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Synthesis of Trioxane Using Heteropolyacids as Catalyst

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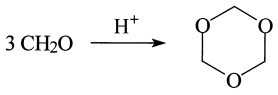
Acetal resin is a term used to describe the high molecular weight polymers and the copolymers of formaldehyde. First commercialized as a homopolymer in 1960 by DuPont, acetal resins are engineering thermoplastics which have found broad use in areas where traditionally metals were applied.[1] Shortly thereafter, researchers at Celanese developed an acetal resin based on the copolymerization of trioxane and cyclic ethers, such as ethylene oxide.[2] In 1962 a commercial plant began producing this acetal copolymer. Since then, a rapid expansion of acetal resin production has occurred worldwide.

Up to 1971 DuPont and Celanese (alone or in joint ventures with other companies) were the sole producers of acetal resins. In 1972 Asahi Chemical started to produce the acetal homopolymer utilizing the world's third type of polyacetal technology.[3] Asahi Chemical also industrialized the acetal copolymer in 1985.[4] At present, the annual demand of acetal resins in the world is about 400000 t per year.

The biggest problem in the case of acetal resins is the energy consumption during its production. The main aspect is the energy requirement in the monomer process. For example, it requires a great deal of energy to get the monomeric trioxane that is needed for the acetal copolymer from aqueous formaldehyde. In the commercial process, trioxane is obtained by heating aqueous formaldehyde in the presence of an acid catalyst like sulfuric acid [Eq. (1)].



(1)

Even though the equilibrium concentration of trioxane is low in the reaction mixture, in the commercial production process trioxane is removed as the distillate from the reaction mixture in the distillation tower.[5] The vapor–liquid equilibrium between trioxane and aqueous formaldehyde is such that when the trioxane concentration in the liquid phase is low, trioxane shows a very high volatility compared to formaldehyde and water in the vapor phase. Thus, almost all the trioxane contained in the vapor phase from the reaction mixture can be concentrated into the distillate in the distillation tower under the proper refluxing conditions. Since the heat of vaporization of the water–formaldehyde mixture is much higher than that of trioxane,[6] most of the energy for trioxane synthesis is consumed in the vaporization of water and formaldehyde.[7] From the viewpoint of the energy requirement, the key point of the trioxane synthesis is the high yield and high selectivity in a one-pass vaporization.

At Asahi Chemical, we developed the *tert*-butyl alcohol process, that is the selective hydration of isobutene using a highly concentrated heteropolyacid as the catalyst.[8] We also developed a new process for producing polyoxytetramethylene glycol with a narrow molecular weight distribution using a heteropolyacid as a catalyst for the polymerization of tetrahydrofuran.[9, 10] With this knowledge, we investigated the catalytic activity of heteropolyacids for the synthesis of trioxane. We observed some interesting phenomena and a superior advantage of heteropolyacids over conventional catalysts like sulfuric acid.

The results for the reaction at atmospheric pressure and 100 °C are shown in Table 1. The best features of using the heteropolyacid, instead of sulfuric acid, as a catalyst for trioxane synthesis were the higher conversion and selectivity. For example, for the same selectivity of 97%, the conversion by sulfuric acid was 20%, while the conversion by the heteropolyacid was 27% (drawn from entries 10 and 6 respectively in Table 1). Heteropolyacids provided a 35% higher yield (yield = conversion × selectivity) than sulfuric acid. A similar result was also obtained for the hydration of isobutene.[8] In this case, high selectivity of heteropolyacids was reported to be related to the big size of their anions.

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Table 1. Results from the synthesis of trioxane with heteropolyacids and with sulfuric acid as the catalyst.[a]

Entry	Catalyst[b]	t [min][c]	Conv. [%][d, e]	S [%][e, f]
1	PW (30)	39	18.3	98.5
2	PW (100)	34	24.6	98.3
3	PW (100)	50	25.5	98.1
4	SiW (30)	23	22.0	99.3
5	SiW (30)	42	22.7	99.2
6	SiW (100)	27	26.7	97.1
7	SiW (100)	41	27.5	95.4
8[g]	SiW (100)	19	28.0	97.1
9	H_2SO_4 (2)	38	14.5	98.5
10	H_2SO_4 (5)	52	17.4	97.5
11	H_2SO_4 (10)	31	17.9	97.4
12	H_2SO_4 (30)	12	21.0	96.5
13	H_2SO_4 (30)	18	22.3	94.5
14	H_2SO_4 (30)	27	23.6	93.5

[a] The reaction was carried out at 100 °C under atmospheric pressure; unless noted otherwise, 55 wt % formalin was used. [b] PW = phosphotungstic acid, SiW = silicotungstic acid; the number in parentheses indicates the amount of catalyst (in g) per initial 100 g of formalin. [c] The contact time t is defined here for simplicity as follows: t [min] = volume of the reaction mixture [mL]/rate of feed formalin [mL min^{-1}], assuming the density of the feed formalin is 1.0 g mL^{-1}. [d] Conversion [%] = {(3[trioxane] + 2[methyl formate] + [methylal])/[feed formalin]} × 100. Almost all the by-product is methyl formate, and only a small amount of methylal was observed. The amount of formic acid was negligibly small. Methyl formate is generated by the Cannizzaro reaction from two molecules of formaldehyde. Methylal is formed by the reaction of two molecules of methanol and one molecule of formaldehyde. [e] For the calculation of conversion and selectivity S concentrations in mol g^{-1} were used. [f] S [%] = {[trioxane]/([trioxane] + 2[methyl formate] + [methylal])} × 100. [g] 61 wt % formalin was used.

