An experimental and thermodynamic study for conversion of CO_2 to CO and methane over Cu-K/Al$_2$O$_3$

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ABSTRACT

Catalytic hydrogenation of CO_2 to CO and hydrocarbons is carried out over a wide range of catalysts. Group of VIIIB transition metals proved high conversion and selectively for CO and methane, however, low cost and effective catalysts are preferable especially in large industrial scale. In this work an experimental and thermodynamic analysis was carried out for conversion of CO_2 to CO and methane over K-Cu/Al$_2$O$_3$ catalyst. Wet impregnation technique was employed to introduce different loadings of copper on the surface of K/Al$_2$O$_3$. The obtained catalysts were characterized for their crystalline phase, surface area, and morphology and pore size distribution. XRD and EDXS illustrated the presence of both K and Cu where a maximum loading of 1.62 wt% of Cu was achieved on a catalyst surface having 0.46 wt% potassium. BET analysis showed a slit mesoporous surface with average size of 0.255 cm^3/g and a total surface area of 114.98 m^2/g.

The obtained catalysts were tested for hydrogenation of CO_2 at different reaction conditions and the results of conversion and selectivity were compared with the theoretical values. It was found that at a given molar ratio of H$_2$/CO$_2$(4:1) the increase in reaction temperature from 500 K to 850 K resulted in decreasing both the conversion (from 98% to 64.5%) and selectivity of CH$_4$ (from 100% to 66%). This decrease was noticeable at lower pressure. Further the increase in temperature above 850 K, increased CO_2 conversion and CO selectivity.

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1. Introduction

Emission of carbon dioxide into atmosphere is a major issue faced by industry and economic development. The atmospheric level of CO_2 has risen from 290 ppm (before industrial revolution) to 398 ppm in 2015. This level is expected to be 570 ppm by the end of this century [1,2]. Therefore, several environmental agencies and government regulations were enforced to control CO_2 emission [3].

Many research efforts were made for downstream CO_2 capture and sequestration [2]. The most feasible treatment methods are membrane technology, absorption and adsorption. In addition, carbon dioxide fixation can be attained by utilizing several bacteria [4] and algae [5]. The limitation of some of these methods is associated with their cost, production of unwanted waste, suitability and selectivity [3].

CO_2 can also be converted to valuable products by means of photocatalysis [6,7], electrocatalysis [8,9] and thermalcatalysis [10–14]. Among these conversion methods, thermalcatalytic process can be feasible in reduction of CO_2 from mobile source with less modification. Different catalysts have already been cited for thermal conversion of CO_2 to CO, methane and higher hydrocarbon products. These catalysts include: Fe, K, Mn, Sr, Ni, Co, Cu, Zr, Pt, Ru, and Rh over Al$_2$O$_3$, γ-Al$_2$O$_3$, SiO$_2$, Al$_2$O$_3$:MgO, CeO$_2$, ZrO$_2$ and Zeolite support [2,10,15–41]. The choice of these catalysts and supports define the type of products, selectivity and conversion on a defined range of operating conditions. Over these catalysts, monometallic (Ru/Al$_2$O$_3$, Ni/Al$_2$O$_3$) and bimetallic (Pd-Mg, Pd-Ni and Pd-Li) on the surface of silica showed high CO_2 conversion (ca. 42∼59%) with 88-95% selectivity to methane obtained at 450 °C [12,42,43]. However, the high reaction temperature and cost of the catalyst encouraged many researchers

to develop a cost effective catalyst that can be used at lower temperature.

Transition elements such as Mn, Fe, Co, Ni showed similar performance but at lower reaction temperature [33,44]. Copper-based catalyst demonstrated a high conversion of CO_2 to carbon monoxide over SiO_2 support. The conversion mechanism was controlled by adsorption of dissociated CO_2 over the catalyst support to yield format and carbonate [45]. Then these intermediate species readily decompose to form CO, while hydrogen acts as reducing agent for oxidized copper. This formation of CO on Cu-based catalyst is related to its weak interaction with adsorbed hydrogen as it is readily desorbed from the surface of the catalyst [46]. This weak adsorption of CO with copper surface was also investigated by Onsgaard et al. (2006) [47] where they found that presence of potassium has decreased its desorption rate from the K-Cu surface [47]. Baussart et al. (1987) [48] stated that a competition between the electron-donor nature of potassium and copper controlled the adsorption of CO and increases its conversion to methane [48].

On the other hand, Cu-based catalyst demonstrated low thermal stability at high temperature that prevents its activity for conversion of CO_2 to methane. Therefore, addition of thermal promoter such as Fe or K on Cu/SiO_2, can enhance its thermal stability, increase its surface area and thus increase its activity [49]. Furthermore, there is a linear relation between the activity of Cu-based catalyst and its surface area, where the addition of alkali promoterscreates new active sites located at the interface between the Cu and the metal [50].

Despite that, much effort has been made for studying the interaction of bimetallic catalysts for conversion of CO_2 to CO and methane; still there is a room for investigation, the interaction of alkali metals with Cu on Al_2O_3 catalyst for hydrogenation of CO_2. Thermodynamic analysis can be used for determination of equilibrium conversion of CO_2 to CO and methane over Cu-K/Al_2O_3 catalyst.

