Overview on the selective lean NO_x reduction by hydrocarbons over Pt-based catalysts

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Selective catalytic reduction of NO_x with hydrocarbons (HC-SCR) has received much attention as one of potential technologies for reducing NO_x emissions under lean-burn conditions. Pt/ZSM-5 prepared by sublimation method and Pt/V/MCM-41 catalysts have been introduced for the wider activity temperature window than those Pt catalysts reported previously. The influence of pre-treatment, oxygen concentration, water and SO_2 on the activities of Pt-based catalysts has been discussed. Combinatorial catalysis, which has been developed recently for discovering the practical HC-SCR catalysts quickly, has been introduced too. Finally, the reaction mechanism of HC-SCR over Pt-based catalysts has been briefly discussed.

KEY WORDS: selective catalytic reduction; NO_x; lean-burn conditions; activity temperature window; combinatorial catalysis.

1. Introduction

Substantial improvement in fuel economy can be achieved for lean-burn gasoline and diesel engines, which are operated under oxygen-rich conditions. However, for these vehicles, the conventional three-way catalysts (TWC) are no longer effective for NO_x reduction due to net-oxidizing conditions of their exhaust streams. Since Held *et al.* [1] and Iwamoto *et al.* [2] reported that selective reduction of NO_x by hydrocarbons proceeded under lean-conditions over Cu-ZSM-5 catalyst in early 1990's, the selective catalytic reduction of NO_x by hydrocarbon has been studied extensively on several different catalytic systems, namely, metal oxide [3–5], ion-exchanged zeolites [6–8] and noble metal catalysts [9]. For zeolite-based catalysts, the major drawbacks are the poor hydrothermal stability and the low activity in the presence of H_2O and SO_2 [10,11]. The activities of metal oxide catalysts are also seriously inhibited by the presence of SO_2 [12]. In contrast, Pt-based catalysts appeared to be active and robust materials to catalyze the de-NO_x reaction [13]. In this article, we focused on some of the recent studies carried out in our laboratory on the selective catalytic reduction of NO_x over Pt-based catalysts.

Previous studies have shown that Pt supported catalysts are active at low temperature region, probably as a result of their high capabilities to oxidize hydrocarbons. However, the narrow activity temperature window is one of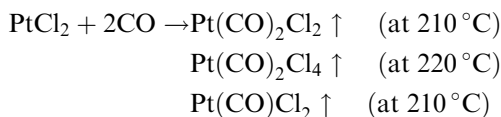 the obstacles for the practical application [12]. At relatively high temperatures, the combustion of reducing agent becomes predominate and there is not enough reducing agent to reduce NO_x. In order to widen the activity temperature window, novel preparation method was used and a second metal was also added. In the following section, details of the preparation of Pt/ZSM-5 and Pt/V/MCM-41 catalysts are first described.

2. Catalyst preparation

The Pt/ZSM-5 catalyst was prepared by two methods: one is conventional ion-exchanged method and the other is sublimation method. For the ion-exchanged method [14], the Na/ZSM-5 was first synthesized with a Si/Al ratio of 30 according to the patent [15]. After exchange in an aqueous solution of $Pt(NH_3)_4Cl_2$ at room temperature for 24 h, the solid was thoroughly washed with deionized water and dried at 100 °C overnight. In some cases, Pt/ZSM-5 catalysts were pre-treated by different ways and were thus designated as follows: (1) heated (4 °C/min) in a flow of He (150 cm^3/min) up to 500 °C and maintain for 2 h (sample-He-500); (2) heated in a flow of oxygen (50 cm^3/min) in the following manner: 20–250 °C (0.7 °C/min), 250–310 °C (0.3 °C/min), and at 310 °C for 3 h (sample-O_2-310); (3) heated (4 °C/min) in a flow of oxygen (50 cm^3/min) up to 500 °C and maintain for 2 h (sample-O_2-500); (4) after pre-treatment of (2) and cooled down in He to room temperature, the sample was then heated (1 °C/min) in flow of H_2 (20 cm^3/min) up to 310 °C and maintained for 2 h (sample-O_2-310-H_2-310).

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For the novel sublimation method [16], the parent NH$_4$-ZSM-5 zeolite was transformed to H-ZSM-5 by calcination in O$_2$ at 500 °C for 4 h. Then the calcined H-ZSM-5 was loaded into one side of a U-shaped reactor and PtCl$_2$ into the other side of the reactor as shown in figure 1. Platinum dicarbonyl chloride, *cis*-Pt(CO)$_2$Cl$_2$, can be obtained by passing CO in a long vertical tube to PtCl$_2$ at 220 °C. The carbonylation of platinum halides occurs as follows:

$$PtCl_2 + 2CO \rightarrow Pt(CO)_2Cl_2 \uparrow \quad \text{(at 210 °C)}$$
$$Pt(CO)_2Cl_4 \uparrow \quad \text{(at 220 °C)}$$
$$Pt(CO)Cl_2 \uparrow \quad \text{(at 210 °C)}$$

Then the sample was washed with doubly deionized water, dried at 110 °C overnight and calcined under O$_2$ at 600 °C for 4 h.

