



CHAPTER I INTRODUCTION

Nitrogen oxides (NO_x) are formed during combustion. These oxides are considered as important pollutants in the air because they can cause the acidification of rain and affect human health through ozone production, and also play a role in visibility degradation by producing photochemical smogs [Teng *et al.* (1999)]. For these reasons, NO_x emissions are controlled.

There are two major catalytic technologies for the abatement of the emission of nitrogen oxides into the atmosphere. Both were developed in the seventies. The first comprises selective catalytic reduction (SCR) using ammonia as a reductant (NH_3 -SCR). This is mainly applied to the emission of coal and oil-fired power plants [Misono *et al.* (1997)]. However, this process suffers from many disadvantages due to the use of an additional gaseous reducing agent such as ammonia slip, equipment corrosion, danger in transportation and storage of ammonia [Illan-Gomez *et al.* (1999)].

The other technology is the three-way catalyst (TWC) that is efficient in the simultaneous reduction of CO, HC, and NO_x . However, it requires an exhaust gas composition operating very close to the stoichiometric point. The emissions from diesel and gas engines are not satisfactorily controlled. Because these emissions are both from small or mobile sources and contain excess oxygen, neither of the above two catalytic technologies is applicable. The same problem exists for such fuel-efficient engines as lean-burn gasoline engines [Fritz and Pichon (1997)].

This is the reason why we need a new catalytic technology which can be applied to dilute nitrogen oxides emitted together with excess oxygen from mobile or small stationary engines [Misono *et al.* (1997)].

The most attractive method for the removal of NO_x is the catalytic decomposition of NO [Iwamoto *et al.* (1995)], because no reducing agent is required.

Because NO is thermodynamically unstable relative to N₂ and O₂. This method is feasible. However, no suitable catalyst with a significant activity in real exhaust gas has been identified. It is widely accepted that the poisoning of the catalyst surface by oxygen from the exhaust gas or from the decomposition itself is the main problem. Therefore, up to now the only way to reduce NO_x emission in lean exhaust gas is the injection of reducing agents into the exhaust gas stream [Forkema and Ying (1998)].

In 1986, Cu-ZSM-5 was reported to be much more active than the earlier known catalysts for the catalytic decomposition of NO. This finding was remarkable, but the catalytic activity decreased sharply with a decrease in the NO concentration and the catalyst suffered from severe deactivation in the presence of oxygen or sulfur oxides. It was later demonstrated that Cu-ZSM-5 showed a significant activity when it was used for a real lean-burn engine and, moreover, the rate increased in the presence of oxygen. It was shown that the reaction-taking place in this case was not the decomposition of NO but the reduction of NO by hydrocarbons contained in the emission gas. Since then (1990-1992), many catalysts such as various kinds of solid acids and bases, including ZSM-5 loaded with metal ions (even with proton), were demonstrated to be active catalysts for this reaction. This reaction is called HC-SCR (selective catalytic reduction by hydrocarbons) [Misono *et al.* (1997)].

The large worldwide reserves of natural gas and the availability of methane at gas-fired power plants make methane an attractive reductant for many applications. However, Cu-ZSM-5 and the acidic oxides that have been found to catalyze the selective catalytic reduction of NO_x with higher hydrocarbons are non-selective when methane is used as a reducing agent. Only a few catalysts have been reported to selectively catalyze the reduction of NO_x, rather than the complete combustion of methane, in an oxidizing atmosphere [Forkema and Ying (1998)].

Much experimental work has been done using zeolite catalyst for NO_x reduction. However, the problems have been found, especially regarding the role of a reactive intermediate generated by hydrocarbons. This intermediate was suspected to react with NO or NO₂ or both. Ansell *et al.* (1993) proposed the term “deposited

coked species” to name the reductant in the reaction over Cu-ZSM-5. Lukyanov *et al.* (1995) suggest that an intermediate is formed on the catalyst surface which can couple with NO or NO₂ to form the N-N bond. Yokoyama and Misono (1994) assume that NO₂ react rapidly with propene to form intermediates, which further decompose into nitrogen over Ce-ZSM-5.

On the other hand, the emission control of particulates from diesel exhaust gases have been concerned worldwide. The formation of particulates (or "soot") and NO_x were the main nuisances of diesel exhaust gases. The simultaneous removal of NO_x and soot particulates in an oxidizing atmosphere is desirable for the aftertreatment of diesel exhausts [Neeft *et al.*(1996)]. The presence of NO_x in gas phase improves the catalytic activity for soot elimination. NO is oxidized to NO₂ that can decrease the temperature needed to burn the soot.[Miro *et al.*(1999)]

For these reasons, there is idea to study about the role of NO_x for the formation and the removal of an intermediate on zeolite catalysts.

The scopes of this study have to be taken into account.

1. Prepare H-ZSM-5 and Cu-ZSM-5 catalysts by using ion exchange method.
2. Intermediate reaction test using nitrogen oxides reduction with various conditions.
3. Characterization of fresh and intermediated catalysts by following methods.
 - the amount of carbon and nitrogen in the intermediate by temperature programmed oxidation (TPO)
 - the carbon radicals of intermediates by electron spin resonance (ESR)
 - the chemical identity by infrared spectroscopy (IR)
 - the surface area by BET
 - the graphitic phase of carbonaceous deposits by x-ray diffraction (XRD)

- the morphology modification by transmission electron microscope (TEM)

This present work is organized as follows:

Chapter II contains literature reviews of the study of mechanism of nitrogen oxides reduction, the formation and the removal the intermediate of nitrogen oxides reduction by various hydrocarbons on zeolite catalysts.

In Chapter III, it provides readers with a detailed overview of theory of nitrogen oxides and zeolite catalysts

Description of experimental systems and the operational procedures are described in chapter IV.

Chapter V demonstrated the experiment results obtained from a laboratory scale reactor, standard measurement including an expanded discussion.

Chapter VI contains the overall conclusions emerged from this research.

At the end of this research, appendices contain calculation of reaction flow rate, nitrogen and carbon content, calibration curve and calculation of temperature in saturator.