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The Production of Methyl Vinyl Ketone by the Vapor-Phase Aldol Condensation between Formaldehyde and Acetone

MAMORU AI

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

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The vapor-phase aldol condensation between formaldehyde and acetone was studied using various kinds of single and binary metal oxides and heteropoly compounds as the catalysts. It was found that the possession of both acidic and basic properties is favorable to promote the reaction and that methyl vinyl ketone is almost the sole product over the acidic catalysts, while a marked amount of by-products is formed over the relatively basic oxides. The best results were obtained with the V_2O_5–P_2O_5 (P/V atomic ratio = 1.06) and Fe_2O_3–P_2O_5 (P/Fe = 4/6) catalysts. The effects of the reaction variables and the stability of catalyst were also studied with the V_2O_5–P_2O_5 catalyst.

INTRODUCTION

The formation of methyl vinyl ketone (MVK) by means of a reaction between formaldehyde (HCHO) and acetone is an aldol condensation which is followed by dehydration to olefin. Moreover, this reaction is also attractive in view of the utilization of C_1-resources in syntheses.

$$CH_3\text{—}CO\text{—}CH_3 + HCHO \rightarrow CH_3\text{—}CO\text{—}CH_2\text{—}CH_2(OH) \rightarrow CH_3\text{—}CO\text{—}CH{=}CH_2 + H_2O$$

Liquid-phase aldol condensations performed at low temperatures using homogeneous base catalysts have been studied extensively (*1*). On the other hand, comparatively little work has been done on vapor-phase reactions at elevated temperatures over heterogeneous catalysts (*2–6*).

Recently, we found that a V_2O_5–P_2O_5 (P/V atomic ratio = 1.06) catalyst, which exhibits an excellent performance in the oxidation of *n*-butane to maleic anhydride, also performs well in the formation of MVK. It is interesting to note that the V_2O_5–P_2O_5 catalyst, which possesses enhanced acidic and redox properties (*7*), is effective in promoting the aldol condensation.

On the other hand, it has been reported by Albanesi and Moggi (*8*) that supported Nb_2O_5, Ta_2O_5, and WO_3, which are different from the known catalysts, i.e., the basic oxides, are effective for the condensation of HCHO with methyl propionate to form methyl methacrylate.

In this study, we first investigated the vapor-phase aldol condensation using a V_2O_5–P_2O_5 (P/V = 1.06) catalyst; then we compared the catalytic behavior of various kinds of metal oxides in order to make a character sketch of the catalytic function for this reaction, since no scientific report has yet been published on this matter.

EXPERIMENTAL

Reaction Procedures

The reaction was 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 as the carrier gas or the diluent, and a mixture of acetone and 37% formalin was

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introduced into a preheating section of the reactor by means of a micro liquid-feeder. Unless otherwise indicated, the reaction conditions were fixed as follows: acetone − HCHO − H_2O − N_2 = 14.2 − 1.6 − 6.5 − 77.8 vol%; flow rate of nitrogen, 140 ml (at 20°C)/min (ca. 0.35 mol/h); feed rate of HCHO, 7.3 mmol/h; acetone/HCHO molar ratio, 8.8; amount of catalyst used, 20 g; temperature, 200°C.

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 was collected (60 ml). The reaction 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 20 *M* at 110°C for aldehydes, ketones, and alcohols. HCHO was analyzed by the sodium sulfite method.

Catalysts

The V_2O_5–P_2O_5 catalysts with *P*/*V* atomic ratios of 0, 0.9, 1.06, 1.2, and 1.6 are the same as those used in a previous study (*9*). Their structures and surface areas have been described in the previous study (*7*). The other metal oxides and heteropoly compounds are also the same as those used in earlier works (*10–15*).

RESULTS

Catalytic Behavior of the V_2O_5–P_2O_5 (P/V = 1.06) Catalyst

Preliminary catalyst-screening tests revealed that the V_2O_5–P_2O_5 (*P*/*V* = 1.06) catalyst is one of the best catalysts for the formation of MVK. Thus, the characteristics of the reaction were studied using this catalyst (surface area = 23 m^2/g).

Reaction products. The reaction was conducted under the conditions described under Experimental, except that the amount of the catalyst used were changed in the range 6–50 g (9.6–80 ml) and, in certain cases, the flow rate of nitrogen was reduced to 110, 75, or 50 ml/min.

