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Heterogeneous catalysis for removal of NO in excess oxygen Progress in 1994

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Abstract

The progress of catalytic decomposition of NO (and N_2O) and selective catalytic reduction of NO by hydrocarbons in the presence of excess oxygen in the past year (1994) have been summarized. There are many reports and suggestions for the active catalysts and the reaction mechanisms in both reaction systems. Several problems, however, remain to be solved at present; for example, enhancement of the catalytic activity, improvement of the life time, suppression of the formation of the harmful by-products and clarification of the reaction mechanisms.

Keywords: NO reduction

1. Introduction

The role of catalysis in environmental improvement is crucial. The concepts or strategies for developing catalysts in the environmental catalysis are quite different from those for the conventional petrochemical catalysis. In the latter case, one can use purified raw materials and apply the best reaction conditions for the production of objective materials. In contrast, environmental catalysts have to work under very severe conditions; very wide temperature range, high space velocity, low concentration of target materials, very high concentration of co-existing gases and poisons, and great change of the reaction conditions. Namely, the environmental catalysts must posses extremely high activity, selectivity and durability. We expect much progress in the near future, both with respect to the development of an environmentally benign technology and in the scientific understanding of the catalytic action.

At present, one of the most significant problems in air pollution is removal of NO_x, which are produced during high-temperature combustion. In particular, the decomposition or reduction of nitrogen monoxide (NO) is a major target to be achieved [1,2]. In this paper the catalytic decomposition of NO and the selective catalytic reduction of NO by hydrocarbons in excess O_2 (SCR–HC) will be introduced. There are a lot of papers dealing with these two catalytic removals of NO. The progress of this field has been reviewed in recent papers [3–14] published in 1994 and, therefore, the results of research in the past year are summarized here.

2. Catalytic decomposition of NO or N_2O

2.1. Catalysts for NO decomposition

It is well known that copper ion-exchanged ZSM-5 (MFI) zeolites are active for direct de-

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composition [3,15]. Much effort has been devoted to enhance the activity and to clarify the reaction mechanism. Eranen et al. found that incorporation of Cu into the zeolite lattice was effective for improvement of the catalytic activity of Cu-MFI, while Co, Ni, or Ag were not [16]. Moretti reported the linear correlation between the turn over frequency of Cu-MFI and the Si/Al ratio when the ion exchange level was 90% or more [17]. Similar results are also revealed by Lee et al. [18]. In addition, they claimed that CuO loaded on zeolite as well as exchanged copper ions is active for the decomposition. In contrast, Zhang et al. reported that CuO supported on the surface of zeolite is inert [19]. On the other hand, there are two interesting reports which clarified that the solid–solid ion exchange between CuO and H-MFI resulted in the formation of Cu-MFI [20] and clarified that the microwave treatment of a mixture of $CuCl_2$ and Na-MFI gave a similar material to Cu-MFI [21]. More detailed investigation would be required to prepare more active catalysts.

Campa et al. [22] showed that the activity of 100% exchanged Cu-MFI was 100 times more than that of the 80% exchanged one and that the kinetic order, with respect to the partial pressure of NO, was 1.1–1.3 and 1.5–1.8 on Cu-MFI and Cu-Y, respectively. The difference between the adsorption of NO on Co-MFI and Co-Y has also been reported; Zhang et al. reported two types of dinitrosyls adsorbates on Co-MFI and only one species on Co-Y [23]. These reports suggest that the high effectiveness of the ZSM-5 zeolite for the decomposition is not only due to the high SiO_2/Al_2O_3 ratio but also due to the structure.

Klier et al. found the high activity of Co–Ce exchanged A-type zeolites [24] but the catalytic activity in flow system should be confirmed to compare the activity. Although La_2O_3 [25] or CeO_2–ZrO_2 [26] has been shown to be active for the decomposition of NO, the active temperatures are still high and the conversion levels have to be improved. As a model catalyst, Xu and Goodman prepared Pd–SiO_2 and concluded that the decomposition proceeded only on the Pd particles with a diameter of 5 nm or more [27].

