PHYSICAL CHEMISTRY OF NANOSTRUCTURED SYSTEMS

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LECTURE No. 5

PROPERTIES OF NANOSTRUCTURED MATERIALS

INTRODUCTION

- Metal based nanomaterials.
- Importance of the size effect in properties of nanomaterials.
- Properties of metal based nanomaterials

OBJECTIVES

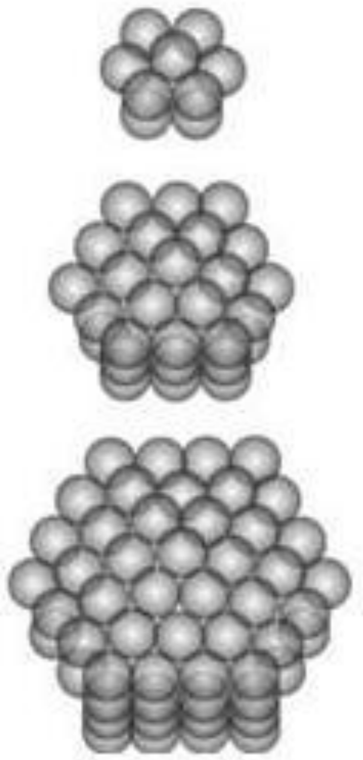
- To analyze the influence of size factor on the chemical equilibrium.
- To discuss the adsorption properties, as very important factor for the application of nanoparticles and nanomaterials.

OUTLINE

- Thermodynamic features of nanoparticles.
- The adsorption properties of nanoparticles and nanomaterials.

Some thermodynamic features of nanoparticles

- Number of atoms



13 atoms (12 on the surface) 92%

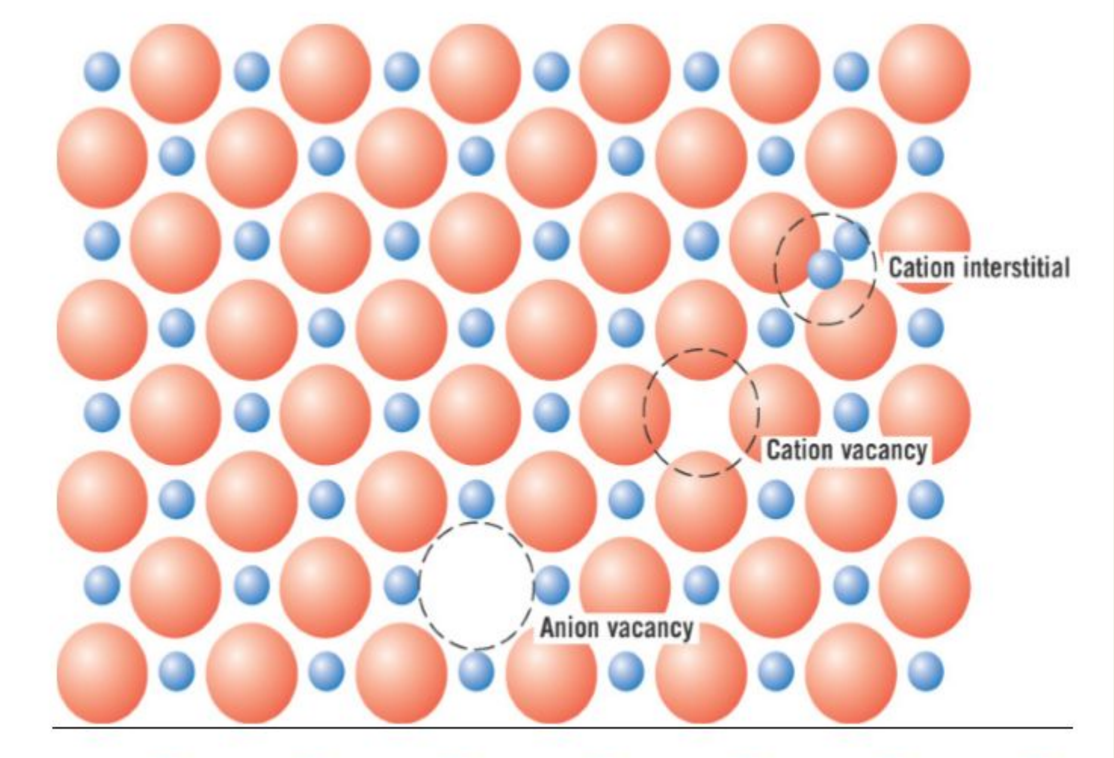
55 atoms (45 on the surface) 76%

147 atoms (93 on the surface) 63%

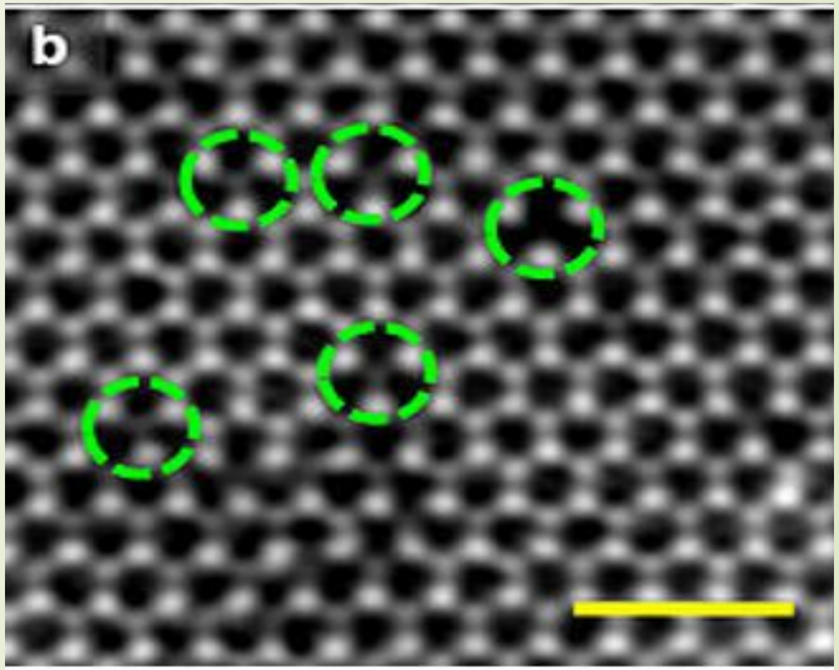
- Surface energy

Concentration of vacancies

Vacancy concentration of nanocrystals (A) and (B) vacancies in a monolayer of molybdenum disulfide.



