Formation of Acrylaldehyde by Vapor-Phase Aldol Condensation I. Basic Oxide Catalysts

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Vapor-phase aldol condensation of formaldehyde with acetaldehyde to form acrylaldehyde was studied with various oxides supported on silica gel using 35% formalin as the source of formaldehyde. The silica gel unsupported catalyst prepared from colloidal silica showed a relatively high activity and selectivity to form acrylaldehyde. The catalytic activity was markedly enhanced by the incorporation of a basic or amphoteric oxide into the silica gel, while it fell with the incorporation of an acidic oxide such as P_2O_5 or B_2O_3. The highest yields of acrylaldehyde were obtained with the Si-Mg, Si-Li, Si-Na, and Si-Zn oxide systems. Effects of reaction variables were also studied using a catalyst with an Si : Mg atomic ratio of 100 : 10.

Acrylaldehyde is currently produced by a partial oxidation of propene, which process has already been well studied. On the other hand, acrylaldehyde is obtained also by an aldol condensation of formaldehyde (HCHO) with acetaldehyde (AcH) in the presence of basic catalyst. This reaction is called "Tollence Reaction":[1,2]

$$CH_3CHO + HCHO \longrightarrow CH_2(OH)CH_2CHO \longrightarrow CH_2{=}CHCHO + H_2O.$$

Schulz and Wanger[3] reported a process involving a contact catalytic conversion of an equimolecular amount of AcH and 30% HCHO aqueous solution on silica gel impregnated with 10% sodium silicate [$Na_2Si_2O_5$] at 305 to 310 °C.[4] The yield of acrylaldehyde was 41 mol% with an AcH conversion of 48%; the selectivity was about 85 mol%. The yield (mol%) is defined as 100×(moles of product)/(moles of AcH fed). The selectivity is defined as 100×(moles of product)/(moles of AcH consumed). Malinowski et al.[5] reported 46—62 mol% yields of acrylaldehyde over alkali and alkaline earth hydroxides.

This reaction is attractive in view of the utilization of C_1 chemical resources. However, aside from the above-cited works,[3,5] very little has been reported on this reaction in the literature. In this study, various kinds of metal oxides were examined as catalysts for this reaction, and then, characteristics of this reaction were studied using a silica gel containing MgO in about 10 mol%.

Experimental

Catalysts. The catalysts used in this study were oxides supported on silica gel. For example, the Si-Mg catalyst with an atomic ratio of 100 : 10 was prepared as follows. Magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] (25.6 g) was dissolved in 100 ml of water and the solution was added to 300 g of colloidal silica "Snowtex O" (Nissan Chem. Ind.) containing SiO_2in 20%. Excess water was evaporated with stirring by means of a hot air current to yield a cake. This cake was dried in an oven for 6 h by gradual heating from 50 to 200 °C. The resulting 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 was carried out with a continuous-flow system at atmospheric pressure. The reactor was made of a stainless steel tube, 50 cm long and 1.8 cm in i.d., mounted vertically and immersed in a lead bath. Nitrogen was fed in from the top of the reactor at a fixed rate of 140 $cm^3\,min^{-1}$ as the carrier or diluent, and a mixture of AcH and 35% formalin (containing methanol in about 8%) was introduced into a preheating section of the reactor by means of a syringe pump. 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. The effluent gas from the reactor was led into four chilled scrubbers to recover the water-soluble compounds. After 1 h time-on-stream, the contents of the scrubbers were collected (100 cm^3). The products were analyzed by gas chromatogarphy using a 6 m column of propylene carbonate for CO_2 and a 2 m column of PEG (polyethylene glycol) 20 M at 110 °C for aldehydes and alcohols.

The contact time, defined as (volume of catalyst)/(flow rate of gaseous feed), was changed by changing the amount of catalyst used with the feed rate fixed.

Results and Discussion

Performance of Metal Oxides Supported on Silica Gel. Various kinds of oxides supported on silica gel were tested as catalysts. The main products were acrylaldehyde, CO_2 and methanol. A very small amount of methyl formate was found in the product, but crotonaldehyde was not detected. In some cases, a large deviation was observed between the acrylaldehyde yield and the AcH conversion. It thus seems likely that the deviation is to be ascribed to formation of unidentified polymers. The conversions and yields obtained for each catalyst tested at a fixed temperature of 320 °C are listed in Tables 1 and 2.

