Preparation and NO reduction property of apatite-type Al₉Si₆O₂₆ (A = Li, Na, K) supported Pt catalyst

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Apatite-type Al₉Si₆O₂₆ (A = Li, Na, K) were prepared by solid state reaction method. The hexagonal unit cell volumes of Al₉Si₆O₂₆ increased with increasing ionic radii of alkali metal ions, indicating that the alkali metal ions were incorporated into the apatite-type lattice. The specific surface areas of Al₉Si₆O₂₆ were less than 1 m²/g. X-ray photoelectron spectroscopy measurement showed that Pt species on as-prepared catalysts were highly oxidized. Reduction temperature of Pt oxides on the catalyst for temperature-programmed reduction by H₂ was decreased by substitution of alkali metal ion at La site in the apatite-type silicate. For C₃H₆-NO₂-O₂ reaction, Pt/NaLa₉Si₆O₂₆ catalyst exhibited a maximum NO conversion of 42%, the highest among Pt/Al₉Si₆O₂₆ catalysts. The temperature for maximum NO conversion over Pt/NaLa₉Si₆O₂₆ catalyst was lower than that over Pt/γ-Al₂O₃ catalyst under the same reaction condition. The temperature of 50% C₃H₆ conversion for C₃H₆-O₂ reaction over Pt/Al₉Si₆O₂₆ catalysts increased in the sequence of A = K < A = Na < A = Li. In addition, C₃H₆ oxidation activity was suppressed by presence of CO₂ and NO on the catalyst. These results suggest that the basic sites on the apatite-type support affect the catalytic activities of Pt/Al₉Si₆O₂₆ catalysts for C₃H₆-NO₂-O₂ and C₃H₆-O₂ reaction.©2013 The Ceramic Society of Japan. All rights reserved.

Key-words : Apatite-type silicate, NO reduction, Pt catalyst, Alkali metal, C₃H₆ oxidation

1. Introduction

Reduction of NO by hydrocarbons (HC) is an efficient way to remove NO from automobile exhaust gas. Platinum, palladium and rhodium (PGM: platinum group metal) catalysts are widely used for NO reduction, and a large number of studies on the catalysts have been reported.1–10 For PGM catalysts, γ-Al₂O₃ is often used as a support.11–12 Recently, it is found that addition of alkali metals to γ-Al₂O₃ supported PGM catalyst increases catalytic activity for NO reduction. Vernoux et al. investigated the influence of Na on catalytic activity of Pt/γ-Al₂O₃ with various loading rates (0.12–5 wt%).13 They showed that the catalytic activity of Pt/γ-Al₂O₃ catalyst for C₃H₆-NO₂-O₂ reaction was improved by addition of Na. The temperatures for 50% C₃H₆ conversion and for the maximum NO conversion to N₂ and N₂O were shifted toward lower temperatures. Konsolakis et al. showed that the NO reduction on Pt/γ-Al₂O₃ catalyst was promoted by addition of Li (0.16–4.7 wt %), K (0.9–8.8 wt %), Rb (1.9–15.5 wt %) and Cs (3.0–24.0 wt %) for C₃H₆-NO₂ reaction.14 In this case, NO conversion and N₂ selectivity were increased by addition of alkali metals. It seems that the catalytic activity of PGM catalyst for NO reduction is promoted by basicity of the catalyst.

In our previous study, it was found that the catalytic activity of the apatite-type La₉Si₆O₂₆ supported Pt catalyst was higher than that of γ-Al₂O₃ supported Pt catalyst.10 Furthermore, the catalytic activity of the apatite-type lanthanum silicate supported Pt catalyst was promoted by substitution of alkaline earth metals (Ca, Sr, Ba) at La site.10 These results suggested that the basicity of the support is an important factor in controlling the catalytic activities.

The alkali metals have low electronegativity compared with lanthanum and alkaline earth metals. Therefore, it is presumed that the basicity of the apatite-type lanthanum silicate support is increased by substitution of alkali metal ions, leading to improvement of the catalytic activities of apatite-type silicates supported Pt catalyst. In this study, we prepared alkali metals containing lanthanum apatite-type silicate, Al₉La₃Si₆O₂₆ (A = Li, Na, K), supported Pt catalysts and evaluated their catalytic activity for NO reduction using C₃H₆ as a reductant. In order to investigate the effects of the alkali metal substitution to the apatite-type silicate support on the reaction including C₃H₆, NO₂ and O₂ as reactants, the catalytic activities for C₃H₆-NO₂-O₂, C₃H₆-O₂ and NO₂-O₂ reactions were also evaluated.

