Formation of Acrylaldehyde by Vapor-Phase Aldol Condensation II. Phosphate Catalysts

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

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Vapor-phase aldol condensation of formaldehyde with acetaldehyde to form acrylaldehyde was studied with various oxide and phosphate catalysts using 35% formalin as the source of formaldehyde. Almost all of the tested oxides exhibited a certain activity as the catalysts. Acidic oxides, such as MoO_3 and WO_3 showed a relatively high selectivity to acrylaldehyde, though the activities were low. V_2O_5 and amphoteric oxides exhibited a much higher activity, but they promoted also the formation of CO_2 and methanol. The catalytic performance was improved, to a certain extent, by combination of an acidic oxide with an amphoteric oxide. Further, the combination of phosphorus with V_2O_5 or an amphoteric oxide induced a large increase in the selectivity to acrylaldehyde. A good performance was obtained with the Ni–P, Mn–P, Fe–P, and V–P systems. The yield of acrylaldehyde reached 86 mol% on the AcH basis with a very slow formation of CO_2 and methanol.

The preceding paper[1)] was concerned with performances of silica-supported basic oxides used as catalysts in the vapor-phase aldol condensation of formaldehyde (HCHO) with acetaldehyde (AcH) to form acrylaldehyde:

$$CH_3CHO + HCHO \longrightarrow CH_2{=}CHCHO + H_2O.$$

It was recently found that the aldol condensation of HCHO with a carboxylic acid, such as acetic acid or propionic acid

$$RCH_2COOH + HCHO \longrightarrow CH_2{=}CRCOOH + H_2O \qquad (R{=}H,\ CH_3),$$

is promoted selectively with phosphate catalysts, for example, V–P,[2,3)] V–Ti–P,[4)] and V–Si–P[5)] oxides. On the other hand, basic oxides were found to be unsuitable as catalysts, because they promote the side-reaction

$$2RCH_2COOH \longrightarrow RCH_2COCH_2R + CO_2 + H_2O \qquad (R{=}H,\ CH_3).$$

This led us to infer that certain phosphates would exhibit performance comparable to that of basic oxides as catalysts for the condensation of HCHO with aldehydes, much as for the reaction with carboxylic acids. In this study, we focused our attention on finding out some phosphate catalysts effective for the formation of acrylaldehyde.

Experimental

Catalysts. The catalysts used in this study were various kinds of single, binary, and ternary oxides. Some of them were the same as those used in our previous studies.[2—4)] For example, the Ni–P oxide with an atomic ratio of 1 : 0.9 was prepared as follows. Nickel nitrate $[Ni(NO_3)_2 \cdot 6H_2O]$ (291 g) was dissolved in 200 ml of water and 104 g of 85% H_3PO_4 was added to the solution. Excess water was evaporated with stirring in a hot air current to yield a viscous paste. This paste was then dried in an oven at 200 °C for 6 h. The obtained solid was ground and sieved to get the 8—20 mesh portion. It was finally calcined at 500 °C for 6 h in a stream of air.

Reaction Procedures. The reaction procedures were almost the same as those described in the preceding paper.[1)] As the source of HCHO, 35% formalin, containing methanol in about 8%, was used. Unless otherwise indicated, the feed rates of AcH, HCHO, methanol, water, and nitrogen were 13, 26, 5.6, 71, and 350 mmol h^{-1}, respectively.

Results and Discussion

Performance of Metal Oxide Catalysts. Since little information has been reported on this reaction, it seems necessary to make a character sketch of catalytic function. Therefore, various kinds of oxides were tested as catalysts. Table 1 shows the conversions of AcH and the yields of acrylaldehyde, CO_2, and methanol obtained at 320 °C with 20 g portions of single and binary oxide catalysts.

The results may be summarized as follows.

(1) The acidic oxides, such as MoO_3 and WO_3, show a relatively high selectivity to form acrylaldehyde, though the activity is low.

(2) V_2O_5 shows a high activity, but it promotes also the formation of CO_2 and the selectivity to acrylaldehyde is low.

(3) Amphoteric oxides, such as TiO_2, SnO_2, and Fe_2O_3, show a high activity, but they also promote the formation of CO_2 and methanol and the selectivity to acrylaldehyde is low.

(4) MgO shows a low activity. The Mg–K=9–1 oxide shows a relatively high activity, but the selectivity to acrylaldehyde is low.