Pt/V/MCM-41 was prepared by step impregnation method [17]. To obtain MCM-41, 37 g Ludox AS-40 (40% colloidal silica in water, stabilized with ammonia) was mixed with a 30 g of 20 wt% tetraethylammonium hydroxide (TEAOH) solution and stirred well for 1 h. Next, 50 g of 20 wt% hexadecyltrimethylammonium bromide (HDTABr) solution was added drop-by-drop to this mixed solution. After stirring for 1 h, the mixture was charged into a 250 ml polypropylene bottle and kept at 100 °C for 5 days. Subsequently, the material formed was filtered, washed with water, dried at 80 °C for 24 h and calcined at 500 °C for 6 h in air. Pt/V/MCM-41 was obtained by first impregnating MCM-41 with a vanadium actylacetonate toluene solution, drying at room temperature, and calcining at 500 °C for 5 h, then impregnating the V/MCM-41 with a platinum acetylacetonate toluene solution, drying at room temperature and calcining at 550 °C for 5 h.

3. Wide activity temperature window

Figure 2 compares the activities of Pt/ZSM-5-9.85 (Pt loading is 9.85%) prepared by the sublimation method and Pt/ZSM-5-9.7 (Pt loading is 9.7%) prepared by the
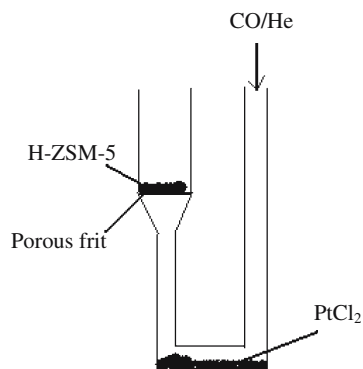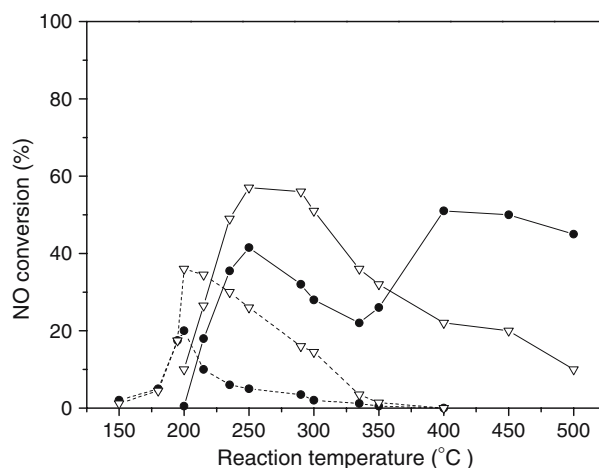

Figure 2. Comparison of conversion of NO to N$_2$ (●, solid line) and N$_2$O (∇, solid line) catalyzed over Pt/ZSM-5-9.85 prepared by sublimation method with that of NO to N$_2$ (●, dashed line) and N$_2$O (∇, dashed line) catalyzed over Pt/ZSM-5-9.7 prepared by the ion-exchanged method (Reaction conditions for Pt/ZSM-5-9.85: 0.27% C$_3$H$_6$, 0.2% NO and 3% O$_2$, GHSV = 42,000 h^{-1}; reaction conditions for Pt/ZSM-5-9.7: 0.1% C$_2$H$_4$, 0.1% NO and 2% O$_2$, GHSV = 72,000 h^{-1}) [16].

ion-exchanged method [16]. The conversion of NO over Pt/ZSM-5 prepared by ion-exchanged method shows a maximum at 200 °C, then it decreased to zero at 400 °C. The curve of NO conversion as a function of reaction temperature, which presents a typical volcano-shape, is similar to those of Pt-based catalysts reported previously. In contrast, the curve is noticeably different over Pt/ZSM-5 prepared by the sublimation method. The curve of NO conversion to N$_2$ showed two maximum peaks, both of which are much larger than that observed on Pt/ZSM-5 prepared by ion-exchanged method. The first maximum conversion of NO to N$_2$ was obtained at 250 °C and the second one was obtained at about 400 °C. Even at 500 °C, the conversion to N$_2$ is still high (40%). In addition, the conversion of NO to N$_2$O is also significantly higher.

