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Room Temperature-Stable Electride as a Synthetic Organic Reagent: Application to Pinacol Coupling Reaction in Aqueous Media

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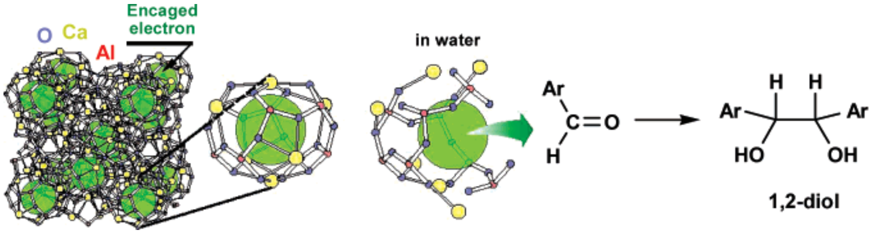
ABSTRACT



Room temperature-stable inorganic electride $[Ca_{24}Al_{28}O_{68}]^{4+}4e^-$ was employed for a pinacol coupling reaction in aqueous media. Ca–Al–O gel formed by the destruction of the crystal structure of an electride by water media played a key role in transferring the electron to electrophilic aldehydes. Aromatic aldehydes reacted smoothly with moderate to high yields.

Electride[1] is a crystalline material that traps electrons at a stoichiometric concentration, and has attracted attention since novel electronic and magnetic properties arising from the exotic electronic structure can be expected. In 2003, we synthesized an inorganic electride by exchanging free oxygen ions in the subnanometer-sized cages of a $12CaO{\cdot}7Al_2O_3$ crystal (C12A7), which is a constituent of commercially available aluminous cement, with electrons.[2] The resulting material, abbreviated as C12A7:e$^-$ (Figure 1), is the first room temperature-stable electride, and the electron concentration can reach the theoretical maximum, which is determined by the total excess charge of the cage framework (2×10^{21} cm^{-3}). It exhibits unique physical properties such as an extremely small work function (2.4 eV)[3] and a metal−insulator transition,[4a] as well as superconductivity.[4b] While

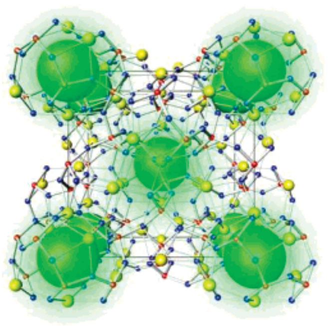


Figure 1. Crystal structure of C12A7:e$^-$. The unit cell (cubic lattice, $a = 1.19$ nm) is composed of 12 cages (inner diameter of ∼0.4 nm), and one-third of these cages are occupied by electrons.

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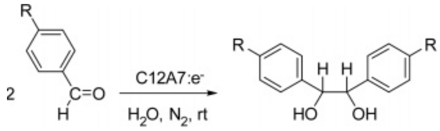
such physical properties have been exploited to date, the examination of electrides as chemical reagents in synthetic organic chemistry remains to be carried out. Although various reducing reagents, such as metal, metal hydrides, and organometallic compounds, are already employed in synthetic organic reactions,[5] there have been no reports on the application of electrons in an electride to synthetic organic reactions. We adopted pinacol coupling of aromatic aldehydes as the first probe of the utility of C12A7:e$^-$ in synthetic organic chemistry, because the reaction is induced by the transfer of electrons from the chemical reagent to the aldehyde. Electrochemically induced pinacol coupling involves an initial transfer of electrons from the electrode to the organic substrate molecules on the surface of the electrode.[6] In this paper, we report the pinacol coupling of aromatic aldehydes promoted efficiently by the electride.

When benzaldehyde (0.094 mmol) and C12A7:e$^-$ (196 mg)[7] are mixed in water (5.0 mL), the dark brown electride gradually dissolves and the mixture slowly becomes a white suspension. Hydrolysis of the white gel by aqueous HCl (1 M), followed by Et_2O extraction produces 1,2-diphenylethyleneglycol, indicating that the pinacol coupling reaction shown by eq 1 took place. The resulting solution showed a pH of 11.6 (26 °C). ^1H NMR analysis of the reaction mixture confirmed the formation of 1,2-diphenylethyleneglycol.



(1)

The C12A7:e$^-$ in the single crystalline form (2×10^{21} electrons cm^{-3})[2] effectively promotes the pinacol coupling of benzaldehyde to yield the corresponding 1,2-diol (71%), when the electride used contains a large excess amount of electrons relative to the aldehyde (Table 1, run 1). The use of polycrystalline C12A7:e$^-$ (10^{19-20} electrons cm^{-3}) leads to a much lower yield of the product (39%) even after reacting for 24 h (run 3). Furthermore, neither stoichiometric C12A7 powder (run 4) nor $Ca(OH)_2$ caused any pinacol coupling. These observations clearly indicate that the electrons in the C12A7:e$^-$ are responsible for promoting the reaction. A mixed solvent system of tetrahydrofuran (THF) and water reduced the saturation yield to 69% for H_2O:THF of 4:1 (run 5) and 33% for 1:1 (run 6), and finally, no reaction was observed in pure THF (run 7), suggesting that water is essential for the release of electrons from the C12A7:e$^-$.

