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Microporous Crystal 12CaO·7Al$_2$O$_3$ Encaging Abundant O$^-$ Radicals

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Received May 1, 2001

Active oxygen species such as O$^-$, O$_2^-$, and O$_3^-$ are key chemical species in the oxidation of hydrocarbons or biochemical reactions.[1−3] In particular, O$^-$ attracts much attention because of its extremely high oxidation power and high reactivity.[4−7] For instance, partial oxidation of CH$_4$ by O$^-$ occurs on MgO even at 130 K.[4] Much effort has been made to create this species thus far. Generally, the active oxygen species are created on the surface of solid oxides with the aid of energetic photons, for example, X-ray irradiation.[1,2] If the material containing a large amount of O$^-$ is obtained in the chemically and thermally stable form, it is anticipated that it exhibits unique chemical properties. In this report, we show that the active oxygens, a pair of O$^-$ and O$_2^-$, can be generated in a wide concentration range up to 6×10^{20} cm^{-3} in 12CaO·7Al$_2$O$_3$ (C12A7)[8−14] by utilizing the *inversed* zeolitic nature of this crystal, that is, anion-accommodation in the cavity of the crystal.

The crystal structure of C12A7, containing two molecules per unit cell, is characterized by a positively charged lattice framework [Ca$_{24}$Al$_{28}$O$_{64}$]$^{4+}$ having 12 crystallographic cages per unit cell ($I\bar{4}3d$ with $a = 1.199$ nm, $Z = 2$) with a free space of ∼0.4 nm in diameter (Figure 1a). The remaining two oxide ions (O^{2-}), referred to as “free oxygen”, are clathrated in the cages to maintain charge neutrality.[8] The high-resolution transmission electron microscopy image shown in Figure 1b visually demonstrates the occurrence of channels connecting the cages. A fundamental difference between C12A7 and conventional zeolites is the charge polarity of the lattice framework; cationic species are introduced to compensate for the negative charge caused by the substitution of Al^{3+} ion for Si^{4+} ion in the zeolites. With C12A7, hydroxide ions (OH$^-$) or halogen anions, X$^-$ (X$^-$ = F$^-$, Cl$^-$), are known to substitute for free oxygen to form the derivatives [Ca$_{24}$Al$_{28}$O$_{64}$]$^{4+}$·4(OH$^-$) or [Ca$_{24}$Al$_{28}$O$_{64}$]$^{4+}$·4(X$^-$).[9,10] The replacement of a free oxygen ion by two monovalent anions likely stabilizes the structure due to charge delocalization. Thus, we anticipate that a large quantity of active oxygen can be trapped in place of free oxygen. This can be accomplished as a result of electron transfer from O^{2-} to O$_2$ (O^{2-} + O$_2$ → O$^-$ + O$_2^-$) if oxygen molecules are introduced into the lattice framework. Since the reaction of H$_2$O with O^{2-} presumably leads to a decrease in free oxygen by forming OH$^-$ (O^{2-} + H$_2$O → 2OH$^-$), a reduction of the H$_2$O vapor pressure in the atmosphere will be crucial for the formation of a large quantity of active oxygen.

We prepared C12A7 powders or ceramics by the solid-state reaction of a mixture of CaCO$_3$ and γ-Al$_2$O$_3$ at 1350 °C for 6 h under controlled partial pressures of oxygen and water.

Paramagnetic susceptibility was obtained for all the samples despite the diamagnetic nature of the lattice framework. The magnetization curve at 5 K and Curie plot (temperature dependence of the susceptibility) from 5 to 300 K for the ceramics sintered in air revealed that it possessed 4×10^{18} cm^{-3} magnetically active ions having $S = {}^1/_2$ spin. As anticipated, the spin concentration dramatically increased with an increase in oxygen pressure (from 0.2 to 1 atm) and a decrease in water vapor pressure (from 4×10^{-2} to 6×10^{-5} atm) during sintering. Spin concentration reached an extraordinarily high value of 6×10^{20} cm^{-3} when annealed in a dry oxygen atmosphere, suggesting that a large number of monovalent active oxygen ions were created in the ceramics.

