

# Synthesis of 1,3-dioxolan-4-one from trioxane and carbon monoxide on HZSM-5 zeolite

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**Cabonylation of formaldehyde with carbon monoxide has been carried out on HZSM-5 zeolite; from spectroscopic analysis of the products obtained, the formation of 1,3-dioxolan-4-one on the Brønsted acid sites of HZSM-5 zeolite has been demonstrated.**

Carbonylation with carbon monoxide (CO) is one of the most important reactions for fundamental and industrial applications, and various kinds of homogeneous and heterogeneous catalysts are used.<sup>1,2</sup> Recently, carbonylation on zeolite catalysts has received considerable attention. It has been shown that CO and H<sub>2</sub>O can react with small alkenes on HZSM-5 zeolite to form carboxylic acids<sup>3,4</sup> and that, under anhydrous conditions, ethene, isobutene and oct-1-ene react to form ketones instead of carboxylic acids.<sup>5</sup> The formation of benzoic acid on HY zeolite from the carbonylation of benzene with CO has also been reported.<sup>6</sup> However, no report is available of the synthesis of lactones. Here we report the formation of 1,3-dioxolan-4-one (1,3-DOX-4) via carbonylation of formaldehyde with CO on HZSM-5.

HZSM-5 zeolites and silicalite were prepared following the previously described procedure.<sup>7</sup> The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios (53, 101, 191 and 3300) were determined by X-ray fluorescence. Prior to the experiments, the zeolite was activated by heating at 400 °C for 8 h. Trioxane was used as the source of formaldehyde, and was purified by crystallization from CH<sub>2</sub>Cl<sub>2</sub> and dried *in vacuo* at room temperature for 1 h. CH<sub>2</sub>Cl<sub>2</sub> (research grade) was used as solvent. When the residual moisture in the CH<sub>2</sub>Cl<sub>2</sub> was greater than 1000 ppm, the carbonylation of formaldehyde with CO did not occur and paraformaldehyde was mainly obtained. Therefore, dehydration of the CH<sub>2</sub>Cl<sub>2</sub> was required using 4 Å molecular sieves, the residual moisture, measured by the Karl Fischer method, was less than 30 ppm.

The carbonylation of formaldehyde with CO was carried out using a 100 ml autoclave as follows. Trioxane (10 g), CH<sub>2</sub>Cl<sub>2</sub> (40 ml) and zeolite (1 g) were placed in the autoclave under a nitrogen atmosphere, and CO (>99.95%) was introduced. 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 zeolite and the solid product were filtered off. The filtrate was distilled under reduced pressure several times. The product (a colourless liquid) obtained by distillation at 85 °C and 60 mmHg was analysed by GC–MS, as well as IR and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The yield of 1,3-DOX-4 obtained was calculated by GC using sulfolane as an internal standard. GC analyses were carried out on a Shimadzu GC-15A gas chromatograph (FID) equipped with a 25 m × 0.22 mm ID HiCap-CBP1 Shimadzu capillary column. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Gemini 300 spectrometer (300 MHz for <sup>1</sup>H, 75.4 MHz for <sup>13</sup>C).

In the <sup>1</sup>H NMR spectrum of the product obtained by distillation, two intense signals were observed at δ 5.5 and 4.2. These signals were assigned to the OCH<sub>2</sub>O and OC(=)CH<sub>2</sub>O methylene groups, respectively. In the <sup>13</sup>C NMR spectrum,

three signals were observed at δ 171.3, 96.1 and 62.4. These signals were assigned to the CO<sub>2</sub> carboxyl carbon and the methylene carbons of the OCH<sub>2</sub>O and OC(=)CH<sub>2</sub>O groups, respectively. Characteristic bands were also observed in the IR spectrum. The 1798 cm<sup>-1</sup> band is characteristic of the stretching vibration of C=O ester groups and the band at about 1210 cm<sup>-1</sup> is characteristic of stretching of C–O ester groups. These results strongly indicate the selective formation of 1,3-DOX-4 on the HZSM-5 zeolite catalyst. The formation of 1,3-DOX-4 (*m/z* 88, 87 and 44) was also confirmed by GC–MS. Although it has already been reported that glycolic acid<sup>8</sup> and the polymer polyglycolide<sup>9,10</sup> can be synthesized from formaldehyde and CO using various acid catalysts, the preferential formation of 1,3-DOX-4 has never been reported.

