Effect of oxide-ion conductivity of apatite-type Ln$_{10}$Si$_6$O$_{27}$ on catalytic activity for toluene combustion

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ABSTRACT

By using apatite-type Ln$_{10}$Si$_6$O$_{27}$ (Ln = La, Sm, Gd) solids with oxide-ion-conduction properties, the effect of conductivity on the catalytic activity of 1 wt% Pt/Ln$_{10}$Si$_6$O$_{27}$ for toluene combustion was clarified. With increasing Ln$^{3+}$ ion size, the lattice volume of Ln$_{10}$Si$_6$O$_{27}$ increased, resulting in the enhancement of the conductivity, likely due to the expansion of the oxide-ion-conducting pathway; that is, the conductivity increased in the order Gd$_{10}$Si$_6$O$_{27}$ < Sm$_{10}$Si$_6$O$_{27}$ < La$_{10}$Si$_6$O$_{27}$. The conductivity of the Ln$_{10}$Si$_6$O$_{27}$ promoter affected the oxygen release ability of 1 wt% Pt/Ln$_{10}$Si$_6$O$_{27}$, which led to the oxidation of Pt$^{4+}$ to Pt$^{2+}$/4+. Correspondingly, the Pt/Ln$_{10}$ Si$_6$O$_{27}$ catalyst facilitated toluene combustion, and the catalytic activity increased in the order 1 wt% Pt/Gd$_{10}$Si$_6$O$_{27}$ < 1 wt% Pt/Sm$_{10}$Si$_6$O$_{27}$ < 1 wt% Pt/La$_{10}$Si$_6$O$_{27}$; this order was not consistent with the surface area, Pt dispersion, or acidity. These results indicate that the catalytic activity was affected by the conductivity of the Ln$_{10}$Si$_6$O$_{27}$ promoter.

1. Introduction

Toluene has been utilized as an organic solvent in the chemical industry for paints, adhesives, printing inks, and other applications. However, toluene is a typical volatile organic compound (VOC) that pollutes the air and causes sick building syndrome [1,2]. Therefore, it is necessary to develop catalysts that can decompose toluene effectively. Among these catalysts, platinum-based ones are known to show relatively high efficiency; for example, Pt supported on γ-Al$_2$O$_3$ completely oxidizes toluene at 170°C [3]. Several factors can improve catalytic activity. In general, catalytic activity depends on the surface area of the supports [4–7]. A high surface area can enhance the dispersibility of the Pt activator, leading to an increase in the number of catalytic active sites. For toluene combustion, the acidity of the support has also been reported to affect the catalytic activity [8,9]. Because toluene is a molecule with weak basicity owing to its aromatic ring, the acidic sites on the support can act as toluene adsorption sites. One important factor is the presence of promoters, which can supply active oxygen species to the Pt activator. CeO$_2$–ZrO$_2$ solid solutions are well-known promoters because of their oxygen release and storage abilities owing to the redox cycle between Ce$^{4+}$ and Ce$^{3+}$ [10–12]. We have studied CeO$_2$–ZrO$_2$ promoters from the viewpoint of oxide ion conduction and found that the introduction of Bi$_2$O$_3$ or NiO into CeO$_2$–ZrO$_2$ improves the oxygen release and storage abilities, because lower-valence Bi$^{3+}$ and Ni$^{2+}$/3+ generate oxygen vacancies to supply oxygen species from the inside of the crystal lattice [13,14].

