CO₂ hydrogenation to methanol and dimethyl ether at atmospheric pressure using Cu-Ho-Ga/γ–Al₂O₃ and Cu-Ho-Ga/ZSM-5: Experimental study and thermodynamic analysis

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Abstract: CO₂ valorization through chemical reactions attracts significant attention due to the mitigation of greenhouse gas effects. This article covers the catalytic hydrogenation of CO₂ to methanol and dimethyl ether using Cu-Ho-Ga containing ZSM-5 and γ-Al₂O₃ at atmospheric pressure and at temperatures of 210 °C and 260 °C using a CO₂:H₂ feed ratio of 1:3 and 1:9. In addition, the thermodynamic limitations of methanol and DME formation from CO₂ was investigated at a temperature range of 100–400 °C. Cu-Ho-Ga/γ–Al₂O₃ catalyst shows the highest formation rate of methanol (90.3 µmol/g cat/h) and DME (13.2 µmol/g cat/h) as well as the highest selectivity towards methanol and DME (39.9 %) at 210 °C using a CO₂:H₂ 1:9 feed ratio. In both the thermodynamic analysis and reaction results, the higher concentration of H₂ in the feed and lower reaction temperature resulted in higher DME selectivity and lower CO production rates.

Key words: CO₂ hydrogenation to methanol, dimethyl ether, atmospheric pressure, holmium, gallium, thermodynamic analysis

1. Introduction

CO₂ emissions to the atmosphere increased 15 billion metric tons from 1990 till 2020 because of the increasing fossil fuel usage in industry, transportation, and electricity generation. After the 2000s, a decreasing trend in CO₂ emissions was observed due to the uses of more environmentally friendly industrial technologies; however, CO₂ concentration in the atmosphere continues to increase (to a value of 410 ppm (v/v) in 2020). As reported by Intergovernmental Panel on Climate Change (IPCC), the concentration of CO₂ in atmosphere is predicted to be nearly 600 ppmv in 2050.

There are several methods for CO₂ removal from the atmosphere such as photosynthesis or biological sequestration by plants and microorganisms and carbon capture and sequestration (CCS) technology. CCS technology can reduce up to 90% of the carbon dioxide emissions from power plants; however, CCS is considered to be only a temporary solution. Instead, efficient utilization of CO₂ in chemical industry is considered to be a more desired solution. Hydrogenation of CO₂ to methanol is particularly important considering the potential of methanol as a feedstock in production of various chemicals such as formaldehyde, dimethyl ether (DME), ethanol, olefins, and formic acid [1]. CO₂ hydrogenation not only reduces the cost of CO₂ disposal, but also provides easier transportation and easier storage through liquid methanol production [2]. There are two main reactions considered for methanol production through CO₂ hydrogenation (see Eq. (1) and (2)).

\[
\begin{align*}
\text{CO}_2 + 3 \text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H^\circ (298 \text{ K}) = -49.5 \text{ kJ/mol} \\
\text{CO}_2 + \text{H}_2 & \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta H^\circ (298 \text{ K}) = 41.2 \text{ kJ/mol}
\end{align*}
\]

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CO₂ can be hydrogenated to produce carbon monoxide or methanol under relatively high-pressure conditions and mild temperatures using Cu-based catalysts. Cu-based traditional catalyst, i.e. Cu/ZnO/Al₂O₃ is used in methanol production from CO₂ hydrogenation at a temperature range of 200–300 °C and pressures between 50 bar and 100 bar [3–6]. However, it is desirable to efficiently conduct the carbon dioxide hydrogenation reaction at lower pressures to decrease the cost of the process. Under low-pressure conditions, selection of a catalyst is crucial to achieve desirable kinetics. Since Cu/ZnO/Al₂O₃ catalyst is not active under low-pressure conditions [7], the rate of methanol formation decreases significantly under atmospheric conditions. For instance, the methanol formation rate was obtained as 1.74 μmol/meOH/gcat/min at 190 °C and 1 atm by using Cu/ZnO catalyst [8]. At atmospheric pressure and high temperatures (higher than 300 °C), Ru, Ni, Fe, and Co catalysts can produce higher production rates of methanol [9]. Ni, Ga/Al₂O₃ catalyst, which is prepared by impregnation method, is more advanced when compared with Cu-based catalyst, reaching a methanol production activity of 125 μmol/meOH/gcat/min at 210 °C and 1 atm (CO₂:H₂ = 1:3) [10].

The low methanol selectivity is one of the main problems at the atmospheric pressure due to the dominant reverse water gas shift reaction. Hence, activity of rWGS reaction should be suppressed to achieve high methanol selectivity values. Cu-based (Cu/ZnO) catalyst, which gives lower methanol selectivity, has higher activity for rWGS reaction compared to the Ni-Ga–based catalyst under low-pressure conditions [9,11,12]. According to Diez-Ramirez, 35% methanol selectivity (and a methanol formation rate of approximately 1.2 μmol/meOH/gcat/min) was obtained from the activity of Cu/ZnO catalyst at 210 °C and atmospheric pressure with a CO₂:H₂ ratio of 1:9 [11]. The catalyst Ni, Ga was reported to show 42.2 μmol/meOH/gcat/min methanol formation rate at 200 °C and atmospheric pressure using a CO₂:H₂ ratio of 1:9 [13]. At a higher temperature, i.e. at 230 °C, and at atmospheric pressure, a methanol and dimethyl ether selectivity of approximately 2.5% was observed on Cu/ZnO/Al₂O₃, whereas methanol and dimethyl ether selectivity increased to approximately 15% on Ni, Ga/Al₂O₃ under the same conditions [9]. Although Ni-rich site performs in both rWGS and methanol production reactions, there is the limitation for poisoning Ni site by adsorbed CO and carbon atoms. Gallium-rich site is reported to be responsible for methanol and DME synthesis reaction due to its effect on providing higher selectivity (%) of both methanol and DME at a temperature range of 200–240 °C and at 1 atm using a CO₂:H₂ ratio of 1:3 [9]. According to Zohour et al. [14] a potential trimetallic catalyst combination for methanol production is Cu–GaO₂-HoO impregnated on γ–Al₂O₃. A combined rate for methanol and dimethyl ether production of 1.6 × 10⁻⁴ s⁻¹ is reported on Cu–GaO₂-HoO/γ–Al₂O₃ at 1 atm and 260 °C (CO₂:H₂ ratio is 1:3) compared to a turnover frequency of 0.45 × 10⁻⁴ s⁻¹ observed on Cu–ZnO/γ–Al₂O₃ [14].

