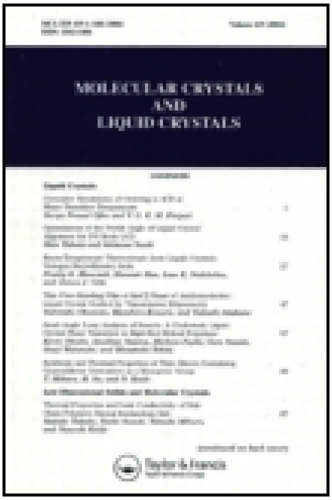

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Reactions in Low Temperature Solid Co-Condensates and Size Effects

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Reactions in Low Temperature Solid Co-Condensates and Size Effects

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The interaction of magnesium atoms, clusters and nanoparticles with different organic and inorganic substances were studied in low temperature solid co-condensates. A combination of matrix isolation techniques and preparative cryochemistry was applied to distinguish the activity of metal species of different sizes.

Keywords: clusters; cryochemistry; magnesium atoms; matrix isolation; nanoparticles; solid co-condensates

INTRODUCTION

At the present time, the attention of many scientists in the fields of physics, chemistry, materials science and biology is devoted to nanoparticles; their synthesis, properties and different reactions. The reason for this lies in the fact that particles of nanometer size show new properties.

The most interesting subject is the connection of chemical properties of metallic particles with their size [1]. Small metal particles with sizes in range from 1 to 10 nm exhibit high and sometimes unusual chemical reactivity, and show a strong variation in their activity depending on cluster size. These are size effects in nanochemistry. Currently, the most successful areas are the study of such effects in gas phase reactions and chemisorption [2].

Low and super-low temperatures may be also used for distinguishing the activity of metal atoms and nanoparticles. This method is based on a combination of matrix isolation techniques and preparative cryochemistry.

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GENERAL REMARKS

In our investigations, we used the condensation of reagent vapors on a cooled surface in special cryostats under conditions which exclude interaction in the gas phase. The scheme in Figure 1 illustrates the fundamental possibility of using low temperature in order to obtain metal clusters, mono- and polynuclear metal complexes and ligand-stabilized nanoparticles. It is important that every possible line in this scheme should be considered as a kind of nanoreactor.

Chemical interactions in low-temperature co-condensates begin with metal atoms. Addition of ligand into the systems may cause the formation of metal particles of different size and their stabilization or reaction with ligand molecules. The aggregation of metal atoms and interaction with ligands occurs practically without an activation barrier.

The high reactivity of small metal species is the main difficulty in establishing the relation between the size of the particles and their chemical activity. There are also problems in producing and isolating the compounds with definite compositions. The reactions shown in scheme Figure 1 are complex multifactor processes taking place under non-equilibrium conditions. Low temperature co-condensates possess internal accumulated energy.

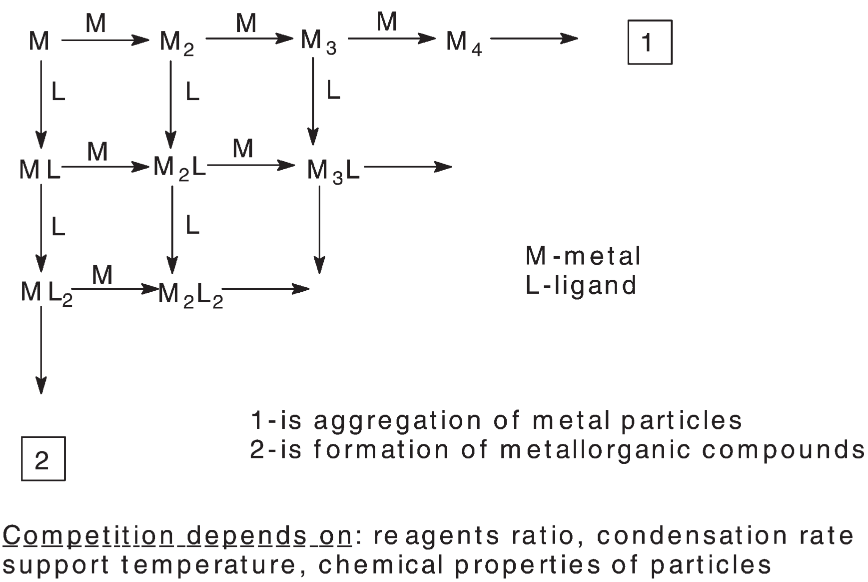

FIGURE 1 Dependence of chemical activity on size of particles.

