Interfaces and heterogeneous catalysis I.
syllabus

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1. Types of interfaces, their classification and significance in the stability of dispersion systems. Definition and interpretation of surface excesses across different interface types. Liquid- gas, solid-gas, solid-liquid, liquid-liquid interfaces-defined adsorption excess functions. The relationship between the structure of the interfacial layer and colloidal stability. Connections between surface excess energy and particle size.
2. The Gibbs definition of surface excess quantities, the introduction of the Gibbs dividing surface and the interpretation of the interface concentration profiles to determine the material excess quantities. The distribution functions of the surface layer concentration of different phase domains. The method of calculating Gibbs's excess by introducing the Gibbs dividing surface. Generic Determination of the of excess functions for extensive state functions.
3. Basics of thermodynamic state functions, extensive and intensive state functions. Extending the thermodynamics of homogeneous systems to the interfacial layers, introducing the excess functions. Thermodynamic state functions of homogeneous phase systems: Derivation of Gibbs-Duhem equation for surface excess quantities. Interfacial tension as an intense state function. The influence of the chemical potential of the bulk phase in determining the surface energy.
4. Extension of the Laplace- equation and Kelvin- equation to nanophase dispersed systems, the role of size dependence at the interpretation of the surface excess properties. Extension of the Laplace- equation and Kelvin- equation on nanophase dispersed systems, the role of size dependence in interpreting surfaces excess properties. Calculation of the surface energy in dispersion systems as a function of the size range of nanoparticles based on the Laplace- and Kelvin- equations. Analysis of the relationship between surface excess energy and kinetic stability. The effect of the adsorption layer structure on the stability of dispersion systems.
5. Interpretation of solid-gas interfaces, the various adsorption isotherms based on different models. Application possibilities for different adsorption isotherms to determine the specific surface area comparison of different adsorption models. Validity of adsorption isothermal equations in the aggregated dispersion systems. Interpretation of surface area determination in the light of aggregation processes.
6. Solid-liquid interfaces, interpretation of the adsorption exesses on the basis of different models. Introduction of the Ostwald-de Izaguire equation in the knowledge of the adsorption material balance. The relationship between the adsorption excess and the effective adsorbed material content. Calculation of the composition of the interfacial layer in binary liquid mixtures. The role of bulk phase activity in controlling the adsorption of excess amounts.
7. The De Boer's adsorption model for calculation of micro- and nanoporous systems and pore size distribution functions. The calculation of the adsorption layer thickness on the bases on the measured adsorption master curve. Calculation of external and internal surface areas as well as pore volume.
8. Characterization of surface hydrophilic / hydrophobic properties in the knowledge of Gibbs equation and adsorption excess isotherms. Functionalization of surfaces

with chemical and ion exchange adsorption, practical possibilities for surface modification. Calculation of the surface hydrophilic/hydrophobic ratio based on the adsorption excess and the activity of the bulk phase.

9. Calculation and calorimetric determination of interfacial enthalpies on solid-liquid interface. Binary mixtures defined by free energy functions and comparing the microcalorimetric measured data to determine interfacial entropy functions. Methods of determining the adsorption enthalpies on solid-liquid and solid-gas interfaces using microcalorimetric measurement techniques. Determination of enthalpy isotherms in flow microcalorimetric systems. Analysis of the relationships between enthalpy isotherms and surface energies. Characterization of the functionalized surfaces.

10. Definition and significance of the catalysis. A brief history of heterogeneous catalysis. The basic concepts of heterogeneous catalysis, activity, reaction rate, selectivity (chemoselectivity, regioselectivity, stereoselectivity). Residence time and their effect on the reaction rate and on the selectivity. The possibilities of the determination of surface active centers of the catalysts.

11. Kinetic characterization of the catalytic reaction. The Langmuir-Hinschelwood mechanism for one and more reacting gases; the determination of the partial orders. Rideal- Eley and Mars-van Krevelen mechanism. Variation of selectivity and yield versus conversion depending on different types of reactions (branched, consecutive, triangular reactions). Temperature dependence of the reaction rate, real and apparent activation energies. The effect of material transport on the kinetics of the reactions.

12. The surfaces of solid materials, defects, disruption, various crystal faults. Theories of heterogeneous catalysts, geometrical and multiplet theories, Polanyi's transition state theory, Vulcan curves. Electron theory of adsorption, electron theory for semiconductor catalysts, Volkenstein's electron theory. The defect structure of oxide-semiconductors and the effect of doping on the conductivity of the oxides. Effect of the support, strong metal support interaction (SMSI), role of the vacancies in the catalytic reactions.

13. Criteria for the selectivity of the catalyst, binding strength, coordination, template effect, and the role of the alloying agents.

14. Characterization of the catalysts, BET method. Temperature programmed processes (desorption, reaction, reduction TPD, TPR, TG, DTA). The theory of TPD, zero, first and second order desorption. The advantages and disadvantages of these methods. Determination of surface carbon deposition. Possibilities for the use of infrared spectroscopy for identifying the species on the surface of the catalysts.

15. Acid-base catalysis. The formation of Brönsted and Lewis acid centers. Methods for determining the acid-base properties of the catalysts (number and strength of acid centers), Hammett indicators, chemical methods, titration, base adsorption, desorption, TPD, infrared spectroscopy and conditions of use, NH_3, pyridine, CO adsorption.

Acid catalyzed reactions of the hydrocarbons through carbocations and carbanions.

16. Preparation of the catalysts. Economics of catalytic processes, possible forms of catalysts. Potential components of the catalysts, the catalytically active phase, the promoters, supports with high surface area. Methods for preparation of the catalysts: precipitation, cooprecipitation, sol-gel method, hydrothermal procedure, impregnation, special procedures eg. sulfidation. Effect of different processes on the particle size of the catalysts.Some important supports, Al_2O_3, SiO_2, TiO_2, activated carbon and oxide or zeolite based catalysts.