The silica gel catalyst, prepared from the colloidal silica "Snowtex O," possesses a certain activity; the yield of acrylaldehyde reached 78 mol% with the selectivity of 98 mol% when the amount of catalyst used was 20 g (the contact time was about 10 s). The

Table 1. Performances of Silica-Supported Alkali and Alkaline Earth Metal Oxide Catalysts[a)]

Catalyst		AcH conv.	Yield/mol%		
(Atomic ratio)	wt/g	%	Acryl[b)]	CO_2	Methanol
Si alone	2	13	13	0	0
	5	32	32	0	0
	20	80	78	0.9	4
Si-Cs (100-4)	2	74	65	1.9	4
	4	85	51	4.7	6
Si-K (100-2)	2	50	44	0	2
	10	88	82	2.0	3
(100-6)	2	58	47	0.5	2
	10	95	63	5.2	12
Si-Na (100-4)	2	45	36	0.7	0
	10	89	87	2.8	3
(100-10)	2	31	28	0.5	2
	20	95	90	4.0	6
Si-Li (100-4)	2	57	47	1.4	0
	10	92	91	9.7	4
Si-Ba (100-10)	2	30	30	0.6	2
	10	54	51	5.0	6
	20	85	74	5.0	6
Si-Ca (100-0)	2	60	58	8.0	22
	6	84	75	19.0	50
Si-Mg (100-0)	1	53	51	4.0	10
	2	75	75	5.9	10
	3	80	80	9.3	28
	4	88	88	15.0	66

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

Table 2. Performances of Silica-Supported Oxide Catalysts[a)]

Catalyst		AcH conv.	Yield/mol%		
(Atomic ratio)	wt/g	%	Acryl[b)]	CO_2	Methanol
Si alone	2	13	13	0	0
	5	32	32	0	0
	20	80	78	0.9	4
Si-P (100-1)	2	low	6	0	0
Si-B (100-10)	20	33	32	0	0
Si-V (100-2)	2	43	38	2	10
	10	83	46	7.1	10
Si-Al (100-4)	2	41	38	0.5	10
	6	73	46	1.7	6
	8	81	40	2.3	6
(100-15)	1	30	25	0.9	10
	2	42	32	1.2	10
	20	99	0	7.5	6
Si-Zn (100-4)	2	52	52	4.7	8
	10	90	90	22.0	50
Si-Fe (100-4)	2	28	27	5.2	15
	8	60	55	35.0	45
Si-Sn (100-4)	2	30	28	3.3	10
	12	74	58	12.0	10
Si-Pb (100-4)	2	66	40	58.0	62
Si-Cu (100-4)	2	low	1	76.0	38

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

incorporation of a basic oxide, such as alkali or alkaline earth oxide, induces a large increase in the activity. However, it seems hard to get a clear correlation between the electronegativity of metal ions and the activity. The acrylaldehyde yield exceeds 85 mol% with the Si-Li, Si-Na, and Si-Mg systems. However, the yield does not exceed 75 mol% with the Si-Cs, Si-Ba, and Si-Ca systems.

The incorporation of an acidic oxide, such as P_2O_5 or B_2O_3, decreases the activity (Table 2). The effect of the amounts of both P_2O_5 and MgO on the activity is shown in Fig. 1. The activity increases sharply with the incorporation of a small amount of MgO, while it decreases sharply with that of P_2O_5. The results strongly suggest that the reaction is promoted by basic sites, as generally believed. However, it should be noted that the silica-supported MgO catalysts are much more active than the unsupported MgO catalyst. Possibly, the combination of silica-gel with metal oxides induces a large increase in surface area and, moreover, a generation of new acidic sites which may also serve to promote the reaction.

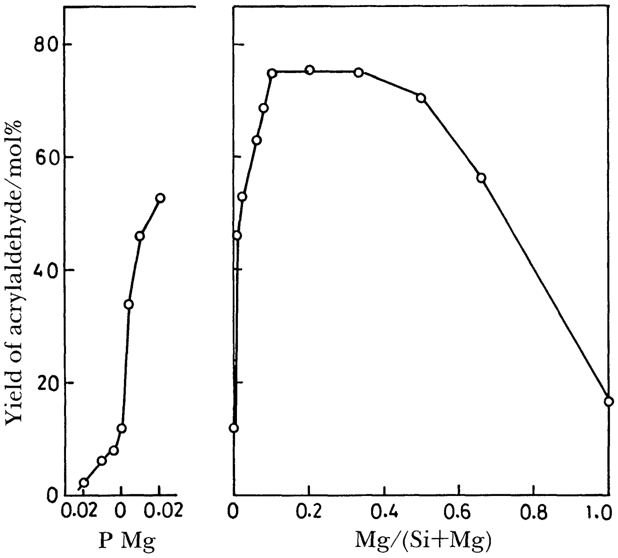

Fig. 1. Effect on activity of the amount of MgO or P_2O_5 incorporated in silica gel. Temperature=320 °C; the amount of catalyst used=20 g.

