

## CHAPTER I

### INTRODUCTION

Direct oxidation of alkanes and aromatic compounds is an important process in petrochemical industry. The partial oxidation reaction can be carried out in either gaseous or liquid phase depended on the thermal stability of the product formed. Usually, the gas phase oxidation is more preferred since the process has lower hydrocarbon inventory than the liquid phase oxidation.

Examples of gas phase oxidation process are the oxidation of o-xylene to phthalic anhydride and benzene to maleic anhydride. In both processes, the aromatic reactants are vapourised and mixed with air in gaseous phase. The concentration of the aromatics is limited by the lower explosive limits of the gas mixture. The gas mixture then flows to a reactor containing several thousands of catalyst tubes. The products formed, the anhydrides, are recovered by cooling the product gas stream using a condenser.

At the condenser, it is known that the lower coolant temperature, the higher product recovery. In practice, the temperature at the condenser is limited by the concentration of water in the product gas stream. If water is allowed to condense, corrosion will occur. The effluent gas leaving the condenser, therefore, still contains traces of organic compounds including the hydrocarbon reactant and the anhydride product.

Eliminating the remaining organic compounds from the effluent gas is necessary. At present, the removal can be carried out by sending the effluent gas, which still contains high oxygen concentration to a furnace or a boiler. This method, however, may cause problem concerning the energy balance of the plant and  $\text{NO}_x$  forming from high temperature combustion. Catalytic combustion is an alternative. There are two catalyst families which can completely oxidise organic compounds. One is the Pt-based catalysts and the other one is the acidic oxide based catalysts.

The Pt-based catalysts can initiate the combustion of the organic compounds at a lower temperature than the acidic metal oxide-based catalysts, typically 100-200°C lower. But the Pt-based catalysts can not withstand prolong operation in a high oxygen concentration atmosphere. The acidic metal oxide-based catalysts work better in the latter case.

An important nature of the acidic metal oxide catalyst is its capability to adsorb acidic organic compounds. On the acidic surface, the acidic organic compounds is less likely to be adsorbed. The further oxidation of the acidic compound to combustion products, therefore, is low. Because of this reason, the acidic metal oxide catalyst becomes a selective oxidation catalyst for the production of anhydrides because it has low ability to further oxidise the anhydrides product formed. On the contrary, this behaviour causes problem when one has to use it as a combustion catalyst.

In order to overcome the aforementioned problem, we propose to dope a basic metal oxide compound to an acidic metal oxide catalyst to enhance the adsorption of the acidic organic compounds. However, the consideration of basic metal oxide is an important. Too strong basic metal oxide cause the catalyst adsorb carbon dioxide leading to carbonate compound formed which deactivated the catalyst. But too weak basic metal oxide led to insufficient ability to adsorb organic acid of the catalyst.

Cobalt oxide is an interesting material in the fields of heterogeneous catalysis. Among the transition metal oxide  $\text{Co}_3\text{O}_4$  shows the highest catalytic activity for the combustion of organic compounds, CO, diesel soot, NO, and ammonia. In addition, it is also active for hydrogenation and hydrodesulphurization reaction [Busca *et al.* (1990)].

MgO is a suitable basic metal oxide because it is not too strong basic metal oxide until adsorb carbon dioxide to form carbonate compound. But it is strong enough to adsorb organic acids [Kanokrattana (1997), Ali *et al.* (2000)].

It has been shown recently that Co-Mg-O catalyst can selectively oxidise C2-C3 alcohols to aldehydes and combustion products. No carboxylic compound is observed [Youngwanishate (1998), Kittikerdkulchai (1999)]. It is likely that the Co-Mg-O catalyst system can oxidise any organic acid, if it is formed, immediately to combustion products.

In this research cobalt-magnesium oxide supported on  $\text{Al}_2\text{O}_3$  is used as catalyst for combustion of phthalic anhydride and maleic anhydride.

In this study the Co-Mg-O/ $\text{Al}_2\text{O}_3$  catalyst with different cobalt and magnesium loading have been used to investigate:

1. The oxidation property of Co-Mg-O/ $\text{Al}_2\text{O}_3$  catalyst for phthalic anhydride and maleic anhydride reactants.
2. The effect of different cobalt and magnesium loading on the oxidation property of Co-Mg-O/ $\text{Al}_2\text{O}_3$  catalyst.

This present work is organized as follows:

Chapter II contains literature reviews of cobalt oxide and supported cobalt catalysts on various reactions

The theory of this research, studies about the oxidation reaction and its possible mechanism, reaction of anhydrides, properties of cobalt oxide and supports are presented in chapter III.

Description of experimental systems and the operational procedures are described in chapter IV.

Chapter V reveals the experimental results of the characterization of Co-Mg-O/ $\text{Al}_2\text{O}_3$  catalysts and the oxidation reaction of phthalic anhydride and maleic anhydride over these catalysts.

Chapter VI contains the overall conclusion emerged from this research.

Finally, the sample of calculation of catalyst preparation, external and internal diffusion limitations, calibration curves from area to mole of phthalic anhydride, maleic anhydride, benzene, toluene, ethylbenzene, and acetic acid, catalytic activity of blank test, and data of this experiment which has emerged from this study are included in appendices at the end of this thesis.



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