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**University profile**

Esther Sulman*

# Tver Technical University

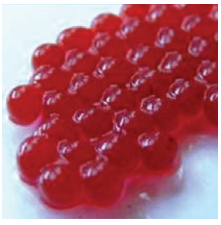
***Corresponding author: Esther Sulman,** Tver Technical University, A. Nikitina Str., 22, Tver 170026, Russian Federation, e-mail: sulman@online.tver.ru

Tver Technical University (TTU) was founded in 1922 as Moscow Peat Institute. Later, it was changed to Kalinin Polytechnical Institute and then to Tver Technical University. Nowadays, TTU is a large educational and scientific center including six daytime departments, evening and correspondence departments, additional educational courses, a postgraduate course, scientific centers, and research laboratories. The Department of Biotechnology and Chemistry of TTU is highly experienced in the study of various catalytic and biocatalytic reactions, development of novel processes, and technologies. Since 2007, the Institute of Nano- and Biotechnologies (INBT) was founded on the base of TTU, which includes the following substructures: Regional Scientifically Educational Complex; Center of Physicochemical and Biotechnological Investigations; Center of Health; Center 'Energy Efficiency'; Scientifically Investigational Laboratory 'Catalyst'; Accredited Analytic Laboratory; 'Ecology – Waste Water (ECOS)'; Laboratories of Nanotechnologies, Biotechnologies and Biomass Processing; and various educational laboratories and centers.

## Biotechnology research

In the field of biotechnology, the research interests of TTU include the following activity:

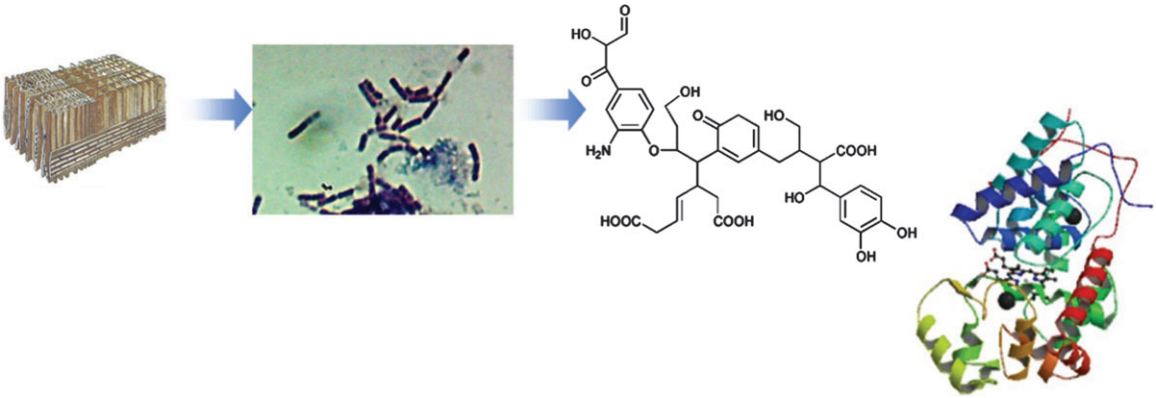
- The investigations on the application of biologically active compounds as food supplements. We are interested in the development of suitable procedures for checking the stability of microcapsules and coatings; the research on different natural polysaccharides and their combinations with regard to their suitability to protect the encapsulated substances against acids, enzymes, and heat; the development of an algorithm, which makes it possible to identify the combination of materials that offer the best protection against certain strains due to production, storage, or digestion. Our research interests include also the encapsulation of biologicals ('bioencapsulation'), the study of the probiotics survival under the encapsulation conditions, and the development of stabilized form of encapsulated probiotic cultures that are both stable and have an increased survival rate. Another interest is a scaling of encapsulation technologies that are designed for large-scale food industrial and medical application;