The low methanol and high CO formation rates reported in the literature for atmospheric pressure conditions can be explained by the thermodynamic analysis of the reactions (1) and (2) at atmospheric pressure [13]. According to the reported thermodynamics analysis, the methanol selectivity decreased from 48% to 0.1% from 127 °C to 277 °C, while CO₂ conversion could only reach 20% at 277 °C (from 8% at 127 °C) [13]. On the other hand, at elevated pressures (P = 50 bar), the equilibrium conversion of CO₂ could reach 45% at 212 °C (with methanol selectivity of 17.5%) [15].

The thermodynamic limit on the CO₂ conversion and methanol selectivity is often tackled by combining the methanol formation with methanol dehydration (Eq. (3)) to form dimethyl ether [15,16]. According to our knowledge, there is no study in the literature on the thermodynamic analysis of CO₂ hydrogenation to methanol and dimethyl ether considering the reactions 1, 2, and 3 at atmospheric pressure.

\[
2 \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad \Delta H^\circ (298 \text{K}) = -23.6 \text{ kJ/mol} \quad (3)
\]

When methanol production catalysts are combined with solid acid catalysts such as g–Al₂O₃ or zeolites, the catalysts become bifunctional for both methanol production and dimethyl ether synthesis. Firstly, methanol is produced on metal-based catalysts, which is then dehydrated to dimethyl ether on solid acid catalysts. The types of solid acid catalyst that can produce dimethyl ether at atmospheric pressure and nearly at 260–300 °C are commercial g–Al₂O₃, or H⁺-zeolites such as H⁺–ZSM-5 zeolite [17–19], which is more acidic than g–Al₂O₃. Since the water produced on the methanol dehydration reaction has an inhibition effect on acid sites of g–Al₂O₃ [20], zeolites are often preferred due to the stability of the zeolites in the presence of water [21]. The active centers for dimethyl ether synthesis in zeolites are Bronsted acid centers [22]. Depending on the pore structure of zeolite, the formation of different hydrocarbons and coke apart from methanol and dimethyl ether can be observed. This can be caused by Bronsted acid centers having different activities.

In this work, the thermodynamic limitations of methanol and dimethyl ether formation from carbon dioxide are studied at the atmospheric pressure. The thermodynamic analysis for CO₂ hydrogenation to methanol and dimethyl ether is performed using a temperature range of 100–400 °C and CO₂:H₂ feed ratios of 1:3 and 1:9. We also examined the effect of H⁺–ZSM-5 and γ–Al₂O₃ as solid acid catalysts including a ternary metal catalyst: Cu–Ho–Ga for carbon dioxide hydrogenation reaction at the atmospheric pressure and temperatures between 210 °C and 260 °C.
2. Materials and methods

2.1. Thermodynamic considerations on CO₂ hydrogenation to DME process

The thermodynamic analysis of CO₂ hydrogenation to methanol and DME at atmospheric pressure was performed using numerical methods in this work. The equilibrium constants are calculated for CO₂ hydrogenation, reverse water gas shift reaction and methanol dehydration reactions (see Eqs. (1)–(3)) using Tables 1 and 2 and Eqs. (4)–(7). \( K_j \) represents the equilibrium constant of reaction \( j \), \( P_i \) represents the partial pressure of species \( i \), \( v_{ij} \) represents the stoichiometric coefficient of species \( i \) in reaction \( j \). \( \Delta G_j \) represents the Gibbs free energy of reaction \( j \) calculated at the specific temperature. The molar heat capacity at constant pressure of the species \( i \) (\( c_p, i \), J/mol/K) is shown in Eq. (8), for which the constants A, B, C, and D can be found in Table 2.

\[
K_j(T) = \prod_i P_i^{v_{ij}} = \exp\left(\frac{-\Delta G_j}{RT}\right) \tag{4}
\]

\[
\frac{d\ln K_j}{dT} = \frac{\Delta_{rxn,j}H^T}{RT^2} = \frac{\Delta_{rxn,j}H_{298K}^{r}+\Delta c_{p,j} T=T_{ref} \Delta c_{p,j} dT}{RT^2} \tag{5}
\]

\[
K_j = K_{j,298K} \times \exp \left[ \frac{-\text{constant}}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) + \frac{\Delta_{rxn,j} H_j}{R} \times \ln \left( \frac{T}{T_{ref}} \right) + \frac{\Delta B_{rxn,j}}{2 R} \times (T - T_{ref}) + \frac{\Delta C_{rxn,j}}{6 R} \times \left( T^2 - T_{ref}^2 \right) \right] \tag{6}
\]

\[
\text{constant} = \Delta_{rxn,j} H_{298K} - \Delta A_{rxn,j} \times T_{ref} - \Delta B_{rxn,j} \frac{T_{ref}^2}{2} - \Delta C_{rxn,j} \frac{T_{ref}^3}{3} - \Delta D_{rxn,j} \frac{T_{ref}^4}{4} \tag{7}
\]

\[
c_{p,i} = A_i + B_i \times T + C_i \times T^2 + D_i \times T^3 \text{ and } \Delta c_{p,i} = \sum c_{p,i} v_{ij} \tag{8}
\]

The mole fractions and selectivity values are calculated based on the extent of the reactions (see Table 3, Eq (21)).

