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Carbonylation of Formaldehyde with Carbon Monoxide over Cation-Exchange Resin Catalysts

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The carbonylation of formaldehyde with carbon monoxide was carried out over two kinds of cation-exchange resins as solid acid catalysts. Effects of reaction conditions on the catalytic performance were studied. From ^{1}H NMR, ^{13}C NMR, IR, and GC-MS analyses of the products obtained, it was found that 1,3-dioxolan-4-one (1,3-DOX-4) is selectively produced over the cation-exchange resins. The carbonylation of formaldehyde with carbon monoxide over the cation-exchange resins proceeds under milder reaction conditions, as compared with HZSM-5 zeolite.

The carbonylation with carbon monoxide (CO) has proved to be of great importance in both fundamental and industrial applications.[1—5] Particularly, the carbonylation with CO is one of important methods for synthesizing ketones and lactones.[6—8] A new efficient and selective synthesis of ketones has been achieved from alkanes or cycloalkanes, CO and silanes in the presence of aprotic superacids[7] and delta-lactones can be synthesized from saturated alcohols and CO.[8] However, the carbonylation reaction was mainly carried out on homogeneous catalysts.[1—3,6,7] Great interest has recently been focused on the carbonylation over solid catalysts, especially zeolite catalysts. It has been reported that butyl alcohols and olefins undergo carbonylation to form carboxylic acids (the Koch reaction) with high conversion over HZSM-5 zeolite at 23—100 °C.[9] The formation of benzoic acid over HY zeolite and benzaldehyde over $AlCl_3$-doped HY from the carbonylation of benzene with CO was also reported.[10]

More recently, we have also investigated the carbonylation ability of protonated zeolite, and we already reported that 1,3-dioxolan-4-one (1,3-DOX-4) is obtained from formaldehyde and CO over various H-type zeolites and that HZSM-5, HY, and Hβ zeolites with the three-dimensional channel system show high activity for the formation of 1,3-DOX-4.[11,12] Based on the effect of the SiO_2/Al_2O_3 ratio of HY zeolite on the carbonylation activity, we concluded that the carbonylation of formaldehyde with CO proceeds mainly on the strong Brønsted acid sites of zeolite. However, the effect of pore size of zeolite on the product distribution is still an open question. In this research, in order to develop a more systematic understanding of the carbonylation of formaldehyde with CO over zeolites, the carbonylation over two kinds of cation-exchange resins with mesopores being strong acid catalysts is investigated. By compared with the catalytic behavior of HZSM-5 zeolite, we try to clarify the effect of the pore size of the solid catalyst on the carbonylation reaction of formaldehyde with CO.

Experimental

Two kinds of cation-exchange resins, whose acid strength is comparable to that of high siliceous zeolites such as ZSM-5 and mordenite, were used as the catalysts. One is Diaion® RCP160M (exchange capacity: ca. 4.3 mequiv g^{-1}, average pore size: ca. 100 Å, BET surface area: 53 $m^2\,g^{-1}$) (Mitsubishi Chemical Co.), a copoly(styrene/divinylbenzene) sulfonic acid resin. The other is Nafion® NR-50 (exchange capacity: ca. 0.8 mequiv g^{-1}, average pore size: ca. 30 Å, BET surface area: ca. 5 $m^2\,g^{-1}$) (Wako Pure Chemical Industries Ltd.), a perfluorinated sulfonic acid resin. The average pore sizes and specific BET surface areas of the cation-exchange resins were measured by mercury porosimetry and nitrogen adsorption at −196 °C. Prior to reaction experiments, the catalyst was activated by heating at 40 °C for 24 h under vacuum. 1,3,5-Trioxane as a source of formaldehyde was purified by crystallization from dichloromethane and dried by evacuating at room temperature for 1 h. Dichloromethane (research grade) was used as a solvent of reaction. When the residual moisture of dichloromethane was more than 1000 ppm, the carbonylation of formaldehyde with CO did not occur and paraformaldehyde was mainly obtained. Therefore, a complete dehydration of dichloromethane was conducted using molecular sieves 4A; the residual moisture measured by Karl Fischer method was less than 30 ppm.

