CHAPTER 1

INTRODUCTION

1.1 Background

Syngas (synthesis gas) or also known as town gas, is made up of hydrogen (H_2) and carbon monoxide (CO). It is a vital feedstock for downstream petrochemical industries. Syngas is the final product of gasification (steam reforming) and is also used as an intermediate compound for the final synthesis of natural gas, ammonia, methanol, and petroleum fuel (Maher, 2010). Due to this, the production of syngas has opened up a wide variety of research opportunities in energy sectors.

Significantly, the massive emissions of carbon dioxide (CO_2) arising from the burning of fossil fuels and subsequently the climate change has become serious environmental issues in recent years. Electricity generation, transportation, agriculture, industrial and residential are the main contributors to the foremost greenhouse gas CO_2 emission. In addition, methane (CH_4) is the second most widespread greenhouse gas released from human activities. Methane is released from natural sources such as wetlands as well as anthropogenic activities such as leakage from natural gas systems and the raising of livestock, i.e. cow rearing industry. The lifetime of methane in the atmosphere is much shorter than carbon dioxide (CO_2). However, CH_4 is more active in trapping radiation than CO_2. Pound for pound, the relative influence of CH_4 on climate change is more than 25 times greater than CO_2 over a 100-year period time (U.S. EPA, 2010). As a consequence, global CH_4 and CO_2 emissions must be greatly reduced in order to mitigate its negative effects. One of the most promising processes to utilize both the greenhouse gases to produce syngas is via dry (CO_2) reforming of methane (DRM) (Xu & Gao, 1999).

Indeed, catalysts play a vital role in speeding up chemical reactions. Catalyst is usually comprised of active metal and support. Generally, transition metals such as Ni and Co have been widely used as catalysts. These catalysts are cheaper and available compared to noble metal based catalysts, hence promoting DRM reaction to be more viable in industrial research. From

previous studies and reviews, Ni-based catalysts have been widely used as they are more effective and promote high catalytic activity and conversion for methane reforming reactions. However, Ni-based catalysts have severe carbon deposition, thus causing catalyst deactivation (Ashok & Kawi, 2013). Therefore, many studies have been researched to improve high catalytic performance and also carbon suppression in DRM. Generally, perovskite-type oxide (ABO_3) is preferred as a catalyst precursor for DRM as it can deactivate carbon deposition, unlike Ni-supported catalysts (Maneerung *et al.,* 2011). In this structure, an A-site ion is generally an alkaline earth metal or rare earth element while B site ions could be transition metal elements. In addition, the partial substitution of the A-site by foreign cations refines structure defects by changing their oxidation state to improve anionic and cationic vacancies. As a result, perovskite-type oxide with the partial substitution of the A-site allows good electronic and ionic conductivity at high temperatures (Meyers *et al.,* 2013). Moreover, the partial substitution of the B-site improves the structural stability and activity in methane reforming reactions. As an outcome, the partial substitution of A and B sites enhances the catalytic performance of perovskite by slightly changing the structure (Sutthiumporn *et al.,* 2012).

1.2 Problem Statement and Motivation

In recent years, utilization of CO_2 and CH_4, which are both greenhouse gases, has been in the focus due to the global warming and irreversible climate change in accordance to environmental and energy concerns. It is well known that both CH_4 and CO_2 are noxious gases and harmful to the environment. Therefore, there is an effort to utilize CO_2 and CH_4 by converting them into useful products such as syngas via methane dry reforming pathway. Nickel (Ni) based catalysts are prone to carbon deposition, thus leading to catalyst deactivation although it is one of the most effective catalysts in methane reforming reaction (Ashok & Kawi, 2013). Therefore, the perovskite-type oxide (ABO_3) has been widely used as a catalyst precursor for DRM as it has been reported to enhance catalytic performance, improve structural stability and suppress coke formation. It has been found that previous catalytic researches are mostly limited to nickel-lanthanum based perovskite oxides. In fact, cobalt (Co) based catalysts have higher carbon resistance compared to the nickel catalysts even though they are slightly more expensive than the Ni (Francisco *et al.,* 2012). An effective way of improving the catalytic performance in dry

methane reforming reaction is by using Co based perovskite oxides. Moreover, it is motivating to explore the possibility of using alkaline earth metals such as strontium as the A-site ion instead of using rare earth elements in this study.

1.3 Objective

To study on the synthesis and characterization of $SrCo_{0.8}M_{0.2}O_{3-\delta}$ perovskite-type oxides where M is Fe or Cu, for methane dry reforming kinetic study.

1.4 Scopes

In order to achieve the outlined objective of this study, the following scopes have been identified:

i) Catalysts Preparation:
    $SrCo_{0.8}M_{0.2}O_{3-\delta}$ perovskite-type oxides where M = Fe and Cu were synthesized via a citrate sol-gel method.

ii) Catalyst Characterization:
    The methods applied in this study were N_2 physisorption, XRD, SEM-EDX and FT-IR. BET method was employed in N_2 physisorption to find out the specific surface area and BJH method for pore size distribution in the solid samples. The crystalline structure and the size of crystallite diameter of the catalysts were determined via XRD. To study surface morphology, the image of fresh catalyst and the coke deposit structure of the used catalysts were captured via SEM while EDX was applied to obtain the elemental composition contained in the sample. Lastly, FT-IR was employed to determine the functional groups present on the catalyst surface.

iii) Catalyst Reaction:
    CO_2 to CH_4 molar ratio was set at unity and reaction temperature was set at 1023 K under the atmospheric pressure in order to study the kinetics of methane dry reforming.