\[
K_1 = \frac{\gamma_{CH_3OH} \gamma_{H_2O}}{p^2 \gamma_{CO_2} \gamma_{H_2}} \tag{9}
\]

\[
K_2 = \frac{\gamma_{CO} \gamma_{H_2O}}{\gamma_{CO_2} \gamma_{H_2}} \tag{10}
\]

\[
K_3 = \frac{\gamma_{CH_3OH} \gamma_{H_2O}}{\gamma_{CH_3OH}^2} \tag{11}
\]

\[
\gamma_{CO_2} = \frac{n_{CO_2} - \xi_1 - \xi_2}{n_{CO_2} + n_{H_2} - 2 \xi_1} \tag{12}
\]

\[
\gamma_{H_2} = \frac{n_{H_2} - 3 \xi_1 - \xi_2}{n_{CO_2} + n_{H_2} - 2 \xi_1} \tag{13}
\]

\[
\gamma_{CO} = \frac{\xi_2}{n_{CO_2} + n_{H_2} - 2 \xi_1} \tag{14}
\]

\[
\gamma_{H_2O} = \frac{\xi_1 + \xi_2 \xi_3}{n_{CO_2} + n_{H_2} - 2 \xi_1} \tag{15}
\]

\[
\gamma_{CH_3OH} = \frac{\xi_1 - 2 \xi_2}{n_{CO_2} + n_{H_2} - 2 \xi_1} \tag{16}
\]
\[
\gamma_{\text{CH}_3\text{OCH}_3} = \frac{\xi_3}{n_{\text{CO}_2+n_{\text{H}_2}-2\times\xi_1}} (17)
\]

\[
S_{\text{DME}} = \frac{2\times\xi_3}{\xi_1+\xi_2} (18)
\]

\[
S_{\text{CH}_3\text{OH}} = \frac{\xi_1-2\times\xi_2}{\xi_1+\xi_2} (19)
\]

\[
S_{\text{CO}} = \frac{\xi_2}{\xi_1+\xi_2} (20)
\]

\[
X_{\text{CO}_2} = \frac{\xi_1+\xi_2}{n_{\text{CO}_2}} (21)
\]

### 2.2. Experimental procedures

#### 2.2.1. Catalyst preparation

**2.2.1.1. Materials for zeolite synthesis**

In zeolite synthesis, colloidal silica LUDOX HS-40 (Aldrich, 40 wt.%, liquid) was used as the silicon source, sodium aluminate (NaAlO\(_2\)) (Sigma-Aldrich, 55 wt.% Al\(_2\)O\(_3\), 44 wt.% solid) was used as the aluminum source and tetrapropylammonium hydroxide (TPAOH) (Merck, 40 wt.%, liquid) was used as the structure-directing agent (SDA). For NH\(_4^+\)-exchange of ZSM-5, NH\(_4\)\(_2\)NO\(_3\) (Sigma-Aldrich, 99 wt.%, solid) was used as the NH\(_4^+\) source.

**Table 1.** Considered reactions and the thermodynamic constants.

| Rxn no. | Reaction stoichiometry     | \(\Delta H^\circ_{298K}\) (kJ/mol) | \(\Delta S^\circ_{298K}\) (kJ/molK) | \(\Delta G^\circ_{298K}\) (kJ/mol) | Extent of rxn \((x_i)\) | \(K_{eq}\) |
|---------|---------------------------|-----------------------------------|-----------------------------------|-----------------------------------|--------------------------|-----------|
| 1       | CO\(_2\) + 3 H\(_2\) ⇌ CH\(_3\)OH + H\(_2\)O | -49.5                             | -0.178                            | 3.574                            | \(x_1\)                  | \(K_1\)   |
| 2       | CO\(_2\) + H\(_2\) ⇌ CO + H\(_2\)O      | 41.20                             | 0.042                             | 28.684                           | \(x_2\)                  | \(K_2\)   |
| 3       | 2 CH\(_3\)OH ⇌ CH\(_3\)OCH\(_3\) + H\(_2\)O | -23.6                             | -0.022                            | -17.004                          | \(x_3\)                  | \(K_3\)   |

**Table 2.** Thermodynamic parameters used for equilibrium constant calculations [37,38].

| Parameters | CO\(_2\) (\(i=1\)) | H\(_2\) (\(i=2\)) | CO (\(i=3\)) | CH\(_3\)OH (\(i=4\)) | H\(_2\)O (\(i=5\)) | CH\(_3\)OCH\(_3\) (\(i=6\)) |
|------------|---------------------|--------------------|--------------|---------------------|---------------------|---------------------------|
| A (J/mol)  | 27.4730             | 25.3990            | 25.5560      | 40.0460             | 33.9330             | 22.6370                   |
| B (\(\times 10^{-3}\)) | 42.3150             | 20.1780            | -6.5807      | -3.8287             | -8.4186             | 164.8000                  |
| C (\(\times 10^{-3}\)) | -1.9558             | -3.8549            | 2.0130       | 24.5290             | 2.9906              | -5.0000                   |
| D (\(\times 10^{-6}\)) | 3.9968              | 31.8800            | -12.2270     | -216.7900           | -17.8250            | 0.3000                    |
| \(\Delta H^\circ_{298K}\) (kJ/mol) | -393.5000            | 0                  | -110.500     | -201.170            | -241.800            | -184.100                  |
| \(\Delta S^\circ_{298K}\) (kJ/molK) | 0.214               | 0.131              | 0.198        | 0.240               | 0.189               | 0.269                     |

**Table 3.** Extent of reactions.

| Reaction no. | CO\(_2\) | H\(_2\) | CO | CH\(_3\)OH | H\(_2\)O | CH\(_3\)OCH\(_3\) |
|--------------|---------|--------|----|------------|--------|-------------------|
| 1            | \(-\xi_1\) | \(-3\xi_1\) | -  | \(+\xi_1\) | \(+\xi_1\) | -                |
| 2            | \(-\xi_1\) | \(-\xi_2\) | \(+\xi_2\) | \(+\xi_2\) | -       | -                |
| 3            | -        | -      | \(+\xi_1\) | \(-2\xi_3\) | \(+\xi_3\) | -                |
| total        | \(n_{\text{CO}_2}\) \(-\xi_1\) | \(n_{\text{H}_2}\) \(-3\xi_1\) | \(\xi_2\) | \(\xi_1+\xi_2\) | \(\xi_3+2\xi_3\) | \(\xi_3\) |
2.2.1.2. Synthesis of ZSM–5

