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Zeolites as Scaffolds for Metal Nanoclusters

Eduard Fron

Abstract

This chapter critically reviews the studies related to structural and photophysical properties of metal clusters within zeolites matrices and summarizes the progress made in understanding the host-guest interactions. The goal is to provide useful insight into the nature of such interactions and experiments used in identifying the excited state dynamics and the reaction mechanisms leading to the emitting species. Especially interesting are the combined experimental and computational approaches used to elucidate the structures and electronic transition of clusters inside the cavity. Although a number of excellent research articles have been published in the last years they only cover rather specific areas like organic photochemistry, confinement, charge transfer, theoretical modeling or photostimulated luminescence.

Keywords: photophysics, structure, time-resolved spectroscopy, absorption, emission

1. Introduction

Noble metal clusters confined in restricted environment of zeolite possess remarkable absorption and emission properties, large Stokes shifts and, with a few exceptions, exceptionally high external quantum efficiencies (EQE's) which are of paramount importance in various processes and applications [1–10]. In the last years, a converging view is that the origin of their optical properties resides in their molecular-like characteristics as a result of a strong quantum confinement leading to discrete energy levels. However, these intriguing effects appear to depend not only on confinement but also on size, structure, and hydration level, charge state of the cluster and host-guest interactions. Electrostatic interactions between zeolite cavity and confined metal nanoparticles govern the photophysical properties of these materials. Metal clusters self-assembled in the well-defined cavities of aluminosilicate crystalline framework of zeolites possess the most fascinating optical properties because of the complex interaction that the clusters develop with the zeolite framework. This is probably the reason that fundamental research on such materials has been less attractive, perhaps because of the difficulties encountered in rigorous determination of the exact nature of these interactions. A number of questions are frequently asked. What is the nature of the electronic transitions and especially of the long-lived emitting species? Is there a charge transfer between zeolite framework and metal cluster involved in the excited state dynamics? Is the luminescence originating from recombination of electrons trapped or simply from species which are not strongly coupled to the zeolite structure? Is an intersystem crossing occurring upon excitation which

indicates a forbidden transition/relaxation and thus the long lifetime of the luminescent electronic state? What is the physics that determines which state decays radiatively and can we map the excited state dynamics?

This chapter critically reviews the studies related to the structural and photo-physical properties of metal clusters within zeolites matrices and summarizes the progress made in understanding the host-guest interactions. The goal is to provide useful insight into the nature of such interactions, methods and experiments used in identifying the excited state dynamics and the reaction mechanisms leading to the emitting species. Although a number of excellent research articles have been published in the last years they only cover rather specific areas like organic photo-chemistry, confinement, charge transfer, theoretical modeling or photostimulated luminescence [11–15]. The chapter is organized in three sections relevant to the interplay cluster-framework and seen from a mechanistic point of view that is further supported by various theoretical and experimental based studies like DFT, diffraction or time-resolved luminescence spectroscopy. The first part presents in short the structure and chemical properties of zeolites which is then followed by the progress in understanding the formation and structure of the metal clusters stabilized in the zeolite cavities, pores and channels. The last part sheds light onto the electronic properties and the origin of intense luminescence and how these depend on the interplay between cluster and framework. Especially interesting are the combined experimental and computational approaches used to elucidate the structures and electronic transition of clusters inside the cavity. Particular emphasis is then placed on various debated mechanisms as models to address the quantized electronic interaction which can lead to new insights into their optical, luminescence, crystal habit, metal-core, ligand-shell, and environmental properties [16].

2. Structure and chemical properties of zeolites

As one of the most important materials used in catalysis, adsorption or ion exchange, zeolites have triggered the interest of scientists because of their structural elements, such as cavities, pores and channels as well as their catalytic properties [10, 17–22]. The molecular-sized open framework forming a periodic array of void spaces, enables confinement of guest particles or molecules and opened interesting research areas like metal-to-insulator transition, charge transfer, solvation and production of trapped electrons [12, 23]. Since their discovery in 1756 the molecular sieve properties are being increasingly used in industry in applications as chemical sensors, medical monitoring or air separation, to name a few [11].

The microporous crystalline aluminosilicate consist of 3-dimentional Si-O/Al-O bond tetrahedral framework of nearly spherical cages connected through sub-nanometric windows with alkali or alkaline earth metals as counterions (**Figure 1**) [24–27]. Basically, they consists of a structure of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra connected via their oxygens. They have the general formula: $(\text{M}^+)_x [(\text{AlO}_2^-)_x (\text{SiO}_2)_y] \cdot m\text{H}_2\text{O}$ where M^+ indicates the alkali metal cation. Depending on how they are connected, the tetrahedra form a three-dimensional framework with pores, channels and cavities [11].

