

Formose Reactions. VII. Some Solid Catalysts for the Formose Reaction

by

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CSH gel which is tobermorite was found to give a selective formose reaction. The catalysis of CSH gel calcined at various temperatures was examined. At calcination temperature, 600°C it was most active, but above 700°C, it became inactive. When CSH gel suspension in water was refluxed for 3 h, it lost the catalysis action. The calcium oxalate precipitated at ORP_{min} , which appeared in the formose reaction catalyzed with $Ca(OH)_2$, was also found to give another selective formose reaction of which the major products were 2-hydroxymethylglycerol, 2,4-bis (hydroxymethyl) -1, 2, 3, 4, 5-pentanepentol, and 3-hydroxymethyl-1, 2, 3, 4, 5-pentanepentol. Catalysis was kept below 300°C, but the catalyst treated at 540°C could not catalyze the formose reaction. The various preparation methods of active calcium oxalate and the effects on the product distribution were investigated.

1. Introduction

In a series of our studies¹⁻⁴⁾ on the formose reaction, the oxidation-reduction potential (ORP) of the reaction mixture has been measured as an indication of the reaction process. The concluding facts are as follows : catalytic species in the induction period of the formose reaction catalyzed with calcium hydroxide is $CaOH^+$. At the formose-forming step, however, $CaOH^+$, dissolved and undissolved $Ca(OH)_2$, and OH^- are also effective species as catalysts. Under the above reaction conditions, the product consists of 30 or more very complex components, as has been already reported.⁵⁾ At the starting point of the formose-forming step, at which ORP shows a minimum, the equivalent amount of oxalic acid to the catalyst, $Ca(OH)_2$, and another metal hydroxide, for example $Mg(OH)_2$, were successively added, then the reaction was immediately initiated by adjusting the mixture to a given pH with conc. KOH. There appeared a marked selectivity in the gas-chromatogram of TMS derivatives of the products. The selective formose reaction was found to occur giving three branched sugar alcohols, 2-hydroxymethylglycerol, 2, 4-bis (hydroxym-

ethyl)-1, 2, 3, 4, 5-pentanepentol, and probably a diastereomeric mixture of 3-hydroxymethyl-1, 2, 3, 4, 5-pentanepentol.

On the other hand, it has been noted that, in some cases, the heterogeneous catalysis promotes a specific reaction which might be minor or simultaneous in the homogeneous system. The solid catalyst, furthermore, has another advantage that it is very easy to separate the products from the catalyst. Despite the advantage gained by empirical and theoretical observations, it is rare that a catalyst can be chosen so that it is entirely specific or unique in its behaviour.

From the above point of view, it is very important to discover such a solid catalyst which gives a selective formose reaction. In this paper, materials which contain calcium, such as xonotlite, portland cement etc, were examined as to whether or not they could catalyze the formose reaction, and the products are unique. Calcium silicates used in this work can be prepared by hydrothermal synthesis and have been spot-lighted as a light construction material of non-in flammable character at the present time.

2. Experimental

Materials. CSH gel prepared by Osaka Packing Mfg. Co. contained CaO 48.0, SiO₂ 39.0, Al₂O₃ 0.3, Fe₂O₃ 0.3, and Ig. loss 12.0%. The structure was estimated as tobermorite gel by X-ray analysis.⁶⁾ When it was used as a catalyst, it was mainly calcined at 180°C for 12 h in air with an electric furnace. Xonotlite slurry supplied by Osaka Packing Mfg. Co, $6\text{CaO} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$, was calcined at given temperatures. Portland cement supplied by Osaka Cement K.K. contained CaO 64.3, SiO₂ 22.2, Al₂O₃ 5.3, Fe₂O₃ 3.6, and Ig. loss 0.6% according to the analysis of JIS R52 02. Calcium oxalate was prepared with different procedures which will be explained precisely in Table 4. The powder used as a catalyst was passed through a 200 mesh sieve. The calcium content of calcined xonotlite was determined as follows: a given xonotlite, ca. 0.1g (weighed exactly) was dissolved into 20 ml of conc. conc. HCl and the solution diluted exactly to 100 ml with water was titrated with EDTA adding NN-reagent as the indicator.⁷⁾ Aqueous formaldehyde solutions were prepared from paraformaldehyde (Merck Co.).²⁾ Other reagents used were of an analytical grade.