Based on the results of the static secondary ion mass spectroscopy (SIMS), it was proposed that the residual chlorine from PtCl$_2$ precursor still remains on Pt/ZSM-5-9.85 catalyst surface after calcining when using the sublimation method [18]. The presence of chlorine increases the acidity of the support [19] and thus results in the formation and deposition of carbonaceous materials [20]. Below 300 °C, the presence of deposited carbon can deactivate the oxidation of propene, resulting in more propene present for the reduction of NO and higher NO conversion obtained than that over Pt/ZSM-5-9.7 catalyst prepared by ion-exchanged method. At high temperatures, although the propene is vanished, the deposited carbonaceous materials can act as reducing agent and react directly with NO to produce N$_2$ over Pt sites located inside channel of ZSM-5. As a result, another NO conversion peak appears above 350 °C. This fact indicates that

Figure 1. Apparatus for the preparation of Pt/ZSM-5 by the sublimation method [16].

novel sublimation preparation method can remarkably improve the activity of Pt-ZSM-5 catalyst.

Besides using novel preparation method, the activity temperature window can also be broadened by designing multifunctional catalyst over which there are several types of reaction sites. For example, Pt/V/MCM-41 catalyst exhibits wide activity temperature window for the selective catalytic reduction of NO with C_3H_6 [17,21]. The maximum NO conversion is sustained over a wide temperature range of 70 °C from 270 to 340 °C. Moreover, the curve of the NO conversion to N_2 versus temperature exhibits three peaks. This is due to three different reactions occurring over Pt/V/MCM-41 catalyst: one is the reaction occurring on usual Pt-based catalyst, the second one is that between NO and carbonaceous species, and the third reaction is that occurring on V/MCM-41 [22].

Over some metal oxide catalysts, such as Ag/Al$_2$O$_3$ catalyst, if the reducing agent is higher alkane (such as octane), the carbon deposition can be occurred and the formation of carbonaceous materials plays a negative role because it covered the active sites and thus inhibited the SCR reaction to proceed [23]. However, over Pt/ZSM-5 prepared by sublimation method and Pt/V/MCM-41 catalysts, the deposited carbon becomes useful since it acts as reducing agent to reduce NO [16,22].

4. Effect of pre-treatment

It is well known that the nature of the active sites plays an important role for the reduction of NO$_x$. For Pt-based catalysts, Burch *et al.* [24] proposed that the platinum metal atoms are active sites. Our research has also demonstrated that reduced platinum sites are active for the reduction of NO. The activities of Pt/ZSM-5 catalysts pre-treated in the different gas atmospheres were compared and the results were shown in figure 3 [14]. It can be seen that the catalyst pre-treated in H$_2$ or He exhibited higher activity than those pre-treated in

oxygen at different temperatures. The activity temperature windows of the oxidized catalysts shifted to higher temperatures and the maximum NO conversions were also decreased. Due to the pre-treatment in H$_2$, the platinum sites are present in reduced state on Pt/ZSM-5 catalyst. Its activity does not vary much as the reaction time prolonged at the maximum conversion temperature indicates the pre-reduced platinum sites are hardly oxidized by oxygen at the similar pre-treated temperatures. So the pre-reduced Pt/ZSM-5 catalyst exhibited high durability in the SCR reaction. For sample-O$_2$-310 and sample-O$_2$-500, the oxidized platinum sites can be reduced by propene only at relatively high temperatures. So both of them start to show reduction activities at temperatures higher than the pre-reduced catalyst. The lowest activity of sample-O$_2$-500 lies in the fact that the high calcination temperature makes the reduction of platinum ions more difficult. This fact also indicated that the presence of propene has two functions: one is acting as reducing agent to react with NO, the other is reducing the platinum ions to active sites.

