CHAPTER I

INTRODUCTION

Carbon dioxide (CO_2) is a greenhouse gas that occurs naturally in the atmosphere. Human activities are increasing the concentration of CO_2 in the atmosphere, thus contributing to Earth global warming. This is an important and urgent problem causing acid rain and the lost of oxygen-carrying molecule in the red blodd cell. CO_2 is emitted when fuel is burnt. It can be also emitted by some other industrial processes. In contrast, chemical CO_2 fixation has become of greater interest in recent years, primarily because of its impact on the environment through the greenhouse gases appeared to warm up the atmosphere [Riedel et al., 1999]. In addition, catalytic hydrogenation of CO_2 has been considered as one of the chemical fixation and recycling technologies for emitted CO_2 [Kusuma et al., 2001]. The current interest in CO_2 hydrogenation (Fischer-Tropsch synthesis) has been extensively studied for years [Suzuki et al., 1993; Saib et al., 2002; Dagle et al., 2007; Panagiotopoulou et al., 2008].

Considering the mechanism of CO_2 hydrogenation Fischer-Tropsch synthesis, the general view is a first RWGS reaction as follow;

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H^\circ = 41.1\ kJ/mol$$

to produce CO which is subsequently consumed in the FT conversion as;

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H^\circ = -206\ kJ/mol$$

However, the additional reaction of a direct CO_2 hydrogenation occurs as;

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H^\circ = -165\ kJ/mol$$

In general, the catalyst properties depend on reaction conditions, catalyst compositions, metal dispersion, and types of inorganic supports used. Cobalt catalysts represent the optimal choice for low temperature, because of higher stability, higher conversion and relatively small negative effect of water on conversion [Khodakov, 2009], preferring for synthesis of high molecular weight paraffins [Dry, 2002; Chu et al., 2007], and lower price compared to those of nobal metal. Furthermore, the

research has emphasized that the supports, such as Al_2O_3, SiO_2, and TiO_2 can significantly enhance the activity, selectivity and catalytic properties as well [Storsaeter et al., 2005]. SiO_2 has been considered to be very attractive because of high surface area, thermal stability and improving the reduction degree of supported cobalt [Khodakov et al., 1997; Backman et al., 1998]. Moreover, Al_2O_3 is one of the most supports for cobalt catalyst because of its favorable mechanical properties and adjustable surface properties. In addition, it significantly improved the catalytic activity of FTS by increasing the dispersion [Zhang et al., 2006]. Furthermore, the effect of SiO_2 modification to Co/Al_2O_3 catalyst was widely studied by improving the properties of the supports and supported cobalt. In reversible, alumina-doped silica was also investigated [Marie et al., 2009; Sun et al., 2010].

The main objective of this present study was to investigate the catalytic behaviors of carbon dioxide hydrogenation over alumina-silica composites-supported cobalt catalyst. The composites supports and catalysts were prepared and characterized by several techniques, such as XRD, BET, DTA/TG, SEM/EDX, TEM, TPR, and CO chemisorptions methods, and then tested for CO_2 hydrogenation reaction in order to mesure activity and selectivity under methanation condition.

Motivation

The Al_2O_3-SiO_2 composites supports can exhibit the novel properties that are not finding in a single oxide support. With combination, the benefit of Al_2O_3 support provided the mechanical properties and adjustable surface properties. In addition, it significantly improved the catalytic activity of FTS by increasing the dispersion and SiO_2 has a sufficiently high surface area, thermal stability and improving the reduction degree of supported cobalt. In this work, I intended to improve activity and selectivity of the cobalt based Al_2O_3-SiO_2 composites catalyst over CO_2 hydrogenation.

Objective

This research objective was to investigate the effect of different Al_2O_3-SiO_2 composites supports on their characteristics by varying composition between Al_2O_3 and SiO_2. Cobalt supported on Al_2O-SiO_2 composites catalysts for CO_2 hydrogenation was further investigated with regard to activity and selectivity.

Research scopes

- Preparation of submicrosphere silica support.

- Characterization of silica support samples by BET surface area X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscope (TEM).

- Preparation of Al_2O_3-SiO_2 composites supports with 25 to 75 wt% of Al_2O_3 on the composites support using hydrolysis of aluminium isopropoxide method.

- Characterization of Al_2O_3-SiO_2 composites supports by BET surface area, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscope (TEM), and differential thermal analysis and thermogravimetric (DTA/TG).

- Preparation of supported Co catalyst on the Al_2O_3-SiO_2 composites supports, which were calcined at 500 to 1000°C, using the incipient wetness impregnation method.

- Characterization of the catalyst samples using BET surface area, X-ray diffraction (XRD), CO chemisorptions, temperature programmed reduction (TPR), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) and transmission electron microscope (TEM).

- Investigation of the catalytic activity of Co/ Al_2O_3-SiO_2 catalyst in the hydrogenation of carbon dioxide (CO_2) at 220°C and 1 atm and a H_2/CO_2 ratio of 10 under methanation condition.

Benefits

- Develop the cobalt base Al_2O_3-SiO composites catalyst for CO_2 hydrogenation.
- Enhance CO_2 fixation system.
- Produce research article based on the results obtained.