The framework is negatively charged in the zeolites containing aluminum and this is due to unbalanced charge of the $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ primary building units (PBUs) which needs to be compensated by the cations. The cations and, eventually, water molecules are distributed inside the cavities which, when aligned, become channels. The presence of H_2O molecules inside the cavities is the reason why zeolites can be hydrated/dehydrated by changing the sample temperature. The PBUs combine by sharing oxygens with adjacent tetrahedra to form a spatial

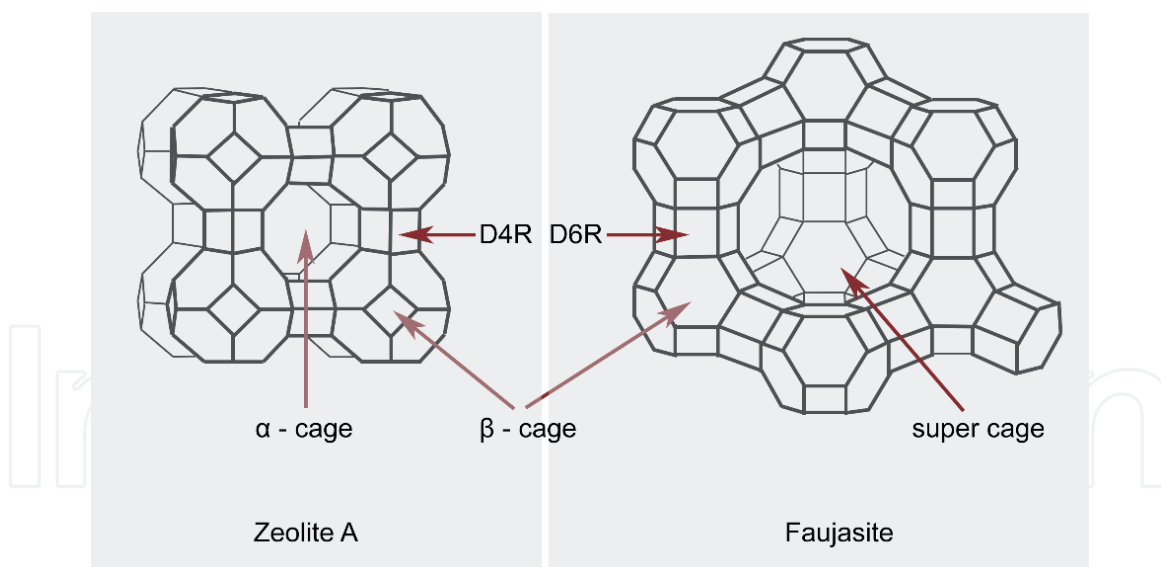


Figure 1.
Framework structure of sodalite-based zeolites.

arrangement of simple geometric forms named the secondary building units (SBU). The crystalline structure is a net product of the special arrangement of SBUs resulting in a large variation in type and morphology of different species of zeolites. The type of zeolites mostly employed in stabilization of metal clusters are A (LTA), FAU (faujasite), and ZSM-5. However, other zeolite morphologies exist while their composition is not limited to the aluminosilicate. For the purpose of this chapter we will limit the description of morphologies to the ones mentioned above.

The structure of zeolite A (LTA) is rather simple and results from connecting the same building unit (β -cage) through a pair of D4R rings (**Figure 1**). Such an arrangement generates a structure with three type of cavities: a D4R square cuboid, an α -cage and of course, the β -cage (**Figure 2**). The largest void present is the α -cage with a diameter of 11 Å and a window of 4.1 Å limiting the size of the potential guests.

Faujasite zeolites exists in two structures X and Y, both constituted from β -cages building blocks. The diameter of the β -cage is 6.6 Å while the window is 2.1 Å and connects to the frame via double D6R. This small window size prohibits the molecular oxygen entering the cage while this remains accessible to water molecules. The difference between X and Y frameworks consists simply in a different Si/Al ratio which is between 1.0 and 1.5 for zeolite X and 1.5 and 3 for zeolite Y. Interestingly, such assembly of β -cages gives rise to a quasi-spherical super cage (**Figure 1**) with a diameter of almost twice the β -cage 13 Å and a window size of 7.4 Å. The mobile counterions needed to compensate the framework charge are distributed inside the β -cage, on the hexagonal faces, at the interface of the supercage 4-ring and D6R unit.

In contrast to LTA and Faujasite topologies, ZSM-5 uses a 5 ring as building unit resulting in a zeolite framework with two type of channels having diameters of 5-6 Å and lengths up to 500 μm . L-type zeolite have a unidimensional channel system as in the mordenite, formed by 6- and 4-membered rings (**Figure 3**).

It is worth mentioning that the electronic structure of the material is in fact a superposition of that of the framework, co-cations, solvent molecules and, eventually, the guest molecules of clusters. The optical bandgap can be as high as 7 eV [2].