The main product was MVK. The formation of methyl formate by the dimerization (Tischenko reaction) of HCHO was less than 0.5 mol% (based on the charged HCHO). Other products, such as carbon oxides, acetaldehyde, and methyl ethyl ketone, were also detected, but their amounts were negligibly small. No formation of mesityl oxide by the condensation of acetone was detected. The yield of MVK 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 large amount of acetone.

Figure 1 shows the yield of MVK as a function of the contact time. The yield is almost proportional to the contact time when the contact time is short, but it levels off at a contact time longer than 35 s. Hence, it does not exceed about 65 mol% (based on the charged HCHO). The values of the maximum yield remains almost unchanged with the variation in the charge rates of HCHO and acetone, so long as the acetone/HCHO molar ratio is fixed. On the other hand, the value increases as the acetone/HCHO ratio increases. These

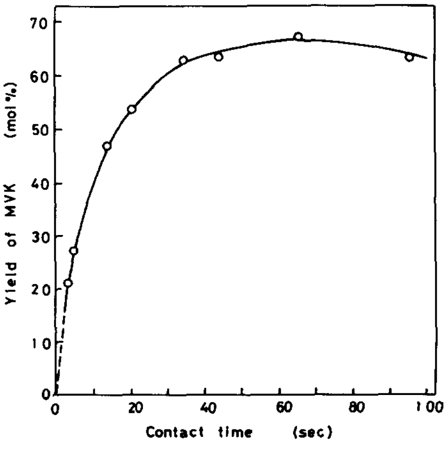

FIG. 1. Yield of MVK as a function of the contact time.

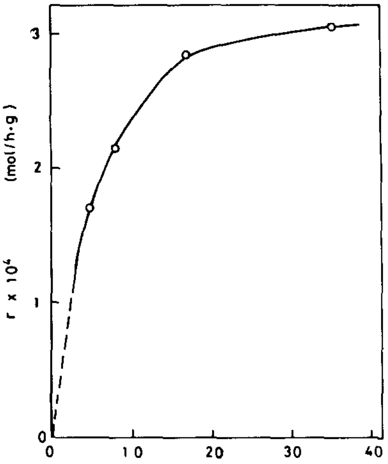

FIG. 2. Effect of the acetone concentration on the rate of MVK formation.

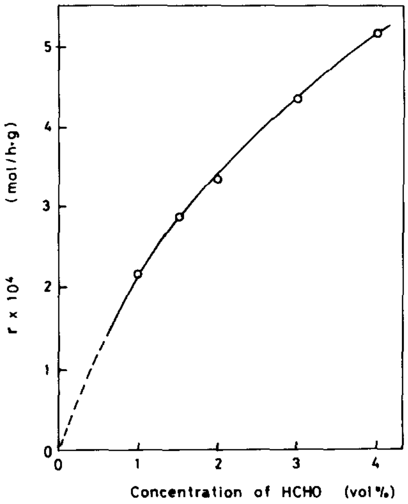

FIG. 3. Effect of the HCHO concentration on the rate of MVK formation.

findings suggest that the yield is limited by the reaction equilibrium.

Effect of the acetone concentration. The reaction was conducted by changing the initial concentration of acetone from 4.6 to 35 vol%, using a 5-g portion of the catalyst, while fixing the other conditions as has been described under Experimental. The rate of MVK formation was calculated from the low-level conversion (below 20%). The results are shown in Fig. 2. The rate increases almost proportionally to the acetone concentration at concentrations below 10 vol%, but it increases less steeply with a further increase in the concentration.

Effect of the HCHO concentration. The reaction was conducted by changing the initial concentration of HCHO from 0.8 to 3.3 vol% using a 5-g portion of the catalyst. The rate of MVK formation is plotted as a function of the HCHO concentration in Fig. 3. The rate is nearly proportional to the concentration.

Effect of the temperature. The reaction was conducted using a 30-g portion of the catalyst under the fixed conditions, while changing the temperature in the range 140–240°C. The results are listed in Table 1. The yield attains 20 mol%, even at a low temperature of 140°C, but it increases, to a small extent, with a further elevation in the temperature until it levels off at a yield of about 60 mol%. The apparent activation energy, as calculated in the temperature range 140–180°C, is about 6 kcal/mol.

