CHAPTER I

INTRODUCTION

Large amounts of fossil fuel, oil, natural gas and coal are burnt to fill the urgent need for energy by both stationary and non-stationary sources. Huge amounts of pollution, solid, liquid and gaseous wastes, are emitted daily with the effluents evolving from these processes as well as fly-ash and dust. The emission of sulphur and nitrogen oxides overloads the environment. These oxides are formed by the burning of fossil fuels. Such emission are blamed for the formation of acid rain and for other environmental problems.

Reduction of emitted NO_x produced by combustion of fossil fuels, can be accomplished by adapting various combustion techniques (*e.g.* low NO_x burners, air staging in the furnace, reburning or flue gas recirculation) or by flue gas treatment. The former, however, can not meet the present strict emission standard. Therefore, the flue gas treatment is usually required. Treatment of the flue gas can be done with selective or non-selective catalytic reduction and can be combined with SO_x removal.

Selective catalytic reduction (SCR) of nitrogen oxides by ammonia in the presence of oxygen is one of the most effective methods for controlling this hazardous emission from stationary sources (*i.e.* power stations). During selective catalytic reduction, the nitrogen oxides contained in flue gas are reduced by ammonia to elemental nitrogen and water vapor according to the following catalytic reaction:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

The superiority of ammonia as compared to other reducing agents (CO, H_2, CH_4) is due to the fact that ammonia is not as susceptible to oxidation by oxygen as the other reducing gases.

Among several catalyst systems studied, such as tungsten oxide, molybdenum oxide, rhenium oxide, chromium oxide, iron oxide, copper oxide and zeolite [Okazumi *et al.* (1985), Kiel *et al.* (1992), Duffy *et al.* (1994a), Matralis *et al.* (1995), Wachs *et al.* (1996), Nova *et al.* (1998)], vanadium (V) oxide (V_2O_5) supported titanium oxide catalyst is the most widely employed and studied catalysts for the SCR of NO_x by ammonia. [Kotter *et al.* (1989), Clarebout *et al.* (1991), Tufano & Turco (1993)] Vanadia/titania catalysts seem to be quite superior to other alternatives due to their high activity, thermal stability and high resistance to poisoning by sulphur dioxide.

It is known that the V_2O_5/TiO_2 system will have the highest turnover frequency (TOF) when the amount of V_2O_5 loaded is about theoretical monolayer coverage. [Amiridis *et al.* (1996), Ciambelli *et al.* (1996), Kijlstra *et al.* (1996)] Hence, many research groups have focused their studies in these regions. [Shikada & Fujimoto (1983), Blanco *et al.* (1989), Clarebout *et al.* (1991), Weng & Lee (1993), Turco *et al.* (1994), Vikulov *et al.* (1994), Marshneva *et al.* (1995), Ciambelli *et al.* (1996), Kijlstra *et al.* (1996), Lietti *et al.* (1996a, b, c), Ramis *et al.* (1996), Kamata *et al.* (1998)] But in this work, we will base our attention on high rate per unit mass or unit volume of the catalyst. Research in our laboratory has shown that the maximum rate per unit mass could be obtained at vanadia loading about 25 wt.%. [Teratrakoonwicha (1997)]

Although the V_2O_5/TiO_2 system possesses high SCR activity, its performance can be changed by the addition of impurities/additives. The surface structure of vanadium species is affected by the pH of the surface moisture layer, which, in turn, is dependent on the nature of additives, for example, acidic or basic compounds. [Deo & Wachs (1991), (1994)]

The performance of the V_2O_5/TiO_2 can be further enhanced by adding metal oxides which are acidic compounds (*e.g.* oxides of W, Mo, Nb). W is a widely used promoter of V_2O_5 based in SCR catalyst. This is because WO_3 can widen the temperature window of SCR, increase the poison resistance to alkali metal oxides and arsenious oxide, and reduce ammonia oxidation as well as SO_2 oxidation. [Alemany *et al.* (1995)] On the other hand, De-NO_xing catalysts can be deactivated by alkali metals that are present in fly ashes. [Tokarz *et al.* (1991)] K is a significant composition in fly ashes. [Lietti & Forzatti (1993)]

Thus, this research is set up to demonstrate the effect of tungsten and potassium on the performance of a high loaded V_2O_5/TiO_2 catalyst for the SCR of NO_x with ammonia.

This thesis is divided into the following chapter:

Chapter II presents a literature reviews of investigation over V_2O_5/TiO_2 catalysts for the SCR of NO_x with ammonia and some comments on the previous papers. The theory of this work, studies about the SCR of NO_x by NH_3 reaction and the by-reaction, molecular structure of titanium oxide supported vanadium oxide catalysts, adsorption and desorption studies on V_2O_5-based catalysts and proposed intermediate species, reaction schemes and reaction mechanism for the SCR of NO_x by NH_3. These topics are presented in chapter III.

In chapter IV, the experimental systems and the operational procedure are described. The experimental results obtained from a laboratory scale reactor is reported and discussed in chapter V. Chapter VI gives overall conclusions emerged from this work and presents some recommendations for any future works.

Finally, sample of calculation, chemical component of TiO_2 support, the operating conditions of NO_x analyzer, the conditions of calcination the catalyst, the data of the reaction testing and the published papers are included in appendix at the end of this thesis.