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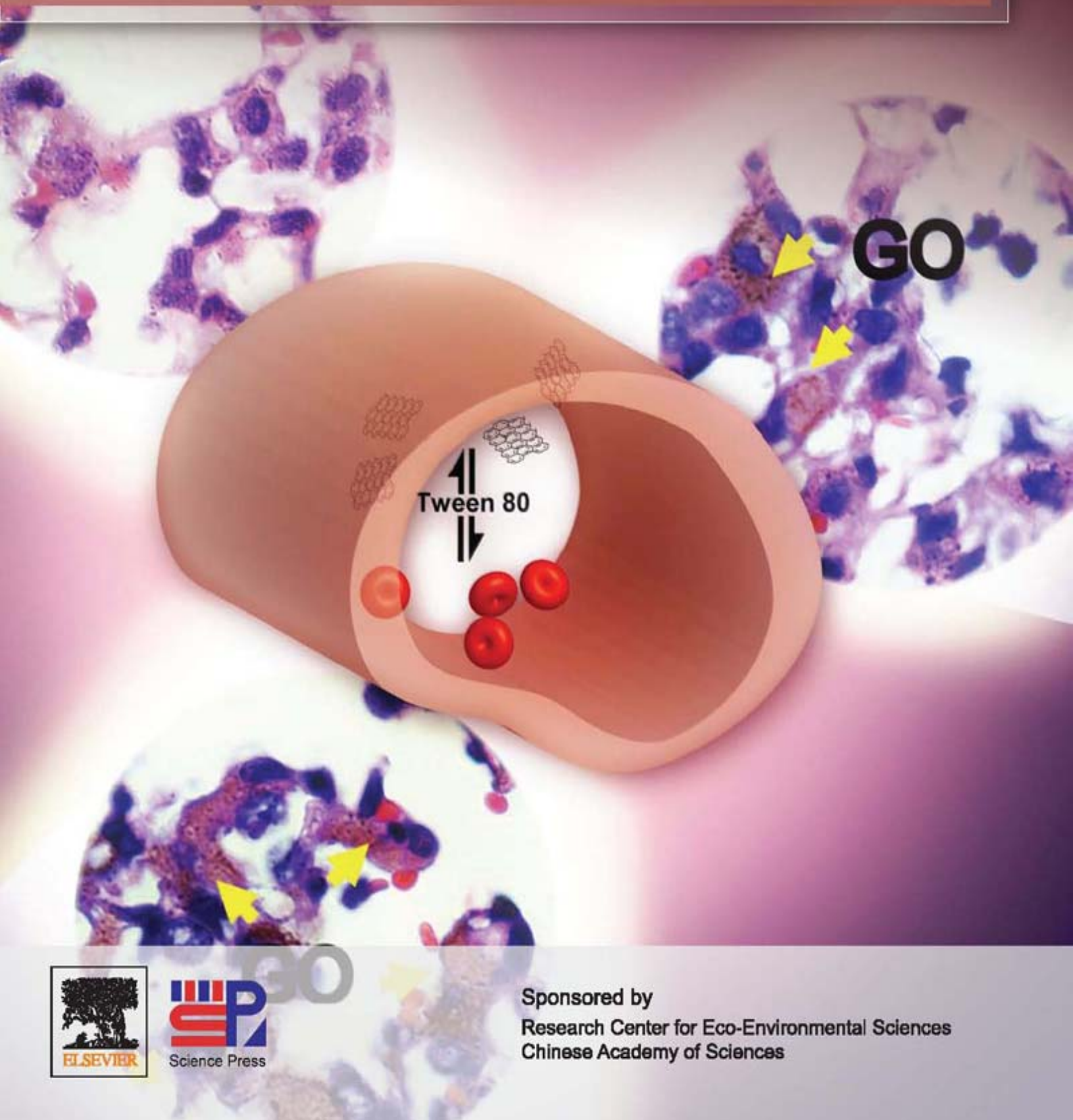

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Characterization and performance of Pt/SBA-15 for low-temperature SCR of NO by C_3H_6

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Abstract

Pt supported on mesoporous silica SBA-15 was investigated as a catalyst for low temperature selective catalytic reduction (SCR) of NO by C_3H_6 in the presence of excess oxygen. The prepared catalysts were characterized by means of XRD, BET surface area, TEM, NO-TPD, NO/C_3H_6-TPO, NH_3-TPD, XPS and ^{27}Al MAS NMR. The effects of Pt loading amount, O_2/C_3H_6 concentration, and incorporation of Al into SBA-15 have been studied. It was found that the removal efficiency increased significantly after Pt loading, but an optimal loading amount was observed. In particular, under an atmosphere of 150 ppm NO, 150 ppm C_3H_6, and 18 vol.% O_2, 0.5% Pt/SBA-15 showed remarkably high catalytic performance giving 80.1% NO*x* reduction and 87.04% C_3H_6 conversion simultaneously at 140°C. The enhanced SCR activity of Pt/SBA-15 is associated with its outstanding oxidation activities of NO to NO_2 and C_3H_6 to CO_2 in low temperature range. The research results also suggested that higher concentration of O_2 and higher concentration of C_3H_6 favored NO removal. The incorporation of Al into SBA-15 improved catalytic performance, which could be ascribed to the enhancement of catalyst surface acidity caused by tetrahedrally coordinated AlO_4. Moreover, the catalysts could be easily reused and possessed good stability.

Key words: low-temperature; selective catalytic reduction; C_3H_6; Pt/SBA-15

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Introduction

NO*x* (NO+NO_2) exhausted from vehicles and stationary combustion engines is one of the important causes of photochemical smog, acid rain, and ozone depletion, which possess serious challenges to human health and environmental protection. With the increase of the motor vehicles, the problems caused by exhaust gas pollution are being much 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. Besides, the low efficiency of TWC during the cold start engine also represents an important issue (Guo et al., 2006; Bera and Hegde, 2011; Granger and Parvulescu, 2011). Therefore, it is of great significance to develop new catalysts with high performance for the treatment of low-concentration exhaust at low temperature.

Selective catalytic reduction (SCR) technique has been proven to be one of the most effective methods for reducing NO*x* emissions due to its high efficiency and simplicity (Liu and Woo, 2006; Roy et al., 2009). It is well known that NH_3-SCR is a widely practiced NO*x* control technology (Brandenberger et al., 2008), but problems such as storage, transportation, leakage, corrosion of NH_3 and catalysts toxicity (vanadium species) are inevitable. Also, hydrocarbons (HCs) are a natural component already present in combustion exhaust, thus it is quite convenient and competitive to use HCs as reducing agent (HC-SCR). Usually, SCR technology requires rather higher reaction temperature (above 300°C), but if SCR of low concentration NO*x* by HC occurs over catalyst with high deNO*x* activity at low temperature, this technology could compete with NH_3-SCR and be more practical for the removal of NO*x* in places such as urban road tunnels and underground parking lots.

