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Comparison of NO adsorbing ability and process on Pt/Mg/Al oxide catalysts prepared by different methods

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Pt/Mg/Al metal oxide catalysts were prepared by impregnation and co-precipitation methods, respectively. These samples were characterized by BET, XRD and NO-TPD; their NO_X storage property and adsorbing intermediate species were investigated with NSC and FTIR. The results showed that the prepared methods exert significant influence on the physical structure properties and the adsorption abilities of NO. (Pt)/Mg/Al samples prepared by impregnation (IM) have larger specific areas and higher NO_X storage capacity than (Pt)/Mg/Al catalysts prepared by co-precipitation (CP). The intermediate species of NO adsorbing process indicated that NO was firstly adsorbed as bridged nitrites both on Pt/Mg/Al (IM) and on Pt/Mg/Al (CP), then on Pt/Mg/Al (IM) the nitrites transferred into monodentate and bidentate nitrate species while on Pt/Mg/Al (CP) the nitrites only transferred into monodentate nitrate species.

KEY WORDS: NO_X; NSR; NO_X storage capacity; FTIR; Pt/Mg/Al.

1. Introduction

The lean-burn engine has been attracted much attention because of its high fuel economy and low environmental impacts. However, three-way catalyst (TWC) used in stoichiometric conditions could not efficiently remove NO_X in lean-burn conditions. NO_X storage reduction (NSR) method, brought forward by TOYOTA Company, is a promising way to eliminate NO_X in lean-burn exhaust gas [1]. NSR system demands a successive sequence of lean and rich operating periods to transfer $NO_X - N_2$. Regarding the NSR catalyst, most of investigations were focused on Pt/Ba/Al/ catalysts [2–10], in which Pt could oxidize NO–NO_2, and BaO could work as a storage material. Therefore, a high NO_X storage capacity (NSC) is significant for real application.

In previous literature, it is reported that Mg/Al material has better low-temperature activity and higher sulfur resistance than Ba/Al material, and MgO has weaker alkalescent than BaO, which is beneficial to NO_X adsorption and desorption [11, 12]. However, most of the catalysts were prepared by co-precipitation method, and the adsorption process was not particularly studied. In this work, the Pt/Mg/Al catalysts were prepared by two different kinds of methods, and their adsorbing property and process were studied in detail.

2. Experimental

2.1. Catalyst preparation

2.1.1. Pt/Mg/Al preparation by impregnation (IM)

γ-Al_2O_3 (calcined from $Al(OH)_3$ in 500 °C for 3 h) was used as catalyst support. Mg/Al metal oxide was prepared by using a two-step incipient wetness impregnation (IM) method. First, MgO was doped on Al_2O_3 support by using incipient wetness impregnation with $Mg(NO_3)_2 \cdot 6H_2O$ (Aldrich, 99%). The ratio of MgO to Al_2O_3 is 30% by weight. After dried at 120 °C overnight, the catalysts were calcined at 500 °C for 2 h in air. Then, the MgO/Al_2O_3 was obtained and denoted as Mg/Al (IM). Noble metal Pt (0.5% by weight of MgO/Al_2O_3) were introduced from $H_2PtCl_6 \cdot 6H_2O$ (Aldrich) using the same incipient wetness impregnation method, followed by drying at 120 °C for 12 h and calcinations at 500 °C in air and then reduced at 500 °C in the flow of H_2 for 2 h. This catalyst was denoted as Pt/Mg/Al (IM). Finally, the catalysts were palletized and crushed to 40–60 mesh for evaluation.

2.1.2. Pt/Mg/Al preparation by co-precipitation (CP)

The Mg/Al metal oxide was prepared in two steps by co-precipitation (CP) from aqueous solutions of nitrates. First, the calculated amounts of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3) \cdot 9H_2O$ were dissolved in distilled water (total metal ions amount 1 mol/L). The ratio of MgO to Al_2O_3 is 30% by weight. The calculated amounts of NaOH and Na_2CO_3 were dissolved in distilled water (total alkali ions amount 3 mol/L). The amount of NaOH was kept at 16 (by mole) on Na_2CO_3.

