Effect of Basicity on Cu Based Catalyst for CO₂ Hydrogenation

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Abstract. The purpose of this research is to study the effect of the MgO loading (0.25, 0.5, 1 and 2 Molar) on the Cu/AC catalysts for CO₂ hydrogenation. The optimum condition of reaction temperature and ratio of H₂:CO₂ for CO₂ hydrogenation were also investigated. Copper based catalysts were characterized by BET, CO₂-TPD, H₂-TPR and CO₂-TPSR. The catalytic performance of catalysts were carried out in the fixed bed reactor at a reaction temperature of 250 °C pressure of 1 atm with mixture gas of 2:1 molar ratio of H₂:CO₂. The result shows that MgO increases the surface basicity of catalyst which enhances the bond strength between CO adsorbed on Cu loading to inhibition the reverse water-gas shift reaction, which can well promote the methane selectivity. The optimum conditions for CO₂ hydrogenation is temperature of reaction at 300 °C and ratio of H₂:CO₂ as 2:1.

1. Introduction
NOWADAY use of fossil fuels give rise to huge amount of greenhouse gases emission to the atmosphere, which has caused the increase of climate change and environmental pollution. A major concern in the regard is the emission of CO₂ from automobile and industrial. Therefore, one alternative to reduce amounts of CO₂ are recycling and recovering. The CO₂ can be primarily used for production of many kinds, such as formate, formic acid, methanol, dimethyl ether and methane. The attractive route to conversion of CO₂ to chemical feed stock is the hydrogenation of CO₂. In recent year, the effect of catalyst on high activity, selectivity and stability is still increase interest to develop. Studies have been conducted on different metal catalysts for CO₂ hydrogenation including Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt support on several oxides [1], Cu metal base catalysts, which were efficient catalyst to hydrogenation of CO₂ into hydrocarbons. Though Cu was inexpensive and commonly used in industrial. To improve the catalytic activity of Cu catalyst, high specific surface area of metal Cu was necessary [2]. Activated carbon (AC) is widely used as catalysts support due to high surface area and thermal stability. Generally, Carbonious materials exhibits high porosity and high surface area which achieve good dispersion of active metal catalyst. Activated carbon is widely used in drinking water treatment wastewater treatment processes as a filter but also across a wide range of other industries and manufacturing processes The MgO associated metal catalysts could promote the CO₂ hydrogenation [3]. In addition, strong basic oxide which exhibits good affinity for the unoccupied orbitals of the CO₂ molecule are required to activate the stable acidic CO₂ molecule [4]. Several
studies have reported on basicity of transition metal catalyst promote on MgO which enhance the catalytic activity in the CO2 hydrogenation.

In this study, to obtain higher conversion and selectivity of CO2 hydrogenation, the Cu/AC catalysts with difference MgO loading were prepared by sol-gel method. The effect of the content of MgO on CO2 hydrogenation was investigated.

2. EXPERIMENTAL

2.1. Preparation of catalyst

The MgO/AC catalysts were prepared by sol-gel method. The Activated Carbon (AC) was used as a support of catalyst obtained from household carbon water tab filter. Briefly, Mg(C3H7O)2 was dissolved in distilled water under vigorous stirring at 85 °C for 60 min, and then AC was dripped slowly into the solution. Then, the solution was heated at 80 °C under reflux and stirring for 60 min and the mixture aged for 30 min. The precipitate gel was obtained and then dried at 50 °C for 24 hr and calcined at 450 °C for 4 hr. The MgO/AC with a series of various MgO loading were used as support. The Cu/MgO/AC catalyst was prepared via the impregnation method with 10wt% of Cu metal. The Cu(NO3)2.3H2O was deposited on MgO/AC support. The product was aging at room temperature for 12 hr. Then the Cu/MgO/AC catalyst was dried at 50 °C for 24 hr. The series of Cu/AC, Cu/0.25MgO/AC, Cu/0.5MgO/AC, Cu/1.0MgO/AC, Cu/2.0MgO/AC were prepared under the same condition but different amounts of Mg(C3H7O)2 loading.