Furthermore, we have demonstrated that Pt/CeO$_2$–ZrO$_2$–MnO$_2$–γ-Al$_2$O$_3$ can completely oxidize toluene at 120°C and 100°C when MnO$_2$ is Bi$_2$O$_3$ or NiO, respectively, which are lower temperatures than that required for Pt/CeO$_2$–ZrO$_2$–MnO$_2$–γ-Al$_2$O$_3$ (140°C) [15,16]. These results suggest that the oxide-ion-conduction properties of the promoter influence its oxygen release and storage abilities, as well as the catalytic activity for toluene combustion. For further discussion, our group investigated the relationships between conductivity and oxygen release and storage abilities in a series of CeO$_2$–ZrO$_2$-based promoters, and we demonstrated that the oxide-ion-conduction properties improved the oxygen release and storage abilities, enhancing the catalytic activity for methane combustion [17]. However, the redox of Ce$^{3+/4+}$ in the CeO$_2$–ZrO$_2$-based promoters showed electronic conduction, which also affects the oxygen release and storage abilities. Therefore, it remains unclear whether oxide ion conductivity influences the oxygen release and storage abilities as well as the catalytic activity. To clarify the effect of the oxide-ion-conduction properties, it is necessary to select pure oxide-ion-conducting solid electrolytes that do not show electronic conduction owing to the valence change of the constituent ions as promoters.

Recently, we demonstrated that apatite-type lanthanum silicate (La$_{10}$Si$_6$O$_{27}$) functioned as a promoter; that is, La$_{10}$Si$_6$O$_{27}$ facilitated catalytic oxidation [18]. Here, the apatite-type structure has a one-dimensional tunnel along the c-axis suitable for oxide ion migration, and lanthanoid silicates
(Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27}) with apatite-type structures are known to be oxide-ion-conducting solid electrolytes [19–21]. We have also reported that a Pt/La\textsubscript{10}Si\textsubscript{6}O\textsubscript{27} catalyst, in which Co\textsuperscript{2+/3+} was introduced into La\textsubscript{10}Si\textsubscript{6}O\textsubscript{27} to provide redox properties, exhibits high catalytic activity; that is, toluene was completely combusted at 120°C [22].

Therefore, apatite-type Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27} solids are expected to be suitable for investigating the effect of oxide ion conductivity on catalytic activity. In the present study, we examined three types of apatite-type solids: La\textsubscript{10}Si\textsubscript{6}O\textsubscript{27}, Sm\textsubscript{10}Si\textsubscript{6}O\textsubscript{27}, and Gd\textsubscript{10}Si\textsubscript{6}O\textsubscript{27}. One reason is that these solids exhibit different oxide ion conductivities, which depend on the size of the Ln\textsuperscript{3+} ions [19,20]. The other is that the Ln (Ln = La, Sm, Gd) ions possess a single trivalent state, which allows them to show pure oxide ion conduction without electronic conduction [19]. The γ-Al\textsubscript{2}O\textsubscript{3} support of our previous catalyst, Pt/La\textsubscript{10}Si\textsubscript{6}O\textsubscript{27}/γ-Al\textsubscript{2}O\textsubscript{3} [22], was excluded to increase the amount of the Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27} promoter and to decrease the effect of the surface area. In addition, while the Pt loading in our previous catalyst was 10 wt % [22], the amount of Pt was reduced to 1 wt% for satisfactory clarification of the powder properties. Based on these concepts, we synthesized 1 wt% Pt/Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27} (Ln = La, Sm, Gd) catalysts and investigated the relationship between the conductivity of the promoter and the catalytic activity for toluene combustion.

2. Experimental

Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27} (Ln = La, Sm, Gd) solids were synthesized via a co-precipitation process similar to that in a previous study [23]. Na\textsubscript{3}SiO\textsubscript{3}·9H\textsubscript{2}O was dissolved in a 15 vol% aqueous ammonia solution, and then an aqueous solution of stoichiometric La(NO\textsubscript{3})\textsubscript{3}, Sm(CH\textsubscript{3}COO)\textsubscript{3}, or Gd(CH\textsubscript{3}COO)\textsubscript{3} was added dropwise in a stoichiometric ratio. After the solution was stirred at 60°C for 1 h, the resulting precipitate was filtered, washed several times with deionized water and ethanol, and then dried at 80°C for 3 h. Subsequently, the powder was calcined at 900°C for 2 h in atmospheric air to obtain Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27}. Pt/Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27} catalysts were prepared by impregnating the Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27} powders with platinum colloids stabilized with polyvinylpyrrolidone (Tanaka Kikinzoku Kogyo); the Pt loading was adjusted to 1 wt%. After impregnation, the sample was dried at 80°C for 12 h and then calcined at 500°C for 4 h in atmospheric air.