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These two solutions were added drop wise to the distilled water produced precipitates while stirred strongly, and the pH was kept between 9 and 10. The precipitates were aged for 10 h in 70 °C in water bath, and then washed by 6 times, dried at 110 °C for 10 h, followed by calcination at 500 °C for 5 h in air. Then the metal oxide catalyst obtained was denoted as Mg/Al (CP). The introduction of Pt to this support is the same process as impregnation method mentioned above, and this catalyst was denoted as Pt/Mg/Al (CP).

2.2. Characterization

BET surface area measurements were performed by using N_2 adsorption. The samples were evacuated at 473 K under vacuum for 4 h. The specific surface area was determined from the linear part of the BET equation.

The X-ray diffraction (XRD) pattern of Pt/Mg/Al (IM) and Pt/Mg/Al (CP) catalyst was recorded with an Automated D/Max B diffractometer. Cu Kα radiation was utilized in X-ray tube operated at 40 kV and 120 mA.

NO_X Sorption Capability (NSC) measurements were carried out in a U-type quartz reactor with inner diameter of 5 mm under normal atmospheric pressure. 0.5 g sample was employed in the test. After pretreatment by flowing pure N_2 (400 mL/min) at 500 °C for 30 min, the samples were cooled to 300 °C in N_2 for adsorption. Then a gas mixture (650 ppm of NO and 8% O_2/N_2) passed through the sample at a space velocity of 30000 h^{-1} for 30 min. An on-line NO_X analyzer (Cheminulene 42HC) was used to measure the NO–NO_2 concentration.

Temperature-programmed desorption (TPD) experiments were carried out in a U-size of fixed-bed reactor with an inner diameter of 5 mm. The temperature was controlled by a programmable temperature controller (CKW-1100). For NO_X adsorption, 0.5 g sample was first treated with nitrogen at 500 °C for 30 min. After the sample was exposed to the flow of 650 ppm NO and 8% O_2/N_2 for 30 min at 300 °C, NO and O_2 were cut, and pure nitrogen was passed through the reactor and nitrogen oxides desorption was performed by ramping the temperature from 300 to 600 °C at 10 °C/min. The total flow rate of the gas mixtures of 650 ppm NO and 8% O_2/N_2 was fixed at 100 mL/min, and the nitrogen flow rate was 400 mL/min.

In situ DRIFTS spectra were recorded on a NEXUS 670-FTIR. The samples were finely ground and placed in a ceramic crucible. The feed gas streamed into the cell at a total flow rate of 100 $cm^3 \cdot min^{-1}$. The temperature in the cell can be programmed from 20 to 800 °C. Prior to analysis, each of the samples was heated firstly in N_2 and O_2 at 500 °C for 30 min followed by pure N_2 at 500 °C for 30 min. The background spectra were collected after dwelling for 30 min at a desired temperature. The sample spectra reported here were collected after dwelling for 30 min. In all cases, 100 scans were recorded at a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Characterizations of the samples

3.1.1. XRD

The XRD patterns of the samples are shown in Figures 1 and 2. It can be seen that the XRD patterns of the samples were of great difference due to the various preparation method. Figure 1 shows the XRD patterns of samples prepared by co-precipitation. The groups at 2θ = 11.24°, 22.9°, 34.66°, 38.9°, 46.4°, 60.34° correspond to the main diffraction peaks of hydrotalcite Mg/Al (CP) sample. The Pt/Mg/Al (CP) sample has the same diffraction peaks as the Mg/Al (CP), which indicates that Pt with a high dispersion on the hydrotalcite does not disturb the intrinsic phase.

