Selective Catalytic Reduction of NO with Methane

Xiang Gao, Qi Yu, Limin Chen
Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China

[Manuscript received October 16, 2003; revised November 14, 2003]

Abstract: The removal of nitrogen oxides from exhaust gases has attracted great attention in recent years, and many approaches have been developed depending on the application. Methane, the main component of natural gas, has great potential as a NO reductant. In this paper, a number of catalysts previous reported for this catalytic reduction of NO have been reviewed, including a direct comparison of the relative activities and effective factors of the catalysts. Reaction mechanisms have also been explored preliminarily.

Key words: selective catalytic, methane, mononitrogen monoxide, reduction

1. Introduction

NO\textsubscript{x} emitted from exhaust gases and fixed sources has caused severe environmental problems. The removal of nitrogen oxides from exhaust gases mainly adopts three-way catalysts made from noble metals such as Pt, Pd, Rh, etc. Nitrogen oxides emitted from fixed sources are removed via selective catalytic reduction (SCR) with NH\textsubscript{3}, which is the most mature technology and most widely applied in commerce at present. The advantage of this technology mainly lies in that NH\textsubscript{3} has a high selectivity in the reduction of NO\textsubscript{x}, and the presence of oxygen will accelerate the reaction. However, the SCR technology, with NH\textsubscript{3} as the reductant, has the following disadvantages[1]:

(1) The excess NH\textsubscript{3} in the reaction will cause secondary pollution, since NH\textsubscript{3} is a poisonous gas;

(2) Storage and transportation are inconvenient because NH\textsubscript{3} is gaseous under normal temperature and pressure;

(3) When V\textsubscript{2}O\textsubscript{5}—WO\textsubscript{3}—TiO\textsubscript{2} is applied in the industrialized process for the reaction of NO\textsubscript{x} with NH\textsubscript{3}, the catalyst may cause harmful effects to the environment because of the toxicity of vanadium.

By considering all the above shortcomings when using NH\textsubscript{3} as the reductant, new approaches for removing NO\textsubscript{x} from both the fixed sources and the exhaust gases have been investigated. Starting from the 1970’s, hydrocarbons as reductant have attracted great attention. The hydrocarbons, however, will undergo combustion simultaneously in the presence of O\textsubscript{2}, thus limiting their commercial utilizations. After Iwamoto has found that Cu-ZSM-5 is a good catalyst for the direct decomposition of NO and the reduction of NO with non-methane hydrocarbons (NMHC), little significant progresses have been made in this field.

A series of metallic ion exchange molecular sieves, including Cu-, Fe-, Pt-, Co-, Ga-, Ce- etc., have been found to catalyze this reaction. Some catalysts other than molecular sieves, such as noble metals and metal oxides, have also been explored [2].

In the early stage, the study of NO reduction by hydrocarbons were generally focused on NMHCs other than methane, such as ethene, propylene, propane, etc., because methane is difficult to be activated. Then, further studies revealed that a series of catalysts such as Co-ZSM-5, Co-FER, Ga-ZSM-5, La\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}, Pt/SiO\textsubscript{2} etc. were effective catalysts when CH\textsubscript{4} was used as the reductant in the presence of O\textsubscript{2}.

* Corresponding author. Tel: 021-65642298; Fax: 021-65642298; E-mail: lmchen@fudan.edu.cn
of oxygen. At present, more and more researches are focusing on CH$_4$ as a selective reactant for NO reduction. The main reasons are as follows:

1. Methane is the main component of natural gas, which is abundant and cheap.

2. About twenty percent of the hydrocarbons present in the exhausted gas under incomplete combustion is methane.

3. The content of methane is abundant in the exhausted gas of natural gas fueled cars.

Therefore, if a kind of catalyst that is suitable for the commercialized SCR with CH$_4$ can be developed, it will not only help to decrease the environmental pollution, but also increase the utilization effectiveness of resources [3,4].

In the following sections, the reactivity, selectivity and impact factors of catalysts for NO reduction by CH$_4$ will be discussed. Also, the reaction mechanisms will be discussed preliminarily.