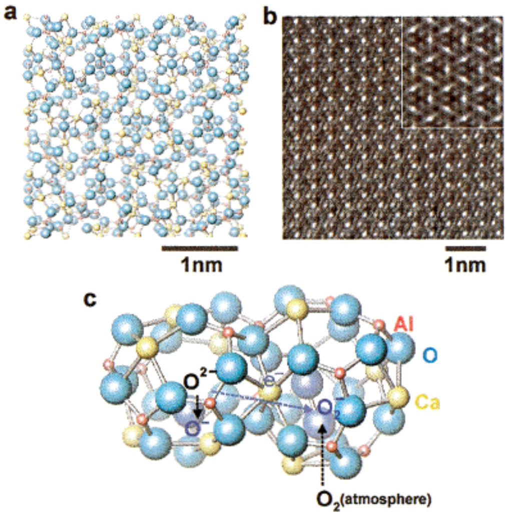

Figure 1. (a) Crystal structure of C12A7 viewed from ⟨111⟩ direction. (b) High-resolution TEM image of C12A7 taken along ⟨111⟩ direction, compared with a simulated image under the Scherzer focus condition (upper right inset). The windows of the connected cages zigzaging along the ⟨111⟩ direction were clearly demonstrated as white spots. (c) Expanded drawing of the two adjacent cages. Entrapped O$_2^-$ and O$^-$ radicals, coordinated with Ca^{2+} ions, are illustrated in the figure. Both radicals are formed as a result of electron transfer from free O^{2-} to ambient O$_2$ molecules.

To identify the active oxygen species, ESR measurements for the ceramics prepared under several atmospheric conditions were performed (Figure 2).[15] An ESR signal attributable to the O$_2^-$ radical[1−2,11,12] ($S = {}^1/_2$, 4×10^{18} spins cm^{-3}, $g_{xx} = 2.002$, $g_{yy} = 2.008$, $g_{zz} = 2.074$) was detected at 77 K in the C12A7 prepared in air. The signal intensity was increased and broadened dramatically with an increase in oxygen pressure and a decrease in water vapor pressure. Further, an additional signal characterized by a peak at $g = \sim 2.04$ appeared superposed on the O$_2^-$ signal. The g-values of the second signal extracted from the spectral simulation were $g_{xx} = g_{yy} = 2.036$ and $g_{zz} = 1.994$. These g-values agree well with those of the O$^-$ radical in the literature.[1,2] All the spectra obtained in different conditions can be reproduced by a simple superposition of O$_2^-$ and O$^-$ with each common set of g-values and different intensity ratio. Since both radicals have $S = {}^1/_2$, the total radical concentration estimated by ESR is consistent with the concentration by the magnetization measurement. The maximum concentration of O$^-$ radical was 2×10^{20} cm^{-3}, while that of O$_2^-$ was 4×10^{20}

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10.1021/ja016112n CCC: $22.00

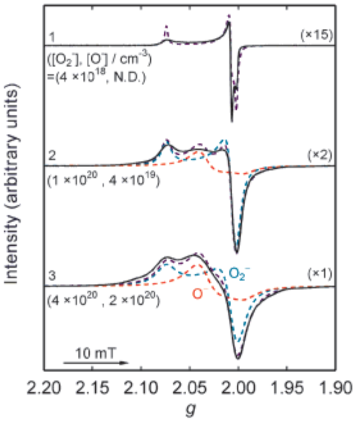

Figure 2. ESR spectra of C12A7 ceramics prepared in different conditions: (sample 1) cooled at 200 °C/h in air $\{p_{O_2} = 2 \times 10^{-1}$ (atm), $p_{H_2O} = 8 \times 10^{-3}\}$ after sintering, (sample 2) quenched followed by heating at 550 °C for 2 h in dry oxygen $\{p_{O_2} = 1, p_{H_2O} = 6 \times 10^{-5}\}$, and (sample 3) cooled at 200 °C/h in dry oxygen. The spectra are recorded at 77 K at an X-band with a field modulation amplitude of 0.1 mT. The observed spectra (black solid lines) were decomposed into simulated powder patterns of O^- (red dashed lines) and O_2^- (blue dashed lines). The purple dashed lines are, therefore, a summation of the two simulated spectra. Spin concentrations were evaluated from the decomposed ESR spectra using $CuSO_4{\cdot}5H_2O$ as a standard. N.D. means "not detected".

cm^{-3}. The positive charge concentration in the lattice framework gives a theoretical maximum of 2.3×10^{21} cm^{-3} monovalent anions. Further optimization of the atmospheric condition may realize the theoretical maximum.

The O^- and O_2^- radicals are likely adsorbed at the Ca^{2+} site on the cage surface at 77 K (Figure 1c), judging from the fact that our obtained *g*-values are close to those of the active oxygen radicals coordinated with divalent metal ions at oxide surfaces.[1,2] Missing hyperfine splitting, due to the ^{27}Al nucleus ($I = {}^5/_2$, abundance = 100%), further supports this conclusion. When the temperature is raised to ~300 K, the ESR signals become broadened and featureless, indicating that the radicals are tumbling in their cages or exchanging the charges with other nearby sites in the lattice.

