



Short communication

Low-temperature selective catalytic reduction of NO with propylene in excess oxygen over the Pt/ZSM-5 catalyst

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ABSTRACT

A 0.5 wt% Pt/ZSM-5 catalyst was used for the low-temperature selective catalytic reduction (SCR) of NO with C₃H₆ in the presence of excess oxygen. Under an atmosphere of 150 ppm NO, 150 ppm C₃H₆ and 18 vol% O₂ (GHSV 72,000 h⁻¹), Pt/ZSM-5 showed remarkably high catalytic performance giving 77.1% NO reduction to N₂ + N₂O and 79.7% C₃H₆ conversion to CO₂ simultaneously at 140 °C. The samples were characterized by means of NO temperature programmed desorption (TPD), NO/C₃H₆ temperature programmed oxidation (TPO), BET surface area, XRD and TEM. The catalytic activities of C₃H₆ combustion and NO oxidation are improved by well-dispersed platinum significantly. It is found that the enhanced activity of Pt/ZSM-5 for the low-temperature SCR is associated with its outstanding activities in the TPO processes of NO to NO₂ and C₃H₆ to CO₂ in low temperature range.

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1. Introduction

NO_x (NO, NO₂) emitted from stationary and mobile sources result in serious air pollutions, e.g., acid rain, photochemical smog and so on, and then evoke serious damages to human health and environmental safety [1,2]. With the increase of the motor vehicles, the problems caused by exhaust gas pollution are being more and more serious. However, the traditional three-way catalysts (TWC) are not effective for the removal of low-concentration, oxygen-rich and low-temperature exhausts emitted from lean-burn engines and diesel vehicles [3]. Therefore, it is urgent to develop new catalysts with high performance for the treatment of low-concentration exhaust at low temperature.

Selective catalytic reduction (SCR) technology is believed to be one of the most promising options for deNO_x. However, SCR usually requires rather high reaction temperature (over 300 °C) when hydrocarbons (HCs) [4] or CO [5] are used as reducing agents. Although low-temperature removal of NO_x by SCR can be achieved with the application of the toxic reducing agent NH₃ [6,7], it is not suitable for mobile engines and immobile constructions (e.g., urban road tunnels, parking lots). If SCR of NO_x with HC occurs over catalyst at low temperature (< 200 °C) with high deNO_x activity, the technology could compete with NH₃-SCR and be more practical for the removal of NO_x at stationary or mobile sources.

Low-temperature SCR of NO_x with HCs has been extensively studied and a large number of catalysts have been evaluated. Noble metals (Pt, Pd, Rh, Ru) doped catalysts, e.g., Pt/Si-MCM-41 [8], Rh/TiO₂ [9], Pt/Al₂O₃ [10], are promising due to their high activity at low temperatures as well as good sulfur resistance and tolerance towards stream.

In our recent work, 0.5 wt% Pt/TiO₂ was found to be the most active catalyst among a series of noble metal (Pt, Pd, Rh and Ru) supported TiO₂ catalysts for the low-temperature SCR of NO with C₃H₆ in excess oxygen. Under an atmosphere of 150 ppm NO, 150 ppm C₃H₆ and 18 vol% O₂ (GHSV 72,000 h⁻¹), the 0.5 wt% Pt/TiO₂ achieved 63% NO_x reduction and 84% C₃H₆ conversion simultaneously at 140 °C [11]. This indicates that Pt loading leads to enhanced low-temperature catalytic activity for C₃H₆-SCR. Moreover, zeolites and other microporous materials have been widely studied for possible lean-burn and diesel engines' exhaust gas purification engineering application. ZSM-5 is one of the most important catalysts and supports used for three way catalysts (TWC) and SCR catalysts [12–14] among them. In the present work, we reported a 0.5 wt% Pt/ZSM-5 catalyst that exhibited remarkably higher catalytic activity for the low temperature C₃H₆-SCR in the presence of excess O₂.

2. Experimental

2.1. Catalyst preparation

The 0.5 wt% Pt/ZSM-5 catalyst was prepared by wetness impregnation method using commercial H-ZSM-5 (Shanghai Fuxu Ltd.,

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Si:Al = 300–500) and $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ as starting materials. The catalysts evaluated in the study were all crushed to 40–60 mesh.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of catalysts were recorded using a Rigaku D/max-2200/PC X-ray Diffractometer with $\text{Cu K}\alpha$ radiation and operated at 49 kV and 20 mA.

