

Reduction of carbon dioxide during the synthesis of metal nano-particles in water

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Received 14 July 2003; accepted 19 July 2003

Published online: 8 August 2003

Abstract

An effort was made to synthesize “carbon-free” metal (Fe⁰, Co⁰, Ni⁰) nano-particles via the reduction of their salts with BH₄⁻ in aqueous solutions. Surprisingly it was found that when the synthesis is carried out in the presence of CO₂, e.g., in aerated solutions, the CO₂ is catalytically reduced by BH₄⁻ on the surface of the metal particles. Carbon-free metals can be prepared by reduction under an inert atmosphere. Thus metal surfaces might have acted as catalysts for CO₂ fixation, probably via the initial formation of carbon clusters, in the reductive atmosphere in the prebiotic era.

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Keywords: Carbon dioxide; Metal nano-particles; Reduction; Sodium borohydride

1. Introduction

In a parallel study [1] the formation of CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ during the partial dissolution of analytical iron powder, and other metal powders, in slightly acidic aqueous solutions was observed. These organic gases stem from the reduction of carbon atoms, or clusters, present in the analytical metal powders. The evolution of light alkanes and alkenes in this process complicates the study of the mechanism of reduction of halogenated organic compounds by iron powder, which was our original aim. Therefore it was decided to synthesize pure metal powders that will not contain any carbon. The synthesis chosen was the reduction of Fe^{II}_(aq), or other M²⁺_(aq) ions by sodium borohydride in aqueous solution, a method used previously [2,3] for the preparation of iron nano-particles. Borohydride reduction of metal ions is currently used extensively for the production of nanoscale metal and metal boride particles [4–8].

2. Results and discussion

Iron nano-particles were synthesized as described in Section 3 in a vessel open to air. Surprisingly it was found that when the reduction is carried out in the presence of CO₂, e.g., in air which is the common practice [6–8], carbon dioxide is reduced during the reduction of the M²⁺_{aq} ions.

Partially dissolving the iron particles thus obtained in phosphate buffer at pH 4.0 results surprisingly in the emission of the organic gases methane, ethane, ethylene and propene (Table 1), determined by GC of the gaseous phase. As the solutions contained no organic compounds this result suggested that CO₂, present in the FeCl₃ solutions, is the source of the organic gases.

In order to verify this assumption the reductions were repeated under CO₂ and under He continuous bubbling during the synthesis. The reactions were performed in a closed three-neck round bottom flask at room temperature. The iron particles thus prepared were immersed in the phosphate buffer and the system was shaken for 24 h. After that the gas concentration and composition

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Table 1
Organic gases emitted during the partial dissolution of metal nano-particles

Metal powder	CH ₄ (ppm)	C ₂ H ₄ (ppm)	C ₂ H ₆ (ppm)
Fe synthesized under He	12	–	–
Fe synthesized under Air	54.3	0.8	2.3
Fe synthesized under CO ₂	95.6	2.3	2.3
Ni synthesized under He	13	–	–
Ni synthesized under CO ₂	75.8	–	1.8
Co synthesized under He	7	–	–
Co synthesized under CO ₂	220.8	–	7.1

3 g metal powder in 3 ml phosphate buffer solution 0.1 M, pH 4.0, $T = 25\text{ }^{\circ}\text{C}$, $t = 24\text{ h}$. The product concentrations in the gaseous phase are reported. Error limit $\pm 15\%$.

were determined by GC. The results (Table 1) clearly demonstrate that the gas concentrations depend on the availability of CO₂ during the synthesis of the iron nano-particles. (The low yield of CH₄ for iron particles prepared under He is probably due to some air penetration during the addition of NaBH₄ to the reaction vessel.)

In order to check whether the CO₂ reduction occurs during the reduction of the iron ions or later on the surface of the iron nano-particles the following experiment was performed: iron nano-particles were synthesized under He and then stored for a week in bulbs saturated with air or CO₂. Then these particles were immersed in the deaerated phosphate buffer for 24 h and the yield of the organic gases measured. The results demonstrate that the yield of the organic gases does not increase due to the storage under air or CO₂. Thus the results clearly demonstrate that the CO₂ is reduced by the BH₄⁻ catalytically on the iron particles as they are formed. No reduction of CO₂ was observed in the absence of iron particles in blank experiments.

Analogous experiments revealed that CO₂ is also reduced during the preparation of nickel and cobalt nano-particles via the same procedure. The results are summed up in Table 1. The concentrations of the emitted organic gases increase dramatically when the synthesis is done under CO₂.

In order to check whether the organic gases stem from carbon atoms or organic compounds, adsorbed to the metal surface during the reduction, the following experiment was performed: nano-particles synthesized under CO₂ were activated by immersing them in H₂SO₄ (0.1 M) for 2 min and then washing the particles 7–8 times by 8 ml portions of pure water. This procedure clearly dissolves the surface of the particles and releases any compounds adsorbed to the surface. The results (Table 2) clearly demonstrate that the activation step increases the concentration of the emitted organic gaseous products considerably. Thus the results point out that the carbon atoms, formed in the CO₂ reduction

Table 2
The influence of the activation of the metal particles synthesized under CO₂ on gas emission

Metal powder	Activation	CH ₄ (ppm)	C ₂ H ₄ (ppm)	C ₂ H ₆ (ppm)
Ni	–	75.8	–	1.8
	+	110.7	–	2.0
Fe	–	95.6	2.3	2.3
	+	135	3.2	3.3
Co	–	220.8	–	7.1
	+	518	–	10

3 g metal powder, 3 ml phosphate buffer solution 0.1 M, pH 4.0, $T = 25\text{ }^{\circ}\text{C}$, $t = 24\text{ h}$. The product concentrations in the gaseous phase are reported. Error limit $\pm 15\%$.

process, are not adsorbed to the metal surface, but are incorporated in the metal particles.

