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# Wide temperature window in the catalytic activity of novel Pt/ZSM-5 prepared by a sublimation method for selective catalytic reduction of NO

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The removal of nitric oxide from the exhaust gas of lean-burn engines is not fully commercialized since the current catalyst technology cannot meet the strict future emission regulations. Although ZSM-5 ion-exchanged with Pt (Pt/ZSM-5) has been considered as a promising catalyst due to its superior low-temperature activity, it has the drawback of a narrow "temperature window" for activity, i.e. an abrupt decrease in the activity above 300 °C. This paper reports on the preparation of novel Pt/ZSM-5 by subliming $Pt(CO)_2Cl_2$ into H-ZSM-5 at 220 °C, resulting in excellent activity within a wide temperature window between 230 and 500 °C. Pre-treatment of this Pt/ZSM-5 can change the width of the temperature window. Moreover, $H_2O$ plays a role as a promoter and $SO_2$ reversibly reduces the activity by less than 20%.

**KEY WORDS:** sublimation; platinum; zeolite; temperature window; DeNOx.

## 1. Introduction

Nitric oxide (NO) emissions from mobile and stationary sources are cause for concern because they are the main source of acid rain and smog [1]. Three-way catalysts whose major ingredients are Pt, Pd and Rh effectively remove NO from gasoline engines. Recent lean-burn gasoline and diesel engines that operate under highly oxidizing conditions are beneficial for the environment in view of their better fuel economy than conventional gasoline engines. Because the conventional three-way catalysts have been known to show little activity for NO reduction under highly oxygen-rich conditions, it is necessary to develop a new catalyst that is applicable for use in lean-burn and diesel-engine vehicles.

The selective catalytic reduction (SCR) of NO by hydrocarbons in the presence of excess oxygen has been studied over various catalysts. Although Cu/ZSM-5 is known to be very active in the rather high temperature region (350–450 °C) and has been studied most intensively, it suffers from severe deactivation in engine tests, mainly due to $SO_2$ and $H_2O$ contained in the exhaust gases [2–4]. Pt/ZSM-5 prepared by the ion-exchange method has been reported to show the highest activity at of low temperatures between 200 and 300 °C [5]. The low-temperature activity of Pt/ZSM-5 is very encouraging and strongly suggests that Pt/ZSM-5 could be adequate for a diesel engine for which the temperature of the exhaust gases is much lower than that of a gasoline engine. In addition, Pt/ZSM-5 is known for its high activity in the presence of water and/or $SO_2$ [6]. However, the large amount of $N_2O$ formation and the narrow temperature window for catalytic activity must be improved for its commercialization [7]. It was reported that sublimation of $FeCl_3$ onto H-ZSM5 is an effective method to prepare Fe/ZSM5 of high iron loading [8,9]. In this paper, we report a novel method for the preparation of Pt/ZSM-5 by sublimation of platinum carbonyl chlorides below its decomposition temperature and its relevant catalytic properties.

## 2. Experimental

### 2.1. Preparation of the catalysts

The parent $NH_4$-ZSM-5 zeolite (ALSI-5, SM-27, Si/Al = 11.75) was transformed to H-ZSM-5 by calcination in $O_2$ flow at 773 K for 4 h. 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. A porous frit kept the H-ZSM-5 separate from the $PtCl_2$. Chemical vapor deposition was carried out under a flow of He (80 $cm^3$/min) and CO (20 $cm^3$/min) at 220 °C. Then the sample was washed with doubly

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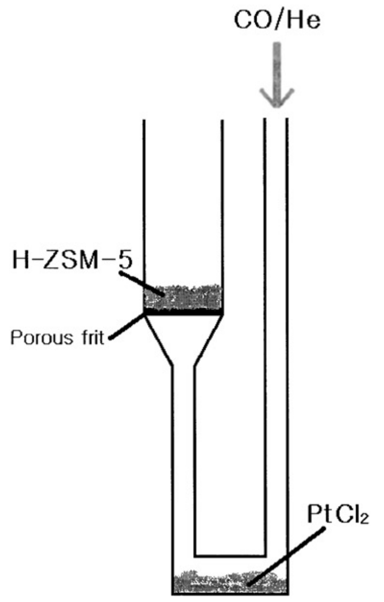

Figure 1. Apparatus for the preparation of Pt/ZSM-5 by the sublimation method.

deionized water, dried at 110 °C overnight, and calcined under $O_2$ flow at 600 °C for 4 h.