2.2. Characterization of catalysts

The BET surface area and pore size distributions were measured by low-temperature N2 adsorption at 77 K. The samples were out-gassed at 250 °C under N2 gas for 3 hr at 250 °C. The BET surface areas were investigated by the Brunauer-Emmett-Teller (BET) method. The pore size distributions were calculated from desorption branch of the adsorption isotherm using the Barrett-Joyner-Halenda (BJH) method.

Temperature-program-reduction (TPR) were performed using BELCET-B instrument. Typically, the sample (0.05 g) was first pretreated in a quartz reactor with a Ar gas flow at 200 °C for 120 min and then cooled down to ambient temperature. Subsequently, the sample was heated to 800 °C at a heating rate of 10 °C/min under 5%H2/Ar mixture at 40 ml/min. TCD signals were recorded from room temperature to 800 °C.

CO2-temperature-program-desorption (CO2-TPD) were performed using BELCET-B instrument. Typically, the sample (0.05 g) was first pretreated in a quartz reactor with a He gas flow at 750 °C for 30 min, followed by purging with high-purity He, the adsorption of CO2 was performed in the pure CO2 at 100 °C for 30 min, and the remaining or weakly adsorbed CO2 was purged by high-purity He. TPD was performed in He flow by raising the temperature to 800 °C at a rate of 10 °C/min. The desorbed molecules were detected with a thermal conductivity detector (TCD).

Temperature programmed surface reaction (TPSR) experiment was carried out in a fixed bed reactor. The sample 0.200 g was reduced under H2 gas at 300 °C for 2 hr. Before the TPSR was performed, a flow of CO2 gas was allowed to the catalyst bed at room temperature for 30 min, following by flushing under He flow. TPSR experiment was studied under the condition of H2 flow at 30 ml/min.

Catalytic reaction

The CO2 hydrogenation reaction over the Cu based catalyst was carried out in a fixed bed reactor (1.00 g of catalyst) at 250 °C, H2:CO ratio of 2:1 at a flow rate of 70 mL/min for 5 h. Prior to the reaction, the catalyst was reduced by H2 flowing at 300°C for 3 h. The effluent gas released from the reactor was analysed with online gas chromatographs (Agilent GC 5890). CO, N2, CH4, and CO2 were analysed by thermal conductivity detector (TCD) with a Heyesep Q/molecular sieve packed column. The liquid products collected in ice-bath cold trap were analysed by an off-line GC (Bruker GC-456) with FID using a HP-1 Methyl Siloxane capillary column. The catalysts activity were
investigated under various reaction temperatures (250, 300 and 350 °C), H₂:CO₂ ratio (1:1, 2:1 and 3:1), under atmospheric pressure, to determine the optimum operating condition.

3. RESULT

3.1. Catalyst characterization

The BET results obtained from Cu/AC, Cu/0.25MgO/AC, Cu/0.5MgO/AC, Cu/1.0MgO/AC and Cu/2.0MgO/AC catalyst were summarized in Table 1. The results indicate the difference in surface area, pore volume and average pore diameter of all catalyst. A surface area of 814.12 m²/g is obtained over the AC supporter, and the value of surface area decreases to 251.67 m²/g after CuO was loaded. The general trend was observed that specific surface area and pore volume decreased with the increase of MgO loading. The specific surface area decreased from 164.87 m²/g to 77.15 m²/g, 22.66 m²/g and 10.76 m²/g for Cu/0.25MgO/AC, Cu/0.5MgO/AC, Cu/1.0MgO/AC and Cu/2.0MgO/AC respectively. The blockage of pores occurs mainly due to high MgO loading.

