Low Temperature Liquid Phase CO_2 Hydrogenation to Methanol over Molybdenum Carbide-Based Catalysts

By
Tianshu Ji

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Thesis advisors/mentors:
Professor Levi T. Thompson, Jr.
Ph.D Student Yuan Chen

ABSTRACT

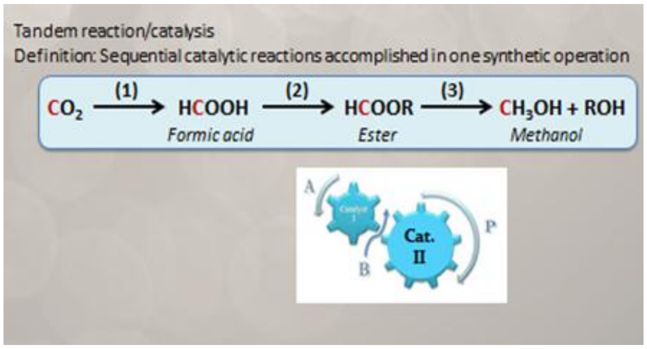
Different metal depositions onto Mo_2C catalysts for the low temperature hydrogenation of CO_2 to methanol was studied in this paper. With the Mo_2C material as a catalyst support, we aim to identify the effect of different metal deposition on the reaction activities and selectivities. Several metal/Mo_2C catalysts were synthesized and characterized using X-ray diffraction, chemisorption, N_2 physisorption and inductively coupled plasma. Our results show that copper, iron and palladium outperformed other tested metal species (cobalt and ruthenium) over Mo_2C to facilitate the CO_2 hydrogenation to methanol. In addition, the kinetic analysis was performed for the CO_2 hydrogenation to methanol over Cu/Mo_2C catalyst. The activation energy was determined to be 82.3 kJ/mol based on Arrhenius law at the low temperatures from 115 to 150 °C. These results provide useful information for the design of metal/Mo_2C catalysts used for CO_2 hydrogenation to methanol via single or cascade catalytic systems.

INTRODUCTION

Carbon dioxide is an abundant and renewable carbon source. It is potentially cheap and can be obtained from power plant exhaust or extracted from air. CO_2 transformation can recycle the CO_2 into useful chemicals that potentially brings economical values with reduced carbon footprints. Therefore, a number of researches have focused on how to convert carbon dioxide into fuels and chemicals such as alcohols and hydrocarbons.[1] Methanol is a commonly used precursor/starting material and solvent in the chemical industry; it can also be used directly to power fuel cells or supplement petroleum products as a clean-burning additive.[1] The hydrogenation of CO_2 to methanol is commercially performed over a single Cu/Zn catalyst that requires high temperature (>200°C); several challenges remained under these operating conditions. The first challenge is associated with thermodynamics: As the CO_2 to methanol reaction is highly exothermic (Eq.1), the theoretical yield of methanol is limited at high temperature. Additionally, the formation of side products (e.g. CO, CH_4) that are favored at high temperatures (>200 °C) can further diminish the selectivity of methanol.[2] The second challenge is operational in that the heat from this exothermic reaction is difficult to remove, causing reactor over-heating and catalyst deactivation. Therefore, it is desired to carry out this reaction at lower temperatures.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O; \Delta H_{298K} = -49.5 \text{ kJ/mol} \qquad \text{Eq. 1}$$

The strategy we utilize to achieve the CO_2 hydrogenation to methanol is through the cascade catalysis, where the overall reaction is accomplished sequentially via several steps within one-pot operation,[3,4] typically with the most effective catalyst identified for each step as illustrated in Figure 1. One cascade pathway takes CO_2 through formic acid and ester formate intermediates to produce methanol (Figure 2). The feasibility of this pathway has been demonstrated by Huff and Sanford using a series of homogeneous catalysts under Lewis acidic condition.[5] However, the material incompatibility was identified to be the main issue for the inefficiency of homogeneous system. Heterogeneous catalysts can potentially provide improved compatibility and easy separation due to its presence in a different phase.[6]



Tandem reaction/catalysis

Definition: Sequential catalytic reactions accomplished in one synthetic operation

Figure 1. Schematic diagram of tandem/cascade catalysis system

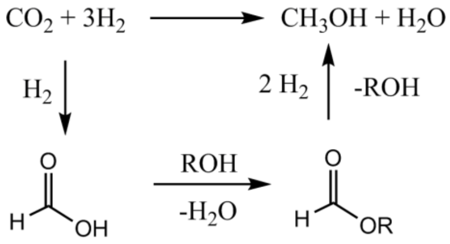


Figure 2. Cascade reaction pathway for CO2 hydrogenation to methanol through formic acid and alkyl formate intermediates.