### 2.2. Reaction test

A typical inlet gas composition for SCR of NO was 0.2% NO, 0.27% $C_3H_6$, 3% $O_2$. When desired, 7.8% $H_2O$ and/or 150 ppm $SO_2$ with He balance was added. An amount of 0.1 g of catalyst was used and the total flow rate was 140 cm$^3$/min (GHSV = 42 000 h$^{-1}$). The reaction temperature was increased stepwise from 200 to 500 °C by 50 °C. The composition of the effluent gas was analyzed by GC (HP 5840; molecular sieve 5A column for $N_2$ and CO and Porapak Q column for $N_2O$, $CO_2$ and $C_3H_6$) at the desired temperature.

## 3. Results and discussion

Platinum dicarbonyl chloride, *cis*-$Pt(CO)_2Cl_2$, can be obtained by passing carbon monoxide in a long vertical tube to $PtCl_2$ at 220 °C [10]. The carbonylation of platinum halides occurs as follows:

$$\begin{aligned} PtCl_2 + 2CO \rightarrow Pt(CO)_2Cl_2\uparrow &\quad \text{(at 210 °C)} \\ Pt_2(CO)_2Cl_4\uparrow &\quad \text{(at 220 °C)} \\ Pt(CO)Cl_2\uparrow &\quad \text{(at 240 °C)} \end{aligned}$$

During sublimation at 220 °C in our experiment, $Pt(CO)_2Cl_2$ and $Pt_2(CO)_2Cl_4$ prevail. Two kinds of Pt/ZSM-5 were prepared by changing the amount of $PtCl_2$. Pt/ZSM-5-9.85 and Pt/ZSM-5-0.34 indicate Pt/ZSM-5 whose Pt loading is 9.85 and 0.34 wt%, respectively.

Figure 2(a) shows a comparison of NO conversion to $N_2$ and $N_2O$ catalyzed over Pt/ZSM-5-9.85 prepared by the sublimation method and that catalyzed over Pt/ZSM-5-9.7 prepared by the ion-exchange method [6]. The first maximum conversion of NO to $N_2$ by Pt/ZSM-5-9.85 occurs around 250 °C and the second occurs around 400 °C. A 40% conversion of NO to $N_2$ was obtained even at 500 °C. H-ZSM-5 can convert NO to $N_2$ in a self-catalytic reaction above 500 °C. The activity above 500 °C must arise from H-ZSM-5 which was used as a support of Pt/ZSM-5-9.85. However, NO conversion to $N_2$ and $N_2O$ by Pt/ZSM-9.7 prepared by the ion-exchange method shows a maximum around 200 °C and monotonously decreases to zero at 400 °C. The area of the conversion curve of NO to $N_2$ by Pt/ZSM-5-9.85 between 200 and 400 °C is 6.1 times greater than that of the conversion curve of NO to $N_2$ by Pt/ZSM-5-9.7. Considering the temperature of exhaust gases from a lean-burn diesel engine varies from ambient temperature to 500 °C depending on the driving conditions, Pt/ZSM-5-9.85 prepared by the sublimation method removed NO much more effectively than