Figure 4 illustrates the effect of pre-treatment condition on the activity of Pt/ZSM-5-9.85 catalyst prepared by sublimation method [16]. It can be seen that the pre-treatment can change the temperature window of the catalyst, although it seldom affects the conversion of NO to N$_2$O (not shown). The maximum conversion of NO over the pre-reduced Pt/ZSM-5-9.85 catalyst shifted to higher temperature compared with those over pre-oxidation catalysts. That means the pre-oxidation catalysts are more active. As described above, the second NO conversion peak is due to the reaction between deposited carbon and NO [18]. In this case, the oxidized platinum sites may be more active for activating the deposited carbon to hydrocarbon intermediates, which then reacted with the activated NO to produce N$_2$. Over the pre-reduced Pt/ZSM-5 catalyst, the deposited carbon can only be activated at elevated temperatures. As a result, the maximum conversion of NO over the pre-reduced Pt/ZSM-5 catalyst was obtained at higher
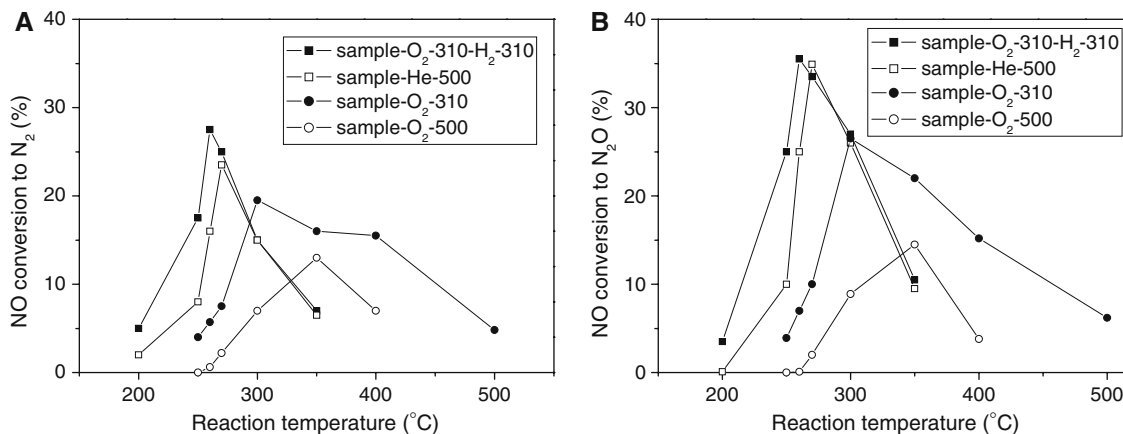

Figure 3. Conversions of NO to N$_2$ (A) and N$_2$O (B) at various temperatures over Pt/ZSM-5 catalysts with different pre-treatment. (Reaction conditions: 0.1% C$_3$H$_6$, 0.1% NO and 2% O$_2$, GHSV = 10,200 h^{-1}) [14].
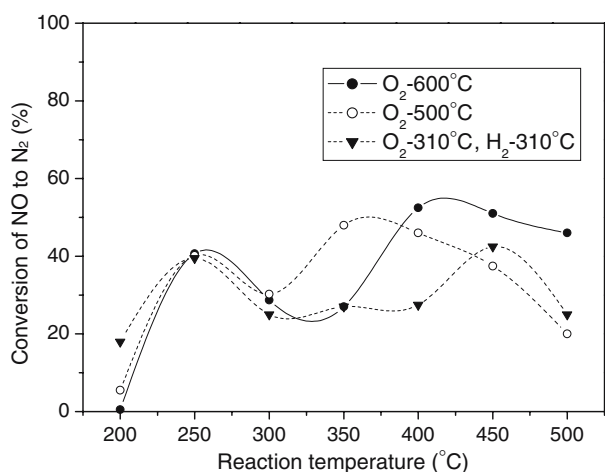
Figure 4. Effect of pre-treatment conditions on the activity of Pt/ZSM-5-9.85 catalyst. (Reaction conditions: 0.27% C$_3$H$_6$, 0.2% NO and 3% O$_2$, GHSV = 42,000 h^{-1}) [16].

temperatures. Combined with the results shown in figure 3, it can be seen that for Pt/ZSM-5 catalyst prepared by different preparation method, the effect of the pre-treatment on the activity is also different. So when preparing the HC-SCR catalyst, using an appropriate preparation method and pre-treatment atmosphere could help to improve its activity.

Besides the nature of the active sites, the activity of Pt-based catalyst was also affected by reaction conditions. Compare with the stoichiometric engines, the noticeable character of diesel engine and lean-burn gasoline engine is that their exhaust contains much more O$_2$. And in the SCR reaction, oxygen also plays an important role. Thus the effect of oxygen concentration on the activity of HC-SCR catalyst has been widely investigated.

5. Effect of O$_2$

Different from the usual Pt-based catalyst, Pt/V/MCM-41catalyst exhibits a complex performance curve as described above. The effect of O$_2$ on the activity of Pt/V/MCM-41catalyst was further studied. It was found that both the conversion of NO to N$_2$ and N$_2$O was increased with the concentration of O$_2$ increased from 0 to 3% and thereafter gradually decreased at further higher O$_2$ concentration [17]. This phenomenon only occurred at relatively low temperatures, at which the function of oxygen may be cleaning the Pt surface by oxidizing the carbonaceous materials deposited on it [24]. Much higher oxygen leads to the combustion of propene and less reducing agent remained for the SCR reaction. As a result, the conversion of NO was decreased. At higher temperatures, even a small amount of oxygen added can lead to the unselective combustion of reducing agent. So at 450, the conversion of NO to N$_2$ reached maximum in the absence of oxygen and it monotonically decreased as adding more oxygen. For