The carbonylation of formaldehyde with CO was carried out using a 100 ml autoclave as follows. Ten grams of 1,3,5-trioxane (formaldehyde source), 40 ml of dichloromethane and 0.05—0.5 g of the cation-exchange resin or 0.7 g of HZSM-5 zeolite (SiO_2/Al_2O_3: 50, pore size: ca. 6 Å, BET surface area: 345 $m^2\,g^{-1}$) were placed in the autoclave under a nitrogen atmosphere, and then CO ($>99.95\%$) was introduced without further purification. The initial CO pressure at room temperature was varied in the range of

15 to 75 MPa. The reaction temperature (40—180 °C) was reached within 1 h. After 2—50 h of reaction, the catalyst and the product were put into acetone and filtered. The filtrate was distilled under reduced pressure several times. The product (colorless liquid) obtained by distillation at bp 85 °C and 60 mmHg (1 mmHg = 133.322 Pa) was analyzed by using GC-MS, IR, ^{1}H NMR and ^{13}C NMR. The yield of 1,3-DOX-4 and the conversion of 1,3,5-trioxane were calculated by GC using sulfolane (tetrahydrothiophene 1,1-dioxide) as an internal standard. GC analysis was carried out on a Shimadzu GC-15A gas chromatograph (FID) equipped with a 25 m, 0.22 mm i.d. HiCap-CBP1 Shimadzu capillary column and GC-MS analysis on a Perkin–Elmer Q-910 mass spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian NMR spectrometer model Gemini 300 (300 MHz for ^{1}H, 75.4 MHz for ^{13}C). IR spectra were recorded on a JASCO Corporation VALOR-III infrared spectrometer.

Molecular weights of polymers obtained were measured by multi-angle laser light scattering method with two TSKgel-GMHHR-H columns. A 1,1,1,3,3,3-hexafluoro-2-propanol solution of sodium trifluoroacetate (5 mmol dm^{-3}) was used as a solvent at a flowing rate of 0.5 ml min^{-1}.

Results and Discussion

The carbonylation of formaldehyde with CO was carried out using Diaion® RCP160M. 1,3,5-Trioxane was used as the formaldehyde source. Characterization of products obtained using Diaion® was carried out first. Formation of many products was confirmed by GC. Figure 1(A) shows the ^{1}H NMR spectrum of the product obtained by distillation (bp 85 °C, 60 mmHg). Two intense signals were observed at 5.5 and 4.2 ppm. These signals were assigned to methylene protons of $-O-CH_2-O-$ and $-OC(=O)-CH_2-O-$ groups, respectively.[13] In the ^{13}C NMR spectrum as shown in Fig. 1(B), three intense signals were observed at 171.3, 96.1, and 62.4 ppm. These signals were assignable to a carboxyl carbon $-OC(=O)-$, methylene carbons of $-O-CH_2-O-$ and $-OC(=O)-CH_2-O-$ groups, respectively.[14] Characteristic bands were observed in the IR spectrum, as shown in Fig. 2. The 1798 cm^{-1} band is characteristic of the stretching vibration of C=O ester groups and the band at about 1210 cm^{-1} is characteristic of the stretching C–O ester groups.[15] The formation of 1,3-DOX-4 (*m*/*z* = 88, 87, 44) was also confirmed by GC-MS. These results strongly indicate that the formation of 1,3-DOX-4 by carbonylation of formaldehyde takes place over the cation-exchange resin as well as HZSM-5 zeolite.

