26 mol%; catalyst, 10 g; SV, 680 h^{-1}.

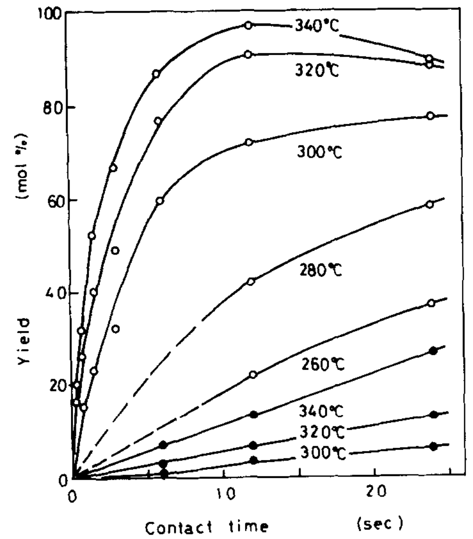

FIG. 8. Effects of the temperature and the contact time on the yields of acrylic acid and carbon oxides in the reaction of trioxane with acetic acid. Yields, based on the charged HCHO; (○) acrylic acid; (●) carbon oxides.

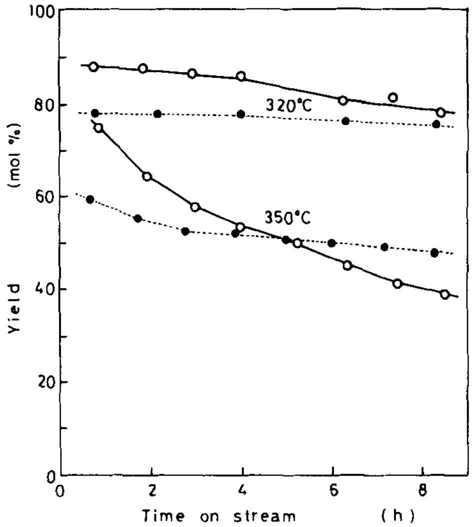

FIG. 9. Stability of the catalytic activity for acrylic acid formation in the reaction of trioxane with acetic acid. Amount of catalyst used: 320°C, 20 g; 350°C, 5 g. Open symbols with solid lines, without oxygen; blocked symbols with dotted lines, with 2.2 vol% oxygen.

ent temperatures and contact times are shown in Fig. 8. The yields of acrylic acid are higher than those obtained in the reaction of formalin (shown in Fig. 2).

The stability of the catalytic activity was also studied (Fig. 9). The activity falls gradually at temperatures above 350°C. However, the addition of a small amount (about 2.2 vol%) of oxygen to the carrier gas suppresses the deactivation, though it also induces a marked formation of carbon oxides.

Effect of the P/V Composition on the Catalytic Performance

The reaction of trioxane with acetic acid was conducted with 20-g portions of a series of V_2O_5–P_2O_5 with different P/V compositions using the feed rate described in the preceding section. The yields of acrylic acid and carbon oxides obtained at 300, 320, and 340°C are shown in Fig. 10. The best results are obtained with the P/V = 1.06 catalyst.

Effect of the Third Components Added to V_2O_5–P_2O_5

Attention was made to modify the V_2O_5–P_2O_5 catalyst by adding a small amount of a

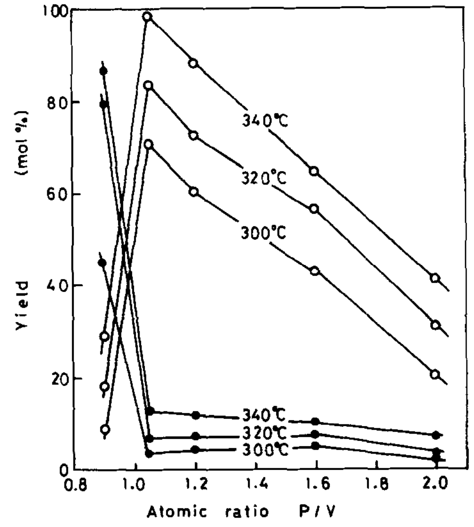

FIG. 10. Effect of the catalyst composition on the yields of acrylic acid and carbon oxides in the reaction of trioxane with acetic acid. (○) acrylic acid; (●) carbon oxides.

third component, such as ZrO_2, Co_3O_4, Nb_2O_5, and TeO_2. The results are summarized in Table 1. The effect of these third components is small, except that the addition of TeO_2 induces a marked formation of carbon oxides.

Reaction of HCHO with Methyl Acetate

Two sets of experiments were conducted on the reaction of HCHO with methyl acetate. In the first set, formalin was used as the source of HCHO. The feed rate was $CH_3COOCH_3/HCHO/CH_3OH/H_2O/N_2$ = 21.9/12.0/2.2/26.8/350 m mol/h; the composition was 5.3/2.9/0.5/6.5/84.7 mol%. In the second set, trioxane was used as the source of HCHO. The feed rate was $CH_3COOCH_3/HCHO/N_2$ = 27.2/15.0/350 m mol/h; the composition was 6.9/3.8/89.3 mol%. The main products were methyl acrylate, carbon oxides, and acetone. The yields of methyl acrylate and carbon oxides obtained with a 20-gram portion of catalyst are shown in Fig. 11. When the temperature was below about 360°C, the yield of methyl acrylate was approximately in accord with the consumption of HCHO.