(5) The catalytic performance is improved by combination of V_2O_5 or an amphoteric oxide with an acidic oxide, such as MoO_3 or WO_3.

(6) The best performances are obtained with the W–Sn and W–Fe oxide systems. The yield of acrylaldehyde reached 67 mol%.

Table 2 shows the results obtained with various phosphate catalysts. The results may be summarized as follows.

Table 1. Performances of Metal Oxide Catalysts[a)]

Catalyst (Atomic ratio)	AcH[b)] conv.	Yield/mol%			Catalyst (Atomic ratio)	AcH[b)] conv.	Yield/mol%		
	%	Acryl[b)]	CO_2	MeOH[b)]		%	Acryl[b)]	CO_2	MeOH[b)]
Mo	15	14	1	1	Ti	89	37	19	19
Mo-V (8-2)	30	30	0	0	Ti-Mo (9-1)	43	42	6	16
Mo-Ti (9-1)	57	15	46	0	(8-2)	52	51	8	22
(8-2)	54	13	47	0	Ti-W (9-1)	67	40	8	24
Mo-Sn (9-1)	54	8	92	0	(7-3)	36	29	1	4
Mo-Fe (9-1)	32	29	1	0	Ti-V (9-1)	82	28	34	36
(7-3)	32	29	2	0	Sn	56	56	27	60
Mo-Bi (8-2)	15	13	2	0	Sn-Mo (9-1)	17	16	60	60
(5-5)	45	21	30	0	(7-3)	61	13	63	36
W	38	35	1	2	Sn-W (7-3)	57	50	6	8
W-V (8-2)	22	20	2	0	(5-5)	55	50	7	10
W-Ti (8-2)	39	28	1	2	Fe	68	42	69	62
(6-4)	50	28	1	0	Fe-Mo (7-3)	58	49	29	23
W-Sn (8-2)	40	40	2	4	Fe-W (7-3)	79	66	38	65
(5-5)	55	50	7	10					
W-Fe (8-2)	48	46	1	4	Sb	Low	2	0	0
(7-3)	62	60	3	12	Sb-V (8-2)	24	21	14	15
(5-5)	73	67	14	15	Mg	18	17	2	0
V	60	28	34	0	Mg-K (9-1)	48	24	34	32

a) Conditions: temperature=320 °C; amount of catalyst used=20 g; contact time=10 to 15 s; AcH/HCHO/methanol/water/nitrogen feed rates=13/26/5.6/71/350 mmol h^{-1}. b) AcH=acetaldehyde; Acryl=acrylaldehyde; MeOH=methanol.

Table 2. Performances of Phosphate Catalysts[a)] (1)

Catalyst (Atomic ratio)	AcH[b)] conv.	Yield/mol%			Catalyst (Atomic ratio)	AcH[b)] conv.	Yield/mol%		
	%	Acryl[b)]	CO_2	MeOH[b)]		%	Acryl[b)]	CO_2	MeOH[b)]
Mo	15	14	1	0	Ni-P (6-4)	94	48	33	50
Mo-P (8-2)	Low	3	0	0	(5-5)	79	66	1	0
W	38	35	1	2	Co-P (6-4)	92	68	21	30
W-P (9-1)	Low	7	1	0	(5-5)	36	35	1	0
V	60	28	34	0	Mn-P (6-4)	86	86	11	23
V-P (1-1.06)	75	70	2	0	(5-5)	Low	4	1	0
Ti	89	37	19	19	Cr-P (5-5)	32	3	3	0
Ti-P (9-1)	67	57	3	5	(4-6)	4	3	0	0
(8-2)	73	66	2	18	Cu-P (6-4)	50	43	21	0
(6-4)	43	42	1	0	(5-5)	Low	1	0	0
Sn	56	56	27	60	B-P (5-5)	20	20	1	0
Sn-P (9-1)	60	59	7	10	Al-P (5-5)	Low	0	0	0
(7-3)	60	60	4	10	Zr-P (5-5)	25	21	0	0
(6-4)	15	15	0	0	Zn-P (6-4)	27	27	4	4
Fe	68	42	69	62	Bi-P (7-3)	37	35	55	62
Fe-P (9-1)	83	21	64	60	(5-5)	42	42	7	12
(8-2)	68	65	33	32	(4-6)	Low	1	0	0
(6-4)	62	55	3	0	Mg-P (5-5)	20	10	0	0
(5-5)	16	15	1	0					
(4-6)	Low	4	0	0					
$Fe_4(P_2O_7)_3$	45	43	1	0					

a) Conditions: temperature=320 °C; amount of catalyst used=20 g; contact time=10 to 15 s; AcH/HCHO/MeOH/water/nitrogen feed rates=13/26/5.6/71/350 mmol h^{-1}. b) AcH=acetaldehyde; Acryl=acrylaldehyde; MeOH=methanol.