The Pt loading was confirmed through X-ray fluorescence (XRF; Supermini200, Rigaku) analysis. The crystal phases of the samples were identified through X-ray powder diffraction (XRD; SmartLab, Rigaku) using Cu Ka radiation at 40 kV and 30 mA, and the lattice volume was calculated by refining the XRD peak angles using α-Al\textsubscript{2}O\textsubscript{3} as a standard. X-ray photoelectron spectroscopy (XPS; PHI 5000 VersaProbe II, ULVAC-Phi) was performed at room temperature using Al Kα radiation. The effect of charging on the binding energies was refined with respect to the C 1s peak (284.6 eV), and the spectra were fitted using a Shirley background and Gaussian–Lorentzian line shapes. To evaluate the conductivity, the Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27} powders were pressed into pellets through uniaxial pressing, and then the pellets were sintered at 900°C for 2 h under an air flow. The obtained pellets were polished with waterproof abrasive papers (#2000, #3000, and then #8000), and platinum-sputtered layers were formed on the center surfaces of the pellets using an ion coater (IB-3, Elko). Subsequently, platinum paste was fixed on the sputtered layer, and then the sample was heated at 800°C for 1 h in atmospheric air. The conductivity (σ) of the sample pellet was measured using the complex impedance method in the frequency range of 13 MHz to 1 Hz (1260 Impedance/Gain-Phase Analyzer, Solartron) between 900°C and 600°C in atmospheric air.

N\textsubscript{2} adsorption–desorption measurements were conducted at −196°C to evaluate the Brunauer-Emmett-Teller (BET) specific surface areas (TriStar 3000, Shimadzu). The Pt dispersion was evaluated using carbon monoxide chemisorption at 50°C with a 10% CO–90% He pulse (0.3 ml) over 0.05 g of the catalyst, under the assumption that one CO molecule adsorbs to one surface Pt atom (BELCAT-B, MicrotracBEL). H\textsubscript{2} temperature-programmed reduction (H\textsubscript{2}-TPR) measurements were carried out at a heating rate of 5°C·min\textsuperscript{-1} over 0.2 g of the catalyst under a reducing gas flow (5% H\textsubscript{2}–95% Ar at 50 ml·min\textsuperscript{-1}) (BELCAT-B, MicrotracBEL). The acidity of the samples was assessed using NH\textsubscript{3} temperature-programmed desorption (NH\textsubscript{3}-TPD) measurements. The sample (0.2 g) was pre-treated at 900°C for 1 h under a helium flow (50 ml·min\textsuperscript{-1}), and then exposed to a flow of 0.5% NH\textsubscript{3}–99.5% He (50 ml·min\textsuperscript{-1}) at 50°C for 30 min and heated at a rate of 10°C·min\textsuperscript{-1} under a helium flow (30 ml·min\textsuperscript{-1}) (BELCAT-B, MicrotracBEL).

Toluene oxidation activity tests were conducted in a conventional fixed-bed reactor with a 10-mm-diameter quartz glass tube by feeding 900 ppm toluene-99.91% air gas at a rate of 20 ml·min\textsuperscript{-1} over 0.1 g of the catalyst with a space velocity of 12,000 L·kg\textsuperscript{-1}·h\textsuperscript{-1}. Prior to the test, the catalyst was pre-treated at 200°C for 2 h under an argon flow (20 ml·min\textsuperscript{-1}). The toluene conversion was determined using gas chromatography with a flame ionization detector (FID; Shimadzu GC-8AIF) using a SunPak-A column (Shinwa Chemical Industries).