2. Thermal reduction of NO without catalyst

The direct reduction of NO by CH$_4$ without a catalyst should be conducted in the absence of oxygen. But since oxygen is always present in the real exhausts, the commercial use of this process is very limited. In the reaction system containing oxygen, there are two competing reactions:

\[
2\text{NO} + \text{CH}_4 + \text{O}_2 \rightarrow \text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (2)
\]

The rate of reaction (2) is much greater than that of reaction (1), that is to say, in the presence of oxygen, the reduction of NO occurs only after the reaction between O$_2$ and CH$_4$ has proceeded to a certain extent. Thus, excess CH$_4$ should be added into the system. Otherwise, the combustion of CH$_4$ will raise the temperature of the system to as high as 1200°C. This high temperature will result in the formation of CO, the by-product of reaction (1), which will then be completely oxidized into CO$_2$. But it will also cause the production of NO, and consequently lower the efficiency of NO removal [3].

In summary, the direct reduction of NO by CH$_4$ without a catalyst will not be widely commercialized because of the high cost and low efficiency.

3. Selective catalytic reduction of NO

3.1. Molecular sieve catalysts

Iwamoto et al. [2] first found that Cu-ZSM-5 could selectively catalyze the reduction of NO. This started the research upsurge of using ion-exchanged molecular sieves as catalysts for NO reduction.

However, in the presence of oxygen, the reactivity of Cu-ZSM-5 for the reduction of NO by CH$_4$ is very low, so Iwamoto et al. classified hydrocarbons as selective (such as C$_2$H$_4$, C$_3$H$_6$ and C$_3$H$_8$) and non-selective (such as CH$_4$ and C$_2$H$_6$). But other researchers found that Co-ZSM-5 exhibited much better selectivity and reactivity for the NO/CH$_4$ system, and the reaction would be promoted when the oxygen concentration was in the range of 1%-21%. At a higher temperature (500°C), the conversion rate of NO was the highest when Co-FER was used. When Co-KL and Co-Y were used, the conversion rate was very low. As for CoO/Al$_2$O$_3$, CoO/TiO$_2$, Co/TiO$_2$, CoO/Silicalite, Co/SiO$_2$-Al$_2$O$_3$ and Co$_3$O$_4$, there were no catalytic reactivities at all.

When no oxygen was present in the system, the reactivity sequence of some catalysts was Rh-ZSM-5>Pt-ZSM-5>Co-ZSM-5>Cu-ZSM-5. But the catalysts followed another sequence of Rh-ZSM-5>Co-ZSM-5>Cu-ZSM-5>Pt-ZSM-5 [5] with the presence of oxygen.

Pd-Na-ZSM-5 showed a poor catalytic activity, while Mn-Na-ZSM-5, Pd-H-ZSM-5 and Pd-H-Ce-ZSM-5 exhibited some good activities for SCR with CH$_4$. The conversion of NO over a Pd-H-ZSM-5 catalyst could reach 70% under the following conditions: reaction temperature 450°C, GHSV 9000 h$^{-1}$, 0.1%NO and 0.2%CH$_4$ in the carrier gas [6].

The reactivity and selectivity of Ga-ZSM-5 and In-ZSM-5 were better than that of Co-ZSM-5 when the reaction temperature was raised to higher than 500°C. But the former ones were more sensitive to water, so that Co-ZSM-5 was better than the other two [3] in a moist gas flow.

For H-type zeolite catalysts, the activities depend on the type of the catalysts. When the reaction was carried out in the absence of SO$_2$ and H$_2$O, the degree of NO conversion at 450°C decreased according to the following sequence: Pd-HZSM-5>Pd-HMOR>Pd-HFER [7].

Berndt et al. studied the potentialities of MFI and MOR zeolites promoted by In and Ce as catalysts for the SCR of NO$_x$ by methane, paying particular emphasis on their stability in the presence of water vapor. They found that the primary role of the CeO$_x$ promoter was to catalyze the oxidation of
NO to NO₂, then NO₂ might react with methane on Lewis-acidic sites and redox active (InO)⁺ species, but further reaction of the intermediates so formed required the presence of residual Brønsted-acid sites. The SCR of NO₂ by methane, however, is partially inhibited by the competitive adsorption between water and the hydrocarbons on the (InO)⁺ species. Higher SCR activity could be achieved by an increase in the hydrocarbon partial pressure in the feed [8].