Table 1. Physical properties of all catalysts.

| Catalyst          | Surface area (m²/g) | Pore volume (cm³/g) | Average pore diameter (nm) |
|-------------------|---------------------|---------------------|---------------------------|
| AC                | 814.12              | 0.45                | 2.2                       |
| Cu/AC             | 251.67              | 0.16                | 2.5                       |
| Cu/0.25MgO/AC     | 164.87              | 0.12                | 2.9                       |
| Cu/0.5MgO/AC      | 77.15               | 0.056               | 2.9                       |
| Cu/1.0MgO/AC      | 22.66               | 0.036               | 6.4                       |
| Cu/2.0MgO/AC      | 10.76               | 0.034               | 12.8                      |

The effect of support modification on the reduction behaviour of copper based catalysts was elucidated by a transient experiment using temperature programmed reduction technique and the resulting TPR profiles for each sample are shown in Figure 1. Herein, two distinct reduction peaks were found at 170- 350 and 360- 460 °C for Cu/AC catalyst. This indicates the reduction of CuO catalyst to metallic Cu via two stages, Cu²⁺ → Cu⁺ → Cu⁰. For MgO catalysts including Cu/0.25MgO/AC, Cu/0.5MgO/AC, Cu/1.0MgO/AC and Cu/2.0MgO/AC, there occurred, on the other hand, one broad peak indicating a single-stage reduction of CuO to Cu⁰. [3] [5] This implies that the modification of the support with MgO positively influenced the reduction behaviour of the catalysts as CuO dispersed better on the surface of MgO modified AC as shown in TPSR results. [3] [6]
Figure 1. TPR profiles of Cu/AC, Cu/0.25MgO/AC, Cu/0.5MgO/AC, Cu/1.0MgO/AC and Cu/2.0MgO/AC catalyst.

TPSR profile obtained from the hydrogenation for pre-adsorbed CO$_2$ on Cu/AC, Cu/0.25MgO/AC, Cu/0.5MgO/AC, Cu/1.0MgO/AC and Cu/2.0MgO/AC catalyst. The profile shows that the hydrogenation of pre-adsorbed CO$_2$ leads to methane, which is the main product. Resulting from TPSR summaries in table 2, the amount of methane on different MgO loading decrease in the order of Cu/1.0MgO/AC > Cu/0.5MgO/AC > Cu/2.0MgO/AC > Cu/0.25MgO/AC > Cu/AC. The higher of methane formation could indicate that active Cu metals are well dispersed on AC supporter. It indicates that the introduced alkaline MgO will promote the formation of Cu species with high dispersion [2]. The peak temperature (T$_{max}$) shift to lower temperature in the order of Cu/AC, Cu/0.25MgO/AC, Cu/0.5MgO/AC, Cu/2.0MgO/AC and Cu/1.0MgO/AC, respectively. It is suggested that this increase in the reactivity of catalyst. It could be concluded that the addition of MgO can improved catalytic activity for CO$_2$ hydrogenation.

Table 2. Amount of methane produced over all catalysts obtained from TPSR profiles.

| Catalyst          | Initial temperature (°C) | T$_{max1}$ (°C) | T$_{max2}$ (°C) | Methane formation (µmol/g of catalyst) |
|-------------------|--------------------------|-----------------|-----------------|----------------------------------------|
| Cu/AC             | 275                      | 484             | 590             | 660                                    |
| Cu/0.25MgO/AC     | 258                      | 467             | 590             | 740                                    |
| Cu/0.5MgO/AC      | 246                      | 413             | -               | 1670                                   |
| Cu/1.0MgO/AC      | 213                      | 400             | -               | 2140                                   |
| Cu/2.0MgO/AC      | 220                      | 380             | 570             | 1259                                   |

The basicity of the all catalysts were further studied by CO$_2$ temperature programmed desorption (CO$_2$-TPD). The CO$_2$-TPD profiles of all catalysts show three desorption peaks in the temperature ranges 100-200 °C ($\alpha$), 200-350 °C ($\beta$), and 560-700 °C ($\gamma$) (Figure 2), presumably due to the presence of weak, medium, and strong basicites in the materials [7]. Table 3, demonstrates that the total basicity
of the Cu/1.0MgO/AC catalyst is higher compared all the supported copper catalysts. However, the strength of the basic sites was varied from loading of MgO.

