Catalysis Letters Vol. 106, Nos. 3–4, February 2006 (© 2006)
DOI: 10.1007/s10562-005-9621-5

Oxidative destruction of hydrocarbons on $Ca_{12}Al_{14-x}Si_xO_{33+0.5x}$ $(0 \leq x \leq 4)$ with radical oxygen occluded in nanopores

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Received 27 June 2005; accepted 7 November 2005

Three types of calcium aluminosilicate, $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$), $Ca_{12}Al_{14}Si_2O_{34}$ ($C_{12}A_6$), and $Ca_{12}Al_{10}Si_4O_{35}$ ($C_{12}A_5$), were prepared by calcining the respective hydrothermally synthesized hydrogarnet, $Ca_3Al_2(OH)_{12}$, $Ca_3Al_2(SiO_4)_{1/3}(OH)_{32/3}$, and $Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$. Different amounts of superoxide (O_2^-) and peroxide (O_2^{2-}) were occluded in the lattice of these calcium aluminosilicates. No activity improvement was observed for the oxidation of propylene and benzene by increasing the amounts of O_2^- and O_2^{2-}.

KEY WORDS: calcium aluminosilicate; hydrocarbons; oxidation; superoxide; peroxide.

1. Introduction

Environmental legislation has imposed increasingly stringent limits for permitted atmospheric emission levels. In particular, the release of hydrocarbons has received much attention. Catalytic combustion is considered to be an effective method for reducing the emission of hydrocarbons. The hydrocarbons are recognized as still increasing contributors to air pollution. The methodology of decreasing polluted chemicals has been established in the last several decades. Catalytic combustion is more flexible than other ways for hydrocarbon removal such as adsorption, condensation, and so on. The use of a catalyst in the oxidative destruction of hydrocarbons can significantly lower the process operating temperature to 300–600 °C [1,2]. This reduction in the temperature is advantageous, because a little or no supplementary fuel is required to sustain a stable combustion. In addition, hydrocarbons with their very low concentration can be combusted with the aid of a catalyst, while such a concentration is too low for thermal combustion.

A prospective catalyst must be active at relatively low temperatures and show high selectivity to carbon oxides. The most widely adopted catalysts are noble metals such as Pt or Pd which are generally supported on alumina or zeolite [3–11]. Those catalysts show high activity for the oxidation of hydrocarbons with high selectivity to carbon oxide products. However, those catalysts are relatively expensive and limited from the point of view of natural resources. Therefore, an attractive catalyst involves non-noble metal materials having the ability of the complete destruction of hydrocarbons. The development of non-noble metal oxide catalysts active for the combustion of a variety of hydrocarbons is a major challenge for future research.

A new phase of $Ca_{12}Al_{10}Si_4O_{35}$ ($C_{12}A_5$) forms a zeolite-like structure with the framework of the (Al, Si)O_4 tetrahedra and accommodates the superoxide anion (O_2^-) and peroxide species (O_2^{2-}) in the nanopores [12,13]. Due to the O_2^- and O_2^{2-} species present, $C_{12}A_5$ exhibited a high activity for the oxidation of hydrocarbons to carbon oxides at >400 °C. It is known that oxide anions such as O_2^{2-}, O_2^- and O^- are generated on the surface of a solid catalyst and play an important role in heterogeneous oxidation reaction [14,15]. The authors reported that the amount of oxygen radicals could be controlled by changing the Al/Si ratio in $Ca_{12}Al_{14-x}Si_xO_{33+0.5x}$ ($x = 0$, 2 and 4 for $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$), $Ca_{12}Al_{12}Si_2O_{34}$ ($C_{12}A_6$) and $Ca_{12}Al_{10}Si_4O_{35}$($C_{12}A_5$), respectively) [16,17]. Therefore, the aim of this study is to reveal the effect of amount of oxygen radicals on the activity for the oxidation of hydrocarbons.

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2. Experimental Section

2.1. Preparation of $Ca_{12}Al_{14\text{-}x}Si_xO_{33+0.5x}$ $(0 \leq x \leq 4)$

$C_{12}A_7$, $C_{12}A_6$ and $C_{12}A_5$ were prepared by heating the respective precursor hydrogarnets $[Ca_3Al_2(SiO_4)_{3\text{-}y}(OH)_{4y}$, $y = 3$, 8/3, and 2.2] at 700 °C. The hydrogarnet was synthesized via hydrothermal reaction of a stoichiometric mixture of alumina-sol, amorphous silica and calcium oxide at 200 °C for 15 h. For $x =$ 0, 2, and 4, $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$ were denoted hereafter.