The size of metal particles and their reactivity are determined by a combination of different experimental conditions. The main experimentally controllable factors are the substrate temperature, metal/ligand ratio, reagent condensation rate, and the rate of sample annealing. Together with the chemical nature of the reagents all factors mentioned determine the pathway of processes.

The general scheme of our cryochemical synthesis and reactions with metals, encapsulated in organic or inert polymer matrices, are presented in Figure 2. The first step is the co-condensation of metal

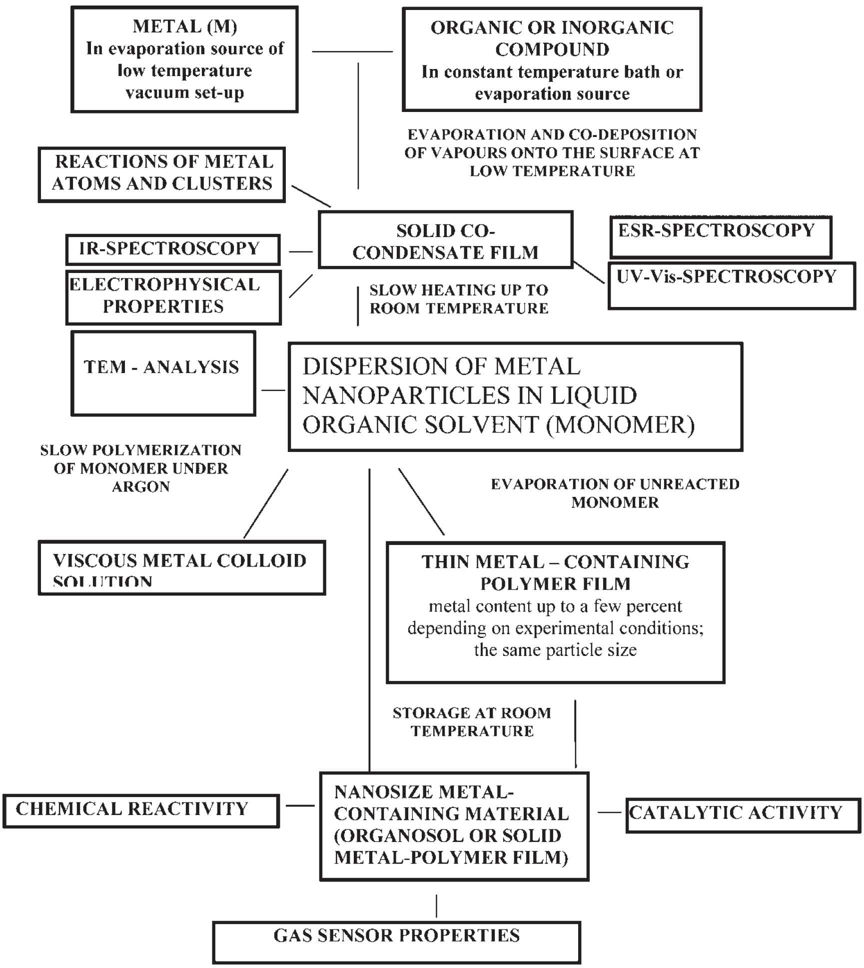

FIGURE 2 Cryochemical synthesis of nanosize metals encapsulated in organic and polymer matrices.

Relative fields of chemistry depending on particle size and number of atoms it contains.

