

CHAPTER I INTRODUCTION



One source of environmental pollution comes from transportation and stationary sources, which emit noxious pollutants produced during high temperature combustion. This combustion process is not so rapid and thermodynamic equilibrium ($\text{CO}_2 + \text{H}_2\text{O}$) is not reached. Therefore, undesired byproducts such as carbon monoxide and soot are formed. Additionally, nitrogen oxides (NO_x) which are toxic pollutants are produced. Among the nitrogen oxides, nitric oxide (NO) is a main component emitted. NO can be oxidized rapidly to NO_2 in the presence of sunlight and hydrocarbon from unburned gasoline. NO_2 is a contributor of so-called acid rain [1]. Furthermore, nitrogen oxides affect the photochemistry of the troposphere and stratosphere. According to a research study, only exposure to 0.05 ppm of nitrogen oxides for 24 h has hazardous effects for human health.

In fact, however, an excessive value frequently exists in the atmosphere during rush hour traffic or in hot climates. Many researchers have paid attention to this problem. Catalysts have been applied for NO removal so far. For automobiles equipped with gasoline engines, so-called "three way catalysts" those composed of noble metals (Pt , Pd or Rh) are powerful for NO removal [2-4]. The efficiency for this application is high when there is a stoichiometric ratio of oxidative and reducing species in exhaust compositions. However, this reaction can be performed well only in suitable condition, the so-called "window" [5].

NO decomposition to N_2 and O_2 , the simplest and most desirable method for NO removal, is an attractive approach to eliminate NO from an exhaust stream. However, no suitable catalyst gives high performance for NO removal and it is difficult to promote high activity in practice [6]. The removal of nitric oxide using ammonia as a reductant is called selective catalytic reduction (SCR) which has been successfully used for the purification of exhaust gas from stationary sources. By using this reaction, NO can be eliminated in the presence of oxygen.

The appropriate amount of oxygen essential to enhance NO removal is shown below [7].



Unfortunately, there are many disadvantages encountered when using vanadium. Ammonia and vanadium are toxic materials. Ammonia has to be kept in storage and unreacted ammonia is a pollutant in the atmosphere as well. Recently, a new method for NO removal has been discovered using hydrocarbons as reductant instead of ammonia. This application is more important for NO removal in the presence of excess oxygen (lean NO_x emission control).



The advantage for NO elimination in the presence of hydrocarbons and excess oxygen that is possible to remove a part of NO in the boiler flue gas without any further hydrocarbon addition. About 1-2% of oxygen is similar to that in flue gases from the boiler for generation [50]. If an effective catalyst can be improved for this reaction, then NO removal will be economical using unreacted hydrocarbons in the stream instead of ammonia as reductant.

Numerous studies concerning catalysts have been investigated for this reaction so far. Variety of metal ion-exchanged zeolites are extensively used. Cu ion exchanged MFI type zeolite (Cu/MFI) discovered by Iwamoto et al. is widely supported to be powerful for NO removal in the condition of excess oxygen [8-13]. Moreover, other kinds of metal ion-exchanged zeolites such as gallium- [14,15], iron- [16,17], cobalt- [18-21], cerium- [22-24], platinum- [25,26], palladium- [27] were studied for this reaction. Protonated form ZSM-5 type zeolite was also studied [28,29]. In addition, other groups of active catalysts such as transition metal and/or metal oxide (Cu, Co, Mn, Fe, Cr, V, Ag) [30-34], perovskites [35,36], faujasite [37], and noble metals [38-41] were considered. Nevertheless, many types of catalysts referred above are easily deactivated during reaction lay high temperature and the coexistence of steam possibly occurred in

practical use [42-46]. As mentioned above, many researchers have tried to find a new catalyst that can handle severe conditions for NO removal. On the other hand, metal incorporated zeolites (metallo-silicates) has been proposed to be effective catalysts which can resist the deterioration under the extreme condition of high temperature even with a large amount of steam [42, 47-49].

This dissertation is separated into 10 chapters. This chapter contains a brief introduction. An overview of the literature was summarised in Chapter II. The background of theory was explained into Chapter III. Chapter IV presents the results obtained in this study. Chapter V discusses the relationship between the amount of copper loaded on MFI zeolite and nitric oxide conversion. From the results, it was decided that 200%Cu/MFI was to be further investigated. Chapter VI describes the trend between the activity for nitric oxide conversion of 200%Cu/MFI and H-Co-silicate and the amount of steam, the so-called hydro-treatment condition. Additionally, the impact of thermal-treatment on nitric oxide conversion of 200%Cu/MFI and H-Co-silicate is described in Chapter VII. The enhancement of the activity for NO removal of H-Co-silicate by high thermal-treatment is also discussed. The characterizations were also repeated in this chapter. Chapter VIII describes the influence of hydrothermal-treatment on the activities of nitric oxide conversions of both Cu/MFI and H-Co-silicate catalysts. Additionally, Pd modification on Cu/MFI catalyst was also taken into account to improve the stability against hydrothermal-treatment. Chapter IX presents results of experiment involving Cu ion-exchanged Co-silicate (Cu/Co-silicate) catalyst to nitric oxide removal in the thermal-treatment condition. This chapter reports on the comparison of Cu/Co-silicate for nitric oxide conversion with Cu/MFI and H-Co-silicate as well. The stability test of these catalysts was also investigated. Finally, overall conclusions were generally summarized in chapter X.