Earlier research in Thompson group has identified that Mo_2C based catalysts especially deposited with active metals, such as Cu and Pd, are active and selective for CO_2 hydrogenation to methanol and all the other sub steps within the proposed pathway.[7] The CO_2 to formic acid step was the rate-limiting step as suggested by the reaction thermodynamics as well as demonstrated by the reaction activity measurements. Through the collaboration in CENTC, this project will be later focused on combining the viable homogeneous catalysts from Sanford group and heterogeneous catalysts from Thompson group for improved performance on methanol production. Research described in this paper is to study the influence of different metal loading over Mo_2C for the reaction activity and selectivity of CO_2 hydrogenation, with methanol being the desirable product. Based on the results, we can rationally select the metal(s) that best facilitate this reaction to design a better catalyst that can be utilized to improve the performance of the cascade catalytic system for CO_2 hydrogenation.

METHODS AND MATERIALS

To prepare the molybdenum carbide catalyst, we used the TPR (Temperature Program Reaction) technique. First, we reduced the precursor ammonia molybdate (AM) under H_2 (400 ml/min, 350 °C, 12 hrs) and followed by a treatment of CH_4/H_2 (400ml/min, 590 °C, 2hrs) to synthesize the Mo_2C. The molybdenum carbide was then introduced into 70 ml deoxygenated water (purged with argon) containing target concentrations of metal precursors. The Mo_2C was kept in contact with the metal precursor solution for 20 hrs with argon being purged to keep the solution agitated and free of oxygen. The resulting catalyst slurry was then dried and reduced under H_2 at 300 °C for 4hrs to remove any anion groups from the metal precursors. The as-synthesized catalyst was then transferred into the glove box for the future reaction usage. A schematic diagram of the synthesis protocol is illustrated in Figure 3. The other details regarding the metal/Mo_2C catalysts synthesis was reported elsewhere.[8]

Surface areas of the materials were measured using a Micromeritics ASAP 2010 analyzer based on N_2 physisorption. All catalysts were degassed at 350 °C for 4 hours before performing the measurements. The bulk crystalline structures were identified using XRD (Rigaku Miniflex 600, Cu Kα radiation) with 2θ ranging from 10 degree to 90 degree at a scan rate of 5 degree per min. Metal compositions of different catalysts were quantified by inductively coupled plasma (ICP-OES) using a Varian 710-ES analyzer. The surface site densities for Mo_2C-based catalysts were determined via CO chemisorption.[9]

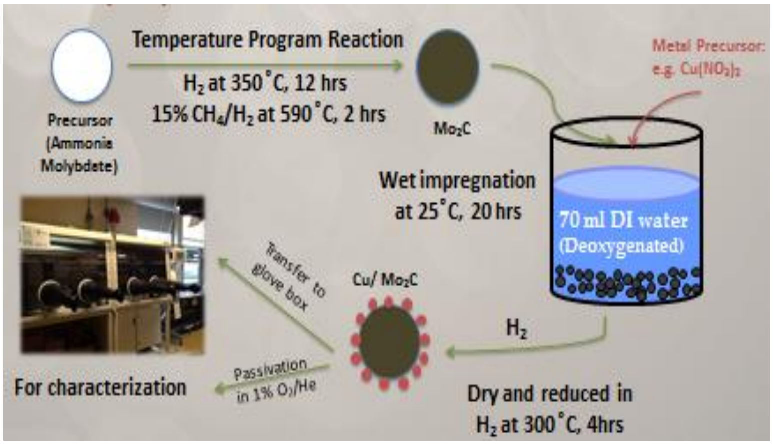


Figure 3. Schematic diagram for catalyst synthesis procedures for metal/Mo_2C catalysts.