5%Sn/Al$_2$O$_3$ and 5%Sn–0.5%Ce/Al$_2$O$_3$ catalysts, the conversion of NO was significantly improved with the increase of oxygen concentration from 1 to 3%. Further increase the oxygen concentration, the NO conversion almost maintained unchanged [25]. The reason is that Sn/Al$_2$O$_3$ catalyst shows poor ability to activate propene and the presence of oxygen not only contributes to the activation of propene but promote the oxidation of NO to NO$_2$, which is more reactive intermediate. Thus, the hydrocarbon-oxidation activity for a given catalyst can be reflected by the effect of O$_2$ on the activity of lean-NO$_x$ reduction.

It seems that oxygen plays two roles in the HC-SCR reaction. On one hand, oxygen reacting with reducing agents decreased the efficiency of reductant for NO$_x$ reduction, especially at higher temperatures. On the other hand, oxygen also shows some positive effects such as activating NO and hydrocarbons, both of which contribute to the NO$_x$ reduction to proceed. For Pt-based catalysts, the former negative effect may be more pronounced. Over some metal-oxide catalysts, the promoting effect of oxygen can be observed due to the latter positive effect.

6. Effect of H$_2$O and SO$_2$

In actual exhaust water and SO$_2$ exist. The resistance against water and SO$_2$ is an important factor in the assessment of any catalyst with potential deNO$_x$ application. So the effect of water and SO$_2$ on the activities of some active HC-SCR catalyst has been investigated. Competitive adsorption between H$_2$O and the reducing agent on the catalyst surface leads to a decrease in the low-temperature activity of the catalyst and a shift of its activity window to higher temperatures [26,27]. And the inhibition of water is usually reversible [26]. For different catalyst system, the effect of water is different. For Sn/Al$_2$O$_3$ catalyst, the inhibition of water was more noticeable at low temperature region while at higher temperatures the inhibition was seldom observed [28]. However, for Pt/V/MCM-41 catalyst, the presence of some water (<3.7%) shows a promoting effect at 250 °C, when the temperature was increased to 350 °C or the concentration of water was increased, the inhibition of water was observed [17]. The promoting effect at low temperatures was proposed to be due to the removal of carbonaceous deposits by water [29]. Carbonaceous deposits block the active sites of Pt on which NO dissociates. After removing the deposits, more active sites play a role in NO dissociation and thus the conversion of NO was improved [17]. When the reducing agent is oxygenated hydrocarbons or longer chain hydrocarbons, the carbonaceous deposits are more easily formed on the surface of the catalyst. The presence of water can decrease the concentration of deposited carbon thus shows a promoting effect [12]. The promoting effect of water was also observed on

Pt/ZSM-5 catalyst prepared by sublimation method [16]. In this case, the possible reason is the presence of water partly inhibited the unselective combustion of propene with oxygen.

Unlike the poisoning mechanism of water, the poisoning caused by SO_2 is assumed that SO_2 reacted with O_2 on the catalyst surface to form stable sulfate under reaction conditions. The sulfate species covered the catalyst surface and reduced the number of chemisorption sites for NO_x. In addition, the presence of SO_2 also leads to the formation of carbonaceous deposits, which results in the deactivation of the active sites, such as over Fe/ZSM-5 catalyst [30]. Compared with the zeolite-based catalysts and metal oxide catalysts [10–12,23], Pt-based catalysts showed high resistance against SO_2. For Pt/V/MCM-41 catalyst, the total conversion of NO was decreased by only 2% even the concentration of co-presence SO_2 is as high as 500 ppm [17]. But it should be noted that the conversion of NO to N_2 was decreased to a larger degree (6%). It is interesting that over Pt/MCM-41 catalyst, after 500 ppm SO_2 has been removed from the feed stream, the NO reduction activity immediately restores to even slightly higher activity than the initial [31]. The weak inhibition of SO_2 was also observed on Pt/ZSM-5 catalyst prepared by sublimation method [16] and Pt/Al$_2$O$_3$ catalyst [32].

From SO_2-TPD experiment, it was found that the adsorption amount of SO_2 over the Pt/MCM-41 catalyst is much less than those over Cu/ZSM-5 and Cu/MCM-41 catalysts, and SO_2 can desorb from Pt/MCM-41 catalyst at a much lower temperature (around 100 °C) [31]. Thus, it is proposed that the higher resistance of Pt-based catalyst against SO_2 is due to the weak interaction between SO_2 and the catalyst.