The concept of Zeolites as 'solvent' has been introduced by Hashimoto [11] to indicate that the pores and cavities can be used to "dissolve" guest entities. The combination of negatively charged framework and cations possessing a large degree

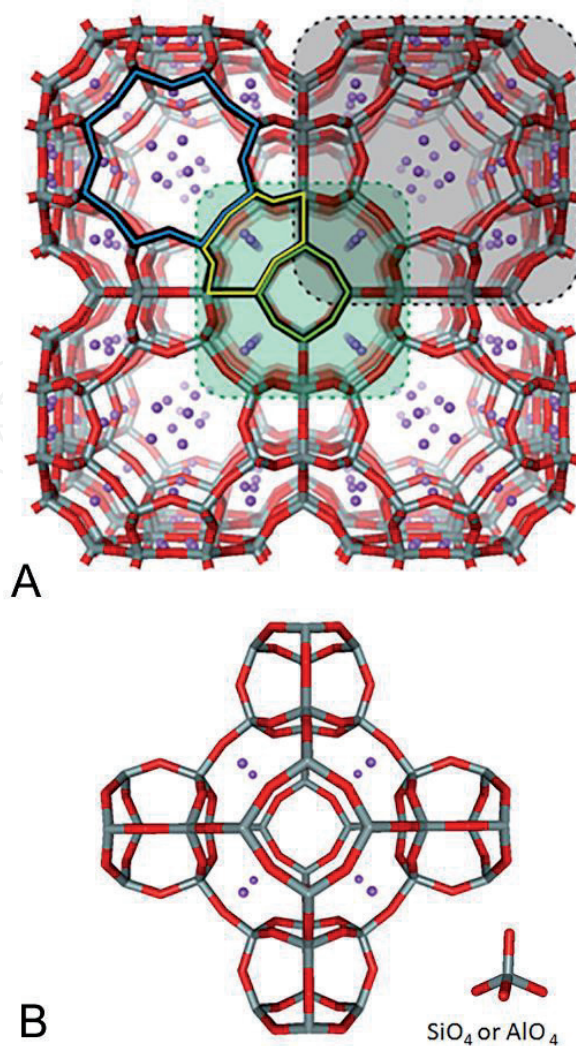


Figure 2. Schematic representation of (A) LTA unit cell displaying the sodalite (green dashed area) and super cage (gray dashed area); the eight ring (8R), six ring (6R), and double four rings (D4R) are highlighted in blue, yellow and green respectively, (B) isolated sodalite cage with D4R connectors.

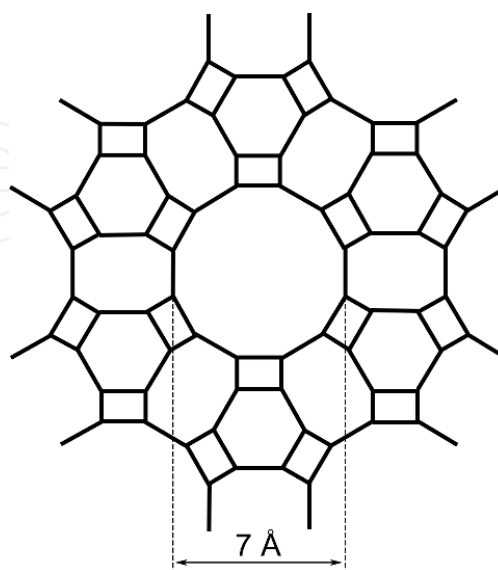


Figure 3. The block unit of zeolite L.

of freedom produce an electrostatic field in which the guest particles are dispersed. Locally, the electric field strength is believed to be extremely high as its intensity hinges on both cation size and Si/Al ratio [28]. In this light, a large number of

molecules have been encapsulated into the zeolite cavities to probe the local electrostatic field and the effects induced by the zeolite framework [29–31].

Exceptional photophysical and photochemical properties are observed when the zeolite crystal dimension is reduced from micrometer size to extremely small nanometer particles with a distribution centered at 10–15 nm [1]. While the micropore volume remains comparable to their corresponding micrometer-sized crystals, the resulted high external surface area, $180 \text{ m}^2 \text{ g}^{-1}$, opens a number of opportunities for processes taking place specifically on this part of the zeolite. The presence of silanes changes the Si/Al ratio and the surface charge of the nanosized zeolites and also the crystal size [8].