2.2. Characterization

X-ray powder diffraction data were obtained with an M18XHF diffractometer (MAC Science, Ltd.) using Ni-filtered Cu$K\alpha$ radiation (40 kV, 100 mA). The BET surface area was measured by a N_2 adsorption–desorption equipment at 77 K (Bell Japan, BELSOPRP 28SP). The Raman spectroscopy experiment was carried out using a spectrometer (SPEX, 1877) with the 514.5 nm line of an Ar^+ laser for excitation, and about 100 mW of power was focused on the sample. The spectrum was recorded with a liquid nitrogen-cooled change-coupled device (CCD) detector (Prinston Instruments, LN/CCD-1100PB) over a scanning range of 790–1150 cm^{-1}. The TG experiment was performed by using TGA-50 (SHIMADZU) under flowing gas mixture of O_2 (20 vol%) and N_2 (80 vol%) or of H_2 (2 vol%) and N_2 (98 vol%).

2.3. Oxidation of hydrocarbons

The oxidation of hydrocarbons was performed using a conventional flow-type quartz glass microreactor in the range from room temperature to 800 °C. The concentration of reaction gases was controlled using synthetic air (80% N_2 and 20% O_2), so that the concentration of hydrocarbons was 1000 ppm by volume. A stream of 1000 ppm of benzene was obtained by passing air through a temperature-controlled saturator. The flow rate was 100 mL/min and the space velocity corresponded to 10,000 h^{-1}. Catalysts were sieved to a size of 300–500 μm and placed in the reactor between silica wool. The effluent gases were analyzed by an on-line gas chromatograph (SHIMADZU, Gas Chromatograph GC-8A) with Porapak P for the organic compounds and active carbon for CO_2 and CO as a separation column.

3. Results and Discussion

Figure 1 shows the crystal structure of $C_{12}A_5$, which is cubic, space group *I43d*. Two tetrahedra of AlO_4 and SiO_4, T(1) and T(2), are linked to each other by bridging O(2) atom to form the framework structure. The species of O(3)–O(3) was assigned to molecular oxygen anions (O_2^- and O_2^{2-}). The crystal structures of $C_{12}A_7$ and $C_{12}A_6$ were also similar to that of $C_{12}A_5$ structure. It was found that the amount of these oxygen species varied among $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$: with this sequence, the amount of O_2^- decreased, while that of O_2^{2-} increased [16]. The BET surface areas of these catalysis were 4~6.5 m^2/g. Figure 2(a), (b) and (c) show Raman spectra taken for $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$, respectively, after reaction with hydrogen or oxygen gas at 600 °C. The Raman band at 1090 cm^{-1} assignable to the O_2^- species was observed for $C_{12}A_7$ and an additional band assignable to the O_2^{2-} species appeared at 880 cm^{-1} for $C_{12}A_6$ and $C_{12}A_5$. All the $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$ decreased the intensity of two Raman bands (1090 and 880 cm^{-1}) after reaction with hydrogen, while the intensity of these two bands was restored after reaction with oxygen. Between these two species, O_2^- was more preferentially consumed under a reductive atmosphere and reproduced again in the oxidative atmosphere. The disappearing and reproducing behavior of molecular oxygen anions was also confirmed from TG measurements (see Figure 3). Reaction with hydrogen decreased the weights of $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$ and reaction of oxygen anion-lacking $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$ with oxygen restored their weights. The observed decrease in the weight and its restoration should result respectively from the consumptions of O_2^- and O_2^{2-} and their reproduction. For $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$, the amounts of O_2^- and O_2^{2-} consumed or restored were, respectively, 0.061, 0.043, and 0.027 wt% at 500 °C and 0.30, 0.19, and 0.072 wt% at 700 °C. Among $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$, the variation in these amounts was in accord with the difference in the intensity of the Raman bands. It should furthermore be noted that the amount of reactive O_2^- and O_2^{2-} increased, as the reaction temperature was elevated. So that the oxygen radicals are separated from the oxygen atoms in