2.2. Reaction mechanism and characterization of Cu

Characterization of Cu^{2+} ions in Y-type and mordenite zeolites has been summarized by Schoonheydt [28]. In MFI, Larsen et al. recently studied the state of Cu^{2+} by EPR [29]. They showed the presence of two kinds of Cu^{2+} ions with square–pyramidal and square–planar structures and the reduction of about half of Cu^{2+} to Cu^+ upon evacuation at high temperature. Dedecek and Wichterlova found two phosphorescence spectra at 480 and 540 nm after the reduction of Cu-MFI by H_2, CO, or vacuum at 623 K [30]. On the basis of the correlation of the spectra with SiO_2/Al_2O_3 ratio or degree of the ion exchange, the former was assigned to a cuprous ion coordinated to two Al ions and the latter to that on one Al ion. Similar spectra have already been reported by Iwamoto et al. [31] and Anpo et al. [32], in which the spectrum at 540 nm was attributed to Cu^+—Cu^+ species. As Wichterlova et al. has recently pointed out [33], the species giving the spectrum at 540 nm seems to be related with the catalytic activity for the decomposition. Further investigation is anticipated to assign the spectrum and clarify the role of the species.

Sarkany and Sachtler measured the change in IR spectra during the redox cycle of copper ions on Cu-MFI. They found a shift of vibration of zeolite lattice resulting from the Cu^{2+} ion exchange (to 918 cm^{-1}) and change in the position to 969–966 cm^{-1} upon the reduction of Cu^{2+} to Cu^+ [34]. Sachtler and co-workers studied the interaction of the Cu species with NO in more detail [35] and concluded the decomposition mechanism, $2Cu + NO \rightarrow Cu^{2+}\text{–}O^{2-}\text{–}Cu^{2+} + N_2O \rightarrow 2Cu^+ + N_2 + O_2$, which was suggested previously [3]. A tracer method has been applied to clarify the reactivity of lattice oxygen in zeolite during the decomposition of NO and N_2O by Valyon et al. [36]. The results demonstrated the high mobility of the lattice oxygen ions in self-diffusion and the exchange of $N^{18}O$ with the catalyst oxygen under reaction conditions. These conclusions are the same as those [37] reported for the exchange of oxygen between water and zeolite oxygen. The formation of extralattice oxygens and the high mobility of zeolite oxygens afford a possible explanation for the problem of how two oxygen atoms combine to form O_2.

The above-introduced papers all suggest the redox cycles of Cu ions during the decomposition, while there is another suggestion from the group of Shelef [38,39]. They found no change in the intensity of EPR signal of Cu^{2+} before and after the high temperature treatment and concluded no importance of the redox cycle in the decomposition reaction. The results are quite different from the others; it is necessary to study in more detail.

Padley et al. reported on Cu/Al_2O_3 that SO_2 adsorbs selectively on Cu^+ and not on Cu^{2+} [40]. This probably explains the poisoning effect of SO_2 on the NO decomposition.

2.3. Decomposition of N_2O

Nitrous oxide is one of the origins for global warming and ozone layer destruction. Cu-Y was reported to be active for the N_2O decomposition about 15 years ago [41]. Cu- and Co-MFI are also reported as the decomposition catalysts for N_2O by Li and Armor [42]. In the subsequent paper [43], Armor and Farris have shown the usefulness of the solid–solid ion exchange method for the preparation of the Co-MFI catalyst. Armor and Farris [44] also found the unusual stability of Co-MFI in the presence of water vapor at high temperature. The reason for the high hydrothermal stability is unknown at present but it implies the possibility that there are some ways to stabilize the zeolite lattice.

Lintz and Turek observed the isothermal oscillations in the catalytic decomposition of N_2O on Cu-MFI [45]. The addition of oxygen did not change the oscillation, while the presence of small amounts of NO immediately quenched the oscillations and increased the conversion of N_2O. The reasons for the oscillation and the effect of NO addition are not clear yet, but these are very interesting phenomena. In addition to the Cu- and Co-MFI, ferrisilicate [46] and hydrotalcites [47] with Ni and Al are reported to be active for the N_2O decomposition. In particular, the latter is active at the temperature as low as 423–473 K and its activity is much higher than those of Cu- and Co-MFI. Detailed study is expected. Photodecomposition of N_2O on Cu-MFI has been reported by Ebitani et al. [48]. They have suggested the Cu^+—Cu^+ sites as the active center for the decomposition based on phosphorescence measurement [49].