The incorporation of V_2O_5 or Al_2O_3 increases strongly the activity. However, the yield of acrylaldehyde does not exceed 50 mol%, though the formation of CO_2 and methanol is relatively slow. Possibly, the acrylaldehyde formed initially is converted to unidentified polymers under the action of strongly acidic sites present on the Si-V and Si-Al oxides:

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

A relatively good performance in both activity and selectivity was obtained with the Si-Zn oxide catalyst. The yield of acrylaldehyde reached 90 mol% with a selectivity of almost 100 mol%, though the formation of by-products such as CO_2 and methanol is relatively fast.

The incorporation of an oxide of heavy metal, such as Fe_2O_3, PbO_2, or CuO, promotes strongly the formation of by-products. The amount of obtained methanol is almost in parallel with that of CO_2, which suggests that these two by-products are formed from HCHO via the process,

$$2HCHO \longrightarrow HCOOCH_3 \longrightarrow CH_3OH + HCOOH \longrightarrow CH_3OH + CO_2 + H_2.$$

It has been reported that the formation of methyl formate by dimerization of HCHO is promoted by an acid-base dual function,[6] and that the decomposition of formic acid to CO_2 and H_2 is promoted very strongly by basic sites.[7] Possibly, the balance of acidic and basic properties of these catalysts may fit for the dimerization of HCHO.

It should also be noted that the incorporation of V_2O_5, an amphoteric oxide, or an oxide of heavy metal can enhance the catalytic activity to the level of catalysts comprising an alkali or alkaline earth metal oxide. This finding leads us to assume that active sites with a strong base, araising from alkali or alkaline earth metal oxide, are poisoned selectively by acidic reactants such as CO_2 and, further, that the reactions, especially the proton-abstraction from AcH

$$CH_3CHO + OH^- \longrightarrow {}^-CH_2CHO + H_2O,$$

are promoted enough by active sites with a very weak base, araising from V_2O_5 and amphoteric oxides.

Effects of Reaction Variables. The study in the preceding section has revealed that the Si-Li, Si-Na, Si-Mg, and Si-Zn catalysts exhibit a good performance for the acrylaldehyde formation. Thus, the characteristics of this reaction were studied using the catalyst with an Si : Mg atomic ratio of 100 : 10.

Product Distribution. The yields of acrylaldehyde, CO_2, and methanol obtained at 280 °C are shown in Fig. 2 as a function of contact time. The yield of acrylaldehyde on the AcH basis reaches 96 mol%, whereas those of CO_2 and methanol reach 12 and 43 mol%, respectively. The sum of the yields of the three products exceeds far 100 mol%. This also indicates that CO_2 and methanol are not formed from AcH but from HCHO.

Effect of Temperature. The yields of acrylaldehyde btained at four temperatures are shown in Fig. 3 as a function of contact time. From the initial rates at 240 and 280 °C, the apparent activation energy was calculated to be about 15 kcal mol^{-1}. The yield of acrylaldehyde reaches 96 mol% at a temperature between 280 and 340 °C.

Effect of AcH Concentration on Rate. The effect of AcH concentration was studied by changing the initial concentration in the feed gas from 0.78 to 5.6 mol%, while fixing the concentrations of HCHO, methanol, and water at about 6, 1.2, and 16 mol%, respectively. The rate increases steadily with the AcH concentration.

Effect of the HCHO/AcH Molar Ratio on the Yield of Acrylaldehyde. The effect of the HCHO/AcH molar ratio on the yield of acrylaldehyde was studied