ZSM–5 zeolite with Si/Al molar ratio is equal to 72 was synthesized hydrothermally using a procedure given by Mei et al. [23]. In the synthesis procedure, 9.654 g of TPAOH was used as the structure directing agent. The molar composition of the synthesis gel mixture was 140SiO₂:1Al₂O₃:8TPAOH:800H₂O. During the synthesis, two solutions were prepared separately. For the first solution, 0.441 g of sodium aluminate and 4.830 g of TPAOH were added in 17.663 g of water. This first solution was stirred for 45 min at room temperature using 300 rpm stirring rate. In another flask, 49.920 g of Ludox LS–40 and 4.830 g of TPAOH were stirred to prepare the second solution at room temperature using 300 rpm stirring rate. After 45 min, the first solution was added to the second solution dropwise. The mixed solution was stirred for 7 h at room temperature using 300 rpm stirring rate. Two autoclaves with Teflon liners (35 mL) were filled with this solution and the hydrothermal synthesis was conducted at 180 °C for 5 days under static conditions. The synthesized zeolite crystals were vacuum filtered using cellulose acetate membrane filter that has 0.2 µm pore diameter and then washed with deionized (DI) water. The mass of ZSM–5 was 19 g after the drying. All samples were dehydrated at 120 °C for 1 h and calcined at 550 °C for 5 h using a 1 °C per min heating rate in a muffle furnace. Then, 5 g of zeolite was exchanged in 0.2 M NH₄NO₃ solution (500 mL DI water) at 80 °C for 3 h using 300 rpm stirring rate. This exchange procedure was repeated 3-times to provide full NH₄⁺ exchange. After the exchange procedure, NH₄⁺-ZSM–5 was heated at 550 °C for 5 h using a 2 °C per min heating rate following drying at 120 °C for 1 h to obtain H⁺-ZSM–5.

2.2.1.3. Materials for metal loading

For metal loading using incipient wetness method, 1.143 g of Cu(II)nitrate trihydrate (Merck, solid), 0.412 g of Ho(III) nitrate pentahydrate (Sigma Aldrich, 100 wt.%, solid), and 1.551 g of Ga(III)nitrate hydrate (Sigma Aldrich, 99.9 wt.%, solid) were used.

2.2.1.4. Catalyst preparation by Cu–Ho–Ga loading for CO₂ hydrogenation reaction

After the heat treatment, the amount of DI water that can be absorbed by 1 g of H⁺-ZSM–5 (Si / Al = 72) was determined (0.8 mL). The metal concentrations to be loaded on support materials were determined to be: 10 wt.% Cu, 5 wt.% Ho, and 5 wt.% Ga. For 3 g of zeolite, 1.143 g of Cu(II) nitrate trihydrate, 1.551 g of Ga(III) nitrate hydrate, and 0.412 g of Ho(III) nitrate pentahydrate were dissolved in 2.4 mL of DI water consecutively. Prepared metal nitrate solution was absorbed by 3 g of H⁺–ZSM–5 (Si/Al = 72). After the H⁺–ZSM–5 was dried at 120 °C for 3 h, calcination was performed at 400 °C for 4 h using a 2 °C per min heating rate following drying at 120 °C for 1 h. This metal loading procedure was repeated for 3 g g–1 of Al₂O₃ in 5.1 mL of DI water. The final samples were pelleted and sieved to result in particle sizes between 200 and 450 µm.

2.2.2. Characterization tests

The characterization of the prepared samples was performed using X-ray powder diffraction, Nₑ adsorption at −196 °C, and scanning electron microscopy. X-ray diffraction (XRD) was performed using a diffractometer (Rigaku Ultima IV, located at the Central Laboratory, Middle East Technical University) using a K-a Cu source (λ = 1.5418 Å) operated at 40 kV and 30 mA. The diffractogram was obtained between 2θ angles of 5-50° and the scanning speed was 1° per min. The images of the prepared ZSM–5 were collected using scanning electron microscopy (QUANTA 400F Field Emission SEM located at the Central Laboratory, Middle East Technical University). The elemental analysis is based on the energy dispersive X-ray spectroscopy analysis (EDX) taken from at least 5 different spots at an accelerating voltage of 30 kV. The textural properties of synthesized and metal-loaded ZSM–5 and metal-loaded γ-Al₂O₃ were investigated using Nₑ adsorption at −196 °C. Prior to Nₑ (Oksan, 99.999%) adsorption experiments, the samples were degassed at 300 °C for 6 h. The adsorption experiments were performed at relative pressure values of 10⁻³ to 0.98 following dead volume measurements using He (Oksan, 99.999%). The temperature of the samples was maintained at −196 °C using liquid Nₑ in a dewar. The micropore volumes of the samples were calculated using statistical thickness, t-plot method.

H₂ TPR experiments were performed on air-exposed calcined samples without any in situ dehydration to be consistent with the reduction procedure prior to the kinetic analysis. Three hundred and fifty milligrams of sample was loaded into a quartz reactor with an inner diameter of 7 mm and an outer diameter of 9 mm. The temperature of the reactor was increased to 625 °C from 30 °C using a heating rate of 5 °C per min. The effluent H₂ was analyzed using an online GC (Agilent 7820A) equipped with a thermal conductivity detector (TCD) and a PoraPlot Q column (CP7554, 25 m × 0.530 mm × 20 mm) every 4 min.

XPS analysis was performed using K-Alpha XPS spectrometer (ThermoFisher Scientific, located at the National Nanotechnology Research Center, Bilkent University) following dehydration of calcined and spent samples at 300 °C for 5 h.