2. Experimental

2.1 Catalyst preparation

The apatite-type silicates containing lanthanum and alkali metal ions, Al₉La₃Si₆O₂₆ (A = Li, Na, K), were synthesized by the solid state reaction method. The powders of La₂O₃, SiO₂ and alkali metal carbonate (A₂CO₃) were used as starting materials. The molar ratios of the starting materials were A₂CO₃:La₂O₃:SiO₂ = x:4.5:6, where, x = 0.65 for A = Li, Na and x = 1 for A = K. These materials were mixed in ethanol by ball-milling. Excess alkali metal carbonates were added to compensate for the loss due to evaporation of alkali metal compounds at high temperature. The mixtures were pressed into pellets of 10 mm diameter and heated at 800–1200°C for 6–12 h in air with intermediate grindings. The synthesis conditions for Al₉La₃Si₆O₂₆ are listed in Table 1. The alkali metal free apatite-type lanthanum
silicate, La$_{9.33}$Si$_6$O$_{26}$, was synthesized by the sol-gel method reported by Tao et al.\textsuperscript{17}) Tetraethyl orthosilicate (TEOS) and La$_2$O$_3$ were used as starting materials. The mixed solution containing 4.0 g of TEOS, 93 cm$^3$ of C$_2$H$_5$OH and 3 cm$^3$ of CH$_3$COOH was stirred at room temperature to obtain a clear solution. Then, 4.52 g of La$_2$O$_3$, 90 cm$^3$ of distilled water and 10 cm$^3$ of 13 mol/dm$^3$ HNO$_3$ were added into the solution and dissolved completely by stirring. The obtained clear solution was heated at 80°C for 6 h, resulting in a sol solution, and an amorphous gel was obtained by drying the solution at 90°C for 12 h. The precursor was obtained by heating the amorphous gel at 600°C for 7 h in air. Apatite-type La$_{9.33}$Si$_6$O$_{26}$ was obtained by heating the precursor at 1250°C for 48 h in air with three intermediate regrindings. Catalysts loaded with 1 mass % of Pt were prepared by impregnating ALa$_9$Si$_6$O$_{26}$ and La$_{9.33}$Si$_6$O$_{26}$ with Pt(NH$_3$)$_2$Cl$_2$-(NO$_3$)$_2$ aqueous solution and heating at 600°C for 3 h in air.

### 2.2 Characterization

Phase identification of the silicates and catalysts was performed by powder X-ray diffraction (XRD) using Cu K$\alpha$ radiation (40 kV, 40 mA). X-ray diffraction patterns were recorded with a Rigaku Ultima IV X-ray diffractometer. The chemical compositions of the ALa$_9$Si$_6$O$_{26}$ were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), using an SII NanoTechnology Inc. SPS 3500-DD. The specific surface areas of the ALa$_9$Si$_6$O$_{26}$ and La$_{9.33}$Si$_6$O$_{26}$ powders were evaluated by the Brunauer-Emmet-Teller (BET) method from N$_2$ adsorption isotherm at −196°C, using a Bel Japan BELSORP-miniII. The chemical states of Pt on the catalyst surface were evaluated by X-ray photoelectron spectroscopy (XPS), using a JEOL JPS-9000SX system with Mg K$\alpha$ radiation and KRATOS AXIS-ULTRA DLD with AlK$\alpha$ radiation. The binding energy (BE) was calibrated using the C1s line (BE = 285.0 eV).