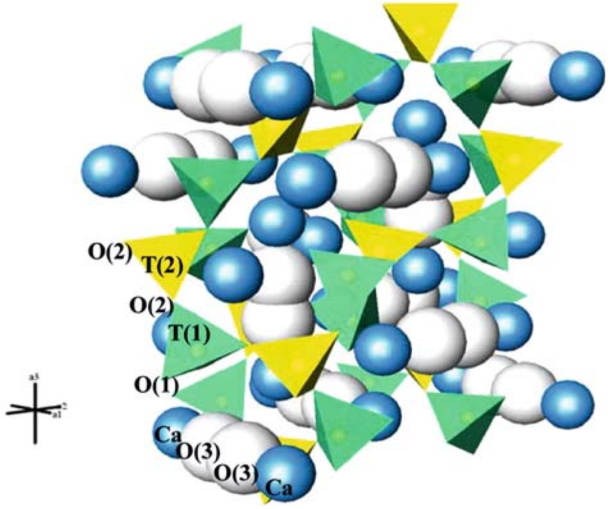

Figure 1. Crystal structure of $Ca_{12}Al_{10}Si_4O_{35}$, showing the links of tetrahedral. The large and small spheres represent O(3) and Ca ions, respectively.

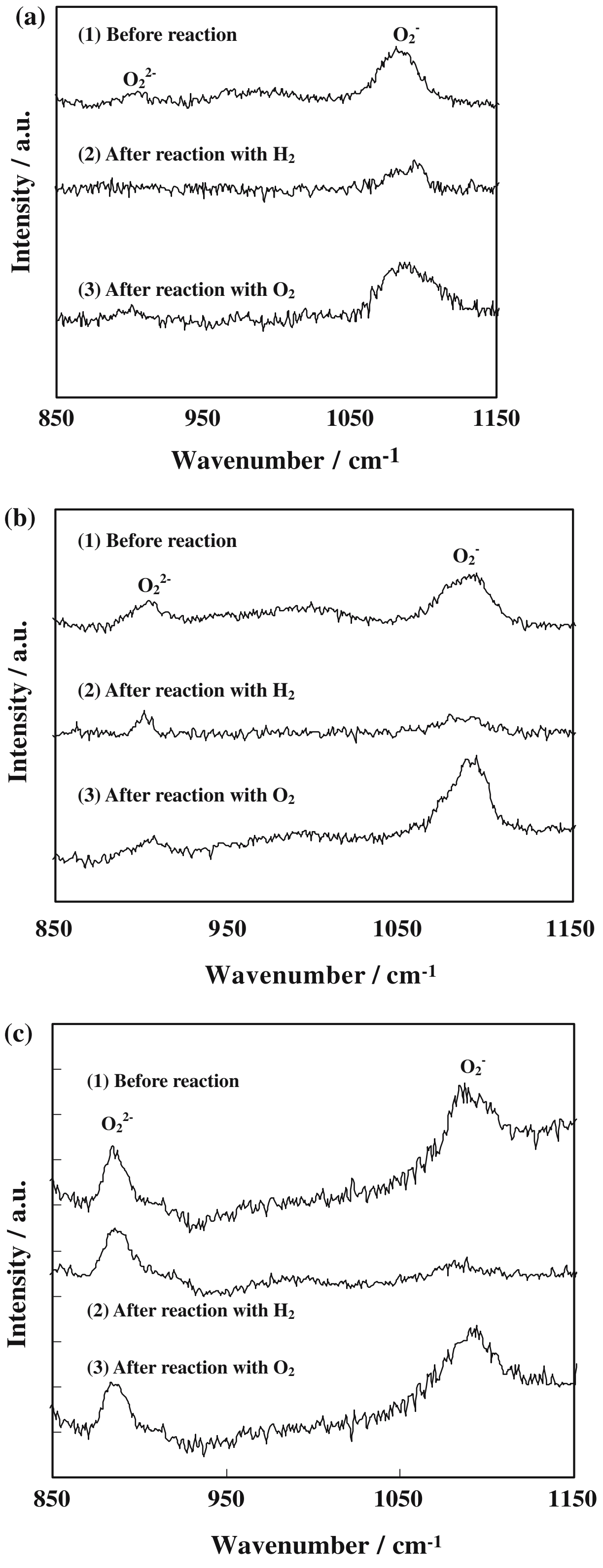

Figure 2. Raman spectra of $C_{12}A_7$ (a), $C_{12}A_6$ (b) and $C_{12}A_5$ (c) after reacting with hydrogen or oxygen gas at 600 °C.

