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Communications

Controlling the Quantity of Radical Oxygen Occluded in a New Aluminum Silicate with Nanopores

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The radical oxygens such as O_2^-, O_2^{2-}, and O^-, which are generally formed on the surface of solid catalysts, play important roles in heterogeneous oxidation reactions.[1−4] Their formations and characterizations have been widely studied in the field of biological and organic chemistry from the viewpoint of biological activators.[5−9] In inorganic solid materials, $Ca_{12}Al_{14}O_{33}$ ($12CaO\cdot 7Al_2O_3$: $C_{12}A_7$), a component of cement clinkers, has been well-known as a material containing O^{2-}, O_2^-, and O^- in the zeolitic lattice.[10−12] Furthermore, it was found that $Ca_{12}Al_{10}Si_4O_{35}$ ($C_{12}A_5$), a new aluminum silicate phase, in which the Al^{3+} site of $C_{12}A_7$ is partly substituted with Si^{4+}, also occludes the O_2^{2-} and O_2^- radicals in the voids of the $(Al,Si)O_4$ framework.[13] However, the mechanism for the formation of radical oxygen occluded in the cavity of the framework remains unclear. This study indicates that the radical oxygen can be generated in the lattice of the new aluminum silicate with different Al/Si ratios. $Ca_{12}Al_{14-x}Si_xO_{33+0.5x}$ with different values of $x = 0$, 1, 2, 3, and 4 have been prepared by heating at 800 °C hydrogarnet [$Ca_3Al_2(SiO_4)_{3-y}(OH)_{4y}$, $y = 3$, 2.8, 2.6, 2.4, and 2.2], which has been synthesized hydrothermally (200 °C, 15 h) from a stoichiometric mixture of alumina-sol, amorphous silica, and calcium oxide (see eqs 1 and 2).

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

$$5Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8} \rightarrow Ca_{12}Al_{10}Si_4O_{35} + 3CaO + 22H_2O \quad (2)$$

The solid solution of $C_{12}A_7$−$C_{12}A_5$ and the CaO phase

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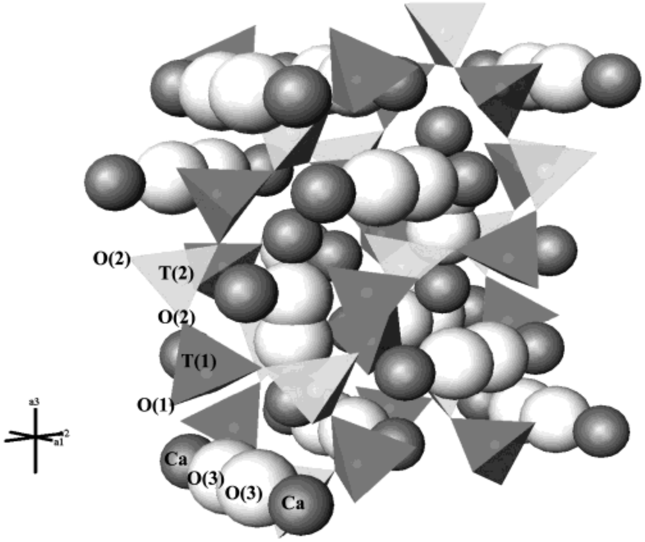

Figure 1. Crystal structure of $C_{12}A_5$, showing the links of tetrahedra. The large and small spheres represent O(3) and Ca ions, respectively.

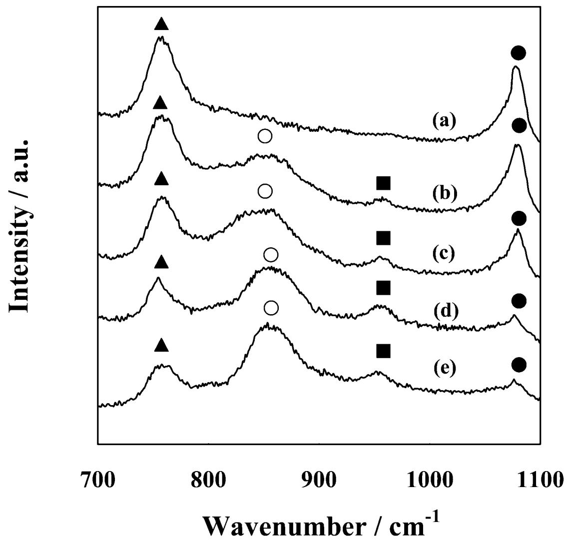

Figure 2. Raman spectra of $C_{12}A_7$ (a), $C_{12}A_{6.5}$ (b), $C_{12}A_6$ (c), $C_{12}A_{5.5}$ (d), and $C_{12}A_5$ (e). ●, superoxide (O_2^-); ○, peroxide (O_2^{2-}); ■, SiO_4 tetrahedron; ▲, AlO_4 tetrahedron.