The dispersion of Pt on the catalysts was evaluated by the CO pulse adsorption method reported by Takeguchi et al.\textsuperscript{18}) A quartz tube reactor was loaded with 0.5 g of catalyst. The catalyst was heated up to 400°C at 10°C/min and held for 10 min in flowing air at 100 cm$^3$/min. Then, the catalyst was purged with He fed at 100 cm$^3$/min for 1 min, and then H$_2$ fed at 100 cm$^3$/min for 10 min, and thereafter cooled down to 50°C under He atmosphere. Subsequently the catalyst was held at 50°C under switched feed gases. The order of the feed gases was: air (5 min), He (1 min), CO$_2$ (10 min), He (1 min), H$_2$ (5 min) and He (5 min), at 100 cm$^3$/min. The CO pulse adsorption was performed at 50°C. The concentration of CO in the effluent gas was evaluated using a Shimadzu GC-8A gas chromatograph with a thermal conductivity detector (TCD). The reduction properties of Pt on the catalysts were investigated by temperature programmed reduction by H$_2$ (H$_2$-TPR). Before the H$_2$-TPR measurement, the catalyst was heated up to 200°C at 10°C/min and held for 1 h to remove adsorbed water, and then cooled down to room temperature under He atmosphere. Then, the measurement was performed in flowing 6%H$_2$-He at 50 cm$^3$/min by heating up to 800°C at 10°C/min. The amounts of H$_2$ consumption were monitored using a gas analyzer (Canon Anelva M-201GA-DM) with a quadrupole mass spectrometer. The amounts of H$_2$ consumption for the reduction of Pt on Pt/La$_{9.33}$Si$_6$O$_{26}$ catalyst were measured by H$_2$ pulse reduction. Before the H$_2$ pulse reduction, the catalyst was heated up to 200°C at 10°C/min and held for 1 h to remove adsorbed water, and then cooled down to room temperature under Ar atmosphere. The measurement was performed in 6%H$_2$-Ar pulse injection at 25 and 250°C. The concentration of H$_2$ in the effluent gas was evaluated using a Shimadzu GC-8A gas chromatograph with a TCD.

### 2.3 Evaluation of catalytic activity

The catalytic activity for NO reduction, C$_3$H$_6$ oxidation and NO oxidation was evaluated using a fixed bed flow reactor. The catalyst was formed into a pellet and crushed. Then, 0.1 g of catalyst, which had been passed through a 26-mesh sieve but trapped on a 42-mesh sieve, was loaded into a quartz tube reactor of 10 mm diameter. Prior to the reaction, the catalyst was heated at 600°C for 10 min in flowing 1.5%O$_2$-He gas. The compositions of the feed gases for C$_3$H$_6$-NO-O$_2$, C$_3$H$_6$-O$_2$ and NO-O$_2$ reactions are shown in Table 2. The reactions were carried out at a gas flow rate of 500 cm$^3$/min (W/F = 0.012 g s/cm$^3$) in the temperature range of 200 to 600°C. The effluent compositions were analyzed using a Shimadzu GC-14B gas chromatograph with a flame ionization detector (FID) and a Shimadzu NOA-70000X analyzer. To investigate the influence of acidic gas adsorption on catalytic activity, evaluation of catalytic activity for C$_3$H$_6$-O$_2$ reaction was performed after CO$_2$ adsorption treatment on the catalyst by exposure to 1%CO$_2$-He gas for 1 h at room temperature.

### 3. Results and discussion

#### 3.1 Catalyst preparation and characterization

**Figure 1 (a)** shows XRD patterns of ALa$_9$Si$_6$O$_{26}$ (A = Li, Na, K) obtained by the solid state reaction method and La$_{9.33}$Si$_6$O$_{26}$ obtained by the sol–gel method. The peaks were indexed on the basis of hexagonal unit cell. The molar ratios of La, Si and A in ALa$_9$Si$_6$O$_{26}$ are 10.15 and 10.19, which are larger than 10.10 and 10.19, which are larger than 10, respectively, suggesting presence of small amounts of excess alkali metal on the catalysts. The lattice constants, hexagonal unit cell volumes of ALa$_9$Si$_6$O$_{26}$ and ionic radii of alkali metal ions\textsuperscript{19}) are listed in Table 3. These ratios are close to stoichiometric composition of ALa$_9$Si$_6$O$_{26}$. For A = Li and Na, ratios of (La + A) are 10.15 and 10.19, which are larger than 10, respectively, suggesting presence of small amounts of excess alkali metal on the catalysts. The lattice constants, hexagonal unit cell volumes of ALa$_9$Si$_6$O$_{26}$ and ionic radii of alkali metal ions\textsuperscript{19}) are listed in Table 4. The volumes of the apatite increased with increasing ionic radii of alkali metal ions. This result indicates that the alkali metal ions were incorporated into the apatite-type lattice. The weak peaks observed at 2\(\theta\) = 26.1 and 28.7°, for alkali metal free-sample, were assigned to La$_2$Si$_2$O$_7$. Figure 1(b) shows XRD patterns of Pt/Ala$_9$Si$_6$O$_{26}$ catalysts and Pt/La$_{9.33}$Si$_6$O$_{26}$ catalyst prepared by the impregnation method. The peaks of apatite-type phase were observed after Pt loading, and no apparent peaks of Pt derived phase, such as Pt, PO or PO$_2$ were detected, suggesting that no large crystalline Pt compounds