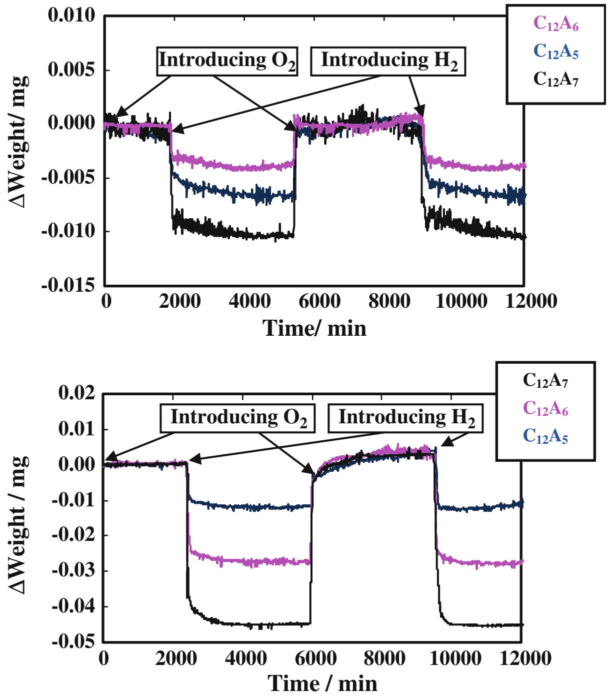

Figure 3. The adsorption and desorption of oxygen in the $C_{12}A_7$, $C_{12}A_6$ and $C_{12}A_5$ crystal under the oxidative and reductive conditions at 500 (a) and 700 °C (b).

the frameworks, $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$ are expressed respectively as $Ca_{12}(Al_{14}O_{32})O$, $Ca_{12}(Al_{12}Si_2O_{32})O_2$, and $Ca_{12}(Al_{10}Si_4O_{32})O_3$, which means that 32 oxygen atoms in the formula unit belong to the framework and the additional one to three oxygen atoms are occluded in the voids of the framework as O_2^- and O_2^{2-}. Following transformations from respective hydrogarnets to $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$ accompany the concomitant production of CaO with different amounts:

$$7Ca_3Al_2(OH)_{12} \rightarrow Ca_{12}Al_{14}O_{33} + 9CaO + 42H_2O \quad (1)$$

$$6Ca_3Al_2(SiO_4)_{1/3}(OH)_{32/3} \rightarrow Ca_{12}Al_{12}Si_2O_{34} + 6CaO + 32H_2O \quad (2)$$

$$5Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8} \rightarrow Ca_{12}Al_{10}Si_4O_{35} + 3CaO + 22H_2O \quad (3)$$

Since a considerable amount of CaO was contained in all samples used for TG measurements, the 'theoretical' amounts of O_2^- and O_2^{2-} were estimated respectively 0.41, 0.24, and 0.081 wt% for $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$ by excluding the amount of CaO from the sample. Taking these values into consideration, a considerable part of O_2^- and O_2^{2-} was incorporated in the reaction with hydrogen at 700 °C, while a limited part was in the reaction at 500 °C. Figure 4 illustrates the activity of $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$ for the oxidation of propylene (a) and benzene (b). Without the catalyst (only fragmented quartz glass packed), the complete oxidation of propylene needed the reaction temperature >725 °C. However, propylene oxidation began at around 400 °C