A few introductory experiments were carried out to investigate the influence of the amount of the cation-exchange

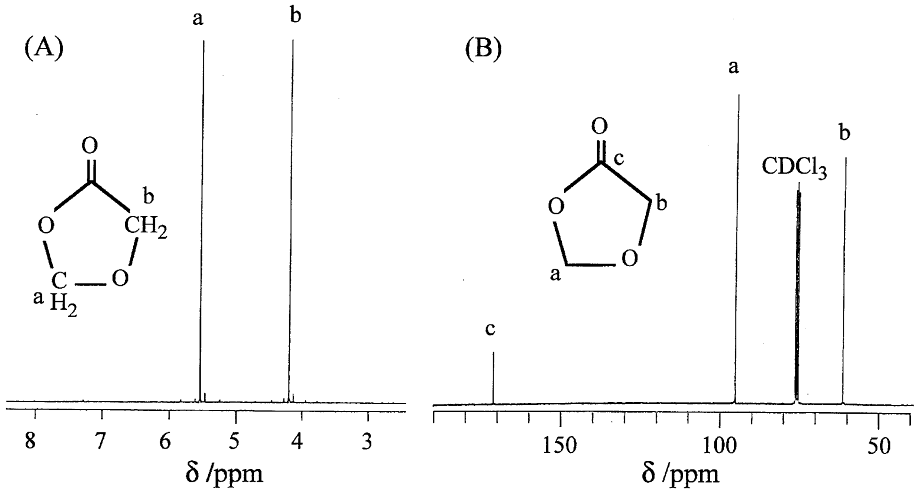

Fig. 1. ^{1}H NMR (A) and ^{13}C NMR (B) spectra of the distilled product obtained over Diaion®.

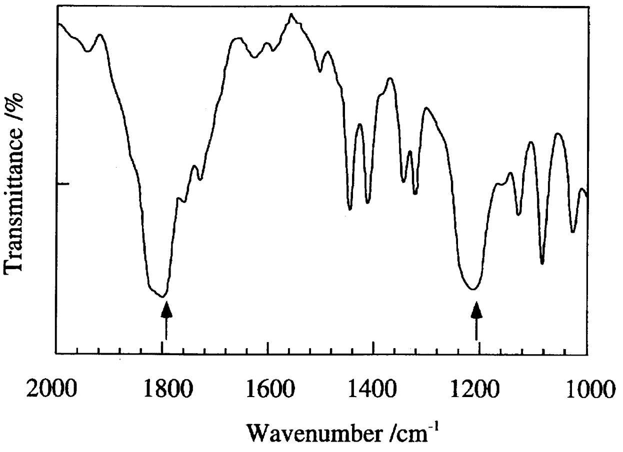

Fig. 2. IR spectrum of the distilled product obtained over Diaion®.

resin (Diaion®) on the 1,3,5-trioxane conversion and 1,3-DOX-4 yield. As listed in Table 1, the 1,3,5-trioxane conversion and 1,3-DOX-4 yield increased with an increase in the amount of Diaion®, suggesting that the carbonylation mainly proceeds on the Brønsted acid sites of Diaion®. It should be noted that diglycolic anhydride (DGAn) is obtained over Diaion. Little DGAn was produced over HZSM-5 zeolite. This may be due to the differences in the pore structures of these two kinds of catalysts. Namely, HZSM-5 zeolite has micropores (ca. 6 Å), while the cation-exchange resin has mesopores (ca. 100 Å). Products other than 1,3-DOX-4 and DGAn could not be identified.

Effects of the reaction temperature on the catalytic performance of Diaion® are illustrated in Fig. 3(A). The results of the carbonylation of 1,3,5-trioxane over HZSM-5 zeolite are also illustrated in Fig. 3(B) in comparison with that over Diaion®. The conversion of 1,3,5-trioxane increased with an increase in the reaction temperature and the maximum yield of 1,3-DOX-4 was obtained at 80 °C. This temperature is lower than that in the case of HZSM-5 zeolite (160 °C) and the maximum yield of 1,3-DOX over Diaion® was higher than that over HZSM-5 zeolite.

