Structure and Electronic Properties of \([\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\cdot4\text{e}^-\) Surfaces: Opportunities for Termination-Controlled Electron Transfer

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Supporting Information

ABSTRACT: We investigate the structure, thermodynamic stability, and electronic properties of (001), (110), and (111) surfaces of mayenite (12CaO·7Al2O3 or C12A7) in its oxygen-deficient phase known as mayenite-derived electride Ca12Al14O32 using simulations based on the density functional theory. Seven types of surface terminations were identified, depending on the orientation of the lattice nanosize cages with respect to the surface plane. We find that the surface termination has a strong effect on the distribution of electron anions in the near-surface region, as demonstrated by the range of the ionic charges and binding energies of adsorbed Au atoms and dimers. Notably, in all cases, Au species acquire a negative charge and preferentially adsorb as isolated ions rather than aggregate into clusters. These results show that C12A7 electride can provide a simple, yet versatile substrate to achieve high adsorption capacity and steric selectivity for single atom catalysts.

INTRODUCTION

Materials exhibiting low-work functions (W) are of interest for their potential applications in energy conversion technologies utilizing thermionic effect, cold electron emitters, and low-temperature catalysis.1−4 However, realization and utilization of these materials is challenging since the low-work function often implies high but uncontrollable chemical reactivity as it is the case with alkali and alkaline-earth metals (\(W_{\text{Li}} = 2.9\) eV, \(W_{\text{Na}} = 2.8\) eV, \(W_{\text{K}} = 2.3\) eV, \(W_{\text{Ca}} = 2.9\) eV).5

A new low work function material was obtained by reducing mayenite (12CaO·7Al2O3 or C12A7) to its stable oxygen-deficient form,6 which is known as electride, i.e., a material in which electrons serve as anions.7 The cubic cell of mayenite consists of two C12A7 molecules and can be represented by the formula \([\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\cdot(\text{O}^{2-})_2\), where \([\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\) is a framework of 12 lattice cages of radius about 0.25 nm (see Figure 1 and Computational Details for structure and composition of the lattice cages). The framework charge is compensated by two extra-framework oxygen ions per cubic cell. These extra-framework \(\text{O}^{2-}\) ions can be replaced with electrons, resulting in the formation of the \([\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\cdot(\text{e}^-)_4\) electride (C12A7·4e−). A series of theoretical and computational studies on the electronic properties of this material reached a consensus that extra-framework electrons localize in the lattice cages.8−12

Although the stoichiometric C12A7 is a wide band-gap insulator, C12A7·e− is a metal13 with the work function of ~2.4 eV,14 which is similar to that of the Na metal. In contrast to Na, C12A7·e− does not react violently with air at ambient conditions. At the same time, C12A7·e− exhibits an unusual chemical activity. For example, it promotes splitting of the CO2 molecules at room temperature15 and enables synthesis of ammonia at a significantly lower pressure than that required in the standard Haber–Bosch process.16,17

This combination of thermodynamical stability and high reactivity is attributed to primarily two factors. First, the lattice cages and electronic anions associated with them form a partially occupied band that has a high Fermi energy, i.e., low-work function, which facilitates electronic transfer to species
adsorbed on C12A7:e− surface. Second, in-diffusion of adsorbed species is suppressed, which prevents runaway decomposition reactions.

Recent experimental and computational reports\textsuperscript{15–18} suggest that C12A7:e− surfaces participate in chemical reactions in at least four ways typical in heterogeneous catalysis: (i) they are a meeting place for the reactants, (ii) the surfaces have special sites at which the reactions occur, (iii) the surfaces, adsorbed species, and catalytically active metal particles engage in electron exchange, and (iv) C12A7:e− surfaces accept and release chemical species, such as O2− and H+. However, relatively little is known about the atomistic structure of C12A7 surfaces. A scanning tunneling microscopy (STM) study\textsuperscript{19} of (001), (110), and (111) surfaces points to the existence of structurally ordered regions separated by larger amorphous or less conductive regions. Qualitatively, the spatial distribution of characteristic features in STM images is consistent with the model of near-surface region being composed of cages as building blocks. However, the atomistic structure of these surfaces was never resolved. On the modeling side, a partially amorphous C12A7:O2\textsuperscript{−} (001) surface was constructed by simulating the lattice cleavage using ab initio molecular dynamics.\textsuperscript{20} The resulting structure was found to contain distorted bulklike cages near the surface. Subsequent studies attributed an unusual chemical reactivity of C12A7:e− to the ability of these near-surface cages to capture and donate electrons in the process of chemical reactions.\textsuperscript{15–18}