Effect of the carrier gas. Air was used in place of nitrogen as the carrier gas. The results obtained using a 30-g portion of the catalyst under the fixed conditions are also compared with those obtained with the nitrogen carrier in Table 1. The yield of MVK is almost the same as that obtained with the nitrogen carrier, and the formation of carbon oxides is small, when the temperature is below 200°C. However, the formation of carbon oxides increases markedly at the expense of a decrease in

TABLE 1

Effects of the Temperature and the Carrier Gas on the Yield of MVK[a,b]

Carrier gas (140 ml/min)	Reaction temperature (°C)					
	140	160	180	200	220	240
Nitrogen	20	34	45	57	60	61
Air			45	54	44	32

[a] Mol% based on the charged HCHO.
[b] Amount of catalyst used, 30 g.

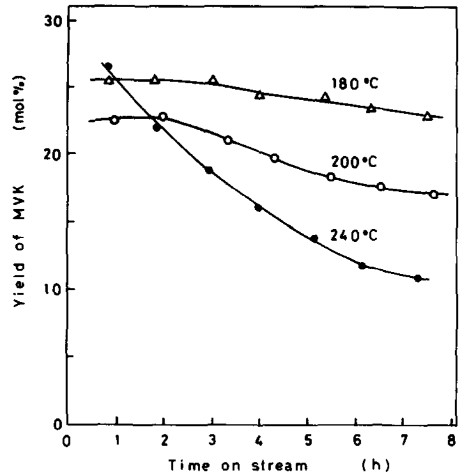

FIG. 4. Stability of the catalytic activity. Amounts of catalyst used: △, 10 g; ○, 5 g; ●, 2.5 g.

the yield of MVK with a further elevation of the temperature, indicating that the consecutive oxidation of MVK takes place.

Stability of the activity. The stability of the catalytic activity was checked. Figure 4 shows the yield of MVK at 180, 200, and 240°C using 10-, 5-, and 2.5-g portions of the catalyst, respectively. The activity is relatively stable at temperatures below 200°C.

It was also found that the V_2O_5–P_2O_5 can be regenerated completely by a heat treatment at 350°C in a stream of air for 2 h.

Performances of Various Metal-Oxide Catalysts

Since little information has been reported on the formation of MVK from HCHO and acetone, it seems necessary to make a character sketch of the catalytic function for this reaction. Therefore, a series of experiments were carried out under the conditions described under Experimental using various kinds of single- and binary-oxide catalysts. Generally, data were taken 1 to 2 h after the start of each run. The results are listed in Table 2, according to the classification of metal oxide in view of both acid–base and oxidizing functions shown in Table 3 (*16*, *17*).

The results may be summarized as follows:

(i) Typical acidic oxides, such as H-zeolite, SiO_2–Al_2O_3, and B_2O_3, are inactive.

(ii) Heteropoly compounds are also inactive.

(iii) Basic oxides, such as MgO and K_2O, show some activity.

(iv) Single oxides, such as WO_3, TiO_2, SnO_2, and Fe_2O_3, exhibit a relatively high activity.

(v) The addition of a small amount of P_2O_5 to an acidic oxide such as WO_3 or MoO_3 strongly decreases the activity, while that to V_2O_5 or an amphoteric oxide enhances the activity.

(vi) The best results are obtained with the V_2O_5–P_2O_5 ($P/V = 1.06$) and Fe_2O_3–P_2O_5 (P/Fe = 4/6) catalysts.

(vii) The next best performances are obtained with the combination of an acidic oxide, such as MoO_3, WO_3, and Sb_2O_4, and an amphoteric oxide, such as TiO_2, SnO_2, and Fe_2O_3.

(viii) The addition of a small amount of K_2O decreases the activity.

(ix) The formation of methyl formate is about 10 mol% with the Zr and Fe–K (9–1) oxides, about 3.5 mol% with the Sn–Mo (7–3) and Sn–V (9–1) oxides, and about 2 mol% with the Ti, Sn, Sn–Sb (7–3), and Sb–Sn (7–3) oxides.

(x) The formation of methyl ethyl ketone is about 20 mol% with the Sn–K (9–1), Ti–K (9–1), and Fe–K (9–1) oxides, about 10 mol% with the Zr, Ti–Ni (8–2), Sn–Sb (7–3), Ni, Ni–K (9–1), Ni–P (9–1), and Al oxides.

(xi) The consumption of HCHO is much greater than the sum of the yields of each product in the cases of the Al, Sn–K (9–1), Sn, Sn–Ni (8–2), Ti–K (9–1), Fe, and K oxides.

