

NO_x Storage-Reduction over Pt/Mg-Al-O Catalysts with Different Mg/Al Atomic Ratios

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Abstract—A series of Pt/Mg-Al-O catalysts with different Mg/Al atomic ratios were prepared. The NO_x storage capacities of these catalysts were measured by isothermal storage at 350 °C. It was found that the NO_x storage capacity increased with increasing Mg/Al atomic ratios. The catalytic behaviors of Pt/Mg-Al-O and Pt/MgO were studied with storage-reduction cycles at 400 °C. Under oxidizing conditions, NO_x concentration in the outlet gas gradually increased with time, which indicated the catalysts could store NO_x effectively. After a switch from oxidizing conditions to reducing conditions, NO_x desorption peak emerged immediately due to the incomplete reduction of stored NO_x, which lowered the total NO_x conversion. With increasing Mg/Al atomic ratio in the catalysts, NO_x conversion increases. Pt/MgO has the highest NO_x conversion because of its best activity in the reduction of NO_x by C₃H₆. It seems that with an increasing amount of MgO in the catalysts, the self-poisoning of Pt-sites by adsorbed species during the reaction of NO_x with C₃H₆ may be inhibited effectively.

Key words: Lean-burn, NO_x Storage-reduction, Platinum, Hydrotalcite, MgO

INTRODUCTION

Lean-burn technologies for gasoline and diesel engines are attractive due to their improved fuel efficiency and low emission of CO₂. However, how to reduce the NO_x emission effectively in a large excess of O₂ has currently become a challenging research topic. Under the net-oxidizing condition, the traditional three-way catalysts will lose nearly all of their NO_x conversion abilities, so DeNO_x catalysts capable of operation in the presence of oxygen are of particular interest. Besides the well-established selective catalytic reduction (SCR) [Burch et al., 2002; Praserthdam et al., 2003], a new solution to this problem, the NO_x storage-reduction (NSR) catalyst, was first presented by Toyota in 1995 [Takahashi et al., 1996]. The NSR catalysts present interesting features and have proven to be a very promising approach to reduce the NO_x emission [Lietti et al., 2001]. According to this strategy, NO_x is stored in the catalyst during the normal lean operation stage of the engine, while regeneration of the catalyst is carried out by short pulses of engine operation in the rich mode, and during these short periods, the NO_x stored is released and reduced over noble metal surfaces [Takahashi et al., 1996].

At present, NSR catalysts based on Pt and Ba have been studied most extensively. Various oxides such as BaO [Fridell et al., 1999; Schmitz and Baird, 2002; Mahzoul et al., 1999], BaAl₂O₄ [Hodjati et al., 1998] and BaSnO₃ [Hodjati et al., 2000] were used as the storage components. During the lean stage, NO was oxidized to NO₂ on platinum site and stored in the storage component, while in the rich stage, the stored NO was released and reduced on platinum group metals to N₂. There is, however, a problem which should be addressed, namely, this kind of catalysts is sensitive to SO₂. The presence of SO₂ in the exhaust can make the catalyst lose its activity due to the formation of BaSO₄, which cannot be decomposed in the exhaust temperatures on the catalyst surfaces [Matsumoto et

al., 2000].

Mg is also an alkaline-earth element. Compared with Ba, Mg has a lower basicity. From the thermodynamic point of view, using MgO as the storage component in the catalysts can obtain a better regeneration ability and a resistance to poisoning by SO₂. Recently, Fornasari et al. have reported that a catalyst derived from Mg-Al hydrotalcite (Mg²⁺:Al³⁺=2:1) showed interesting characteristics as novel NSR catalyst, with improved low-temperature activity and a better resistance to deactivation by SO₂ [Fornasari et al., 2002; Centi et al., 2002].

