

Synthesis of Dimethyl Ether from Supercritical Methanol in the Presence of Aluminum

Yuma Usui, Chihiro Wakai, Nobuyuki Matubayasi, and Masaru Nakahara*
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011

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A novel method to synthesize dimethyl ether (DME) is presented. When methanol is treated with aluminum metal in supercritical conditions at a density of 0.39 kg/dm^3 , it is found that DME is generated above 275°C through a single-step procedure. The DME production increases with the temperature elevation, and it becomes the main product above 300°C with by-products of hydrogen and methane. DME is considered to be produced at the formation step of methyl derivative of boehmite and/or its surface catalytic effect.

Dimethyl ether (DME) liquefies at -25°C and 0.1 MPa or at room temperature and 0.6 MPa . It costs low for transportation and storage compared to the liquefied natural gas, which is conveyed and stored at -160°C . In addition, SO_x and soot are not produced at all with few NO_x when DME is burned. Therefore, the potential of DME as a clean energy source is promising and its application is in preparation.¹

In the synthesis of DME, the catalyst improvement is supposed to be indispensable.²⁻⁴ For example, with solid-acid catalysts, such as $\gamma\text{-Al}_2\text{O}_3$, H-ZSM-5, amorphous alumina-silicas, and titania-modified zirconia, the catalytic conversion of methanol to DME is well characterized. Since DME needs to be produced on a large scale in the near future, its clean and convenient method of synthesis is desirable to be established. In this study, a novel synthetic method of DME is presented utilizing a modification of aluminum. The starting materials in our method are only methanol and aluminum metal, which is abundant in our surroundings and changes into unique forms in organic solvents.

Aluminum powder (Kojundo Chemical Laboratory) and

magnesium powder (Nacalai Tesque) were used without further purification. The powder size of aluminum was $850\text{--}425 \mu\text{m}$ (about 18–35 mesh), and that of magnesium was $20\text{--}70 \mu\text{m}$ (about 740–210 μm). In a quartz tube reactor of 1.45 mm i.d. , $3.2 \pm 0.2 \text{ mg}$ (0.12 mmol) of aluminium powder or $2.8 \pm 0.1 \text{ mg}$ (0.12 mmol) of magnesium powder was placed, and methanol (Wako) was added to 50% of the reactor volume ($1.3 \times 10^{-4} \text{ dm}^3$). The air in the reactor was replaced by argon. The reactor was then put into an electric furnace kept at $200\text{--}325^\circ\text{C}$; the temperature was controlled within $\pm 1^\circ\text{C}$. Since the critical temperature of methanol is 239°C , the solution system at supercritical temperatures is homogeneous with interfaces to metal powders and involves the methanol density of 0.39 kg/dm^3 . After the reaction time, the sample was removed from the furnace and quenched in a water bath. After the reaction, aluminium and magnesium powders were observed to be changed into white or gray particles, and the liquid and gas phases coexisted in the sample vessel. The liquid and gas phases were separately measured by ^1H and ^{13}C NMR at room temperature (JEOL ECA-400N). A D_2O solution of 1,3,5-trioxane was used as an external reference, which was filled in the NMR tube with the sample vessel. In addition to metal aluminum, aluminum triethoxide (Aldrich) was examined at 300°C . In this case, the used solvent was methanol and ethanol.

Figure 1 shows the proton spectra for the gas phase of the sample with aluminum metal before and after the reaction. Before the reaction, only two peaks assigned to the external reference were detected; one peak at 2.6 ppm represents 1,3,5-trioxane, and another at 2.1 ppm stands for impurity HDO in D_2O .

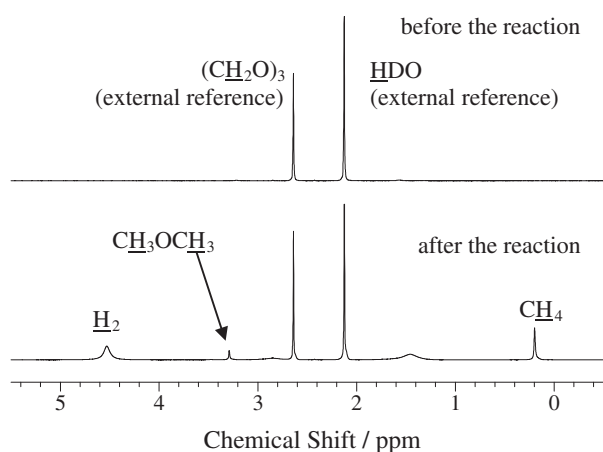


Figure 1. The gas-phase ^1H NMR spectra of methanol with aluminum metal. The reaction was performed for 1 h at 300°C and the methanol density of 0.39 kg/dm^3 . 1,3,5-trioxane employed as an external reference is set at 2.6 ppm . A broad peak at 1.4 ppm is methyl signal of liquid methanol which adheres to the reactor wall.

