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Assimilatory and Dissimilatory Reductions of NO_n^- $(n = 2, 3)$ Catalyzed by MoFeS Cluster

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Nitrate and nitrite ions are selectively reduced to NH_3 by a $(Bu_4N)_4[MoFe_3S_4(SPh)_3(O_2C_6Cl_4)]_2$-modified glassy carbon electrode under the electrolysis at −1.25 V vs. SCE in H_2O (pH 10.0), while nitrite ion is predominantly reduced to N_2 under the same electrolysis at −1.00 V.

Biological assimilatory and dissimilatory reductions of NO_3^- regulate the amounts of inorganic nitrogen compounds such as N_2, NH_3, and NO_3^- on earth (nitrogen cycle). Although the mechanisms of those enzymatic NO_3^- reductions have not been clearly elucidated, NO_3^- is first reduced to NO_2^- with molybdenum containing nitrate reductases. Assimilatory reduction of NO_2^- has generally been considered to proceed *via* NO^- (or HNO), NH_2OH to NH_3. On the other hand, the pathway of dissimilatory reduction of NO_2^- to N_2 (Scheme 1) has been still confused in the four-electron jump from NO_2^- to N_2O, and various 1N and 2N species such as NO^+, NO, NO^-, $N_2O_2^{2-}$, N_2O_3, and $N_2O_3^{2-}$ have been proposed as the intermediates in that process.[1] Recently, we have confirmed $N_2O_2^{2-}$ in the dissimilatory reduction of NO_2^- by $[Fe_4S_4(SPh)_4]^{2-}$ in CH_3CN,[2] and NH_2OH in the assimilatory reduction of NO_2^- by the triply bridged double cubane cluster $(Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$-modified glassy carbon electrode in H_2O.[3] This letter reports the identification of NO as a common intermediate of the assimilatory and dissimilatory reduction of NO_n^- $(n = 2, 3)$ by a doubly bridged double cubane cluster $(Bu_4N)_4[MoFe_3S_4(SPh)_3(cat)]_2$ (cat = $O_2C_6Cl_4$)[4]-modified glassy carbon electrode[5] in H_2O.

$$2NO_3^- \longrightarrow 2NO_2^- \longrightarrow ? \longrightarrow N_2O \longrightarrow N_2$$

Scheme 1. The pathway of the dissimilatory reduction of NO_3^-

The $(Bu_4N)_4[MoFe_3S_4(SPh)_3(cat)]_2$ (50 nmol cm^{-2})-modified electrode ($[MoFe_3S_4]/GC$) effectively catalyzes the reduction of NO_3^- under the electrolysis at −1.25 V vs. SCE in an aqueous $NaNO_3$ solution (pH 10) to produce NO_2^- (Eq. 1), NH_3 (Eq. 2), and H_2 with current efficiencies η = 42, 37, and 20%, respectively, as shown in Fig. 1a. The present assimilatory reduction of