Remains not understood is the link between catalytic activity exhibited by metal-loaded C12A7:e− surfaces\textsuperscript{16} and the local atomic structure and electronic properties of the surface sites: which structural motifs are responsible for a dramatic enhancement of metal catalyst supported on C12A7:e−? Here, we investigate thermodynamic stability and electronic properties of C12A7:e− surfaces. We explore a plethora of the surface structures and categorize them into seven types, determined by the surface orientation and by the relative positions of the lattice cages (see Figure 1) with respect to the surface plane. To quantify the local concentration of electron anions, we considered the interaction of these surfaces with Au atoms and dimers. Our results suggest that C12A7:e− surfaces can provide a versatile platform to achieve high adsorption capacity and enhanced catalytic activity for single atom catalysts.

\section*{COMPUTATIONAL DETAILS}

Shown in Figure 1 is a cubic conventional unit cell of the bulk C12A7:e−; it has the calculated lattice parameter of 12.117 Å and contains 12 lattice cages of about 6.5 Å in size. Each cage has an S\textsubscript{4} symmetry axis oriented along [100] or [010] or [001] lattice vectors. For brevity, we refer to these cages as X, Y, and Z, respectively. C12A7:e− surfaces (001), (110), and (111) were modeled using the periodic slab approach. The slabs were assembled from an integer number of full lattice cages in the same stacking sequence as they appear in the bulk lattice along the [001], [110], and [111] crystallographic axes. Slab supercell models of these surfaces consist of several cage layers and a 15 Å wide vacuum gap. In-plane lattice vectors of the slabs were a = a\textsubscript{x} X, b = a\textsubscript{y} Y for (001) slabs; a = a\textsubscript{x} X, b = a\textsubscript{y} (X − Y) for (110) slabs; and a = a\textsubscript{y} (Y − Z), b = a\textsubscript{x} (Z − X) for (111) slabs, where a\textsubscript{x} is the lattice constant obtained for the fully relaxed bulk C12A7:e−, and X, Y, and Z are unit vectors that correspond to the bulk crystallographic cell vectors. Dependence of surface energy on slab thickness was studied to ensure a convergence within 10−2 J/m\textsuperscript{2}, which corresponds to a slab thickness of 19.5−24.6 Å, depending on the surface orientation. Dipole correction to the total energy and local potential is applied to correct the errors induced by the interaction between the periodic slab images.

Calculations were performed within the framework of density functional theory and the projector augmented-wave formalism for electron-ion potential,\textsuperscript{21} as implemented in the Vienna ab initio simulation package.\textsuperscript{22,23} Exchange–correlation interaction was treated within the Perdew–Burke–Ernzerhof (PBE) functional form of the generalized gradient approximation (GGA).\textsuperscript{24} The plane-wave basis with a 500 eV cutoff was used. The 3×3×1 Monkhorst–Pack k-point mesh with its origin at the Γ point was used for the calculations of the total energy and forces and the 5×5×1 k-point mesh for calculating the density of states (DOS). The energies of self-consistent calculations were converged to 10−4 eV/cell, and the lattice and atomic positions were relaxed until the forces on the ions were less than 10−2 eV/Å.