Capsules with doxorubicine

Capsules with retinol acetate

- The biodestruction of organic wastes (sawdust, sheave, etc.) through a combination of physical and biological action. Especially, we are interested in (i) the biotransformation of lignocellulose and lignin pretreated with ultrasound to obtain humic acids and (ii) the biotransformation and detoxification of oil slimes;
- The proposed investigations allow the solving of the problems of waste utilization and avoiding the use of aggressive mediums formed during the hydrolysis of vegetable material. Finding will allow the process of raw material pretreatment to be more economical and be of benefit and safe.
- The ultrasonic extraction of plant biologically active substances, i.e., heteropolysaccharides. The derived glycans are promising components for functional foods and can also be used as substrates for the enzymatic hydrolysis using free or immobilized glycolytic enzyme complexes. The optimum conditions of the enzymatic hydrolysis of polysaccharides allow the accumulation of the maximum quantity of physiologically active three- and pentaoligosaccharides;




- The investigation of enzyme (oxidoreductases) immobilization on the various heterogeneous supports and the application of synthesized catalysts in environmentally important reactions of waste water purification from phenolic compounds as well as intermediates;
- The development of biocatalytic polysaccharide membranes to produce biosensors for the determination of phenols in aqueous and non-aqueous media.

## Catalysis research

In the field of catalysis, the scientific interests of the Tver group are the chemo- and enantioselectve catalytic hydrogenation, selective deoxygenation, and oxidation using the catalytic systems of different natures varying from conventional catalysts to nanoparticulate polymeric catalysts and biocatalysts. Among them, the metal-containing polymeric nanocatalysts based on amphiphilic block-copolymers, the ultrathin polyelectrolyte layers deposited onto inorganic supports, and the heterogeneous polymeric matrices were successfully tested by the TTU group in various catalytic processes.

TTU has experience in working on international projects. TTU has participated as a partner in the FP6 project NANOCAT ('Tailored nanosized metal catalysts for improving activity and selectivity *via* engineering of their structure and local environment') and in two NATO Science for Peace projects. In the framework of the current FP7 project POLYCAT, the TTU group developed novel polymer nanocatalysts based on hypercrosslinked polystyrene (HPS).

HPS is a highly porous polymer consisting of rigid cavities, the size of which can be varied depending on the reaction conditions. HPS is produced by Purolite Ltd (UK) as a sorbent, but HPS can be also used for the controlled formation of catalytic nanoparticles (NPs). Figure 1 shows the HPS granules containing Pt NPs (left) and the HPS internal structure (right).

HPS-based catalysts allow the control over NP formation due to a 'cage' effect (by limiting the NP size with the pore size) along with controlling the precursors and reduction conditions. It is noteworthy that the HPS matrix also provides excellent stability of the catalysts developed due to trapping the NPs and preventing the leaching of metal species. The above advantages of HPS-based catalysts allow the regeneration and multiple reuse of the catalysts developed and, thus, seem to be especially promising for exploitation in the industry.

## Goals and achievements in the POLYCAT project

In the framework of the POLYCAT project, we developed mono- (Pt, Pd, Ru, Au) and polymetallic (Pd-Pt, Pd-Zn, Pd-Au-Zn, etc.) HPS-based catalytic systems using various commercial HPS (nonfunctional, HPS materials bearing amino and sulfo groups). Besides, the nature of the metal

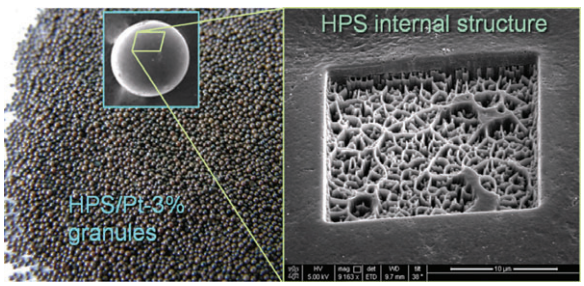



**Figure 1** The structure of HPS-based Pt catalyst. Left: HPS/Pt 3% granules; right: the internal HPS structure imaged by scanning electron microscopy.