The purpose of this study is to examine the effect of Mg/Al atomic ratios on the performance of Pt/Mg-Al-O catalysts. A series of Pt/Mg-Al-O catalysts with different atomic ratios of Mg/Al were prepared and characterized by XRD, N₂-BET-surface area and TPD, and their catalytic activities were evaluated by NO_x isothermal storage as well as dynamic storage-reduction experiments.

EXPERIMENTAL

1. Preparation of Catalytic Materials

Mg-Al hydrotalcites were prepared by co-precipitation at pH≈10 and 60 °C under vigorous stirring. A solution ([Mg²⁺]+[Al³⁺]=1.25 M) containing Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O in a certain atomic ratio and a mixed solution of NaOH and Na₂CO₃ ([OH⁻]/[CO₃²⁻]=16) were added dropwise simultaneously to a three-necked round-bottom flask containing 200 ml of distilled water. The resulting precipitate was aged in the mother liquor at 70 °C for 10 h, and then filtered and washed with distilled water for six times. After washing, the precipitate was collected by centrifugation and dried overnight at 110 °C. The dried samples were calcined for 5 h at 600 °C to make them decompose into the Mg-Al-O mixed oxide. In this paper, the Mg-Al-O mixed oxide with different atomic ratios is designated as Mg-AL_x, where x indicates the value of atomic ratio of Mg/Al. The results of X-fluorescence analysis showed that no sodium oxide existed. Pure MgO was prepared by using the same meth-

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od, and pure γ -Al₂O₃ was obtained from the Shandong Aluminum Corporation of China, with a surface area of about 120 m²·g⁻¹. For convenience, in the figures and tables of this paper, the value *x* for Al₂O₃ and MgO is designated as 0 and ∞. The calcined samples were crushed and granules with a size range of 0.15 to 0.25 mm were collected to prepare the catalysts. Pt/Mg-Al_{*x*}, Pt/MgO and Pt/Al₂O₃ catalysts were prepared by incipient wetness impregnation of the corresponding supports with a Pt(NH₃)₄(OH)₂ aqueous solution, and the Pt content was 1 wt%. The calcination temperature of the catalysts was 500 °C.

2. Catalyst Characterization

Surface areas of the samples were measured by N₂ adsorption at liquid nitrogen temperature (77 K) by using the BET method. The X-ray diffraction (XRD) patterns of the hydrotalcites and the mixed oxide formed by their thermal decomposition were obtained with a Rigaku D/MAX- γ B diffractometer using CuK α radiation. The patterns were recorded over 2θ angles ranging from 5° to 70°.

3. Catalyst Tests

All catalyst tests were performed in a vertical flow fixed-bed quartz reactor. The gas flow rate was set at 1 l·min⁻¹ (STP). N₂ was used as the carrier gas. The mass of the catalyst was 0.75 g and the gas hourly space velocity was about 55,000 h⁻¹. The total NO_{*x*} concentration in the outflow of the reactor was analyzed with a chemiluminescence NO-NO_{*x*} analyzer (Model 44, manufactured by Thermo Electron Corporation). Another analyzer specially designed for automobile gas analysis (Model FGA4015, manufactured by the Fushan Xinyu Instrument Co., China) was used to analyze the concentrations of O₂, C₃H₆ and NO on-line.

The amount of NO_{*x*} stored in all catalysts at saturation was tested at 350 °C. Before each test, the catalyst was pretreated *in situ* in the reactor by the following procedure: the catalysts were reduced in 8% H₂ at 400 °C for 1 h, and then stabilized in 8% O₂ for 1 h. After the pretreatment, the temperature of the catalyst bed was lowered from 400 °C to 350 °C, and the reaction feed (8% O₂, 550 ppm NO, N₂ balance) was introduced into the reactor. The amount of NO_{*x*} stored at saturation (*A_s*) in the catalyst was calculated by using the following Eq. (1):

$$A_s = \frac{([\text{NO}]_{in} \times (t_2 - t_1) - \int_{t_1}^{t_2} [\text{NO}]_{out} dt) \times v}{22.4 \times m_{cat}} \quad (1)$$

where [NO]_{*in*}, [NO]_{*out*} are the inlet and outlet NO_{*x*} concentration; *t*₁ and *t*₂ are the time at the beginning and the ending of storage process; *v* is the gas flow rate and *m_{cat}* is the mass of the catalyst.