(1) The combination of phosphorus with an acidic oxide, such as MoO_3 or WO_3, decreases the activity markedly.

(2) The V-P oxide consisting of divanadium(IV) dioxide pyrophosphate [$V_2O_2(P_2O_7)$] exhibits a relatively good performance in both activity and selectivity.

(3) The combination of phosphorus with a certain

amphoteric oxide, such as TiO_2, SnO_2, Fe_2O_3, NiO, Co_3O_4, MnO_2, Cr_2O_3, or CuO, induces a large increase in the selectivity to acrylaldehyde, though the activity decreases gradually as the content of phosphorus increases. Therefore, there exists an optimum value in the amount of phosphorus.

(4) The combination of phosphorus with an oxide without oxidizing function, such as B_2O_3, Al_2O_3, ZrO_2, ZnO, Bi_2O_3, or MgO, is less effective.

(5) The best performances are obtained with the Ni–P, Co–P, Mn–P, Fe–P, and V–P oxide systems.

To get more detailed information about the catalytic functions, the effect of contact time on the AcH conversion and yields was examined for several phosphate catalysts which had showed a good performance. The results are listed in Table 3. The results may be summarized as follows.

(1) The best performance in the yield of acrylaldehyde is obtained with the Ni–P oxide with a P/Ni atomic ratio of 0.9/1.

(2) The next best catalyst is the Fe–P oxide with a P/Fe atomic ratio of 0.75/1.

(3) The combination of TiO_2 with the V–P oxide, which improves the performance for the reaction of HCHO with acetic acid,[4] increases the activity markedly, but the maximum yield of acrylaldehyde decreases from 79 to 63 mol%.

Table 3. Performances of Phosphate Catalysts[a] (2)

Catalyst			AcH conv.	Yield/mol%		
	(Atomic ratio)	wt/g	%	Acryl[b]	CO_2	Methanol
V–P	(1–1.06)	2	17	16	0	0
		20	74	70	2	1
		40	87	79	3	4
V–Ti–P	(1–2–5.5)	2	46	45	0	0
		4	71	63	1	2
		6	78	63	2	4
		8	89	63	3	4
Fe–P	(1–0.75)	2	30	30	1	0
		16	86	80	9	13
Ni–P	(1–0.67)	2	42	41	3	4
		5	77	72	20	40
		20	94	48	33	50
	(1–0.9)	2	37	37	0	0
		15	91	86	1	8
		20	94	80	2	8
	(1–1)	20	79	66	1	0
		40	86	75	1	0
Co–P	(1–0.67)	2	42	41	3	0
		10	77	75	9	15
		20	92	68	21	30
	(1–0.75)	2	20	20	0	0
		12	75	65	2	0
		20	90	63	12	0
Mn–P	(1–0.67)	2	37	37	1	0
		5	53	52	6	8
		20	86	86	11	23

a) Conditions: temperature=320 °C; AcH/HCHO/methanol/water/nitrogen feed rates=13/26/5.6/71/350 mmol h^{-1}. b) Acryl=acrylaldehyde.

The Mo–P and W–P oxides consisting of heteropoly compounds, such as $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$, which possess strongly acidic sites, are not active as catalysts for this reaction, which suggests that the reaction is not promoted solely by acidic sites. V_2O_5, amphoteric oxides, and oxides of heavy metals, which are considered to be more basic than MoO_3 and WO_3 because of the lower electronegativity of metal ions, show a higher catalytic activity. Further, the activity of these oxides falls with the incorporation of phosphorus. These findings suggest that the reaction is catalyzed by basic sites. However, the sites required to promote the acrylaldehyde formation seem to consist of very weakly basic sites, present in metal tungstates, molybdates, and phosphates, but not of strongly basic sites, which is in conformity with the results obtained in the preceding study.[1]

The formation of acrylaldehyde is accompanied by the following side-reactions, as has been pointed out in the preceding work:[1] (i) formation of CO_2 and methanol from HCHO via methyl formate, which is promoted mainly by basic sites, and (ii) polymerization of acrylaldehyde to unidentified polymers, which is promoted by strongly acidic sites.