It was found that methyl acetate is less reactive than acetic acid and that the yield of methyl acrylate is lower than that of acrylic acid obtained in the reaction with acetic acid.

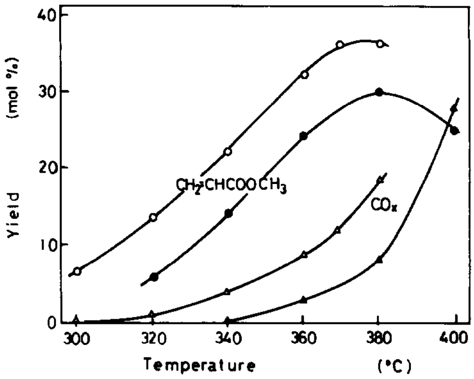

FIG. 11. Reaction of HCHO with methyl acetate. Product: (○, ●) methyl acrylate, (△, ▲) carbon oxides. Source of HCHO: (●, ▲) formalin, (○, △) trioxane. SV, 330 h^{-1}.

TABLE 1

Performances of the V_2O_5–P_2O_5–M_nO_m Catalysts[a]

Products (mol%)[b]	Temperature (°C)			
	300		320	
	AA[c]	CO_x	AA[c]	CO_x
V/P(1/1.06)	70	6	83	13
V/P(1/1.2)	60	10	72	13
V/P/Zr(1/1.3/0.1)	70	10	75	14
V/P/Co(1/1.3/0.1)	59	4	71	12
V/P/Nb(1/1.1/0.1)	65	4	83	12
V/P/Te(1/1.2/0.15)	49	42	44	55

[a] Conditions: catalyst, 20 g; feed rate of $CH_3COOH/HCHO/N_2$, 38.0/17.0/350 m mol/h; SV, about 340 h^{-1}.
[b] Yields based on the charged HCHO.
[c] AA, acrylic acid.

Reaction of HCHO with Acetaldehyde

Acetaldehyde–formalin mixtures of four different compositions were introduced, together with the nitrogen carrier gas, into the reactor. The reaction occurs to a great extent, even at the low temperature of 240°C. Acrolein was almost the sole product and the formation of carbon oxides was very small. The yield of acrolein was approximately in accord with the consumption of HCHO. The yields of acrolein (based on the charged HCHO) obtained with a 20-gram portion of catalyst (SV = about 330 h^{-1} at different concentrations of acetaldehyde and HCHO are shown in Fig. 12. It was found that the yield is strongly affected by the concentrations of the reactants.

DISCUSSION

The methyl acetate and methyl acrylate formed in the reaction of formalin with acetic acid (Fig. 1) are ascribed to the esterification of acetic acid with the methanol present in the formalin used, but not to the reaction of HCHO. Therefore, they are not formed when trioxane is used as the source of HCHO.

The main side-reaction is the formation

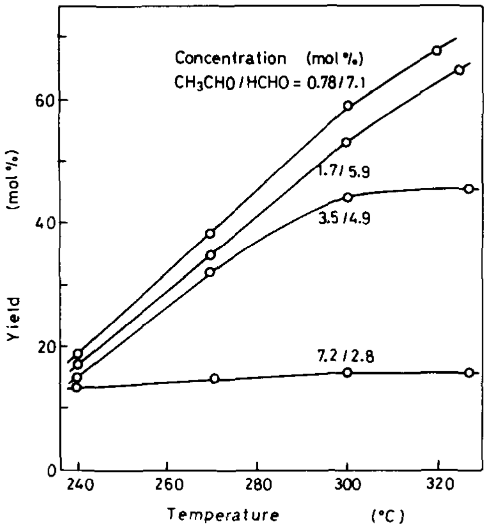

FIG. 12. Reaction of HCHO with acetaldehyde to form acrolein. Figures show the concentrations of CH_3CHO and HCHO in the feed gas. Ordinate: yield of acrolein based on the charged CH_3CHO. SV, about 330 h^{-1}.

of carbon oxides—above all, CO_2—and acetone. A set of experiments was carried out by using nitrogen gases containing acetic acid, an acetic acid : water (volumetric ratio of 2 : 1) mixture, an acetic acid : formalin (2 : 1) mixture, acrylic acid, and formalin as the feeds, and the formation of carbon oxides was studied. As may be seen in Fig. 13, HCHO is stable enough, even at 400°C, and acrylic acid is more stable than acetic acid. Therefore, it seems that carbon oxides are formed mainly from the decomposition of acetic acid, but not from that of acrylic acid or HCHO. This may be the reason why the sum of the yields (based on the charged HCHO) of acrylic acid and carbon oxides exceeds 100 mol% at higher temperatures (Fig. 8). Further, this is supported by the finding that the yield of acrylic acid in the reaction of trioxane with acetic acid is approximately in accord with the consumption of HCHO.