DISCUSSION

It has been considered (*3*, *6*) that vapor-phase aldol condensation is controlled by

TABLE 2

Catalytic Activity of Metal Oxides for Formation of Methyl Vinyl Ketone[a]

Catalyst (atom ratio)	Yield (mol%)[b]	Catalyst (atom ratio)	Yield (mol%)[b]	Catalyst (atom ratio)	Yield (mol%)[b]
Mo	8.0	Ti	24	$H_3PMo_{12}O_{40}$	0.5
Mo–P (9–1)	0.5	Ti–P (9–1)	24	$Cs_2HPMo_{12}O_{40}$	0.5
Mo–W (8–2)	7	(7–3)	30	$Ag_2HPMo_{12}O_{40}$	0.5
Mo–V (8–2)	28	(5–5)	30	$H_5PMo_{10}V_2O_{40}$	1.5
Mo–Ti (6–4)	23	Ti–Mo (8–2)	17	$H_3PW_{12}O_{40}$	0.5
Mo–Sn (6–4)	11	Ti–W (7–3)	20		
Mo–Fe (7–3)	10	Ti–V (9–1)	34		
Mo–Bi (5–5)	6	Ti–Ni (8–2)	10	Zeolite 13×[c]	0.0
Mo–K (9–1)	5	Ti–K (9–1)	21	Si–Al (8–2)	0.0
W	27	(7–3)	13		
W–P (9–1)	0.5	Sn	22	B	0.0
W–Mo (8–2)	9	Sn–P (8–2)	24		
W–V (8–2)	7	Sn–Mo (7–3)	28	Zr	11
W–Ti (8–2)	26	Sn–W (7–3)	33	Zr–Mo (7–3)	11
W–Sn (8–2)	28	Sn–V (8–2)	36	Sb	21
W–Fe (8–2)	32	Sn–Sb (7–3)	30	Sb–Mo (9–1)	9
W–Ni (8–2)	30	Sn–K (9–1)	17	Sb–Sn (7–3)	37
W–K (9–1)	30	(8–2)	13	Al	9
V	13	Fe	34	Al–P (9–1)	6
V–P (1–0.9)	18	Fe–P (8–2)	40	Zn	15
(1–1.06)	52	(7–3)	48	Zn–P (9–1)	20
(1–1.2)	42	(6–4)	50	Zn–K (9–1)	6
(1–1.6)	25	Fe–Mo (7–3)	32	(8–2)	4
V–Mo (8–2)	24	Fe–W (7–3)	25	Mg	8
V–W (8–2)	19	Fe–V (9–1)	33	K	9
V–Ti (9–1)	25	Fe–K (9–1)	23		
V–Sn (9–1)	19	Ni	17		
V–Fe (9–1)	19	Ni–P (9–1)	26		
V–K (9–1)	6	Ni–K (9–1)	11		

[a] Conditions: catalyst, 20 g; temperature, 200°C; N_2 carrier, 140 ml/min; HCHO feed rate, 7.4 mmol/h; acetone/HCHO ratio, 6.8.

[b] Based on the charged HCHO.

[c] H^+ exchanged.

the abstraction of a H atom at the α-position to the carbonyl function on the basic sites. Certainly, the possession of a basic property is indispensable for a catalyst in this reaction. In line with this thought, it is likely that the acidic oxides, such as H-zeolite, SiO_2–Al_2O_3, and B_2O_3, are lacking in a basic property; as a result, they are inactive. Similarly, the W–P and Mo–P oxides and heteropoly compounds must be deficient in their basic property. Possibly, the basic property of WO_3 and MoO_3 may be extinguished, to a significant extent, by the P_2O_5.

However, as may be seen in Table 2, the single-alkali and alkaline-earth metal oxides and the amphoteric oxides combined with K_2O are markedly less active than many other more-acidic oxides. In this connection, the yields of MVK are plotted in Fig. 5 as a function of the amounts of P_2O_5 and K_2O added to amphoteric oxides, such as TiO_2, SnO_2, Fe_2O_3, NiO, and ZnO. It is clear that the activity is related to the acidic

TABLE 3

Acid–Base Properties of Metal Oxides

(i) Oxides with Oxidation Activity

No.	1	2	3	4	5	6	7	8	9	10				
Oxide	W	Mo	V	U	Ti	Sn	Fe	Bi	Zn	Mn	Cr	Co	Ni	Cu
Group	A	A	A	B	B	B	B	B′	B′	C	C	C	C	C
	Acidic ←													→ Basic

(ii) Oxides without Oxidation Activity

No.	1′	2′	3′	4′	5′	6′	7′	8′	9′	
Oxide	S	P	B	As	Sb	Al	Mg	Ca	Na	K
Group	A′	A′	A′	A′	A′	A′	D	D	D	D
	Acidic ←									→ Basic

property, but not to the basic property. This finding indicates that, as far as these oxides are concerned, the reaction is controlled by the action of acidic sites rather than by that of basic sites.