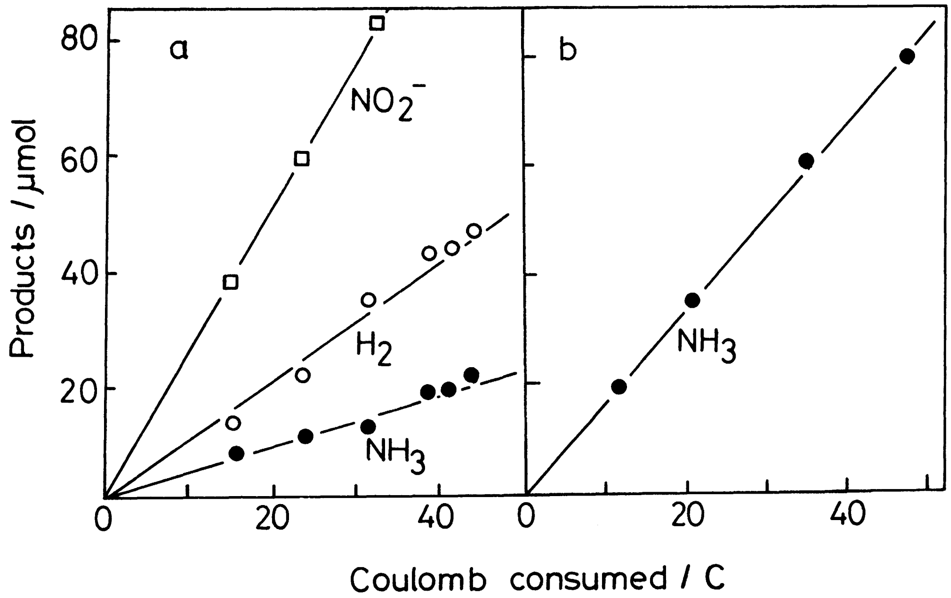

Fig. 1. Reduction of NO_n^- (n = 2, 3) by the $[MoFe_3S_4]$/GC under the controlled-potential electrolysis at -1.25 V *vs*. SCE in aqueous $NaNO_3$ (50 mmol dm^{-3}) (a) and $NaNO_2$ (50 mmol dm^{-3}) (b) solutions at pH 10.0.

$$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O \qquad (1)$$

$$NO_3^- + 9H^+ + 8e^- \longrightarrow NH_3 + 3H_2O \qquad (2)$$

NO_3^- affording NH_3 is apparently *via* NO_2^- since NO_2^- (50 mmol dm^{-3}) is also smoothly reduced to NH_3 with a current efficiency 98% under the same electrolysis conditions (Fig. 1b). Thus, NO_n^- (n = 2, 3) selectively undergoes the assimilatory reduction by the $[MoFe_3S_4]$/GC under the electrolysis at -1.25 V *vs*. SCE. On the other hand, the dissimilatory reduction of NO_2^- predominantly took place in addition to the assimilatory reduction under the controlled-potential electrolysis at -1.00 V in an aqueous $NaNO_2$ (50 mmol dm^{-3}) to produce N_2 (Eq. 3) and NH_3 with η = 90 and 6%, respectively. Such an

$$2NO_2^- + 8H^+ + 6e^- \longrightarrow N_2 + 4H_2O \qquad (3)$$

alternation of the main reaction path from assimilatory to dissimilatory reduction by the change of the electrolysis potential of the $[MoFe_3S_4]$/GC suggests that both reductions proceed *via* a common reaction intermediate.
The intermediate involved in the reduction of NO_2^-, therefore, was investigated by use of a rotating ring-disk electrode (RRDE), in which only the disk-electrode was modified with $(Bu_4N)_4[MoFe_3S_4(SPh)_3(O_2C_6Cl_4)]_2$. When the disk electrode of the RRDE was applied the potential at more negative than -1.0 V with 1000 rpm in the aqueous $NaNO_2$ (0.10 mol dm^{-3}), the reduction of NO_2^- took

place on the disk electrode. At the same time, the glassy carbon ring electrode detected an anodic current of free NO.[6)] In the previous electrochemical NO_3^- reduction conducted under acidic conditions (pH < 4), free NO is formed by the disproportionation reaction of the protonated NO_2^- (Eq. 4).[7)]

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O \qquad (4)$$

On the basis of the fact that NO_2^- does not undergo protonation in H_2O at pH 10, the formation of free NO apparently results from the one-electron reduction of NO_2^- by the $[MoFe_3S_4]$/GC (Eq. 5). This result is distinct contrast to the

$$NO_2^- + e^- + 2H^+ \longrightarrow NO + H_2O \qquad (5)$$

assimilatory and dissimilatory reduction of NO_2^- by $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ [3)] and $[Fe_4S_4(SPh)_4]^{2-}$,[2)] where NO can not be detected at all, and NH_2OH and $N_2O_2^{2-}$ formed by the two-electron reduction of NO^- and dimerization of NO^-, respectively, are identified as the reaction intermediates.