Figure 2 shows the XRD patterns of samples prepared by impregnation method. The groups at 2θ = 37.02°, 45.78°, 66.58° correspond to the main diffraction peaks of γ-Al_2O_3, but Mg/Al (IM) has two peaks at 2θ = 42.9°, 62.26° corresponded to the main diffraction peaks as MgO, which indicated that the quantity of Mg beyond the quantity of the maximum monolayer dispersion. When Pt is loaded on sample, both have no other diffraction peaks, which indicate that Pt was well dispersed on samples.

The different XRD patterns of these two kinds of catalysts indicate that the Pt/Mg/Al (CP) and Pt/Mg/Al (IM) catalysts have different physical structure properties. The Pt/Mg/Al (CP) catalysts have only hydrotalcite structure, while on the Pt/Mg/Al (IM) catalysts, MgO have two kinds of patterns, one is monolayer dispersion

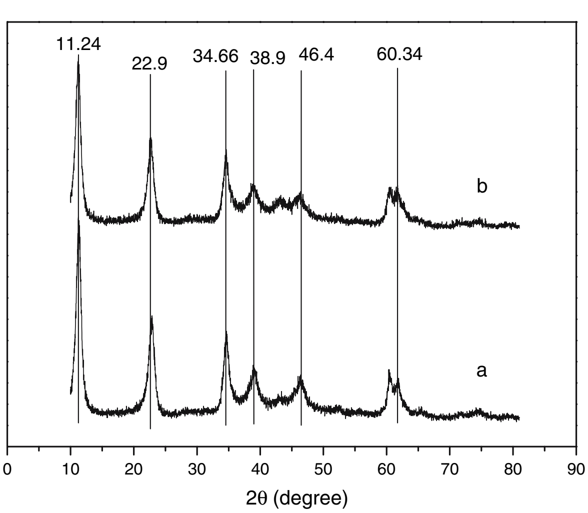


Figure 1. XRD patterns of various samples prepared by co-precipitation. (a) Mg/Al (CP); (b) Pt/Mg/Al (CP).

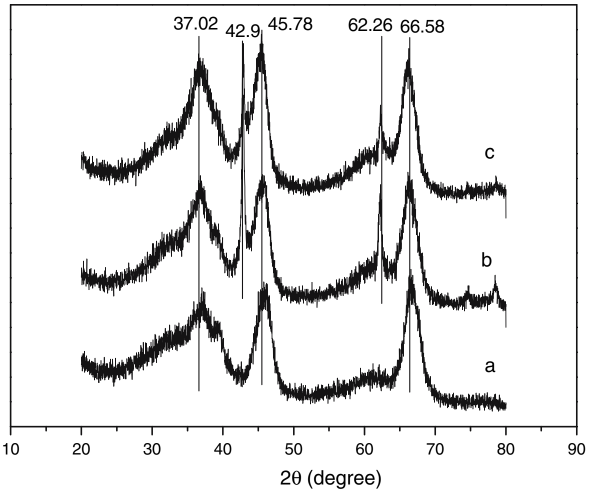


Figure 2. XRD patterns of various catalysts prepared by impregnation. (a) Al_2O_3; (b) Mg/Al (IM); (c) Pt/Mg/Al (IM).

on Al_2O_3, and the other is the excessive bulk MgO. These differences in physical structure properties may be lead to the different specific area and NO_X storage capacities.

3.1.2. *BET*

The specific surface areas of (Pt)/Mg/Al prepared by two different methods were summarized in Table 1. It can be seen that the specific surface area of the samples were of great difference due to the various preparation method. The specific area of (Pt)/Mg/Al (IM) were much larger than (Pt)/Mg/Al (CP), and the specific area of Mg/Al (IM) is about three times of Mg/Al (CP). The great difference of specific area was probably due to the different crystal structures that were formed with various preparation methods. Both for Mg/Al (IM) and Mg/Al (CP), the addition of 0.5 wt% Pt has only slight effect on the specific area.