The kinetics of the gas emission (Fig. 1) revealed different behavior for the different metals. In the case of iron the process is very quick and ends within 30 min, but in the case of Ni and Co the process continues for considerably longer periods. The different dissolution rates might be due to:

1. Differences in the redox potential: Fe (–0.44 V), Co (–0.28 V), Ni (–0.25 V).
2. Differences in the pH at which the metal is covered by hydroxides and/or phosphates, which inhibit the continuation of the process.
3. As the process is a heterogeneous one its rate depends on the surface structure of the nano-particles.

In summary the results demonstrate that:

1. The metal particles and/or metal–boron particles [4,7] are catalysts for CO₂ reduction by NaBH₄ during the metal powder synthesis.
2. Preparation of pure metal nano-particles requires a synthesis in the absence of CO₂.

Finally it is tempting to suggest that metal surfaces, metal clusters, might have acted as catalysts for CO₂ fixation, probably via the production of carbon atoms, carbides, or carbon clusters in the reductive atmosphere in the prebiotic era [9]. Then these carbon atoms, carbides were transformed into alkanes or alkenes upon contact with water.

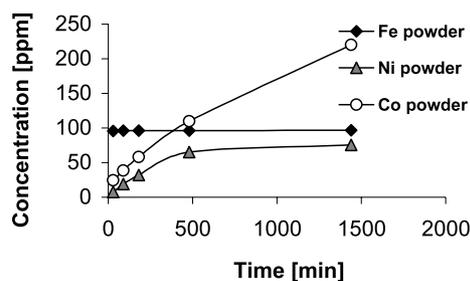


Fig. 1. Kinetic study of the CH₄ emission process. 3 g of non-activated metal powder, 3 ml phosphate buffer solution 0.1 M, pH 4.0, $T = 25\text{ }^{\circ}\text{C}$, $t = 24\text{ h}$. Error limit $\pm 15\%$.

3. Experimental

All the chemicals used this study were of A.R. grade and were used without further purification. The water used was deionized and further purified by a Millipore Milli-Q setup with a final resistivity of $>10 \text{ M}\Omega$.

The metal synthesis was performed in a three-neck round bottom flask at room temperature. The system was continuously stirred and bubbled with He or CO_2 when air presence was undesired.

Synthesis of iron nano-particles: NaBH_4 (10 g) in small portions was added to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (27 g) dissolved in 1 liter of pure water. The Fe^{III} ions are clearly initially reduced to Fe^{II} ions. After that the metal powder was filtered and dried.

Synthesis of Co and Ni nano-particles: NaBH_4 (6.5 g) in small portions was added to $\text{NiCl}_2/\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (23.8 g) dissolved in 1 liter of pure water. After that the powder was filtered and dried.

The phosphate buffer solutions (0.1 M) at pH 4.0 were deaerated by bubbling He through them for 15 min using the syringe technique. Then the solutions (3 ml) were introduced into He deaerated glass bulbs (15 ml) sealed with rubber septums containing the synthesized metal powders (3 g) which in some experiments were previously activated by H_2SO_4 (0.1 M) for 2 min followed by 7–8 washings with 8 ml portions of pure water.

The analysis of the gaseous phase was done on HP 5890 GC FID detector (Poropaq QS GC column 10 ft 1/

8 in. Supelco). The carrying gas was He (30 ml/min, $T = 70 \text{ }^\circ\text{C}$).

Acknowledgements

This study was supported in part by a grant from the Budgeting and Planning Committee of The Council of Higher Education and the Israel Atomic Energy Commission. D.M. wishes to express his thanks to Mrs. Irene Evens for her ongoing interest and support.

References

- [1] I. Rusonik, H. Polat, H. Cohen, D. Meyerstein, submitted.
- [2] S.M. Ponder, J.G. Darab, T.E. Mallouk, *Environ. Sci. Technol.* 34 (2000) 2564.
- [3] C.B. Wang, W.X. Znan, *Environ. Sci. Technol.* 31 (1997) 2154.
- [4] G.N. Glavee, K.J. Klabunde, C.M. Sorencen, G.C. Hadjipanayis, *Langmuir* 10 (1994) 4726.
- [5] G.N. Glavee, K.J. Klabunde, C.M. Sorencen, G.C. Hadjipanayis, *Langmuir* 9 (1993) 162.
- [6] Z. Hu, Y. Hsia, J. Zheng, J. Shen, Q. Yan, L. Dai, *J. Appl. Phys.* 70 (1991) 436.
- [7] S. Linderoth, M. Steen, *J. Appl. Phys.* 69 (1991) 5256.
- [8] S. Wells, S.W. Charles, S. Moerup, S. Linderoth, J. Van Wouterghem, J. Larsen, M.B. Madsen, *J. Phys.: Condens. Matter* 1 (1989) 8199.
- [9] S. Miyakawa, H. Yamanashi, K. Kobayashi, H.J. Cleaves, S.L. Miller, *PNAS* 99 (2002) 14628.