All the experiments were performed in a semi-batch (Parr) reactor system as shown in Figure 4. The reactor supports the high temperature (up to 350 °C) and high pressure (up to 200 bar) operation and equipped with a shaft to keep the reaction species well-mixed; a filter was also installed to separate the catalyst particles from reaction liquid samples.

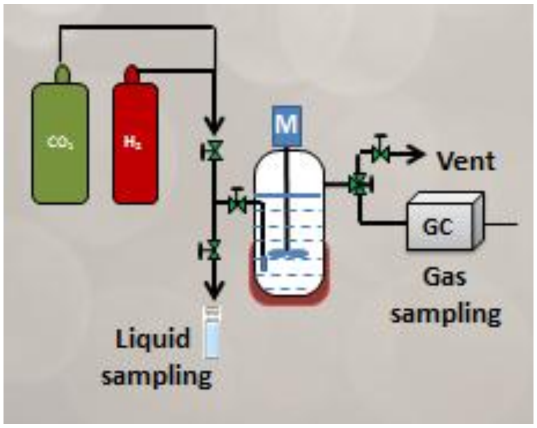


Figure 4. Semi-batch reactor system for liquid phase CO_2 hydrogenation.

The reaction solution was prepared by combining 37.5 ml 1,4-dioxane with 10 µl of decane (as an internal standard for GC analysis). Then we took 400 µl of the solution as the initial liquid sample. The reaction solution and 200 mg of catalyst were then introduced into the reactor. The reactor loading was performed in a glove box (filled with Ar) since the native Mo_2C-based catalysts are pyrophoric. The reactant gases of 10 bar CO_2 and 30 bar H_2 were then charged into the reactor. After the system was heated up to the desired reaction temperature (135 °C for this study), we took the 0h samples of both the gas and liquid phases. Followed by that, the samples at 2h, 4h, 6h, 8h (and sometimes 24h) were also taken periodically. We determined the concentrations of products at different time using GC analysis and calculate the reaction rate and turn over frequency (TOF) over the catalysts. The reaction rate was calculated by normalizing the total amount of product formation (in mmol) by reaction time (2h, to approximate the initial rate) and catalyst weight (200mg). The TOF was determined by dividing the reaction rate by the catalyst site density.

RESULTS AND DISCUSSION

The physical properties of a series of metal/Mo_2C catalysts were characterized and the results are shown in Table 1. The metal content for all the catalysts achieved ~ 5wt%, the target loading. The Co/Mo_2C showed a relatively lower loading compared to the other catalysts, as Co deposition reached saturation via the wet impregnation technique at the current conditions, possibly governed by a surface re-dox equilibrium.[8] The surface coverage was determined based on the measured site density by assuming 10^{19} sites/m^2. The surface areas for the metal/Mo_2C catalysts were in general lower than that of Mo_2C, possibly suggesting that the metal domains has partially blocked the pores of the Mo_2C support.

Table 1 Physical properties of Mo_2C-based catalysts

Catalyst	**Metal Content (wt%)**	**Site density (µmol/g)**	**Surface coverage (% ML)**	**Surface Area (m2/g)**
Cu/Mo_2C	5.3	298	35.1	135
Pd/Mo_2C	5.2	346	20.5	138
Cu-Pd/ Mo_2C	Cu (3.8) Pd (1.4)	328	30.7	132
Co/Mo_2C	1.7	383	11.7	124
Ru/Mo_2C	5.2	216	21.6	96
Fe/Mo_2C	4.7	306	35.1	118
Mo_2C	NA	406	NA	151

The XRD was performed to identify the crystallite structures and phase purity of these catalysts as shown in Figure 5. The pattern on top (the light blue line) is for the bulk Mo_2C material. We observed both alpha- and beta-phase carbides where no molybdenum oxide peaks were detected. This observation indicated that the Mo_2C catalyst was phase pure with complete carburization. The bottom five patterns corresponded to the metal/Mo_2C catalysts. However, the peaks associated with the metal were not obviously observed. There are two reasons to explain this observation: First, the metal loaded on the Mo_2C is not too much in quantity with some characteristic peaks overlapped with the ones of molybdenum carbide; second, the crystallite size of the metal is comparable or below the detection limit of the XRD (~ 5nm), which could indicate that metal was well distributed on the catalyst surface.