3. Results and discussion

The crystal structures and conductivities of the Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27} (Ln = La, Sm, Gd) promoters were examined. Figure 1 shows the XRD patterns of Ln\textsubscript{10}Si\textsubscript{6}O\textsubscript{27}. All samples were indexed to single-phase apatite-type structures, and no impurity phases were observed. From the XRD patterns refined using α-Al\textsubscript{2}O\textsubscript{3} as
a standard (Figure S1), the lattice volumes of the apatite-type structures were estimated, yielding the following results: La$_{10}$Si$_6$O$_{27}$ (0.587 nm$^3$) > Sm$_{10}$Si$_6$O$_{27}$ (0.535 nm$^3$) > Gd$_{10}$Si$_6$O$_{27}$ (0.528 nm$^3$). This trend is consistent with the Ln$^{3+}$ ion size (La$^{3+}$: 0.117 nm, Sm$^{3+}$: 0.110 nm, Gd$^{3+}$: 0.108 nm, coordination number: 6 [24]), similar to the findings of a previous study [19,20]. Figure 2(a) shows the conductivities of the Ln$_{10}$Si$_6$O$_{27}$ solids as functions of temperature, where the typical Nyquist plots are given in Figure S2. As expected, La$_{10}$Si$_6$O$_{27}$ showed the highest conductivity, followed by Sm$_{10}$Si$_6$O$_{27}$ and then Gd$_{10}$Si$_6$O$_{27}$. Figure 2(b) displays the lattice volume dependence of the conductivity at 900°C, and the activation energy for ion conduction, calculated from Arrhenius plots (Figure S3). As the lattice volume increased, the conductivity increased and the activation energy decreased, indicating that a large crystal lattice results in the expansion of the oxide-ion-conducting pathway. This tendency is consistent with the results of previous studies [19,20].

For the Pt-loaded on Ln$_{10}$Si$_6$O$_{27}$ catalysts, the XRD patterns displayed only peaks attributable to the apatite-type structure, and peaks derived from Pt species could not be identified because of the low Pt loading (Figure S4). The presence of Pt was confirmed using XRF analysis. The measured Pt loadings in Pt/Ln$_{10}$Si$_6$O$_{27}$ were 1.04 wt% (Ln = La), 0.98 wt% (Ln = Sm), and 0.97 wt% (Ln = Gd), which were in good agreement with the feed values within experimental errors. The BET specific surface areas and Pt dispersions of Pt/Ln$_{10}$Si$_6$O$_{27}$ are summarized in Table 1. The samples had similar values for both. In addition, the BET specific surface areas were low (ca. 15 m$^2$ g$^{-1}$) because the Ln$_{10}$Si$_6$O$_{27}$ solids were calcined at an elevated temperature of 900°C.

To investigate the effect of the Ln$_{10}$Si$_6$O$_{27}$ promoters on the oxidation state of the surface Pt species, XPS measurements were carried out. The XPS spectra of the Pt 4f core levels of Pt/Ln$_{10}$Si$_6$O$_{27}$ are shown in Figure 3. For each sample, the Pt 4f$_{5/2}$ and Pt 4f$_{7/2}$ peaks could be divided into Pt$^0$, Pt$^{2+}$, and Pt$^{4+}$ peaks; the ratios of the Pt species are listed in Table 2. The Pt$^{2+}$ and Pt$^{4+}$ ratios both increased in the order Pt/Gd$_{10}$Si$_6$O$_{27}$ < Pt/Sm$_{10}$Si$_6$O$_{27}$ < Pt/La$_{10}$Si$_6$O$_{27}$. Although the surface areas and Pt dispersions can influence the oxidation state of Pt [4–8], the Pt/Ln$_{10}$Si$_6$O$_{27}$ catalysts showed similar surface areas and Pt dispersions (Table 1). In contrast, the trend of the cationic Pt ratio matches that of the oxide ion conductivity (Figure 2). Therefore, promoters with higher
The oxide-ion conductivities can supply more oxygen species to the Pt activators, accelerating the oxidation of the Pt species.