Procedure. The apparatus and the experimental procedure were virtually the same as those described previously.^{2,3)} The formaldehyde consumption, the sugar yield, the concentration of the dissolved calcium ion species, and the ORP were measured by the method described in the previous papers. The preparation of trimethyl silylated (TMS) derivatives of products and its gas-chromatography were carried out in the same manner as described previously.⁸⁾

3. Results and Discussion

The formose reaction catalyzed with $\text{Ca}(\text{OH})_2$ or CaO was strongly affected by pH of the reaction mixture.^{2,3,9)} This result was explained on the basis of the concentration of CaOH^+ which is determined by the dissociation constant of $\text{Ca}(\text{OH})_2$ and the concentration of dissolved calcium.³⁾ These are also determined by the pH of the solution. In the case of CSH gel catalyst, pH influences strongly the formose reaction as shown in Fig. 1, but the effects are somewhat different from those in

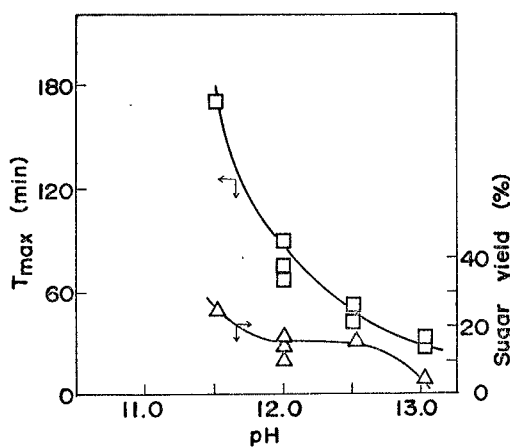


Fig. 1 Effect of the pH of the reaction mixture.

[HCHO]=1.0 M [CSH gel]=0.15 M as CaO ; Temp., 60°C . The pH was controlled by conc. KOH. CSH gel was calcined at 180°C for 12 h in air.

Table 1. Effect of CSH gel on the formose reaction^{a)}

CSH gel ^{b)} (M as CaO)	T_{\max} (min)	Sugar yield (%)	Products (glc%)				
			2HG	11	3HPP	22	2,4BHPP
0.10	75	14	13	15	33	4	5
0.15	75	10	1	19	14	5	2
0.30	80	12	5	19	25	2	3
—	(85.3) ^{c)} ₂₀₀	—					

a) [HCHO]=1.0M ; pH=12.0 adjusted by KOH ; Temp., 60°C ; Total volume=200 ml ; N_2 .

b) Calcined at 180°C for 12 h.

c) T_{\max} was not observed and the data mean the formaldehyde consumption at 200 min.

the reaction catalyzed with $\text{Ca}(\text{OH})_2$.

Figure 1 shows that T_{\max} , the time length of the reaction at which the formaldehyde consumption is over 90%, decreases with the increasing pH of the reaction mixture. On the other hand, T_{\max} in the formose reaction catalyzed with $\text{Ca}(\text{OH})_2$ increased due to decreasing the dissolved calcium ion concentration ($[\text{Ca}]$) above pH 11.5.^{2,3)} In this paper, the reaction was carried out at pH 12.0 (adjusted by conc. KOH) to suppress the effects of the dissolved calcium ion, because $[\text{Ca}]$ is less than 2×10^{-2} M at pH 12.0.³⁾

Product analyses by gas chromatography of TMS derivatives are shown in Table 1. Product distribution and the sugar yield were not influenced by the amount of CSH gel, but it could be notable that GLC peak 11 is a major product in the gas chromatogram, and CSH gel might give a useful selective formose reaction.