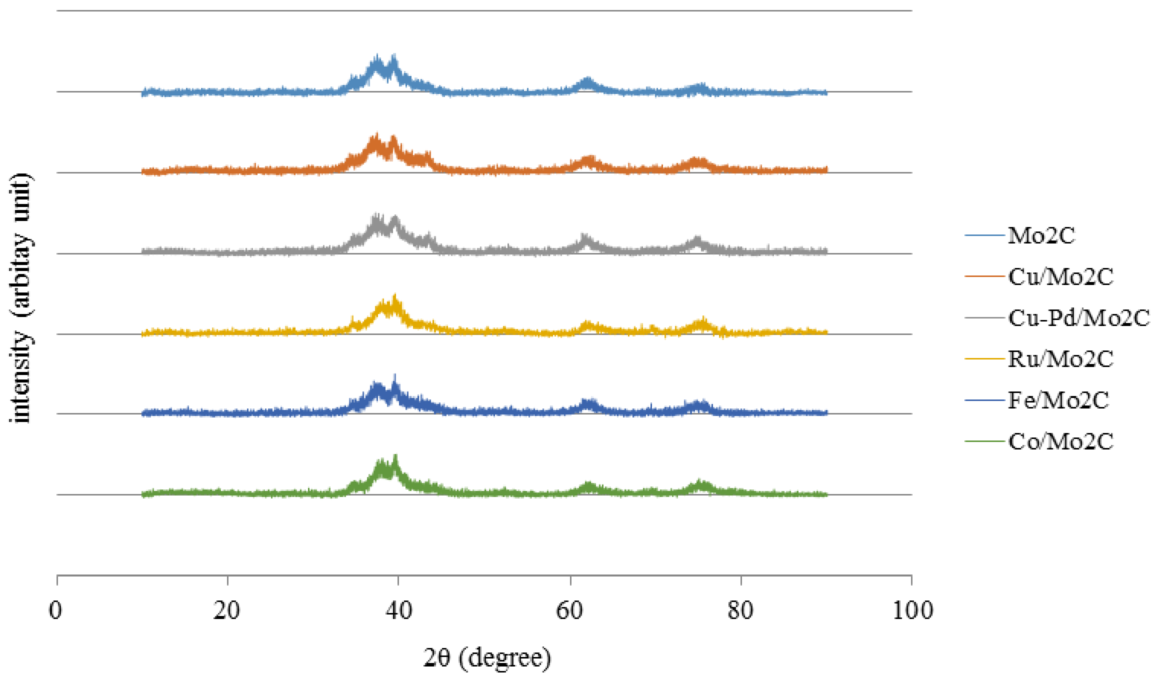


Figure 5. X-ray diffraction patterns for a series of metal/Mo_2C catalysts.

The hydrogenation of CO_2 was measured at 135 °C, 10 bar CO_2, and 30 bar H_2 in 37.5 ml 1,4-dioxane. Under these conditions, the corresponding loading for CO_2 and H_2 are approximately 56 mmol and 9 mmol based on their solubilities in 1,4-dioxane.