Table 3. Total amount of basic site obtained from CO$_2$-TPD for all catalysts.

| Catalyst      | Weak | Moderate | Strong | Total basicity |
|---------------|------|----------|--------|----------------|
| Cu/AC         | 0.03 | 0.06     | 0.07   | 0.15           |
| Cu/0.25MgO/AC | 0.09 | 0.31     | 0.14   | 0.53           |
| Cu/0.5MgO/AC  | 0.15 | 0.24     | 0.14   | 0.52           |
| Cu/1.0MgO/AC  | 0.32 | 2.16     | 0.38   | 2.86           |
| Cu/2.0MgO/AC  | 0.30 | 1.94     | 0.38   | 2.61           |

Figure 2. CO$_2$-TPD profiles of Cu/AC, Cu/0.25MgO/AC, Cu/0.5MgO/AC, Cu/1.0MgO/AC and Cu/2.0MgO/AC catalyst

3.2. Effect of MgO loading during hydrogenation of CO$_2$.

The surface basicity of the catalyst was investigated (Figure 3). According to the CO$_2$-TPD analysis results. The Lewis acidic CO$_2$ should be adsorbed on MgO basic sites, the amount of CO$_2$ would be correlated with the number of basic sites of catalyst. As far as the desorption of CO$_2$ from Cu/MgO/AC catalysts demonstrates a new desorption CO$_2$ peak at low temperature between 150 - 300 °C with corresponding to weak basicity surface. It could suggest that MgO addition led to increase surface weak basicity sites and directly involved for strong adsorption of CO$_2$ molecule. As propose above, an increase of weak basic site due to MgO addition effected to CO$_2$ conversion in the order of Cu/AC (19.40%) < Cu/0.25MgO/AC (38.74%) < Cu/0.5MgO/AC (46.50%) < Cu/2.0/MgO/AC (47.73%) < Cu/1.0/MgO/AC (58.74%). The result suggested that the weak acid site could be active site for activation of CO$_2$ conversion which is accordance with the result obtain from TPSR. It can be observed that both CO$_2$ conversion and methane formation from TPSR increase with the increasing of MgO loading.
The selectivity for series of basic catalyst are reported in Figure 4 and the corresponding selectivity values, conversion and CH$_3$OH production rate are tabulated in Table 4. The result showed that an increase of catalyst surface basicity was decreased selectivity of CO and then increased methane formation. It was possible due to the concept that adsorption and hydrogenation of CO$_2$ has been described by following two step reactions. First step, CO$_2$ adsorbed onto basic site of catalyst and subsequent converted to CO. Subsequently, direct conversion CO to methane was occurred by reacting with H$_2$ gas. The result showed that MgO increased the surface basicity of catalyst which enhanced the bond strength between CO and the surface of catalyst. The reverse water-gas shift reaction was inhibited that can well promote the methane selectivity.

Table 4. Effect of MgO loading on Cu/AC towards conversion, selectivity and production rate of CH$_3$OH.

| Catalyst       | % CO$_2$ Conversion | % Selectivity | CH$_3$OH (mol s$^{-1}$ g$^{-1}$ catalyst) |
|----------------|---------------------|---------------|------------------------------------------|
| Cu/AC          | 19.4                | 0.27          | 4.26                                     | 95.47                                   |
| Cu/0.25MgO/AC  | 38.75               | 0.17          | 25.03                                    | 74.80                                   |
| Cu/0.5MgO/AC   | 46.50               | 0.12          | 22.76                                    | 77.12                                   |
| Cu/1.0MgO/AC   | 58.74               | 0.08          | 29.27                                    | 70.65                                   |
| Cu/2.0MgO/AC   | 47.73               | 0.31          | 3.35                                     | 96.33                                   |