Timecourses of ORP, the formaldehyde consumption, and the sugar yield in the formose reaction catalyzed with CSH gel are shown in Fig. 2. The same relationships between them are observed as those in the formose reaction catalyzed with Ca -

(OH)₂. Namely, at ORP_{min} the formose-forming step begins, then formaldehyde consumption occurs rapidly with smooth sugar production.

As shown in Table 2, xonotlite slurry was not as active as the catalyst for the formose reaction. In the case of CSH gel, when the calcination temperature was below 600°C, T_{max} decreased by increasing the temperature, but [Ca], the sugar yield, and the product distribution were independent of the calcination temperature. Above 700°C, catalysis was lacking in spite of increasing the dissolved calcium ion concentration. Iizuka *et al.*¹⁰⁾ reported as follows: The basicity of calcium oxide calcined at various temperatures attains a maximum value at 500°C. The decrease in observed basicity at higher temperature of calcination seems to indicate that

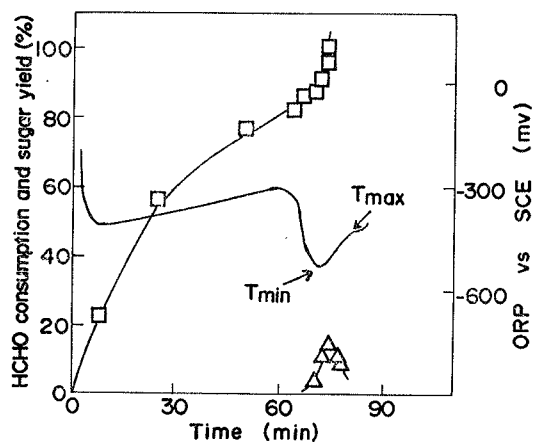


Fig. 2 Timecourses of ORP, HCHO consumption and sugar yield in the formose reaction catalyzed by CSH gel.

[HCHO]=1.0M; [CSH gel]=0.1M as CaO (calcined at 180°C for 12 h); pH=12.0 adjusted by KOH; Temp., 60°C. □, HCHO consumption; △, Sugar yield; —, ORP.

Table 2. Effects of calcination temp. on the formose reaction^{a)}

Catalyst ^{b)}	Calcination Temp. (°C)	[Ca] (10 ⁻⁴ M)	T _{max} (min)	Sugar yield (%)
CSH gel	r.t.	9.6	79	11
CSH gel	180	5.2	75	10
CSH gel	300	9.5	70	13
CSH gel	500	10.0	53	13
CSH gel	600	7.0	54	13
CSH gel	700	10.1	(97) ₁₈₀ ^{d)}	e)
CSH gel	1000	25.0	(96) ₁₈₀ ^{d)}	e)
Xonotlite slurry	180	5.0	(91) ₁₈₀ ^{d)}	e)
Xonotlite slurry	300	3.0	(92) ₁₈₀ ^{d)}	e)
Xonotlite slurry	500	0.5	(90) ₁₈₀ ^{d)}	e)
Xonotlite slurry	800	0.3	(92) ₁₈₀ ^{d)}	e)

a) [HCHO]=1.0M; pH=12.0 adjusted by KOH; Temp., 60°C.

b) The concentration of CSH gel and xonotlite slurry were 0.15 and 0.3 M as CaO respectively.

d) The data mean the formaldehyde consumption at 180 min.

e) Benedict's reaction was negative.

the basic sites are associated with unstable crystal structures of calcium oxide. Namely, the basicity decrease is considered due to the stabilization of the unstable structure. Furthermore, Asano *et al.*¹¹⁾ postulated that, in the carbonation of xonotlite and tobermorite, the former is less reactive than the latter, because, owing to the different hydrothermal synthesis conditions (under saturated steam, xonotlite 150-400°C, tobermorite 110-140°C), xonotlite has a packing structure and tobermorite is a semicrystalline. CSH gel used has a tobermorite structure, so it could be assumed that the catalysis for the formose reaction might be controlled by its basicity and structure.