Low temperature HC-SCR has been extensively studied and a large number of catalysts have been evaluated. Noble metal doped catalysts, e.g., Pt/Al_2O_3 (Salem et al., 2008;

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Seker and Gulari, 2002), Rh/TiO_2 (Halkides et al., 2002), Pt/V/MCM-41 (Jeon et al., 2003), Pt-Sn/Al_2O_3 (Corro et al., 2003), are promising due to the high activity at low temperatures and high SO_2 tolerance as well as good water resistance. In our recent work, 0.5% Pt/TiO_2 (anatase) was found to be the most active catalyst among a series of Pt supported TiO_2 catalysts for the low temperature C_3H_6-SCR in excess oxygen. Under the condition of 150 ppm NO, 150 ppm C_3H_6, and 18 vol.% O_2, this 0.5% Pt/TiO_2 catalyst could achieve a complete C_3H_6 conversion and 47.03% NO*x* reduction simultaneously at 180°C (Liu et al., 2011). This indicates again that Pt loaded catalyst is promising for low temperature C_3H_6-SCR process.

Mesoporous molecular sieves have been recognized as the good catalytic supports for their high specific surface area, porous volume and adjustable pore size diameter as well as the uniform pore size distribution (Beck et al., 1992). Within the family of mesoporous materials, SBA-15 materials synthesized under acidic conditions exhibit larger pore size and thicker pore volume wall compared with M41S (Zhao et al., 1998). Its remarkably high surface area and large pore volume favoring a high dispersion of the active component on the surface of the catalytic support as well as the improved accessibility of active sites should have a favorable impact on catalytic activity (Sayari, 1996; Corma, 1997). Such mesoporous silica SBA-15 based catalysts were already studied in SCR of NO by ammonia (Rico et al., 2010; Segura et al., 2005; Chmielarz et al., 2006), CO (Patel et al., 2011) and by ethanol (Boutros et al., 2009), and exhibited various reduction activities toward NO*x* at higher temperature (> 300°C). However, this pure siliceous mesoporous material is lack of acid sites and acidity, incorporation of Al into the structure of SBA-15 is an effective way to enhance its acidity which may promotes the SCR reactions (Giroir-Fendler et al., 2001; Brandhorst et al., 2005).

In the present work, we reported a Pt/SBA-15 catalyst that exhibited high activity for low temperature C_3H_6-SCR in the presence of excess O_2. Special emphasis is given to the possible correlations among Pt loading amount, O_2/C_3H_6 concentration, Al incorporation, and NO conversion efficiency of the catalysts. For practical consideration, catalytic stability of the prepared catalysts was investigated as well.

1 Experimental

1.1 Catalyst preparation

SBA-15 materials were synthesized according to the procedure reported in other literature (Zhao et al., 1998). In a typical synthesis, 4 g of the P123 (EO_{20}-PO_{70}-EO_{20}, Aldrich) was dissolved in 30 g of H_2O and 120 g of 2 mol/L HCl. The mixture was continually stirred for a few hours until the copolymer was completely dissolved. Then 8.5 g of tetraethylorthosilicate (TEOS) was slowly added dropwise and the resulting mixture was stirred for 20 hr at 40°C. Afterward, the samples were aged at 100°C in the autoclave for 24 hr. After cooling, the solids were washed and filtered with deionized water, and then allowed to air-dry. Finally, the as-synthesized samples were calcined at 550°C for 6 hr in air to obtain mesoporous SBA-15.

In a typical Al-SBA-15 synthesis (Yue et al., 1999): 8.5 g TEOS and a calculated amount isopropoxide aluminium, to obtain a given Si/Al ratio (10), were added to 10 mL of aqueous HCl at pH 1.5. This mixture was stirred for 4 hr at room temperature and then added to a second solution containing 4 g of P123 in 150 g of aqueous HCl at pH 1.5. The resulting solution was stirred for 20 hr at 40°C, followed by aging at 100°C for 24 hr under static conditions. The solid product was recovered by filtration, dried at room temperature and calcined at 550°C for 6 hr. The as-synthesized sample was denoted as Al-SBA-15(10), where 10 is the Si/Al ratio.

All Pt supported catalysts were prepared by impregnating weighted supports with calculated amounts of $Pt(NH_3)_2(NO_2)_2$ aqueous solution, followed by 30 min of ultrasonic dispersion. Then all catalysts were dried at 110°C for 12 hr followed by calcination in air at 450°C for 4 hr. All the above catalysts were ground and sieved to 40–60 mesh for evaluation.

1.2 Characterization of catalysts

The powder X-ray diffraction (XRD) measurements were carried out with a Rigaku D/max-2200/PC X-ray diffractometer (Rigaku Corporation, Japan) with Cu *K*α radiation and operated at 49 kV and 20 mA.

Measurements of the BET surface area were performed by nitrogen adsorption data from Quantachrome NOVA1000a Sorptomatic apparatus (Quantachrome, USA).

Transmission electron microscopic (TEM) images were obtained by employing a JEM-2010 (JEOL, Japan) device with a 200-kV accelerating voltage.

X-ray photoelectron spectroscopy (XPS) spectra were acquired with a Kratos Axis Ultra^{DLD} spectrometer (Shimadzu-Kratos, Japan) using a monochromatic Al *K*α source (1486.6 eV). The BE scale was calibrated according to the C1s peak (284.8 eV) for adventitious carbon on the analyzed sample surface.

^{27}Al MAS NMR experiment was performed at room temperature with a 4.0 mm MAS probe on a Bruker Avance III-400 spectrometer (Bruker, Swiss) in a magnetic field strength of 9.4 T at a frequency of 104.263 MHz. Powder sample was packed inside zirconia MAS rotors and spun at 10 kHz. A single pulse 2.0 μS followed by acquisition of 1 K points was repeated at a recycle rate of 3 sec.

1.3 Catalytic activity test

Catalytic activity of the catalysts for NO reduction was determined in a continuous fixed bed U-type quartz reactor (Shanghai Zhiying, China) (4 mm i.d.) using 0.2 g of

catalyst. The standard reactant composition was as follows: 150 ppm C_3H_6, 150 ppm NO, 18 vol.% O_2, and Ar balance at a total flow rate of 120 mL/min. The concentrations of NO, NO_2 and NOx were monitored by a chemiluminescent NO/NO_2 analyzer (Thermo Environmental Instruments Inc., 42i LS, Thermo, USA). C_3H_6 and CO_2 were determined by a gas chromatograph (GC, Shanghai Huaai, China) equipped with a flame ionization detector (FID) detector, and a quadrupole mass spectrometer (Ametek Process Instruments, Dycor DM 100M, USA) was also used combined with a GC. The data were collected when the reactions reached the steady state around 40 min at each temperature point. Unless otherwise specified, the gas flow rates in this article were all fixed at 120 mL/min. The NOx removal efficiency (R, %) was calculated as follows:

$$R = \frac{[NOx]_{in} - [NOx]_{out}}{[NOx]_{in}} \times 100\% \quad (1)$$

where, $[NOx]_{in}$ is the inlet concentration of NOx and $[NOx]_{out}$ is the outlet concentration of NOx.

