CHAPTER I

INTRODUCTION

Direct oxidation of hydrocarbons compounds is an important process in petrochemical industry. Examples of oxidation of aromatic compounds in oxidation process are the oxidation of o-xylene to phthalic anhydride and benzene to maleic anhydride. In both processes, the aromatic reactants are mixed with air in gaseous phase. The concentration of aromatics is limited by the lower explosive limits. The gas mixture then flows to 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 the coolant temperature, the higher the 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.

The elimination of 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 a high oxygen concentration to a furnace or a boiler. This method, however, may cause problem concerning the energy balance of the plant. There are two catalyst families which can completely oxidise organic compounds. One is Pt-based catalysts and the other is acidic oxide 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 metal oxide catalysts is the capability to adsorbed acidic organic compounds. On the acidic surface, acidic organic compounds are less likely to be adsorbed. The further oxidation of the acidic compound to combustion products, therefore, is low. In this reaction, metal oxide catalyst becomes a selective oxidation catalyst for the production of anhydride because it has low ability to further oxidise the anhydride product formed. On the contrary, this behavior 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. In this research, magnesium oxide is added to vanadium oxide catalyst to new compound, V-Mg-O catalyst, it is an interesting catalyst because its basic property and not difficult to prepare. It is convenient to find raw materials and cost is not expensive. Besides the structure of catalyst is no complexity. Vanadium-magnesium oxide is a well known catalysts for the oxidative dehydrogenation of hydrocarbons, as in the transformation of propane to propene, butane to butene and butadiene, and ethylbenzene to styrene.[Pimanmas (1999)]

In a magnesium oxide supported vanadium oxide system, vanadium oxide does not form the monolayer structure like the titanium oxide supported vanadium oxide system because of the acid-base reaction between the acidic vanadium oxide and basic magnesium oxide. The strong interaction between vanadium oxide and magnesium oxide results in the formation of a mixed metal oxide compound, V-Mg-O, rather than a stable surface vanadia overlayer on the magnesia support.

V-Mg-O catalyst is prepared from V_2O_5 on titania and magnesium oxide. In chemical industry and environment process, supported vanadium oxide is more interesting because it is used to oxidise SO_2 to SO_3, eliminate NO from exhaust gas of combustion in industry by ammonia, oxidise toluene to benzoic acid, oxidise butane, butene, benzene to maleic anhydride etc.

Acid-basic properties of support are dependent on the structure of vanadium oxide on support. Vanadium oxide on titania support has high activity and high selective for the oxidation *o*-xylene to phthalic anhydride whereas vanadium oxide interaction with magnesium oxide to form a new complex oxide compound. Additionally, it is possible to have the other elements that are more active and selective than VMgOTi catalysts such as MoO_3 and P catalysts etc. Thus the other elements may be used for combustion anhydride. However, there is no information about properties of V-Mg-O catalysts in combustion and appropriate ratio for combustion anhydride.

The present work is arranged as follows:

Chapter II presents literature reviews of investigation related to supported vanadia systems on the combustion

The theory related to this work and studies about the structure and reactivity of vanadium oxide species on oxide support especially TiO_2 and MgO are described in chapter III.

Chapter IV presents the experimental systems and the operational procedure.

Chapter V shows the experimental results of the characterization of catalysts and the benzene, toluene, ethyl-benzene, phthalic anhydride and maleic anhydride reactions on V-Mg-O/TiO_2 catalyst.

In the last chapter, the overall conclusion emerged from this research is given.

Finally, the sample of calculation of catalyst preparation, diffusional limitation effect, calculation of specific surface, the details of gas chromatograph including the operating conditions, the calibration curves and the samples of chromatogram, data of experiments and a published paper which has emerged form this study are included in appendices at the end of this thesis.