It has previously been proposed as a general rule (*10*, *16*, *17*) that the combination of an amphoteric oxide such as TiO_2, SnO_2, Fe_2O_3, or NiO with a smaller amount of an acidic oxide such as P_2O_5, WO_3, MoO_3, or V_2O_5 often makes it possible to possess two enhanced opposite-properties, i.e., acid and base sites, on the surface. Indeed, the yield of MVK shown in Table 2 seems to be in accord with this rule, at least to a certain extent. This finding leads us to consider that the reaction is catalyzed by acid-base bifunctional properties.

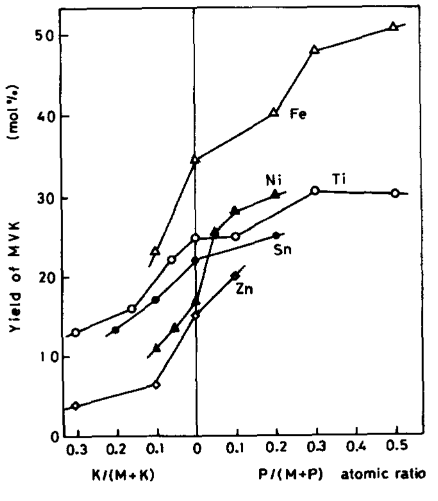

FIG. 5. Effect of the amounts of P_2O_5 and K_2O on the yield of MVK.

This view is also supported by the rate data shown in Figs. 2 and 3, where the rate is almost proportional to the concentrations of both HCHO and acetone. This finding indicates that the rate is controlled not only by the action of basic sites for the abstraction of a H atom from acetone, but also by the activation of both HCHO and acetone.

It is known that aldol condensation is also catalyzed by the action of acid for the protonation of the carbonyl function, resulting in an increase in the electrophilicity of the carbon atom; e.g.,

$$H_2CO + H^+ \rightarrow H_2C^+OH$$

On the other hand, it is also probable that the acidic sites play a role in enhancing the affinity of the catalyst with the reactant feeds or in promoting the dehydration of hydrated formaldehyde,

$$H_2C(OH)_2 \rightarrow HCHO + H_2O$$

At present, it seems hard to describe clearly the action of acidic sites.

Actually, it has already been reported (*2–6*) that composite oxides, such as Li_2O–

P_2O_5, ThO_2–ZnO, Na_2O–SiO_2, and Na_2O–SiO_2–Al_2O_3, are more effective than single alkali and alkaline earth metal oxides. This leads us to assume that the combination of metal oxides induces the generation of acidic sites, which play a role in promoting the reaction.

On the other hand, it has been shown in previous studies (*12, 13*) that the vapor-phase dimerization of HCHO to methyl formate (Tischenko reaction) is promoted effectively by metal oxides possessing acid–base bifunctional properties, though this reaction in a liquid phase can be promoted only by a base catalyst. This finding also indicates that the presence of acidic sites is required in promoting the vapor-phase reaction.

However, the situation seems to be complex: the balance between acidic and basic properties, which is an important factor deciding the catalytic activity, differs depending on the difference in the reaction. For example, in the formation of MVK, a more acidic and a less basic property is required than in the dimerization of HCHO to methyl formate.

As for the selectivity, MVK is almost the sole product over relatively acidic oxides, while the formation of by-products is enhanced over relatively basic oxides, indicating that the selectivity is governed also by the balance between acidic and basic properties.

It is very interesting and important to clarify in more detail the relation between the catalytic behavior and the acid–base property of metal oxides. However, oxides of transition metals are colored and the titration method is not available for their acid–base determination. As a result, clear information especially about acid–base strength are lacking. Further studies on the acid–base properties of mixed oxides containing transition metal oxides are awaited.

It should also be noted that the reaction is conducted in a reducing atmosphere and, accordingly, that during the reaction the catalysts suffer a reduction which induces a change in their acid–base properties. By way of example, a relatively high activity is obtained with oxides containing either P_2O_5 or WO_3, both of which are lacking in any redox function. This lack of redox function seems to be beneficial for avoiding the reduction.

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