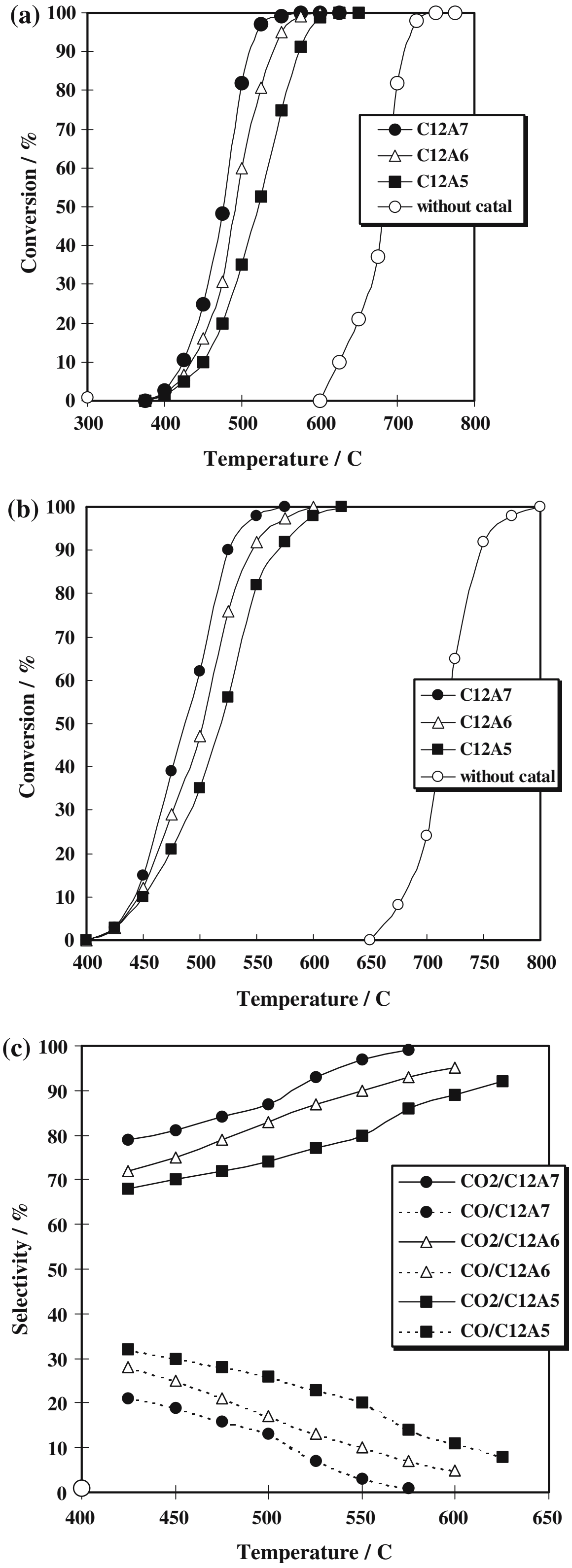

Figure 4. The conversion and carbon oxide selectivity for each hydrocarbons at various temperatures over catalysts. (a) propylene, (b) benzene, (c) carbon oxide selectivity by oxidation of benzene.

on $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$ and is completed at 575, 600, and 625 °C on $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$, respectively. Benzene oxidation also began at 400 °C on $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$ and was completed at 575, 600, and 625 °C on $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$, respectively. The selectivity for CO and CO_2 calculated from the following equations, S_{CO} and $S_{CO}2$, is displayed in Figure 4(c).

$$S_{CO} = CO/(CO + CO_2) \times 100(\%)$$
$$S_{CO2} = CO_2/(CO + CO_2) \times 100(\%)$$

Both CO and CO_2 were formed from the oxidation of benzene, whereas only CO_2 was from the oxidation of propylene. The values of CO selectivity decrease with increasing temperature, and also with changing composition from $C_{12}A_5$ to $C_{12}A_7$. It is reasonable that the temperature at which oxidation begins was the same among $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$, although the amount of O_2^- and O_2^{2-} was different among them. This is because the oxidation ability of O_2^- and O_2^{2-} should not be different among $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$. It is interesting to compare the present result with the authors' recent papers describing that the oxidation ability of O_2^- was highly improved by substituting a part of Ca^{2+} ions with some kinds of transition metal ions [18,19]. In other words, the variation in the amount of O_2^- and O_2^{2-} occluded in calcium aluminosilicate did not lead to the activity improvement for the oxidation of hydrocarbons, but the substitution of a part of Ca^{2+} with some kinds of transition metal ions did. However, the oxidation completion temperature was found to be different among $C_{12}A_7$, $C_{12}A_6$, and $C_{12}A_5$. For this finding, a following explanation is possible: a large amount of O_2^- and O_2^{2-} is favorable for exothermic oxidation, which leads to a temperature elevation in a limited area of a catalyst, resulting in lowering temperature for the completion of oxidation. It is difficult to differentiate the reactivity between O_2^- and O_2^{2-} for the oxidation of hydrocarbons. However, the O_2^- signal disappeared by reacting with hydrogen and appeared again by reacting with oxygen more preferentially than the O_2^{2-} signal. This preferential disappearing/appearing behavior suggests the higher reactivity of O_2^- species for the oxidation of hydrocarbons.

4. Conclusions

Calcium aluminosilicate, $C_{12}A_7$, $C_{12}A_6$ and $C_{12}A_5$, with different amounts of O_2^- and O_2^{2-} were active for the oxidation of propylene and benzene. However, the increase in the amount of O_2^- and O_2^{2-} did not lead to the activity improvement.

Acknowledgements

We are grateful to Mr. S. Komai of Nagoya University for measurement of Raman spectra.

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