The promoting effect of SO_2 was also observed on some HC-SCR catalysts. Over Pt/B$_2$O$_3$–Al$_2$O$_3$–SiO$_2$ catalyst, the enhancement of NO conversion by SO_2 is due to the inhibition of propene oxidation by oxygen [33]. While for Ga$_2$O$_3$–Al$_2$O$_3$ catalyst, the promoting effect is ascribed to the increase of acidity due to the presence of sulphate species, which facilitates the activation of hydrocarbon [34].

7. Combinatorial catalysis

Combinatorial catalysis, which has been developed recently, promises to significantly accelerate the process

Table 1
Composition of catalyst library[a] [38]

#	Loading (mole %)				#	Loading (mole %)			
	Pt	Cu	Fe	Co		Pt	Cu	Fe	Co
1	0	0	1	0	29	0.4	0.2	0.2	0.2
2	0.2	0	0.8	0	30	0.2	0.4	0.2	0.2
3	0	0.2	0.8	0	31	0	0.6	0.2	0.2
4	0.4	0	0.6	0	32	0.8	0	0	0.2
5	0.2	0.2	0.6	0	33	0.6	0.2	0	0.2
6	0	0.4	0.6	0	34	0.4	0.4	0	0.2
7	0.6	0	0.4	0	35	0.2	0.6	0	0.2
8	0.4	0.2	0.4	0	36	0	0.8	0	0.2
9	0.2	0.4	0.4	0	37	0	0	0.6	0.4
10	0	0.6	0.4	0	38	0.2	0	0.4	0.4
11	0.8	0	0.2	0	39	0	0.2	0.4	0.4
12	0.6	0.2	0.2	0	40	0.4	0	0.2	0.4
13	0.4	0.4	0.2	0	41	0.2	0.2	0.2	0.4
14	0.2	0.6	0.2	0	42	0	0.4	0.2	0.4
15	0	0.8	0.2	0	43	0.6	0	0	0.4
16	1	0	0	0	44	0.4	0.2	0	0.4
17	0.8	0.2	0	0	45	0.2	0.4	0	0.4
18	0.6	0.4	0	0	46	0	0.6	0	0.4
19	0.4	0.6	0	0	47	0	0	0.4	0.6
20	0.2	0.8	0	0	48	0.2	0	0.2	0.6
21	0	1	0	0	49	0	0.2	0.2	0.6
22	0	0	0.8	0.2	50	0.4	0	0	0.6
23	0.2	0	0.6	0.2	51	0.2	0.2	0	0.6
24	0	0.2	0.6	0.2	52	0	0.4	0	0.6
25	0.4	0	0.4	0.2	53	0	0	0.2	0.8
26	0.2	0.2	0.4	0.2	54	0.2	0	0	0.8
27	0	0.4	0.4	0.2	55	0	0.2	0	0.8
28	0.6	0	0.2	0.2	56	0	0	0	1

[a]The maximum loading was set to 0.5 mmol/g of Cu, Fe, Co and 0.125 mmol/g of Pt leading to single-component catalyst samples of 2.30 wt% Pt/AlSBA-15, 3.00 wt% Cu/AlSBA-15, 2.70 wt% Fe/AlSBA-15 and 2.80 wt% Co/AlSBA-15.

of discovering and optimizing of lean-NO$_x$ catalyst by exploring vast parameters within short period of time [35,36]. Using the combinatorial method, Ozturk and Senkan [37] discovered that CuOs/13X catalyst was very active for the catalytic reduction of NO by hydrocarbons. Compared with Cu-ZSM-5 catalyst, much higher conversion of NO was obtained over CuOs/13X catalyst over a wider temperature range. More importantly, CuOs/13X catalyst exhibited higher low-temperature activity and superior durability in steam. Recently, a quaternary catalyst library of 56 samples composed of Pt, Cu, Fe and Co supported AlSBA15 was also optimized in our laboratory. Composition of catalyst library is shown in table 1 and the results are shown in figure 5 [38]. It can be seen that Pt$_{0.8}$Fe$_{0.2}$(#11) and Pt$_{0.8}$Co$_{0.2}$(#32) at 250 °C, Pt$_{0.6}$Fe$_{0.2}$Co$_{0.2}$(#28) and Pt$_{0.8}$Co$_{0.2}$(#32) at 300 °C, Pt$_{0.4}$Fe$_{0.4}$Co$_{0.2}$(#25) and Pt$_{0.6}$Fe$_{0.2}$Co$_{0.2}$(#28) at 350 °C, and Pt$_{0.4}$Fe$_{0.6}$(#4), Pt$_{1.0}$ (#16) at 400 °C showed higher activity. The important finding is that these bimetallic and tri-metallic catalysts are more active than the monometallic Pt catalyst at some temperatures. From the cost issues, these catalysts are also superior to Pt catalyst since Fe and Co are not costly compared with Pt. Further investigation should be focused on analysing the exact nature of the reaction products, especially the selectivity towards N$_2$. At the same time, the chemical and physical structures of these active catalysts should be characterized to reveal the relationship between activity as well as selectivity and structure.