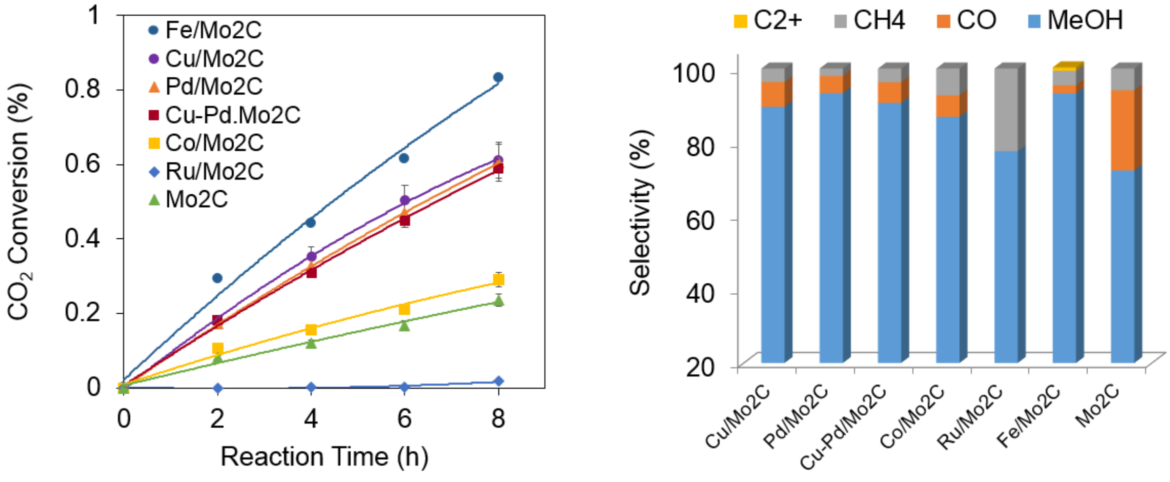
The major objective is to understand the effects of depositing different active metals to Mo_2C on reaction performance. We looked into several types of metal deposition: Copper, palladium, bimetallic of copper and palladium, cobalt, ruthenium, iron and a bulk Mo_2C catalyst (as a control experiment). The results of reaction activities and selectivities are shown in Table 2.

Table 2. CO_2 hydrogenation over metal loaded Mo_2C based catalysts

Catalysts	**CO_2 Conv. rate (mmol/g_{cat}/hr)**	**MeOH production rate (mmol/g_{cat}/hr)**	**Selectivity (%) at 8 hr**	**MeOH production TOF at 2 hr (hr^{-1})**
Cu/Mo_2C	0.22	0.19	89.8	0.70
Pd/Mo_2C	0.21	0.21	93.4	0.59
Cu-Pd/Mo_2C	0.21	0.18	90.6	0.66
Co/Mo_2C	0.10	0.08	86.6	0.35
Ru/Mo_2C	0.006	0.006	80	0
Fe/Mo_2C	0.28	0.26	93.2	1.28
Mo_2C	0.08	0.59	72.3	0.14

Most of metal deposition exhibited improved performance compared to the bulk Mo_2C for CO_2 conversion rate. Among these metals, Fe, Cu and Pd are the most active promoters, while Co slightly enhanced the performance likely due to its lower metal loading content. The deposition of Ru seemed to inhibit the performance of Mo_2C catalyst; this deactivation was likely a consequence of the surface complexation between the Cl^- anion (from the $RuCl_2$ precursor) and the Mo_2C support as suggested from previous study.[9] The CO_2 conversion as a function of reaction time is shown in Figure 6a. The CO_2 conversions of <1% were achieved over all the catalysts after 8h of reaction, much lower than the equilibrium conversion (~ 11% based on the thermodynamics at the current reaction conditions). At these low CO_2 conversion values, the CO_2 concentration in the reaction system can be considered as a constant, which explains the linear correlation ($R^2 > 95\%$), between the CO_2 conversion and the reaction time.

The product selectivities over each metal/Mo_2C is shown in Figure 6b. Improvements on methanol selectivity were observed when Cu, Pd, Fe or Co were deposited onto the Mo_2C support. This finding indicated that these metals further facilitated the methanol synthesis over Mo_2C catalyst, likely by providing additional dissociative hydrogenation. Meanwhile, both Cu and Pd based catalysts has been reported to be active methanol synthesis catalysts; Co and Fe are active species during the Fisher Tropsch Synthesis (FTS) for alcohol synthesis. No obvious synergy was observed over the bimetallic Pd-Cu/Mo_2C compared to the Cu/Mo_2C or Pd/Mo_2C individually, suggesting Cu and Pd domains exhibited similar catalytic performance over the Mo_2C support. The deposition of Ru resulted in comparable methanol selectivity, while substantial amount of CH_4 was produced. This observation is consistent with Ru being a methanation catalyst as reported in previous studies.[10] In addition, ethane and propane were also produced over Fe/Mo_2C, suggesting that Fe species was capable to promote the FTS at low temperatures over Mo_2C support for the C_{2+} hydrocarbon formation.