3.3. Effect of catalyst activity temperature
The effect of different temperature on activity of catalysts was performed at difference temperature including 250, 300 and 350 °C. Further, catalyst was carried on optimize condition at 1 bar under 2:1 mole ratio of H\textsubscript{2}:CO\textsubscript{2}. The CO\textsubscript{2} conversion was shown in Figure 5, which revealed that the CO\textsubscript{2} conversion was achieved under temperature range from 250 to 350 °C. It can be found that CO selectivity increase with the increase of temperature. The data of Table 5 showed that both temperature at 300 and 350 °C lead to 98.46 and 99.95 % selectivity of CO. It is also possible that CO\textsubscript{2} hydrogenation to CO formed via RWGS reaction at high temperature [8] [9].

![Figure 5. Effect of temperature toward conversion and selectivity of Cu/1.0MgO/AC](image)

**Table 5. Effect of Cu/1.0MgO/AC on CO\textsubscript{2} conversion, selectivity and production rate of CH\textsubscript{3}OH.**

| Operating Condition | % CO\textsubscript{2} Conversion | % Selectivity | CH\textsubscript{3}OH | CH\textsubscript{4} | CO | CH\textsubscript{3}OH (mol s\textsuperscript{-1}g\textsuperscript{-1} catalyst) |
|---------------------|--------------------------------|---------------|-----------------|----------------|---|----------------------|
| Temp. (°C)          |                               |               |                 |                |    |                      |
| 250                 | 58.74                         | 0.08          | 29.27           | 70.65          |    | 1.26 \times 10\textsuperscript{-9} |
| 300                 | 60.77                         | 0.06          | 1.48            | 98.46          |    | 1.27 \times 10\textsuperscript{-9} |
| 350                 | 61.77                         | 0.03          | 0.39            | 99.95          |    | 1.26 \times 10\textsuperscript{-9} |
| H\textsubscript{2}:CO\textsubscript{2} ratio |                  |               |                 |                |    |                      |
| 1:1                 | 41.64                         | 0.05          | 0               | 99.95          |    | 1.28 \times 10\textsuperscript{-9} |
| 2:1                 | 60.77                         | 0.06          | 1.48            | 98.45          |    | 1.26 \times 10\textsuperscript{-9} |
| 3:1                 | 83.22                         | 0.04          | 0               | 99.96          |    | 1.27 \times 10\textsuperscript{-9} |

3.4. Effect of H\textsubscript{2}:CO\textsubscript{2} ratio on activity and selectivity of catalysts

The effect of catalyst activity and selectivity over Cu/1.0MgO/AC was carried on optimize condition at 300 °C under 1 bar of H\textsubscript{2} gas with difference H\textsubscript{2}:CO\textsubscript{2} ratio at 1:1, 2:1 and 3:1. The effect of H\textsubscript{2}:CO\textsubscript{2} ratio was shown in Figure 6 and Table 5. It can be found that CO\textsubscript{2} conversion was increased with H\textsubscript{2}:CO\textsubscript{2} ratio. The H\textsubscript{2}:CO\textsubscript{2} ratio at 3:1 showed the highest CO\textsubscript{2} conversion follow by the ratio of 2:1 and 1:1 respectively. It should be due the fact that increase H\textsubscript{2}:CO\textsubscript{2} ratio was favored the reverse water–gas shift (RWGS) [9]. However, it can be clearly found that difference H\textsubscript{2}:CO\textsubscript{2} ratio has no effect on selectivity.
4. Conclusions
In summary, the basicity of the catalyst was increased by addition of MgO. The Cu/1.0MgO/AC exhibited the strongest total basicity. The MgO addition provided surface basicity which increased adsorption of CO2 gas and then inhibited the reverse water gas shift reaction. In addition, the surface basicity increased the methane selectivity. The Cu/1.0MgO/AC catalyst was found to inhibit excellent on RWGS activity and the highest methane selectivity was occurred.

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