Measurement of the BET surface area was based on N_2 adsorption data from a Quantachrome NOVA1000a Sorptomatic apparatus.

TEM images were obtained by employing a JEOL-2010 device with 200 kV accelerating voltage.

2.3. Catalytic activity tests

The SCR activity of the prepared catalysts was determined in a continuous fixed-bed U-tube quartz reactor (1/4" o.d.) using a 200 mg catalyst. Experiments were conducted in the temperature range of 120–350 °C with a gas mixture containing 150 ppm NO, 150 ppm C_3H_6 , 18 vol% O_2 and Ar balanced at a total flow rate of 120 cm^3/min (GHSV 72,000 h^{-1}). CO , CO_2 and C_3H_6 were determined by a gas chromatograph (GC) equipped with hydrogen flame ionization detector (FID). CO , CO_2 and C_3H_6 were determined by a gas chromatograph (GC) equipped with hydrogen flame ionization detector (FID) in SCR reactions. The NO_x (NO , NO_2) concentration was measured by a chemiluminescence NO/NO_2 analyzer (Thermo Environmental Instruments, 42i LS) in this paper. The activity data was collected after the reactions reached near steady state for at least 30 min at each temperature.

2.4. NO and C_3H_6 temperature programmed desorption

TPD experiments were conducted in the same reactor as described in Section 2.3. Prior to the TPD experiment, the catalyst (200 mg, 40–60 mesh) was loaded in the reactor, supported by quartz wool, and heated at 350 °C under Ar flow for 30 min and then cooled down to 50 °C. Adsorption of NO was performed by passing a flow of 150 ppm NO and 18 vol% O_2 balanced with Ar through the sample bed at 50 °C for 1 h. After the sample was purged with Ar for 20 min at 50 °C, the TPD measurements were carried out up to 350 °C with a heating rate 4 °C/min in Ar flow. CO_2 and C_3H_6 were continuously analyzed with a quadrupole mass spectrometer (Ametek Process Instruments, Dycor DM100M) in the temperature-programmed experiments. The gas flow rates in this paper were all fixed at 120 cm^3/min .

2.5. NO + O_2 and C_3H_6 + O_2 temperature programmed oxidations

$\text{NO}/\text{C}_3\text{H}_6$ -TPO was performed in the continuous fixed-bed U-tube quartz reactor (see Section 2.3). The feed gas mixture balanced with Ar contained 150 ppm NO and 18 vol% O_2 in the NO-TPO, and 150 ppm C_3H_6 and 18 vol% O_2 in the C_3H_6 -TPO, respectively.

3. Results and discussion

3.1. Characterization of catalyst

The BET surface areas of bare ZSM-5 and 0.5 wt% Pt/ZSM-5 are 370 and 355 m^2/g respectively, indicating that noble metal impregnation brought a slight decrease of BET surface area, which is a normal phenomenon for the impregnation process due to the coverage of surface by low surface area active component clusters.

The XRD patterns of the bare ZSM-5 and Pt/ZSM-5 are given in Fig. 1. All showed a MFI structure of zeolite. Moreover, no diffraction

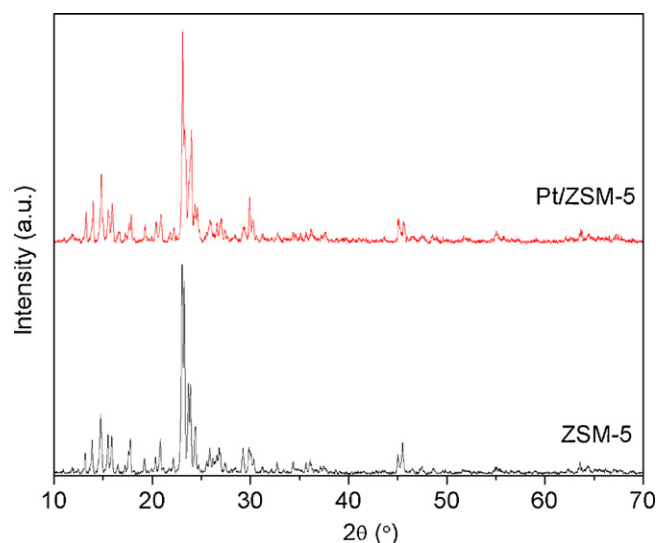


Fig. 1. XRD patterns of ZSM-5 and 0.5 wt% Pt/ZSM-5.

peak corresponding to Pt or PtO was observed for supported ZSM-5, suggesting that noble metal was well dispersed over the support or the formed particles were too tiny to be detected by XRD.