2.2.3. Apparatus used for CO₂ hydrogenation in catalytic reaction

The reaction setup can be seen in Figure 1. The gas flows were controlled using digital mass flow controllers (Alicat, MC-100SCCM-D/5M). A glass bubble flowmeter was used to measure the gas volumetric flow rates at the exit of the reactor.
A quartz tube with an inner diameter of 7 mm and an outer diameter of 9 mm was used as the reactor. In this reactor, 1.7 cm bed length and 350 mg zeolite was loaded and supported by glass wool. A cylindrical furnace around the reactor tube was used as a heater and was controlled by a thermocouple attached to the center of the zeolite outside the quartz cylinder tube in a spiral fashion. The quantitative analysis of effluent gas of the reactor was performed using a gas chromatograph (GC) (Agilent 7820A). The carrier inert gas of GC was He together with H₂ and dry air for flame ionization detector (FID). A PoraPlot Q column (CP7554, 25 m × 0.530 mm × 20 mm) was used for product separation. A flame ionization detector (FID) was used for element qualification and quantification. The split ratio of GC set to 1/5. The temperature of the GC oven was set initially at 40 °C with 5 min holding time in order to separate the light gases. Then the temperature of the oven inside the GC was set to rise from 40 °C to 160 °C at a 10 °C per min ramping rate with 3 min holding time, giving a total of 20 min method time. The sample was taken every 20 min using an autosampling valve with an inlet temperature of 150 °C and FID temperature of 300 °C.

2.2.4. Reaction procedure for CO₂ hydrogenation
The reaction procedure included two steps. The first step was reduction of catalysts using 50 sccm He and 50 sccm H₂. The temperature of the reactor was set to 250 °C using a 5 °C per min heating rate. The temperature was then held at 250 °C for 2 h for reduction. In the second step of CO₂ hydrogenation, CO₂ flow was set to 25 sccm and H₂ flow was set to 75 sccm in order to provide a CO₂:H₂ ratio of 1:3 or 10 sccm vs 90 sccm for a CO₂:H₂ ratio of 1:9 (The total volumetric flow rates were measured as 115 cm³ per min at 25 °C). The reaction was performed at 210 °C, the temperature was set to 210 °C using a heating rate of 5 °C per min. The reaction was performed for 2 h while taking online samples every 20 min. The reaction was also repeated at 260 °C with a CO₂:H₂ ratio of 1:3 and 1:9. The selectivity values and CO₂ conversion were calculated based on equations given in Eqs. (22)–(25), where FCO₂ is the molar flow rate of CO₂ in µmol/h.

\[
\text{Selectivity, } S_{\text{CH₃OH}} \%, = \frac{r_{\text{CH₃OH}}}{r_{\text{CH₃OH}+2r_{\text{DME}}+r_{\text{CH₄}}+r_{\text{CO}}}} \tag{22}
\]

\[
\text{Selectivity, } S_{\text{DME}} \%, = \frac{2r_{\text{DME}}}{r_{\text{CH₃OH}+2r_{\text{DME}}+r_{\text{CH₄}}+r_{\text{CO}}}} \tag{23}
\]

\[
\text{Selectivity, } S_{\text{CO}} \%, = \frac{r_{\text{CO}}}{r_{\text{CH₃OH}+2r_{\text{DME}}+r_{\text{CH₄}}+r_{\text{CO}}}} \tag{24}
\]

\[
\text{Conversion, } X_{\text{CO₂}} \%, = \frac{r_{\text{CH₃OH}+2r_{\text{DME}}+r_{\text{CH₄}}+r_{\text{CO}}}}{F_{\text{CO₂}}/8\text{cat}} \tag{25}
\]
3. Results and discussion

3.1. Thermodynamic analysis

The thermodynamic analyses were performed for CO$_2$ hydrogenation with or without dimethyl ether production (see Figures 2a–2d and 3a–3c). Figure 2a represents the equilibrium conversion of CO$_2$ to methanol and dimethyl ether with respect to temperature using different feed ratios. According to Figure 2a, higher CO$_2$ conversion can be achieved at atmospheric pressure when CO$_2$:H$_2$ ratio is 1:9 (when compared to 1:3 CO$_2$:H$_2$ ratio). The equilibrium CO$_2$ conversion increases from 17.3% to 28.3% at 260 °C for a CO$_2$:H$_2$ ratio of 1:9 when DME production is considered. On the other hand, when DME production is not taken into account (see Figure 3a), the equilibrium CO$_2$ conversion increases from 13.6% to 22.6% at 260 °C when CO$_2$:H$_2$ ratio increases from 1:3 to 1:9.

Figure 2b represents the equilibrium selectivity of CO with respect to temperature using different feed ratios. According to Figure 2b, when CO$_2$:H$_2$ ratio is 1:9, selectivity of CO is less than that for CO$_2$:H$_2$ ratio of 1:3, indicating less favorable reverse water gas shift reaction at higher H$_2$ ratios. A similar case is observed in the absence of dimethyl ether (see Figure 3b). Figure 2c represents the equilibrium selectivity of methanol (MeOH) with respect to temperature with different feed ratios. Slightly higher methanol selectivity could be achieved when CO$_2$:H$_2$ ratio is 1:9; nevertheless, the equilibrium methanol selectivity is very low (<1%) at temperatures higher than 200 °C. Figure 2d represents the equilibrium selectivity of DME with respect to temperature with different feed ratios, again showing a higher selectivity value when CO$_2$:H$_2$ ratio is 1:9. Both methanol and dimethyl ether selectivity values practically reach zero as temperature is increased to values higher than 250 °C.

According to the thermodynamic analysis, higher CO$_2$ conversion, higher methanol selectivity and higher dimethyl ether selectivity can be achieved when H$_2$ is used in higher concentrations in the feed. This is expected due to the higher H$_2$ stoichiometric coefficient in methanol formation when compared to reverse water gas shift reaction.

![Figure 2](image1.png)

**Figure 2.** (a) Equilibrium conversion of CO$_2$ and equilibrium selectivities of (b) CO, (c) MeOH, and (d) DME with respect to temperature at different feed ratios.
At low temperatures, DME and methanol selectivity are higher than those at high temperatures. This is due to the fact that the equilibrium constants for reactions 1 and 3 are decreasing at higher temperatures (due to exothermic nature of the reactions) when compared to increasing equilibrium constant for CO production (Figure 4). This results in increasing CO production and decreasing methanol and DME production at higher temperatures.

