Evaluation of Nanoporous Aluminum Silicate Including Active Oxygen Species

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The catalytic activities of propylene oxidation on different aluminum silicates with the mayenite structure \([\text{Ca}_{12}\text{Al}_{14-x}\text{Si}_x\text{O}_{33-x}\text{O}_x] \) \((x = 0, 0.4, 0.8, 1.0, 1.2, 1.4)\) formed at 500, 800 and 1000°C were investigated. The aluminum silicates were prepared by the hydrothermal and solid-state reactions of a stoichiometric mixture of calcium oxide, alumina sol and silica. The XRD results of the aluminum silicates obtained by the solid-state reaction showed that the peak intensities of the mayenite phases became larger as the calcination temperature increased. The aluminum silicates included two kinds of active oxygen species \((\text{O}_2^+, \text{O}_2^{-})\) related to Raman shifts of around 887 and 1092 cm\(^{-1}\), respectively. As a result, the aluminum silicates exhibited oxidation activities based on the easily reducible active oxygen species. Notably, the \(\text{Ca}_{12}\text{Al}_{10}\text{Si}_6\text{O}_{35}\) calcined at 1000°C without the hydrothermal treatment showed the highest activity of all catalysts, indicating that the crystal structures play an important role in determining the catalytic activity.

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1. Introduction

In recent years, a great concern about environmental problems, water pollution, acid precipitation and so on, has risen worldwide, and legislation has imposed increasingly stringent limits. The release of hydrocarbons, especially volatile organic compounds (VOCs), has also been receiving much attention due to the potentially carcinogenic nature of VOCs. Thermal combustion is one way to reduce VOCs in the atmosphere, although it requires temperatures greater than 800°C. The use of an oxidation catalyst can significantly lower the operating temperature. Indeed, the oxide of metals such as cobalt, copper, or manganese is active for the combustion of hydrocarbons in the temperature range 200–600°C.\(^{1,2}\)

Active oxygen species such as \(\text{O}^+, \text{O}_2^-\) and \(\text{O}_2^{2-}\) are key chemical species in the catalytic oxidation of hydrocarbons or biochemical reactions. In particular, \(\text{O}_2^-\) and \(\text{O}_2^{2-}\) attract much attention because of their extremely high oxidation activity.\(^{3,4}\) Fujita et al. pointed out that aluminum silicate \((\text{Ca}_{12}\text{Al}_{14-x}\text{Si}_x\text{O}_{33-x}\text{O}_x)\), a component of cement clinkers, has been well-known as a material containing \(\text{O}_2^-\), \(\text{O}_2^{2-}\), and \(\text{O}^+\) in the zeolitic lattice. The nanoporous crystal structure of \(\text{Ca}_{12}\text{Al}_{14-x}\text{Si}_x\text{O}_{33-x}\text{O}_x\), containing several oxygen molecules per unit cell, is characterized by a positively charged lattice framework having 6 crystallographic cages per unit cell with a free space of \(\sim 0.4\) nm in diameter.\(^{5-8}\)

Several examples of the catalytic oxidation of hydrocarbons using \(\text{Ca}_{12}\text{Al}_{14-x}\text{Si}_x\text{O}_{33-x}\text{O}_x\) have been demonstrated, such as \(\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}\) \((x = 0)\) and \(\text{Ca}_{12}\text{Al}_{14}\text{Si}_{10}\text{O}_{35}\) \((x = 4)\). In particular, \(\text{Ca}_{12}\text{Al}_{14}\text{Si}_{10}\text{O}_{35}\) successfully exhibited a high level of activity for the oxidation of hydrocarbons such as benzene, toluene and propylene to carbon oxides due to the \(\text{O}_2^-\) and \(\text{O}_2^{2-}\) species present.\(^9\) However, preparing them by the conventional method which requires two steps, hydrothermal reaction and calcination, is very complex and is relatively expensive. In addition, undesirable by-products, \(\text{CaO}\), are formed, since the synthesis reaction of \(\text{Ca}_{12}\text{Al}_{10}\text{Si}_6\text{O}_{35}\) passes through an intermediate hydrogrossular \((\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{10})\) form.