3. Selective catalytic reduction of NO by hydrocarbons

3.1. Catalysts

With zeolite, catalysts Pt-MFI [50] and Co-silicate [51] were reported to be active for the SCR–HC reaction even in the presence of H_2O and SO_2, respectively. The high activity of Cu-SAPO at high temperature in H_2O was also claimed [52]. With oxide catalysts, Ni/ [53] and Ag/Al_2O_3 [54] were found to be active at relatively high temperatures. Especially, the former was active even after the treatment at 973 K. The catalytic activity of La_2O_3 was also reported in the CH_4 system [25] but it was still low compared to those reported so far. Tabata et al. reported the promotive effect of Sn on the catalytic activity of alumina in the NO–O_2–methanol system [55]. Cu–Zr oxides are suggested as an active catalyst, in which propene is a good reductant but propane is not [56].

It should be noted that the physical mixing of two or three kinds of materials was found to be very effective to enhance the catalytic activity. For example, Shpiro et al. reported the increase in the reduction activity by mixing of Cu/Na-

MFI with H-MFI [57]. Yokoyama and Misono found the effectiveness of the mixing of Ce-MFI [58] with CeO_2 or Mn_2O_3, in which the active temperature became lower and the activity higher upon mixing [59]. These reports suggest that the separation of roles of catalysts in the SCR–HC reaction and the good combination of them could result in the increment in the catalytic activity. There lies the possibility that we might have a better catalytic system than those reported so far.

Teraoka et al. observed the simultaneous removal of NO_x and soot particulates on perovskite-type oxides [60]. $La_{0.9}K_{0.1}Cu_{0.7}V_{0.3}O_x$ was the most active and the oxidation of soot and the reduction of NO_x proceeded simultaneously at 573–673 K. Witzel et al. examined the effect of the molecular dimensions of the reductants on the reduction ability [61]. Radtke et al. measured the production of harmful by-products during the SCR–HC reaction. They found HCN on Cu-MFI [62] and HCN and NH_3 on Al_2O_3 [63] as by-products and gave a warning to the production.

Although, the purpose of the research is not to reduce NO, a few papers treated NO as a reactant. Buckles and Hutchings found the enhancement of the catalytic activity for the partial oxidation of propane to propene or benzene by addition of NO into the reaction system [64]. In this study, the mixture of Ga_2O_3 and H-MFI was used as a catalyst, which is a similar combination to those employed in the SCR–HC reaction. Inoue et al. obtained nitrile compounds from NO–alkane or –alkene reaction on Pt–Sn/SiO_2 [65].

3.2. Reaction mechanism

As for the reaction mechanism, there are many suggestions and it is under investigations. At present, three kinds of reaction schemes can be proposed: (a) Decomposition of NO proceeds to yield N_2 and then the hydrocarbons clean up the surface oxygen, or the oxidation reaction of hydrocarbon by oxygen is used to adjust the oxidation state of an active metal ion, (b) some reaction intermediates (HC^*) formed in the oxidation of the hydrocarbon have ability to reduce NO selectively and (c) nitrogen oxides generated from NO and O_2, for example NO_2, can preferentially react with the hydrocarbon.

(a) $2NO \rightarrow N_2 + 2O(ads)$
$HC + O(ads) \rightarrow CO_2 + H_2O$
(b) $HC + O_2\ (\text{or } NO_x) \rightarrow HC^* + CO_2 + H_2O$
$HC^* + NO_x \rightarrow N_2 + CO_2 + H_2O$
(c) $NO + \frac{1}{2}O_2 \rightarrow NO_2$
$HC + NO_2 \rightarrow N_2 + CO_2 + H_2O$

To discuss the reaction mechanism, the following questions should be answered: (1) How does the selective catalytic reduction begin? (2) Where is the active site? What are the roles of metal ions, proton or zeolite cages? (3) What is/are the final intermediate(s) which yields N_2?