### Table 1. Synthesis conditions of ALa$_9$Si$_6$O$_{26}$ (A = Li, Na, K)

| A | Synthesis condition |
|---|---------------------|
| Li | 800°C 12 h and 1100°C 12 h |
| Na | 800°C 12 h and 1100°C 24 h |
| K | 800°C 6 h and 1200°C 12 h |

### Table 2. Composition of feed gases for C$_3$H$_6$-NO-O$_2$, C$_3$H$_6$-O$_2$ and NO-O$_2$ reactions

| Gas | C$_3$H$_6$-NO-O$_2$ reaction | C$_3$H$_6$-O$_2$ reaction | NO-O$_2$ reaction |
|-----|----------------------------|-------------------------|-------------------|
| C$_3$H$_6$ | 1500 | 1500 | — |
| NO | 1000 | — | 1000 |
| O$_2$ | 9000 | 9000 | 9000 |
| He | Balance | Balance | Balance |
formed on the catalysts. Specific surface areas of supports and CO/Pt for catalysts are listed in Table 5. All of the specific surface areas for the apatite-type silicate supports were small (0.4–0.7 m²/g), because the apatite-type silicate supports were synthesized at high temperature (1100–1250°C). The CO/Pt for the Pt/ALa9Si6O26 and Pt/La9.33Si6O26 catalysts was 0.02, 0.06, 0.04 and 0.05 for A = Li, Na, K and Pt/La9.33Si6O26, respectively. These values indicate that the amounts of exposed Pt atoms on catalyst surface were small, and no significant difference of Pt dispersion was observed among the catalysts. The XPS spectra of the Pt 4f region for the as-prepared apatite-type silicate supported Pt catalysts are shown in Figure 2. The Pt 4f spectra for all the catalysts could be fit to two doublets. The Pt 4f7/2 peaks were observed at 72.0–72.1 and 73.7–73.9 eV. The binding energies of the Pt 4f7/2 peaks are listed in Table 6. Hecq et al. reported that the binding energies of Pt 4f7/2 were 72.3 eV for PtO and 73.6 eV for PtO2 in the case of oxygen-platinum compounds.20) From their results, the two doublets of Pt 4f spectra for the catalysts were assigned to Pt²⁺ and Pt⁴⁺ species. The molar fractions of Pt²⁺ and Pt⁴⁺ calculated by curve fitting of the spectra are listed in Table 6. The fraction of Pt⁴⁺ was more than 70% for Pt/ALa9Si6O26 catalysts, and 37% for Pt/La9.33Si6O26, indicating that Pt on these catalysts was highly oxidized. Figure 3 shows the H₂-TPR curves of the apatite-type silicate supported Pt catalysts. Hydrogen consumption peak was observed at 94, 96, 87 and 383°C for A = Li, Na, K and Pt/La9.33Si6O26 catalysts. The reduction temperature for Pt/La9.33Si6O26 was much higher than that for Pt/ALa9Si6O26, and broad H₂ consumption was observed in the temperature range of 100–300°C. The amounts of H₂ consumption for Pt reduction on Pt/La9.33Si6O26 catalyst at 25 and 250°C were measured by H₂ pulse reduction. Hydrogen consumption was less than 0.1, and 1.05 mol/g-cat. at 25 and 250°C, respectively. Figure 4 shows XPS spectra of the Pt 4f region for Pt/La9.33Si6O26 after H₂ pulse reduction at 25 and 250°C. The Pt 4f7/2 peaks for Pt/La9.33Si6O26

Table 3. Molar ratios of La, Si and A (A = Li, Na, K) in ALa9Si6O26

| ALa9Si6O26 | Molar ratios (–) | A | Si²⁺ | A |
|------------|-----------------|---|-------|---|
| A = Li     | 9.16            | 6.00 | 0.99 |
| A = Na     | 9.15            | 6.00 | 1.04 |
| A = K      | 8.89            | 6.00 | 1.00 |

* Molar ratios of Si are fixed at 6.00.