The oxygen supply abilities of Pt/Ln₁₀Si₆O₂₇ were assessed using H₂-TPR measurements, and the profiles are shown in Figure 4. The peak maximum was observed at ca. 350°C for all samples, because the reduction temperature is predominantly influenced by the electronic conductivity rather than the oxide ion conductivity [17]. In contrast, the total H₂ consumption amount, estimated from the peak area, increased in the following order: Pt/Gd₁₀Si₆O₂₇ (43.5 μmol·g⁻¹) < Pt/Sm₁₀Si₆O₂₇ (57.6 μmol·g⁻¹) < Pt/La₁₀Si₆O₂₇ (99.0 μmol·g⁻¹). This tendency is influenced by the Pt⁴⁺ and Pt⁶⁺ ratios (Table 2), because H₂ consumption is related to the reduction of the cationic Pt species involved with oxygen release. The cationic Pt ratio was affected by the oxide-ion conductivity, indicating that the oxygen supply ability of Pt/Ln₁₀Si₆O₂₇ is improved when the conductivity of the Ln₁₀Si₆O₂₇ promoter is high.

Because the acidity of the supports has been reported to affect the catalytic activity [8,9], NH₃-TPD measurements were performed (Figure S5). The number of acidic sites increased in the order Sm₁₀Si₆O₂₇ (69 μmol·g⁻¹) < Gd₁₀Si₆O₂₇ (91 μmol·g⁻¹) < La₁₀Si₆O₂₇ (118 μmol·g⁻¹), which was not consistent with the conductivity or the oxygen supply ability.

Catalytic activity tests for toluene combustion were carried out for the Pt/Ln₁₀Si₆O₂₇ catalysts, and the temperature dependence of toluene conversion is shown in Figure 5. Here, the Ln₁₀Si₆O₂₇ solids themselves acted as the promoter, not the active species, as toluene decomposition was not observed at temperatures below 250°C. As shown in Figure 5, the catalytic activity increased in the order Pt/Gd₁₀Si₆O₂₇ < Pt/Sm₁₀Si₆O₂₇ < Pt/La₁₀Si₆O₂₇, despite similar surface areas and Pt dispersions. In other words, the catalytic activity was obviously dependent on the promoter property, while Pt/Ln₁₀Si₆O₂₇ showed lower activities than that of the previous 10 wt% Pt/La₁₀Si₆O₂₇/γ-Al₂O₃ catalyst [22] (Figure S6) owing to the exclusion of the γ-Al₂O₃ support with high surface area and the high Pt loading amount. In addition, no correlation was observed between the acidity of Ln₁₀Si₆O₂₇ and catalytic activity. Thus, the catalytic activity is predominantly affected by the oxygen supply ability and conductivity. Figure 6 shows the relationships between the conductivity of the Ln₁₀Si₆O₂₇ solids at 900°C and the H₂ consumption amount and complete toluene oxidation temperature for the Pt/Ln₁₀Si₆O₂₇ catalysts. The conductivities of the Ln₁₀Si₆O₂₇ promoters were

Table 1. BET surface areas and Pt dispersions of Pt/Ln₁₀Si₆O₂₇ (Ln = La, Sm, Gd).

| Samples       | BET surface area/m²·g⁻¹ | Pt dispersion/% |
|---------------|-------------------------|-----------------|
| Pt/Sm₁₀Si₆O₂₇ | 20.2                    | 23.2            |
| Pt/La₁₀Si₆O₂₇ | 29.4                    | 25.3            |
| Pt/Gd₁₀Si₆O₂₇ | 36.1                    | 28.8            |

Table 2. Ratios of the Pt species in Pt/Ln₁₀Si₆O₂₇ (Ln = La, Sm, Gd) estimated from XPS results.

| Samples       | Pt⁰ % | Pt⁶⁺ % | Pt⁴⁺ % |
|---------------|-------|--------|--------|
| Pt/Sm₁₀Si₆O₂₇ | 21.0  | 35.0   | 44.0   |
| Pt/La₁₀Si₆O₂₇ | 36.1  | 29.4   | 34.5   |
| Pt/Gd₁₀Si₆O₂₇ | 51.0  | 28.8   | 20.2   |

Figure 3. XPS spectra of Pt 4f core levels of the Pt/Ln₁₀Si₆O₂₇ (Ln = La, Sm, Gd) catalysts.