\section*{RESULTS AND DISCUSSION}

Structural Models. Figure 2 shows the ordering of cage layers along the normal to the (001)-oriented slab. Each layer has only one type of the lattice cages: X, Y, or Z. The repeat unit of the layer sequence is Y−Z−X−Z, and the interlayer distance is 1.515 Å. Each Z layer contains only one cage per lateral cell, whereas X and Y layers contain two cages that have the same orientation of the S\textsubscript{4} axes but different chirality. In the case of the (001)-oriented slab, the layers formed by the X and Y cages are equivalent with respect to the c-axis. Hence, the cage sequence can be represented as ...[XZ][XZ][XZ]... or [XZ]\textsubscript{m}. This sequence gives rise to three types of (001)-oriented slabs: [XZ]X, [XZ]\textsubscript{m}, and [Z][XZ]\textsubscript{m}. We denote them according to the orientation of the surface cages: X∥X, X∥Z, and Z∥Z, respectively. Thus, there are only two types of nonequivalent (001) surface terminations: X-type, terminated with X or Y cages and Z-type, terminated with Z cages.

The sequence of cage layers along the normal to the (110)-oriented slab is shown in Figure 3. The repeat unit, in this case, is more complex than that in the (001)-oriented slab and consists of two lamella-like units XZX and YZY separated by a relatively large distance of 2.142 Å. Within each lamella-like unit, cage layers are evenly spaced by a shorter distance of...
1.071 Å. Since X and Y cages are equivalent with respect to the [110] vector, the smallest repeat unit can be taken as either XZX or YZY, where cages in different X or, respectively, Y layers have different chiralities. For convenience, we classify the manifold of possible cage sequences in terms of distances between the neighboring planes. For example, X and Y layers (Figure 3) are separated by the long distance (l), whereas X and Z layers, as well as Y and Z layers, are separated by the short distances (s). In these notations, the stacking sequence of (110) cage layers can be represented as ...ssllssls ... or ...[ss][ssl][sss]... Six types of non-equivalent (110)-slabs can be constructed for this sequence: [ss], [ssl], [ssl], [ssls], [ssl], and [sls][ssl]. Consequently, there are only three nonequivalent surface terminations: ...[ss]s, ...[ssl], and ...[ssls], where the right-most symbols s and l indicate the location of the lattice cleavage planes. Accordingly, the terminating surfaces are denoted as Xl, Xs, and Zs.

Finally, ordering of cage layers along the normal to the (111)-oriented slab is shown in Figure 4. In this case, X, Y, and Z cages are equivalent with respect to the surface normal, and the centers of all cage types are located in the same plane. Hence, we can denote a cage layer by X3, and the corresponding stacking sequence is [X3]l. Due to the asymmetric distribution of ionic charge of a cage along a [111] direction, the two surfaces of this slab are not equivalent. We define these surfaces as Xs and Xl, where subscripts indicate local excess of positive or negative charge, respectively.

The relationships between the (001), (110), and (111) lattice planes, the models of slabs oriented parallel to these planes, and nonequivalent surface terminations are shown in Figure 5. The 10 nonequivalent slab models considered here give rise to seven nonequivalent surface terminations: X and Z for (100); Xs, Xl, and Zs for (110), and X3 and X2 for (111).

**Thermodynamic Stability.** Figure 6 shows the dependence of C12A7-e− thermodynamic stability on Oxygen and Ca chemical potentials ΔHIO and ΔHICa, respectively. Method used to determine the stability region is described elsewhere.25–27 The C12A7-e− is stable in a relatively narrow region bounded by precipitation of CaO, Al2O3, and Al metal. The color palette corresponds to the free energy (G′) of the (001)X surface. Within the relevant interval of ΔHIO and ΔHICa, G′ ranges from 0.9 J/m2 at O-rich/Ca-poor conditions to 1.3 J/m2 at O-poor/Ca-rich conditions. These values are comparable to the surface energies found for other oxides, including rutile TiO2(110) (0.5−0.8 J/m2)28,29 and MgO(001) (1.04−1.20 J/m2).30

Since the stability region is narrow, we can introduce a linear relationship between the relevant values of ΔHICa and ΔHIO along a bisector of the region and use it to express C12A7-e− surface energy as a function of a single variable, either ΔHICa or ΔHIO. Surface energies for all of the C12A7-e− terminations considered here are shown in Figure 7. For polar surface (111) X3 and X2, we present their average free energy that corresponds to (X3 + X2)/2. These results show that the (001)X surface is the most stable at O-rich/Ca-poor conditions and (001)Z the most stable at O-poor/Ca-rich conditions. The (111) surfaces are the least stable at all conditions. This is attributed to the electrostatic polarity of these surfaces. The (110) surface energies are in the middle range with Xl and Zs being more stable at O-poor/Ca-rich and O-rich/Ca-poor conditions, respectively.