Table 4. Lattice constants, unit cell volume of ALa9Si6O26 (A = Li, Na, K) and ionic radius of A⁺

| ALa9Si6O26 | Lattice constants | Unit cell volume | Ionic radius of A⁺ |
|------------|-------------------|-----------------|--------------------|
| A = Li     | a (nm) 0.96901(7) | c (nm) 0.71524(5) | V (nm³) 0.5816 | 0.106 |
| A = Na     | a (nm) 0.96940(10)| c (nm) 0.71880(7) | V (nm³) 0.5850 | 0.132 |
| A = K      | a (nm) 0.97291(5) | c (nm) 0.72442(3) | V (nm³) 0.5930 | 0.165 |

*8-coordination environment.

Table 5. Specific surface area of supports and CO/Pt of Pt/ALa9Si6O26 (A = Li, Na, K) and Pt/La9.33Si6O26 catalysts

| Catalyst | Specific surface area (m²/g) | CO/Pt |
|----------|------------------------------|-------|
| Pt/ALa9Si6O26 | 0.7                           | 0.05  |
| Pt/LiLa9Si6O26 | 0.4                           | 0.02  |
| Pt/NaLa9Si6O26 | 0.4                           | 0.06  |
| Pt/KLa9Si6O26 | 0.4                           | 0.04  |

Fig. 1. XRD patterns of (a) ALa9Si6O26 (A = Li, Na, K), La9.33Si6O26 and (b) apatite-type silicate supported Pt catalysts.
Table 6. Binding energy of Pt 4f/2 and relative peak area for Pt/Ala9Si6O26 (A = Li, Na, K) and Pt/La9.33Si6O26 catalysts.

| Catalyst                  | Binding energy of 4f/2 (eV) | Relative peak area (%) | Assignment |
|---------------------------|-----------------------------|------------------------|------------|
| Pt/La9.33Si6O26           | 72.1                        | 63                     | Pt⁺        |
|                           | 73.9                        | 37                     | Pt²⁺       |
| Pt/LiLa9.33Si6O26         | 72.0                        | 28                     | Pt⁺        |
|                           | 73.9                        | 72                     | Pt⁺        |
| Pt/NaLa9.33Si6O26         | 72.0                        | 25                     | Pt⁺        |
|                           | 73.7                        | 75                     | Pt⁺        |
| Pt/KtLa9.33Si6O26         | 72.1                        | 29                     | Pt⁺        |
|                           | 73.8                        | 71                     | Pt⁺        |

The H₂-TPR results of Pt/Ala9Si6O26 catalysts indicate that the reduction temperature of Pt oxides on the catalysts was decreased by substitution of alkali metal ion at La site in the apatite-type silicate support. In our previous study, H₂-TPR measurement was performed for Pt/La₉.₃₃Si₆O₂₆ (A' = Ca, Sr, Ba) under the same condition. Hydrogen consumption peaks observed at 95 and 89°C for A' = Sr and Ba. These temperatures were close to those observed in the case of Pt/Ala9Si6O26 catalysts. On the other hand, H₂ consumption peak was observed at 145°C for A' = Ca, which is higher than that for A' = Sr and Ba. From these results, it is presumed that the reduction temperature of Pt oxides was affected by basicity of the apatite-type silicate support, but the difference of effect on lowering the reduction temperature among Pt/Ala9Si6O26 catalysts is small.

