

MECHANISM OF ELECTRON TRANSFER IN DINITROGEN
FIXATION IN THE SYSTEM Ti(III)-Mo(III)

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Mo(III) and N_2 together inhibit H_2 evolution in the dinitrogen fixing system Ti(III)-Mo(III) in alcohol-water media. It is concluded that the formation of a Mo_2N_2 complex changes the collective properties of Ti(III) hydroxide. The catalytic action of Mo(III) in N_2 reduction is explained by the possibility of electron transfer to the Mo_2N_2 complex from a number of Ti(III) atoms situated around the catalyst complex.

Mo(III) и N_2 совместно ингибируют выделение H_2 в фиксирующей азот системе Ti(III)-Mo(III) в водно-спиртовой среде. Сделано заключение, что образование комплекса Mo_2N_2 изменяет коллективные свойства гидроокиси Ti(III). Каталитическое действие Mo(III) в восстановлении азота объяснено с точки зрения возможности переноса электронов к комплексу Mo_2N_2 от большого числа атомов Ti(III) расположенных рядом с каталитическим комплексом.

Mo(III) compounds catalyze the reduction of N_2 by Ti(III) hydroxide activated by Mg(II) in water and alcohol-water /1-5/. At temperatures higher than 80 °C, up to 100 N_2H_4 and NH_3 molecules are formed per each molybdenum atom. The suggested mechanism of N_2 reduction includes the formation of a dinuclear Mo(III) complex with dinitrogen and subsequent electron or H-atom transfer to the activated N_2 molecule /3, 4/. It is also suggested that Mo(III) atoms are bound to Ti(III) by hydroxo or oxo bridges. In the process of N_2 reduction to N_2H_4 , Mo(IV) and Ti(IV)

are formed. To ensure catalysis, the Mo(III) compound has to be regenerated, thus Mo(IV) must be reduced by Ti(III) to Mo(III). The mechanism of this process must include either Mo(IV) transfer to unreacted Ti(III) (possibly via the intermediate formation of soluble Mo(IV) compounds) or electron transfer from surrounding Ti(III) ions to Mo(IV), which remains bound to Ti.

Some conclusions about the mechanism can be drawn from dihydrogen evolution from water occurring along with N_2 reduction.

It has been found that the oxidation of Ti(III) by water in Ar atmosphere is 10^2 to 10^3 times faster at 83–127 °C than hydrazine formation at 100 atm N_2 /5/. The hydrazine yield at 127 °C is a few percent of added Ti(III), i. e. a much higher value than could be expected from the ratio of N_2 reduction and H_2 formation without N_2 . Besides, at 120–130 °C in the absence of N_2 atmosphere the accumulation of N_2H_4 requires 30–40 min., and Ti(III) oxidation is much slower. It may be assumed from these data that the oxidation of Ti(III) by water is inhibited by dinitrogen. Indeed special experiments have shown that this is the case and inhibition is observed only in the presence of molybdenum. It may be seen from Table 1 that the increase of N_2 pressure decreases the consumption of Ti(III).

Table 1

P_{N_2} (atm)	0	10	25	50	80	150
Ti ^{III} (10^4 mol)	2.2	2.0	1.78	1.68	1.64	1.54

This dependence is opposite to that of the N_2H_4 yield (Fig. 1), saturation being reached in both cases at pressures higher than 150 atm.

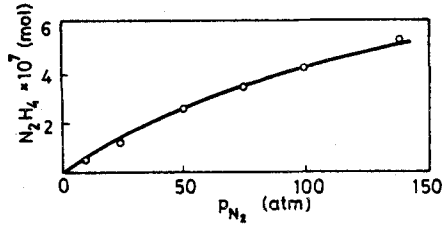


Fig. 1. Dependence of the N_2H_4 yield on the N_2 pressure, $TiCl_3 = 3 \times 10^{-4}$ mol; $MoCl_5 = 3 \times 10^{-7}$ mol; $Mg/Ti = 0.5$, $T = 86^\circ C$, reaction time = 10 min

Table 2 shows the effect of the Ti/Mo ratio on the inhibition at 100 atm of N_2 . Upon increasing the Mo content, the rate of the Ti(III) reaction with water decreases.

Table 2

Ti/Mo	∞	3 000	1 000	200	30
W_{H_2} (rel)	1	0.9	0.78	0.67	0.53

If it is assumed that each Mo_2N_2 complex prevents \underline{n} Ti(III) ions from reacting with H_2O , then \underline{n} may be estimated as several hundred.

These results can be explained in terms of the collective properties of solid Ti(III)-Mg(II) hydroxide, assuming that in the presence of N_2 the electrons of a number of Ti(III) ions are at least partly "switched over" to the reduction of activated N_2 , the formation of H_2 thus being slowed down.

It is of interest to consider from the point of view of this hypothesis the dependence of the N_2H_4 yield on the Mo/Ti ratio (Fig. 2). At very small ratios both the absolute and relative $\left(\frac{[N_2H_4]}{[Mo]} \right)$ yields increase with increasing Mo/Ti, the latter presumably because of the necessity of a Mo_2 dimer for N_2 activation. At Mo/Ti

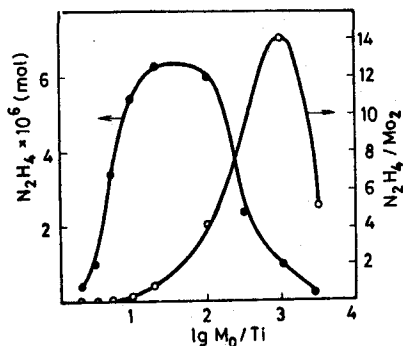


Fig. 2. Dependence of the absolute and relative yield of N_2H_4 on the Ti^{3+}/Mo^{5+} ratio. $TiCl_3 = 3 \times 10^{-4}$ mol, $P_{N_2} = 100$ atm; $T = 86$ °C; $mg/Ti = 0.5$; reaction time = 10 min

ratios in the range of $10^{-3} - 10^{-2}$, the relative yield decreases while the absolute yield still increases. At higher ratios even the absolute N_2H_4 yield decreases. This fall of activity toward N_2 may be due to changes in the electron transfer properties of Ti(III). Measurements of the electric conductivity of the hydroxides dried in vacuum show that the addition of Ti(IV) and Mo(III) decreases the specific conductivity of Ti(III) hydroxide. Thus the addition of 3% Mo(III) to Ti(III)-Mg(II) hydroxide changes κ from 10^{-6} to $5 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$.

It may be noted that compounds of V(III) and V(IV) with Mg^{2+} , having a spinel structure at $Mg/V = 0.5$ show semiconductor properties (for a monocrystal, $\kappa = 1 - 2.5 \Omega^{-1} \text{ cm}^{-1}$, $E = 0.15$ eV /6/).

As mentioned earlier /3, 4/ some properties of the Ti(III)-Mg(II)-Mo(III) system are similar to those of the N_2 -fixing enzyme nitrogenase. The phenomena described in this paper make this similarity even closer. According to Shilov and Likhtenshtein /7/, the enzymatic process includes electron transfer via a polymeric iron cluster in Fe and

Mo-Fe proteins to the N_2 molecule activated in a dinuclear molybdenum complex. In the model system, the Ti(III) ions form an electron transfer chain and transfer electrons to a similar molybdenum complex of the activated N_2 molecule.

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