(a) (b)

Figure 6. (a) CO_2 conversion as a function of reaction time; (b) product selectivities from CO_2 hydrogenation at 8 h of reaction, over a series of metal/Mo_2C catalysts.

We also conducted reactions at temperatures ranging from 115 to 150 °C over Cu/Mo_2C catalyst to study its Arrhenius behavior and determine the activation energy for CO_2 hydrogenation to methanol. We selected Cu/Mo_2C catalyst in this study due to its relatively high activity and selectivity based on the previous catalyst screening. The activity measurements were performed under three different temperatures, 115 °C, 135 °C, and 150 °C as shown in Figure 7a. The activity data were fit to the Arrhenius equation, expressed as $k = A*\exp[-E_a/RT]$, where k is the reaction rate, T is temperature in K, E_a is activation energy, A is a pre-exponential factor and R is gas constant.

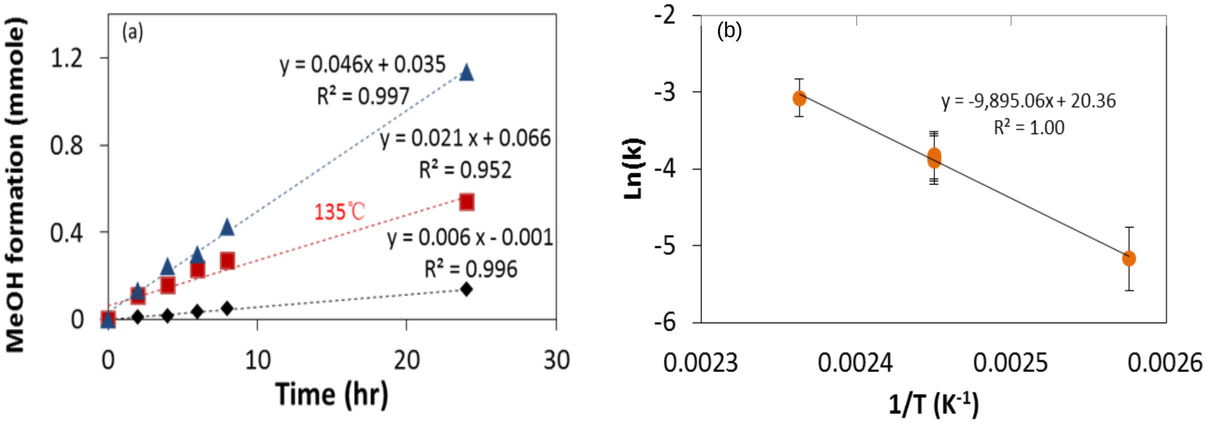


Figure 7. (a) Kinetic data and (b) Arrhenius plot for CO_2 hydrogenation to methanol over Cu/Mo_2C catalyst. 115 - 150 °C, 30 bar H_2 and 37.5 ml 1,4-dioxane.

Figure 7b shows the fitting of the kinetic data after taking the logarithm on both sides of the Arrhenius equation; the slope of this linear fitting is equal to $-E_a/R$. The activation energy is calculated to be 82.3 kJ/mol and can be used later to predict the activity at other temperatures without running the reactions.

CONCLUSION

To sum up, we have studied the effect of metal deposition over Mo_2C based catalysts for the low temperature (135 °C) liquid phase CO_2 hydrogenation to methanol. Of the metals we examined, Cu, Pd and Fe are among the most effective to facilitate the methanol production. Fe also appears to promote the FTS over Mo_2C to produce ethane and propane from CO_2. The addition of Co resulted in slight enhancement in reaction rate and methanol selectivity, possibly due to its low metal loading and surface coverage compared to other metal/Mo_2C catalysts. The Ru deposition seemed to deactivate Mo_2C activity, producing substantial amount of CH_4. The activation energy was determined to be 82.3 kJ/mol over Cu/Mo_2C within the low temperature range of 115-150 °C. Some of the metal/Mo_2C catalysts will be combined with a series of homogeneous catalysts to promote the CO_2 hydrogenation using a homo-/heterogeneous cascade system. The finding of this project will provide useful knowledge on designing heterogeneous-based cascade catalytic systems for CO_2 hydrogenation as well as other complex conversions that involve multi-step transformations.

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