3.2 Catalytic activity

Figure 5(a) shows temperature dependence of NO conversion for C₃H₆+NO+O₂ reaction over Pt/Ala9Si6O26 (A = Li, Na, K) and Pt/La₉.₃₃Si₆O₂₆ catalysts in the range of 200–600°C. The maximum NO conversion of Pt/Ala9Si6O26 catalysts decreased in the sequence of A = Na (42%) > A = Li (35%) > Pt/La₉.₃₃Si₆O₂₆ (29%) > A = K (23%) and the temperatures for maximum NO conversion were 350, 275, 350 and 325°C for A = Li, Na, K and Pt/La₉.₃₃Si₆O₂₆ catalyst, respectively. This result suggests that the substitution of alkali metal ion at La site in apatite-type silicate support affects NO reduction behavior of the Pt/Ala9Si6O26 and Pt/La₉.₃₃Si₆O₂₆ catalysts for C₃H₆+NO+O₂ reaction. In our previous study, Pt/γ-Al₂O₃ exhibited a maximum NO conversion of 46% at 325°C, under the same reaction condition. Although the specific surface area of Pt/NaLa₉.₃₃Si₆O₂₆ catalyst (0.4 m²/g) was smaller than that of Pt/γ-Al₂O₃ catalyst (159 m²/g), the maximum NO conversion for Pt/NaLa₉.₃₃Si₆O₂₆ catalyst was comparable to that of Pt/γ-Al₂O₃ catalyst. Burch et al. performed kinetics measurements for C₃H₆+NO+O₂ reaction over Pt/γ-Al₂O₃ and Pt/Al₂O₃. They proposed that C₃H₆ adsorption and formation of carbonaceous species occur on Pt surface during the reaction, and that oxidized Pt is inactive for NO dissociation. 1,2 This suggests that the chemical state and reduction property of Pt species affect the catalytic behavior for C₃H₆+NO+O₂ reaction. The higher Pt reduction temperature of Pt/La₉.₃₃Si₆O₂₆ would be one of reason for the lower activity below 275°C compared with Pt/Ala9Si6O26 (A = Li, Na, K). On the other hand, no significant difference was observed in the chemical state (Fig. 2) and reduction property (Fig. 3) of Pt species on the Pt/Ala9Si6O26 catalysts. Therefore, it is suggested that the C₃H₆ adsorption and formation of carbonaceous species over Pt on Pt/Ala9Si6O26 catalysts are not dominant factors causing difference of catalytic activities among the catalysts for C₃H₆+NO+O₂ reaction.

In the case of catalytic NO reduction by hydrocarbon in the presence of O₂, it is also known that NO₂ is formed by NO oxidation as one of the reactive intermediates. 23,24 To investigate the influence of the apatite-type silicate supports on NO₂ formation, catalytic activities for the NO₂ reaction over Pt/Ala9Si6O26 and Pt/La₉.₃₃Si₆O₂₆ catalysts were evaluated. Figure 6 shows temperature dependence of NO conversion into NO₂ over the catalysts and Pt/γ-Al₂O₃ catalyst in the range of 200–600°C. All of the maximum NO conversions over Pt/Ala9Si6O26 and Pt/La₉.₃₃Si₆O₂₆ catalysts were less than 9%. On the other hand, Pt/γ-Al₂O₃ exhibited higher maximum conversion of 17% at 400°C. Thus, no significant difference was observed for NO oxidation properties among Pt/Ala9Si6O26 and Pt/La₉.₃₃Si₆O₂₆ catalysts. These results suggest...
that the alkali metal ion substitution at La site in the apatite-type silicate supports has no effect on the catalytic activity for NO oxidation.

In order to investigate the effect of the apatite-type silicate supports on C_3H_6 containing reaction, catalytic activity for C_3H_6–O_2 reaction of Pt/ALa_9Si_6O_26, Pt/La_9.33Si_6O_26 and Pt/La_9Si_6O_26 were evaluated. Figure 7 shows temperature dependence of C_3H_6 conversion for C_3H_6–O_2 reaction over Pt/ALa_9Si_6O_26, Pt/La_9.33Si_6O_26 catalysts and KLa_9Si_6O_26 in the range of 100–600°C. Propene conversion increased sharply at 225°C for Pt/La_9.33Si_6O_26 and at 200 and 175°C for Pt/ALa_9Si_6O_26 (A = Li, Na, K), respectively. This result indicates that C_3H_6 oxidation activity was improved by substitution of alkali metal ions at La site in the apatite-type silicate support. The temperatures for 50% conversion of C_3H_6, T_50(C_3H_6), for C_3H_6–O_2 reaction over Pt/ALa_9Si_6O_26 and Pt/La_9.33Si_6O_26 catalysts are listed in Table 7. The T_50(C_3H_6) for C_3H_6–O_2 reaction decreased in the sequence of Pt/ALa_9Si_6O_26 > Pt/La_9.33Si_6O_26 > Pt/LiLa_9Si_6O_26 > Pt/NaLa_9Si_6O_26 > Pt/KLa_9Si_6O_26 > Pt/KLa_9Si_6O_26, which agrees with the decreasing order of the electronegativity of lanthanum and alkali metals. The catalytic performance of KLa_9Si_6O_26 without Pt loading was also investigated as shown in Fig. 7. The C_3H_6 conversion over KLa_9Si_6O_26 was less than 2% below 600°C, indicating that C_3H_6 oxidation occurred over Pt on the Pt/KLa_9Si_6O_26 catalyst. As described above, no difference of chemical state and reduction property of Pt were observed among Pt/ALa_9Si_6O_26 catalysts. Therefore, it is suggested that the basicity ofapatite-type silicate supports affect the C_3H_6 activation over the supports.