1.4 NO temperature programmed desorption

Before the TPD experiment, the samples were pretreated in pure Ar flow at 350°C for 30 min then cooled down to 50°C. Adsorption of NO was carried out over 0.2 g catalyst 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 hr. After the sample was purged with Ar for 20 min at 50°C, the TPD experiment was performed with a heating rate 4°C/min.

1.5 Oxidation of NO and oxidation of C_3H_6

Oxidation of NO/C_3H_6 was also carried out with a heating rate 4°C/min. The feed gas mixture was 150 ppm NO/150 ppm C_3H_6 and 18 vol.% O_2 balanced with Ar, 0.2 g catalyst was used as well.

1.6 NH_3 temperature programmed desorption

The surface acidity of the samples was determined by a temperature programmed desorption of ammonia (NH_3-TPD) in a fixed-bed quartz reactor. The 0.2 g catalyst sample was first pretreated in pure N_2 at 500°C for 1 hr to yield a clear surface, and was then cooled down to 50°C. The cooled sample was exposed and saturated with 600 ppm NH_3/N_2 at a flow rate of 150 mL/min for 1–2 hr, and was then purged by N_2 until constant baseline level was attained. In the desorption process, the carried gas N_2 was kept at a flow rate of 150 mL/min while the temperature was raised from 50 to 500°C with a heating rate of 5°C/min. The effluent composition was analyzed continuously with a FT-IR spectrometer (Thermo Nicolet 6700, USA).

2 Results and discussion

2.1 Catalysts characterization

Small-angle and wide-angle X-ray diffraction patterns of the synthesized catalysts are presented in **Fig. 1**. As can be seen from **Fig. 1a**, both samples exhibited well resolved diffraction peaks that can be indexed as the (100), (110) and (200) reflections associated with *P6mm* hexagonal symmetry typical of SBA-15 materials (Zhao et al., 1998). Comparing two samples, the diffraction peaks of Al-SBA-15(10) were slightly shifted to lower values than those of SBA-15. This fact is related with the longer Al–O bond length compared to the Si–O bond (Calleja et al., 2007).

Figure 1b illustrates the wide-angle XRD patterns of the synthesized catalysts. All materials exhibited a broad diffraction peak between 15°–35°, corresponding to the amorphous silica. No diffraction peak of alumina was found on the wide-angle XRD pattern of Al-SBA-15(10), meaning the well dispersion of alumina and no formation of Al_2O_3 crystallites in this sample. Additionally, the XRD pattern of Pt supported catalysts also showed weak reflection peaks at about 39.7°, 46.2° and 67.5°, attributed

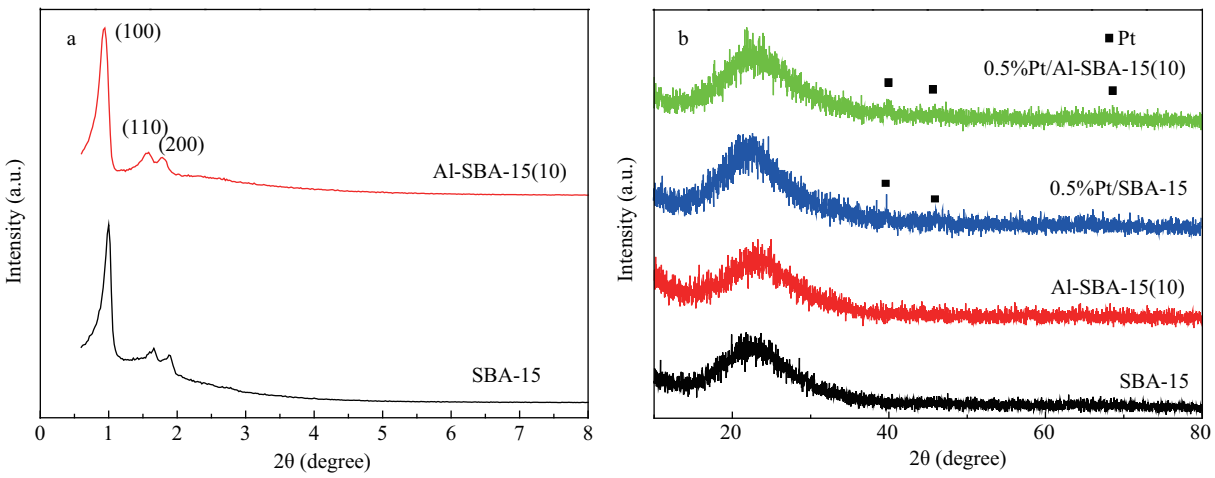

Fig. 1 XRD-patterns of synthesized catalysts. (a) small angle XRD; (b) wide angle XRD.

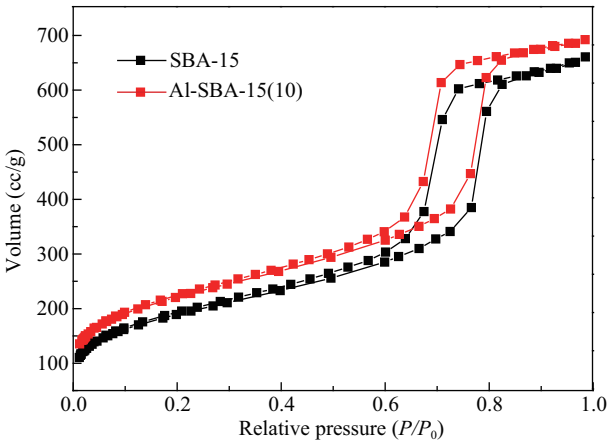

Fig. 2 Nitrogen adsorption-desorption isotherms of SBA-15 and Al-SBA-15(10).

to the metallic state platinum.

The nitrogen adsorption-desorption isotherms of SBA-15 and Al-SBA-15 materials are depicted in **Fig. 2**. It is obvious that both isotherms are Type IV (IUPAC classification) with H1 hysteresis loops at high relative pressure values (Ravikovitch and Neimark, 2001; Jang et al., 2004), corresponding to the mesoporous materials consisting of well-defined cylindrical-like pore channels and a high degree of pore size uniformity, which can also be observed in **Fig. 3**. BET surface areas were calculated from physisorption data of the samples. **Table 1** gives the textural properties of the Al-SBA-15(10) sample, together with the data of SBA-15 for comparison.