The high dispersion degree can also be confirmed by the TEM image of 0.5 wt% Pt/ZSM-5 (Fig. 2a and b), on which Pt particles are uniformly distributed with a size smaller than 8 nm. The well-dispersed Pt particles could be very important for the outstanding low-temperature SCR activity of Pt/ZSM-5.

3.2. Catalytic activity tests

A comparative study of NO catalytic reduction by C_3H_6 in the presence of 18 vol% O_2 was carried out over ZSM-5 and 0.5 wt% Pt/ZSM-5 (Fig. 3a–c). The 0.5 wt% Pt/ZSM-5 achieved 77.1% NO reduction to $\text{N}_2 + \text{N}_2\text{O}$ (Fig. 3a) and 79.7% C_3H_6 oxidation to CO_2 (Fig. 3b) simultaneously at 140 °C, which were significantly higher than those of ZSM-5. In Fig. 3a, with the temperature increasing from 120 to 350 °C, the NO reduction to $\text{N}_2 + \text{N}_2\text{O}$ over Pt/ZSM-5 and support increased until reached the maximum, and then decreased. The lowering NO reduction efficiency could probably be caused by competitive reactions of C_3H_6 oxidation involving in SCR and direct C_3H_6 combustion. In other words, C_3H_6 were more readily oxidized by O_2 other than to form $\text{C}_x\text{H}_y\text{O}_z$ at high temperature, which was supposed to be selectively oxidized by nitrates. The volcanic variation of catalytic activity versus temperature is similar to that of Pt/TiO₂ reported [11,15]. As shown in Fig. 3b, the C_3H_6 conversion to CO_2 increased with temperature increasing before reaching the 100% platform. Additionally, only CO_2 was detected as the product of C_3H_6 oxidation during the low-temperature SCR of ZSM-5 support and Pt/ZSM-5 catalyst, which indicates that the catalyst and support have 100% selectivity towards CO_2 . At higher temperatures (>200 °C), the NO was mostly converted to NO_2 rather than reduced to N_2 and N_2O (Fig. 3c) over the Pt/ZSM-5.

3.3. NO and C_3H_6 temperature programmed desorption

Fig. 4 shows the TPD profiles corresponding to the NO concentration. Compared to noble metal (Pt, Pd, Rh and Ru) supported TiO₂ [11], quite smaller amounts of NO desorption were detected during NO-TPD (Pt/ZSM-5: 19.7 $\mu\text{mol}/\text{g}$; ZSM-5: 12.0 $\mu\text{mol}/\text{g}$), which suggested that both the Pt/ZSM-5 catalyst and the ZSM-5 support have limited capacity for NO adsorption. Nevertheless,