3.1.3. *NO_X adsorption capacity*

NSC of (Pt)/Mg/Al samples prepared by two different methods were summarized in Table 2. The preparation method exerts a significant influence on the NSC, in addition, the addition of Pt on the Mg/Al has obvious effect on the NSC both for the samples by IM and CP. The largest NSC (4234 μ mol/g) was attained on the Pt/Mg/Al (IM) catalyst among all the samples during co-adsorption of NO_X and O_2. It was 2.5 times of NSC compared to Pt/Mg/Al (CP) sample. From the results of BET and XRD, the different crystal structure and specific surface area are the main reason for the great difference of NSC, the influence of Pt is due to the oxidation of NO–NO_2 over Pt active sites and NO_2 is easier to adsorb on surface of the samples.

Table 1
The BET surfaces of samples

Catalyst	BET surface (m^2/g)
Mg/Al (IM)	140.30
Pt/Mg/Al (IM)	146.25
Mg/Al (CP)	49.85
Pt/Mg/Al (CP)	42.56

Table 2
NO_X storage capacity of the samples under different adsorption conditions at 300 °C

Sample	NO_X storage capacity (μmol/g)
Mg/Al (IM)	1403
Pt/Mg/Al (IM)	4234
Mg/Al (CP)	840
Pt/Mg/Al (CP)	1684

3.1.4. *NO-TPD*

The NO-TPD profiles of different samples are presented in Figur 3. It contains the NO_X desorption curves on various catalysts pretreated with co-adsorbing NO (650 ppm) and O_2 (8%) at 300 °C. Both for Mg/Al (IM) and Mg/Al (CP), there are two peaks in the NO-TPD profile, one is small peak around 350 °C, and another is large around 550 °C. In comparison, only one peak was observed with the addition of Pt on the Mg/Al samples prepared by IM or CP, and the peak-temperature is centered on 450 °C. However, the (Pt)/Mg/Al (IM) catalysts have much larger desorption areas than the (Pt)/Mg/Al (CP) catalysts, which is in accordance with the NSC data. The (Pt)/Mg/Al (IM) catalysts have much larger BET areas, and this is helpful for the NO_X adsorption.

Analyzing the components of the desorption gas of each sample, it indicates that the stored species of NO_X on the catalysts mainly attribute to nitrates which were decomposed to NO_2 accompanying with O_2 in the process of TPD, while the stored species of NO_X on the catalysts without Pt should mainly attribute to nitrites which were decomposed to NO in the process of TPD. For each kind of catalysts, the one containing Pt has much larger amount of NO_X desorption. Because the main desorption species were nitrates which could be more easily storage on the surface of the catalysts than nitrites, it indicates that the presence of Pt promoted the NO oxidization to NO_2 and then resulted in the increase of NO_X storage, but the stability of the nitrates formed on the surface of the catalysts decreased, which is beneficial to NO_X release and reduction in rich condition.

3.2. *FTIR data*

3.2.1. *Mg/Al (CP) and Pt/Mg/Al (CP)*

The FTIR spectra of Mg/Al (CP) sample exposed to 650 ppm NO in N_2 and O_2 mixture at 300 °C for 30 min are shown in Figure 4. According to previous literature,