are easily recognized in the X-ray powder diffraction patterns. (See Supporting Information (Rietveld refinement patterns)). Figure 1 shows the crystal structure of $C_{12}A_5$. The crystal structure of $Ca_{12}Al_{14-x}Si_xO_{33+0.5x}$ is cubic, space group $I\bar{4}3d$. Two tetrahedra of AlO_4 and SiO_4, T(1) and T(2), are linked to each other by a bridging O(2) atom to form the framework structure. The Ca ion forms a seven-coordinate polyhedron consisting of two O(1), four O(2), and one O(3) atoms. The O(3) atom, which is statistically located on the crystallographic 24d position in the cavity of the framework and is assignable to a diatomic molecule (O(3)−O(3)), is linearly bonded with two Ca atoms. The Si^{4+} ions might be preferentially located in the T(2) site, as shown in the case of other mayenite-related compounds.[14−16] To emphasize the occupation of the O(3) atom, the formula of $Ca_{12}Al_{14-x}Si_xO_{33+0.5x}$ is expressed as $[Ca_{12}Al_{14-x}Si_xO_{32}][O_{0.5x+1}]$ since 32 pfu for the number of oxygen atoms is the sum of the O(1) and O(2) atoms belonging to the aluminosilicate framework. The total number of cages is 6 in each formula unit and these positions are statistically shared by the oxygen radical species, O(3). The empirical formula estimated from the occupancy factor of the O(3) site is $[Ca_{12}Al_{14}O_{32}][O_{1.5}]$, $[Ca_{12}Al_{13}SiO_{32}][O_{2.0}]$, $[Ca_{12}Al_{12}Si_2O_{32}][O_{2.6}]$, $[Ca_{12}Al_{11}Si_3O_{32}][O_{2.8}]$, and $[Ca_{12}Al_{10}Si_4O_{32}][O_{3.9}]$ for $C_{12}A_7$, $C_{12}A_{6.5}$, $C_{12}A_6$, $C_{12}A_{5.5}$, and $C_{12}A_5$, respectively. Figure 2 shows the Raman spectra of $C_{12}A_7$−$C_{12}A_5$. The Raman band at 1075 cm^{-1}, which is assignable to the O_2^- species, was observed for $C_{12}A_7$, and furthermore, the additional band, which corresponds to the O_2^{2-} species, appeared at 853 cm^{-1} for $C_{12}A_{6.5}$, $C_{12}A_6$, $C_{12}A_{5.5}$, and $C_{12}A_5$. The bands at 950 and 755 cm^{-1} are assigned to the stretching vibrations of the SiO_4 and AlO_4 tetrahedra constituting the framework, respectively, because these agree with those of zeolite which have been extensively investigated as a function of the Si/Al ratio.[17,18] Furthermore, O_2^{2-} occluded in the void of framework would predominantly exist compared to O_2^- with the increasing Si content in the $Ca_{12}Al_{14}O_{33}$ crystal based on the intensity of the spectrum. Although a part of the incorporated active oxygen was desorbed by the reduction treatment with a hydrocarbon or hydrogen under inert conditions, the active oxygen species are regenerated by the oxygen gas flow.[13] The above assignment of the O−O stretching vibrations for O_2^- and O_2^{2-} also has been confirmed based on the following finding: Figure 3 demonstrates the isotope effect that the Raman bands for $[Ca_{12}Al_{10}Si_4O_{32}][O_{3.9}]$ crystal, at 853 and 1075 cm^{-1} corresponding to the O−O stretching vibrations of O_2^{2-} and O_2^-, respectively, shift to 819 and 1036 cm^{-1}, using $^{18}O_2$ gas instead of $^{16}O_2$. The above assignment is clear from the observed isotope shifts, although the degree of the isotope shifts of 34 and 39 cm^{-1} is slightly smaller than the theoretical value $\Delta\nu(O-O) =$ ca. 49 cm^{-1}. The diatomic molecule O(3)−O(3) in the $Ca_{12}Al_{14-x}Si_xO_{33+0.5x}$ may be explained by the following two possible interpretations: one is that one of the two sites is statistically shared[12] and another one is that these sites are occupied by O_2^- or O_2^{2-}. The three-dimensional structure of $Ca_{12}Al_{14-x}Si_xO_{33+0.5x}$ yields positively charged tetrahedral frameworks having molecular size pores occupied by charge-balancing dioxygen species such as O_2^- and O_2^{2-}. The positive charge variability is caused by the substitution of Al^{3+} for Si^{4+} as in zeolites.