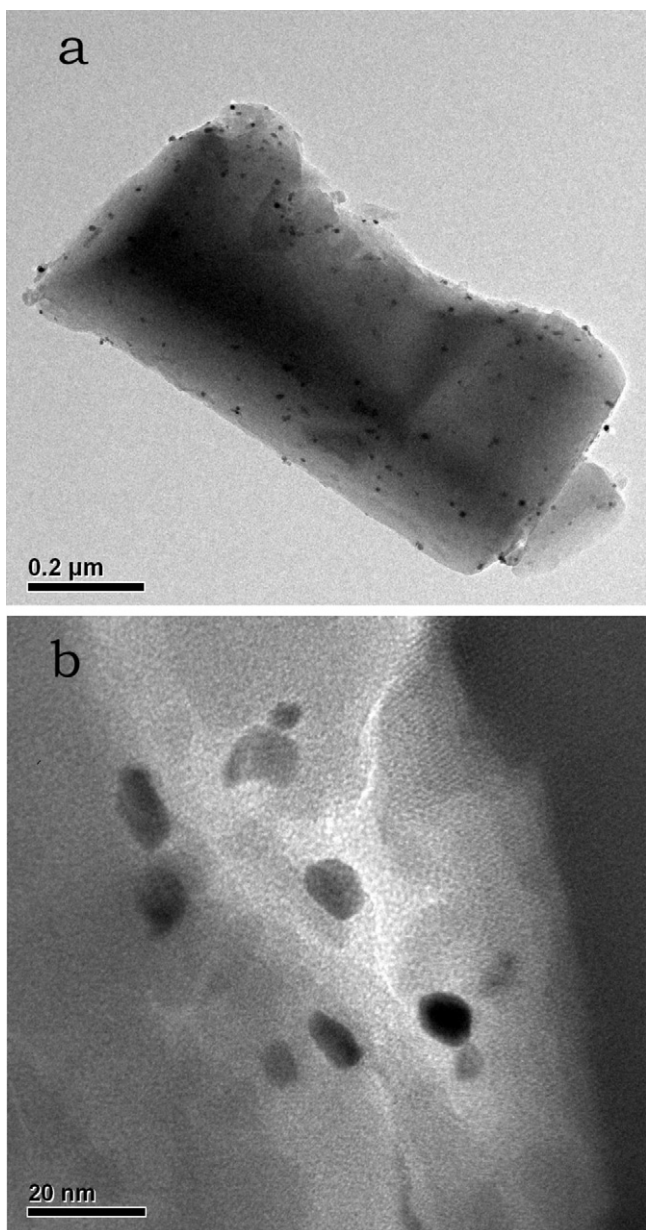


Fig. 2. TEM images of 0.5 wt% Pt/ZSM-5.

Pt loading can also favor the adsorption of NO over catalyst despite a slight BET surface area decrease caused by impregnation process, which could be explained by Pt-NO species formation mechanism [16,17].

By contrast, 0.5 wt% Pt/ZSM-5 and ZSM-5 have remarkably large C_3H_6 adsorption capacity, whereas noble metal supported TiO_2 and bare TiO_2 could hardly adsorb C_3H_6 [11]. The C_3H_6 -TPD profiles of ZSM-5 and Pt/ZSM-5 are presented as Fig. 5. The curves of C_3H_6 desorbed from catalyst and support both show a maximum at $\sim 165^\circ C$, but the profile of Pt/ZSM-5 has one more tiny shoulder around $235^\circ C$. This suggests that two different types of adsorption sites exist on the surface of Pt/ZSM-5. Additionally, Pt/ZSM-5 yields a significantly higher NO desorption amount compared to bare ZSM-5 (Pt/ZSM-5: $207.7 \mu mol/g$; ZSM-5: $90.3 \mu mol/g$). The reason for the increased amount of C_3H_6 desorption over Pt/ZSM-5 is not clear yet.