When equilibrium results containing methanol dehydration (dimethyl ether production) are compared to those found by Ahmad et al. for CO\textsubscript{2} hydrogenation to methanol without dimethyl ether production [13], a similar trend of higher methanol selectivity is observed at low temperatures at atmospheric pressure. When production of DME reaction is also considered at atmospheric pressure, methanol selectivity shows a maximum selectivity of 9.3% at 142 °C and then decreases with higher temperatures (see Figure 2c). When the DME reaction is not taken into account, methanol selectivity shows a steadily decreasing trend (Figure 3c). This may be due to the higher values of equilibrium constant of the DME production reaction when compared to those of the other reactions, as shown in Figure 4. Due to the lowest minus Gibbs free energy in the third reaction, the equilibrium constant of 3rd reaction gets higher values and therefore increasing the DME selectivity.

3.2. Characterization of catalysts

3.2.1. XRD powder patterns

Powder X-Ray diffraction patterns for H\textsuperscript{+}-ZSM-5 and Cu-Ho-Ga/ZSM-5 following calcination are shown in Figure 5a and the pattern for Cu-Ho-Ga/γ-Al\textsubscript{2}O\textsubscript{3} is shown in Figure 5b. H\textsuperscript{+}-ZSM-5 was observed to have high crystallinity with signature peaks for MFI framework as expected. In XRD patterns of Cu-Ho-Ga/ZSM-5 and Cu-Ho-Ga/γ-Al\textsubscript{2}O\textsubscript{3}, formation of CuO can be observed following Cu-Ho-Ga loading and calcination in air. Presence of CuO was determined on Cu-Ho-Ga/ZSM-5 and Cu-Ho-Ga/γ-Al\textsubscript{2}O\textsubscript{3} from the diffraction peak observed at the 2q angle of 38.7° (belonging to CuO (111) [24]) and at the 2q angle of 35.6° (belonging to CuO (002)[25]), respectively.
3.2.2. \( \text{N}_2 \) adsorption tests

\( \text{N}_2 \) adsorption isotherms obtained at \(-196 \, ^\circ\text{C}\) on \( \text{H}^+\)-ZSM-5, Cu-Ho-Ga/ZSM-5, \( \gamma \text{-Al}_2\text{O}_3 \), and Cu-Ho-Ga/\( \gamma \text{-Al}_2\text{O}_3 \) can be seen in Figures 6a and 6b. The surface areas, total pore volumes, and micropore and mesopore volumes of the samples before and after the metal loading of \( \text{H}^+\)-ZSM-5 and after the metal loading of \( \gamma \text{-Al}_2\text{O}_3 \) are given in Table 4. \( \text{H}^+\)-ZSM-5 contains both micropore volume and mesopore volume. Cu-Ho-Ga/\( \gamma \text{-Al}_2\text{O}_3 \) contains mesopore volume. The micropore volumes of pure \( \text{H}^+\)-ZSM-5 and Cu-Ho-Ga/ZSM-5 were measured as 0.129 cm\(^3\)/g and 0.104 cm\(^3\)/g, respectively. Following the loading of Cu-Ho-Ga, it was observed that the volume of micropores as well as surface areas on \( \text{H}^+\)-ZSM-5 decrease. This could be because of some of the dissolved Cu(II), Ho(III), or Ga(III) cations exchanged inside the micropore voids of the zeolites.

3.2.3. Morphology and elemental analysis

The scanning electron microscopy (SEM) image of Cu-Ho-Ga/ZSM-5 can be seen in Figure 7. ZSM-5 crystals have crystal sizes between 5 and 15 \( \mu \text{m} \) (Figure 7a) and \( \text{Al}_2\text{O}_3 \) having particle sizes approximately 200 nm (Figure 7b) without any clear evidence of metal clusters. When the elemental analysis was performed using energy dispersive X-ray spectrometry (EDX), the average weight percentages were found to be 9.7 wt.% for Cu, 4.8 wt.% for Ho, and 3.6 wt.% for Ga on ZSM-5, in agreement with the intended metal loading percentages: 10 wt.% Cu, 5 wt.% Ho, and 5 wt.% Ga. For \( \text{Al}_2\text{O}_3 \), weight percentages were found to be 15.9 wt.% for Cu, 10.6 wt.% for Ho and 4.7 wt.% for Ga.

3.3. Catalytic \( \text{CO}_2 \) hydrogenation reaction results

The kinetic results of the reaction were obtained by performing reactions at 210 \( ^\circ\text{C} \) and 260 \( ^\circ\text{C} \) and at atmospheric pressure using ZSM-5- and \( \gamma \text{-Al}_2\text{O}_3 \)-based 0.35 g catalysts. According to these results, methanol, DME, and CO were observed as the main products with a small amount of CH\(_4\) formed.

Figure 4. Calculated equilibrium constants for (a) reaction 1, (b) reaction 2, and (c) reaction 3.
By examining two different catalysts; Cu–Ho–Ga/ZSM-5 and Cu–Ho–Ga/g–Al₂O₃, at the same feed ratio (1:3 CO₂:H₂) and at the same temperature (260 °C), the total methanol and DME formation rates of g–Al₂O₃-based catalyst are nearly two times of that of ZSM-5-based catalyst (See Table 5). The reason for the lower methanol formation activity (per gram of the catalyst) on Cu–Ho–Ga/ZSM-5 could be due to the inactive Cu(II) or Ho(III), Ga(III) cations that are residing inside the micropores, which cannot be reduced as freely as the nanoclusters of CuO at the surface of the ZSM-5 crystals.
TPR experiments conducted on calcined samples show complete reduction of CuO on g-\(\text{Al}_2\text{O}_3\) at 230 °C (see Figure 8), similar to TPR profile of commercial Cu/ZnO/g-\(\text{Al}_2\text{O}_3\) catalyst [26]. On the other hand, for complete reduction of Cu(II) on ZSM-5, temperatures above 300 °C are needed on ZSM-5 (see Figure 8) [27]. Reduction of Ga\(\text{2O}_3\) and Ho\(\text{2O}_3\) are expected at temperatures higher than 500 °C [28,29]. Reduction at 250 °C reduces only 51% of the reducible metals on ZSM-5 (1051 μmol H\(_2\) per g cat out of total 2073 μmol H\(_2\)/g cat), whereas this ratio is found to be 72% on g-\(\text{Al}_2\text{O}_3\) (948 μmol H\(_2\)/g cat out of total 1311 μmol H\(_2\)/g cat) based on TPR analysis.