Burch and co-workers have investigated the mechanism on Pt-catalysts [66,67] and metal ion-exchanged zeolites [68] and concluded that the key reaction is the decomposition of NO and hydrocarbons are used to remove the surface oxygen species.

Misono and co-workers claimed on Ce-MFI [69] and Pt/SiO_2 [70] that the reaction includes the oxidation of NO to NO_2, the formation of nitro-compounds from NO_2 and the reaction of the nitro-compounds with NO or O_2. With Ce-MFI, the Ce ions were suggested to be active sites for the 1st and 3rd steps. Shelef et al. also suggested the significant role of NO_2 during the reduction on Cu-MFI [71].

Chajar et al. concluded that the role of NO_2 is not so important, though there is the production of NO_2 in the course of the reaction [72]. On the basis of the characterization of the Cu-MFI catalysts by EXAFS and XANES, Liu and Robota have clarified that at high temperature copper existed as Cu^+ even in the oxidative atmosphere and that hydrocarbons were activated on this site and reacted with NO [73].

The states of copper ions during the SCR–HC reaction have been studied by several workers. Grunert et al. found by ESCA, ESR, EXAFS, XANES that there were 6 kinds of copper ions in Cu-MFI and the ionic states (+1 and +2) of copper were dependent on the atmosphere [74]. Chajar et al. indicated the linear correlation between the amount of Cu^+ ions in the zeolite structure and the reduction activity [75]. Itoh et al. found that there were two kinds of cupric ions and the ions were reversibly displaced depending on the presence or absence of a alcohol molecule [76]. The change in Cu^{2+} concentration or zeolite structure with the partial pressure of O_2 has been measured by Pentunchi and Hall [77]. In contrast to these reports, Kucherov et al. again claimed that there was no reduction of copper during the SCR–HC reaction [78]. Taking their papers reported for the decomposition [38,39] into account, Kucherov et al.'s Cu-MFI appears to be hardly reduced.

Another type of NO_x adsorbate, N_2O_3, was suggested on Cu-MFI by Adelman et al. [79]. Tabata et al. clarified that molecular O_2 was not activated on Ga-MFI but adsorbed as atomic species on Cu-MFI [80]. This is in good agreement with the fact that Cu-MFI is a good catalyst for the oxidation of hydrocarbons. The chemisorption of alkenes was also investigated [81].

Very recently, Cowan et al. [82] has compared the reaction rates of CH_4 and CD_4 on Co-MFI and revealed that the former was 2.05–2.4 times faster than the latter. This lead to the conclusion that the rate-limiting step is the dissociation of the C–H bond of methane. Although, the formation of NO_2 is probably the essential step in the methane reaction system as suggested by several workers, the results concluded that the activation of methane is a more significant step. On the other hand, Li et al. [83,84] suggested that the Co–NO_2 species reacts with CH_4 to form a CH_3 radical and the resulting radical further reacts with another Co–NO_2. In the NO–O_2–CH_4 system, the need of the presence of proton sites were clarified on Ga-zeolites [85] and Pd-zeolites [86] at the same time.

Bell et al. [87], Hayes et al. [88] and Bamwenda et al. [89] suggested several intermediates for the reduction but there remain some contradictions; for example, CN species are reported to give N_2 and CO_2 upon the reaction with O_2 on Cu-MFI [88], while no reaction occurs on Rh/Al_2O_3 [89].

4. The future

From the above works can be concluded that the direct decomposition and selective reduction by hydrocarbons are the potential ways to remove NO. The catalytic technologies described in this paper are one of the major breakthroughs in the catalytic chemistry but is not as yet practical. Several problems remain to be solved; for example, enhancement of the catalytic activity, improvement of the life time, suppression of the formation of the harmful by-products and clarification of the reaction mechanisms. The decomposition process is clearly the best method, but the selective catalytic reduction of NO by hydrocarbons in an oxidizing atmosphere would be nearer to an alternative practical method to the present systems [90] than the decomposition process.

This review has been based on the papers published up to the end of February 1995.

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