To obtain more information related to carbonylation on HZSM-5 zeolite, the catalytic performance of HZSM-5 zeolite was examined under various reaction conditions. At first, to clarify the active site of the formation of 1,3-DOX-4, the carbonylation was conducted on various HZSM-5 zeolites with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. As shown in Table 1, the yield of 1,3-DOX-4 decreased with an increase in the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (entries 1–4). In the case of silicalite, which has almost no Brønsted acid sites, 1,3-DOX-4 was not obtained. This indicates that the carbonylation is promoted on the acid sites of HZSM-5 zeolite. Next, the influence of the reaction temperature and CO pressure on the 1,3-DOX-4 yield was studied. 1,3-DOX-4 was obtained in very low yields at 40 and 80 °C (entries 5 and 6). At reaction temperatures higher than 80 °C, the yield increased with the reaction temperature and then decreased after reaching a maximum yield at 160 °C (entries 7–9). The yield of 1,3-DOX-4 was dependent on the initial CO pressure (entries 8, 10–12). The yield increased with the initial CO pressure and a

**Table 1** Synthesis of 1,3-DOX-4 from trioxane and CO on zeolite catalysts<sup>a</sup>

Entry	Zeolite (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> )	Reaction conditions			
		T/°C	P <sub>CO</sub> /MPa <sup>b</sup>	t/h	Yield/mmol (%)
1	HZSM-5 (53)	120	35	2	101 (60.7)
2	HZSM-5 (101)	120	35	2	51 (30.6)
3	HZSM-5 (191)	120	35	2	46 (27.6)
4	Silicalite (3300)	120	35	2	0 (0)
5	HZSM-5 (191)	40	35	5	0 (0)
6	HZSM-5 (191)	80	35	5	2 (1.2)
7	HZSM-5 (191)	120	35	5	93 (55.9)
8	HZSM-5 (191)	160	35	5	102 (61.3)
9	HZSM-5 (191)	180	35	5	83 (49.8)
10	HZSM-5 (191)	160	15	5	60 (36.0)
11	HZSM-5 (191)	160	55	5	114 (68.5)
12	HZSM-5 (191)	160	75	5	89 (53.5)
13	HZSM-5 (191)	160	35	2	71 (42.6)
14	HZSM-5 (191)	160	35	13	61 (36.6)
15	HZSM-5 (191)	160	35	50	6 (3.6)

<sup>a</sup> Reaction conditions: trioxane (10 g, 111 mmol), CH<sub>2</sub>Cl<sub>2</sub> (40 ml), zeolite (1 g). <sup>b</sup> Initial CO pressure at room temperature.

maximum yield of 114 mmol was obtained at a CO pressure of 55 MPa. As the maximum yield of 1,3-DOX-4 calculated from the amount of trioxane (111 mmol) used is 166.5 mmol, this indicates the preferential formation of 1,3-DOX-4. The time dependence of the 1,3-DOX-4 yield was also studied. The yield increased with the reaction time, and then decreased markedly after the maximum yield was reached at a reaction time of *ca.* 5 h (entries 8, 13–15). Taking into account the fact that the yield of solid product increased with an increase in the reaction time, this seems to indicate that 1,3-DOX-4 is the initial product and that the decrease in the yield is attributable to the later ring opening polymerization of 1,3-DOX-4 to form polyglycolide, probably inside the zeolite crystals.<sup>9,10</sup>

From the above results, it has been shown that 1,3-DOX-4 is selectively synthesized from trioxane and CO, although the CO pressure needed for the synthesis is higher than 15 MPa. Although the detailed reaction mechanism has not been clarified at the present time due to limited data, the preferential formation of 1,3-DOX-4 appears to be due to the suppression of formation of polymers because the active sites (Brønsted acid sites) are in zeolitic pores.

## Footnote and References

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