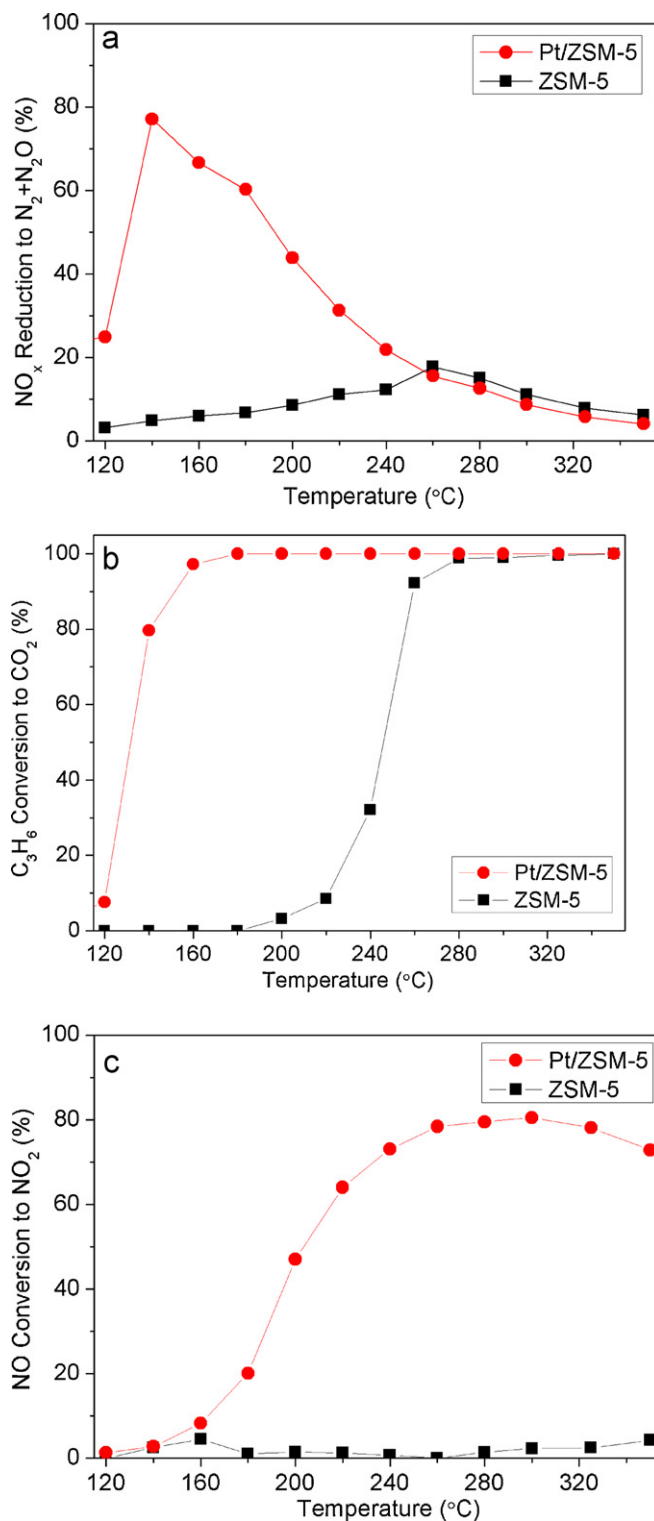


Fig. 3. Activity as a function of temperature in $C_3H_6 + NO + O_2$ SCR reactions over ZSM-5 and 0.5 wt% Pt/ZSM-5 for (a) NO conversion to $N_2 + N_2O$, (b) C_3H_6 conversion to CO_2 and (c) NO conversion to NO_2 . Reaction conditions: 150 ppm C_3H_6 , 150 ppm NO, 18 vol% O_2 , Ar balance; 200 mg catalyst; total flow rate $120 \text{ cm}^3/\text{min}$.

3.4. $NO + O_2$ and $C_3H_6 + O_2$ temperature programmed oxidations

TPO activities of NO to NO_2 by O_2 on ZSM-5 and Pt/ZSM-5 were compared in Fig. 6. The oxidative activities of NO to NO_2 on catalysts increased rapidly with temperature increasing, and then kept a high level. The Pt/ZSM-5 showed absolutely higher oxidation

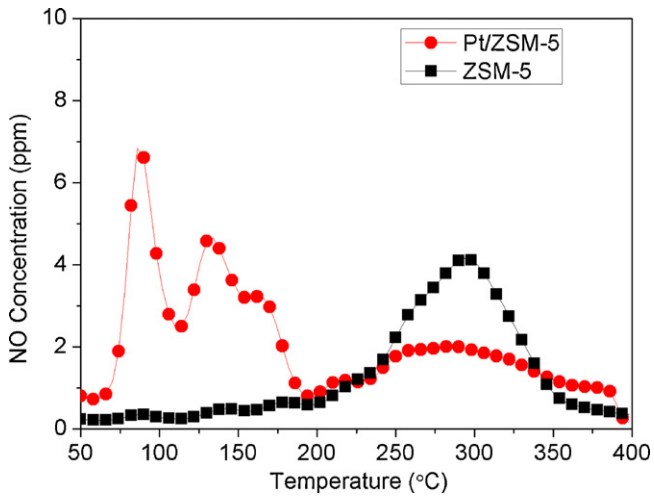


Fig. 4. NO-TPD profiles of ZSM-5 and 0.5 wt% Pt/ZSM-5.