We note that the surface energies depend on the approximation used to describe exchange−correlation energy. Surface energies obtained using PBE-GGA are typically underestimated by about 30%, compared to that obtained by the local density approximation (LDA).30 For the C12A7-e− surfaces, our calculations show that the reduction is in the range from 25 to 35% (see Figure S1).

In practice, C12A7-e− surfaces were prepared in ultrahigh vacuum with a base pressure ~10−9 Pa (7.5 × 10−11 Torr) and subjected to temperature variations from 900 to 1050 °C.19 Under these conditions, ΔμOc varies from −3.3 to −2.8 eV (see Figure S2). Both GGA and LDA simulations show that several terminations have similar surface energies within this ΔHIO range (Figure 7). Moreover, changing the exchange−correlation functional from GGA to LDA results in the reversal of the relative stability for Xl and Zs surfaces, which suggests that real samples may exhibit several competing terminations simultaneously.

**Electronic Structure.** Surface work function (W) was determined using the formula Wc12a7-e = Evac − EF, where Evac and EF are vacuum level and Fermi energy, respectively. Values of Wc12a7-e were calculated for surfaces: (001)X (2.8 eV), (001)Z (2.9 eV), (110)X (2.7 eV), (110)Z (2.8 eV), (111)X3 (3.3 eV), (111)X2 (3.2 eV), and (111)X1 (2.6 eV). We suggest that the work function of macroscopic samples will be determined by the lowest work function value for the most stable terminations which, according to Figure 7, corresponds to (001)X and (110)X terminations and 2.7−2.8 eV. This is larger than the experimental intrinsic work function of 2.4
eV,14 but still as low as those of alkali and alkaline-earth metals.5 It should be noted that \( WC_{12}A_7:e^{-} \) can increase up to a value of 3.1 eV, depending on surface treatment.31 The one-electron densities of states (DOS) for the slabs terminated with most stable surfaces for each crystallographic orientation, (001) \( X \parallel X \), (111) \( X \parallel X \), (111) \( X \parallel X \), and (110) \( X \parallel X \), are shown in Figure 8. In all cases with the exception of the (110) \( S \parallel S \) slab, the systems are metallic. The cage conduction band is broader than that in the bulk \( C_{12}A_7:e^{-} \), and the narrow gap between the cage conduction band and the framework conduction band disappears. In contrast, in the case of the (110) \( S \parallel S \) slab, the cage conduction band splits into a narrow occupied part and an unoccupied part separated by a \( \sim 0.5 \) eV wide gap.

To characterize the distribution of the electron anions in the near-surface region, we calculate the formal ionic charge associated with each cage wall. Taking the ionic charges of the Ca, Al, and O species to be +2, +3, and \(-2\) (in atomic units), respectively, the cage-wall charge in the bulk is +1/3. This charge is compensated by 1/3 of an electron anion associated with each cage on average. The situation is different near the surface. Here (see Figure S3), the cage-wall charge at the surface is more positive and, in contrast, the cage-wall charge in the subsurface region is less positive than that in the bulk. This induces redistribution of the compensating electron anions, whereby their density at the surface becomes higher than that is the bulk and, accordingly, in the subsurface region, lower.

Local density of states (LDOS) is often used to relate the surface electronic properties to the results of STM experiments. Figure 9 shows LDOS due to the states within +2.5 eV above the Fermi level, consistent with the sample bias voltage of +2.5 V used in the STM measurements.19 The same area of 2.42 \( \times \) 2.42 nm\(^2\) is examined for all of the surfaces. The LDOS of the (001) \( X \parallel X \) surface exhibits stripes of \( \sim 7.4 \) Å in length. They are formed by the electron anions accumulating on the surface. Bright spots at the two ends of each stripe mark Ca sites. The (110) \( X \parallel X \) surface has a high LDOS intensity at Ca and Al sites. In contrast, LDOS intensity of the (110) \( S \parallel S \) is very low,
consistent with the DOS calculated for the (001) slab (Figure 8). This would result in an STM image that is flat due to vanishing tunneling current almost everywhere, except for the narrow \( \sim 3.5 \) Å long regions.