3. Formation and structure of the metal clusters in zeolite framework

3.1 Progress

Already in the years 1970s, the high temperature hydrogen reduction of Ag ion to metallic silver in zeolite Y was known but it was only in 1978 when Kellerman and Texter reported the first optical measurements [32]. By measuring the Shuster-Kubelka-Munk re-emission function and fluorescence of a vacuum dehydrated sample of silver clusters they presented and characterized for the very first time the excited electronic state of monodispersed atoms as well as optical absorption of collaterally produced clusters and particles. They assigned the broad absorption peaking at 3.3 eV to “intrazeolitic silver particles”. The results triggered a large interest among scientist. Three years later Gellens *et al* reported the formation of the so called “color centers” in Ag-A zeolites, as a result of the reduction of Ag^+ ions upon dehydration. The authors assigned the process to the formation of linear Ag_3^{2+} clusters with Ag^0 located inside the sodalite cage opposite the framework D4R and in between two Ag^+ cations located at the D6R [33]. It was then believed that the yellow color is due to isolated cluster whereas the observed red color was associated to the formation of two or more interacting Ag_3^{2+} clusters in the sodalite cage to a maximum of four.

As stated above, the silicon-to-aluminum ratio is an important parameter of zeolite as this determines the number of exchangeable cations. In 1984, Johnson *and al.* detected distinct species following the reaction of sodium-exchanged zeolite Y with sodium, potassium, or rubidium vapor in dehydrated samples of zeolite Y [34]. Upon exposure to high concentrations of metal vapor he obtained stable ionic clusters (Na_4^{3+} , K_4^{3+} and Rb_4^{3+}) characteristic of small metallic particles located inside the zeolite cavities. Also interesting is that the researchers observed cluster species Ag_6^{q+} ($q = 1, 3, 5$) in which an unpaired electron is trapped at a cluster of six equivalent silver cations. In the same year ESR measurements on silver particles in zeolite A proved that during the reduction of silver-loaded zeolite A certain stages of cluster formation can be followed and detected the presence of Ag_6^{x+} and Ag_8^{y+} clusters which fit in the sodalite cage [35]. Two years later, Wang and Herron succeeded in encapsulation of CdS and PbS in zeolite Y matrix and indicated that zeolites can be thought as providing a solid solvent for this type of clusters [36]. Impressive work since, through simple experiments, they showed that their optical properties were dependent on size and state of aggregation, a property well-known already for metal particles. A fascinating conclusion was drawn: due to the fact that the transition from clusters to aggregates is not continuous but abrupt they suggested that aggregation inside the zeolite is a percolative process.

The first important review on the structure and chemistry of silver clusters in zeolites has been published by Sun and Self and the reader is encouraged to read

this excellent work which inspired many scientists [9]. The spectroscopy and light induced processes of silver clusters in zeolites have been incipiently discussed by Chen *et al.* [37] For the first time they looked at photostimulated luminescence of silver-exchanged zeolite-Y. Once irradiated with 254 nm wavelength, the photoluminescence intensity of silver atoms centered at 505 nm decreases and a new absorption band shows up around 840 nm. By photostimulation of this absorption band, the fluorescence of silver atoms is observed and the photoluminescence intensity of silver atoms increases slightly. These phenomena were considered to be caused by the charge transfer between the zeolite framework and the entrapped silver atoms. The photostimulated luminescence of silver clusters encapsulated in zeolite-Y was caused by the recombination of luminescence centers with electrons released from their traps by photo-stimulation. Charge transfer from the framework oxygens to silver cations was also reported by Seff and Kim based on a color change from brick-red to yellow [38].

Following the pioneering work presented above, small metal particles started to attract the real interest of scientists due to their peculiar optical, electronic and catalytic activity that change from bulk properties to molecular-like properties once the size decreases under a certain range. For instance, a change in the electronic properties from a band structure to molecular orbitals levels was common for isolated species of a few atoms particle. Such change was almost invariable of the nature of the constituent atoms. Of a particular interest was to control the size and coordination because these would allow fine-tuning of electronic and luminescent properties of the clusters. However, to achieve that, a deep understanding of the electronic state was much desired. Based on such understanding the revealed structure-to-function relationship could finally open perspectives for practical applications.

The exact structure of metal clusters stabilized by the zeolite matrix remained under debate for a long time. Gellens *et al.* investigated the electronic properties of silver clusters using extended Hückel framework [39]. They calculated isolated Ag_3 molecules in linear or nearly linear geometries and a strong similarity with the electronic spectrum of yellow Ag clusters were found. The proposed model for Ag_3 engaged in the zeolite framework appeared to be weakly interacting with the zeolite lattice. Very interesting is that the scientists suggest the occurrence of an electron transfer of approximately two electrons from the cluster toward the zeolite framework increasing the charge density on the Si/Al model.