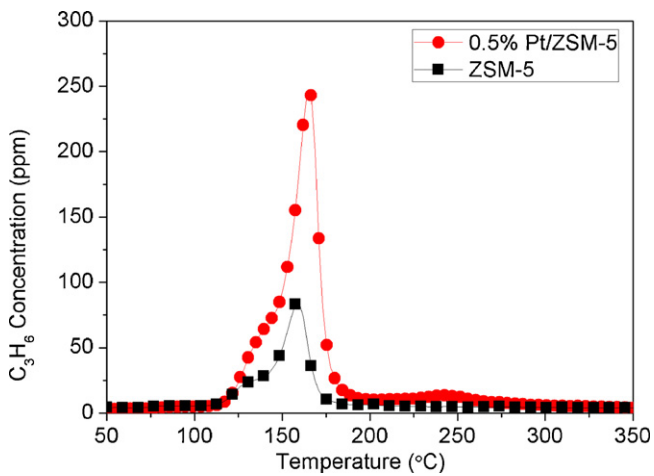


Fig. 5. C_3H_6 -TPD profiles of ZSM-5 and 0.5 wt% Pt/ZSM-5.

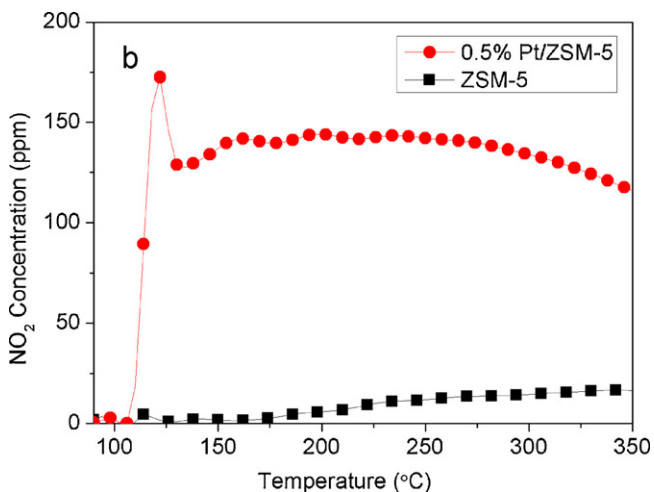


Fig. 6. Temperature programmed oxidation of NO by O_2 over ZSM-5 and 0.5 wt% Pt/ZSM-5. Reaction conditions: 150 ppm NO, 18 vol% O_2 , Ar balance; 200 mg catalyst; total flow rate $120\text{ cm}^3/\text{min}$.

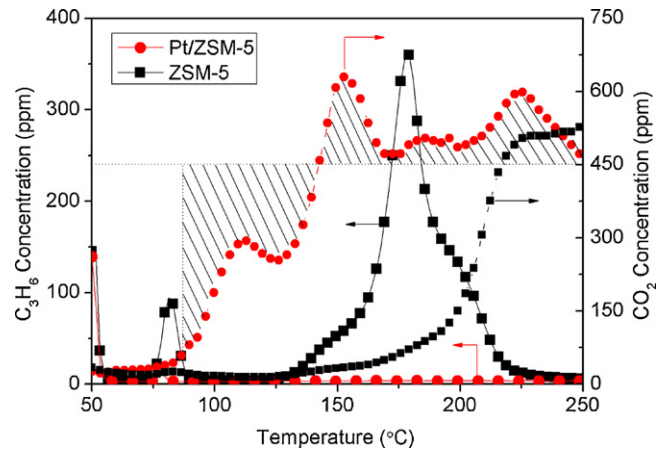


Fig. 7. Temperature programmed oxidation of C_3H_6 by O_2 over ZSM-5 and 0.5 wt% Pt/ZSM-5. Reaction conditions: 150 ppm C_3H_6 , 18 vol% O_2 , Ar balance; 200 mg catalyst; total flow rate $120\text{ cm}^3/\text{min}$.

activity in the whole temperature range than ZSM-5 and even Pt/TiO₂ [11]. This is in good agreement with the catalytic performance obtained in SCR reactions (Fig. 3c). The as-formed NO₂ is easily to form nitrates over catalyst surface in the presence of active Pt sites, which were regarded as important intermediate of SCR reactions [11,15,18]. Compared the oxidation of NO to NO₂ (Fig. 6) with the conversion of NO to NO₂ (Fig. 3c), it is found that NO₂ formation was somewhat inhibited by C_3H_6 introducing, as also reported by Yentekakis [19]. It was suggested that part of NO₂ was transformed to nitrates intermediates, which was readily reduced to N₂ and N₂O by oxygenated species originated from C_3H_6 on the surface of catalyst subsequently [20].