Figure 4. H₂-TPR profiles of the Pt/Ln₁₀Si₆O₂₇ (Ln = La, Sm, Gd) catalysts.
clearly correlated with the amount of $H_2$ consumed, that is, the oxygen supply ability. Because high oxygen supply ability improves the catalytic activity, a clear relationship between the complete toluene oxidation temperature and the conductivity was observed. Therefore, the conductivity of the Ln$_{10}$Si$_6$O$_{27}$ promoter influences toluene oxidation on the Pt activator.

Finally, we discuss the catalytic reaction mechanism when a Ln$_{10}$Si$_6$O$_{27}$ promoter is used together with a Pt activator. In general, toluene is oxidized by adsorbed oxygen species ($O^{\bullet}_{\text{Pt}}$) on the active sites of the platinum activator, and this active oxygen is supplied by atmospheric air (Eq. (1)).

$$O_2(\text{gas}) \rightarrow 2O^{\bullet}_{\text{Pt}}$$  \hspace{1cm} (1)

The use of an apatite-type Ln$_{10}$Si$_6$O$_{27}$ promoter with oxide-ion-conduction properties enables the active oxygen species to be supplied via an additional route through oxide ion migration; that is, metallic Pt$^0$ would be oxidized to PtO or PtO$_2$ by the oxide ion (Eqs. (2) and (3)) involved in the formation of oxygen vacancies ($V_O$) in the Ln$_{10}$Si$_6$O$_{27}$ lattice and electrons.

$$Pt^0 + O^{2-} \rightarrow PtO + V_O + 2e^-$$ \hspace{1cm} (2)

$$Pt^0 + 2O^{2-} \rightarrow PtO_2 + 2V_O + 4e^-$$ \hspace{1cm} (3)

It has been reported that cationic Pt species are more active than metallic Pt$^0$ [25–27]. The generated electrons are conducted through the Pt activator, and then the adsorbed oxygen species on the promoter ($O^{\bullet}_{\text{promoter}}$) are reduced to oxide ions near the catalyst-promoter-gas interface (Eq. (4)).

$$2e^- + O^{\bullet}_{\text{promoter}} \rightarrow O^{2-}$$ \hspace{1cm} (4)

Oxide ions also migrate into the promoter lattice and eventually combine with $V_O$ formed in Eq. (2) or (3). As a result, toluene combustion may be facilitated catalytically. Consequently, the oxide-ion-conduction properties may improve the catalytic activity of apatite-type Ln$_{10}$Si$_6$O$_{27}$-based catalysts for toluene combustion.

**Figure 5.** Temperature dependence of toluene conversion over the Pt/Ln$_{10}$Si$_6$O$_{27}$ (Ln = La, Sm, Gd) catalysts.

**Figure 6.** Relationships between the conductivities of the Ln$_{10}$Si$_6$O$_{27}$ solids at 900°C and $H_2$ consumption amount and complete toluene oxidation temperature for the Pt/Ln$_{10}$Si$_6$O$_{27}$ (Ln = La, Sm, Gd) catalysts.
4. Conclusions