3.2. Metal oxide catalysts

Generally speaking, the thermal and hydrothermal stabilities of metal oxides are much better than those of the molecular sieves [9]. SnO₂ is more active for the reaction of NO/C₂H₄ than Cu-ZSM-5, because of its greater hydrothermal stability, but SnO₂ is much less active for the reaction of NO/CH₄, as compared to the Co-ZSM-5. Li/MgO and MgO have certain activities for the reaction of NOₓ/CH₄, and the activity of Li/MgO is slightly better than that of the MgO [3].

The catalytic activities of Group IIIB nanocrystalline metal oxides for the reduction of nitric oxide with methane were found to be comparable to that of Co-ZSM-5. Although Group IIA, Group IIIB, and lanthanide oxide catalysts are not as active as certain zeolitic catalysts for the selective catalytic reduction of NOₓ with methane, these materials do exhibit significantly better hydrothermal and high-temperature stabilities than many of the zeolitic systems that have been studied [10].

The performances of Scandium, Yttrium and Lanthanum oxides have also been studied. The activity begins at 400 °C and reaches the maximum at about 625 °C. The activities and selectivities of Sc₂O₃ and Y₂O₃ were higher than those of La₂O₃ in the presence of oxygen. The stability of Y₂O₃ against water and heat was rather good, and the activity loss of Y₂O₃ in the presence of water vapor was not serious [11].

La₂O₃ is more active than Li/MgO. At the similar conversion of NO, the reaction temperature over La₂O₃ catalyst is about 100 °C higher than that of the reaction over Co-ZSM-5. Unlike Li/MgO, La₂O₃ only exhibits activity in the presence of oxygen. At a higher temperature (800–1000 °C), La₂O₃ with 4% (Sr) has a better activity in the reaction NO/CH₄. La₂O₃ loaded on δ- or γ-Al₂O₃ is more active than that of the pure one. At 700 °C, the conversion of NO over La₂O₃ was 60% higher than that over Cu-ZSM-5 [12,13].

It was found that Ga₂O₃ loaded on Al₂O₃ exhibited high activity and selectivity for NO/CH₄, while pure Ga₂O₃ and Al₂O₃ supported on other materials had no activity at all. For Ga₂O₃/Al₂O₃, the activity varies with different ratios of Ga₂O₃, and the highest activity can be achieved when the ratio of Ga₂O₃ is 30%. The high activity and selectivity are caused by the high dispersion of Ga₂O₃ on the Al₂O₃ surface. The reaction activity of Ga₂O₃/Al₂O₃ has been compared with that of the Ga-ZSM-5 and Co-ZSM-5. The results showed that at a high temperature, Ga₂O₃/Al₂O₃ had the highest activity and selectivity, and the resistance against water was better than Ga-ZSM-5 [14].

3.3. Noble metal catalyst

Platinum, Palladium and Rhodium, carried on Al or Si separately, can catalyze the NO/CH₄ reaction to a certain extent. The activity sequence is: Pt/Si>Pt/Al>Pd/Al>Pd/Si>Rh/Al>Rh/Si. The sequence for SCR of NO with CH₄ is different from that for the CH₄ oxidation reaction, in which Pd has the highest catalytic reactivity, while for the NO/CH₄ reaction, Pt exhibits the highest activity. In addition, it can seen that Si is a good support for Pt, while Al is a good support for Pd or Rh.

It has been thought that the controlling step of the reaction is the breaking of the C—H bonds in CH₄, but this hypothesis is not true, because the catalytic activities of Pt, Pd and Rh for the oxidation of CH₄ and the catalytic activities for NO/CH₄ are different. The conversion of NO to N₂ involves the dissociation of NO on the reduced surface sites, which may be metal atoms in the case of Pt, or oxygen anion vacancies in the case of Pd and Rh. Moreover, formation of N₂O was found when Pt or Pd was used as catalysts [15].

Ohtsuka found that the effects of noble metals toward NO₂ reduction by methane can be categorized into the following three groups: (1) low activity for NO oxidation to NO₂, and high activity for NO₂ reduction to N₂ (Pd, Rh); (2) high activity for NO oxidation to NO₂, and low activity for NO₂ reduction to N₂ (Ru, Ir, Pt); (3) low activity for both reactions (Ag, Au) [16].