Figure 3 shows an IR spectrum of CSH gel calcined at various temperatures. Below 600°C, there is no change in the IR spectrum, but above 700°C there appears

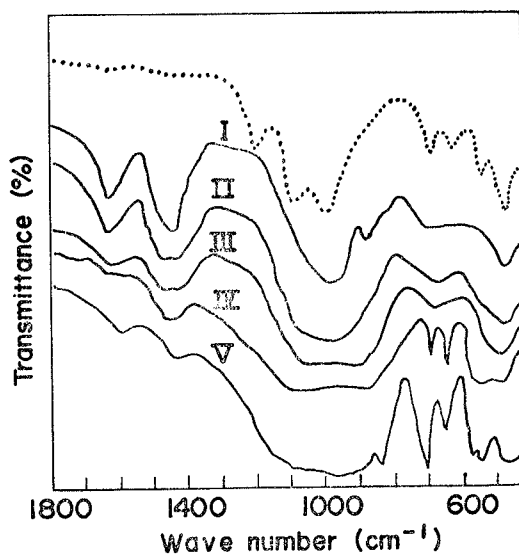


Fig. 3 IR spectrum of CSH gel calcined at various temperatures.
Calcination temp. : I, r.t. ; II, 600°C ; III, 700°C ; IV, 1000°C ; V, 1200°C. Calcinations were carried out for 12 h in air. ..., Xonotlite slurry calcined at 500°C.

appreciable changes in the IR spectrum of calcined CSH gel which is not able to catalyze the formose reaction. Namely, by increasing the calcination temperature, the broad absorption at 1620 cm^{-1} decreases and the two sharp absorptions at 650 and 720 cm^{-1} increase. The IR spectrum of xonotlite slurry is apparently different from that of CSH gel. From the results of X-ray analysis of CSH gel calcined at various temperatures, it was qualitatively estimated, but not quantitatively, that the crystallinity of CSH gel which catalyzed the formose reaction was generally less.

From these results, it might be natural to conclude that the catalytic action of xonotlite is controlled by its structure. Furthermore, the fact that

the ignition loss of CSH gel was relatively large, *ca.* 12%, might imply that water of crystallization in CSH gel is important for the catalysis.

In order to examine the effects of water on the catalysis of CSH gel, CSH gel calcined at 180°C for 12 h was suspended in water at 60 and 100°C before the formose reaction was carried out, and the results obtained are shown in Table 3. The catalyst which was suspended in water for a long time, for example 3 h at 100°C, could not catalyze the formose reaction. Furthermore, when the catalyst was used repeatedly, two or three times, it became inactive, but calcining it again, it became

Table 3. Catalysis of CSH gel suspended in water^{a)}

Temp. (°C)	Time (h)	T _{max} (min)	Sugar yield (%)	[Ca]
—	—	75	10	nil
60	12	73	9	nil
60	24	91	10	nil
60	144	199	9	nil
60	336	(94) ^{b)} ₁₈₀		nil
60	456	(87) ^{b)} ₁₈₀		nil
100	1	100	8	nil
100	3	(90) ^{b)} ₁₈₀		nil
100	12	(96) ^{b)} ₁₈₀		nil

a) Reaction conditions : [HCHO]=1.0M ; [CSH gel] =0.15M as CaO ; pH=12.0 ; Temp., 60°C ; N₂.

b) The data mean the formaldehyde consumption (%) at 180 min.

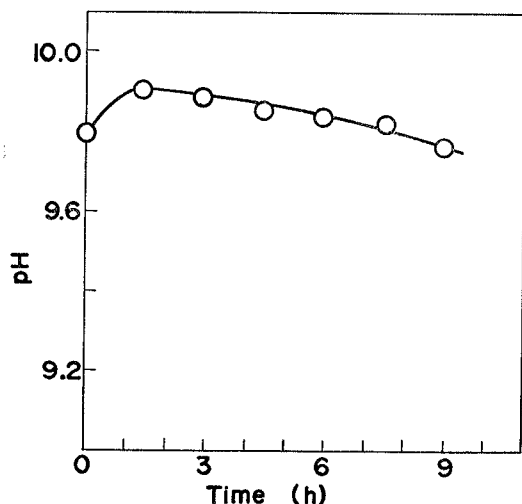


Fig. 4 Timecourse of the pH of CSH gel suspension.
[CSH gel]=0.3M as CaO(calced at 180°C for 12 h) ; Temp., 100°C.

into the solution and as a result a hydrous SiO₂ layer is formed at the crystal surfaces. When the thickness of this layer reaches a certain value, it usually begins to

be possible to use it as a catalyst for the formose reaction. When the reaction was catalyzed by CSH gel, which was suspended in water and calcined again, the product distribution was not so selective as that obtained with freshly prepared CSH gel.