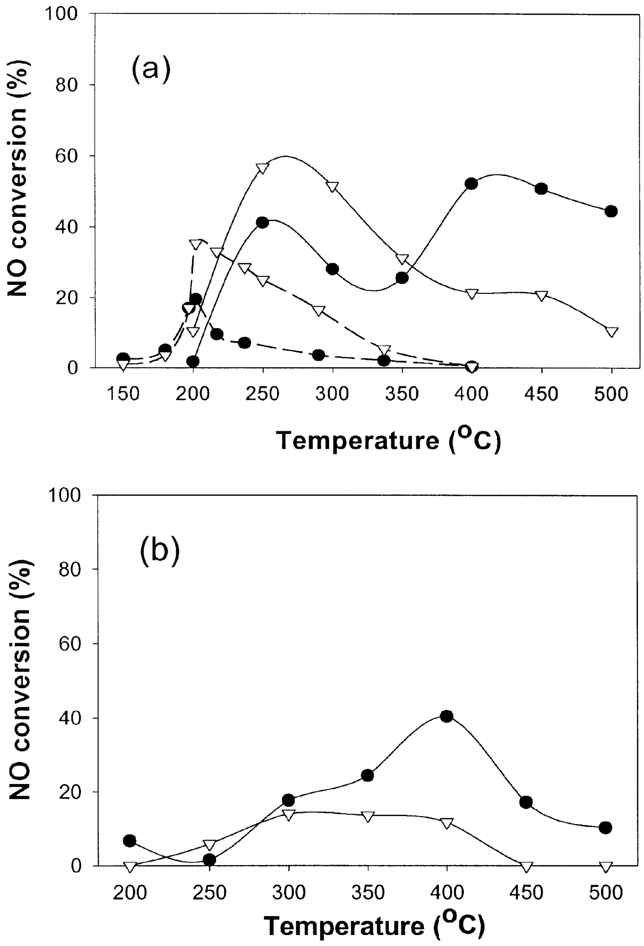

Figure 2. (a) Comparison of conversion of NO to $N_2$ (—●—) and $N_2O$ (—▽—) catalyzed over Pt/ZSM-5-9.85 prepared by the sublimation method with that of NO to $N_2$ (– –●– –) and $N_2O$ (– –▽– –) catalyzed over Pt/ZSM-5-9.7 prepared by the ion-exchange method [6]. (Reaction conditions of Ref. [6]: GHSV = 72 000 h$^{-1}$, 0.1% $C_2H_4$, 0.1% NO and 2% $O_2$). (b) Conversion of NO to $N_2$ (—●—) and $N_2O$ (—▽—) catalyzed over Pt/ZSM-5-0.34 prepared by the sublimation method.

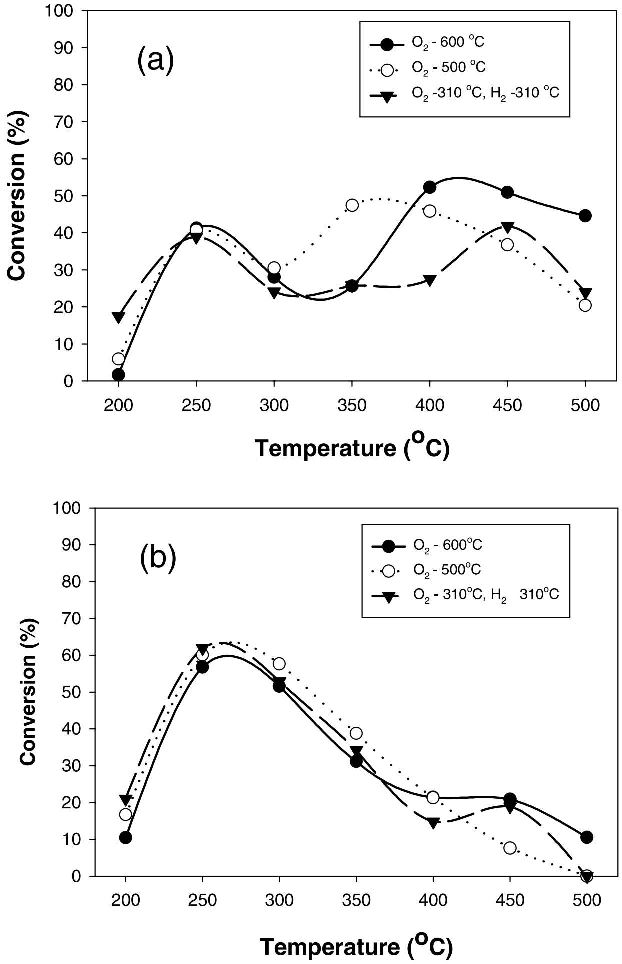

Figure 3. Effect of the pre-treatment conditions of Pt/ZSM-5-9.85 on the conversion of NO to (a) $N_2$ and (b) $N_2O$.