The LDOS of (001) slab exhibits triangles with bright spots at their vertices. The spots with higher and lower LDOS intensity are Ca and Al sites, respectively. Surface charge density is significantly high only inside the triangular areas. It should be noted that due to similar surface energies (Figure 7), the surfaces can have mixed terminations and, therefore, more complex LDOS patterns. Nevertheless, stripe and triangular patterns were observed in the STM images for (001) and (111) surfaces, indicating superposition of several types of LDOS.

**Adsorption of Au Atoms.** Finally, we assess how control of the density of electron anions could be used to control oxidation states of adsorbed metal species. Electron-rich C12A7:e⁻ surfaces can promote electron transfer between the surfaces and adsorbates and, hence, enhance the surface adsorptive capacity or catalytic activity.\(^{15,17,18}\) We find that C12A7 surfaces also offer a way to modify electron density by controlling the concentration of anions, such as O⁻² ions clathrated in C12A7 cages.\(^{6}\) To this end, we consider adsorption of a single gold atom (\( \text{Au}_1 \)), two separated monomers (\( \text{Au}_1 \times 2 \)), and a dimer (\( \text{Au}_2 \)), as shown in Figure 10 for (001)X surfaces. We distinguish between individual Au atoms with the help of superscripts \( \alpha \) and \( \beta \). Table 1 shows Bader charges and adsorption energies (\( E_{\text{ads}} \)) at the most energetically favorable adsorption sites.

For the C12A7:e⁻ slabs, Bader charge analysis shows that all Au ions are negatively charged, nominally in the \( \text{Au}^\alpha \) or \( \text{Au}^\beta \) charge states and bind to surface Ca or Al. We note that although in most cases, the Bader charge of adsorbed Au species is close to formal +1 el, in the case of the (110)X\(_s\) surface, these charges are close to −2 el. This is an indication that Au⁺ resides at a site that hosts a large amount of charge associated with C12A7:e⁻ electron anions. Indeed, analysis of the cage-wall charge for this termination (see Figure S3) shows that the surface layer of cages has the highest positive charge among all considered surfaces. Accordingly, electron anions that compensate this charge have the highest density for this surface termination and function as strong reducing species.

In the Au₂ configuration, the Au–Au distance varies from 2.72 to 2.97 Å. Au dimers on oxide surface were extensively studied in the past, and the reported Au–Au distances are 2.52–2.56 Å for \( \text{Au}_n \) on insulating MgO(001)\(^{32,33}\) and 2.88 Å for \( \text{Au}_n \) adsorbed on a surface F-center.\(^{35}\) This comparison suggests that the elongation of the Au–Au bond on C12A7:e⁻ is constrained by the surface topographic features, resulting in, potentially different activities of the dimer.

We calculate adsorption energy \( E_{\text{ads}} \) by referring energy of the whole system (\( \text{Au}_n \times m \text{/slab} \)) to that of an isolated Au atom and the slab without or with an existing Au ion (\( \text{Au}_1 \times m' \text{/slab}, m' = 0 \) or \( 1 \), respectively): \( E_{\text{ads}} = E(\text{Au}_n \times m \text{/slab}) − E(\text{Au}) − E(\text{Au}_1 \times m' \text{/slab}) \), where \( n, m \leq 2 \). For the Au₁ and Au₂ configurations, \( E_{\text{ads}} \) values of \( \text{Au}^\alpha \) and \( \text{Au}^\beta \) are in the range from −3.6 to −4.5 eV. For comparison, for a Au/MgO system, \( E_{\text{ads}} \) is between −1.35 and −1.01 eV. An enhanced adsorption with \( E_{\text{ads}} \) from −1.44 to −2.27 eV was predicted for MgO bilayer deposited on Mo substrate. In this case, the higher binding energy is due to electron transfer from Mo substrate to the adsorbed Au ions.\(^{34}\) An alternative way to stabilize adsorbed metals is to create oxygen vacancies which then transfer electrons to the adsorbates, as in the case of, e.g., Pt/TiO₂.\(^{35}\)

