CHAPTER I

INTRODUCTION

The enhanced volume of air pollutants have become a serious global environmental problem. These pollutants must be removed as much as possible from the atmosphere. Nitric oxides(NOx) is one of pollutants come mostly from the exhausting gas mostly from engines of vehicles and partly from boilers and stationary engines in industries. NOx is a strong poison, which has threshold limit about 10 ppm[1]. It can reach all parts of the respiratory system and their functions throughout the lungs. Besides, oxides of nitrogen play a major role in the photo chemical reaction in the stratosphere which is one of key substance destroying the ozone in atmosphere[2].

Thermodynamically, nitric oxide can decompose to dinitrogen under 800 °C but, kinetically, it remains stable in the absence of suitable catalyst[3]. NO decomposition became a widespread topic in the last decade since Iwamoto[4,5] found the outstanding activity of Cu/ZSM-5 compared to catalysts that had been studied so far. The process is easy and simple because it involves only one reactant. Hence, it was considered applicabel to real-life problems. Unfortunately, Cu/ZSM-5 was not highly active enough for practical systems with extremely severe conditions and high GHSV such as in exhaust stream from an engine. Non selective reduction of NO by CO and H_2 has been known for decades. In the presence of oxygen, selective reduction of NO where both NO and O_2 competitively react with reducing a agent.

In selective reduction, a molecule of nitric oxide could be better reduced by a reactant containing a nitrogen atom in order to easily form dinitrogen. There are numbers of N-containing reductants that have been proposed, for example, urea, cyanuric acid and ammonia[6]. However, NH_3 is always applied in practice because of its availability and ease of use. Units for of selective

catalytic reduction(SCR) of NO by NH_3 have been installed for treating exhaust gas from stationary plant such as boilers and engines in several countries[3,7]. On the other hand, SCR of NH_3 also has disadvantages compared with the ordinary reductants like CO ,H_2 and CH_4. Since NH_3 is a poisonous gas, there are requirements for careful storage and precise control of the use of NH_3 in order not to allow the unreacted NH_3 gas to disperses in atmosphere and turn in to another pollutant. One well-achieved invention of NOx abatement technology is the catalytic converter which has been attached in exhaust line of gasoline-engines since 1990 in USA and become a standard part of gasoline vehicles[8], currently. Use of conventional three-way catalyst(Pt-Rh/Al_2O_3) in converting NO, CO and hydrocarbon simultaneously is limited by a very narrow range of oxygen content[9]. This is the reason why it is exploited only for gasoline engine which operates in a rich condition. However, the lean burning internal combustion engine is inherently more efficient than the same engine operating at a stoichiometric air-fuel ratio which will make it favoured in the future. Accordingly, a new approach to eliminating NOx in high oxygen environments is necessary. Fortunately, the pioneer work of Iwamoto et al.[10-13] and Held et al.[6] brought us to proposing the selective reduction of NO by hydrocarbon. Unlike the conventional catalytic converter for gasoline engine, this process can be operated even under a highly oxidizing atmosphere. Therefore, it would be a better process for exhaust gas treatment with lean burn engines. In recent years, catalysts for the SCR of NO has been studied by many researchers, for instance, Cu/ZSM-5 [10-17], Co/ZSM-5 [18-21], H-ZSM-5 [22-24], Metal/Al_2O_3 [23,25-27], Metal-ZrO_2 [28-30] and metal/mordenite [31-33]. Among all, however, Cu/ZSM-5 is one of the catalysts which is the most active and the most widely studied because of its remarkable property in the SCR of NO by hydrocarbons. Thorough understanding of the catalyst functions and mechanisms is important for the development of a practical NO removal process, so that it is worth studying some functions and roles of active sites on the catalysts which remained unclear. Residue cations which are still on the surface of ZSM-5 after

ion-exchanging with copper is a factor which may affect the efficiency of catalyst.