Structure Determination and Refinement. The X-ray powder diffraction data of the solids were obtained using a M18XHF diffractometer (MAC Science, Ltd.) using Ni-filtered Cu Kα radiation (50 kV, 150 mA). The

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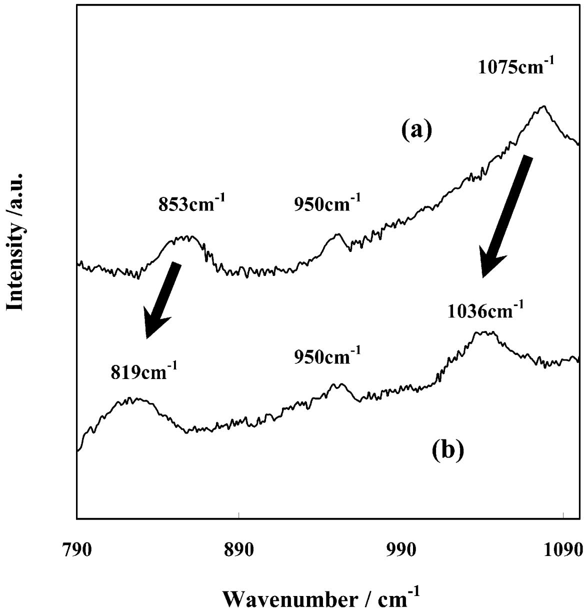

Figure 3. Raman spectra of superoxide (O_2^-) and peroxide (O_2^{2-}) regenerated by the flow of $^{16}O_2$ (a) and $^{18}O_2$ (b) after reduction of $C_{12}A_5$. 950 cm^{-1}: the stretching vibration of the SiO_4 tetrahedron.

sample was placed in a vacuum vessel immediately after cooling the sample from 800 °C to room temperature and then evacuated during the measurements. The diffraction patterns were measured over a diffraction angle range from 10 to 120° with a 2θ step increment of 0.01° and a counting time of 1.2 s for each step. The refinement of the crystal structure was carried out by the Rietveld method using RIETAN 94[19] dealing with the sample consisting of two phases ($Ca_{12}Al_{14-x}Si_xO_{33+0.5x}$ and CaO). The refinement of $Ca_{12}Al_{14-x}Si_xO_{33+0.5x}$ was initiated with the positional parameters of $Ca_{12}Al_{14}O_{33}$.[20] The equivalent isotropic atomic displacement parameters of T(1) and T(2) and of O(1), O(2), and O(3) were constrained to have the same values. The crystal structure (see Supporting Information (Tables 1 and 2)) of $Ca_{12}Al_{14-x}Si_xO_{33+0.5x}$ is cubic, space group $I\bar{4}3d$. The residuals of the refinement are $R_{wp}(\%) = 7.03$; $R_p = 5.44$; $R_e = 5.90$; $s = 1.19$; ($C_{12}A_7$: $R_I(\%) = 2.54$; $R_F = 1.57$, CaO: $R_I = 2.48$; $R_F = 1.13\%$) for $C_{12}A_7$ ($a = 11.9920(13)$Å), $R_{wp} = 14.31$; $R_p = 10.74$; $R_e = 5.84$; $s = 2.44$; ($C_{12}A_{6.5}$: $R_I = 6.89$; $R_F = 3.43$, CaO: $R_I = 6.11$; $R_F = 3.34$) for $C_{12}A_{6.5}$ ($a = 11.9888(8)$Å), $R_{wp} = 9.81$; $R_p = 7.53$; $R_e = 5.95$; $s = 1.65$; ($C_{12}A_6$: $R_I = 4.99$; $R_F = 2.45$, CaO: $R_I = 2.98$; $R_F = 1.50$) for $C_{12}A_6$ ($a = 11.9882(23)$ Å), $R_{wp} = 11.54$; $R_p = 8.74$; $R_e = 5.77$; $s = 2.00$; ($C_{12}A_{5.5}$: $R_I = 6.89$; $R_F = 3.59$, CaO: $R_I = 3.75$; $R_F = 1.67$) for $C_{12}Al_{5.5}$ ($a = 11.9855(16)$ Å) and $R_{wp} = 13.80$; $R_p = 10.74$; $R_e = 5.89$; $s = 2.34$; ($C_{12}A_5$: $R_I = 9.31$; $R_F = 5.93$, CaO: $R_I = 6.88$; $R_F = 4.09$) for $C_{12}A_5$ ($a = 11.9756(7)$Å), where R_{wp}, R_p, R_e, R_I, R_F, and s are weighted pattern, pattern, expected, integrated, structure factor R-factor, and goodness of fit indicator (R_{wp}/R_e), respectively.

Raman Spectra. The Raman spectra were measured using a spectrometer (SPEX, 1877) with the 514.5-nm excited line of an Ar^+ laser, and about 100 mW of power was focused on the sample. The spectra were recorded by a liquid nitrogen-cooled charge-coupled device (CCD) detector (Princeton Instruments, LN/CCD-1100PB) over a scanning range of 700−1200 cm^{-1}.

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Supporting Information Available: Figures showing Rietveld refinement patterns and tables giving the interatomic distances and atomic positions and occupancy factors for $C_{12}A_7$−$C_{12}A_5$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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