Until 1990s, simple structures as dimers and trimers of alkali-metal elements or noble metals were only experimentally investigated with UV-VIS and IR spectroscopy, Raman, ESR and EXAFS techniques [40–42]. These experiments indicated various shapes such as linear, bent or triangular structure and even interconversions between such structures were proposed. Precise studies of the effect of cluster shape, structure and interactions with the zeolite environment have been rather limited mainly due to a combination of instrumentation and techniques used. Other difficulties were found due to a distribution of particle size or problems with high mobility of precursors. Zeolite X and Y have been utilized as scaffolds to restrict and stabilize metal agglomeration. In such matrices, for instance, geometric models based on EXAFS experimental results revealed the formation of Pd_2 , Pd_3 and Pd_4 clusters occupying adequate positions of the sodalite cages [43]. This showed again a “molecular” cluster elegantly stabilized in an open-framework zeolite. Texter *et al* encountered similar difficulties when investigated the formation of charged silver clusters of activated dehydration of zeolite A [44]. The nuclearity of these clusters formed in the sodalite unit was uncertain, believed to be between 6 and 14 while the dominant cluster had an absorption band centered at 2.72 eV and a higher band at 3.8 eV. Closely, more details about the cluster nuclearity and interactions

with the framework have been brought via far-infrared experiments [45]. The cage vibrational mode characteristic for Ag_0 atoms isolated in zeolite Y has been identified at 89 cm^{-1} while silver-silver stretching modes were identified for zeolites A and Y encapsulated Ag_n^{q+} clusters with $n = 2, 3$ and 6 . Via IR spectroscopy the presence of silver microcrystals located on the external surface of zeolite has been also demonstrated. Although important steps have been made, the structure of the metal cluster remains largely uncertain and very few have succeeded in providing strong evidences. Spectroscopic experiments, although widely qualitative, remain the basis in identifying a cluster species. Generally, larger clusters give rise to lower optical bandgap and inconsistencies in assignment of these bands were sometimes observed in literature.

A first attempt to establish the structure of the model Ag clusters in zeolite sample was made in 2004 by employing a combination of steady-state spectroscopy and K-edge XANES/EXAFS analyses [46]. The absorption spectra showed bands at 255 and 305 nm and from Ag K-edge EXAFS results, the structure of the cluster was presumably identified as Ag_4^{2+} . The coordination number 3.3 and the Ag-Ag distance of 2.7 Å suggest that the cluster consisted of 3 or 4 Ag atoms. The amount of the clusters increases with the Ag/Al ratio of Ag zeolites. Further spectroscopic investigations on very small particles Ag_2S and PbS in zeolite A showed photoluminescence in the visible range and lifetimes as long as 300 μs and these properties were shown to be strongly dependent on co-cations [47]. A broad investigation has been carried out for Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , and Sr^{2+} . Interestingly, the unusual long luminescence lifetime has been interpreted as excitation energy transfer between Ag_2S and Ag_4S_2 , a concept that comes often forward in literature.

3.2 State of the art

The long pathway laid and impressive work of scientists toward structural characterization of metal clusters provided a momentum wisely used by the recent scientists who combined time-resolved spectroscopy, X-ray excited optical luminescence (XEOL), electron spin resonance (ESR), X-ray crystallographic, Ag K-edge Extended X-ray Absorption Fine Structure (EXAFS) and density functional theory (DFT), time-resolved density functional theory (TD-DFT), X-ray photoelectron spectrometry (XPS), and used all the tools at hand to reveal with astonishing details the shape of these “molecules” and tag their luminescence properties [2–5, 11, 48–50].

A general and versatile synthesis protocol used for encapsulation of metal clusters within zeolite micropores enabled selective incorporation of a broad range of metals (Pt, Pd, Ir, Rh, and Ag) within NaA, a zeolite with channel windows too small for post synthesis encapsulation of metal precursors [51]. Encapsulation provides protection for clusters against sintering and contact with toxic impurities within environments. Better conditions of stabilization of Ag and Cu clusters in zeolite voids with formation of a self-assembled clusters system were found by Gurin *et al.* [52] As expected, zeolite voids could incorporate and stabilize clusters of smaller size than a void size. A few geometric structures have been proposed fitting erionite and mordenite voids (0.63–0.70 nm). The structures belong to the following point groups: Oh (cube), Td (tetrahedron), D4h (rectangular parallelepiped), and C2v (3D polyhedron). A stable geometry (rhombus) is found for Ag_4^+ in accordance with calculations presented earlier.

Restricted by the chapter size, we will further focus on the case of Ag clusters as these appear to be representative for these class of luminescent systems [49]. In this field, notable studies investigating the geometry and energetic properties of Ag_n clusters $3 \leq n \leq 6$ have been carried out using density functional theory

(DFT) calculations. FAU topologies predominantly accommodate Ag_2 , Ag_3 , Ag_4 and Ag_8 clusters while LTA frameworks prefer Ag_3 and Ag_6 clusters [3–5, 9, 33, 39, 53]. A number of geometries have been optimized inside a ZSM-5 zeolite whose ten-membered ring contains different numbers of Al atoms substituted for Si atoms of the SiO_2 framework. For Ag_5^+ , a ditrigonal orthogonal geometry appeared as the most energetically stable configuration while a triangle Ag_3 cluster while for Ag_4 both a square and a tetragonal clusters have been considered. Ag_6 clusters inside ZSM-5(Al1) and ZSM-5(Al2) cavities preserve two stable configurations: a tetragon pair with a shared bond and edge and a pair with shared bonds [54]. DFT calculations also show that the cluster has two 5 s electrons populating the totally symmetric frontier orbitals, which leads to a stabilization of the cluster structure. The totally symmetric 5 s-based orbital corresponds to a super atom S-orbital. The optical transition modeled through time-dependent DFT calculations attributed the absorption peaks to an electronic transitions based on 5 s-type orbitals from the totally symmetric occupied orbital (S-orbital) to an unoccupied orbital with one node (P-orbital) [54].