The 1,3-DOX-4 yield was also dependent on the initial CO pressure, as shown in Table 2. The yield increased with the initial CO pressure and a maximum yield of 77.6% (132 mmol) was obtained at the CO pressure of 25 MPa. As the maximum yield of 1,3-DOX-4 calculated from the amount of 1,3,5-trioxane (111 mmol) is 166.5 mmol, this indicates the selective formation of 1,3-DOX-4. In the case of HZSM-5 zeolite, a maximum yield of 67.2% (114 mmol) was obtained at the CO pressure of 55 MPa.

Although it is difficult to compare the catalytic activity of Diaion® with that of HZSM-5 zeolite due to large differences in the surface area and the pore size, the above results indicate that the carbonylation of 1,3,5-trioxane with CO over the cation-exchange resin proceeds under milder conditions than over HZSM-5 zeolite. The swelling of the cation-exchange resin may affect the catalytic performance of Diaion. Therefore, the lower catalytic activity of HZSM-5 zeolite seems to be attributable to the controlled diffusion of 1,3,5-trioxane or formaldehyde to the active sites of zeolite pores with ca. 6 Å.

The time dependence of the 1,3-DOX-4 yield was also studied. The yield increased with the reaction time, and decreased markedly after the maximum yield at the reaction time of ca. 5 h, as shown in Fig. 4. On the other hand, the yield of DGAn increased monotonously with the increase in the reaction time. Since the yields of solid product and DGAn increased with an increase in the reaction time, the

Table 1. Effects of Amount of Cation-Exchange Resin on Catalytic Activity

Amount of Diaion®/g	Conversion of 1,3,5-trioxane/%	Yield of 1,3-DOX-4/%	Yield of DGAn/%
0.05	34.2	13.9	1.8
0.1	61.3	51.0	4.2
0.2	82.4	57.2	4.3
0.3	92.4	65.2	3.8
0.5	98.2	77.6	4.2

Reaction conditions; P_{CO}: 25 MPa, Temperature: 80 °C, Time: 5 h, 1,3,5-Trioxane: 10 g, CH_2Cl_2: 40 ml.

Table 2. Effects of Initial CO Pressure over Diaion®

P_{CO} MPa	Conversion of 1,3,5-trioxane/%	Yield of 1,3-DOX-4/%	Yield of DGAn/%
15	28.1	2.4	2.8
25	98.2	77.6	4.2
35	99.8	73.8	1.3
55	82.1	64.8	0.8
75	64.3	50.2	0.4

Reaction conditions; Temperature: 80 °C, Time: 5 h, 1,3,5-Trioxane: 10 g, CH_2Cl_2: 40 ml, Diaion: 0.5 g.