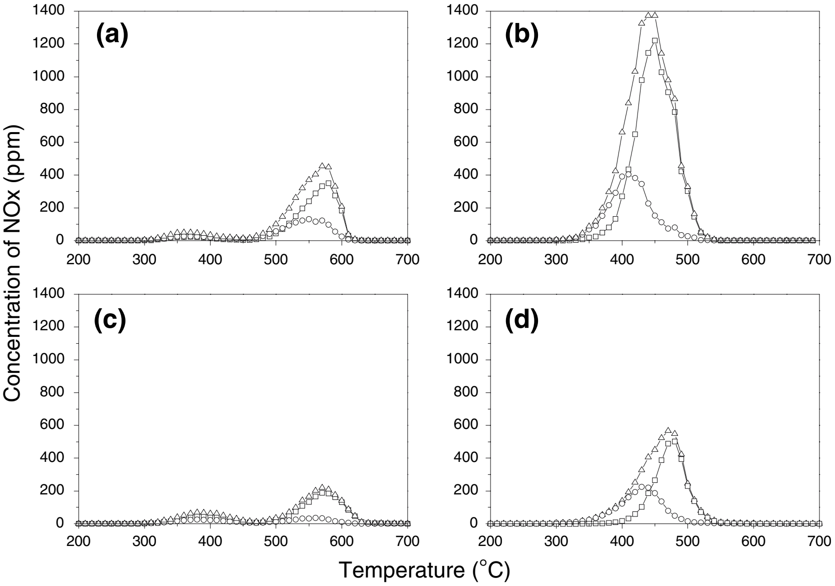


Figure 3. NO-TPD profiles of different catalysts prior to co-adsorbing NO and O_2 at 300 °C. (Reaction conditions: 650 ppm NO, 8% O_2/N_2, GHSV = 30000 h^{-1}, pretreated at 500 °C for 30 min in N_2) (a) Mg/Al (IM), (b) Pt/Mg/Al (IM), (c) Mg/Al (CP), (d) Pt/Mg/Al (CP); (□) NO, (○) NO_2, (△) NO_X.

all peaks between 1000 and 2000 cm^{-1} can be assigned to different types of surface nitrate and nitrite species associated with the samples. For example, the peaks at 1230 cm^{-1} can be assigned to bridged nitrite species, while the peaks at 1321, 1284, 1531, 1630 cm^{-1} can be assigned to bidentate, monodentate and bridging nitrate species [13, 14]. For Mg/Al (CP), there are major peaks at 1230 and 1321 cm^{-1}, which indicate that the NO was mainly adsorbed as nitrite. For Pt/Mg/Al (CP), the similar peaks were observed in the spectra, while the intensity of the nitrate peaks slightly increased. Therefore, there are two steps for NO_X adsorption. Firstly, NO was mainly adsorbed as bridged nitrite species on the catalyst surface; then NO was mainly adsorbed as monodentate nitrate species (1531 and 1284 cm^{-1}). The peaks at 1630 cm^{-1} were so unconspicuous at both samples, which indicated that there were hardly bridging nitrate species produced. This adsorption process indicated that NO_X was primarily existed on the catalyst as NO_3^- surface at 300 °C. Combined with BET and XRD data, the Pt had little influence to the specific areas and physical structure property, but considering the results of NO-TPD and NSC, the amount of NO desorption and storage were obviously different between these two samples, this indicated Pt could serve as an active site to oxidize nitrites to nitrates, which have better adsorption and desorption abilities, so as to increase the NSC of the catalysts.