The curious case of Ag_3 cluster. Experimental crystallographic data showed that Ag_3^+ and Ag_3^{2+} clusters form a linear configuration (with the later slightly bent) along the 3-fold axes through double six-rings of dehydrated zeolite X [55]. A weakly attractive interaction between $\text{Ag}^+ - \text{Ag}^+$ could be concluded. Later, the assumption of a linear clusters has been confirmed by Zhao *et al* in a comprehensive series of DFT calculations [56]. The optimized geometries and binding energies of the most stable Ag^n , Ag^{n-} , Ag^{n+} , Ag^nH , Ag^nH^- and Ag^nH^+ with $2 \leq n \leq 7$ showed remarkable odd-even alternation behaviors. Silver behaves like an alkali-metal atom in the interaction between H and silver clusters. Surprisingly, in a different and fascinating DFT modeling study, the geometry of Ag_3 inside the void of ZSM-5 was demonstrated as a triangle and that the Ag-Ag orbital interaction as well as Ag-O electrostatic interactions determine such a different structure [57]. The structure is the same in both lower and high spin states, however, the high spin state leads to two types of triangles significantly distorted from the D_{3h} configuration. The authors also established that the structural and electronic features are governed by the number of Al atoms through Ag-Ag and Ag-O interactions. The modeling calculations support both a linear and a triangular structure [58].

Ag_4 , a clear tetrahedron. Using already classical X-ray absorption measurements, the geometry of Ag_4 cluster has been carefully investigated in the FAU or LTA topologies [3–5, 48, 49, 59]. About 67% of Ag atoms constitute the oligomeric Ag_4 clusters and found located inside the sodalite cage [4]. Each Ag atom is bonded in to 2.2 water molecules and surrounded mostly by ca. 33% of Ag isolated cations located at the center of the S6R rings of the sodalite cage (18%) and in the center of the hexagonal prisms connecting the sodalite cages (15%). The fully Ag-exchanged sample FAUY contains a similar Ag_4 geometry, with the difference that the cation distribution is slightly changed with of Ag_4 cluster surrounded by ca. 25% of silver ions located close to the center of the S6Rs and ca. 13% of silver atoms located in the center of the hexagonal prisms. This excellent study is particularly interesting for its extensive characterization which indicates a strong and direct influence of silver loading and host environment on the cluster ionization potential. This new finding is also correlated to the cluster's optical and structural properties. By fine-tuning of the zeolite environment the researches achieved clusters with photoluminescence quantum yield approaching unity. Another Ag_4 cluster (dehydrated $\text{Ag}_1\text{Li}_{11}$ -LTA zeolite) was found to feature a remarkable EQE of 83% with an emission maxima around 545 nm when excited between 300 and 400 nm [48]. The presence of Li^+ clearly changes the luminescence properties of this cluster in two ways: by shielding the interaction between cluster and zeolite oxygen framework and by contraction of

the lattice parameter leading to a tightly confined cluster inside the sodalite cage of LTA zeolite.

The octahedron cluster, Ag₆. Using a different, Ag clusters in LTA and FAU zeolites have been characterized via luminescence properties which were shown before to depend on the nature of the co-cation, the amount of exchanged silver, and the host topology. A broad pallet of emissive species Ag_n,Na-X and Ag_n,Na-Y, $1 \leq n \leq 12$ were observed with spectral properties ranging from 380 to 700 nm and further used as “fingerprint” in cluster type identification [3]. The luminescence decays on a time scale ranging from ns to μ s and the transitions were attributed to excited state processes involving spin forbidden transitions and intersystem crossing. A singlet-triplet transition in the case of Ag₆²⁺ cluster or a doublet-quadruplet transition in the case of Ag₆⁺ have been suggested. Similar long luminescence decay times were also found in other types of silver-zeolite systems. The exact structure of each luminescent species and the nature of the luminescent electronic state still remain a subject of investigations. The structure of hexasilver molecule Ag₆⁰ has been further resolved by the group of Seff *et al* via single crystal diffraction experiments and showed that these crystals contains octahedral subunits [60]. Ag₆⁰ had formed in varying amounts in up to 60% in the sodalite cavities of the crystals studied. The hexasilver was shown to be surrounded by eight Ag⁺ ions distributed in a cub, one in each face of the octahedron. In addition, the presence of even larger clusters is Ag₈⁺ or Ag₁₄⁸⁺ was detected.