Chemistry of atoms	Nanochemistry					Solid State Chemistry
	Number of atoms in the particle					
Single atoms	10	10^2	10^3	10^4	10^6	Bulk compound
Particle diameter, nm	1	2	3 5	7	10	> 100

FIGURE 3 Size effects in chemistry.

and ligand vapors on a surface at low or very low temperature. Thus we produce a solid co-condensate film. It is possible to observe the stabilization or reactions of metal species in such films using IR, UV-vis and ESR spectroscopy and electrical measurements. During the annealing to room temperature, the dispersion of metal nanoparticles or metal-containing polymer films are formed. Here we used TEM to determine the size of particles. Finally, we produce nanosized metal-containing organosols or solid films and use these materials to study various chemical transformations, catalytic activity, and gas sensor properties.

The lifetime of highly active species such as metal atoms, their dimers or trimers, during the co-condensation on a cold surface is inversely proportional to the condensation rate and depends on the nature of relaxation and diffusion processes in the system. The intensity of the particle beam determines the number of collisions of the atoms and molecules with the surface and with each other.

Working with low-temperature co-condensates we can face several size effects. Corresponding definitions are presented in the table shown in Figure 3 [3]. In low temperature co-condensates the following size dependencies are possible: film thickness, size (number of atoms) and combinations of both.

REACTIONS OF MAGNESIUM PARTICLES

In the organic chemistry of polyhalogen compounds it is known that at room temperature in solution carbon tetrachloride does not react with bulk magnesium. The situation changes dramatically in Mg-CCl_4

co-condensates on a cold surface at temperatures close to the that of liquid nitrogen (77 K). In the case of carbon tetrachloride we have competition between chemical reactions and formation of different chemical intermediates and products: Grignard reagent (CCl_3MgCl), trichloromethyl radical (CCl_3), dichlorocarbene (CCl_2). The reaction mechanism has been studied in detail [4].

Magnesium clusters of different nuclearity can be obtained in low temperature matrices. The process of cluster formation is simply controlled by changing the reagent ratio. The particle size and the C–Hal bond energy are important. We have studied the interaction of magnesium species with halogenated butanes and compared the yields of octane (product of recombination) with the C–Hal bond energy. The results are correlated with the C–Hal bond energy and our scheme of reaction [5].

New data were obtained for reactions of magnesium particles with polyhalomethanes in the temperature range 12–70 K [6]. The system magnesium-carbon tetrachloride was studied in detail. UV-vis spectra of magnesium particles in argon are shown here in Figure 4. The magnesium particles were identified using the literature. Atoms, dimers, trimers and tetramers are all stable at 12 K and may be found in the matrix immediately after the condensation. Annealing of the condensate, leads to simultaneous linear decrease of all absorption peaks with increasing temperature. The spectrum totally disappears at 35 K.

Addition of 10% of CCl_4 changes the annealing behavior of the system. The data, presented in the next figure (Fig. 5) clearly shows that dimers and trimers are consumed first. Magnesium tetramers and

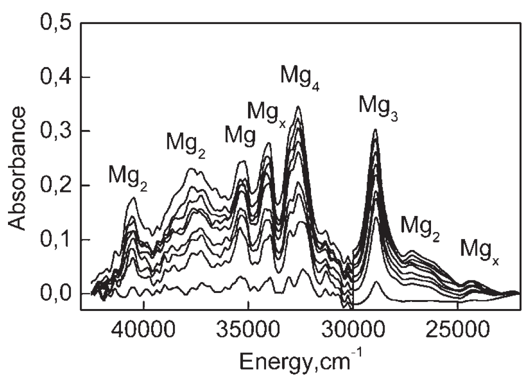

FIGURE 4 Temperature dependence of UV-Vis spectra of Mg/Ar = 1/1000 condensate. Shown are traces in the range (from top to bottom 12–34 K).

