



## Benzyl methyl ether production from benzyl alcohol and methanol in carbonic water



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### ABSTRACT

Synthesis of benzyl methyl ether from benzyl alcohol and methanol in high-temperature carbonic water was studied in a batch reactor. Benzyl methyl ether formation was not observed by reacting benzyl alcohol with only methanol under supercritical conditions at 573 K. On the other hand, benzyl methyl ether was formed by the treatment of benzyl alcohol in an aqueous methanol solution at 573 K. 12% of benzyl methyl ether yield was obtained in aqueous methanol solution (methanol to water molar ratio of 0.025 mol/0.11 mol) at 573 K in 60 min and the yield enhanced to 33% by the addition of 18 MPa of carbon dioxide to the aqueous solution. As the etherification is an acid catalyzed reaction, the protons derived from the dissociation of water molecules could be responsible for the etherification of benzyl alcohol in an aqueous methanol solution at 573 K. The enhancement of benzyl methyl ether yield by the addition of carbon dioxide in aqueous methanol solution is caused by the increase of the number of protons derived from carbonic acid, which is formed in high-temperature liquid water under high-pressured carbon dioxide.

### 1. Introduction

Asymmetrical ether can be formed from organo halide and deprotonated alcohol, such as sodium alkoxide, in aprotic polar solvents (Williamson ether method); however, inorganic salt is a by-product of such process. An atom-efficient process for ether formation is the intermolecular dehydration of alcohols with an acid catalyst; however, symmetric ether is also produced. Inorganic acid, such as sulfonic acid, is effective for the etherification; however, it requires a neutralization step by base and involves the formation of salt as the by-product.

High-temperature liquid water can act as a green reaction medium for acidic and basic reactions of organic compounds, because the solubilities of organic compounds are higher and the number of protons and hydroxyl ions are in larger concentration in high-temperature liquid water at around 573 K [1,2]. There are several reports for the application of high-temperature liquid water as a green medium for organic reactions, such as hydrolysis of organic polymers [3–5]. The dehydration mechanism by the proton in high-temperature liquid water is also studied by *ab initio* calculation [6]. There are also several reports about the etherification in high-temperature liquid water. Poliakoff et al. reported that symmetric ethers, such as di-*n*-propyl ether and di-*n*-hexyl ether, could be formed in aqueous alcohol solution at 473 K with

a continuous system [7]. Antal et al. reported acid catalyzed formation of *tert*-butyl ethyl ether from *tert*-butanol and ethanol in high-temperature liquid water [8].

The addition of high-pressure carbon dioxide into water to form carbonic acid, accelerates the acid catalysis of high-temperature liquid water. An acidic solvent composed of water and carbon dioxide is environmentally-benign not only because both water and carbon dioxide are non-toxic, but also separation and recycling of these two components can be easily performed by depressurization of the system after reaction. Savage et al. reported that tetrahydrofuran was formed by intramolecular dehydration of 1,4-butanediol in high-temperature liquid water and the dehydration rate was enhanced by the addition of carbon dioxide [9–11]. Yamaguchi et al. reported that intramolecular dehydration of several polyalcohols, which were the chemical blocks of biomass, proceeded in high-temperature liquid water and that the dehydration rates were enhanced by the addition of high-pressure carbon dioxide [12–17].

In this study, we applied high-temperature carbonic acid water to etherification reaction. We studied benzyl methyl ether formation by the treatment of benzyl alcohol in an aqueous methanol solution at 573 K and the enhancement of ether formation rates by the addition of high-pressure carbon dioxide.

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## 2. Experimental

Benzyl alcohol (Wako Pure Chemical Industries), benzyl methyl ether (Wako Pure Chemical Industries) and *n*-butanol (Wako Pure Chemical Industries) were purchased and used without any further purification. The dehydration reaction of benzyl alcohol and methanol was carried out in a batch reactor (inner volume: 6.0 cm<sup>3</sup>) made of a SUS316 tube [18,19]. Benzyl alcohol (0.50 mmol) and solvent (0–3.0 mL (0–0.2 mol) of water and 3.0–0 mL (0.075–0 mol) of methanol) were loaded into the reactor and it was purged with nitrogen gas to remove the air. 10–14 MPa of carbon dioxide was fed to the reactor at 323 K. The partial pressure of carbon dioxide in the reactor at 573 K was estimated to be 18 or 25 MPa, based on the equation of Charles's law, corresponding to the initial pressure of 10 and 14 MPa at 323 K, respectively. The reactor was then submerged into a sand bath at 573 K for a given reaction time, and then submerged into a water bath for cooling quickly to ambient temperature after the reaction. The carbon dioxide gas in the reactor was removed by depressurization after cooling. A mixture of the reactant and liquid products was taken out from the reactor using *n*-butanol. The quantitative analyses of the reactant and liquid products were conducted by gas chromatography with a flame ionization detector (GC-FID, SHIMAZU GC-14 B and Agilent Technologies 6890) and GC-MS (Agilent Technologies HP-7890) using tetrahydrofurfuryl alcohol as an internal standard. The products were identified by comparing them with the retention times of the standard material: benzyl alcohol, benzyl methyl ether, and dibenzyl alcohol. The yield of benzyl methyl ether was calculated as follows,

Yield (%) = (the amount of benzyl methyl ether formed)/(the amount of benzyl alcohol fed) × 100.

Initial formation rates of benzyl methyl ether were estimated from initial slopes of the fitting curves of their profiles.