Representative TEM images of the synthesized catalysts are displayed in **Fig. 3**. **Figure 3a** and **c** show representative images along the [100] direction of SBA-15 and [001] direction of Al-SBA-15(10), respectively. The high degree of order and the characteristic hexagonal features of SBA-15 are maintained in Al-SBA-15(10) after aluminium incorporation, which is in good agreement with the small-angle XRD results above. **Figure 3b** and **d** reveal the long ordered arrangement of the channels in SBA-15 and Al-SBA-15(10) on which platinum nanoparticles are uniformly distributed, indicating that the ordered frameworks were retained after the impregnation process. These particles are present in a good distribution of size smaller than 8.0 nm.

Figure 4 shows the XPS spectra of Pt 4f region on Pt/SBA-15 with the fitting result presented in the table. For the sample, metallic Pt^0 (binding energy at 71.2 and 74.6 eV), $Pt^{II}O$ (binding energy at 72.3 and 75.6 eV) (Pitchon and Fritz, 1999) and $Pt^{IV}O_2$ (binding energy at 74.3 and

Table 1 Physicochemical properties of synthesized catalysts

Sample	Al_{tetra}/Al_{octa}	S_{BET} (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
SBA-15	–	645.4	6.295	1.016
Al-SBA-15(10)	1.67	737.5	7.12	1.160

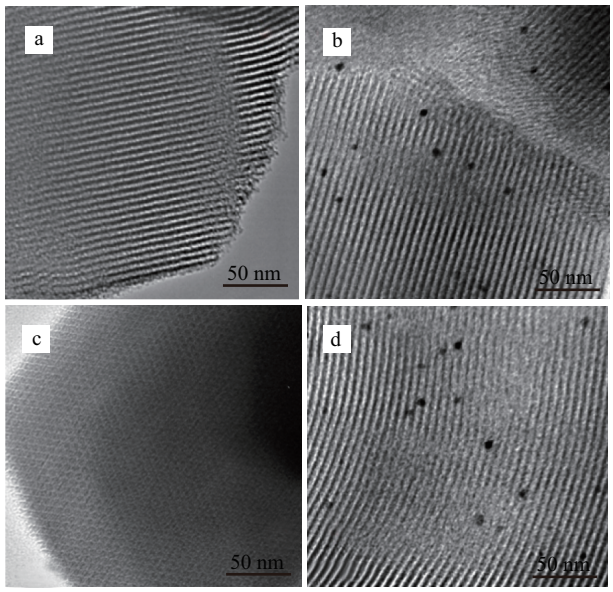

Fig. 3 TEM images of synthesized catalysts. (a) SBA-15; (b) 0.5% Pt/SBA-15; (c) Al-SBA-15(10); (d) 0.5% Pt/Al-SBA-15(10).

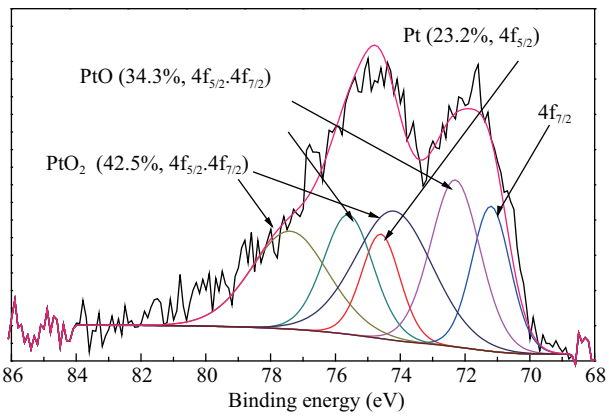

Fig. 4 Pt 4f XPS spectra of Pt/SBA-15.

77.8 eV) (Li et al., 2011) were all observed on SBA-15 support. In particular, the relative peak areas of PtO_2 were somewhat larger compared with the other Pt species. This suggests that the PtO_2 species might play a role as an active site in deNO*x*. In the meantime, the analysis of Pt 4d region was utilized to detect Pt species supported on Al-SBA-15. For the aluminosilica sample, Pt (314.4 eV), PtO (314.9 eV) and PtO_2 (317.9 eV) (www.lasurface.com) were also observed on the support, however, the fitting result was not so accurate as Pt/SBA-15 sample.

2.2 Catalytic activity tests

A comparative study of NO catalytic reduction by C_3H_6 in the presence of 18% O_2 was carried out over SBA-15 and 0.5% Pt/SBA-15. The 0.5% Pt/SBA-15 achieved 80.1% NO reduction (**Fig. 5a**) and 87.04% C_3H_6 conversion to CO_2 (**Fig. 5b**) simultaneously at 140°C, which were significantly higher than those of SBA-15. As shown in **Fig. 5a**, with the temperature increasing from 100 to 340°C, the NO*x* reduction efficiency of the catalysts increased until

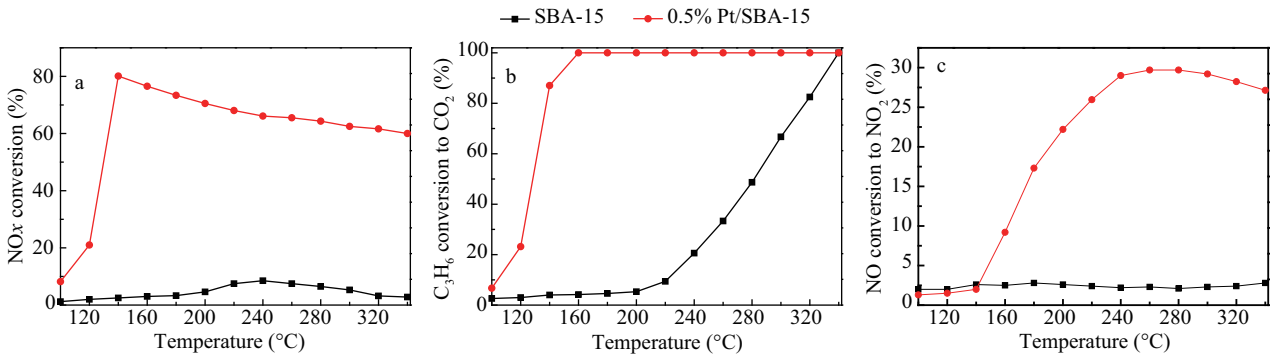

Fig. 5 Catalytic activity as a function of reaction temperatures in C_3H_6-SCR process over SBA-15 and 0.5% Pt/SBA-15. (a) NO*x* conversion; (b) C_3H_6 conversion to CO_2; (c) NO conversion to NO_2. Reaction conditions: [NO] = [C_3H_6] = 150 ppm, [O_2] =18%, balance Ar, total flow rate 120 mL/min.

reached the maximum, and then decreased. The lowering NO*x* reduction efficiency at high temperature range could be ascribed to 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 C*x*H*y*O*z* at high temperature, which was supposed to be critical intermediate in HC-SCR reaction. As shown in **Fig. 5b**, 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 SCR reaction of SBA-15 support and Pt/SBA-15 catalyst, which indicates that the catalyst and support have 100% selectivity towards CO_2.