NO-TPD experiments were carried out in the same reactor, and the analyses of the gases NO, NO₂ and N₂O at the reactor outlet were performed by FT-IR spectroscopy (Nicolet Nexus 470, with OMNIC QuantPad software). The catalysts were pretreated in the same method as mentioned above. After the pretreatment, the samples were cooled down to 350 °C, and then exposed to the feed gas (8% O₂, 550 ppm NO, N₂ balance) until saturation. After being saturated with NO_{*x*}, the catalysts were cooled down to 80 °C in nitrogen, and followed by desorptions. All TPD experiments were performed under pure N₂, with a flow rate of 2 l·min⁻¹ and a heating rate of 20 °C·min⁻¹.

The dynamic storage-reduction experiments were performed by using a series of periodic operations from lean conditions (190 s: 8% O₂, 550 ppm NO, N₂ balance) to rich conditions (110 s: 800

ppm C₃H₆, 550 ppm NO, N₂ balance) at 400 °C, namely, there are 12 cycles in one hour. After 5-7 cycles, a steady state of the catalyst was established. The total NO_{*x*} conversion was calculated by using the following equations:

NO_{*x*} total conversion

$$X_{NO_x} = \frac{[\text{NO}_x]_{in} \times (t_2 - t_1) - \int_{t_1}^{t_2} [\text{NO}_x]_{out} dt}{[\text{NO}_x]_{in} \times (t_2 - t_1)} \quad (2)$$

where [NO]_{*in*} and [NO]_{*out*} are the inlet and outlet NO_{*x*} concentrations; *t*₁ and *t*₂ are the time at the beginning and the ending time of each cycle, respectively.

RESULTS AND DISCUSSION

1. Catalyst Characterization

The XRD patterns of the calcined samples are presented in Fig. 1. From the patterns of the calcined samples, it can be seen that pure MgO has sharp and symmetric peaks, while Mg-Al_{*x*}, Mg-Al₂ and Mg-Al₁ have weak and broad peaks, resembling a metal oxide solid solution (MOSS) of the constituent oxides [Alcaraz et al., 1998]. The diffraction peaks of Mg-Al_{0.5} and Mg-Al_{0.33} are very weak, implying very poor crystallinity of these samples.

The surface areas of Mg-Al-O supports with different atomic ratios are shown comparatively in Table 1. Compared with pure MgO, the Mg-Al mixed oxides have higher surface areas and for Mg-Al_{*x*}; the influence of Mg/Al atomic ratio (*x*) is not significant.

2. Catalyst Tests

2-1. NO_{*x*} Isothermal Storage

The isothermal storage of NO_{*x*} was performed at 350 °C. The outlet concentrations of NO_{*x*} were plotted versus time in Fig. 2. It is shown that at the beginning of the storage process, there is a period during which NO_{*x*} is adsorbed over the catalysts completely. This period with zero NO_{*x*} concentration is defined as the break-

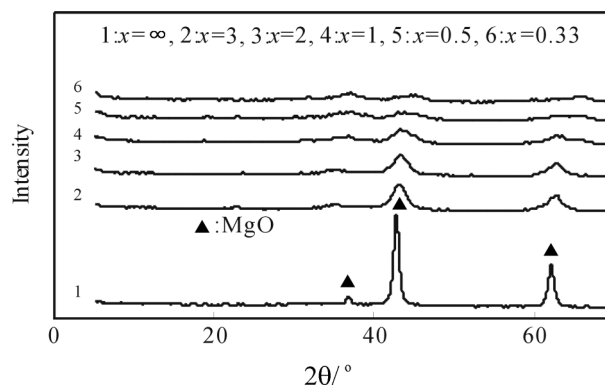


Fig. 1. XRD patterns of Mg-Al_{*x*} support with different Mg/Al atomic ratio.