4. Effects of some factors for the reaction activity and selectivity of the catalysts

4.1. The effect of the support
As we all know, the support has a great influence on the activity of a catalyst, but the studies on the influence of the supports are still superficial, which can not explain why different kinds of supports have different activities. For example, there is no proper explanation why Ferrierite is better than ZSM-5, and Co-FER has a higher activity than Co-ZSM-5 under the same conditions [17].

Co$_3$O$_4$ in cluster forms, and CoO loaded on Al$_2$O$_3$ or SiO$_2$-Al$_2$O$_3$ have no catalytic activities for the NO/CH$_4$/O$_2$ reaction. This may indicate that the uniformly and finely dispersed Co ions have an effect on the activity [2]. Moreover, it was found that the dispersion of the molecules in the Co-mordenite molecule sieve channels also has some influence on the reactivity. [18] It has also been found that there is a large amount of Pd particles on the surface of Pd-H-ZSM-5 [7].

In conclusion, the inner crystalline dispersion on the support, the porosity, and the distribution state of the metal atoms are all important factors for the catalytic activity as well as the hydrothermal stability of the supporter.

4.2. The effect of the states of active species

The particle size and the chemical state of the active species have great effects on the NO/CH$_4$ reaction.

NO is selectively reduced by CH$_4$ to N$_2$ over well-defined Ru nanoparticles supported on γ-Al$_2$O$_3$, which starts from 450 °C. At 450 °C, CH$_4$ is selectively oxidized by NO to CO$_2$ and H$_2$O over the catalyst (12%Ru/Al$_2$O$_3$) with larger Ru nanoparticles (d ≥5 nm), but over small Ru nanoparticles (d <5 nm), CH$_4$ is directly converted by NO to CO and H$_2$ in the temperature range 450–600 °C. And the stabilities of the two kinds of Ru nanoparticles are also different. The catalyst with a large fraction of small Ru nanoparticles (6% Ru/Al$_2$O$_3$) is easily to be deactivated under the presence of air or NO, whereas the catalyst with large Ru nanoparticles (12% Ru/Al$_2$O$_3$) is less sensitive to oxygen poisoning [19].

The promotion of Ag-ZSM-5 by cerium for the selective catalytic reduction (SCR) of NO with methane in the presence of excess oxygen was studied. The results showed that silver existed mainly as dispersed Ag$^+$ ions in low Ag-content (Ag/Al<0.5–0.6) Ce-Ag-ZSM-5 samples, while nanoparticle silver with about 10 nm was also found on the surface of high Ag-content samples. The Ag$^+$ in a dispersed state was more active for the SCR reaction than the nanoparticle silver, whereas silver particles effectively catalyzed the methane combustion reaction [20].

Four kinds of Pd/H-ZSM-5 catalysts with different states of Pd (high or low dispersion, and with preoxidized or prereduced treatments) and Pd/Na-ZSM-5 were also investigated. The focus was on the relations between the states of Pd and the catalytic performance. The results showed that the Pd atoms in the Pd/H-ZSM-5 (high dispersion and preoxidized) were mostly in the isolated Pd$^{2+}$ state, and distributed almost uniformly in the zeolite particle. The catalyst showed a high activity for NO reduction in the early stage, and reached a steady state rapidly. The Pd on the Pd/H-ZSM-5 (high dispersion and prereduced), which was initially in a highly dispersed metallic state, was oxidized very quickly in the NO-CH$_4$-O$_2$ stream. The state of Pd and the catalytic performance after the oxidation exhibited a similar behavior as the Pd/H-ZSM-5 (high dispersion and preoxidized). Pd/H-ZSM-5 (low dispersion, preoxidized or prereduced) had initially large PdO and Pd$^0$ particles (14–16 nm) on the external surface, which were dispersed gradually into the micropores as isolated Pd$^{2+}$ because of the quick oxidation of Pd$^0$. The catalytic performance changed correspondingly, that is, the catalyst showed a high activity for NO reduction and a low activity for CH$_4$ oxidation. In the steady state at 673 K, all four kinds of catalysts showed the same high activity for NO reduction and modest activity for the CH$_4$ oxidation, corresponding to the same state of Pd. For the preoxidized Pd/Na-ZSM-5, it showed a low activity for the NO reduction. The preoxidized Pd atoms on Pd/Na-ZSM-5 existed mainly in the form of PdO particles (17 nm) on the external surface, and they changed little during the reaction. These results clearly demonstrate that isolated Pd$^{2+}$ ions in the zeolite micropores are active and selective species for NO reduction, and PdO particles on the external surface are active mainly for the CH$_4$ oxidation [21].