8. Reaction mechanism of HC-SCR

So far, considerable research has been carried out in order to understand the reaction mechanism of HC-SCR over Pt-based catalysts and some possible mechanisms have been proposed. Base on the FTIR studies the direct-decomposition mechanism was put forward on Pt/ZSM-5 catalyst [39,40]. The overall reaction consists three major steps, which may occur simultaneously.
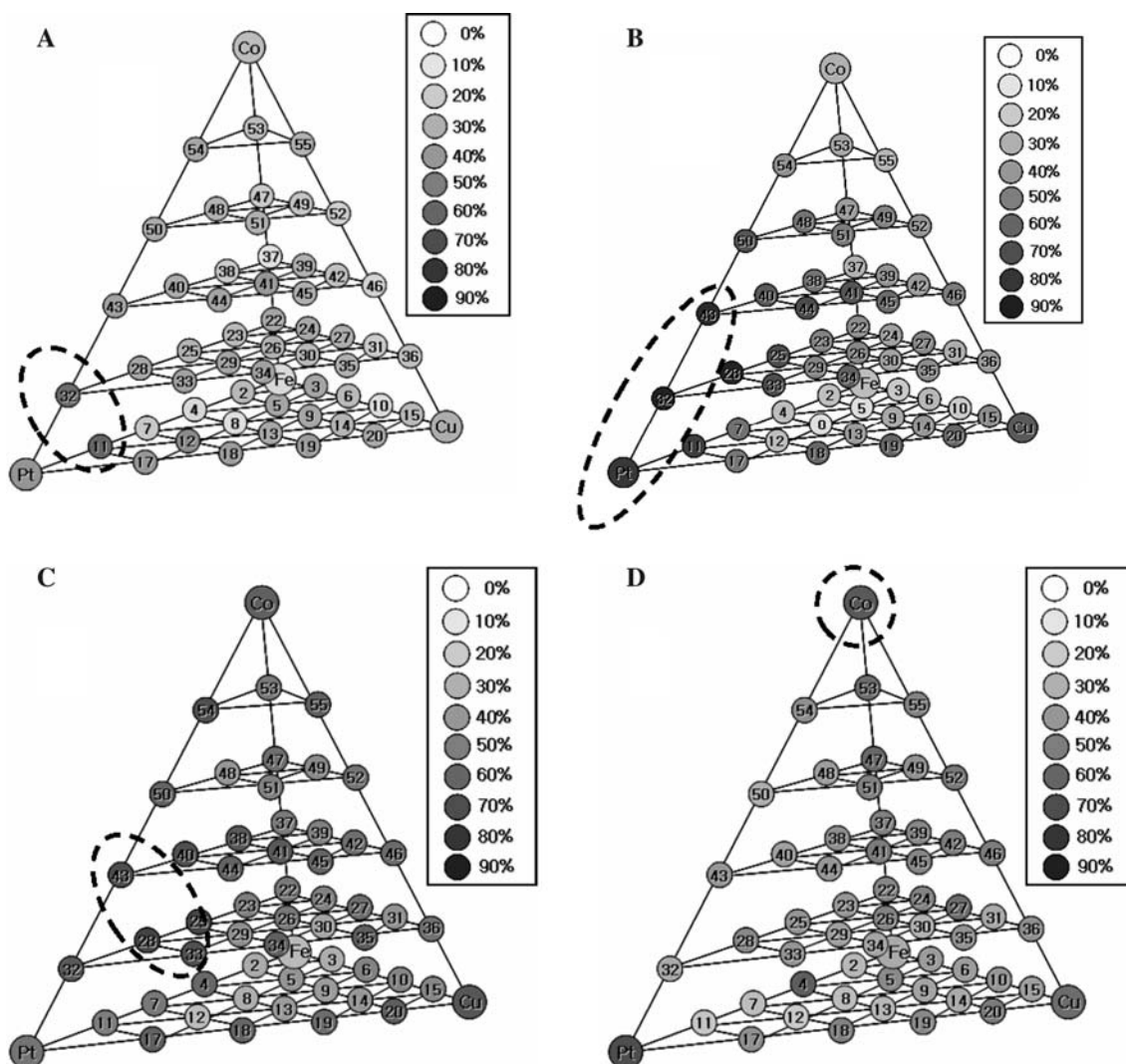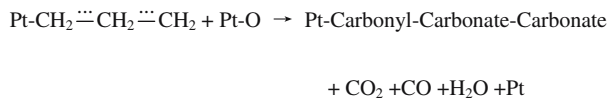