Generally, Cu/ZSM-5 zeolite can be prepared by ion-exchanging Cu ion into either Na- or H- form of ZSM-5. The choice of the primary form of ZSM-5 used by a researcher likely depended upon his or her preference rather than for reasons. For instance, in order to avoid the effect of Na^+ ion, H-ZSM-5 should be used[3]. However, Na^+ on catalyst surface can be exchanged with Cu ion easier than H^+. Although overexchanged Cu/ZSM-5, which is the most active catalyst for the SCR of NO by hydrocarbon[14], has a degree of Cu^{2+} exchange above 100%, based on the assumption that one Cu^{2+} ion exchanges with two Na^+ ions or two protons, this sample still has a significant amount of other cations remaining on the surface[3,34]

H-ZSM-5 is one of the catalysts that shows quite high activity in the SCR of NO[22-24] whereas the poor activity of Na-ZSM-5 has also been observed[16, 22, 35]. The difference in activity between Na-ZSM-5 and H-ZSM-5 resulted totally from the difference of cations on the catalyst surface. The cation neutralizes the zeolite structure caused by the negative charge of the alumina tretahedral. The Na^+ ion is located near the tetrahedral while the proton on the zeolite surface always interacts with oxygen adjacent to the Al tetrahedral and acts as Brønsted acid bridging hydroxyl group. Somehow, after high temperature treatment, two Brønsted acid sites dehydrate to form one Lewis acid site. The Cu/ZSM-5 surface would mainly consist of copper ion sites which are believed to be the main active sites of Cu/ZSM-5 catalyst for the SCR reaction [15, 16, 36-38] and, partly, unexchanged cations which are Na^+ ions and/or protons. However, these remaining cations may influence either the active site or the mechanism of reaction. To distinguish the exact effect of these remaining cations, this study would focus on reactions over Cu/Na-ZSM-5 and Cu/H-ZSM-5. Moreover, the characteristics of both catalysts were observed in order to determine how the remaining cations affect the ZSM-5 catalysts and to understand the participation of these cations in the SCR. The objectives and scope of this study will be describe as follows:

1.1 The Objectives of This Study

1.1.1 To study the different catalytic activities between Cu ion-exchanged Na-form ZSM-5 and H-form ZSM-5 in the various reactions.

1.1.2 To distinguish catalytic properties between both catalysts.

1.1.3 To investigate factors inwhich influence the activity in selective catalytic reduction of NO by propane over both catalysts.

1.2 The Scope of This Study

1.2.1 Preparation of parent Na-ZSM-5 by rapid crystallization method and H-ZSM-5, Cu/Na-ZSM-5 and Cu/H-ZSM-5 by ion exchanging Na-ZSM-5 in an appropriate procedure.

1.2.2 Characterization of catalysts by following methods:

a) Specific surface area by N_2 adsorption based on BET method
b) Quantitative analysis of substance in catalysts by AA, ICP and XRF
c) Structure and crystallity of catalysts by X-Ray Diffraction
d) acidic properties by Pyridine adsorption
e) ex-situ FT-IR
f) Oxygen adsorption
g) CO adsorption
h) Dealumination by Al-NMR
i) Coke deposition by Temperature Programmed Oxidation (TPO)

1.2.3 Steady state kinetic experiments over catalysts at 150 - 600 ^{o}C in various feeds as follows:

a) NO + He

b) NO + C_3H_8 + He

c) C_3H_8 + O_2 + He

d) NO + C_3H_8 + O_2 + He

1.2.4 Experiment over catalysts at high GHSV at various concentration of each gas as shown below:

a) 400 - 2000 ppm NO at constant C_3H_8 and O_2.

b) 400 - 2000 ppm C_3H_8 at constant NO and O_2.

c) 3 - 6 % O_2 at constant C_3H_8 and NO.

1.2.5 Transient experiment over catalysts at various step change of each reaction as follows:

a) switching from N_2 to NO + N_2

b) switching from N_2 to NO + O_2 + N_2

c) switching from N_2 to C_3H_8 + N_2 and adding NO

d) switching from N_2 to C_3H_8 + O_2 + N_2 and adding NO