2.3 NO temperature programmed desorption

Figure 6 shows the TPD profiles corresponding to the NO concentration. It is obvious that Pt loading favored the adsorption of NO, namely, the desorption amount is six times higher in Pt/SBA-15 than in SBA-15 (Pt/SBA-15: 25.18 μmol/g; SBA-15: 4.01 μmol/g), which could be explained by Pt–NO species formation mechanism (Kotsifa et al., 2007; Ivanova et al., 2007).

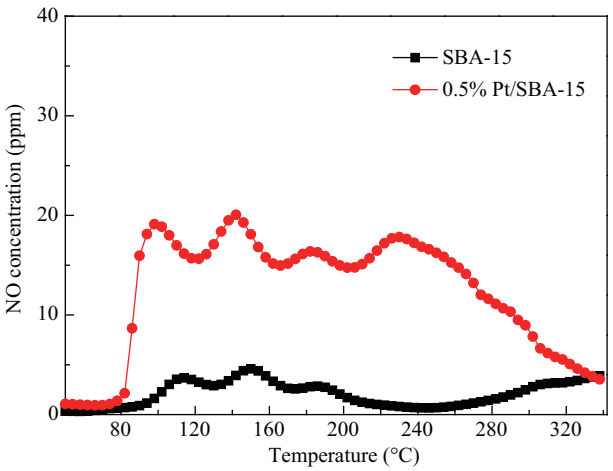

Fig. 6 NO-TPD profiles of SBA-15 and 0.5% Pt/SBA-15.

2.4 Oxidation of NO and oxidation of C_3H_6

Oxidation activities of NO to NO_2 by O_2 on SBA-15 and Pt/SBA-15 were investigated and compared in **Fig. 7a**. SBA-15 had very poor oxidizing ability in the whole temperature range, while the oxidative activity on Pt/SBA-15 increased rapidly with temperature increasing, and then kept a high level followed by a little decrease at elevated temperatures (above 280°C), this decrease could be ascribed to the thermodynamic equilibrium, i.e., $NO_2 \longleftrightarrow NO+1/2O_2$. The Pt/SBA-15 showed absolutely higher oxidation activity in the whole temperature range than SBA-15 and even Pt/TiO_2 (Liu et al., 2011). This is in good accordance with the catalytic performance obtained in SCR reaction (**Fig. 5**). Some researchers even found that the conversion of NO*x* was significantly improved by replacing the feed reaction gas NO with NO_2 directly (Li et al., 2004; Liu and Woo, 2006). The as-formed NO_2 is easily to form nitrates (nitrites) over the catalyst surface, which were regarded as important intermediates of SCR reaction. It was generally accepted that the nitrates derived from NO_2 can be readily reduced to N_2 by oxygenated species originated from HCs on the catalyst surface subsequently (García-Cortés et al., 2000; Matyshak et al., 2009; Nguyen et al., 2010). Compared the NO_2 formation in NO oxidation reaction (**Fig. 7a**) with SCR reaction (**Fig. 5c**), it is found that NO_2 formation was somewhat inhibited by the introduction of C_3H_6, as also reported in other literature (Yentekakis et al., 2005).

C_3H_6 oxidation activities of SBA-15 and Pt/SBA-15 are plotted in **Fig. 7b**. SBA-15 could oxidize C_3H_6 (*m*/*e* = 41 signal) completely at about 285°C, whereas Pt/SBA-15 oxidized C_3H_6 completely to CO_2 at much lower temperature, say, at around 115°C, indicating that Pt loading favors the C_3H_6 oxidation. By the way, this temperature is about 20°C lower than that of Pt/TiO_2 (Liu et al., 2011). C_3H_6 is activated on the surface of the noble metal loaded catalyst by forming oxygenated species (C*x*H*y*O*z*) with the participation of oxygen (Gorce et al., 2004; Adamowska et al., 2009); and an efficient catalyst should preferentially promote oxidation of adsorbed C_3H_6 with Pt–O (Kotsifa

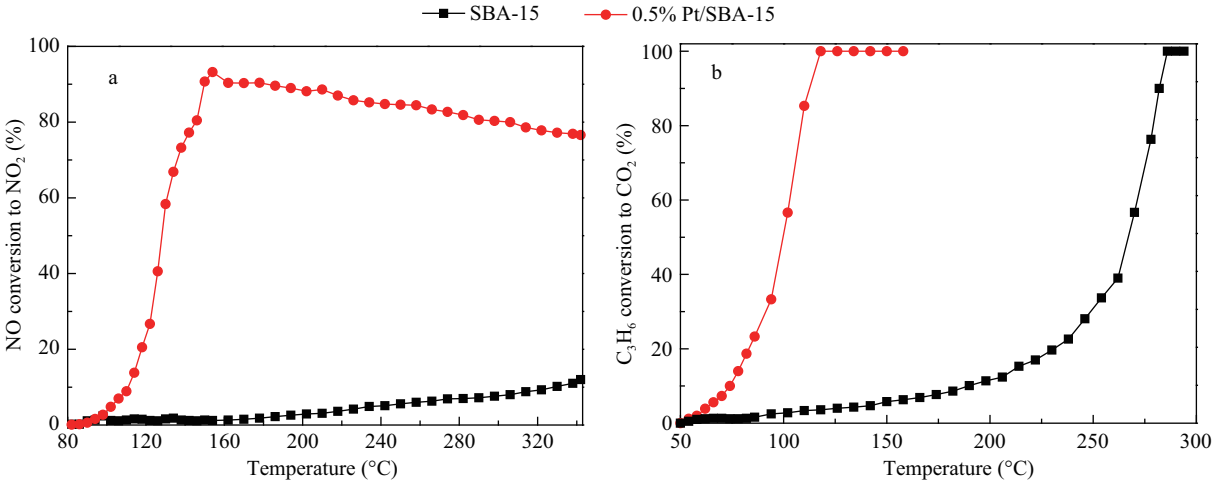

Fig. 7 NO oxidation (a) and C_3H_6 oxidation (b) profiles of SBA-15 and 0.5% Pt/SBA-15.

et al., 2007). Comparing **Fig. 7b** and **Fig. 5b**, it could be observed that the presence of NO in the C_3H_6-SCR reaction increased the C_3H_6 light-off temperature and the temperature of 100% C_3H_6 conversion by 50–60°C; the C_3H_6 oxidation was also somewhat inhibited by NO participation in SCR. It is presumed that the inhibition of C_3H_6 oxidation induced by NO and that of NO_2 formation caused by C_3H_6 at low temperatures are due to the competition of reaction intermediates for active surface sites (Yentekakis et al., 2005). Concerning the results obtained in the catalytic activity tests (Section 2.2), it could be concluded that the remarkable low temperature C_3H_6-SCR performance was correlative well with the enhanced oxidation activities of NO to NO_2 and C_3H_6 to CO_2 at low temperature.