Figure 5. NO$_x$ conversion (gray-scale) of the 56-member catalyst library at (A) 250 °C, (B) 300 °C, (C) 350 °C, (D) 400 °C. (Reaction condition: 0.2% NO, 3.2% O$_2$, 0.27% C$_3$H$_6$, total gas flow rate: 10 ml/min, catalyst amount: 10 mg with each chamber.)

1. The adsorption and/or decomposition of reactants on Pt/ZSM-5

$$NO + Pt \rightarrow Pt\text{-}NO \rightarrow Pt\text{-}N + Pt\text{-}O$$

$$C_3H_6 + Pt/ZSM\text{-}5 \rightarrow Pt\text{-}CH_2 \cdots CH_2 \cdots CH_2 \quad (\pi\text{-allyl complex})$$

2. The oxidation of surface organic compounds

$$Pt\text{-}CH_2 \cdots CH_2 \cdots CH_2 + Pt\text{-}O \rightarrow Pt\text{-}Carbonyl\text{-}Carbonate\text{-}Carbonate$$

$$+ CO_2 + CO + H_2O + Pt$$

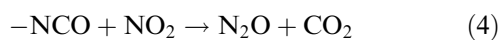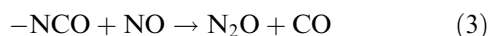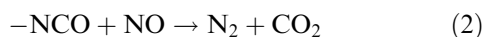3. The formation of reduced products

$$2Pt - N \rightarrow N_2$$

$$Pt - -N + Pt - NO \rightarrow N_2O + 2Pt$$

In the first step, Pt–N and Pt–O were produced by the dissociated adsorption of NO, at the same time, propene was activated by Pt to form π-allyl complex. Then two dissociated N combine to produce N_2. One un-dissociated NO combines with one dissociated N to form N_2O. The role of step 2 is regenerating the "reduced" platinum sites, which are active for NO decomposition, by the reaction between propene π-allyl complex adsorbed on or very close to platinum clusters and surface oxygen species.

Different catalyst support can lead to different reaction mechanism. Jentys et al. [41] have found that the formation of –NCO species plays an important role for the reaction to proceed over Pt/MCM-41 catalyst. The following are the possible reaction steps:

$$NO + CO \rightarrow -NCO + O \qquad (1)$$

$$-NCO + NO \rightarrow N_2 + CO_2 \qquad (2)$$

$$-NCO + NO \rightarrow N_2O + CO \qquad (3)$$

$$-NCO + NO_2 \rightarrow N_2O + CO_2 \qquad (4)$$

CO was formed by the partially oxidation of propene on Pt active sites. Then NO reacted with CO to form –NCO, which subsequently reacts with adsorbed NO/NO_2 to form N_2 and N_2O. Similar reaction steps were also observed on Cu/ZSM-5 catalyst [42,43]. However, Acke et al. [44] have proposed that over Pt/Al$_2$O$_3$ catalyst even if –NCO species are formed, as evidenced by the IR studies, they may not be directly involved in the NO reduction step. They further emphasized NH_x(ads) species was the possible important reaction intermediates. For Pt-based catalysts, some studies have also showed that organic nitro, nitrite, and carbonyl surface species are key reaction intermediates for the formation of nitrogen and nitrous oxide [12,45].

In addition, the reaction mechanism of Pt-based catalyst also depends on the type of reducing agent. For Pt/Al$_2$O$_3$ catalyst, the NO reduction occur on the Pt surface when propene is reducing agent, whereas for propane the NO is reduced over the support by a reaction between reducing species derived from propane and NO_2, which formed by the oxidation of NO on the Pt surface [46,47].

9. Conclusions

Pt/ZSM-5 catalyst prepared by the sublimation method and Pt/V/MCM-41 exhibit wider activity temperature windows than the usual Pt catalysts reported previously. In order to make the two catalysts closer to the practical application, improving the selectivity to nitrogen is our further research target, although it is very challenging. In addition, combinatorial catalysis may be helpful to find the novel catalyst that is active, cheap and suitable for practical application. Although some possible mechanisms of the lean NO_x reduction over Pt-based catalysts have been proposed and some key reaction intermediates have been identified, there is still a need for further study to fully understand the mechanism, which can provide some valuable information concerning the design of more active catalysts for the selective reduction of NO_x with hydrocarbons.

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