The activity and selectivity may, therefore, be governed by the balance of acidic and basic properties. When the basic property is too strong, the formation of CO_2 and methanol is promoted. On the other hand, when the basic property is suppressed too much by the incorporation of an acidic oxide, the catalyst loses the activity.

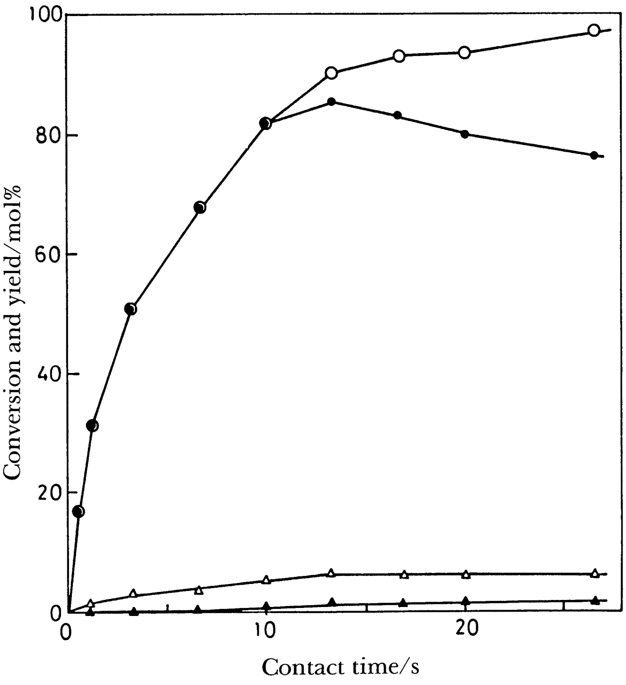

Fig. 1. Performance of the catalyst with an Ni : P atomic ratio=1 : 0.9. ○ AcH conversion; ● acrylaldehyde; ▲ CO_2; △ methanol.

The control of the acid-base property of catalysts is performed by the combination of an acidic oxide with a more basic oxide. It is, therefore, considered that the acid-base properties of the Ni–P, Mn–P, Co–P, Fe–P, and V–P oxide systems are best fit for promoting solely the formation of acrylaldehyde.

Performance of the Ni–P=1–0.9 Catalyst. The study in the preceding section has revealed that the best results for the formation of acrylaldehyde are obtained with the nickel phosphate with a P/Ni atomic ratio of 0.9/1. Thus, the characteristics of this catalyst were studied.

Product Distribution. The conversion of AcH and the yields of acrylaldehyde, CO_2, and methanol obtained at 280 °C are plotted in Fig. 1 as a function of contact time. The selectivity to acrylaldehyde is almost 100 mol% up to the AcH conversion of 80%, but it falls gradually with a further increase in the conversion. The results indicate that the acrylaldehyde formed initially is converted to polymers. The maximum yield of acrylaldehyde is about 85 mol%. This value is lower than those obtained with silica-supported basic oxides (96 mol%).[1)] However, the formation of CO_2 and methanol is clearly slower than that obtained with the silica-supported basic oxides.[1)] Possibly, the Ni–P oxide catalyst possesses strongly acidic sites, while the silica-supported basic oxides possess strongly basic sites.

Effect of Temperature. The yield of acrylaldehyde obtained with 2 g portions of catalyst (contact time 1.3 s) are plotted in Fig. 2 as a function of temperature. It was found that the effect of temperature on the rate is very small. The apparent activation energy was calculated to be about 3.5 kcal mol^{-1}. This value is clearly lower than that observed with the Si–Mg catalyst (15 kcal mol^{-1}),[1)] which suggests that the active sites of the Ni–P catalyst are different from those of the Si–Mg catalyst. Possibly, the rate determining step is different; for example, it is the protonation of HCHO by acidic sites, $HCHO+H^+\longrightarrow H_2C^+OH+H_2O$, over the Si–Mg catalyst, whereas over the Ni–P catalyst it is the proton abstraction from AcH by basic sites, $CH_3CHO+OH^-\longrightarrow {}^-CH_2CHO+H_2O$.