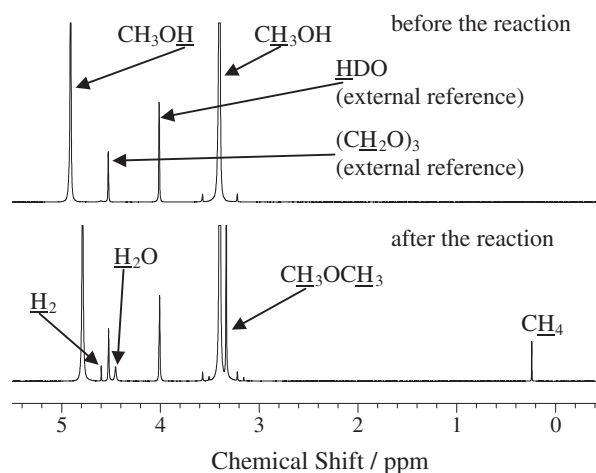


Figure 2. The liquid-phase ^1H NMR spectra of methanol with aluminum metal. The reaction was performed for 1 h at 300°C and the methanol density of 0.39 kg/dm^3 . 1,3,5-trioxane employed as an external reference is set at 4.5 ppm . After the reaction, the methanol OH peak was shifted to the lower magnetic field.

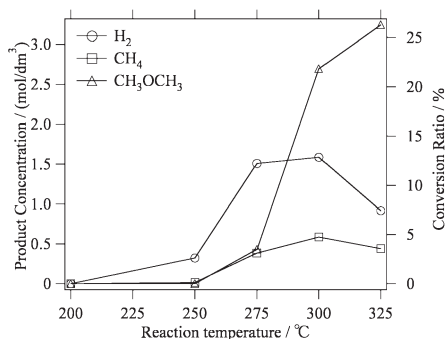


Figure 3. Temperature dependence of the product concentration from the methanol reaction with aluminum metal for 1 h. The conversion ratios of H₂, CH₄, and DME refer to their mole ratios to 0.5, 1, and 0.5 times of the initial methanol load, respectively.

After the 1 h reaction at 300 °C, three new peaks emerged; the peaks at 0.2, 3.3, and 4.6 ppm represent methane, DME, and hydrogen, respectively. Figure 2 shows the corresponding spectra for the liquid phase. Before the reaction, two peaks at 3.4 ppm and ≈5 ppm are assigned to methanol as a solvent. 1,3,5-trioxane gives a peak at 4.5 ppm, and the impurity HDO in D₂O at 4.0 ppm. After the reaction, three peaks at 0.2, 3.3, and 4.6 ppm appeared similarly and represent methane, DME, and hydrogen, respectively. The H₂O peak also emerged at 4.4 ppm after the reaction. This shows that the dehydration is a step to form DME from methanol. Without metals, those products were not detected.

Figure 3 plots the concentrations and conversion ratios of hydrogen, methane, and DME from the 1 h reaction against the temperature. At 200 °C, no products are generated. Hydrogen is the main product at 250 and 275 °C, and is overwhelmed by DME at higher temperatures. At 325 °C, DME is produced as ≈3 times as hydrogen. In other words, the selectivity of DME increases with the temperature rise. Figure 4 shows the product concentrations and conversion ratios at 300 °C against the reaction time. The concentrations of hydrogen and methane increase with the reaction time, and converge at 1.6 and 0.6 mol/dm³, respectively. At the initial stage of the reaction, DME is slowly generated in comparison to hydrogen. At later stages, its concentration rises to ≈3 times of that of hydrogen, and exhibits a converging behavior at 4.5 mol/dm³.

When the magnesium metal is used, DME was not detected as a product. Only hydrogen was generated at a concentration of 1.4 mol/dm³ above 150 °C with a small amount of methane above 200 °C.⁵ Thus, the magnesium metal is not useful for the DME production.

The known reactions which generate hydrogen from methanol are the partial oxidation of methanol, steam reforming reaction, and metal oxidation reaction.⁶ If our reaction is either the partial oxidation or steam reforming reaction, CO or CO₂ will be generated along with hydrogen. According to ¹³C NMR, however, only methane and DME were observed, and CO and CO₂ were not. In addition, the total amount of hydrogen and methane converged at ≈1.2 times of the mole amount of aluminum metal added.⁵ From these results, it is concluded that the metal oxidation generates hydrogen and methane. In other words, the transformation of aluminum into aluminum methoxide leads to the

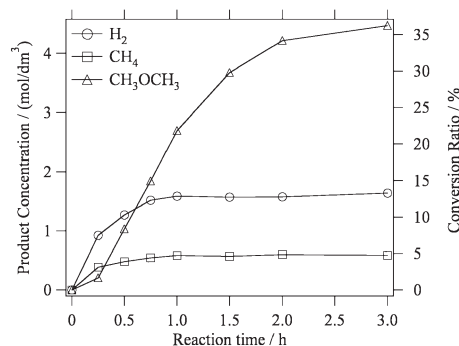


Figure 4. Time dependence of the product concentration and the conversion ratio from the methanol reaction with aluminum metal at 300 °C.

generation of hydrogen, and the transformation into aluminum oxides produces methane.

Inoue et al. found that aluminum was transformed at 250–300 °C into a layer structure of boehmite with alkyl pendant groups derived from solvent alcohol via aluminum alkoxide.^{7,8} If the aluminum transformation proceeds through the scheme as Inoue et al. suggested, it is considered that DME is produced at the formation step of the methyl derivative of boehmite from aluminum methoxide and/or through the surface reaction on boehmite. To further confirm the production of a symmetric alkyl ether from the corresponding alcohol in the presence of aluminum alkoxides, we also examined the reaction of methanol and ethanol at 300 °C in the presence of aluminum ethoxide. As a result, only DME was produced from methanol and only diethyl ether was produced from ethanol.

In this communication, we demonstrated that DME is formed from methanol in the presence of aluminum metal. This synthetic method opens a possibility of a simple and mass production of DME.

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References and Notes

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