## 3. Results and discussion

### 3.1. Benzyl methyl ether formation from benzyl alcohol in aqueous methanol solution

Benzyl methyl ether was not detected by GC when only methanol solution of benzyl alcohol was treated at 573 K for 60 min, indicating that etherification of benzyl alcohol and methanol did not proceed in supercritical methanol in absence of water or acid catalyst. Dibenzyl ether was not detected by GC analysis of aqueous solution of benzyl alcohol treated at 573 K for 60 min, indicating that intermolecular etherification of benzyl alcohol did not proceed under the reaction condition. The intermolecular dehydration of methanol would not proceed in this system because methanol recovery was high and strong acid is need for the dehydration.

Benzyl methyl ether was formed in the aqueous methanol solution of benzyl alcohol treated at 573 K for 60 min, and the benzyl methyl ether yield depended on methanol to water ratio in the aqueous methanol solution. Fig. 1 shows the benzyl methyl ether yield obtained after the treatment of benzyl alcohol in aqueous methanol solution at 573 K for 60 min as a function of methanol to water ratio. About 10% yield of benzyl methyl ether was obtained after the treatment of aqueous methanol solution of benzyl alcohol at methanol to water ratio of 1 mL/2 mL (0.025 mol/0.11 mol) and 1.5 mL/1.5 mL (0.037/0.083) at 573 K for 60 min in the absence of acid catalyst. There are several reports that cyclic etherification [9,12] and symmetric etherification [7] proceed in high-temperature liquid water at between 473 and 573 K. Water is a neutral solvent; however, protons dissociated from water molecules in the aqueous solution at 573 K would catalyze the asymmetric etherification of benzyl alcohol and methanol.

We also studied the temperature dependence of etherification of benzyl alcohol and methanol in the aqueous methanol solution. Benzyl

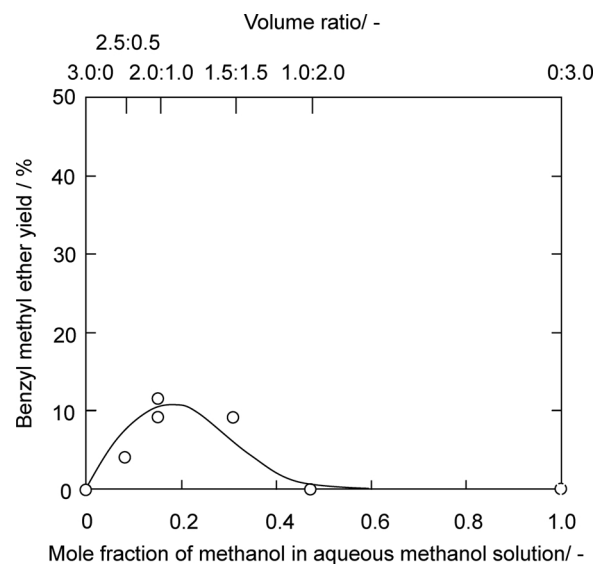


Fig. 1. Effect of mole ratio of methanol to water on benzyl methyl ether yield in aqueous methanol solution (Reaction conditions; reaction temperature, 573 K and reaction time, 30 min).

methyl ether was not formed at 473 K while its yield was only 3% at 623 K in aqueous methanol solution at methanol to water ratio of 0.025 mol/0.11 mol. We found that the optimum temperature and methanol to water ratio are 573 K and 0.025 mol/0.11 mol, respectively, in a batch operation.

The reaction profile of benzyl methyl ether production from aqueous methanol solution of benzyl alcohol is shown in Fig. 2. The amount of benzyl alcohol increased linearly with the initial formation rate of  $3.1 \times 10^{-4}$  mol L<sup>-1</sup> min<sup>-1</sup>. The yield increased to 33% after 180 min.

### 3.2. Effect of carbon dioxide on benzyl methyl ether yield

The effect of high-pressure carbon dioxide on benzyl methyl ether production was also studied. The etherification profile of the aqueous methanol solution of benzyl alcohol under high-pressure carbon dioxide is shown in Fig. 3. In the presence of 18 MPa of carbon dioxide, the initial benzyl methyl ether yields were larger than that in the absence of carbon dioxide. The introduction of carbon dioxide into the aqueous methanol solution would increase the number of protons by the

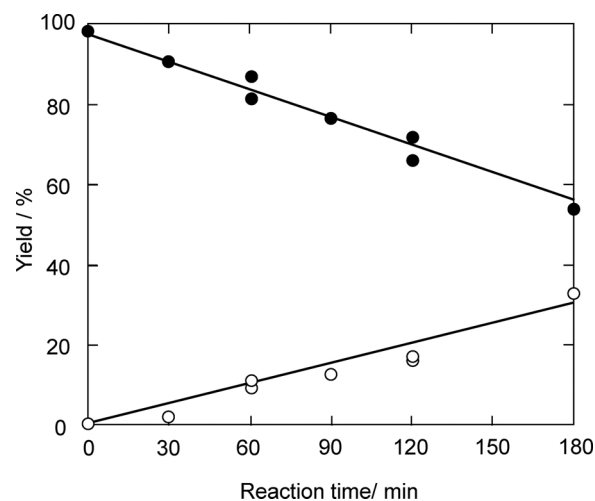


Fig. 2. Benzyl methyl ether yield in aqueous methanol solution (Reaction conditions; water to methanol ratio, 0.11 mol/0.025 mol; reaction temperature, 573 K). Benzyl methyl ether yield (○), benzyl alcohol recovery yield (●).

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