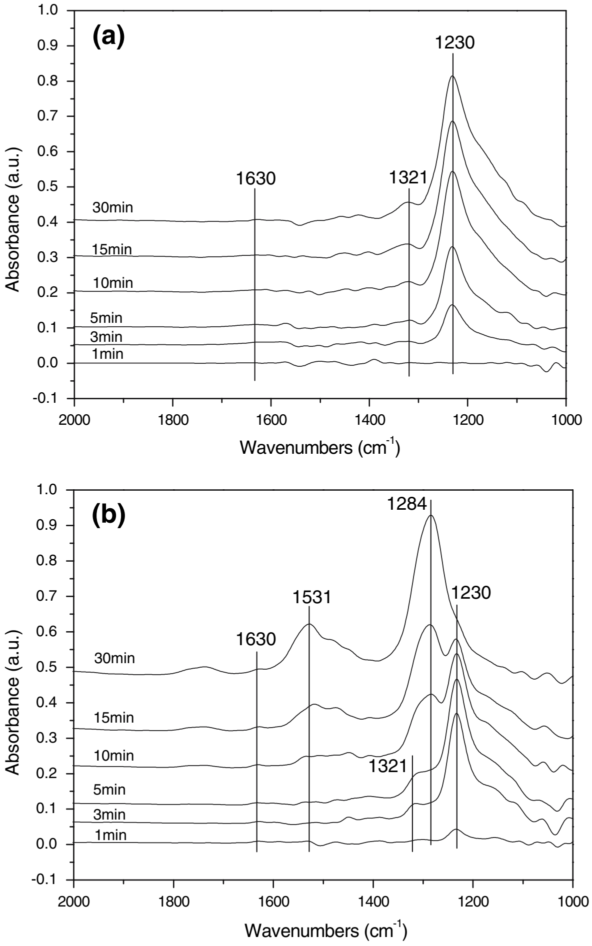


Figure 4. FTIR spectra of NO and O_2 co-adsorption onto the catalysts prepared by CP at 300 °C. (a) Mg/Al (CP); (b) Pt/Mg/Al (CP). (Feed composition: 650 ppm NO, 8% O_2, N_2 as the balance gas, pretreated at 500 °C for 30 min in N_2).

3.2.2. Mg/Al (IM) and Pt/Mg/Al (IM)

The FTIR spectra of a Pt/Mg/Al(IM) sample exposed to 650 ppm NO in N_2 and O_2 mixture at 300 °C for 30 min are shown in Figure 5. This spectra contain

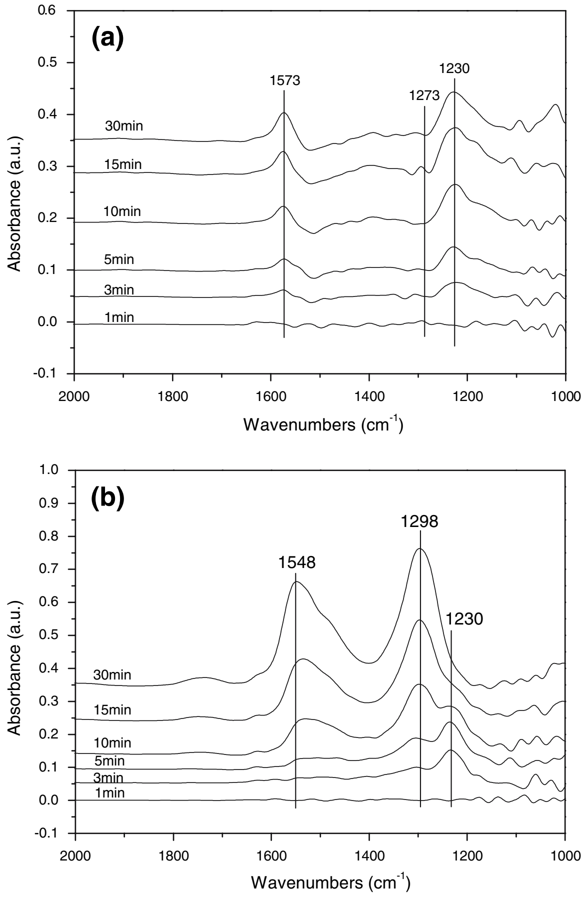
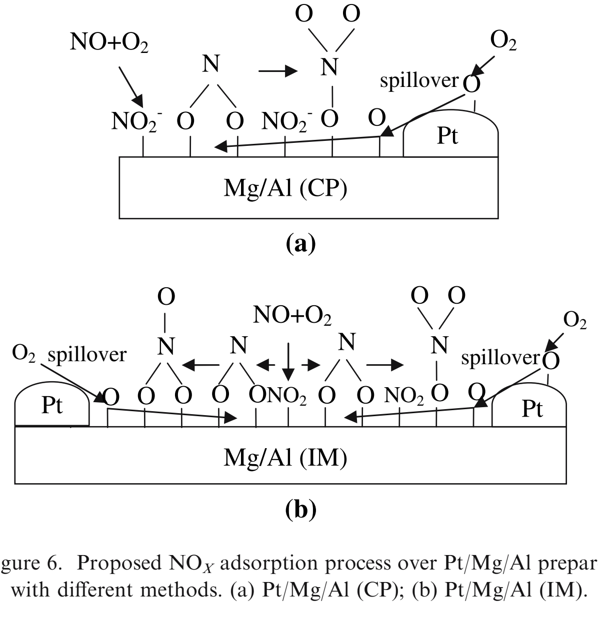