Table 1. BET results of Mg-Al_{*x*} support with different Mg/Al atomic ratio

	Mg/Al atomic ratio (<i>x</i>)						
	0*	0.33	0.5	1	2	3	∞
<i>S</i> _{BET} (m ² ·g ⁻¹)	121	249	238	228	237	222	131

*: a kind of commercial Al₂O₃.

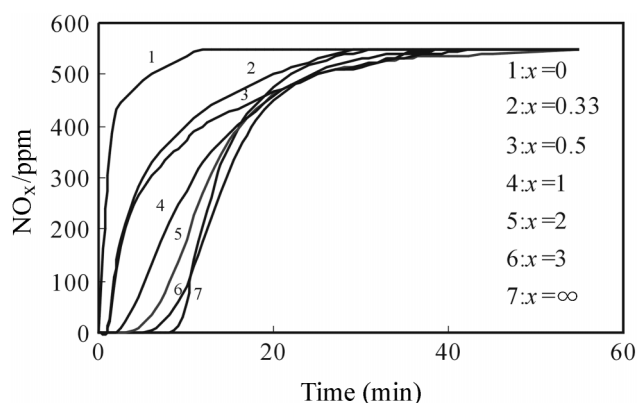


Fig. 2. Outlet NO_x concentrations profile during the storage process over the catalysts at 350 °C (550 ppm NO, 8% O₂, N₂ balance).

Table 2. Amount of NO_x stored at saturation over catalysts with different Mg/Al atomic ratios at 350 °C

	Mg/Al atomic ratio (x)						
	0	0.33	0.5	1	2	3	∞
A _x (μmol·g ⁻¹)	61	244	305	401	469	505	474

through time of the NSR catalysts. When the catalysts were saturated at 350 °C, a significant fraction of the total amount of injected NO was converted to NO₂. The concentration of NO₂ was calculated by the difference of the concentration of NO_x and NO. For Pt/Mg-Al_x and Pt/MgO, the fraction of NO₂ in the total NO_x varied in the range of 0.6 to 0.68. The NO₂/NO_x ratio over Pt/Al₂O₃ was low, being about 0.39. Pt/Mg-Al_x and Pt/MgO, compared with Pt/Al₂O₃, could catalyze the oxidation reaction of NO more effectively. The amount of NO_x stored in every catalyst to saturation is listed in Table 2. As shown in Table 2, the amount of NO_x stored in Pt/Al₂O₃ is very low, implying that MgO is the main storage component in the catalyst. For Pt/Mg-Al_x, with increasing Mg/Al atomic ratio in the catalysts, an increased amount of NO_x stored in the catalyst was observed. The surface areas of the catalysts could also influence the NO_x storage capacity, but in this study, this effect was less significant than that of the Mg/Al atomic ratio. The amount of NO_x stored in the Pt/Mg-Al₃ is slightly higher than that in Pt/MgO but the breakthrough time of Pt/Mg-Al₃ is less than Pt/MgO. The breakthrough time, a more important parameter for NSR catalyst, is always prolonged with the increasing of the Mg/Al atomic ratio at 350 °C. Increasing the Mg/Al atomic ratio is more preferable to the NO_x storage.

2-2. TPD Measurement

Pt/Al₂O₃, Pt/Mg-Al₁ and Pt/MgO were selected to carry out the TPD experiments. The TPD results are summarized in Table 3. The stored NO_x is released in the form of NO and NO₂ and only one peak for NO, NO₂ and NO_x is observed. The amount of desorbed NO, NO₂ and NO_x was also calculated. As listed in Table 3, the NO_x desorption peaks for Pt/Al₂O₃, Pt/Mg-Al₁ and Pt/MgO are located at 428 °C, 451 °C and 506 °C, respectively. The NO_x desorption peak at this temperature range can be assigned to the decomposition of nitrates on the catalyst [Sedlmair et al., 2003]. So it can be concluded that the presence of Al lowered the stability of nitrates on the catalyst surfaces.

