CHAPTER I

INTRODUCTION

Technology of conversion of methane, a major component of natural gas, to other useful chemicals and fuels has been an important issue that attracts interest from many researchers. Although the production of methane rises progressively in each year, only a small fraction of methane (approximately 7%) is converted to useful chemicals. Most of methane is used for heating and power generation purposes. Around 4% is flared and vented directly to atmosphere, thereby accounting for loss of natural resources and increase of pollutant emissions.

There are two routes of methane conversion to other chemicals; i.e. indirect and direct routes. In the indirect method, methane is initially converted to synthesis gas which then reacts further to produce other chemicals such as C_1-compounds (methanol and formaldehyde) and C_2-compounds (ethane and ethene). This method is currently employed in commercial production. The direct route, on the other hand, is able to produce a desired chemical in one step, bypassing the step of the synthesis gas production that is an energy-intensive step. The direct method as a promising route for future production is still under research and development.

The oxidative coupling of methane for production of C_2-compounds, abbreviated OCM thereafter, was proposed firstly by Keller and Bhasin in 1982. Although developments on designs of both catalysts and reactor configurations have been carried out throughout the world, the commercialization of the conventional OCM process is limited by enormous problems. A serious obstacle is hot-spot temperature since the highly exothermic OCM reaction requires high temperature operation (above 973 K). In addition, because of the explosion limit of oxygen concentrations in the feed, the extent of the reaction is restricted. As a result, the application of membrane process to the OCM reaction is a good remedy. In a membrane reactor, oxygen supplied to react with methane can be evenly controlled so that the heat generated by the reaction can be very much more flat across the reactor. Moreover, oxygen and methane are separated from each other and, therefore, oxygen concentration in feed is not restricted.

Consequently, high methane conversion can be accomplished and the separation of oxygen usually from air is not essential.

The membrane reactor for the OCM can be categorized according to types of oxygen transport through a membrane into oxygen molecule transport, oxygen lattice diffusion, and oxygen ion conduction. The corresponding membranes are porous membrane, dense metal and metal oxide membrane, and dense oxygen ionic conducting solid oxide electrolyte membrane, respectively. In many researches, it was found that the first two membranes showed low C_2-yield because oxygen molecules transfer through the porous membrane unselectively and oxygen lattices diffuse through dense membrane very slowly when using air as an oxygen source. Membrane reactor using a solid oxide electrolyte membrane has been, therefore, received much attention. It is due to the membrane in this reactor permits oxygen supplied to react with methane in an ionic state that is suitable to formation of C_2-compounds. In addition, this membrane reactor makes it possible to operate the reaction in the manner of both fuel cell and oxygen pump. This reactor is named a solid oxide fuel cell reactor, abbreviated SOFC thereafter, when it is operated as a fuel cell. This reactor is regarded as a chemical-energy co-generation system as the C_2-hydrocarbon and electricity are generated simultaneously. The hot-spot problem is alleviated as energy is converted to useful electrical energy. Furthermore, it was found that the emission of pollutants, NOx and COx, from the SOFC reactor was very low.

The main components of the SOFC reactor are solid oxide electrolyte, anode electrode, cathode electrode and external circuit. The solid oxide electrolyte as a selective membrane acts as a barrier between anode and cathode chambers. It should posses high ionic conductivity. On the cathode side, oxygen usually from air is activated by electrons from an external circuit and becomes an ionic form. Then, oxygen ions move through the solid oxide electrolyte to the anode side where oxygen ions react with methane to form C_2-compound products. Electrons from the reaction move out from the anode side to the cathode side via the external circuit.

Nevertheless, at the present time the SOFC reactor has offered yield insufficiently high to be commercialized. It is particularly due to low C_2-hydrocarbon formation and the electric current. Consequently, developments of anode catalyst and solid oxide electrolyte are essential for the SOFC reactor.

A number of issues need to be taken into account for selection of an anode catalyst. Under the severe operation of a SOFC reactor, the anode catalyst should be able to resist both thermal and chemical conditions- it must have high melting point and stability to active gases such as methane and carbon dioxide.

From many experiments, it was found that among the OCM catalysts, a catalyst containing a rare earth metal or a transition metal showed the best C_2-yield, it was normally concluded to be due to their high basic characteristics. However, the pure rare earth oxide or transition oxide was insufficiently active, therefore there was a development of the catalyst by adding an alkali earth oxide or an alkali oxide to the rare earth oxide, and the C_2 yield was improved markedly. However, it was found that the promoter action was declined due to formation of stable carbonates or hydroxides (Tsai *et al.*, 1999; Yide *et al.*, 1997). Besides the alkali earth and alkali promoter, the fluoride containing catalyst was able to improve the C_2 yield due to ability to prevent CO_2 poisoning (Wan *et al.*, 1999), nevertheless, the fluoride content was unstable at high temperature condition. Furthermore, the rare earth oxide promoted by aluminum, La-Al-O catalyst, was investigated; it was found to be active and stable under high temperature condition (Tagawa *et al.*, 1998).

This research is aimed to study the application of the SOFC reactor to the oxidative coupling of methane for simultaneous generation of useful chemicals and electric power. It is particularly focused on the development of an anode catalyst of a rare earth oxide, Sm_2O_3, containing Al as a promoter for the SOFC reactor.