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Review

Nucleation, growth and properties of nanoclusters studied by radiation chemistry
Application to catalysis

J. Belloni

Laboratoire de Chimie Physique, ELYSE, UMR CNRS/UPS 8000, Université Paris-Sud, 91405 Orsay, France

Abstract

For more than three decades, extensive research work has been devoted to the unique properties of clusters. They are made of a small number (or nuclearity) of atoms or molecules only, and therefore constitute a new state of matter, with specific properties. New methods have been developed in physics and chemistry for their synthesis, their direct observation, the study of their properties, and of their crucial role in number of processes, such as phase transition, catalysis, surface phenomena, imaging. Owing to its specific approach, radiation chemistry offered first the opportunity to reveal the existence of nuclearity-dependent properties of clusters. Pulse radiolysis has then proven to be a powerful method to study the mechanisms of cluster formation, induced by irradiation as well as by chemical reduction, and the reactivity in solution or at the interfaces.

Keywords: Metal clusters; Core-shell structure; Alloyed clusters; Redox potential; Growth kinetics; Nucleation mechanism; Catalytic mechanism

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E-mail address: jacqueline.belloni@lcp.u-psud.fr.

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1. Introduction

Ionizing radiations are known since their discovery, X-rays by Roentgen in 1895 [1] and uranium rays by Becquerel in 1896 [2], to fog the photographic plates, that is to reduce silver ions into atoms, and finally into tiny metal clusters in the emulsion. Progressively, the chemical effects of the absorption of high-energy radiation by liquids were better understood. Particularly, since Fricke's works [3], it was established that the energy is essentially absorbed by the electrons of the solvent which are by far the most abundant. Solutes are only indirectly transformed in a secondary step when they react with the ions, radicals, molecules or excited states generated radiolytically from the solvent. A great deal of comparative studies by X- and γ-rays or electron pulse radiolysis of aqueous solutions of these solutes, used as radical scavengers, converged to the determination of the yields of ions, radicals and molecules produced in water by the radiation:

$$H_2O \rightsquigarrow e_{aq}{}^-,\ H_3O^+,\ H^\bullet,\ OH^\bullet,\ H_2,\ H_2O_2,\ HO_2{}^\bullet \qquad (1)$$

When noble metal ions were used as scavengers of the reducing radicals, colloids of zerovalent metal were indeed formed. However, the reduction yield presented some irreproducibility and discrepancy with the expected value, or some induction dose was required before the metal colloid appeared [4]. The phenomenon could be related to the well known but unexplained image regression of the latent image in photographic emulsions used for radiation track detection [5]. Moreover, Baxendale et al. [6] observed by pulse radiolysis that silver atoms Ag^0 or charged dimers $Ag_2{}^+$, produced by the scavenging of hydrated electrons $e_{aq}{}^-$ and radicals $H^\bullet$, were easily oxidized by oxygen back to Ag^+. All these facts contradicted the noble character of silver metal [4,5].

According to other results on the radiolysis of Cu^+, also used as a scavenger of reducing species in liquid ammonia [7], no copper clusters were formed and molecular hydrogen was instead produced, as in a subsequent corrosion of copper in its nascent state. We, therefore, explained all these apparent anomalies in concluding that atoms and aggregates of a few atoms presented, in this 'quasi-atomic state', a redox potential much more negative than the bulk metal, making them easily oxidable by oxygen or solvent. The specific properties of clusters were thus due to their highly divided state, constituting a new state of matter, or mesoscopic phase, as later named, between the atom and the crystal [8]. Walker's group [9] determined, by photoionization of transient zerovalent silver species, that their redox potential was lower than that of the bulk metal. Henglein [10] derived from a thermodynamical cycle that the redox potential of silver atoms in water was indeed $E^\circ(Ag^+/Ag^0) = -1.8V_{NHE}$ (2.6 V lower than that of the bulk metal $E^\circ(Ag^+/Ag_{met}) = 0.79V_{NHE}$). This was confirmed by the pulse radiolysis studies showing that atoms are oxidized by a series of moderate oxidizing molecules [11].

Since then, the nucleation of atoms, growth and properties of various metal clusters induced by radiolysis were actively investigated [12–14], as well as the conditions under which ultra-small metal clusters could be stabilized to be applicable to catalysis [12]. The main hypothesis to examine was whether the catalytic efficiency of a cluster could result, not only from its high specific area favoring encounters with the reactants, but also from the specific thermodynamical properties due to its low nuclearity [15]. Various types of catalyzed reactions were studied [12].

The aim of this review is to summarize how the radiation chemistry methods, in the continuous or the pulse regime, are unique tools to determine the mechanism of nucleation and growth of metal clusters and their nuclearity-dependent properties, and how these conclusions can be used to control the synthesis, by irradiation or by chemical methods, particularly in view of applications such as catalysis. The mechanism of some catalytic reactions have also been investigated by the pulse radiolysis method.

2. Radiolytic cluster formation

2.1. Metal ion reduction

The atoms are produced in solution by radiation-induced reduction of the metal ion precursors. The species arising from the radiolysis of water, solvated electrons $e_{aq}{}^-$ and $H^\bullet$ atoms (1), are indeed the strongest reducing agents. They easily reduce all metal ions, possibly complexed by a ligand, up to the zerovalent state M^0 (Fig. 1). In contrast, sibling radicals which are also formed in radiolysis, such as $OH^\bullet$ in water, are able to oxidize the ions or the atoms into a higher oxidation state. To prevent this oxidation, the solution is added with a scavenger of $OH^\bullet$ radicals such as secondary alcohols (Fig. 1) or formate anions. The secondary radicals formed, α-methyl-hydroxyethyl $H_3C{-}^\bullet COH{-}CH_3$ or formyl $^\bullet CO_2{}^-$ radicals, respectively, are almost as strong reducing species as primary $H^\bullet$ atoms (reaction (1)), also scavenged:

$$H_3C{-}HCOH{-}CH_3 + OH^\bullet\,(H^\bullet) \rightarrow H_3C{-}^\bullet COH{-}CH_3 + H_2O\,(H_2) \qquad (2)$$