Higher ratio of formation rates of DME over methanol at 260 °C were observed for ZSM-5-based catalyst when compared to g-\(\text{Al}_2\text{O}_3\)-based catalyst (see Table 5). The reason for this is stronger Bronsted acid sites on ZSM-5 as expected. The weaker acidity on g-\(\text{Al}_2\text{O}_3\) causes lower methanol dehydration rates as well as lower water stability compared to ZSM-5 [30].

Lower temperatures (210 °C) affected the methanol and DME formation rates differently in two different catalysts (see Figure 9). For Cu-Ho-Ga/ZSM-5, a decreasing trend in methanol and DME formation rates have been observed, which is opposite to what is observed on Cu-Ho-Ga/g-\(\text{Al}_2\text{O}_3\). Decreased methanol and DME formation rates at 210 °C could be due to the slower CO\(_2\) hydrogenation kinetics, and methanol dehydration reactions, could cause blockage of the Bronsted acid sites as well as oxidation of Cu(0) metals into Cu(II) on zeolites [31,32] that would decrease the DME and methanol production. Especially at 200 °C, presence of water could cause competitive adsorption, similar to the case of NO oxidation, where decreased catalytic activity was reported due to the competitive adsorption of water and NO on Cu-ZSM-5 [33].

XPS analyses of calcined and spent samples are given in Figures 10a–10f. A visibly higher Cu(II) fraction is evident on Cu-Ho-Ga/ZSM-5 when compared to that on Cu-Ho-Ga/g-\(\text{Al}_2\text{O}_3\) (peaks at 933.7 eV and 934.3 eV for Cu(II) 2p\(_{3/2}\), and 932.8 eV for Cu(0) 2p\(_{3/2}\) [34], see Figures 10g and 10h), indicating either inefficient reducibility of Cu(II) as mentioned before, or oxidation due to the abundant production of water. Oxidized Ga and Ho were also observed (Ga 2p\(_{3/2}\) at 1118 eV for Ga\(\text{2O}_3\) [35] Ho 4d\(_{5/2}\) at 161.2 eV for Ho\(\text{2O}_3\) [36]) on spent catalysts that are exposed to air (see Figures 10c–10f).

Table 5. Methanol, DME, and CO formation rates on 0.5 g of Cu-Ho-Ga/H\(_+\)-ZSM-5 and Cu-Ho-Ga/g-\(\text{Al}_2\text{O}_3\) at 260 °C and at 1 atm for a CO\(_2\)/H\(_2\) of 1:3.

| Catalyst                | CH\(_3\)OH formation rate (μmolCH\(_3\)OH/g\(_{\text{cat}}\)/h) | DME formation rate (μmol\(_{\text{DME}}\)/g\(_{\text{cat}}\)/h) | CO formation rate (μmol\(_{\text{CO}}\)/g\(_{\text{cat}}\)/h) | Selectivity of CH\(_3\)OH+DME (%) |
|-------------------------|---------------------------------|---------------------------------|---------------------------------|-------------------------------|
| Cu-Ho-Ga/g-\(\text{Al}_2\text{O}_3\) | 41.7 ± 0.9                      | 3.2 ± 0.2                       | 6825 ± 400                      | 0.7                           |
| Cu-Ho-Ga/ZSM-5          | 23 ± 1                           | 5.6 ± 0.4                       | 553 ± 56                        | 5.9                           |

Figure 7. SEM images of a) Cu-Ho-Ga/ZSM-5 and b) Cu-Ho-Ga/g-\(\text{Al}_2\text{O}_3\).
Figure 8. $H_2$ TPR analyses of Cu-Ho-Ga/ZSM-5 and Cu-Ho-Ga/g–Al$_2$O$_3$.

(a) Cu-Ho-Ga/ZSM-5

| Parameter                  | Cu-Ho-Ga/ZSM-5 | Cu-Ho-Ga/γ–Al$_2$O$_3$ |
|----------------------------|----------------|------------------------|
| CO formation rate (μmolCO/gcat/h) | 553            | 6825                   |
| DME formation rate (μmolDME/gcat/h)  | 0.6            | 1.4                    |
| CH$_3$OH formation rate (μmolCH$_3$OH/gcat/h) | 23.0           | 42                     |

Figure 9. Product formation rates on a) Cu-Ho-Ga/ZSM-5 and b) Cu-Ho-Ga/γ–Al$_2$O$_3$ at 210 and 260 °C and CO$_2$:H$_2$ ratios of 1:3 and 1:9.
Figure 10. XPS analysis on oxidized and spent a,c,e) Cu-Ho-Ga/ZSM-5 and b,d,f) Cu-Ho-Ga/g–Al$_2$O$_3$, XPS Cu 2p$_{3/2}$ region for spent g) Cu-Ho-Ga/ZSM-5 and h) Cu-Ho-Ga/g–Al$_2$O$_3$. 
In contrast to Cu-Ho-Ga/ZSM-5, increased methanol and DME formation rates are observed on Cu-Ho-Ga/g–Al₂O₃ at 210 °C with suppressed CO formation. This could be due to the exothermicity of the methanol and DME formation reactions as well as endothermicity of the reverse water gas shift reaction, favoring methanol and DME formation at lower temperatures. Increased methanol and DME formation rates sum up to 103 µmol/gcat/h (90.3 µmolCH₃OH/gcat/h and 13.2 µmolDME/gcat/h) at 210 °C and a CO₂:H₂ feed ratio of 1:9. Even though these values are lower than 5625 µmolCH₃OH/gcat/h and a CO₂:H₂ feed ratio of 1:9 observed on Ni₃Ga₂/SiO₂ at 210 °C and 1 atm (CO₂:H₂ = 1:3) [10], it is higher than 72 µmolCH₃OH/gcat/h methanol formation rate obtained on Cu/ZnO catalyst at 210 °C and 1 atm (CO₂:H₂ feed ratio of 1:9) [11].