Wakabayashi et al. investigated the oxidation of hydrocarbon and the reduction of NO by hydrocarbon species over apatite-type La_7.33BaYSi_6O_25.5 supported Pt catalyst. They performed infrared (IR) spectroscopy measurement for La_7.33BaYSi_6O_25.5 after treatment in flowing 0.25% C_3H_6–N_2 gas, and observed adsorbed carbonous species such as ones completely oxidized to carbonate and partially oxidized to methanol, formaldehyde and dimethylether. In their study, they presumed that the catalytic activity of apatite-type La_7.33BaYSi_6O_25.5.

| Catalyst       | T_50(C_3H_6) (°C) | T_50(C_3H_6) (°C) |
|----------------|------------------|------------------|
| Pt/ALa_9Si_6O_26 | 251              | 255              |
| Pt/La_9.33Si_6O_26 | 240              | 264              |
| Pt/NaLa_9Si_6O_26 | 197              | 217              |
| Pt/KLa_9Si_6O_26  | 190              | 251              |

Fig. 5. Temperature dependences of (a) NO and (b) C_3H_6 conversions for C_3H_6–NO–O_2 reaction over Pt/ALa_9Si_6O_26 (A = Li, Na, K) and Pt/La_9Si_6O_26 catalysts.

Fig. 6. Temperature dependence of NO conversion for NO–O_2 reaction over Pt/ALa_9Si_6O_26 (A = Li, Na, K), Pt/La_9.33Si_6O_26 and Pt/LiAl_2O_3 catalysts.

Table 7. T_50(C_3H_6) for C_3H_6–O_2 reactions.
supported Pt catalyst for NO reduction by C\textsubscript{3}H\textsubscript{6} was affected by the adsorbed form of oxidized carbonous species on La\textsubscript{3.33}BaY\textsubscript{0.67}Si\textsubscript{6}O\textsubscript{26}. In the case of Pt/Al\textsubscript{2}O\textsubscript{3}, basic sites on the apatite-type silicate supports would occur, resulting in degradation of catalytic activity. Therefore, optimization of basicity of the support would be necessary for improving the catalytic activity for C\textsubscript{3}H\textsubscript{6}−NO\textsubscript{2} reaction.

**4. Conclusion**

Apatite-type Al\textsubscript{2}O\textsubscript{3} (A = Li, Na, K) supported Pt catalysts were prepared and investigated for their catalytic activity for C\textsubscript{3}H\textsubscript{6}−NO\textsubscript{2}, C\textsubscript{3}H\textsubscript{6}−O\textsubscript{2} and NO−O\textsubscript{2} reactions. Pt/Al\textsubscript{2}O\textsubscript{3} catalyst exhibited the highest maximum NO conversion at the lowest temperature among Pt/Al\textsubscript{2}O\textsubscript{3} catalysts.

Catalytic activity of apatite-type silicate supported Pt catalyst for C\textsubscript{3}H\textsubscript{6} oxidation was improved by substitution of alkali metal ions on La site in the apatite-type silicate supports. However, C\textsubscript{3}H\textsubscript{6} oxidation on apatite-type silicate supported Pt catalysts was suppressed by presence of acidic gases such as CO\textsubscript{2} and NO. From these results, it seems that the reaction intermediate formed over basic sites on the apatite-type silicate support, resulting in enhancement of the catalytic activity. On the other hand, adsorption of CO\textsubscript{2} and NO on the basic site would inhibit formation of the intermediates. Therefore, optimization of basicity of the support would be necessary for improving the catalytic activity for C\textsubscript{3}H\textsubscript{6}−NO\textsubscript{2} reaction.

**Acknowledgements** This work was partly supported by Grant-in-Aid for Scientific Research (C) (23510089) from Japan Society for Promotion of Science (JSPS).

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