In the present paper, we describe the evaluation of oxidation activities for propylene combustion over the aluminum silicate catalysts prepared simply by a solid-state reaction of the stoichiometric mixture of calcium oxide, alumina-sol and silica.

2. Experimental

\(\text{Ca}_{12}\text{Al}_{14-x}\text{Si}_x\text{O}_{33-x}\text{O}_x\) \((x = 0.4, 0.8, 0.5, 0.55, 1.0)\) was formed by heating a stoichiometric mixture of calcium oxide, alumina-sol and various extents of silica at 500, 800 and 1000°C for 5 h at atmospheric pressure. The conventional preparation method of \(\text{Ca}_{12}\text{Al}_{14-x}\text{Si}_x\text{O}_{33-x}\text{O}_x\) is described elsewhere. The X-ray powder diffraction data were obtained by the RINT-TTR diffractometer (Rigaku-Denki) using Ni-filtered CuK\(_\alpha\) radiation \((50\text{ kV}, 100\text{ mA})\). The specific surface area was measured by N\(_2\) adsorption–desorption equipment at 77 K (Monosorb, Quantachrome). The Raman spectroscopy experiment was carried out using the spectrometer (NRS-1000, Jasco) with a 532 nm line of a green laser for excitation at room temperature. The spectrum was recorded in the scanning range of 850–1150 cm\(^{-1}\). The evaluation of oxidation activity was carried out in a conventional flow-type microreactor of quartz glass in the temperature range of 300 to 900°C. Synthetic air \((80\% \text{He} \text{ and } 20\% \text{O}_2)\) was used. The concentration of propylene was adjusted to 1000 vol ppm. The total gas flow was 20 mL min\(^{-1}\) and the space velocity was 9500 h\(^{-1}\). The catalyst was sieved to a size of 300–500 \(\mu\text{m}\) and placed in the reactor between silica wool. The effluent gases were analyzed by an on-line gas chromatograph (SHIMADZU, GC-8A) with Porapak Q for the organic compounds.

3. Results and Discussion

3.1 X-ray diffraction of aluminum silicate

Figure 1(a) shows the XRD patterns of the \(\text{Ca}_{12}\text{Al}_{14}\text{Si}_{33}\) \((x = 0)\) calcined at several temperatures by solid-state reaction. Diffraction peaks corresponding to the mayenite

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phase and raw material phases were observed in the patterns of Ca$_{12}$Al$_{14}$O$_{33}$ ($x = 0$) catalyst synthesized at any temperatures. The peak intensities of the mayenite phase became larger with the increase in calcination temperature. These results reflect that the crystal of the mayenite is grown at higher temperatures. Similar results were obtained in that of Ca$_{12}$Al$_{10}$Si$_4$O$_{35}$ which had mayenite structure with the Si contents as shown in Fig. 1(b).

Figure 2 shows comparisons of the XRD results of the catalysts prepared by conventional methods and the method described in this paper. As shown in Figs. 2(a), (b), both Ca$_{12}$Al$_{14}$O$_{33}$ and Ca$_{12}$Al$_{10}$Si$_4$O$_{35}$ phases successfully synthesized in their crystal structures by solid-state reaction. In particular, the undesired quartz peaks were observed in the pattern of Ca$_{12}$Al$_{10}$Si$_4$O$_{35}$ catalysts as shown in Fig. 2(b). This result may be due to the insolubility of SiO$_2$ as a raw material in the hydrothermal reaction at a low temperature, 180°C.