It should also be noted that the formation of carbon oxides from the neat acetic acid is much more rapid than that from the acetic acid–water or acetic acid–formalin mixtures, indicating that the presence of water vapor and HCHO plays a role in suppressing the decomposition of acetic acid.

Then, a nitrogen gas containing 11.6 mol% of acetic acid was passed over a 30-g portion of the catalyst, and the distribution of the products was studied. CO_2 and acetone were almost the sole products; their amounts were approximately equal to one-half of the amount of the acetic acid consumed. The formation of CO was less than 0.5 mol%, and that of methane was not detected. Those findings indicate that acetic acid is decomposed exclusively by the reaction

$$2\,CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O.$$

It is known that this reaction is promoted by basic oxide catalysts, such as CaO (*11*) and Bi_2O_3 (*12*).

Though both the formation of acrylic acid and the decomposition of acetic acid are inhibited by water vapor, higher yields of acrylic acid and lower yields of carbon oxides are obtained when the reaction is conducted in the absence of water vapor. Possibly, the absence of water vapor makes it possible to achieve the reaction at a lower

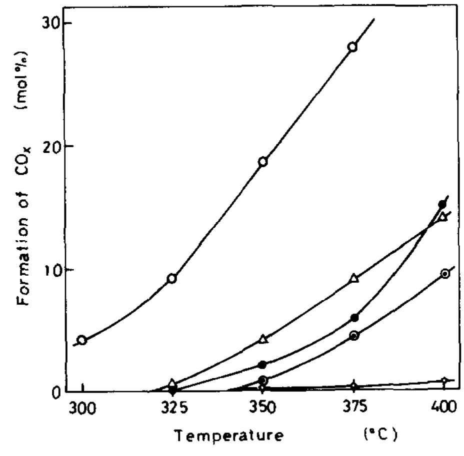

FIG. 13. Formation of CO_2. Feed: (○) 11.6 mol% CH_3COOH, (●) 7.1 mol% CH_3COOH + 11.4 mol% H_2O, (⊙) 7.3 mol% CH_3COOH + 2.9 mol% HCHO + 6.4 mol% H_2O, (△) 9.9 mol% CH_2=HCOOH, (◇) 7.6 mol% HCHO + 17.0 mol% H_2O. Catalyst, 10 g; SV, about 660 h^{-1}.

temperature, which results in a marked decrease in the formation of carbon oxides, for the formation of carbon oxides increases much more sharply than that of acrylic acid with an elevation of the temperature.

As may be seen in Figs. 5 and 6, the rate levels off at the HCHO concentration of 2 mol%, while it levels off at the acetic acid concentration of 7 mol%, indicating that the affinity of HCHO to the catalyst is greater than that of acetic acid. Accordingly, the use of an excess of acetic acid with respect to HCHO is desirable for this reaction.

It has been considered (*13, 14*) that vapor-phase aldol condensation is controlled by the abstraction of a proton at the α-position to the carbonyl group by the basic sites of catalyst surface; for example, $CH_3COOH + B \rightarrow H_2C^-COOH + BH^+$. Certainly, the possession of a basic property is indispensable for a catalyst in this reaction. However, as may be seen in Fig. 10, the catalytic activity for the formation of acrylic acid varies in a manner similar to that of the acidic properties of the V_2O_5–P_2O_5 binary oxides, but not to that of the basic properties (*6*), indicating that the activity is related to the acidic property, but not to the basic property. This finding suggests that, as far as the V_2O_5–P_2O_5 catalysts are concerned, the reaction is controlled by the action of acidic sites rather than by that of basic sites. Possibly, acidic sites play a role in the protonation of the carbonyl group, resulting in an increase in the electrophilicity of the carbon atom; for example, $H_2CO + H^+ \rightarrow H_2C^+OH$.

It may be true that phosphorus added to V_2O_5 plays a role in suppressing the basic property (*6*) which promotes the decomposition of acetic acid (Fig. 10), though the presence of a certain extent of basic property is indispensable for the aldol condensation.

A comparison of the results shown in Figs. 2, 8, and 11 reveals that the V_2O_5–P_2O_5 catalysts are more effective for the reaction of acetic acid than for that of methyl acetate. This may be ascribed to the fact that the V_2O_5–P_2O_5 catalysts are eminent in their acidic property and poor in their basic property (*6*). Possibly, the interaction between the acidic compounds and the catalyst surface may be weak and, as a result, the acrylic acid produced can easily leave from the surface.

In the case of the reaction of HCHO with acetaldehyde, the aspects of the reaction are different from those observed in the reactions with acetic acid and methyl acetate. That is, the reaction can occur at a lower temperature without an appreciable accompanying decomposition of acetaldehyde, but the reaction is blocked when the concentration of acetaldehyde is high. Possibly, the affinity of acetaldehyde with the catalyst surface is so strong that the surface is covered uniquely with acetaldehyde when the concentration is not low. Accordingly, the use of a large excess of HCHO with respect to acetaldehyde is desirable for this reaction.

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