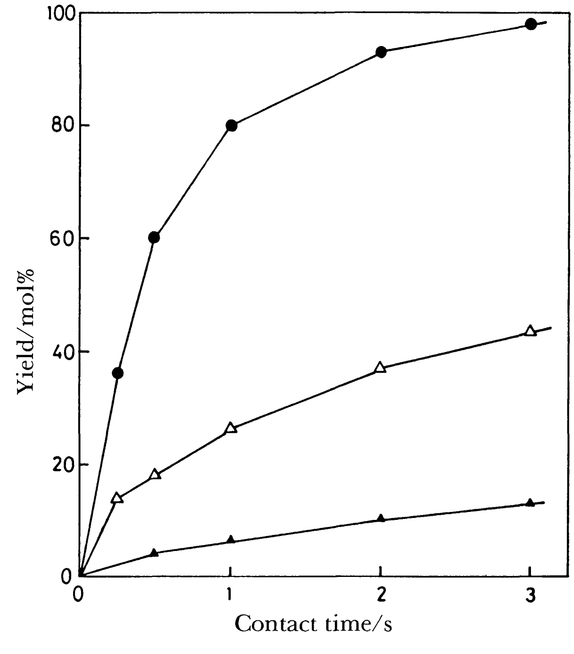

Fig. 2. Reaction of HCHO with AcH with the Si : Mg=100 : 10 catalyst. ● Acrylaldehyde; ▲ CO_2; △ methanol.

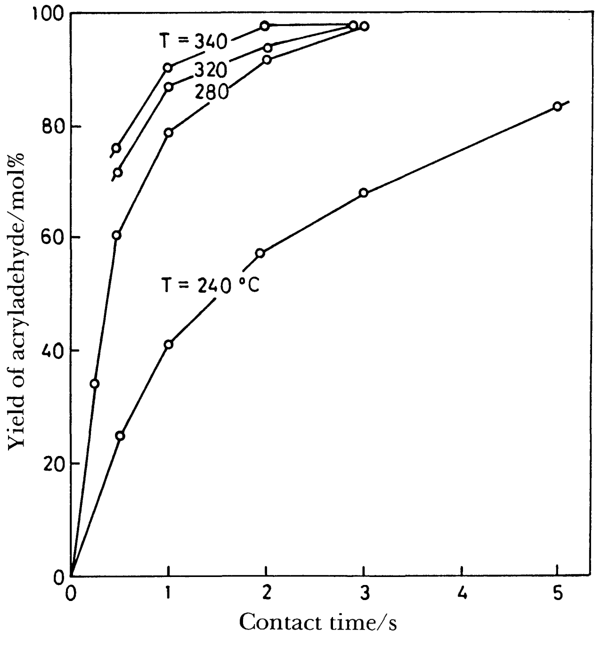

Fig. 3. Effect of temperature on the yield of acrylaldehyde.

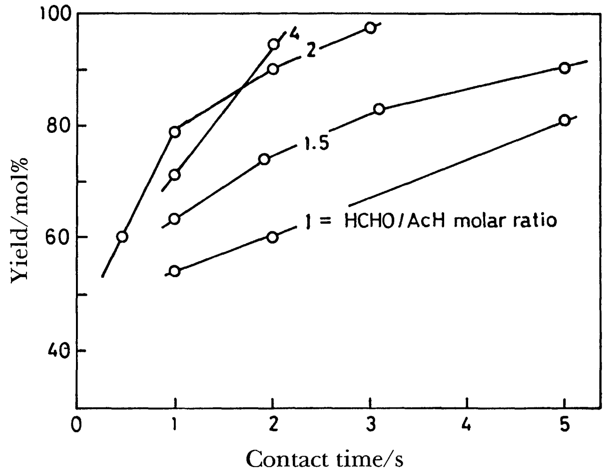

Fig. 4. Effect of the HCHO/AcH molar ratio on the yield of acrylaldehyde. Temperature=280 °C.

at a fixed AcH feed rate of about 13 mmol h^{-1} by changing the feed rate of formalin. Figure 4 shows the yields obtained at 280 °C with four different HCHO/AcH ratios. Longer contact time is required to achieve a certain level of acrylaldehyde yield as the HCHO/AcH ratio decreases, which indicates that the rate increases with the HCHO concentration, too.

Effect of Feed Rate. The reaction was conducted by changing the feed rates of AcH and HCHO, while fixing the HCHO/AcH molar ratio at 2. The initial rate of acrylaldehyde formation at 240 °C increased steadily with the increase in the feed rate, as reasonably expected from the above-mentioned results.

Conclusion. The silica gel prepared from the colloidal silica exhibits a relatively good catalytic performance in both activity and selectivity to form acrylaldehyde by aldol condensation of HCHO with AcH. The incorporation of a small amount of alkali or alkaline earth oxide, V_2O_5, an amphoteric oxide, or an oxide of heavy metal enhances markedly the activity. However, the formation of acrylaldehyde is accompanied by two side-reactions the polymerization of produced acrylaldehyde to unidentified polymers and the dimerization of HCHO to methyl formate which is decomposed readily to methanol and CO_2. The highest acrylaldehyde yields are obtained with the Si–Na, Si–Li, Si–Mg, and Si–Zn oxides.

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