Figure 5. FTIR spectra of NO and O_2 co-adsorption onto catalysts prepared by IM at 300 °C. (a) Mg/Al (IM); (b) Pt/Mg/Al (IM). (Feed composition: 650 ppm NO, 8% O_2, N_2 as the balance gas, pretreated at 500 °C for 30 min in N_2).

several major peaks at 1230 and 1573 cm^{-1}, which can be assigned to surface bridged nitrite and bidentate nitrate species respectively. The peaks at 1573 cm^{-1} indicates that NO will be more easily oxidized to NO_2 on the Mg/Al (IM) catalyst than Mg/Al (CP) catalyst. For Pt/Mg/Al (IM) samples, there are also two steps for NO_X adsorption. On the first step, NO was mainly adsorbed as bridged nitrite species (1230 cm^{-1}) on the catalyst surface which is similar with those results on the catalyst Pt/Mg/Al (CP); with the reaction time passing, NO was mainly adsorbed as bidentate and monodentate nitrate species (1298 and 1548 cm^{-1}). Combined with BET, XRD and NO-TPD data, the Pt had the same influence as in the catalyst Pt/Mg/Al (CP).



(a)

(b)

Figure 6. Proposed NO_X adsorption process over Pt/Mg/Al prepared with different methods. (a) Pt/Mg/Al (CP); (b) Pt/Mg/Al (IM).

Typically, there are two approaches of NO_X storage on the Pt/Mg/Al catalysts: One is that NO was first transferred into bridged nitrite species, then the nitrite species were oxidized by the oxygen atoms spilling over Pt sites on catalyst surface to bidentate nitrate species. The other is that NO was firstly oxidized to the NO_2 adsorption species over Pt sites of the catalyst, then NO_2 species reacted with O_2 to form monodentate nitrate species.

The FTIR spectra indicate that the NO was first adsorbed on the surface on these two kinds of catalysts which is in accordance with the first approach. On the catalyst Pt/Mg/Al (CP), after about 15 min, the NO was adsorbed on the surface as the first approach to form nitrates. On the catalyst Pt/Mg/Al (IM), after 10 min, along with the first NO adsorption approach, the NO was adsorbed over the Pt sites as the second approach at the same time. Figure 6 shows the reaction pathways of NO_X oxidation and adsorption onto the Pt/Mg/Al (CP) and Pt/Mg/Al (IM) catalysts. In comparison, the intermediate species of NO absorbing process indicated that NO was firstly adsorbed as bridged nitrites both on Pt/Mg/Al (IM) and on Pt/Mg/Al (CP), then on Pt/Mg/Al (IM) the nitrite transferred into monodentate and bidentate nitrate species while Pt/Mg/Al (CP) only transferred into monodentate nitrate species. The different NO adsorption approaches were caused by different physical structure properties of the two kinds of catalysts, which were characterized by the XRD patterns. On the Pt/Mg/Al (CP) catalysts, MgO has only the hydrotalcite pattern, while on the Pt/Mg/Al (IM) catalysts MgO has two kinds of patterns. The differences in physical structure properties also leaded to the different NO_X storage capacities, and also resulted in the differences of the NSC.

4. Conclusion

The different prepared methods exert significant influence on the physical structure property and the adsorption ability of NO. The different crystal structures were obtained on the samples prepared by two methods. The samples Pt/Mg/Al (IM) have large BET surface areas and high NO_X storage ability compared with Pt/Mg/Al (CP). The addition of Pt on Mg/Al (CP) and Mg/

Al (IM) resulted in the decrease of the stability of nitrates formed on the sample surfaces, and the peak temperature of NO-TPD profile shifted to low temperature region, which indicates that the presence of Pt decreased the stability of NO_X adsorption species. The FTIR results indicated that NO was firstly transferred into bridged nitrite species, and then the nitrite species were oxidized to nitrate species with different approaches.

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