The effect of conductivity on catalytic activity for toluene combustion was investigated using Pt-loaded on apatite-type Ln$_{10}$Si$_6$O$_{27}$ (Ln = La, Sm, Gd) solids with an oxide-ion-conducting pathway. The conductivities of the Ln$_{10}$Si$_6$O$_{27}$ promoters increased in the order Gd$_{10}$Si$_6$O$_{27}$ < Sm$_{10}$Si$_6$O$_{27}$ < La$_{10}$Si$_6$O$_{27}$. This trend was consistent with that of the lattice volume of Ln$_{10}$Si$_6$O$_{27}$ (Ln = La, Sm, Gd), because a large lattice volume leads to the expansion of the oxide ion migration pathway. For the Pt/Ln$_{10}$Si$_6$O$_{27}$ catalysts, the ratios of the cationic Pt species (Pt$^{2+}$ and Pt$^{4+}$) increased; this was related to improvements in oxygen supply ability. The oxygen supply was enhanced by the high conductivity of the Ln$_{10}$Si$_6$O$_{27}$ promoter. The catalytic activity for toluene combustion increased in the following order: Pt/Gd$_{10}$Si$_6$O$_{27}$ < Pt/Sm$_{10}$Si$_6$O$_{27}$ < Pt/La$_{10}$Si$_6$O$_{27}$. This tendency was not influenced by the surface area, Pt dispersion, or acidity, but was predominantly correlated with oxygen supply ability. The oxide-ion-conduction properties of the promoter facilitated oxygen supply into the lattice, resulting in high catalytic activity for toluene combustion.

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Disclosure statement

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References

[1] Atkinson R, Arey J. Atmospheric degradation of volatile organic compounds. Chem Rev. 2003;103 (12):4605–4638.
[2] Kostiainen R. Volatile organic compounds in the indoor air of normal and sick houses. Atmos Environ. 1995;29(6):693–702.
[3] Sager SM, Kondarides DI, Verykios EX. Catalytic activity of supported platinum and metal oxide catalysts for toluene oxidation. Top Catal. 2009;52 (5):517–527.
[4] Lai YT, Chen TC, Lan YK, et al. Pt/SBA-15 as a highly efficient catalyst for catalytic toluene oxidation. ACS Catal. 2014;4(11):3824–3836.
[5] Zhang J, Rao C, Peng H, et al. Enhanced toluene combustion performance over Pt loaded hierarchical porous MOR zeolite. Chem Eng J. 2018;334:10–18.
[6] Wu HC, Chen TC, Budi CS, et al. Confinement of Pt nanoparticles in cage-type mesoporous silica SBA-16 as efficient catalysts for toluene oxidation: the effect of carboxylic groups on the mesopore surface. Catal Sci Technol. 2019;9(24):6852–6862.
[7] Liu G, Tian Y, Zhang B, et al. Catalytic combustion of VOC on sandwich-structured Pt@ZSM-5 nanosheets prepared by controllable intercalation. J Hazard Mater. 2019;367:568–576.
[8] Gan T, Chu X, Qi H, et al. Pt/Al$_2$O$_3$ with ultralow Pt-loading catalyze toluene oxidation: promotional synergistic effect of Pt nanoparticles and Al$_2$O$_3$ support. Appl Catal B: Environ. 2019;257:117943.
[9] Hou Z, Zhou X, Lin T, et al. The promotion effect of tungsten on monolith Pt/CE$_{0.65}$Zr$_{0.35}$O$_2$ catalysts for the catalytic oxidation of toluene. New J Chem. 2019;43(15):5719–5726.
[10] Fornasiero P, Balducci G, Monte RD, et al. Modification of the redox behaviour of CeO$_2$ induced by structural doping with ZrO$_2$. J Catal. 1996;164(1):173–183.
[11] Kaśpar J, Fornasiero P, Graziani M. Use of Ce$_2$O$_3$-based oxides in the three-way catalytic wall. Catal Today. 1999;50 (2):285–298.
[12] Nagai Y, Yamamoto T, Tanaka T, et al. X-ray absorption fine structure analysis of local structure of Ce$_2$O$_3$-ZrO$_2$ mixed oxides with the same composition ratio (Ce/Zr = 1). Catal Today. 2002;74(3–4):225–234.
[13] Imanaka N, Masui T, Koyabu K, et al. Significant low-temperature redox activity of Ce$_{0.64}$Gd$_{0.16}$Bi$_{2.0}$O$_{1.90}$ supported on γ-Al$_2$O$_3$. Adv Mater. 2007;19 (12):1608–1611.
[14] Jeong M, Nunotani N, Moriyyama N, et al. High methane combustion activity of PdO/Ce$_2$O$_3$-ZrO$_2$-NiO/γ-Al$_2$O$_3$ catalysts. J Asian Ceram Soc. 2016;4(3):259–262.
[15] Masui T, Imadzu H, Matsuyama N, et al. Total oxidation of toluene on Pt/Ce$_2$O$_3$-ZrO$_2$: Bi$_2$O$_3$/γ-Al$_2$O$_3$ catalysts prepared in the presence of polyvinyl pyrrolidone. J Hazard Mater. 2010;176(1–3):1106–1109.
[16] Jeong M, Nunotani N, Moriyyama N, et al. Introduction of NO in Pt/Ce$_2$O$_3$-ZrO$_2$:γ-Al$_2$O$_3$ catalysts for removing toluene in indoor air. Mater Lett. 2017;208:43–45.
[17] Jeong M, Nunotani N, Imanaka N. Relationship between the conductivities of Ce$_2$O$_3$-ZrO$_2$:MO$_x$ (M = Bi, Ca, Sn, Ni, Fe) solid solutions and catalytic activities during methane oxidation. Bull Chem Soc Jpn. 2018;91 (2):158–164.
[18] Nunotani N, Moriyyama N, Matsuo K, et al. Catalytic methane combustion over novel catalyst based on oxide-ion-conducting lanthanum silicate. J Ceram Soc Jpn. 2017;125(10):773–775.
[19] Nakayama S, Kageyama T, Aono H, et al. Ionic conductivity of lanthanoid silicates, Ln$_{10}$(SiO$_4$)$_2$O$_3$(Ln = La, Nd, Sm, Gd, Dy, Y, Ho, Er and Yb). J Mater Chem. 1995;5 (11):1801–1805.
[20] Nakayama S, Sakamoto M. Electrical properties of new type high oxide ionic conductor $RE_{10}Si_6O_{27}$ ($RE = La, Pr, Nd, Sm, Gd, Dy$). J Eur Ceram Soc. 1998;18 (10):1413–1418.