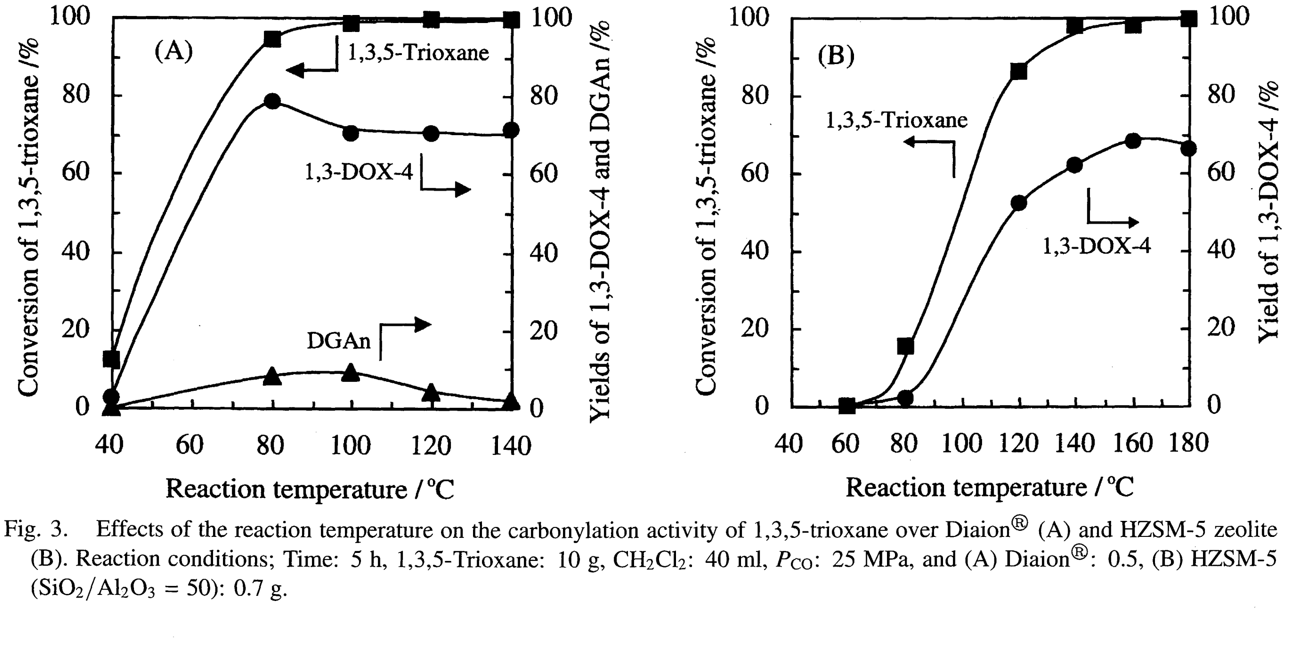

Fig. 3. Effects of the reaction temperature on the carbonylation activity of 1,3,5-trioxane over Diaion® (A) and HZSM-5 zeolite (B). Reaction conditions; Time: 5 h, 1,3,5-Trioxane: 10 g, CH_2Cl_2: 40 ml, P_{CO}: 25 MPa, and (A) Diaion®: 0.5, (B) HZSM-5 (SiO_2/Al_2O_3 = 50): 0.7 g.

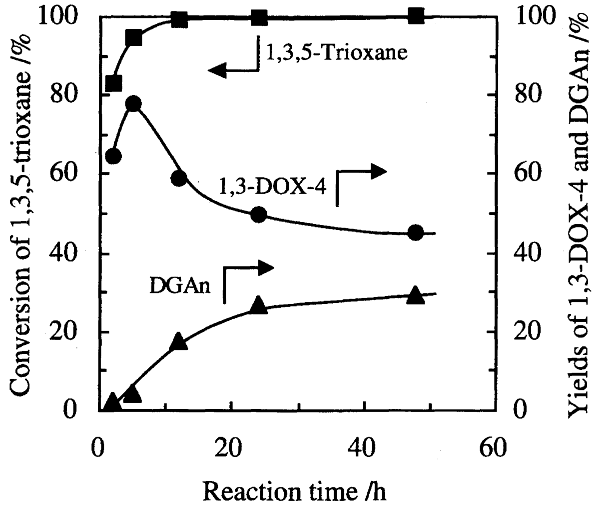

Fig. 4. Time dependence of 1,3,5-trioxane conversion and yield of 1,3-DOX-4 over Diaion®. Reaction conditions; Temperature: 80 °C, P_{CO}: 25 MPa, 1,3,5-Trioxane: 10 g, CH_2Cl_2: 40 ml, Diaion®: 0.5 g.

results indicate that 1,3-DOX-4 is the initial product and that the decrease of the 1,3-DOX-4 yield is attributable to the production of DGAn and the ring opening polymerization of 1,3-DOX-4 to form polyglycolide.[16,17]

The carbonylation of 1,3,5-trioxane with CO over Nafion® NR-50 was also performed. Figure 5 shows the effects of the reaction temperature and the reaction time on the conversion of 1,3,5-trioxane and the yields of 1,3-DOX-4 and DGAn. The maximum yield of 1,3-DOX-4 (86.2%) was obtained at 80 °C for 5 h under the CO pressure of 25 MPa. The yield of 1,3-DOX-4 increased with an increase of the reaction time over Nafion® NR-50 catalyst and decreased markedly after the maximum yield at the reaction time of ca. 5 h as well as over Diaion®.