4.3. The effect of cooperative action

When some other catalytic active components are added into the catalyst, the effect may be changed.

The activity of Pd-Pt/SZ (sulfated zirconia) was noticeably higher than that of either Pd/SZ or Pt/SZ. A cooperative action of Pd and Pt, in which the Pd acts as the sites for the reaction of NO$_2$ with methane and the Pt catalyzes NO oxidation to NO$_2$, was sug-
gested. The addition of Pt to Pd/MOR showed a similar improvement, but the effect was much more pronounced for the Pd/SZ [22].

Tonetto et al. found that the activity of Pd-Mo/Al₂O₃ for the NO/CH₄ reaction was higher than the corresponding Pd- and Mo-supported catalysts prepared by the same method in the temperature range 200–500 °C. On the other hand, a decrease in the activity (at 500 °C) was observed over the Pd-Mo/Al₂O₃ samples after 2 h under the reaction conditions, being similar to the activity displayed by the Pd/Al₂O₃. This is thought to be associated with a poisoning of the MoO₃ sites by the oxygen formed during the dissociation of NO. The oxygen taken up by the MoO₃ species does not seem to be removed by methane. The higher initial activity on bimetallic catalysts is attributed to the greater number of active sites and a synergetic effect between Pd and Mo [23].

4.4. The effect of water vapor

The existence of water has a great effect on the rates and thermodynamics of the reactions. It was found that aluminum atoms will leak out irreversibly from the skeleton of Cu-ZSM-5 molecule sieve when water vapor exists at 683 K. So, it is thought that under high temperatures and high water vapor concentrations, aluminum atoms in the skeleton of the sieves will permanently lose, which will lead to the loss of catalytic activity of the copper ions loaded on those aluminum atoms.

Unlike Cu-ZSM-5, a decrease in catalytic activity of Co-ZSM-5 or Co-FER in the presence of water vapor has been found. For example, for the Co-ZSM-5, when there was 10% of water vapor, the rate of NO conversion fell sharply, but this decrease was reversible. Such effect can be offset by raising the reaction temperature, because higher temperatures can decrease the partial pressure of water vapor.

The Langmuir-Hinshelwood dynamic model is sometimes used to explain this effect:

\[ r = \frac{k[N\text{O}][\text{CH}_4]}{1 + k_1[N\text{O}] + k_2[\text{H}_2\text{O}]} \]

According to this model, NO is in competition with H₂O. A rise in temperature will reduce the partial pressure of water vapor, and thus accelerate the adsorption and reduction of NO. TPD (Temperature Programmed Desorption) experiment results of Co-ZSM-5 agrees with this explanation [2].

Pd-MOR (0.47%Pd) showed a stable activity in the absence of water vapor at 450 °C for more than 30 h, while the NO₂ conversion decreased gradually in the presence of water vapor. Pd-ZSM-5 (0.58%Pd) showed a gradual decrease in NO₂ conversion even in the absence of water vapor and almost lost the activity completely in 20 h in the presence of water vapor. CO adsorption measurements revealed that Pd-ZSM-5 tested in the presence of water suffered from the severest decrease in Pd dispersion. These results suggested that deactivation of the Pd-zeolite is caused by Pd agglomeration to form PdO, and water vapor promotes the agglomeration [24].

4.5. The effect of sulfur dioxide

Natural gas contains traces of sulfur, which is usually in the form of sulfur dioxide. Over a Co-ZSM-5 catalyst, in the absence of water, the addition of 53 ppm SO₂ slightly decreased the conversion of NO at 500 °C, but doubled the decrease in NO conversion at 550 and 600 °C. In the presence of both SO₂ and 2%H₂O, a substantial decrease in the NO conversion was found at a temperature below 500 °C, but no change was observed at 600 °C. Over a Co-FER catalyst, the addition of 53 ppm SO₂ caused a sharp decrease in NO conversion. Thus, the Co-FER catalyst is more sensitive to SO₂ than the Co-ZSM-5 [3].