Furthermore, the $C_3H_6 + O_2$ TPO experiments were also carried out to evaluate the catalytic oxidation ability of ZSM-5 and Pt/ZSM-5. C_3H_6 is activated on the surface of the noble metal loading catalysts by forming oxygenated species ($C_xH_yO_z$) with the participation of oxygen, which are originated from the dissociative adsorption of O_2 , surface adsorbed oxygen atoms (e.g., Pt–O) and even the limited decomposition of NO_x species formed on the surface of catalysts in SCR [11]. Nevertheless, an efficient catalyst should preferentially promote oxidation of adsorbed C_3H_6 with Pt–O [16]. Owing to strong C_3H_6 and CO₂ adsorption capability of Pt/ZSM-5 and ZSM-5, it is hard to determine the exact light-off temperature for C_3H_6 combustion by variation of C_3H_6 concentration alone. Therefore C_3H_6 ($m/e=41$ signal) and CO₂ ($m/e=44$ signal) on prepared catalysts as a function of temperature were plotted complementarily in Fig. 7. Almost no C_3H_6 was detected during the C_3H_6 -TPO of Pt/ZSM-5, which was caused by adsorption at lower temperature and complete combustion at higher temperature. Meanwhile, a considerable amount of C_3H_6 desorbed around 175 °C, as shown in the C_3H_6 -TPO profile of ZSM-5. The proximate light-off temperature for C_3H_6 combustion of Pt/ZSM-5 could be possibly located at ~85 °C, at which the integrating area of CO₂ curves under dashed line (450 ppm) equals to that of upper part (140~250 °C). The C_3H_6 light-off temperature of Pt/ZSM-5 is at least 100 °C lower than that of ZSM-5.

Comparing C_3H_6 conversion profiles in TPO (Fig. 7) and SCR (Fig. 3b) indicates that C_3H_6 oxidation was also evidently inhibited by NO oxidation in SCR. The participation of NO into SCR increased the light-off temperature of C_3H_6 and the 100% C_3H_6 conversion temperature significantly. It is presumed that the inhibition of C_3H_6 oxidation induced by NO and that of NO₂ formation caused by C_3H_6 at low temperatures are due to the competition of reaction intermediates for active surface sites. Additionally, the interactive effect could be responsible for the differences of SCR activities between

Pt/ZSM-5 and Pt/TiO₂. Additionally, the Pt/ZSM-5 with stronger catalytic NO oxidation activity could compete more active surface sites than Pt/TiO₂, and then showed higher NO reduction but lower C₃H₆ oxidation efficiency during C₃H₆-SCR.

Concerning the results obtained in catalytic activity tests (Section 3.2), it could be concluded that the performance of Pt/ZSM-5 catalyst for the low-temperature SCR was correlative well with the enhanced oxidation activities of NO to NO₂ and C₃H₆ to CO₂ by O₂ in TPO at low temperature. The formed nitrates and oxygenated C_xH_yO_z species over the surface of Pt/ZSM-5 are believed to be two essential intermediates for the low-temperature SCR, which was evaluated specifically in many literatures [15,18,20].

4. Conclusion

The low-temperature SCR of NO with C₃H₆ has been investigated over 0.5 wt% Pt/ZSM-5 and ZSM-5. The Pt/ZSM-5 catalyst achieved remarkably high 77.1% NO reduction to N₂ + N₂O and 79.7% C₃H₆ conversion to CO₂ simultaneously at a relatively low temperature of 140 °C. NO-TPD and TPO results indicate that the Pt/ZSM-5 catalyst has outstanding oxidation activities of NO to NO₂ and C₃H₆ to CO₂ by O₂ at low temperature. The well-dispersed Pt significantly improved the catalytic activities of C₃H₆ combustion as well as NO oxidation. The differences of SCR activity between Pt/ZSM-5 and reported Pt/TiO₂ are thought to be further evidence for the mutual inhibition of NO oxidation and C₃H₆ oxidation. The catalytic performance of low-temperature SCR correlates well with the oxidation activities shown in C₃H₆/NO-TPO. Further studies are in progress for a deep understanding of the reaction mechanism of the low-temperature C₃H₆-SCR over Pt/ZSM-5 catalyst.

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