(A)



(B)

Size effect influencing on the chemical equilibrium

$$\sum_i \nu_i A_i = \sum_j \mu_j B_j$$

Where:

-ν_i and μ_j - corresponding stoichiometric coefficients.

-A and B are reactant and final product.

Size effect influencing on the chemical equilibrium

Standard change in the Gibbs energy equation:

$$-kT\ln K_p = \Delta G^0$$

Where:
k is the Boltzman constant,
T is the temperature,
Kp is the equilibrium constant.

Size effect influencing on the chemical equilibrium

Standard state ΔG^{O} :

$$\Delta G^{0} = \sum_{j} \mu_{j} G^{0}_{B_{j}} - \sum_{i} v_{i} G^{0}_{A_{i}} = G^{0}_{j} - G^{0}_{i}$$ (Normal T and P)

$$\Delta G^{0} = \Delta H^{0} + T\Delta S^{0}$$ (Only for massive phase)

Where:
ΔH^{0} is enthalpy,
ΔS^{0} is entropy,
T is the temperature.

Size effect influencing on the chemical equilibrium

For reactions between substances in a state of change Nano dispersed Gibbs potential can be written as:

$$\delta G_i = \frac{2}{3}\frac{A}{N_a}\frac{\sigma_i F_i}{\rho_i V_i} - kT(C_R - C_\infty) = \frac{A}{\rho_i N_A}\frac{2\sigma}{R_i} - kT(C_R - C_\infty)$$

Where:

- σ surface-tension,
- F surface area,
- V volume of the dispersed particles,
- ρ density,
- C_R relative number of vacancies per atom,
- Ri radius of the particles,
- C∞ concentration of vacancies in the array,
- A atomic weight,
- N_A Avogadro's number.

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1 : Contribution of the Surface energy

2 : Contribution of vacancies

Size effect influencing on the chemical equilibrium

If the reaction product is dispersed:

$$\Delta G = \Delta G^{0} + \sum_{j} \mu_{j} \delta G_{j} - \sum_{i} \nu_{i} \delta G_{i}$$

Standard state

Nano dispersed reagents

Gi › Gj, then ΔG ‹ 0

Size effect influencing on the chemical equilibrium

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$$\Delta G = \Delta G^0 + \sum_j \mu_j \delta G_j - \sum_i v_i \delta G_i$$

$$-kT \ln K_p = \Delta G^0$$

Size effect influencing on the chemical equilibrium

$$K_p = K_p^{\infty} \exp\left\{ \frac{2}{N_A} \left[\sum_i v_i \frac{\sigma_i A_i}{\rho_i R_i} - \sum_j \mu_j \frac{\sigma_j A_j}{\rho_j R_j} \right] \right\} \frac{1}{kT} - \sum_i v_i (C_R^i - C_R^{\infty}) + \sum_j \mu_j (C_R^j - C_{\infty}^j)$$

Where:

Kp∞ - bulk sample constant,

Kp - nanoparticle sample constant,

Ri - radius value representing the size effect.

Only for reactions between nanoparticles

Size effect influencing on the chemical equilibrium

могут возникать реакции между наночастицами, термодинамически запрещенными для массивных материалов, поскольку константа равновесия для реакций между наночастицами включает, в отличие от реакции с массивными материалами, многие другие факторы, такие как: радиус, поверхностные натяжения, плотность, концентрации вакансий и т.д.

The adsorption properties of nanoparticles and nanomaterials.

Application:

- ✔ Chromatography
- ✔ Purification filters
- ✔ Gas analyzers

Inverse gas chromatgraphy

The adsorption properties of nanoparticles and nanomaterials.

Normal alkanes (C6-C8) in 3 Å, 4 Å and 5 Å zeolites. The results showed that:

- With increasing the number of carbon atoms increases linearly adsorption parameters.
- In addition, the heat of adsorption on zeolite 3 Å is higher than 5 Å zeolite. (Å=0,1 nm)

The adsorption properties of nanoparticles and nanomaterials.

Cabon nanotubes: The nanotubes obtained by high-temperature annealing and thermal oxidation have similar structure, but they have great specific interactions around 10-30 % of the total surface area.

Metal nanoparticles: It was shown the feature of hydrogen sorption at the surface of magnesium nanoparticle. They have a minimum defects and their small size give the possibility to use them as hydrogen accumulators.

The adsorption properties of nanoparticles and nanomaterials.

Metal nanoparticles deposited on oxide supports

- Gold and platinum nanoparticles supported on alumina or zirconium oxide, modify the heat capacity.

Adsorptive properties of the nanoparticles are different on different substrates and the particle size also influences.

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Control questions

1. Explain two properties of metal based nanoparticles.

2. Analyze some factors, that explain the change in the thermodynamic variables of Nano dispersed particles.

3. Why are important the adsorption properties of nanoparticles and nanomaterials?

THANK YOU FOR YOUR ATTENTION!