4. Electronic properties and the origin of intense luminescence

Validated by various research groups, the photophysical properties of metal clusters engaged in zeolite matrices are strongly dependent on numerous factors like ligand, spatial confinement, charge state, water content, electrostatic charge of the cavity or co-cation type [11]. Perhaps one of the largest scientific debates among scientist in this field is understanding the size dependent properties of a metal cluster [9]. Although the strong quantum confinement of the electrons separating the continues density of states into discrete energy levels is generally recognized as the origin of the optical transition, the fundamental photophysical mechanisms underlying their emission are poorly understood [61]. Metal clusters in various size regimes display molecule-like optical characteristics featuring HOMO-LUMO bandgap with transition to metal properties at high nuclearity. Obtaining well-defined clusters often remains questionable in designing nanostructures with specific functional properties. An understanding of both structural and electronic features by invoking their familiar aspects like the discrete electronic shell has led to a few concepts which attempt to rule the characteristics of the molecular-like entity. Substantial theoretical and computational efforts were made to understand and predict the fundamental properties associated with the existing and emerging metal clusters and develop a general valid theory [4, 7, 16].

In the examples presented earlier, the intense or dim luminescence has been attributed to various phenomena occurring in the excited state, effects mainly related to intersystem crossing (leading to phosphorescence), charge transfer and recombination, ion migration or structural changes [12, 62, 63]. Intriguingly enough, limited time-resolved spectroscopy experiments have shown that the luminescence decays on time scales ranging from fs to ms, a characteristic similar to molecules undergoing a complex excited-state dynamics. Several kinetic schemes have been proposed indicating luminescence either as a spin forbidden radiative transition to the ground state (phosphorescence) or recombination of electrons and holes trapped in the zeolite matrix (fluorescence) [2, 13, 59, 64].

The electronic configuration of the main constituent atoms Cu, Ag, and Au is situated at 3d, 4d, and 5d period, respectively. When a silver atoms with an electronic configuration of $4d^{10}5s^1$ forms a cluster, the electronic properties are determined by the frontier orbitals resulted from a linear combination of the 5 s orbitals [50, 54]. The 5 s orbitals can be regarded within the concept of “super atom” in analogy to the orbitals in hydrogen-like atoms. In gas-phase, clusters are assumed to behave like giant atoms and obey the same rules as atoms. Similarly, principles like orbital hybridization or Hund’s rule can be applied. Inspired by the Jellium model, the confined electrons move within a smeared positive region that is evenly distributed over about the cluster volume [65]. In this model, the frontier orbitals with different numbers of nodes can be classified as S, P, and D and have an angular momentum quantum number $L = 0, 1,$ and 2 for the S, P, and D orbitals, respectively) corresponding to the number of nodes of the 5 s-based orbitals.^{67,72} In this light, the magic number of bare silver clusters and the selection rule in their electronic transitions ($\Delta L = \pm 1$) can be resolved [7, 66].

Utilizing the super-atom orbital concept to understand properties of silver clusters inside ZSM-5 zeolite, Yumura *et al.* investigated the energetic properties of Ag_n clusters by using DFT and TD-TDF calculations [54]. TD-DFT optimized geometries of Ag_n -ZSM-5(Al_m), where $3 < n < 6$ and $1 < m < 5$, showed an intense oscillator strength at the electronic transition between 5 s-based orbitals from the totally symmetric orbital (S-orbital) to that with one node (P-orbital). The $S \rightarrow P$ electronic transitions obeys the selection rule for cluster in gas-phase. Previously, DFT calculations of the Ag_3 and Ag_4 clusters inside a 10-membered ring of the ZSM-5 zeolite showed that photon absorption is due to a transitions from a completely symmetric 5 s-based orbital to a 5 s-based orbital with one node [67]. The absorptions spectra are “modulated” or strongly affected by the encapsulations as this induces cluster distortion leading to interactions between clusters and the framework oxygen atoms. The optical properties of Ag_4 and Ag_6 encapsulated inside the sodalite cavity of LTA zeolite were investigated using similar DFT and TD-DFT methods by Cuong *et al.* [50] Hydrated quadruply charged silver hexamer features a strong absorption band at 420 nm which is very sensitive to its charge. In the case of hydrated doubly charged silver tetramer cluster, the absorption band shifts slightly and steadily to lower energy with the increasing amount of interacting water molecules. The presence of water molecules pushes the silver tetramer away from the cavity center. Water molecules take the role as ligands and induce a splitting of the energy levels of excited states of both Ag_4^{2+} and Ag_6^{4+} clusters. As we will see bellow, this splitting causes the optical properties of the clusters to change significantly.