3.2 Raman spectra of aluminum silicate

A very attractive feature of Ca$_{12}$Al$_{14}$O$_{33}$ and Ca$_{12}$Al$_{10}$Si$_4$O$_{35}$ is that the active oxygen species are occluded in their mayenite structures.$^{9,10}$ These radical species are associated with Raman shifts of O$_2^2$ and O$_2^-$ observed around 850 and 1070 cm$^{-1}$, respectively. In the present study, the Raman spectra of Ca$_{12}$Al$_{14}$O$_{33}$ and Ca$_{12}$Al$_{10}$Si$_4$O$_{35}$ showed that the absorption bands assigned to peroxide (O$_2^-$) and superoxide (O$_2^-$) were observed at 887 and 1092 cm$^{-1}$, respectively (Fig. 3). It was also confirmed that the Raman absorption of Ca$_{12}$Al$_{14}$O$_{33}$ due to the O$_2^-$ were larger than that of O$_2^-$, while the Raman absorption of Ca$_{12}$Al$_{10}$Si$_4$O$_{35}$ due to the O$_2^-$ was almost the same as that of O$_2^2$. It was reported that the nanopores structured in
mayenite crystals are charged in positive\(^5\) and they could include several oxide radical anions such as O\(_2^-\), O\(_3^{2-}\), OH\(^-\) and O\(_{2\cdot}\).\(^{5,11-13}\) Detected O\(_2^-\) and O\(_{2\cdot}\) radicals are likely to be formed by absorbing oxygen molecules in atmosphere, and then oxidized by electron (e\(^-\)) stabilized in the cavities as follows:

\[
O_2(\text{gas}) \rightleftharpoons O_2(\text{ads}) \rightleftharpoons O_2^- (\text{cavity}) \rightleftharpoons O_{2\cdot}^-(\text{cavity}).
\]

3.3 Catalytic activities towards propylene oxidation

3.3.1 Catalytic activities of various aluminum silicates

Figure 4 displays the oxidation curves for propylene as a function of the reaction temperature over Ca\(_{12}\)Al\(_{14-x}\)Si\(_x\)O\(_{35}\) catalysts. Concerning the Ca\(_{12}\)Al\(_{10}\)Si\(_4\)O\(_{35}\) catalysts, the oxidation began at 400, 300 and 300\(^\circ\)C and is completed at 700, 600 and 600\(^\circ\)C for the catalysts calcined at 500, 800, 1000\(^\circ\)C, respectively, as shown in Fig. 4(a). This result indicates that the catalytic activity of Ca\(_{12}\)Al\(_{10}\)Si\(_4\)O\(_{35}\) becomes higher with an increase in calcination temperature. As described above, the mayenite crystals grow at higher temperature, providing higher activities of catalysts calcined at higher temperatures. Figure 4(b) showed that the Ca\(_{12}\)Al\(_{10}\)Si\(_4\)O\(_{35}\) catalyst exhibited higher oxidation activities than Ca\(_{12}\)Al\(_{14}\)O\(_{35}\) catalyst. These results may be explained by the difference of the kind of active oxygen species that predominantly exist in the crystal structure.

Next, we discuss the effect of preparation methods of the Ca\(_{12}\)Al\(_{10}\)Si\(_4\)O\(_{35}\) catalyst on its activity. In general, the crystal structure forms faster at higher temperatures. Therefore, it can be seen that the calcination temperature plays an important role in determining the activities of the catalysts. Indeed, the Ca\(_{12}\)Al\(_{10}\)Si\(_4\)O\(_{35}\) catalyst obtained by solid-state reaction showed higher activities than those obtained by hydrothermal reaction [see Fig. 4(b)]. This can be explained by the difference of formation temperature of the mayenite structure. Indeed, the formation of the hydrogrossular as the precursor structure of mayenite was remarkably low (<200\(^\circ\)C). As a result, the XRD intensity corresponding to the mayenite structure formed by hydrothermal reaction was slightly lower than that formed by solid-state reaction. Therefore, the oxidation over the Ca\(_{12}\)Al\(_{10}\)Si\(_4\)O\(_{35}\) catalyst obtained by solid-state reaction occurred at a slightly lower temperature than that synthesized by hydrothermal reaction, although the calcination temperature was the same.