2.5 Factors influencing NO conversion

2.5.1 Effect of O_2 concentration

The effect of O_2 concentration on the C_3H_6-SCR activity of the 0.5% Pt/SBA-15 catalyst was examined. The oxygen concentration increased from 6% to 18%, while its effect on NO*x* reduction and C_3H_6 conversion over this catalyst is plotted in **Fig. 8**. Higher O_2 concentration in the feed increased the maximum NO*x* reduction activity from 77.6% (6% O_2) to 78.37% (12% O_2) and finally to 80.1% (18% O_2). At the same time, the T_{max} (temperature for maximum NO*x* conversion) lowered from 180°C to 160°C and 140°C, respectively. The conversion of C_3H_6 was also shifted toward the low temperature range with the increase of oxygen concentration. The positive effect of excess O_2 is also reported in other literature (Haneda et al., 2003; Yentekakis et al., 2005; Li et al., 2004). These results indicate that oxygen plays a key role in C_3H_6-SCR, and could be explained as follows (Li et al., 2004; Iliopoulou et al., 2004; Wang et al., 2005). Oxygen would contribute to several reaction steps such as hydrocarbon partially oxidized forming intermediate active species C*x*H*y*O*z*, reacting with NO*x* (NO, NO(a) + O(a) ⟶ NO_2), which leads to NO*x* removal. Increasing the O_2 concentration enhances the formation of intermediate active species of hydrocarbons and the activation of NO, thus increasing NO*x* reduction.

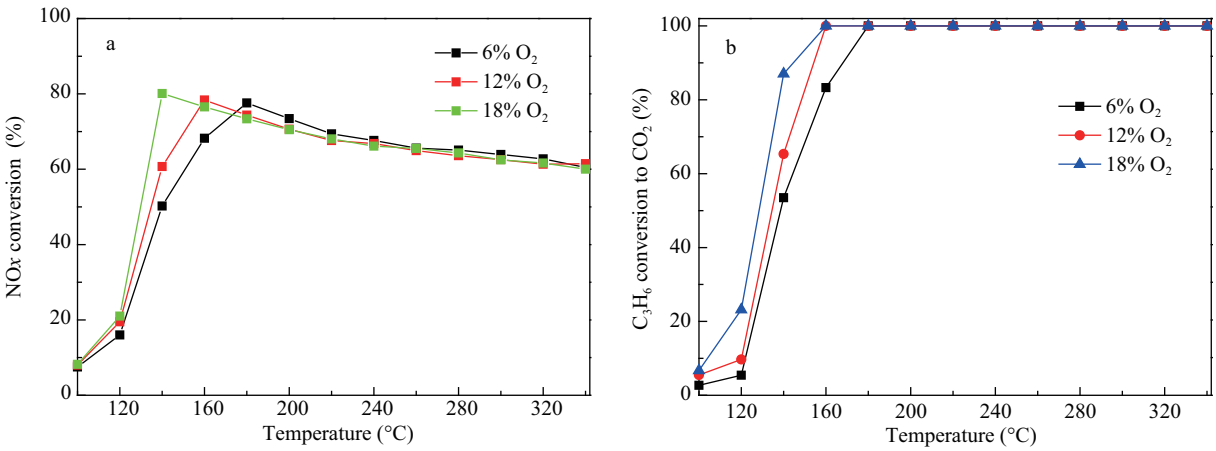

Fig. 8 Effect of O_2 concentration on NO*x* conversion and C_3H_6 conversion over 0.5% Pt/SBA-15 catalyst. Reaction conditions: [NO] = [C_3H_6] = 150 ppm, balance Ar, total flow rate 120 mL/min.

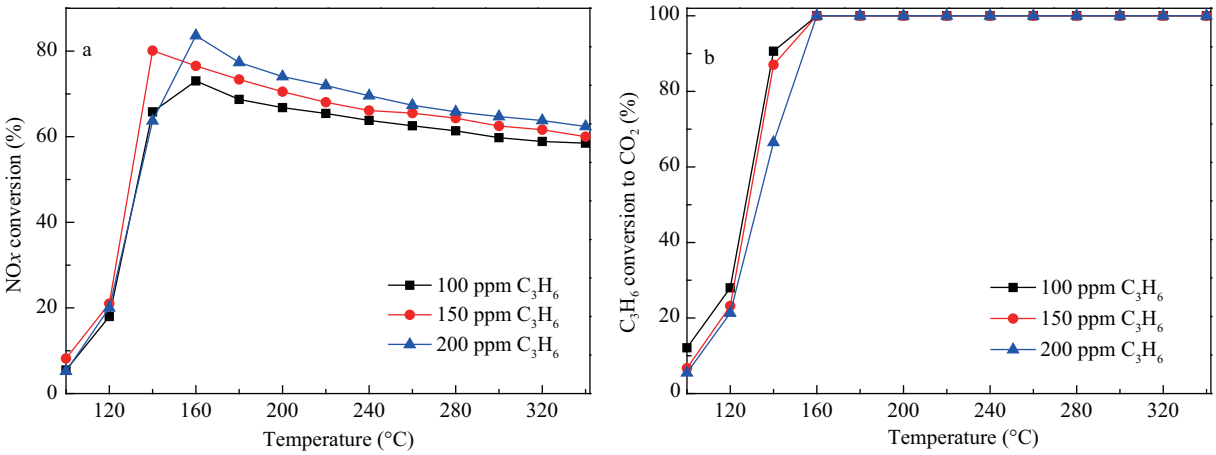

Fig. 9 Effect of C_3H_6 concentration on NOx conversion and C_3H_6 conversion over 0.5% Pt/SBA-15 catalyst. Reaction conditions: [NO] = 150 ppm, [O_2] = 18%, balance Ar, total flow rate 120 mL/min.

2.5.2 Effect of C_3H_6 concentration

The effect of C_3H_6 concentration on NOx reduction over 0.5% Pt/SBA-15 was evaluated and compared. As shown in **Fig. 9a**, with the increase of C_3H_6 concentration, the maximum NOx reduction activity increased from 73.02% (100 ppm C_3H_6) to 80.1% (150 ppm C_3H_6) and finally to 83.6% (200 ppm C_3H_6). However, the T_{max} varied from 140°C (150 ppm C_3H_6) to 160°C (100 ppm C_3H_6; 200 ppm C_3H_6). In the meantime, the conversion of C_3H_6 shifted toward high temperature range as well. The result indicates that higher concentration of reductant is beneficial to the reduction of NOx, which is in good agreement with previous reports (Jen, 1998; Lanza et al., 2009). Increasing C_3H_6 concentration enhances the formation of CxHyOz, which is well regarded as a crucial intermediate active species in NOx removal by HC-SCR, thereby facilitating NO reduction.