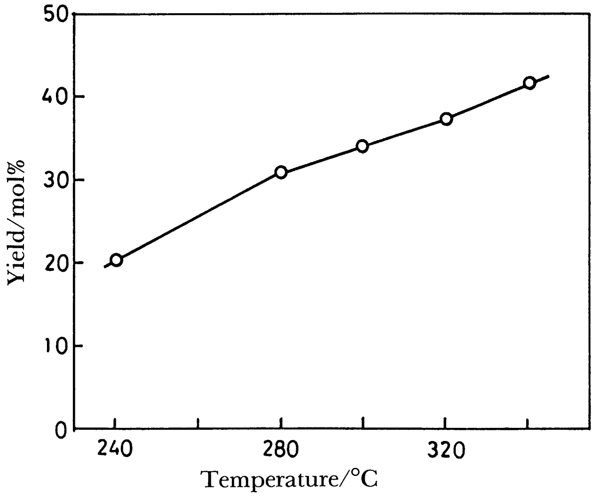

Fig. 2. Effect of temperature on the yield of acrylaldehyde. Contact time=1.3 s.

The effect of temperature on the selectivity to acrylaldehyde was studied. The results obtained at the AcH conversion of around 90% are shown in Table 4. It was found that the selectivity is scarcely affected by temperature up to 320 °C. It is, therefore, concluded that the optimum temperature is 320 °C.

Effect of Feed Rate. The effects of the AcH concentration and AcH-HCHO feed rate on reaction rate were studied at 280 °C. The results were similar to those obtained with the Si–Mg catalyst in the preceding study;[1)] the rate increases steadily with the increase in either the AcH concentration or AcH-HCHO feed rate (the HCHO/AcH molar ratio was fixed at 2).

Table 5 shows the effect of the HCHO/AcH molar

Table 4. Effect of Temperature on Acrylaldehyde Formation

Temp. °C	Contact time s	Conversion of AcH %	Yield of acryl[a)] mol%	Selectivity to acryl[a)] mol%
250	27	89	79	88
280	13	91	85	93
300	13	94	85	90
320	10	91	86	94
360	6	84	81	96
	10	92	71	77

a) Acryl=acrylaldehyde.

Table 5. Effect of HCHO/AcH Molar Ratio on Acrylaldehyde Formation[a)]

HCHO/AcH Molar ratio	Contact time s	Conversion of AcH %	Yield of acryl[b)] mol%	Selectivity to acryl[b)] mol%
1.5	20	90	85	94
2.0	13	91	85	93
4.0	5	92	90	98

a) Temperature=280 °C. b) Acryl=acrylaldehyde.

Table 6. Effect of AcH-HCHO Feed Rate on Acrylaldehyde Formation[a)]

HCHO/AcH Feed rate[a)] mmol/h	Contact time s	Conversion of AcH %	Yield of acryl[b)] mol%	Selectivity to acryl[b)] mol%
17/8.5	10	88	85	97
26/13	13	91	85	93
52/26	27	75	73	98
52/26*	27	90	86	95
104/52**	27	89	73	82

a) Temperature=280 °C; *320 °C; **360 °C. b) Acryl=acrylaldehyde.

ratio on the selectivity to acrylaldehyde. It was found that the selectivity is scarcely affected by the change in the HCHO/AcH molar ratio, though the rate decreases as the HCHO/AcH ratio decreases. This is understood from the finding that the Ni–P catalyst is inactive for the formation of CO_2 and methanol, which proceeds in parallel with the formation of acrylaldehyde.

The effect of the AcH-HCHO feed rate on the selectivity to acrylaldehyde was studied with the HCHO/AcH molar ratio fixed at 2. As is seen in Table 6, the effect of the feed rate on the selectivity is small. This is also understood from the finding that the catalyst is inactive for the side-reaction.

References

1) M. Ai, *Bull. Chem. Soc. Jpn.*, **64**, 1342 (1991).
2) M. Ai, *J. Catal.*, **107**, 201 (1987).
3) M. Ai, *Appl. Catal.*, **36**, 221 (1988).
4) M. Ai, *Appl. Catal.*, **48**, 51 (1989).
5) M. Ai, *Bull. Chem. Soc. Jpn.*, **63**, 1217 (1990).