Table 1. Pinacol Coupling of Aldehydes (RC_6H_4CHO) by C12A7:e$^-$ [a]

run	R	electrons/ aldehyde[b]	solvent	temp/ °C	time/ h	yield[c]/ %	dl:meso[d]
1	H	2.9	H_2O	rt	3	71	55:45
2	H	1	H_2O	rt	3	21	38:62
3[e]	H	20	H_2O	rt	24	39	52:48
4[f]	H		H_2O	rt	24	0	
5	H	2.9	H_2O:THF (4:1)	rt	18	69	50:50
6	H	2.9	H_2O:THF (1:1)	rt	18	33	67:33
7	H	2.9	THF	rt	24	0	
8	CH_3	2.9	H_2O	100	12	35	40:60
9	$(CH_3)_3C$	2.9	H_2O	100	12	11	41:59
10	Cl	2.9	H_2O	100	24	33	53:47
11	CH_3CO	2.9	H_2O	100	24	11	*g*

[a] Reaction conditions: [aldehyde] = 0.094 mmol, solvent = 5.0 mL. [b] Molar ratio of electrons in C12A7:e$^-$ to aldehyde. [c] Determined by ^1H NMR with 4-methoxybiphenyl as an internal standard. [d] Ratios of the stereoisomers of the products determined by ^1H NMR. [e] Polycrystalline C12A7:e$^-$ was employed (solvent = 50 mL). [f] C12A7 powder was used in the same amount as the electride in run 1. [g] Not determined due to severe overlap of the signals due to the stereoisomers.

The results of run 1 indicate that 30% of the electrons in the C12A7:e$^-$ are utilized in the reaction at maximum. Olga reported that the thermodynamic potential of the electron within C12A7:e$^-$ is high enough to promote the reduction of water.[8] Actually, Na intercalated in silica gel, which is effective for the reduction of organic compounds,[5b] preferentially produces hydrogen gas in the presence of water.[9] However, the reactions with C12A7:e$^-$ are accompanied by some reduction of water, but the electrons are consumed effectively for the reduction of aldehyde rather than the reduction of water. This observation implies that some reaction medium produced from C12A7:e$^-$ acts as a reaction selector.

Table 1 shows the reactions of other substituted aldehydes in water (runs 8−11), and indicates that they proceeded at 100 °C to form the corresponding diols as the products with moderate yields. The reactivity of the C12A7:e$^-$ system changes apparently depending on the substituents of the aromatic ring among these four aldehydes, and no direct relationship is observed between the electron-withdrawing (or releasing) properties of the substituents and the product yield. The aldehyde group of *p*-acetylbenzaldehyde was selectively reduced to pinacol, whereas the carbonyl group in the ketone moiety remained unreacted (run 11).

The XRD analysis of the residual powder after the completion of the reaction confirmed that the reaction is

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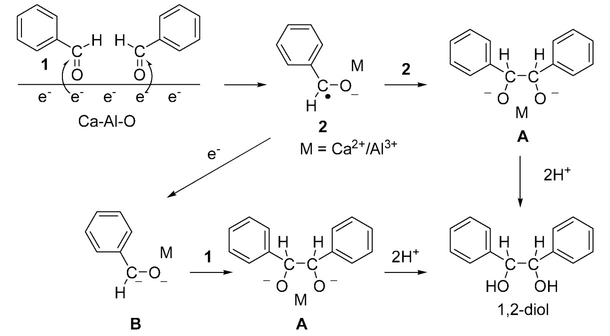
accompanied by the decomposition of the electride framework upon contact with water. C12A7:e$^-$ undergoes slow decomposition of the framework in water and forms a gel layer on the surface during hydrolysis in a similar way as the aluminous cement.[10]

Scheme 1. Possible Mechanism of Pinacol Coupling Mediated by C12A7:e$^-$



Scheme 1 depicts a plausible mechanism for the pinacol coupling promoted by the C12A7:e$^-$. The pinacol coupling is presumed to take place within the gel. The transfer of electrons to carbonyl carbon atoms of the aldehyde occurs on the surface of the C12A7:e$^-$. The formed anion radicals are concentrated within the gel layer and may be stabilized by coordination to metal cations (Ca^{2+} or Al^{3+}) in the gel or on the surface of the solid electride (**2**). Dimerization of the anion radical coordinated to the metal would form the pinacolate dianion (**A**), while one-electron reduction of **2** and subsequent nucleophilic addition of the resulting dianion (**B**) to the carbonyl group of aldehyde would also yield **A**.[5] Both of the C−C bond-forming reactions are possible in the pinacol coupling. The coordination of the intermediate to calcium and/or aluminum cations in the gel or on the surface serves to stabilize and concentrate them and to enhance the coupling in the presence of a large amount of water.

In conclusion, we have demonstrated that the inorganic electride C12A7:e$^-$ acts as a single-electron donor reagent in synthetic organic reactions in aqueous media. It appears to be inactive in the absence of water, even in polar organic solvents, but releases electrons slowly upon the addition of water. Electrons released from the electride act as a reducing agent, probably within the Ca−Al−O gel, that results from the decomposition of the electride framework in water. The electride is nontoxic and can be handled easily in an ambient atmosphere, i.e., it is thermally and chemically stable irrespective of its small work function (2.4 eV) comparable to metal potassium but can induce efficient electron transfer to the aldehyde in water medium. Since this process is controlled by the decomposition of the network frame, the reaction is gentle even in aqueous media unlike conventional reducing reagents. Further, the resulting Ca−Al−O gel may provide a favorable environment for the present reaction over H_2 generation from water. Such unique characteristics make the reaction procedure very simple without electrochemical electrodes, suggesting applicability for various organic reactions in aqueous media.

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Supporting Information Available: General procedure for the preparation of C12A7 electride and NMRs of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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