As described above, results suggest that 1,3-DOX-4 is the initial product and that the decrease of the yield is attributable to the production of DGAn and the ring opening polymerization of 1,3-DOX-4 to form polyglycolide. To confirm this, the reaction of 1,3-DOX-4 with CO was conducted under the same reaction conditions as were used for the carbonylation of 1,3,5-trioxane (Table 3). The results over various H-type zeolites are also shown in Table 3 in comparison with those over cation-exchange resins. The conversion of 1,3-DOX-4 was higher than 30% over cation-exchange resins and zeolites, except over H-type mordenite (denoted as M). Considerable amounts of solid product and DGAn were obtained over cation-exchange resins, as compared with zeolites. Formation of many by-products which were not identified was also confirmed by GC.

The FT-IR spectrum and the ^{1}H NMR and ^{13}C NMR spectra of the solid product dissolved in a solvent of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were measured; the results are shown in Figs. 6 and 7. Two characteristic bands were observed in the IR spectrum, as shown in Fig. 6. The 1798 cm^{-1} band is characteristic of the stretching vibration of C=O ester groups and the band at about 1210 cm^{-1} is characteristic of the stretching C–O ester groups.[15] In the ^{1}H NMR spectrum as shown in Fig. 7(A), one intense signal was observed at 4.8 ppm assigned to methylene protons of $-O-CH_2-CO-$ group.[13] In the ^{13}C NMR spectrum as shown in Fig. 7(B), two intense signals were observed at 171.3 and 62.4 ppm. These signals were assignable to carboxyl $-C(=O)-$ and methylene carbons of $-C(=O)-CH_2-O-$ group, respectively.[14] These results were consistent with the spectra of polyglycolide reagent, indicating the formation of polyglycolide during the carbonylation of 1,3,5-trioxane with CO over cation-exchange resins. The number-average molecular weight of polyglycolide obtained using Diaion® was ca. 2.9×10^4.

The detailed reaction mechanism of the preferential formation of 1,3-DOX-4 and the production of DGAn has not yet been clarified. Taking into account that cyclic ethers such as 1,3,5,7-tetraoxocane are not detected by GC-MS and that 1,3,5-trioxane is easily decomposed to formaldehyde,