Thermogravimetric measurements with heating−cooling cycle between room temperature and 1350 °C in the dry oxygen revealed that a weight loss of ~1% occurs when heated to ~700 °C, and the loss was restored when cooled below ~700 °C. The amount of weight loss agrees well with the desorption of oxygen species which are reformed from the encapsulated O_2^- and O^- radicals. If the sample initially contains the OH^- ion in the cage, the heating procedure to >1100 °C in dry atmosphere removes the OH^- ion and is indispensable for the formation of O_2^- and O^- radicals.

The oxygen-activated C12A7 also shows outstanding oxidative reactivity. We placed a Pt metal plate in contact with the surface of C12A7. When a C12A7 pellet in contact with a metal platinum plate was annealed at 1350 °C in dry oxygen, the contacted area became brown. It remained colorless when annealed in wet air (Figure 3a). No such color development was observed in other materials in the alkaline-earth aluminate system.[13,14] The XPS measurement (Figure 3b) in the contacted area shows the presence of Pt oxidized to the tetravalent state.[16] The Pt(IV) is formed by the deposition on the sample surface and subsequent oxidation by active oxygen, most likely O^-. Thermodynamically, neutral metallic Pt is much more stable than the oxidized state above 500 °C.

An extremely large amount of O^- and O_2^- can be formed and trapped stably in the cages of C12A7 up to ~700 °C by fully utilizing free O^{2-}-accommodating zeolitic feature of C12A7 crystal, that is, by tuning heat-treatment temperature and O_2 and H_2O pressures. The state of the radicals is similar to those adsorbed on the oxide surface.[1,2] Hence, for these species the inner cage provides an adsorption site protected from the ambient atmosphere. Thus, C12A7 should be of great value for spectroscopic investigations of entrapped oxygenic species. We expect that this type of active anion manipulation in C12A7 provides a unique opportunity for applications.

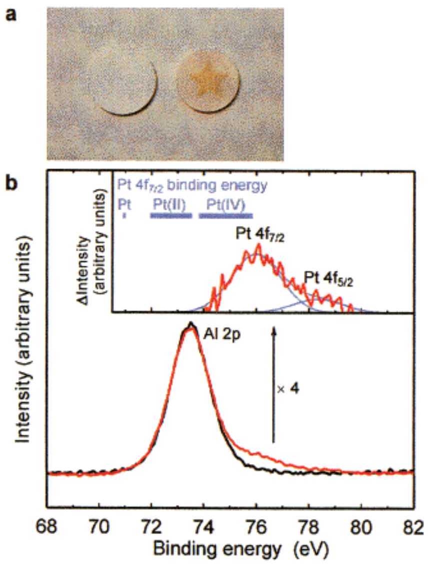

Figure 3. (a) Photographs of C12A7 ceramics sintered in wet air (left; $p_{O_2} = 2 \times 10^{-1}$ atm and $p_{H_2O} = 4 \times 10^{-2}$ atm, $[O_2^-] = 1 \times 10^{18}$ cm^{-3}) and in dry oxygen (right; $p_{O_2} = 1$ and $p_{H_2O} = 6 \times 10^{-5}$, $[O_2^-] = 4 \times 10^{20}$ and $[O^-] = 2 \times 10^{20}$). Star-shaped Pt plates were placed in contact with the top surface of the samples during sintering. (b) XPS spectra for the brown-colored area (red line) and for the uncolored area (black line). Main peak corresponds to tetrahedrally coordinated Al-2p band. No Pt was detected in the uncolored area. Inset is the difference between the two spectra. The resultant band was further decomposed into two parts, which are respectively attributed to the spin−orbit split $4f_{7/2}$ and $4f_{5/2}$ bands of Pt. A large chemical shift from Pt metal indicates the Pt was oxidized to Pt(IV).

Acknowledgment. We thank Dr. T. Yamamoto (School of Frontier Science, The University of Tokyo) for TEM observation.

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(15) The decomposition was optimized by *g*-value and peak-to-peak line width, ΔH, in Lorentzian line shape. The estimated ΔH were 0.3 mT for O_2^- in sample 1, 1.2 mT for O_2^- and 2.5 mT for O^- in sample 2 and 2 mT for O_2^- and 3 mT for O^- in sample 3. Despite the large dipolar broadening of line width of O_2^- and O^-, the relationships $g_{\|} < g_{\perp}$ for O_2^- and $g_{\perp} < g_{\|}$ for O^- substantiates the assignment of each radical.[1,2] Similar line shapes of coexistence of O_2^- and O^- were seen on CeO_2 surface. (Soria, J.; Martinez-Arias, A.; Conesa, J. C.; Munuera, G.; Gonzalez-Elipe, A. R. *Surf. Sci.* **1991**, *251/252*, 990−994.)
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JA016112N