The effect of SO₂ on the activities of Co-FER and Co-ZSM-5 can be explained by the adsorption effect. Temperature-programming adsorption/desorption experiments showed that, when both catalysts are exposed to a gas flow containing SO₂, thirty percent of the cobalt adsorption sites are taken by SO₂, and so the adsorption sites for NO will decrease, which makes the catalyst more active for the oxidation of CH₄ than for the reduction of NO [2].

Other researches showed that over catalysts of Pd supported on pentasil zeolites, sulfur dioxide alone had no apparent effect on the activities for NO₂ reduction, but the coexistence of water and SO₂ inhibited both NOₓ and methane conversions. The extent of inhibition by water and SO₂ on NOₓ reduction is Pd-HFER>Pd-HZSM-5>Pd-HMOR. Acid mordenite doped with low levels of Pt and Pd leads to an active catalyst that is more tolerant to the presence of either water or SO₂ than the corresponding monometallic Pt- and Pd-MOR. Nevertheless, NOₓ reduction is also inhibited at temperatures below 450 °C when SO₂ and water are both present. TPD experiments
of water over calcined samples of Pd supported on protionic pentasil zeolites, Pd/γ-Al₂O₃ and Pt-Pd-HMOR with and without pretreatment in SO₂+O₂ atmosphere indicated that sulfation of the surface could increase water chemisorption by the support. Therefore, when SO₂ and H₂O coexist in the feed stream, the decrease in NO₂ reduction on Pd loaded zeolite catalysts may be due to the enhanced water inhibition and presumably active site poisoning [7].

In summary, the effect of SO₂ is strongly related to the operation temperature, the presence of water vapor, and the type of molecular sieve.

4.6. The effect of feed stream

Fliatoura et al. have investigated the effects of O₂, CO₂, H₂O in the feed stream on the CaO catalyst. They found that when a CaO catalyst is used, the addition of O₂ at concentrations as high as 10 mol% had no effect on the activity of the CaO catalyst at 650 ℃, but at 770 ℃ a significant decrease in NO conversion was evident. CO₂ (2.5 mol% in the feed stream) was found to inhibit the reduction of NO, especially in the range of 500–650 ℃. However, the inhibiting effect of 5 mol%H₂O in the feed stream was small in the range of 500–650 ℃, while the influence of water on NO conversion in the range of 700–850 ℃ appeared to be slightly positive [25].

5. Reaction mechanisms

The discussion of mechanisms is not limited to the NO/CH₄ reaction, because the mechanisms vary a lot with the catalyst and the reductant when hydrocarbons are chosen to be the reductant of NO. Yet whatever the catalyst or reductant is, the reactions are of the same type, there should be some similarity and comparability. No matter what the details of the mechanisms are, there will be two key questions:

(1) How are the hydrocarbons activated, i.e. how is the C—H bond broken?
(2) How is nitrogen formed, i.e. how is the N—N bond formed?

In the following section, some mechanisms will be reviewed [2,26,27]:

(1) Mechanism put forward by Iwamoto and Mizuno. The key step is the production of the intermediate oxidation product. The mechanism is as follows:

\[
\text{C}_2\text{H}_y \xrightarrow{\text{O}_{2/\text{NO}}^2} \text{C}_2\text{H}_y(\text{O}, \text{N})(\text{intermidate})
\]

\[
\text{NO/O}_2 \xrightarrow{} \text{CO}_2(\text{CO})
\]

Hydrocarbons are partially oxidized by oxygen, forming a certain kind of intermediate product which will further react with NO for producing nitrogen.

(2) Another mechanism which includes the formation of NO₂.

\[
\text{NO} \xrightarrow{\text{O}_2} \text{NO}_2 \xrightarrow{\text{C}_2\text{H}_y} \text{C}_2\text{H}_y\text{O}_2
\]

\[
\text{NO}_x \xrightarrow{\text{CO}_2(\text{CO}) + \text{N}_2 + \text{H}_2\text{O}}
\]

NO is oxidized homogeneously into NO₂, which further oxidizes hydrocarbons into intermediate oxidation products, and finally produces N₂. The mechanism is similar to the first one, but it explicitly describes that the intermediate product C₂H₉O₂ is formed via the formation of NO₂.

