



## CHAPTER I

### INTRODUCTION

Air pollution caused by the emissions of nitrogen oxides ( $\text{NO}_x$ ) in stack gases from thermal power stations and industrial process facilities has been the object of major environmental concern worldwide over the last decades. In the combustion processes, nitrogen oxides ( $\text{NO}_x$ ) are formed due to the reaction between  $\text{N}_2$  and  $\text{O}_2$  at high temperatures (thermal  $\text{NO}_x$ ), as well as from oxidation of the organic nitrogen present in the fuel (fuel  $\text{NO}_x$ ) and from HCN formed from fuel nitrogen (prompt  $\text{NO}_x$ ) [Bosch and Janssen 1988]. On increasing the flame temperature the contribution of fuel  $\text{NO}_x$  decreases and thermal  $\text{NO}_x$  represents most of the total  $\text{NO}_x$  formed.  $\text{NO}_x$  typically consists of a mixture of 95% NO and 5%  $\text{NO}_2$ .  $\text{NO}_x$  emissions from stationary sources roughly account for half of man-made  $\text{NO}_x$  and are blamed for the production of acid rain and human respiratory problems.

Accordingly, the removal of  $\text{NO}_x$  from exhaust gases released from stationary sources is an important research for today environmental problem. Techniques developed for controlling the emissions of  $\text{NO}_x$  can be classified into two groups [Forzatti and Lietti 1996]: that consisting combustion modification of  $\text{NO}_x$  (primary measures) and those consisting of effluent treatments to remove  $\text{NO}_x$  (secondary measures).

Combustion modifications, including low- $\text{NO}_x$  burners, flue gas recirculation, fuel reburning, staged combustion and water or steam injection, have been extensively applied. The  $\text{NO}_x$  reduction ensured by these primary measures can be as 50-60%, but it may not meet the most stringent emissions limits previously discussed.

Among the flue gas treatment methods the selective catalytic reduction (SCR) is best developed and is used worldwide due to its efficiency, selectivity and economics. The removal of  $\text{NO}_x$  can be accomplished by selective reduction with a suitable reductant *e.g.* hydrocarbon and/or ammonia. The selective catalytic reduction

of  $\text{NO}_x$  by  $\text{NH}_3$ , however, represents only today the practical process for the removal of  $\text{NO}_x$  from exhaust gases of stationary sources [Cai *et al.* 1991, Baiker *et al.* 1992, and Duff *et al.* 1993].

In the midst of several catalyst systems studied, vanadium(V)oxide ( $\text{V}_2\text{O}_5$ ) supported on titanium(IV)oxide catalyst is the most widely employed in this process. Though the  $\text{V}_2\text{O}_5/\text{TiO}_2$  system possesses high SCR activity, its performance can be further enhanced by adding metal oxides *e.g.* oxides of W, Mo, Nb, Ge, and Y [Odenbrand *et al.* 1994, and Vikulov *et al.* 1994]. It has been reported that the activity of the catalysts depends on vanadia loading [Srnak *et al.* 1992], and that both monomeric vanadyls and polymeric vanadates are present in sub-monolayer samples [Went *et al.* 1992a]. It has also been reported that polymeric vanadate species are more active although less selective than isolated vanadyls in the SCR reaction [Weng *et al.* 1992b]. Although it is generally accepted that the vanadia portion of the catalyst is essential for this reaction, the nature of the active sites and the mechanism of the reaction over the catalyst are quite controversial. Several literatures have suggested that the reactivity of  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts relates to the surface acidity of the catalysts [Saur *et al.* 1986, Matralis *et al.* 1986, Bosch and Jassen 1988, Gutberlet and Schallent 1990, Ramis *et al.* 1990a, Ramis *et al.* 1990b, Topsøe 1991, Topsøe 1992, and Hu and Apple 1996]. A generally accepted agreement, however, has yet to be reached.

Because of the above reasons, a  $\text{V}_2\text{O}_5/\text{TiO}_2$  system is developed and modified by adding tungsten (W) and potassium (K) to alter the performance of the catalyst on the SCR of NO with  $\text{NH}_3$ . This work was set up to investigate:

1. The effect of acidity property of  $\text{V}_2\text{O}_5/\text{TiO}_2$  with W and K on SCR activity.
2. The relationship between the  $\text{V}_2\text{O}_5/\text{TiO}_2$  based catalysts and their reactivity.

The present work is arranged as follows:

Chapter II shows literature reviews of investigation over the SCR of  $\text{NO}_x$  with  $\text{NH}_3$ .

The theory of this research, studied about the acid-base properties of the catalyst is described in chapter III.

Chapter IV presents the experimental systems and the operational procedure.

The experimental results of the characterization of catalysts and the SCR of NO with  $\text{NH}_3$  over the  $\text{V}_2\text{O}_5/\text{TiO}_2$  based catalysts are reported and discussed in chapter V.

In the last chapter, the overall conclusion emerged from this work and some recommendations for any future works are present.

Finally, a briefly theory of reduction of NO, IR spectra of the spent catalysts with and without  $\text{SO}_2$  at reaction temperatures of 200 °C and 450 °C, sample of calculation, chemical component of  $\text{TiO}_2$  support, operating condition of  $\text{NO}_x$  analyzer, conditions of calcination the catalyst, and the published papers which have emerged from this study are included in appendices at the end of this thesis.

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