For Cu-Ho-Ga/ZSM-5, major decrease in CO formation rate is observed by increasing the H₂ content of the feed to a CO₂:H₂ feed ratio of 1:9 at 260 °C, in accordance with the thermodynamic expectance. At these conditions, a methanol formation rate of 31 µmolCH₃OH/gcat/h and a combined methanol and DME selectivity of 31% are observed on Cu-Ho-Ga/ZSM-5, which is higher than reported methanol and DME selectivity of 15% on Ni₃Ga₂/SiO₂ at 230 °C [9]. However, at 210 °C, the CO formation rate did not differ much from the value of 98 µmolCO赴/gcat/h obtained at 260 °C and CO₂:H₂ feed ratio of 1:9 (see Figure 9). Considering low CO formation together with decreased methanol and dimethyl ether rates, we can conclude that blockage of Cu and Bronsted acid sites rendered 210 °C an unfavorable temperature for all three reactions (Eqs. (1)–(3)) on Cu-Ho-Ga/ZSM-5.

On the other hand, effect of temperature and CO₂:H₂ ratio in the feed is clearly observable for Cu-Ho-Ga/g–Al₂O₃. At 210 °C, lower CO selectivity values can be achieved with higher methanol and DME formation rates. For a CO₂:H₂ ratio of 1:9, 59.8% CO selectivity and 30.9% methanol selectivity were observed using Cu-Ho-Ga/g–Al₂O₃ (see Table 6). At 260 °C a lower methanol selectivity value of 1.5% on Cu-Ho-Ga/g–Al₂O₃ was noted for the same CO₂:H₂ ratio, in accordance with the thermodynamic analysis. Therefore, we can conclude that lower temperature (210 °C) and 1:9 CO₂:H₂ resulted in higher methanol+ DME selectivity on Cu-Ho-Ga/g–Al₂O₃ (see Table 6). This is due to the exothermicity of reactions 1 and 3 and stoichiometric coefficients of the 3 main reactions in Table 1. The methanol and DME formation rates are expected to increase when the H₂ ratio in the feed is higher.

CO₂ conversion results are shown in Figure 11. According to the catalytic activity of both Cu-Ho-Ga/γ-Al₂O₃ and Cu-Ho-Ga/ZSM-5, the highest conversion of CO₂ (%) was recorded at 260 °C and at 1:9 CO₂:H₂ ratio. The calculated CO₂ conversion values (such as 5.3% at 260 °C and at 1:9 CO₂:H₂ ratio on Cu-Ho-Ga/γ-Al₂O₃) are lower than the calculated equilibrium conversion values (28% at 260 °C and at 1:9 CO₂:H₂ ratio), indicating room for improvement for the observed rates on these catalysts.

4. Conclusions
This study reports the kinetic and thermodynamic analysis of DME and methanol synthesis from CO₂ hydrogenation reaction at atmospheric pressure. Cu-Ho-Ga/γ-Al₂O₃ was found to be a more efficient catalyst with methanol formation rate reaching 90.3 µmolCH₃OH/gcat/h and a DME formation rate of 13.2 µmolDME/gcat/h. A combined methanol and DME selectivity of 39.9% was observed at 210 °C and a 1:9 CO₂:H₂ feed ratio. Temperature increase affected the methanol formation rate and selectivity values on Cu-Ho-Ga/γ-Al₂O₃ and Cu-Ho-Ga/ZSM-5 differently. On Cu-Ho-Ga/γ-Al₂O₃, increased temperature resulted in decreased methanol formation and accelerated CO formation (and therefore much lower methanol selectivity) as expected from the thermodynamic analysis. However, for Cu-Ho-Ga/ZSM-5, 210 °C was disadvantageous due to high CO formation rate.

Table 6. The methanol + DME and CO selectivity values of 0.5 g of Cu-Ho-Ga/ZSM-5 and Cu-Ho-Ga/g–Al₂O₃ at 210 °C and 260 °C and at 1 atm with different feed ratios.

| Catalyst          | Reaction temperature (°C) | CO₂:H₂ feed ratio | S₃CH₃OH (%) | S₃CH₃OH + S₃DME (%) | S₃CO (%) |
|-------------------|---------------------------|-------------------|-------------|---------------------|---------|
| Cu-Ho-Ga/g–Al₂O₃  | 210                       | 1:9               | 30.9        | 39.9                | 59.8    |
|                   |                            | 1:3               | 18.8        | 21.6                | 78.3    |
|                   | 260                       | 1:9               | 1.52        | 1.9                 | 98.1    |
|                   |                            | 1:3               | 0.61        | 0.7                 | 99.3    |
| Cu-Ho-Ga/ZSM-5    | 210                       | 1:9               | 12          | 14.5                | 85.2    |
|                   |                            | 1:3               | 12.8        | 14.3                | 85.2    |
|                   | 260                       | 1:9               | 21.8        | 31.0                | 68.6    |
|                   |                            | 1:3               | 4.0         | 5.9                 | 93.9    |
found to be a low temperature for significant methanol and dimethyl ether production as well as reverse water gas shift reaction due to the inactivation of the Cu and Bronsted acid sites in presence of water vapor. Only at 260 °C, the reaction results followed thermodynamic trends by showing enhanced methanol selectivity with an increased H₂ content in the feed. An increase in the methanol and DME selectivity from 5.9% to 31% was observed with decreased CO₂:H₂ ratio from 1:3 to 1:9. Higher CO₂ conversions were observed at 260 °C with the highest value of 5.3% using a CO₂:H₂ ratio of 1:9. Optimization of the catalysts is encouraged for enhancing the observed methanol formation rates and selectivity values as the results were found to be away from the equilibrium. At the investigated conditions, the highest methanol formation rate and selectivity were found as 90.3 µmolCH₃OH/gcat/h and 30.9%, respectively.

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