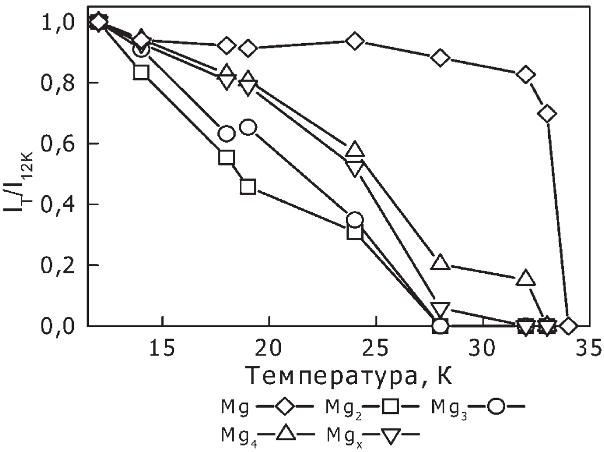

FIGURE 5 Temperature dependence of UV-Vis spectra of $Mg/CCl_4/Ar =$ 1/100/1000 co-condensate. Variation of relative peak intensity of several absorption lines.

Mgx oligomers are a bit more stable. The adsorption of atoms was nearly constant and does not change up to 27 K, while the absorption of all clusters decreases. Only when less than 20% of the initial cluster concentration remained did the atomic peak also start to decrease. One can see that atoms start to react after clusters and the reactivity changes in the sequence $Mg_2 \geq Mg_3 > Mg_4 \geq Mg$.

IR-spectroscopic studies have shown that the only stable products of the reaction are C_2Cl_4 and C_2Cl_6. The formation of Grignard reagent was not detected (Fig. 6). We suppose that the reaction proceeds by the sequential abstraction of chlorine atoms accompanied by metal cluster decomposition. The intermediate product is probably the complex between magnesium chloride and dichlorocarbene. Further transformation of this complex leads to formation of stable products. This scheme of the reaction agrees with theoretical calculations [7].

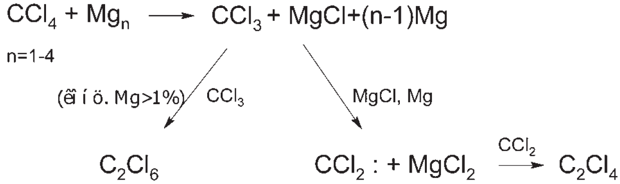

FIGURE 6 Proposed scheme of the reactions in Mg/CCl_4 co-condensate at 12–40 K.

We also studied reaction of magnesium particles with other polyhalomethanes. The interaction with $CHCl_3$ in the temperature range 12–70 K was not observed. Reaction with $CFCl_3$ occurs only at temperature T = 70 K. We consider these observed facts to be a result of the higher bond energy in these compounds.

Size effects have been also found in the reaction of Mg with alkyl and aryl halides. In this case we have seen the influence of the film thickness on reaction rate. Under some critical conditions, explosions are observed [8].

At the present time, we suppose that in the reactions with metal particles the combination of two size effects takes place – the film thickness and particle size. Thus, low temperature co-condensates possess redundant energy. This energy can be released in various chemical reactions. The main forms of the accumulated energy are energy of chemical transformation, excess energy of non-equilibrium phase state, energy of defects in amorphous and crystalline substances, and energy of mechanical stresses.

Explosive reactions at low temperatures take place also in systems which do not contain metal particles. Such a reaction was found for acetyl chloride and diethylamine [9].

We have also shown size effects in water condensate films. The experiments were carried out using an original low temperature thin film setup for differential calorimetry. Spontaneous fast release of heat was observed at 80 K, when the water film thickness increased to a critical value [10]. In our opinion, the fast process is connected to the crystallization of the amorphous water. The decrease of stresses was observed when film thickness reached its critical value. The formation of a crack network in the film was detected at the same time.

A general scheme for the processes that took place in the growing solid co-condensate film during its formation are presented in the literature [11]. There are different forms of the accumulated energy and competition between different chemical transformations (fast and slow).

CONCLUSIONS

Low and super-low temperatures allow the study of reactions of active metal species: atoms, small clusters and their nanosized aggregates.

Such processes can be accompanied by unusual chemical reactions. The formation of hybrid metal-organic supramolecular structures, metal clusters, and nanosized metal particles can take place during the low-temperature co-condensation and during further thermal treatment of the samples.

The most interesting findings in cryochemistry of metal nanoparticles are the size effects of various sorts [12]. As such effects we consider the influence of metal species size (the number of atoms in the structure) or film thickness on their reactivity.

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