The timecourse of pH of CSH gel suspension is shown in Fig. 4. The increase of pH as seen in Fig. 4 is considered to be caused by a dissolution of Ca(OH)₂ from xonotlite into the solution as reported by Maki *et al.*¹²⁾ Namely, when xonotlite crystals come in contact with the solution, Ca²⁺ ions at and near the surfaces of the crystals dissolve

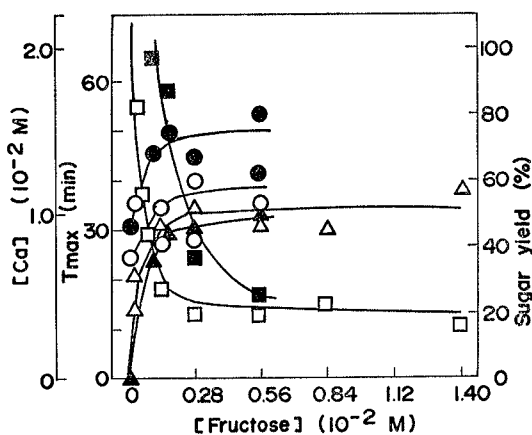


Fig. 5 Effect of fructose concentration on the formose reaction catalyzed with Portland cement.

[HCHO]=1.0M ; [Portland Cement] = 0.5M as CaO ; Temp., 60°C ; pH was adjusted by conc. KOH to a given pH.

pH=11.5 : ■, T_{max} ; ▲, Sugar yield ; ●, [Ca].
pH=12.0 : □, T_{max} ; △, Sugar yield ; ○, [Ca].

break down into tiny flakes.¹³⁾ The gradual decrease in pH after their maxima as seen in Fig.4 was caused by dissolution of SiO_3^{2-} from these SiO_2 flakes.

Figure 5 shows the effects of the fructose concentration on the formose reaction catalyzed with Portland Cement. In the absence of fructose, the reaction did not occur. Above 2.8×10^{-3} M of the fructose concentration, further addition of fructose did not influence T_{max} and the sugar yield. The product components became complex.

In order to obtain some information for designing a catalyst which gives a selective formose reaction, the properties of calcium oxalate precipitated at $\text{ORP}_{\text{min}}^{\text{a)}}$ were examined and the results obtained are shown in Table 4. The calcium oxalate had better catalysis than the calcium phosphate. Both product distributions were the same and the major products were 2-hydroxymethylglycerol, 2,4-bis(hydroxymethyl)-1, 2, 3, 4, 5-pentanepentol, and 3-hydroxymethyl-1, 2, 3, 4, 5-pentanepentol.

Table 4. Formose reactions catalyzed by the calcium salts precipitated at $\text{ORP}_{\text{min}}^{\text{a)}}$

Calcium salt (M)	T_{max} (min)	Sugar yield (%)
	(74) ₁₈₀ ^{c)}	(0.1) ₁₈₀
Calcium oxalate precipitated ^{b)}	0.1	60
Commercial calcium oxalate	0.3	(88) ₁₈₀ ^{c)}
Calcium phosphate precipitated ^{b)}	0.03	(75) ₁₈₀ ^{c)}
Calcium phosphate precipitated ^{b)}	0.1	129
		14
		(0.4) ₁₈₀
		(3.8) ₁₈₀
		12

a) $[\text{HCHO}] = 1.0$ M ; pH=12.0 adjusted by KOH ; Temp., 60°C.

b) The formose reaction was carried out under $[\text{HCHO}] = 1.0$ M, $[\text{Ca}(\text{OH})_2] = 0.1$ M, and Temp., 60°C. After equivalent amounts of oxalic acid or phosphoric acid to $\text{Ca}(\text{OH})_2$ used were added at ORP_{min} , the precipitated salts were separated and dried at r.t. in air.

c) The data mean the formaldehyde consumption(%) at 180 min.