Interestingly, adsorption of Au as separated species \( \text{Au}^\alpha \) and \( \text{Au}^\beta \) is energetically preferred over the formation of \( \text{Au}_2 \) dimer (this is with the one exception of the (001)X surface, where

![Figure 9. Local density of states due to states within +2.5 eV above the Fermi level for the (001)X, (110)X, (110)Z, and (111)X surfaces. The image area is 2.42 × 2.42 nm² in all cases. Dashed lines mark a single lateral cell. Yellow and blue circles indicate the positions of the top-most Ca and Al atoms, respectively.](image1)

![Figure 10. Adsorption of Au atoms on the (001)X surface of C12A7:e⁻: (a) two Au monomers and (b) Au dimer. (c) A single Au atom on the same surface of C12A7:e⁻ with clathrated O²⁻ ions. Numerals indicate bond lengths (in Å) and Bader charges of Au species.](image2)
the difference between the energies to such configurations is less than 0.2 eV). Hence, we conclude that it is more energetically favorable for Au atoms to be dispersed over the surfaces rather than aggregate into clusters.

To demonstrate the ability to control charge state and adsorption site of Au ions through controlling electron density, we introduce two clathrated oxygen atoms into two cages on the (001) surface. These extra oxygen atoms will partially absorb the extra-framework electrons to become O$_2^−$ ions and hence reduce electron density. As a result, the adsorbed Au ion becomes positively charged (+0.29 lel). At the same time, its binding energy is significantly decreased (from 4.5 to 3.8 eV) (Table 1: Au$_1$). Moreover, Figure 10c shows that such Au ion forms bonds with oxygen anions, rather than with surface cations.

Therefore, the C12A7: e$^−$ surfaces not only offer an efficient way to achieve a much stronger binding interaction and hence higher adsorption capacity for Au species but also to control charge state and adsorption site of Au atoms. Such an ability to stabilize positive and negative metal species by modifying the bulk compositions can provide a high degree of control over surface catalytic processes.

**CONCLUSIONS**

To summarize, we provide insight, based on the density functional theory simulations, into the structure, thermodynamic stability, and electronic and chemical properties of C12A7: e$^−$ surfaces. We explored a plethora of C12A7: e$^−$ slab structures and categorized their surfaces into seven basic types of termination, depending on the direction of cage symmetry axis and the separation of surface and subsurface cage layers. We found that the surface termination and the concentration of the electron anions in the near-surface region have a strong effect on the binding on metal species. Au species adsorbed on C12A7: e$^−$ surfaces trap the electron anions and bind to the surface cations. These extra oxygen atoms will partially absorb the extra-framework electrons to become O$_2^−$ ions and hence reduce electron density. As a result, the adsorbed Au ion becomes positively charged (+0.29 lel). At the same time, its binding energy is significantly decreased (from 4.5 to 3.8 eV) (Table 1: Au$_1$). Moreover, Figure 10c shows that such Au ion forms bonds with oxygen anions, rather than with surface cations.

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**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b11866.

Effect of the density functional on the stability of C12A7: e$^−$ surfaces, relation of ΔH$_{TO}$ to the experimental conditions, analysis of the charge distribution, atomic coordinates of the most stable (001), (110), and (111) surfaces (PDF).

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Accelerated Innovation Research Initiative Turning Top Science and Ideas into High-Impact Values (ACCEL) program of the Japan Science and Technology Agency. H.H. was supported by a MEXT Grant-in-Aid Scientific Research (No. 17H06153). P.V.S. was supported by the Laboratory Directed Research and Development program at Pacific Northwest National Laboratory (PNNL), a multiprogram national laboratory operated by Battelle for the US Department of Energy under Contract DE-AC05-76RL01830. Calculations were performed using PNNL Institutional Computing (PIC) resources.

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