

CHAPTER I

INTRODUCTION

Methane, the principal component of natural gas, has been mainly utilized as an important fuel in power generation plants, industry, or households for a long time. Instead, for the past thirty years, utilization of methane has increased, as a well-known gas-to-liquids (GTL) technology has emerged to be a commercially feasible industry (Wood et al., 2012). Methane utilization has been widely developed into a major research area in this period.

Generally, methane is first converted into the synthesis gas (CO and H₂) by several different methods including steam methane reforming (SMR), autothermal reforming (ATR), catalytic partial oxidation (CPO) (Smet, 2000; Wood et al., 2012), carbon dioxide reforming (dry reforming) or simultaneous carbon dioxide and steam reforming (Choudhary et al., 1996; Demidov et al., 2011), and, recently, the solar thermal reforming (Agrafiotis et al., 2014; Wikipedia, 2014). Synthesis gas is the versatile intermediate that can be used in many manufacturing processes such as liquid fuels and high quality wax production (via the Fischer-Tropsch synthesis process), dimethyl ether (DME) production, methanol production, ammonia production, and other chemical production.

In addition to the two-step process mentioned above, various one-step processes to convert methane into higher valuable chemicals have also been proposed and investigated, for instance, gas to methanol (GTM) (De Klerk, 2012; Wood et al., 2012), gas to di-methy-ether (DME) (Fleisch et al., 2012; Wood et al., 2012), gas to olefins (GTO), and gas to gasoline (GTG) (Hamilton, 2008; Wood et al., 2012). This makes methane recognized as being more precious than ever and methane as a feedstock for the chemical industry is currently attractive and will be important in the future. This is as a result of limited supplies of liquid-petroleum based hydrocarbons and more stringent environmental legislation. Therefore, it is important to carry out research in this field aimed at either improving current technology or generating new ways of utilizing methane. Work in this thesis focused on two aspects of methane utilization. First, methylation of benzene with methane, where methane directly reacts with benzene, with the aim of producing xylenes.

Second, gas-to-liquids (GTL) focusing on Fischer-Tropsch synthesis (FTS), the core step of GTL, was studied with the target to improve Co-based FTS catalyst performance.

In the aromatics complex process, benzene, toluene, and xylenes are the major products. For the last decade, the petrochemical industry has been drastically developed throughout the world, thereby making the demand and price of xylenes, especially *p*-xylene, increased significantly. The methylation of benzene to make xylenes by using methane as an alkylating agent is attractive. This benefits not only the prices of benzene and methane, but also the product flexibility of an aromatics complex plant.

It is well-known that methane is very thermodynamically stable and has very low reactivity; therefore, the reaction of methane with benzene is extremely difficult to activate and selectively transform to more valuable chemicals such as xylenes. Nonetheless, the fact that catalysts can accelerate the rates of reaction along with providing desirable product selectivity, by controlling the relative rates of pathways, is considered for this challenge. Therefore, many efforts have been devoted to finding a suitable catalyst for methylation of benzene with methane. In fact, with the old technologies, the alkylation of aromatics with light alkane can be achieved by often using strong mineral acids or Lewis acids (e.g., HF, H₂SO₄, AlCl₃), the so-called Friedel-Crafts catalysts (Olah et al., 2003; Perego et al., 2009). Although they are very active and require less energy consumption, some serious drawbacks, such as the fact that highly toxic and corrosive, cause them to be unattractive. With respect to worldwide environmental awareness, the environmentally-friendly solid acids catalysts as a substitute for Friedel Crafts catalyst have received much more attention (Perego et al., 2009).

So far, the methylation of benzene with methane has been conducted using ZSM-5 zeolite based catalyst. The first achievement was report by He and co-workers in 1995, in which several types of zeolites were used (He et al., 1995). Later, Adebajo and co-worker first suggested that oxygen is required for accelerating the reaction and this reaction is the so-called oxidative methylation (Adebajo et al., 2000). Accordingly, the reaction route can be classified in 2 ways, which are non-oxidative methylation (Baba et al., 2002; He et al., 1995) and oxidative methylation

(Adebajo et al., 2000). However, the latter is less significant due to an emission of CO and CO₂ by-products and a difficult-to-operate process. The present thesis therefore focuses on a non-oxidative methylation route using metal loaded HZSM-5 catalysts.

Gas-to-liquids (GTL) technology generally consists of three principal processes, which are (1) the methane reforming process, converting methane into synthesis gas (CO and H₂) by various processes mentioned previously, (2) Fischer-Tropsch synthesis, processing the synthesis gas to create a mixture of naphtha, synthetic fuels, as well as heavy paraffinic wax, and (3) product refining, upgrading the synthetic fuels into finished products (e.g., diesel, motor gasoline, jet fuels, lubricants, waxes, and other high-quality FT products, with ultralow sulfur content and low aromatics content), respectively (ESP, 2014). The Fischer-Tropsch process is the heart of this technology, in which gas-to-liquids is realized. It was invented in Germany prior to the Second World War and has been developed and deployed at a commercial scale until the present. In particular, for the past three decades, this process has received much more attention, as a result of increasingly more rare crude oil reserves and more stringent environmental regulations.

The heart of the Fischer-Tropsch process is the catalyst. Co-based catalysts are effective and now being used at the commercial scale. However, research is still continuously conducted to address specific issues and, in turn, to improve performance (e.g., activity, selectivity, and stability). For example, to improve the activity of the Co/Al₂O₃ FT catalyst, the most popular one, adding reduction promoters is necessary because a strong interaction between Co and Al₂O₃ support make Co difficult to be reduced into metallic Co, the surface of which provides active sites (Guczi et al., 2002; Jacobs et al., 2002).

This work investigates reduction promoters for the Co/Al₂O₃ FT catalyst. Various metals, including Pt, Ru, Ag, Au, Rh, Ir, were utilized to study their promotion capability after regeneration cycles. Moreover, the local atomic structure of some metal-promoted Co/Al₂O₃ catalysts was also explored using the EXAFS technique. Besides a strong interaction issue, the size of Co is also a matter for the catalyst performance, especially from the standpoint of stability. It has been observed by XANES that net reduction of cobalt catalyst occurs during the initial decay period

prior to leveling off, and EXAFS spectra that suggest a complex sintering mechanism, involving agglomeration of cobalt oxides, re-reduction, and sintering of the metal, based on increased Co-Co metallic coordination (Das et al., 2003; Jacobs et al., 2006; Moodley et al., 2011; Saib et al., 2006). Nevertheless, the observation by XANES found that a fraction of cobalt in spent samples is due to a cobalt support compound not present at such concentrations in the freshly activated catalyst. The question remains as to the original source of this species. Therefore, the present work aims to investigate that whether small Co^0 crystallites undergo re-oxidation (Van Steen et al., 2005) at the onset of reaction to CoO and become a source of CoO, in addition to unreduced CoO left from activation.