

CHAPTER I

INTRODUCTION

Nowadays, the conversion and utilization of methane, a major component of natural gas, becomes an interesting topic due to its availability, economical price, environmental friendly, and etc. However, due to highly thermodynamic stability of methane it is quite difficult to directly convert methane into chemicals or synthetic fuels. Therefore, an indirect conversion of methane to desired products through more reactive chemical intermediate seems most possible.

Methane activation by halogen free radical reaction is one of the most extensively studied methane functionalization pathways. This method involves extracting hydrogen from methane molecule and producing methyl halide under relatively mild condition, then the catalytic methyl halide to achieve the production of higher hydrocarbon or oxygenates. The accomplishment of methane activation by halogen depends on the ability to synthesize monohalomethane with highest selectivity against polyhalomethanes.

Halogenation of alkane, particularly methane, has been intensively studied in the past by Weissman *et al.* (1984). The process required the use of chlorine as a catalyst, but the corrosive of substances, hydrochloric acid, was the drawback in commercialization. Therefore, bromine stands out as being the best halogen with slightly exothermic. Zhou *et al.* (2003) developed an integrated multi-step process using solid metal bromides/oxides as mediators via bromination and recovery step. The significant formation of polybromomethanes obstructs the high selectivity of methyl bromide. By adding small amount of iodine could be improved the conversion of methane and methyl bromide selectivity (Ding *et al.*, 2013). Nevertheless, the barriers of these processes were unfavourable selectivity to monosubstituted alkyl bromide dominated by free-radical reaction occurring in the gas phase, the large quantity of bromine is hazardous oxidant, and regeneration of step is not easy.

Another halogenation approach is the oxidative bromination of methane (OBM) by using HBr/H₂O and O₂ instead of bromine. Compared to the existing processes; steam reforming and partial oxidation of methane to produce synthesis gas, (CO & H₂), OBM process has more advantages, for instance producing a more

reactive methyl bromide intermediate, less energy consumption, and less greenhouse gases emission.

Many literatures verify that the OBM reaction could be the effective way to convert methane to valued products, for example, acetic acid (Wang *et al.*, 2005, Wang *et al.*, 2006), dimethyl ether (Xu *et al.*, 2005, You *et al.*, 2009), and higher hydrocarbon (Liu *et al.*, 2007). Additionally, some researchers focused on the role of catalyst in the OBM reaction. Yang *et al.* (2008) used Rh/SiO₂ as a catalyst and studied the reaction pathways in order to achieve in high selectivity of methyl bromide. An inexpensive catalysts was also investigated by replacing noble catalysts with a series of non-noble catalyst (Lin *et al.*, 2009) or FePO₄/SiO₂ (Lin *et al.*, 2010). However, noble catalysts (Ru/SiO₂, Rh/SiO₂) still provide the excellent performance in terms of high methyl bromide selectivity.

The purpose of this work is to investigate the activity of Rh/SiO₂ catalysts for the oxidative bromination of methane and the appropriate conditions in order to obtain high yield of methyl bromide, which could be used as alkylating agent for methylation reaction.