2.5.3 Effect of Pt loading

In **Fig. 10a**, the catalytic activities of NOx reduction over SBA-15 with various Pt loading contents are shown as a function of reaction temperature. Among all samples, 0.5% Pt/SBA-15 performed the most efficiently giving 80.1% NOx reduction and 87.04% C_3H_6 conversion simultaneously at 140°C. In contrast, 0.2% Pt/SBA-15 reached maximum NOx conversion efficiency of 33.3% and 100% C_3H_6 conversion at 180°C. Further increasing Pt content in the catalysts from 0.5% to 2% led to a decrease of maximum NOx reduction activity from 80.1% (0.5% Pt) to 76.56% (1% Pt) and finally to 73.2% (2% Pt), but the T_{max} was not changed. However, as shown in **Fig. 10b**, the C_3H_6 conversions increased monotonously with reaction temperature increasing, and the temperatures at which C_3H_6 was completely consumed were decreased on higher Pt loading samples.

Considering the correlations between Pt loading amount and NOx removal efficiency, the intermediate Pt loading of 0.5% is the optimum amount for NOx reduction, which is similar to previous studies (Hoost et al., 1997; Luo et al., 2004; Iliopoulou et al., 2004). The Pt species (Pt, PtOx) over catalyst surface are regarded as vital active sites for catalytic reactions. The number of active sites available

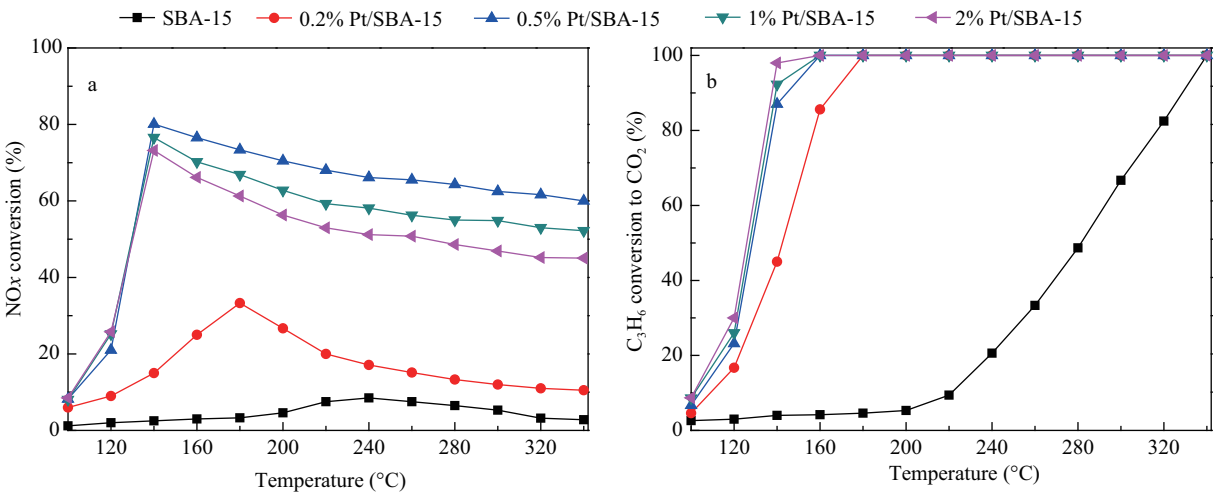

Fig. 10 NOx conversion and C_3H_6 oxidation over Pt/SBA-15 with various Pt loadings. Reaction conditions: [NO] = [C_3H_6] = 150 ppm, [O_2] = 18%, balance Ar, total flow rate 120 mL/min.

for NOx reduction increased with the increase of the Pt loading, but there was an optimum Pt loading amount (0.5% Pt), at which the number of active sites just meet the needs of NOx SCR reaction. In other words, the Pt content of 0.5% was enough to activate the SCR reaction, while weakening the direct combustion of C_3H_6 with O_2. In case of 1% Pt and 2% Pt supported SBA-15, higher amount Pt would lead to a fortified direct combustion of C_3H_6, resulting in decreasing the amount of reductant remaining for the SCR reaction, which may in part explain their lower catalytic activities (Iliopoulou et al., 2004; Kumar et al., 2008).

2.5.4 Effect of Al incorporation

Al-SBA-15 was prepared by direct hydrothermal synthesis where isopropoxide aluminium used as Al source. The ^{27}Al MAS NMR spectrum of the Al-SBA-15 sample is displayed in **Fig. 11**. There were two resolved peaks in the spectrum at approx. 53 and 0 ppm, respectively. The former, which is attributable to tetrahedrally coordinated aluminum species, indicates that aluminum atoms have been incorporated into the framework of the siliceous samples (AlO_4 structural unit, Al(tet), and the aluminum is covalently bonded to four Si atoms by oxygen bridges). The resonance at 0 ppm can be assigned to octahedral aluminum corresponding to extra-framework aluminum species (AlO_6 structure unit, Al(oct)) (Sumiya et al., 2001). Also, a small shoulder peak at around 30 ppm could be attributed to pentahedrally coordinated aluminum species (Al(penta)) (Yue et al., 1999). From the results of ^{27}Al MAS NMR spectrum and according to the peak area ratio of the tetrahedrally coordinated Al to octahedrally Al (Area 50 ppm/Area 0 ppm=1.67, **Table 1**), it can be proved that most of aluminum had been incorporated into the framework of SBA-15 sample.

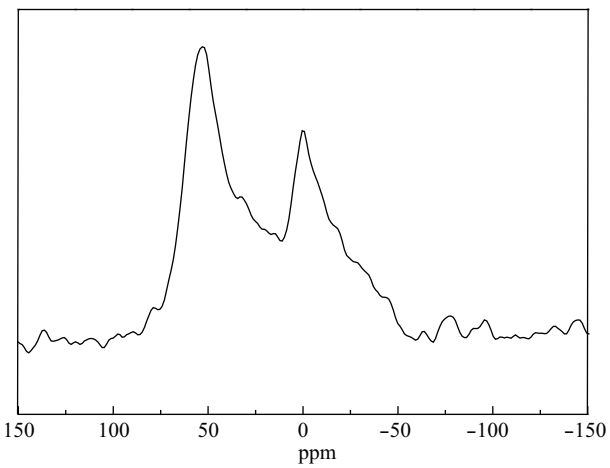

Fig. 11 Solid ^{27}Al MAS NMR spectrum of Al-SBA-15(10).

Figure 12 shows that the catalytic activity for C_3H_6-SCR over Pt/SBA-15 was improved by the Al incorporation. The 0.5% Pt/Al-SBA-15(10) catalyst exhibited remarkably high activity in low temperature C_3H_6-SCR process, giving 86.06% NOx reduction efficiency at T_{max} of 140°C. Improvement of the activity could be reasoned by the enhancement of surface acidity after Al incorporation which was evidenced by NH_3-TPD. As shown in **Fig. 13**, the TPD profile of Pt/SBA-15 material showed no evident peaks, indicating that Pt/SBA-15 material has no acid sites. In the meantime, the TPD profile of Pt/Al-SBA-15(10) material showed a main peak at about 120°C and a shoulder peak at around 200°C related to weak and mild acid sites, respectively, whereas the desorption peak of NH_3 is too broadened to be detected at a temperature higher than 300°C corresponding to strong acid sites. NH_3-TPD plots show that there is a substantial increase in acidity and acid strength after Al incorporation. Based on the NMR analysis results, NH_3-TPD profiles and other literature (Li et al., 2004), we can propose that the tetrahedrally coordinated AlO_4 contributes to the acidity greatly.