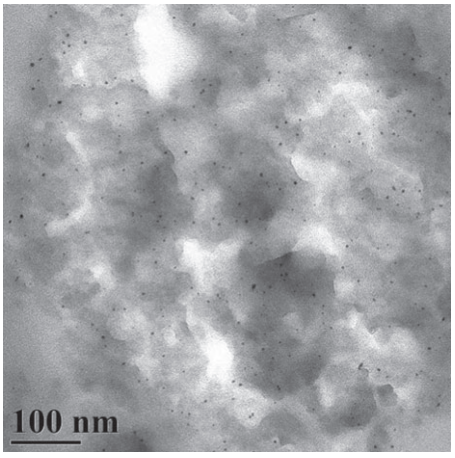



**Figure 2** TEM of HPS-stabilized Pd NPs.

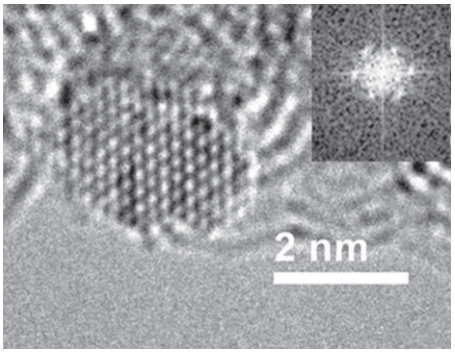



**Figure 3** HRTEM of HPS-stabilized Ru NP.

precursor compounds was varied to design nanoparticulate catalysts containing monodisperse NPs.

The catalytic systems developed were tested in the reactions of fine organic chemistry of both fundamental and industrial importance: the oxidation of mono- and disaccharides, the hydrogenation of monosaccharides, and the Lindlar-type hydrogenation of acetylene alcohols. For all the reactions studied, the promising results were obtained with HPS-based catalysts.

To illustrate the behavior of the catalysts developed, we will provide a few examples. For one, in the case of the selective hydrogenation of acetylene alcohol $C_5$ (semiproduct of the synthesis of vitamins A, E, K, and fragrant substances), 0.1% Pd/HPS catalyst (Figure 2) provides selectivity higher than 97% (at 100% conversion), which significantly exceeds the selectivity of the conventional industrial catalysts (e.g., Lindlar catalyst) at higher metal loading, the use of hazardous modifiers, and metal leaching.

The other reaction of interest where the HPS catalysts were tested is the syntheses of ultrapure D-gluconic acid by the oxidation of D-glucose over gold NPs incorporated in the HPS (1%-Au/HPS). The use of Au/HPS catalyst characterized by a high stability in multiple reaction cycles resulted in the 98–99% yield of gluconic acid.

The Ru-containing HPS is a prospective catalyst of the D-glucose selective hydrogenation for sorbitol production. The high-resolution transmission electron microscopy (HRTEM) image of a single Ru particle is presented in Figure 3. The use of 3% Ru/HPS allowed us to achieve a selectivity >98% at 100% of glucose conversion without the use of any modifiers, the formation of side products, the pollution of the target product with $Ni^{2+}$ ions as what occurs with the conventional saccharide hydrogenation catalyst, Ni-Raney.

The general advantages of the HPS-based catalytic systems developed by TTU in the POLYCAT project in comparison with the existing industrial catalysts include (i) the large specific surface area (usually near 1000–1500 $m^2/g$); (ii) the possibility to work in virtually any solvent; (iii) the high catalyst activity at a lower metal loading due to the formation of well-defined NPs vs. their aggregation in conventional catalysts; (iv) the higher stability and lifetime due to the minimization of metal loss; (v) the high selectivity without the necessity to use catalytic poisons and metal modifiers; and (vi) the prevention of NP aggregation during the reaction.