[21] Tao S, Irvine JTS. Preparation and characterisation of apatite-type lanthanum silicates by a sol-gel process. Mater Res Bull. 2001;36(7–8):1245–1258.

[22] Matsuo K, Nunotani N, Imanaka N. Catalytic toluene combustion over Pt loaded on lanthanum silicate with apatite-type structure. Funct Mater Lett. 2019;12 (5):1950074.

[23] Ma Y, Moliere M, Yu Z, et al. Novel chemical reaction co-precipitation method for the synthesis of apatite-type lanthanum silicate as an electrolyte in SOFC. J Alloys Compd. 2017;723:418–424.

[24] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr Sect A. 1976;32 (5):751–767.

[25] Fu X, Liu Y, Deng J, et al. Intermetallic compound PtMn$_y$-derived Pt-MnO$_x$ supported on mesoporous CeO$_2$: highly efficient catalysts for the combustion of toluene. Appl Catal A Gen. 2020;595:117509.

[26] Wang Q, Li Y, Serrano-Lotina A, et al. Operando investigation of toluene oxidation over 1D Pt@CeO$_2$ Derived from Pt cluster-containing MOF. J Am Chem Soc. 2021;143(1):196–205.

[27] Hu J, Gao X, Fan Q, et al. Facial controlled synthesis of Pt/MnO$_2$ catalysts with high efficiency for VOCs combustion. RSC Adv. 2021;11(27):16547–16556.