

CHAPTER II

LITERATURE REVIEWS

Removal of NO in exhaust gases from diesel engines and other lean-burn combustion facilities has been one of the most important target for pollution control but no practical methods have been developed. Thus, intensive effort has been made to overcome this difficulty. Most recently, some studies on the NO elimination under the condition of an excess oxygen with a low concentration of hydrocarbon were reported using zeolitic catalysts such as H-type zeolite, metal-ion-exchanged ZSM-5, Cu-incorporated zeolites, and some kinds of metallosilicates. Some of the recent investigations and the evolution of these catalysts are summarized below.

Hamada et al. [22] compared the catalytic activities of copper ion-exchanged ZSM-5 (Cu/ZSM-5) with other catalysts. They had shown that the order of activity was $\text{Cu/ZSM-5} > \text{Ag-Co}_3\text{O}_4 > \text{La-Sr-Co(Cu)-O} > \text{Pt/Al}_2\text{O}_3 > \text{Y-Ba-Cu-O/MgO}$. The extent of conversion over Cu/ZSM-5 was higher than those others at temperature as low as 773 K. The results indicated that Cu/ZSM-5 was the most active catalyst at 773 K for the decomposition of dilute NO gas.

Iwamoto et al. [23] found that the catalytic activity of one cupric ion exchanged into ZSM-5 zeolite was much higher than that in mordenite, ferrierite, and L-type zeolites. In addition, it was noted that the mordenite with molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3=18.9$ showed higher catalytic activity than that with molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3=10.5$, in spite of the smaller amount of copper ions included in the

former than that in the latter. They suggested that the zeolite structure and the aluminum content (or $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio) were more important factors for controlling catalytic activity.

The selective reduction of nitric oxide by ethene in the presence of oxygen was studied by Iwamoto et al. [24]. They observed that copper ion-exchanged ZSM-5 zeolite was the most active at temperature as low as 437-573 K compared with transition metal ion- and proton-exchanged zeolites, and Al_2O_3 . The order of active temperature regions of cation-exchanged ZSM-5 zeolites was Cu (the most active temperature, 523 K) < Co (623 K) < H (673 K) < Ag (723-873 K) < Zn (873 K). Moreover, the activity of copper ion-exchanged ZSM-5 zeolite did not decrease even in gas hourly space velocity (GHSV) of more than 10000 h^{-1} .

Hamada et al. [10] studied the selective reduction of nitric oxide with hydrocarbons over zeolite catalysts in oxygen rich atmosphere. The most active catalyst of the three H-form zeolites was H-mordenite, which gave the maximum nitric oxide conversion of 65% at 673 K, followed by H-ZSM-5 and HY. It was interesting that Na-ZSM-5 and silicalite were also active for the reaction although the activity was not so high. On the other hand, silica gel showed no activity. For each catalyst, the percentage conversion of nitric oxide to nitrogen had a maximum value at a certain reaction temperature. This optimum temperature varied with the type of zeolite catalysts. The use of propene instead of propane as the reducing agent lowered this temperature for H-ZSM-5 and HY. This suggested that the efficiency of the selective reduction depended not only on the reduction temperature but also on the type of zeolites and hydrocarbons.

The removal of nitric oxide over copper ion-exchanged zeolite catalysts were studied by Iwamoto et al. [25]. They found that direct decomposition and selective reduction of nitric oxide over copper ion-exchanged zeolite catalysts were new methods for removal of nitric oxide. The copper ion exchanged zeolite (Cu/Z) was the most active catalyst for decomposition of nitric oxide. The activity of Cu/Z zeolites increased with increase in the exchange level. The zeolites with copper ion-exchange levels of 100% or more, which could be prepared by repeating ion exchange of the ZSM-5 zeolite using aqueous copper(II) acetate solution or addition of ammonia into the aqueous copper(II) nitrate solution, showed significantly high activity even in the presence of oxygen and high GHSV region. Characterization of Cu/Z, by using infrared spectroscopy (IR), electron spin resonance (ESR), phosphorescence, temperature programmed desorption (TPD), and CO adsorption measurements indicated that (1) the Cu^{2+} ions exchanged into zeolite were reduced to Cu^+ and/or Cu^+ through evacuation at elevated temperature, (2) after exposure to oxygen at 773 K and subsequent evacuation, about 40% copper ions in zeolite existed as Cu^+ ions, (3) the NO^- species formed by adsorption of NO on Cu^+ would be an intermediate in the NO decomposition, and (4) redox cycle of $\text{Cu}^+ = \text{Cu}^{2+}$ in the zeolite was probably a key step to achieve the decomposition reaction. Selective reduction of NO by hydrocarbon in the presence of oxygen was first found by them [19,20,22] and Cu/Z was remarkably effective for NO removal at temperature as low as 523-673 K. Furthermore, they had reported that the NO reduction rate over Cu/Z at 573 K was higher than those over H-zeolite and alumina catalysts at 723 and 773 K, respectively.