2-3. Dynamic NO_x Storage-reduction

Fig. 3 shows the NO_x concentration profiles over each sample during the cyclic reaction. The reaction temperature was set at 400 °C, and when the conditions were switched from lean to rich, there was a fluctuation in temperature of about 7 °C. Total NO_x conversion is shown in Table 4.

As shown in Fig. 3, for Pt/Al₂O₃ and Pt/Mg-Al_x, there are three NO_x breakthrough peaks in a storage-reduction cycle. The highest peak is located at the beginning of the reduction stage after switching from lean conditions to rich conditions. The second highest peak is at 230-240 s of each cycle, and the third one is at the beginning of the storage stage after switching from rich conditions to lean conditions. The breakthrough peak at the switching point from lean to rich was observed and discussed by Fridell et al. [1999], Bögner et al. [1995], and Huang et al. [2001]. Huang et al. attributed this breakthrough peak to two reasons. One was that the rate of storage of NO_x decreased when oxygen was cut off; the other was that in the first few seconds of the rich phase, a certain amount of oxygen was remaining on the noble metal sites, which impeded the reduction of NO_x by noble metals. Bögner et al. considered that reduction of the noble metal sites was relatively slow, as compared with the decomposition of the nitrates. Fridell et al. believed that this peak was caused by a rapid reduction of the noble metal sites and the adsorption properties of NO_x on the noble metal surface changed radically. In our study, compared with the NO_x concentration, C₃H₆ was in large excess, but during the period from the switching point to the emergence point of the second NO_x peak, the C₃H₆ concentration was always zero. So in our opinion, at the initial period of the reduction stage, the rate of storage of NO_x decreased and C₃H₆ was also consumed by the oxygen adsorbed on the catalyst surfaces at the storage stage. This caused the rate of reduction of NO_x to be less than the rate of decomposition of the nitrates formed at the storage stage, and resulted in the largest breakthrough peak. It seemed that the amount of oxygen adsorbed on the catalyst surface was an important factor affecting the reduction of NO_x by C₃H₆. At the initial period of the reduction stage, oxygen inhibited the reduction of NO_x, but when the amount of oxygen adsorbed on the catalyst sur-

Table 3. Summary of the TPD results over Pt/Al₂O₃, Pt/Mg-Al₁ and Pt/MgO, after storage up to saturation at 350 °C

	Desorption peaks for		
	NO ₂	NO	NO _x
Pt/Al ₂ O ₃	391 °C, 21 μmol·g ⁻¹	431 °C, 44 μmol·g ⁻¹	428 °C, 65 μmol·g ⁻¹
Pt/Mg-Al ₁	410 °C, 111 μmol·g ⁻¹	463 °C, 294 μmol·g ⁻¹	451 °C, 405 μmol·g ⁻¹
Pt/MgO	448 °C, 122 μmol·g ⁻¹	512 °C, 356 μmol·g ⁻¹	506 °C, 478 μmol·g ⁻¹