This work aims at studying the experimental and theoretical interpretations of hydrogenation of CO_2 over Cu-K/Al_2O_3. Effect of reaction conditions such as reactor temperature and pressure, and molar ratio of H_2/CO_2 using Gibbs free energy minimization will be studied and optimized.

2. Material and Methods

2.1. Materials

GammaAl$_2$O$_3$ was purchased from Honeywell Riedel-deHaën and used as a support for synthesized catalysts. KNO_3 and Cu $(NO_3)_2.3H_2O$ were brought from Panreac with purity of 98% for both salts and utilized as a source for K and Cu catalysts. All the chemicals were utilized without further purification.

2.2. Synthesis and Characterization of Catalyst

All catalyst samples were prepared using wet impregnation method. In a typical run, 2.6 g of potassium nitrate and 1.91 g of copper nitrate trihydrate were mixed in 100 ml distilled water to obtain 0.25 and 0.08 mol/L of K^+ and Cu^{+2} respectively. To this solution alumina powder (8.5 g) was added and mixed thoroughly for 30 min and was allowed to equilibrium for 24 h. The impregnated Cu-K/Al_2O_3 catalyst was filtered after 24 h and aged at 110 °C with ramp of 16 °C/min for 8 hr. Then the catalyst was calcinated at 550 °C for 6 h with a ramp of 5 °C/min in the open air atmosphere. The calcinated catalyst was then stored in closed-cap container for further use. This procedure was repeated to obtain the other catalysts having different loading of Cu (1, 1.25 and 1.62 wt%).

The prepared catalyst was characterized by using x-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy-dispersive X-Ray spectroscopy (EDXS) techniques to check its crystalline phase, surface morphology and the presence of impregnated metals. XRD was conducted using Phillips diffraction Unit (Model PW 1140/90), operated with monochromatic Cu-Kα radiation source at 50 mA and 40 kV. Scanning speed was set at 4° 2θ min^{-1} with a step size of 0.1° in the range of 10−80° 2θ.

SEM imaging was obtained using JEOL JSM-5600. Particles first carbon glued and gold coated under vacuum for 60 sec. The analysis conditions were set at an accelerating voltage of 15 KV, a beam current of 1 nA and a Si (Li) detector located at 10 nm from the sample. X-ray detection limit was set at 0.1%. The amount of copper and potassium impregnated into the alumina was determined by using Energy-dispersive X-Ray spectroscopy (OXFORD INCAx-SIGHT) at 137eVand a resolution of 5.9 KeV. Surface area and pore size distribution were obtained using ASAP 2020 Micrometritics. Samples of ca. 0.35 g were first degassed at 250 °C, followed by N_2 adsorption-desorption at 77 K.
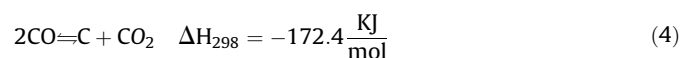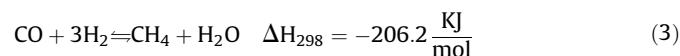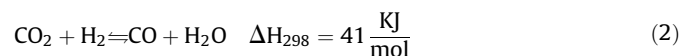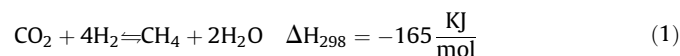
2.3. Catalytic Conversion

A packed bed reactor was used for conversion of carbon dioxide as shown in Fig. 1. A stainless steel reaction column with 3 mm ID and 22.7 cm length was placed in a tubular muffle furnace and connected with a pressure regulators and flow meters at both the ends. The column filled with 2 g of Cu-K/Al_2O_3 was connected with H_2/CO_2 cylinders through 2 mm stainless steel tubes, while the outlet of the reactor was connected to online GC-MS having FID connected with HP-PLOT/Q column, TCD connected with two column (SUPELCO Analytical 12% UCW-98, SUPELCO 80/100 HAYESEPQ) and MS connected with DB-624 column.

Prior to reaction, the catalyst was reduced by H_2 at flow rate of 50 ml/min and a temperature of 400 °C for 6 h with a heating rate of 4 °C/min. Then, mixture of H_2 and CO_2 gases with different molar feed ratios of 4:1 and 2:1 was introduced individually at outlet flow rate of 10 ml/min, GHSV of 1400 h^{-1} and a pressure of 7 bar. The reaction temperature was fixed at 230 °C, 400 °C, and 600 °C by using PID controller. The conversion of the CO_2 was measured by using GC-MS.

2.4. Thermodynamic analysis

Thermodynamic analysis was conducted to predict the maximum theoretical conversion of CO_2 and the selectivity of the expected products based on minimum Gibbs free energy[51]. Hence, all the expected main products are included to get the real composition profile of the process. The major species present during the hydrogenation of CO_2 are H_2, CO_2, CO, C, CH_4 and H_2O. The main proposed reactions during hydrogenation of carbon dioxide are summarized by[52].

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H_{298} = -165\frac{KJ}{mol} \tag{1}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H_{298} = 41\frac{KJ}{mol} \tag{2}$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad \Delta H_{298} = -206.2\frac{KJ}{mol} \tag{3}$$

$$2CO \rightleftharpoons C + CO_2 \quad \Delta H_{298} = -172.4\frac{KJ}{mol} \tag{4}$$