Iwamoto and Mizuno [26] studied catalytic activity of copper ion-exchanged ZSM-5 (Cu/ZSM-5) for NO reduction. They found that the activity of

Cu/ZSM-5 depended on the exchange level of copper ion. The activity increased with the increment of the exchange level, reached a maximum at the exchange level of 80-100% and then decreased a little.

Hamada et al. [27] investigated mechanism of the selective reduction of nitric oxide with propane by Cu/ZSM-5. They suggested that nitric oxide was oxidized to nitrogen dioxide intermediate which was reduced to nitrogen by reaction with propane. The direct oxidation of propane with oxygen was a side reaction. Probably the high selectivity of the reduction was caused by the higher reactivity of nitrogen dioxide to hydrocarbons than that of oxygen. Moreover, they suggested that the decrease in nitric oxide conversion to nitrogen at high temperatures could be explained by the high rate of propane - oxygen reaction.

The catalytic activity of Cu/ZSM-5 (Cu exchanged extent from 23 to 210%) and Cu/Y (Cu exchanged extent from 5 to 100%) zeolites in NO decomposition at 773 K was studied by Campa et al. [28] The results showed that the decomposition rate increased by roughly 100-fold when the extent of exchange with copper in the ZSM-5 framework increased from 20% to 100%. This phenomena showed that not all Cu sites were equivalent in their decomposition activity. In addition, they found that Cu-Na-ZSM-5, which was prepared by impregnation, was as active for NO decomposition as ion-exchanged ZSM-5 catalysts when the excess copper in Cu-Na-ZSM-5 was removed by H₂O washing after impregnation.

The catalytic reduction of NO_x in actual diesel engine exhaust over copper ion-exchanged ZSM-5 zeolite catalyst in the presence of oxygen and hydrocarbons were reported by Iwamoto et al. [29]. Copper ion exchanged ZSM-5 zeolite effectively reduced NO_x by 25% in normal engine operation, and

by 40% when C_2H_4 , C_3H_6 , or C_4H_8 was added. The temperature of maximum activation was observed at 400 °C irrespective of hydrocarbon species. However, the effect of CH_4 was small, indicating that the reduction effect depends on the type of hydrocarbon.

Teraoka et al. [30] studied the cocation effect on copper ion-exchanged ZSM-5 zeolite for reduction of nitric oxide with ethene in an oxidizing atmosphere. They found that the coexistence of alkaline earth (Ca and Sr) and transition metal (Fe, Co and Ni) cation was effective in the promotion of the maximum activity and the expansion of the active temperature range of the reduction of nitric oxide. They suggested that the results obtained might be due to increase selectivity of main reaction (NO reduction) by cocation or might be due to chemical and/or physical change, location, aggregation state, or electronic state of Cu ions.

Yang et al. [31] found that the activity for selective catalytic reduction (SRC) of NO by ethene of Cu^{2+} exchanged TiO_2 -pillared clay (Cu/ TiO_2 -PILC) was higher than that of Cu/ZSM-5 catalyst, even in the presence of H_2O (5% by vol.) and SO_2 (500 ppm). It might be the cation exchange capacity (CEC) of pillared clay was higher than that of Cu/ZSM-5 or the pore dimensions in the pillared clay was considerably larger than that in ZSM-5. Moreover, it was possible that there existed a more favorable chemical environment for redox for the Cu^{2+} ion in the pillared clay than in the structure of zeolite, and this might also be the reason for the H_2O resistance of the pillared clay catalyst. Due to Cu/ TiO_2 -PILC could tolerate to SO_2 better than Cu/ZSM-5, thus it was claimed as a new class of catalysts for this reaction.