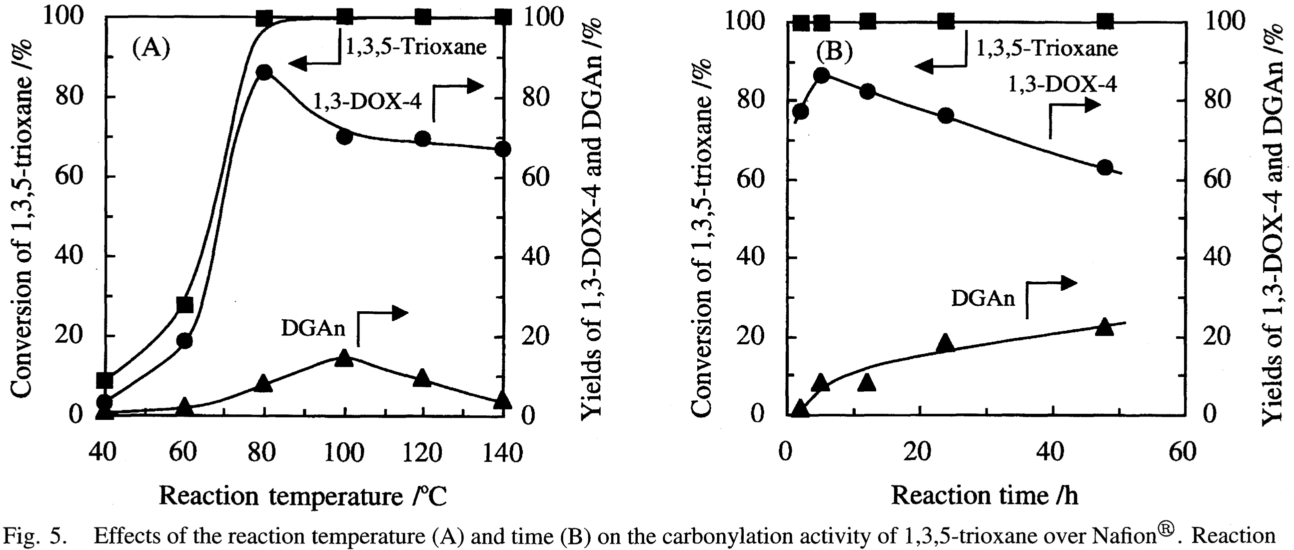

Fig. 5. Effects of the reaction temperature (A) and time (B) on the carbonylation activity of 1,3,5-trioxane over Nafion®. Reaction conditions; 1,3,5-Trioxane: 10 g, CH_2Cl_2: 40 ml, P_{CO}: 25 MPa, Nafion®: 0.5 g, and (A) Time: 5 h, (B) Temperature: 80 °C.

Table 3. Carbonylation of 1,3-DOX-4 over Cation-Exchange Resins and H-Type Zeolites

Catalyst	Reaction conditions			Conversion of	Yield of	Solid
(SiO_2/Al_2O_3)	P_{CO}/MPa	Temp/°C	Time/h	1,3-DOX-4/%	DGAn/%	product/g
Diaion®	25	80	2	36.9	10.2	0.8
Nafion®	25	80	2	46.7	8.1	0.6
ZSM-5(53)	35	120	5	37.0	Trace	—
Y(30)	35	120	5	55.0	0.3	0.4
M(20)	35	120	5	10.5	0.5	—
MCM-41(78)	35	120	10	31.0	1.5	—

Reaction conditions; 1,3-DOX-4: 5 g, CH_2Cl_2: 40 ml, Cation-exchange resin: 0.5 g, Zeolite: 1.0 g.

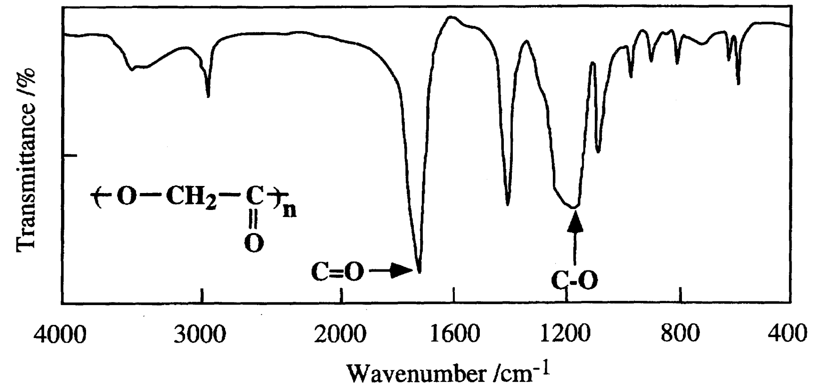

Fig. 6. IR spectrum of the solid product dissolved in a solvent of HFIP (1,1,1,3,3,3-hexafluoro-2-propanol).