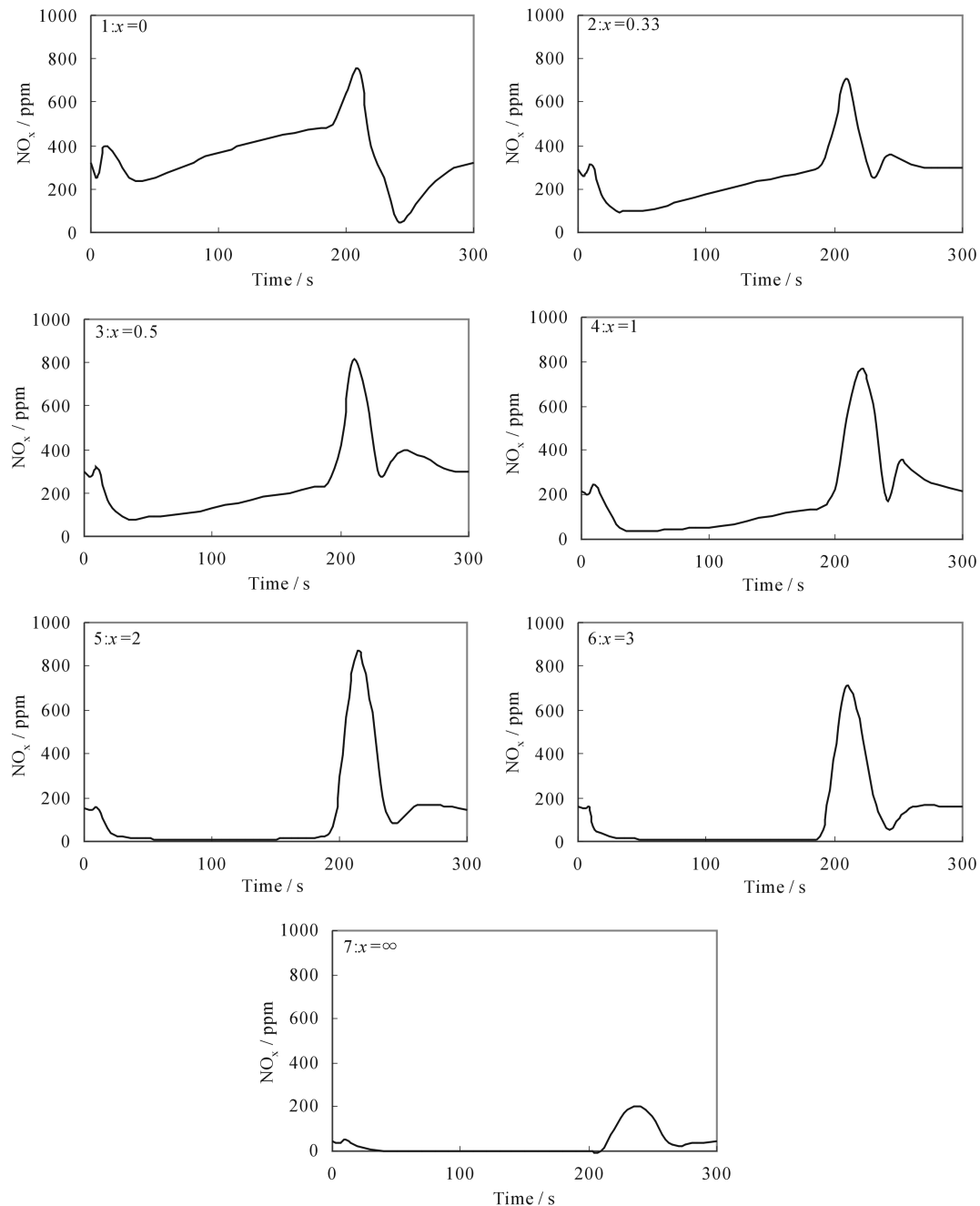


Fig. 3. NO_x concentration profile over catalysts in the storage-reduction cycle at 400°C (storage stage: 190 s, 8% O_2 , 550 ppm NO , N_2 balance; reduction stage: 110 s, 800 ppm C_3H_6 , 550 ppm NO , N_2 balance).

Table 4. NO_x total conversion over catalysts with different Mg/Al atomic ratios in Dynamic NO_x storage-reduction at 400°C

	Mg/Al atomic ratio (x)						
	0	0.33	0.5	1	2	3	∞
X_{total} (%)	36.1	52.8	54.2	65.6	78.1	80.9	94.3

face was consumed to a certain extent, the presence of oxygen could promote the reduction of NO_x by C_3H_6 . It can be seen that NO_x concentration always dropped first to a certain value, then increased again in 230–240 s of each cycle, which led to the second NO_x peak.