Pt/ZSM-5-9.7 prepared by the ion-exchange method [11,12]. The plausible reason for this wide temperature window for the removal of NO will be published in a future paper [13].

Figure 2(b) shows the NO conversion over Pt/ZSM-5-0.34 prepared by the sublimation method. Although the conversion of NO decreased compared with that of Pt/ZSM-5-9.85, it shows a higher selectivity to $N_2$ and less formation of $N_2O$. The conversion of NO to $N_2$ increases and passes through a maximum at about 400 °C. The maximum conversion of NO to $N_2$ is about 40% at 400 °C. The conversion of NO to $N_2O$ shows a broad pattern between 250 and 400 °C, which is different from that of Pt/ZSM-5-9.85.

Woo and co-authors [14] reported that pre-treatment conditions of Pt/ZSM-5 prepared by the ion-exchange method show a considerable effect on the activity and selectivity for reduction of NO. As shown in figure 3(b), there is little change in the conversion and temperature of the maximum conversion of NO to $N_2O$ on Pt/ZSM-5 pre-treated under various conditions (calcined at 500 or 600 °C, and calcined at 310 °C, then reduced at 310 °C). These pre-treatments do not affect the conversion and temperature of the maximum conversion of NO to $N_2$ below 325 °C, as shown in figure 3(a). However, the temperature of the maximum conversion of NO to $N_2$ above 325 °C depends on the pre-treatment conditions. When the catalyst is reduced before reaction (calcined with $O_2$ at 310 °C followed by reduction with $H_2$ at 310 °C), the maximum conversion is shifted to a higher temperature. It is noticeable that the temperature window of activity of Pt/ZSM-5-9.85 can be controlled by changing the pre-treatment conditions.

A high durability of the catalyst in the presence of $SO_2$ and $H_2O$ is required because they always exist in exhaust gases. Table 1 shows the effect of adding $SO_2$ and $H_2O$ to the reactant on the catalytic activity of Pt/ZSM-5-9.85 at 250 °C. When 150 ppm of $SO_2$ is added, the conversion of NO to $N_2$ does not change, while that of NO to $N_2O$ decreases a little. Consequently, the NO conversion is reduced from 93 to 73%. When $SO_2$ is not added, the conversion of NO recovers to 82.2%. $H_2O$ does not play a role as an inhibitor for $N_2$ and $N_2O$ formation, but as a promoter because the NO conversion increased to 95.3% upon the addition of 7.8% $H_2O$. Moreover, the activity for the $N_2$ conversion in the presence of $H_2O$ and $SO_2$ is higher than in the presence of $SO_2$ only. Although $SO_2$ deactivates the Pt/ZSM-5-9.85, the degree of deactivation is not so high and is partially reversible.

## 4. Conclusion

Pt/ZSM-5 catalysts are prepared by sublimation of $PtCl_2$ with CO into H-ZSM-5. They showed a better performance in SCR of NO and a wider temperature window for activity than Pt/ZSM-5 prepared by the ion-exchange method. The width of the temperature

Table 1
Change in the catalytic activity upon the addition of $SO_2$ and $H_2O$ over Pt/ZSM-5-9.85 at 250 °C[a]

| Conversion to | Reactant only | Reactant with $SO_2$ | Reactant only | Reactant with $H_2O$ | Reactant only | Reactant with $H_2O$ and $SO_2$ |
|---|---|---|---|---|---|---|
| $N_2$ (%) | 31.9 | 29.7 | 27.7 | 32.7 | 27.4 | 32.6 |
| $N_2O$ (%) | 61.1 | 43.3 | 54.5 | 62.6 | 60.0 | 46.2 |
| $N_2+N_2O$ (%) | 93.0 | 73.0 | 82.2 | 95.3 | 87.4 | 78.8 |

[a] The reaction was carried out sequentially (reactant only → $SO_2$ was added → $SO_2$ was removed → $H_2O$ was added → $H_2O$ was removed → $H_2O$ and $SO_2$ were added simultaneously).

window for activity is controllable depending on the pretreatment conditions. A high durability against $SO_2$ and $H_2O$ is also demonstrated.

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