With continuous feeding of 55 wt % formalin to the reaction mixture, no scale formation was observed for the heteropolyacids; that is, no paraformaldehyde was formed. However, for sulfuric acid, some whitening of the reaction mixture—that is, formation of paraformaldehyde—was observed. Thus the upper limit of the feed formaldehyde concentration using sulfuric acid as catalyst was considered to be 55 wt %. On the other hand, for the heteropolyacids, by increasing the amount of the heteropolyacid in the reaction mixture from 30 to 100 g (per initial 100 g of formalin), continuous feeding of 61 wt % formalin to the reaction mixture was possible without any problems of scale formation. This phenomenon meant an increase in the solubility of formalin in the presence of heteropolyacids, which might result from the interaction of the heteropolyacids with an ether linkage of the oligooxymethylene glycol.

Increasing the formaldehyde concentration from 55 to 61 wt % with the same conversion and same selectivity means an increase of 10 % in the yield of trioxane per energy for trioxane synthesis.[7] Thus, considering the increase in conversion and the increase in feed formalin concentration, an increase of 50 % for the yield of trioxane per energy for trioxane synthesis may be possible.

We investigated the solubility of formalin in the heteropolyacids. Figure 1 shows that increasing the weight percent of heteropolyacid enhanced the solubility of formalin. The reaction temperature was changed by altering the vaporizing pressure. We thus determined the whitening temperature for the reaction mixtures. With an increase in the weight percent

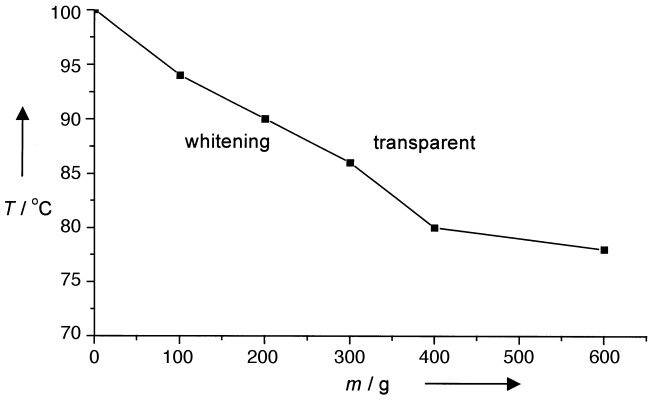

Figure 1. Plot of the lowest temperature T for which upon cooling no whitening (paraformaldehyde formation) occurs as a function of the amount m of heteropolyacid per 100 g of formalin. The catalyst was phosphotungstic acid; 55 wt % formalin was used; contact time 12 – 30 min.

of heteropolyacid, ever lower temperatures could be reached without whitening. In the case of a conventional catalyst like sulfuric acid, with feeding of 55 wt % formalin, the critical temperature was around 100 °C. However, through the use of heteropolyacids, we could work at lower reaction temperatures without whitening by increasing the amount of the heteropolyacids in the reaction mixtures. In Figure 1, we show the example of using phosphotungstic acid as catalyst. Similar results were obtained in the case of silicotungstic acid. These facts suggested that the heteropolyacids have a high solvation power for formalin.

The effect of temperature on the trioxane synthesis is shown in Table 2. An increase in temperature results in a decrease in conversion and selectivity of trioxane formation. Thus, high selectivity and high conversion were attained using highly concentrated heteropolyacids under reduced pressure (to achieve reaction temperatures of 81 – 84 °C; entries 7 – 10). These phenomena are thought to be characteristic for heteropolyacids and could not be achieved using a conventional catalyst like sulfuric acid, considering the fact that in the sulfuric acid catalyst system the critical temperature was 100 °C for the 55 wt % formalin feed.

In Figure 2, the relationships between the yield and selectivity obtained under various conditions are shown. With

Table 2. Effects of temperature T on conversion and selectivity S in the synthesis of trioxane.[a]

Entry	Catalyst[b]	T [°C]	t [min][c]	Conv. [%][d, e]	S [%][e, f]
1[g]	PW (30)	110	15	17.7	98.6
2[g]	PW (30)	110	20	18.3	98.1
3[g]	PW (30)	110	48	22.9	97.3
4[h]	PW (30)	100	39	18.3	98.5
5[h]	PW (100)	100	34	24.6	98.3
6[h]	PW (100)	100	50	25.5	98.1
7[i]	PW (300)	84	25	30.1	98.4
8[j]	PW (400)	83	15	27.5	99.2
9[j]	PW (400)	83	37	28.9	98.6
10[k]	PW (600)	81	36	31.2	99.2

[a] 55 wt % formalin was used. [b] – [f] See footnotes [b] – [f] of Table 1. [g] p = 2.65 atm. [h] p = 1 atm. [i] p = 0.44 atm. [j] p = 0.42 atm. [k] p = 0.33 atm.