2.6 Stability of the catalysts

To evaluate the stability of the catalysts, the recycling experiments were performed for eight successive cycles under standard reaction condition in the temperature range between 100 and 340°C. It can be seen from **Fig. 14** that the maximum NOx conversion of both samples hardly decreased by and large after the fifth cycle even after the sixth cycle, whereas the T_{max} did not increase to 160°C until the sixth cycle. This indicated that the catalytic

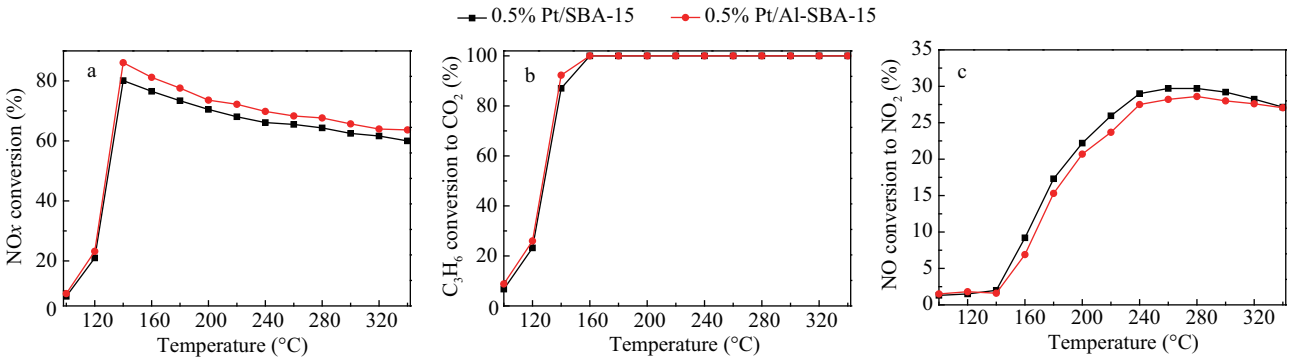

Fig. 12 Conversion of NOx with the function of temperature over 0.5% Pt/SBA-15 and 0.5% Pt/Al-SBA-15. (a) NOx conversion; (b) C_3H_6 conversion to CO_2; (c) NO conversion to NO_2. Reaction conditions: [NO] = [C_3H_6] = 150 ppm, [O_2] = 18%, balance Ar, total flow rate 120 mL/min.

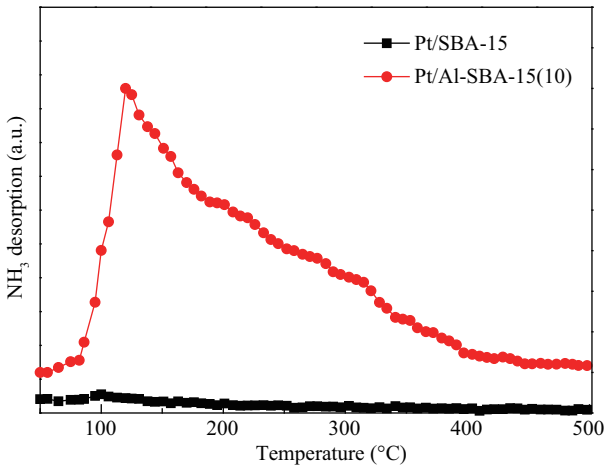

Fig. 13 NH_3-TPD profiles of Pt/SBA-15 and Pt/Al-SBA-15(10)

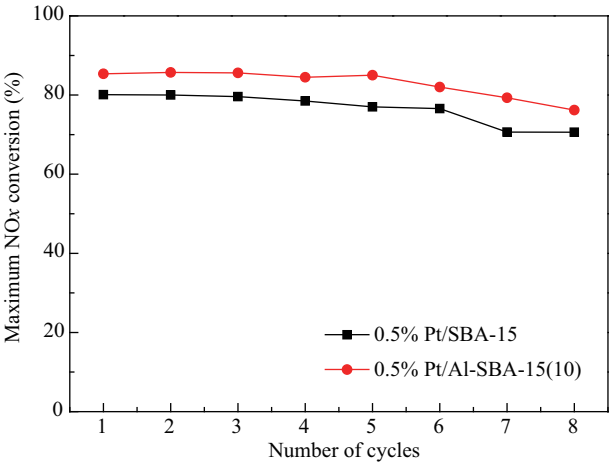

Fig. 14 Recycling investigations of 0.5% Pt/SBA-15 and 0.5% Pt/Al-SBA-15(10) in SCR reaction. T_{max} of the cycle 1–5 was 140°C, and T_{max} of the cycle 6–8 was 160°C. Reaction conditions: [NO] = [C_3H_6] = 150 ppm, [O_2] = 18%, balance Ar, total flow rate 120 mL/min.

performance of both catalysts is well-sustained. However, obvious deactivation was observed after the seventh and the eighth cycle for both catalysts, say, the maximum NO*x* conversion efficiency of the eighth cycle were 70.6% for 0.5% Pt/SBA-15 and 76.2% for 0.5% Pt/Al-SBA-15(10) respectively. In addition, the T_{max} of these catalysts did not change for the seventh and the eighth cycle. In a word, it is far not enough to mention the industrial application of these catalysts only based on the results presented and further work is in progress.

3 Conclusions

The low temperature C_3H_6-SCR has been investigated over 0.5% Pt/SBA-15 and 0.5% Pt/Al-SBA-15 catalysts. The 0.5% Pt/SBA-15 sample achieved markedly high 80.1% NO*x* reduction and 87.04% C_3H_6 conversion simultaneously at 140°C. Such high catalytic activity correlates well with the outstanding oxidation activities shown in NO/C_3H_6 oxidation reactions. Higher concentrations of $O_2$and C_3H_6 led to higher NO*x* conversion efficiencies. Higher Pt loading favored NO*x* conversion, but an optimum content of 0.5 wt.% Pt was observed. The XPS results suggested that Pt, PtO and PtO_2 were all presented in the catalyst, whereas PtO_2 species might play a role as main active site of Pt/SBA-15. The incorporation of appropriate amount Al into SBA-15 improved catalytic performance, which could be ascribed to the enhancement of catalyst surface acidity caused by tetrahedrally coordinated AlO_4. Further studies are in progress for a deep understanding of the mechanism of low temperature C_3H_6-SCR.

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