

## CHAPTER II

### LITERATURE REVIEWS

Selective reduction of nitrogen oxides under an oxidizing atmosphere by hydrocarbons has attracted attention as a process for the catalytic removal of NO in the exhaust gas of diesel or lean-burn engines. Recently, some studies on the NO elimination under the condition of an excess oxygen with a low concentration of hydrocarbon were reported using many kinds of solid catalysts as follows.

Hamada et al. [21] compared the respective catalytic activities by using their own experimental apparatus. The catalytic properties of a copper ion-exchanged ZSM-5 zeolite (Cu-ZSM-5) can be compared with other catalysts. The order of activity is Cu-ZSM-5 > Ag-Co<sub>3</sub>O<sub>4</sub> > La-Sr-Co(Cu)-O > Pt/Al<sub>2</sub>O<sub>3</sub> > Y-Ba-Cu-O/MgO. The extent of conversion over Cu-ZSM-5 is higher than those others at temperature as low as 773 K. The results indicate that Cu-ZSM-5 is the most active catalyst at 773 K for the decomposition of dilute NO gas.

Iwamoto et al. [22] found that the catalytic activity of one cupric ion exchanged into ZSM-5 zeolite is much higher than that in mordenite, ferrierite, and L-type zeolites. In addition, it is noted that the mordenite with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=18.9 showed higher catalytic activity than that with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=10.5, in spite of the smaller amount of copper ions included in the former than that in the latter. It is very significant to investigate which of the zeolite structure and the aluminum content (or SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio) is more important factor for controlling catalytic activity.

The selective reduction of nitric oxide by ethene in the presence of oxygen was studied by Iwamoto et al. [23]. They observed that copper ion-exchanged ZSM-5 zeolite is the most active at temperature as low as 437-573 K compared with transition metal ion- and proton-exchanged zeolites, and  $\text{Al}_2\text{O}_3$ . 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).

Li and Armor [24] discovered a family of catalysts that can effectively reduce  $\text{NO}_x$  with methane in the presence of excess oxygen. This new catalytic chemistry offers an alternative means for controlling  $\text{NO}_x$  emissions. Complete reduction of nitric oxide was obtained at 400 °C over Co-ZSM-5 catalyst. The presence of oxygen in the feed greatly enhances the nitric oxide reduction activity on Co-ZSM-5, and the nitric oxide conversion is strongly related to the inlet methane level. On the other hand, Cu-ZSM-5, which is a unique catalyst for the direct nitric oxide decomposition, is a poor catalyst for nitric oxide reduction by methane in the presence of excess oxygen.

Hamada et al. [7] 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 is 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 all the catalysts, the percentage conversion of nitric oxide to nitrogen had a maximum 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 suggests that the efficiency of the selective reduction depends not only on the reduction temperature but also on the type of zeolites and hydrocarbons.

Ault and Ayen [25] compared the conversion data for the reaction of nitric oxide with C1 to C8 hydrocarbons over a barium-promoted copper chromite catalyst operated in an integral flow reactor at atmospheric pressure and temperatures of 225° - 525 °C. In general, an increase in carbon number in the hydrocarbon studied resulted in a decrease in the required temperature for a given nitric oxide conversion. For a given carbon number, the required temperature for a given nitric oxide conversion decreased with degree of saturation.

NO decomposition in the presence of excess O<sub>2</sub> with a low concentration straight chain saturated C<sub>8</sub>-C<sub>16</sub> hydrocarbons on copper containing A-type zeolite was observed by Inui et al. [26]. The amount of added hydrocarbons was set at about 0.6 molar ratio of complete combustion stoichiometry. The order of magnitude of the NO conversion was n-C<sub>8</sub> < n-C<sub>10</sub> < n-C<sub>16</sub>, and around 300-350 °C each NO conversion attained maximum.

Petunchi et al. [27] studied the selective reduction of nitric oxide with isobutane in the presence and absence of oxygen over Cu-ZSM-5-14-114. The effect of adding nitric oxide to the HC/He stream in the absence of oxygen was small; the conversion to nitrogen was little affected by the hydrocarbon. When oxygen was added, however, the decomposition was complete at 573 K even at high space velocities (e.g. SVH  $\approx 10^4$ ) even though the combustion was not. Isobutane (an alkane) was more effective than C<sub>3</sub>H<sub>6</sub> (an alkene) for the selective reduction; this is not generally the case.

Cho [28] investigated the steady-state activity of a Cu-ZSM-5 catalyst for NO reduction by hydrocarbons under highly lean conditions. The efficiency of ethylene and propylene, both individually and collectively, as selective reductant for NO reduction is compared at different space velocities in order to characterize their kinetic behavior. Results have revealed that ethylene is a more efficient reductant than propylene due to its superior selectivity.