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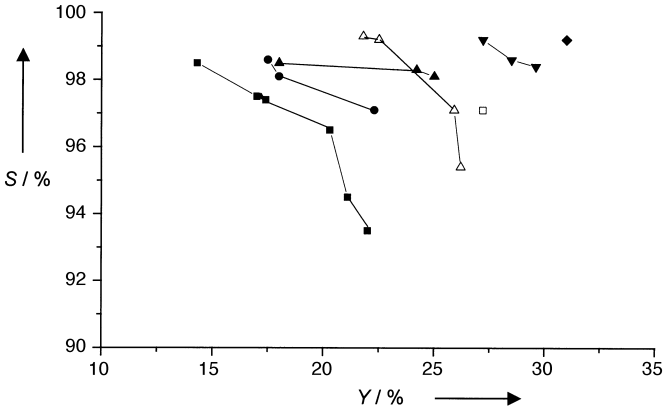

Figure 2. Relationships between yield *Y* and selectivity *S* under various conditions (see Tables 1 and 2). Unless noted otherwise, 55 wt% formalin was used. The catalyst and reaction temperature are as follows: ■ sulfuric acid at 100 °C, ● phosphotungstic acid at 110 °C, ▲ phosphotungstic acid at 100 °C, ▼ phosphotungstic acid at 83–84 °C, ◆ phosphotungstic acid at 81 °C, △ silicotungstic acid at 100 °C, □ silicotungstic acid at 100 °C using 61 wt% formalin.

an increase in yield, a decrease in selectivity was observed. However, a decrease in reaction temperature was accompanied by an increase in selectivity. Comparing the results obtained using heteropolyacids with those obtained using sulfuric acid, it is apparent that the heteropolyacid provides a higher yield and higher selectivity than sulfuric acid. Especially, by lowering the reaction temperature, a higher yield and higher selectivity can be attained.

In conclusion, considering the increase in conversion and selectivity as well as the increase in formalin solubility upon the use of heteropolyacids as a catalyst for trioxane synthesis, it might be possible to increase the yield of trioxane by over 50% yield of trioxane per energy for trioxane synthesis.[7] Therefore, heteropolyacids are worth developing as a catalyst for the commercial production of trioxane. This would open a new aspect for the industrial application of heteropolyacids as a catalyst in addition to the synthesis of *tert*-butyl alcohol (selective hydration of isobutene)[8] and polymerization of tetrahydrofuran to polyoxytetramethylene glycol.[9]

Experimental Section

We mainly used a 55 wt% aqueous formaldehyde solution, which was prepared by dissolving the 84 wt% paraformaldehyde flake (Sumitomo Chemical) in water at 100 °C. For the heteropolyacids, we used the commercial chemical grade of silicotungstic acid ($H_4SiW_{12}O_{40} \cdot 26H_2O$) and phosphotungstic acid ($H_3PW_{12}O_{40} \cdot 29H_2O$), supplied by Nippon Inorganic Color and Chemical, without further purification.

For the reactions, a 200-mL glass reactor was used. A thermal jacket, which was added to the top cover of the reactor, was heated with steam so that the vapor phase in the reactor did not condense on the inner face of the top cover. Thus, the reaction gas mixture was correctly carried (without change in composition) to the condenser without inner refluxing. (If partial condensation occurred on the inside surface of the top cover, the relative amount of trioxane was higher and thus the data measured gave the wrong results.) The reaction mixture (100 mL) consisting of the catalyst and 55 wt% formalin feed was heated in an oil bath. Formalin was continuously fed to the reactor, and the reaction product continuously vaporized from the homogenous liquid reaction mixture. The vapor phase condensed in the condenser, and the condensate (water/formaldehyde/trioxane) was analyzed by gas chromatography. The level of the reaction mixture was controlled by a photo level controller, and the feed rate of formalin was adjusted to obtain a constant level of the reaction mixture. The contact time was regulated by changing the vaporizing speed, which was adjusted by changing the oil bath temperature. The measurement for the reaction was carried out after the stationary state was confirmed; the carbon balance (wt%) in feed formalin and distillate was equal.

For the trioxane synthesis above 100 °C (that is, under pressure, 110 °C), a stainless steel reactor was used, feeding 55 wt% formalin and drawing out the vapor phase into a condenser at low pressure until atmospheric pressure was reached. For the trioxane synthesis below 100 °C (that is, the reaction under reduced pressure), the same system was used as for reactions at atmospheric pressure.

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