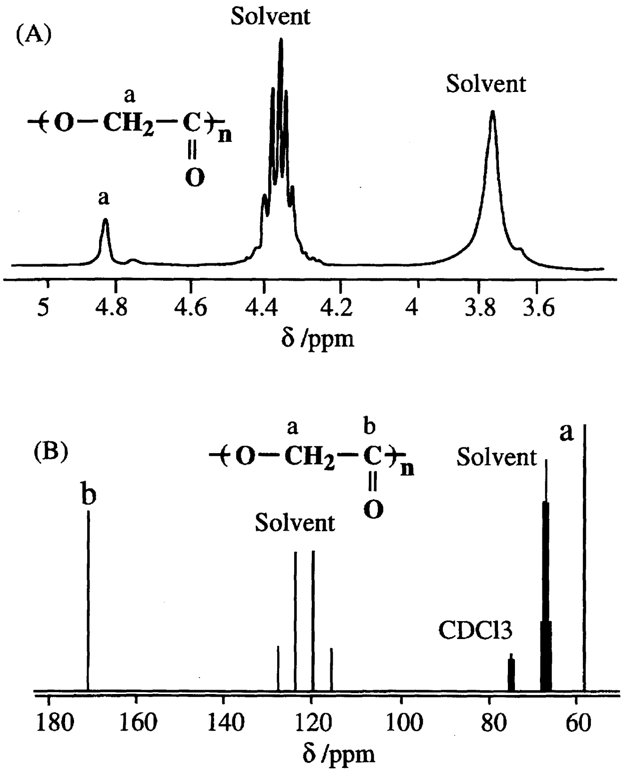

Fig. 7. ${}^1H$ NMR (A) and ${}^{13}C$ NMR (B) spectra of the solid product dissolved in a solvent of HFIP.

however, we have speculated the mechanism for formation of 1,3-DOX-4 shown in Fig. 8. Namely, the process may be explained by the decomposition of 1,3,5-trioxane to formaldehyde, the formation of methylol cation on acid sites and the generation of acylium cation by the insertion of CO to methylol cation.[9,18] The acylium cation is reacted with formaldehyde to give 1,3-DOX-4.

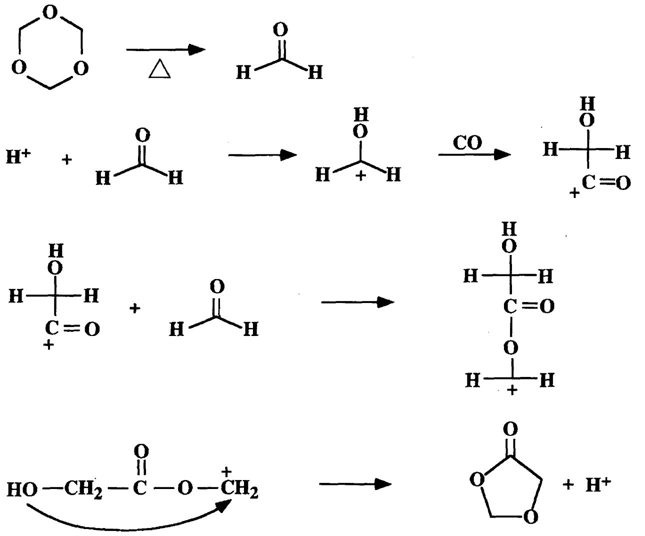

Fig. 8. A speculated mechanism of formation of 1,3-DOX-4.

Conclusions

1,3-DOX-4 is selectively synthesized from 1,3,5-trioxane (formaldehyde source) and CO over cation-exchange resins as well as HZSM-5 zeolite, although the CO pressure needed for this synthesis is higher than 15 MPa. As compared with

HZSM-5 zeolite, the carbonylation of 1,3,5-trioxane with CO over cation-exchange resins proceeds under milder reaction conditions. Diglycolic anhydride and polyglycolide are markedly produced over cation-exchange resins due to their large pores, while only minor amounts are produced over HZSM-5 zeolite.

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