This NO_x peak was always accompanied by a rapid increase of the C_3H_6 concentration. It is possible that the oxygen adsorbed on the catalyst surface at the storage stage was used up and the reduction of NO_x proceeded in the absence of oxygen at this time. The NO_x breakthrough peak at the beginning of the storage stage was not pronounced for Pt/Mg- Al_2 , Pt/Mg- Al_3 and Pt/MgO. This result is similar to that obtained by Salasc et al. [Salasc et al., 2002], who found that this peak was most significant for Pt/ Al_2O_3 , but weak and just as an indication for Pt/BaO/ Al_2O_3 . They suggested that this peak originates from the desorption of the NO adsorbed on Pt during the rich phase. As for the samples that contained storage components, this peak was weakened by the storage of NO when O_2

was introduced into the catalyst surface.

Pt/MgO yielded the best NO_x conversion at 400 °C. We attributed this result to two reasons. First, from the TPD experimental results, the rate of decomposition of the nitrates formed on the Pt/MgO surface was lower than that over Pt/Mg-Al_x and Pt/Al₂O₃. Second, the rate of NO_x reduction by C₃H₆ on the Pt/MgO surface was the fastest of all catalysts in this study. For the Pt/MgO, in the runs with prolonged reduction time, the final NO_x concentration was 55 ppm, while for Pt/Mg-Al₂ and Pt/Mg-Al₃, the NO_x concentration was stabilized at 120 ppm and 140 ppm, respectively, and for Pt/Al₂O₃ and Pt/Mg-Al_x (x<1), the reduction of NO_x was more incomplete. It was believed that in the absence of oxygen, the reduction of NO_x by C₃H₆ was a self-poisoning reaction because the noble metal sites were occupied by NO or by propylene or propylene derived species [Salasc et al., 2002]. Therefore, it can be concluded that MgO can inhibit the self-poisoning of the reaction. Similar results have been obtained by Salasc et al. [Salasc et al., 2002]. They pointed out that in Pt/BaO/Al₂O₃, barium oxide could prevent self-poisoning in the reduction of NO_x. The reason given by them was that NO_x originating from the decomposition of barium nitrate and hydrocarbons that adsorbed on BaO could migrate to the noble metal sites *via* spill-over, and these migrating species may then react with adsorbed species on the noble metal sites.

CONCLUSIONS

In this paper a series of Pt/Mg-Al-O and Pt/MgO catalysts for the removal of NO_x were prepared. The performance of these catalysts was evaluated and summarized as follows:

At 350 °C, the stored amount of NO_x at saturation and breakthrough time increase with the increase of the Mg/Al atomic ratio in the catalyst. NO_x is stored in the form of nitrates, and nitrates formed over Pt/MgO are more stable than that over Pt/Mg-Al-O. During the dynamic storage-reduction experiments, three NO_x breakthrough peaks could be observed, which lowered NO_x conversion. Oxygen adsorbed over the catalyst surface can influence the reduction of NO_x by C₃H₆. With increasing Mg/Al atomic ratio in the catalysts, NO_x conversion increases. Pt/MgO has the highest total NO_x conversion due to its high activity in the reduction of NO_x by C₃H₆. MgO could inhibit self-poisoning of the reaction of NO_x and C₃H₆.

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NOMENCLATURE

A_x : the amount of NO_x stored to saturation over the catalyst [μmol·g⁻¹]
 m_{cat} : mass of the catalyst [g]
 [NO_x]: NO_x concentration [ppm]
 v : feed gas flow rate [L·min⁻¹]
 X_{NO_x} : NO_x total conversion in storage-reduction cycles [%]

Subscripts

in : inlet

out : outlet

x : Mg/Al atomic ratio of the catalyst

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