3.3.2 Influence of atmospheric oxygen content on catalytic activity over aluminum silicate

Fujita et al. reported that the catalytic performances of the hydrocarbon oxidation over the aluminum silicate were strongly influenced by the oxygen concentration in the atmosphere, and the catalytic oxidation proceeded by the active oxygen species in the crystal structure.\(^5\) They also indicated that the oxygen radicals directly migrated from the atmosphere even if the oxygen radicals were consumed by the hydrocarbon oxidation. To study the details of behavior, we investigated the effects of oxygen concentration on the catalytic performance at 500 and 600\(^\circ\)C. The conversions of propylene were plotted as a function of time in Fig. 5. The oxygen concentration in the reaction gas was controlled at 0 vol% from 0 to 30 min where the oxygen flow was cut off and replaced to carrier flow, and then changed to 20 vol% after 30 min. The temperature was adjusted to 500 and 600\(^\circ\)C in order to investigate the temperature dependence of the conversion responses as a result of the above procedure. The
conversion decreased without oxygen supply, and then increased with oxygen supply due to the effects of the oxygen concentration on the catalytic performances as described above. The decrement of the conversion at 500°C was larger than that at 600°C, while the increment of the conversion at 500°C was smaller than that at 600°C. These results reflected that the oxygen supplied into the crystal structure was slower at lower temperature.

3.3.3 Catalytic activity under repetitious changes of oxygen concentration

The influence of the repetitious changes of oxygen concentration on catalytic activity was examined by the following method as shown in Fig. 6. The investigation was carried out using two kinds of feed gases, one containing 1000 vol ppm propylene without oxygen; (I) and the other containing 20 vol% oxygen without propylene; (II). Six cycles with feeding (I) and (II) were repeated at 500 and 600°C. The time-conversion curves showed that the conversions consistently decreased during exposure to (I) without oxygen, and increased after exposure to (II) with oxygen. The conversion value at 600°C consistently decreased to 60% and increased to 90%, however the value at 500°C was changed irregularly at every cycle and the conversion tended to decrease through the 6 cycles. These results indicate that the migration of the oxygen is fast at 600°C and slower at 500°C, providing that the catalytic activity at 600°C was not more influenced by the repetitious operation in 6 cycles.

4. Summary

Aluminum silicate catalysts are very interesting and attractive in view of the oxidation mechanism. In the present work, we prepared five kinds of aluminum silicate catalysts through solid-state and hydrothermal reactions. We investigated the basic oxidation performances of the aluminum-silicate catalysts obtained by different methods. In addition, the influence of oxygen content in the atmosphere was reported to examine the behavior of oxidation performances.

The following findings were obtained:

(1) The Ca_{12}Al_{14}O_{33} and Ca_{12}Al_{10}Si_{4}O_{35} catalysts with mayenite phase were successfully synthesized by solid-state reaction. The XRD results of the direct-synthesized Ca_{12}Al_{14}O_{33} and Ca_{12}Al_{10}Si_{4}O_{35} catalysts showed that the mayenite phases related to the catalytic activity grew by solid-state reactions with the increase of calcination temperature.

(2) The aluminum silicate obtained by solid-state reaction occluded two active oxygen species, O^{2-} and O_{2}. It was also found that the O^{2-} radical on the Ca_{12}Al_{14}O_{33} catalyst was detected to have a larger Raman absorption than that of the O^{2-} radical, while the absorption of O_{2} on the Ca_{12}Al_{10}Si_{4}O_{35} catalyst was almost the same as that of O^{2-}.

(3) The oxidation activity of the aluminum silicate catalysts obtained by solid-state reaction rose with the increase of the calcination temperature. The Ca_{12}Al_{10}Si_{4}O_{35} catalyst synthesized at 1000°C had the highest oxidation activity of all catalysts. The oxygen contents affected the catalytic activities more strongly at lower temperatures. Additionally, repetitious testing indicated that the catalytic activity at 600°C consistently recovered in every cycle, while the activity at 500°C varied irregularly and degraded after a few cycles because of the lower transportation rate at lower temperatures.

REFERENCES