The reduction of NO_2^- by the $[MoFe_3S_4]$/GC electrode is initiated by the the coordination of NO_2^- on either Mo or Fe of the $MoFe_3S_4$ core of the cluster since NO_2^- is not reduced by the glassy carbon plate at more positive potentials than -1.70 V <u>vs</u>. SCE at pH 10.0.[3)] The interaction between the cluster and NO_2^- was studied in DMF in order to elucidate the coordination site of NO_2^- though the cluster on the $[MoFe_3S_4]$/GC exists in a solid state. It is well-known that $[MoFe_3S_4(SR)_3(cat)]_2^{4-}$ (R = alkyl and aryl) dissociates into two single cubane clusters $[MoFe_3S_4(SR)_3(cat)(solvent)]^{2-}$ in polar solvents such as DMF, CH_3CN, THF, DMSO, and acetone by coordination of those solvents to the molybdenum atom, and those solvent molecules are easily substituted by various donor molecules such as PR_3 RS^-, N_3^- and NH_2NH_2 to afford the 1:1 adduct.[4)] In accordance with this, an addition of $NaNO_2$ to the DMF solution of $(Bu_4N)_2[MoFe_3S_4(SPh)_3(cat)(DMF)]$ (0.10 mmol dm^{-3}) results in a gradual decrease of the CT band at 450 nm of the DMF solvated cluster[4)] with appearance of the isosbestic point at 335 nm (Fig. 2), suggesting that DMF

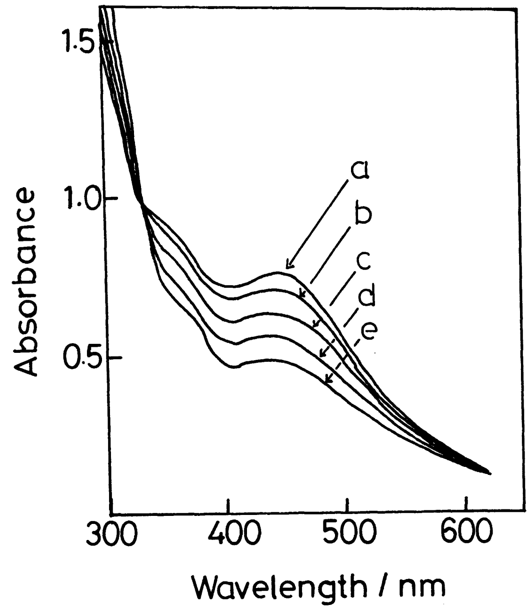

Fig. 2. Electronic absorption spectra of $(Bu_4N)_2[MoFe_3S_4(SPh)_3(cat)(DMF)]$ (0.60 mmol dm^{-3}) under the various concentrations of $NaNO_2$; 0 (a), 6.0 (b), 18.0 (c), 30.0 (d), and 54.0 mmol dm^{-3} in DMF.

$$[\mathrm{MoFe_3S_4(SPh)_3(cat)(DMF)}]^{2-} + \mathrm{NO_2}^- \rightleftharpoons [\mathrm{MoFe_3S_4(SPh)_3(cat)(NO_2)}]^{3-} + \mathrm{DMF} \qquad (6)$$

coodinated on the Mo atom of the $MoFe_3S_4$ core is substituted by NO_2^- (Eq. 6). Thus, NO_2^- binds to Mo rather than Fe of the present MoFeS cluster and the equilibrium constant calculated from the change of the absorbance at 310 nm was 30 dm^3 mol^{-1} (298 K) in DMF. On the other hand, NO_2^- coordinates on the Fe atoms of the reduced species of $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ by the substitution reaction of the terminal PhS^- ligand. Such a difference of the coordination sites of NO_2^- may be associated with the formation of NO^- and NO as the first reduction products of NO_2^-. Recently, electrochemical[8)] and photochemical[9)] reductions of NO_3^- have been much interested in connection with key reactions of the nitrogen cycle. The first reduction products of NO_2^- in those reductions, however, have hardly been examined. The present study demonstrates that both NO and NO^- are feasible intermediates as the first reduction product of NO_2^- in not only the assimilatory but also the dissimilatory reductions, and their formation is largely dependent on the coordination sites.

References

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5) The $[MoFe_3S_4]$/GC was prepared by an addition of a given amount of a CH_3CN solution (0.10 mmol dm^{-3}) of $(Bu_4N)_4[MoFe_3S_4(SPh)_3(cat)]_2$ on a polished surface of the glassy carbon plates (1.0 and 3.0 cm^2) by a syringe technique and dried for *ca*. 30 min under N_2 steam.[3)]
6) Not only the threshold potential (+0.45 V) of an increase of the anodic ring current but also the current-potential curve of the ring electrode are consistent with those of free NO at pH 10.0.
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