In a remarkable study, Grandjean *et al* investigated the structure and electronic properties at the origin of the luminescence of Ag_4 clusters confined in Ag-LTA-zeolite by a unique combination of XEOL-EXAFS, (TD)-DFT calculations and time-resolved spectroscopy [5]. XEOL experiments showed that the species at the origin of the bright green luminescence observed in Ag_3K_9 -exchanged LTA zeolites are Ag_4 clusters with short Ag-Ag distances of 2.82 Å in which each Ag atom is bonded in average to 2 water molecules at 2.36 Å. This results suggested the presence of two isomers $Ag_4(H_2O)_4$ and $Ag_4(H_2O)_2$ clusters with a 40/60 ratio in this Ag_3K_9 -LTA sample. DFT calculations confirmed the presence of the two stable isomers. The best agreement between both the calculated structures and absorption spectra with those measured experimentally were obtained when applying a + 2 charge preferentially localized on the Ag_4 cluster. The calculated frontier orbitals for both $Ag_4(H_2O)_4^{2+}$ and $Ag_4(H_2O)_2^{2+}$ isomers are a superposition of 50% from Ag 5 s atomic orbitals and of up to 25% from the oxygen states of the surrounding framework oxygens and water molecules. The lowest cluster configuration is formed from a doubly occupied 1S_0 HOMO of totally symmetric s-type and two sets

of three singlet 1P and three triplet 3P LUMOs of p-type character with one node which corresponds to the assumed two electron model cluster. The coordination with water molecules lifts the degeneracy of the LUMOs orbitals. As a result LUMOs in $Ag_4(H_2O)_4^{2+}$ and $Ag_4(H_2O)_2^{2+}$ clusters are split into six excited states i.e. three singlet $^1P(S = 0, L = 1, m_l = -1, +1 \text{ or } 0)$ and three triplet $^3P(S = 1, L = 1, m_l = -1, +1 \text{ or } 0)$ states. Due to the quasi isoenergetic position of the high-energy triplet $^3P(S = 1, L = 1, m_l = 0)$ state with the 1P singlet states corroborated to a silver large *spin-orbit* coupling, an intersystem crossing takes place. Photon absorption promotes the clusters in the excited singlet state. A fraction of 1P singlet states population is transferred to the high-lying triplet state that finally decays via internal conversion into the low-lying $^3P(S = 1, L = 1, m_l = -1 \text{ or } +1)$ triplet state. Although a spin forbidden process, the bright green emission takes place as a radiative transition from the lowest triplet excited state $^3P(S = 1, L = 1, m_l = -1)$ to the ground singlet state 1S_0 .

5. Conclusions and outlook

Even though the super atom model could provide a qualitative description of the luminescence properties, the exact picture to contain the dynamics and kinetics of electron transition of the excited state remains blurred. By judiciously manipulating the interactions at the interface between cluster and zeolite framework together with a careful calculation of time-dependent density functional theory, a few proposed kinetic scheme claim to elucidate the long-lived emitting state. Simply considering an excited state intersystem crossing process followed by a radiative decay to the ground state would not fully explain the presence of a complex array of decay components observed on a fs and ps time scales, decay observed in the photophysics of many clusters. Ultrafast decay components would indeed indicate the occurrence of an intersystem crossing phenomena but can also suggest internal conversion or fast structural relaxation which are so common for molecules. The ns components would suggest decays between states of the same spin multiplicity, like fluorescence. Are these components considered at all when concluding the excited state dynamics? Why do these emissions indicate a Stokes shift as large as $12\text{--}15000\text{ cm}^{-1}$? Are there other intermediate states that are not yet experimentally revealed? When all is said and done, are all the fruits from the tree harvested?

As shown above, the lack of full understanding of the photophysics of metal clusters resides in its optical properties which depend on so many factors including cluster size, temperature, surface ligands geometry, cluster assembly structure, humidity, etc. One think is clear. Dedicated time-resolved spectroscopy techniques like transient absorption and fluorescence up-conversion at the femtosecond scale should come more consistently into play to provide precise and reliable information. Only then a complete picture of the relaxation and decay pathways of excited electrons immediately after the population of the Franck-Condon state can be achieved. More modern time-resolved spectroscopy techniques, like for instance X-ray diffraction based on X-Ray Free-Electron Laser (XFEL) methods, could elucidate changes in structural dynamics immediately after excitation. Most importantly, with respect to the paramount importance, universality and complexity of the model, the experimental part, be that spectroscopy, diffraction or ESR techniques, should take the first place in providing the arguments while modeling and computation could shortly support the experimental findings. Only when a complete picture of the excited state processes is achieved one can tune the electronic structure and thus interfere with the optical properties of the metals clusters. Hence, the advance achieved will be of immediate interest to a broader pool of researchers and will open real pathways for practical applications.

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