(3) Armor et al. put forward a mechanism on how Co exchanged molecular sieves catalytically reduce the reaction NO/CH₄/O₂ as below:

(a) \(\text{Z—Co+NO} \iff \text{Z—Co—NO}\)
(b) \(\text{Z—Co—NO}+1/2\text{O}_2 \iff \text{Z—Co+NO}_2\)
(c) \(\text{CH}_4+\text{Z—Co+NO}_2 \rightarrow \text{CH}_3^+\text{Z—Co—HNO}_2\)
(d) \(\text{CH}_3+\text{Z—Co+NO}_2 \rightarrow \text{Z—Co+NO}_2\text{CH}_3\)
(e) \(\text{Z—Co+NO}_2\text{CH}_3+\text{NO} \rightarrow \text{N}_2+\text{CO}+\text{H}_2\text{O}+\text{Z—Co—OH}\)
(f) \(\text{Z—Co—OH+NO} \rightarrow \text{Z—Co—HNO}_2\)
(g) \(2\text{Z—Co—HNO}_2 \rightarrow \text{NO+NO}_2+\text{H}_2\text{O}+2\text{Z—Co}\)

The mechanism explains why the existence of gaseous oxygen can accelerate the reaction. NO is adsorbed on the active sites of Co, and reacts with O₂ to form Z—Co—NO₂. It is the Z—Co—NO₂ that activates CH₄ to form Z—Co—NO₂CH₃, which reacts with NO to form N₂.

(4) Cant et al. explained selective catalytic reduction with methane on Co-MFI as follows:

(a) \(\text{CH}_4 + \text{NO}_2(\text{ads}) \rightarrow \text{CH}_3+\text{HONO}\)
(b) \(\text{CH}_3+\text{NO} \rightarrow \text{CH}_3\text{NO}\)
(c) \(\text{CH}_3+\text{NO}_2 \rightarrow \text{CH}_3\text{NO}_2\)
(d) \(\text{CH}_3\text{NO}_2 \rightarrow \text{CO}_2+\text{NH}_3\)
(d) \(4\text{NH}_3+4\text{NO}+\text{O}_2 \rightarrow 4\text{N}_2+6\text{H}_2\text{O}\)
They thought that NO must first be oxidized to NO$_2$ to provide a site which can abstract hydrogen from the hydrocarbon. The same or another NO$_x$ then produces a nitroso or nitro intermediate, which generates through a series of rearrangement and degradation steps a reduced nitrogen centre. The conversion to N$_2$ then requires another NO$_2$ molecule. Hydrogen abstraction by an adsorbed NO$_x$ species is the rate determining step when methane is used as the reductant over Co-MFI, and a nitro route appears to be marginally favoured over a nitroso one.

(5) Liese et al. have done some researches on the selective catalytic reduction of NO by methane over CeO$_2$-Zeolite, and explained their experiment results as follows:

It is suggested that a short-lived intermediate (nitro- or nitroso- methane) is formed from adsorbed NO$_2$ or nitrate and methane on the CeO$_2$ surface, which can activate both NO and methane. The intermediate is detached from CeO$_2$ sites and transformed to nitroso and carbon oxides over Bronsted sites of the adjacent zeolite. In the voids of inactive zeolites (e.g. Na forms) or upon further contact with CeO$_2$, the intermediate undergoes unselective radical reactions, resulting in the formation of carbon oxides and NO. This mechanism is basically different from other bi-functional mechanisms for HC-SCR discussed in the literature so far.

In this paper the activities of various catalysts for the reaction NO/CH$_4$ and their impacting factors are reviewed, and a preliminarily exploration on the reaction mechanisms is discussed. All the catalysts, Co-ZSM-5, Co-FER, Mn-Na-ZSM-5, Pd-H-ZSM-5, Pd-H-Ce-ZSM-5, Sc$_2$O$_3$, Y$_2$O$_3$, La$_2$O$_3$, Ga$_2$O$_3$, Pt, Pd, Rh, etc. have certain reactivity, but they are affected by SO$_2$ and H$_2$O. And their reactivities are also related to the existence of gaseous oxygen and the properties of the carriers. At present, these catalysts are still not suitable for commercial applications. Further researches are required to find out catalysts which have high activities in an aerobic condition, not easy to be affected by SO$_2$ and H$_2$O, and have good stabilities.

References