Inui et al. [32] studied effects of coexistence of H₂O, CO₂ and SO₂ in the selective reduction of nitric oxide by cetane on catalytic performance of cobalt containing silicate having ZSM-5 (MFI) structure (Co-silicate). They found that water vapor retarded only the cetane conversion to CO₂ but no effect was observed on NO conversion and hydrocarbon combustion. The stability of H-Co-silicate would be ascribed to the state of cobalt species which was stabilized by incorporation into crystal framework. Therefore, cobalt silicate was demonstrated to be one of practical catalysts for this reaction.

Effect of Cu/ZSM-5 catalyst preparation on the activity of "over-exchanged" copper for NO decomposition were investigated by Zhang et al. [33]. They showed that a single step ion-exchange from an aqueous cupric acetate solution at pH>6.5 could achieve a high copper loading in ZSM-5, but not all the copper exists in ion-exchange state in the zeolite channels. A fraction of the copper was on the surface which could be easily formed to be oxidic particle after calcination and could be identified by scanning transmission electron microscopy/energy dispersion x-ray (STEM/EDX) analysis. The over-exchanged copper was inactive for NO decomposition. Short time wash with aqueous ammonia removed this copper. Consequently, the catalyst activity correlated very well with the amount of copper remaining in the ZSM-5 channels.

Inui et al. [34] reported catalytic removal of NO under condition of large excess oxygen by using different kinds of metallosilicates having ZSM-5 structure. In presence of a low concentration of cetane, H-Fe-silicate, which had both acidity and redox properties, exhibited the maximum performance at a fairly lower temperature range, around 350 °C, and the NO was totally

converted. The temperature dependence of NO conversion was consistently similar to that of cetane combustion.

The effect of SO₂ on catalytic performance for the NO/CH₄/O₂ reaction over Co-ZSM-5 and Co-ferrierite with and without the presence of water vapor was reported by Li et al. [35]. Co-ZSM-5 and Co-ferrierite behaved differently in response to SO₂ addition in dry feed. Over Co-ZSM-5, SO₂ significantly enhanced the NO conversion at T > 500°C in dry feed ; while over Co-ferrierite, SO₂ greatly reduced the NO conversion. However, when both SO₂ and H₂O were presence in feed, Co/ZSM-5 suffered significant activity loss, while Co-ferrierite showed improved activity. In addition, CH₄ combustion of both catalysts were depressed in the presence of SO₂ and/or H₂O in feed gas.

Iwamoto et al. [36] studied selective reduction of NO by hydrocarbons over copper ion-exchanged zeolite in the presence of O₂, SO₂, and H₂O. Simultaneous presence of O₂ and hydrocarbons such as ethene, propene, and propane with NO in the reactant gas markedly promoted NO removal at low temperature (473-673°C). On the other hand, the addition of CO, H₂ or CH₄ to the NO+O₂ system did not cause any selective reduction of NO. When SO₂ or H₂O was added to NO+O₂+hydrocarbons, it resulted in slight decrement in the catalytic activity. Furthermore, the activity was gradually restored after the supplement of SO₂ and/or H₂O was stopped.

The reviewed papers demonstrate that copper ion-exchanged ZSM-5 zeolite (Cu/ZSM-5) has capacity to selectively reduce nitric oxide with hydrocarbon in the presence of excess oxygen. However, the catalytic activity of Cu/ZSM-5 is limited in a rather narrow temperature range. Its activity decreases when temperature is more than 300 °C. This limitation inhibits the

application of ZSM-5 to real life problem. Thus, this study was set up to develop a catalyst which can perform high catalytic activity and a wider temperature window for nitric oxide reduction by hydrocarbon in oxidizing atmosphere. J. Pincharoenthaworn [37] reported that Al content may affect the catalyst activity for nitric oxide removal. In addition, Iwamoto et al. [25] reported that Cu ion-exchanged catalyst showed lower temperature for NO reduction. Consequently, bimetallosilicate, which both Cu and Al are in the crystal, was prepared and its catalytic activity for the removal of nitric oxide by hydrocarbon in oxidizing atmosphere was studied.