The catalytic reduction of NO<sub>x</sub> 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<sub>x</sub> by 25% in normal engine operation, and by 40% when C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, or C<sub>4</sub>H<sub>8</sub> was added. The temperature of maximum activation was observed at 400 °C irrespective of hydrocarbon species. However, the effect of CH<sub>4</sub> was small, indicating that the reduction effect depends on the type of hydrocarbon.

The role of oxygen in the selective reduction of nitrogen monoxide by either propane or propene over excessively ion-exchanged Cu/ZSM-5 was observed by d'Itri and Sachtler [30]. In a wide temperature region and in the absence of additives such as steam, propane is a more effective reductant than propene; with propane and in the presence of oxygen reduction of nitric oxide to nitrogen approaches 100% above 600 K.

Burch and Scire [31] studied the selective reduction of nitric oxide by methane or ethane, in the presence and in the absence of a large excess of oxygen on Cu/ZSM-5, Co/ZSM-5, Rh/ZSM-5, and Pt/ZSM-5 catalysts over a wide range of temperatures. It has been found that the maximum nitric oxide conversion is higher with ethane than with methane and the temperature of this maximum is lower with ethane.

The removal of nitric oxide over copper ion-exchanged zeolite catalysts were studied by Iwamoto et al. [32]. They found that direct decomposition and selective reduction of nitric oxide over copper ion-exchanged zeolite catalysts are 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. It was clarified concerning Cu-Z, by using IR, ESR, phosphorescence, TPD, and CO adsorption measurements that (1) the  $\text{Cu}^{2+}$  ions exchanged into zeolite were reduced to  $\text{Cu}^+$  and/or  $\text{Cu}^+ - \text{Cu}^+$  through evacuation at elevated temperature, (2) after exposure to oxygen at 773 K and subsequent evacuation, about 40% copper ions in zeolite existed as  $\text{Cu}^+$  ions, (3) the  $\text{NO}^-$  species formed by adsorption of NO on  $\text{Cu}^+$  would be and the intermediate in the NO decomposition, and (4) redox cycle of  $\text{Cu}^+ = \text{Cu}^{2+}$  in the zeolite is 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 and Cu-Z was remarkably effective for NO removal at temperature as low as 523-673 K. The activity for this selective reduction in  $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$  system was not poisoned very much by addition of  $\text{SO}_2$ . The conversion into nitrogen was changed to 85% (773K) in the presence of  $\text{SO}_2$ , from 100% in absence of  $\text{SO}_2$  which is in contrast with the fact that the catalytic activity for direct decomposition NO was completely lost on adding the same amount of  $\text{SO}_2$ . Furthermore, the reduction rate over Cu-Z at 573 K was higher than those over H-zeolite and alumina catalysts at

723 and 773 K, respectively, which have been reported to be active, after findings by the authors.

d'Itri and Sachtler [33] reported that Cu/ZSM-5 catalysts prepared by impregnation of Cu acetate were active for NO reduction. In mixtures containing both NO and O<sub>2</sub>, reductants such as CO or CH<sub>4</sub> preferentially react with O<sub>2</sub>, but propane reacts preferentially with NO.

Hamada et al. [34] studied the selective reduction of nitric oxide with propane. They suggested that nitric oxide was oxidized to nitrogen dioxide intermediate which is reduced to nitrogen by reaction with propane. The direct oxidation of propane with oxygen is a side reaction. Probably the high selectivity of the reduction is caused by the higher reactivity of nitrogen dioxide to hydrocarbons than that of oxygen over alumina and H-ZSM-5, which are poor catalysts for the activation molecular oxygen. The decrease in nitric oxide conversion to nitrogen at high temperatures could be explained by the high rate of propane - oxygen reaction.

Catalytic reduction of NO<sub>x</sub> with methane in an oxidizing atmosphere over metal exchanged zeolites was studied by Li and Armor [35]. They found the nitric oxide conversion as a function of Si/Al ratio of Co-ZSM-5. The nitric oxide conversions increase rather linearly with decreasing Si/Al ratio, i.e. with increasing the cation exchange capacity. Thus the overall activity of a catalyst was proportional to the number of the exchanged Co<sup>+2</sup> in the zeolite.

Iwamoto and Mizuno [36] found that the activity of Cu-MFI 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.

The previous works clearly demonstrate that copper ion-exchanged ZSM-5 zeolite has capability to selectively reduce nitric oxide with hydrocarbon in the presence of excess oxygen. The reviewed papers also indicate that the catalytic activity of the catalyst depends on zeolite structure, type of hydrocarbon, Si/Al ratio, and the exchange level of copper ion. However, the catalytic activity of ZSM-5 developed so far is limited in a rather narrow temperature range. This limitation inhibits the application of ZSM-5 to real life problem. Thus, this study way 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.