Table 5. Thermo stability of the calcium oxalate precipitated at $\text{ORP}_{\text{min}}^{\text{a)}}$

Heating temp. ^{b)} (°C)	T_{max} (min)	Sugar yield (%)
40	60	16
150	60	14
300	63	12
540	(90) ₁₈₀ ^{c)}	(0.2) ₁₈₀

a) The reaction conditions and the procedure of calcium oxalate preparation were same as Table 4.

b) Heating time was 4 h.

c) The data mean the formaldehyde consumption (%) at 180 min.

The thermostability of the calcium oxalate precipitated at ORP_{min} is shown in Table 5. Its catalysis was kept below $300^{\circ}C$. From these results, it could be concluded that the catalysis might be due to a slight amount of products which were formed in the induction period. Namely, it could be supposed that the main reason why the catalyst treated at $540^{\circ}C$ could not catalyze the formose reaction cannot be explained by the change from calcium oxalate to calcium carbonate, but by the decomposition of the slight amount of organic substances formed in the induction period owing to such a high temperature.

The active calcium oxalate was prepared using three procedures : The formose reaction was started under the conditions, $[HCHO]=1.0$ M, $[Ca(OH)_2]=0.1$ M, and temperature= $60^{\circ}C$, then 0.1 M phosphoric acid was added to the reaction mixture at ORP_{min} . After the mixture was cooled with an ice bath, it was separated into a precipitate and a filtrate. Into 200 ml of the filtrate, 0.1 M calcium hydroxide and 0.1 M oxalic acid were added successively, then the precipitated calcium oxalate (1) was dried in air at room temperature. In the same manner, the calcium oxalate (2) was prepared by adding oxalic acid and calcium hydroxide successively, and the calcium oxalate (3) was prepared by adding calcium chloride and oxalic acid successively. The selectivity in the formose reaction decreased when the catalyst varied in the order (1)>(2)>(3). These results suggest that in order to make a catalyst which gives a selective formose reaction it is necessary to absorb the effective substances on the surface of calcium hydroxide.

By the same method as described above, except that 0.02 M glycolaldehyde aqueous solution was used in place of

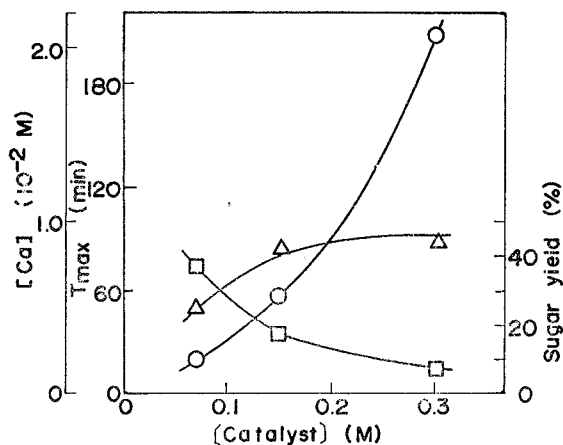


Fig. 6 Effect of the concentration of $Ca(OH)_2$ containing glycolaldehyde on the formose reaction.

$[HCHO]=1.0$ M ; pH = 12.0 adjusted by KOH. Temp., $60^{\circ}C$. \square , T_{max} ; \triangle , Sugar yield ; \circ , $[Ca]$.

of the filtrate, the active calcium oxalate was prepared and the results are shown in Fig.6. When the dissolved calcium ion concentration was low, ca. 1.0×10^{-3} M, it gave a selective formose reaction with three major products, but in the presence of such a high dissolved calcium ion concentration as 2×10^{-2} M, the products were very complex. It is necessary to investigate the relationship between other organic substances as a cocatalyst and the product distribution.

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