

Национальный исследовательский Томский государственный университет

**Новые катализаторы и каталитические процессы для
решения задач экологически чистой и
ресурсосберегающей энергетики**

Сборник тезисов докладов научной школы молодых ученых

9 – 10 сентября 2021

Томск 2021

Model catalysts synthesized by the *di*-block copolymer inverse micelle method: insights on nanoparticle formation and network stability within the environmental TEM

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The *di*-block copolymer inverse micelle method, where an amphiphilic *di*-block copolymer dissolved in toluene creates a system of inverse micelles, is a rather simple method to obtain well controlled supported metallic nanoparticles once the micelle core is charged with metallic salts. Supported metallic catalysts can be obtained in this way on both flat (model catalysts) and powder (realistic catalysts) supports [1]. Our main interest deals with applications of bimetallic catalyst systems that we investigate from extended catalytic surfaces [2] to realistic catalysts [3]; the idea being to isolate and understand the role of important physico-chemical parameters on the catalytic behaviour of these systems in the shape of model catalytic surfaces and try to extrapolate them to realistic catalysts. This is very important for the controlled design of catalysts with specific properties. In this way we can, not only spend less active material (often rare and expensive), but also avoid unnecessary poisoning while keeping high activity (stability) and finely tune the selectivity to avoid deleterious unwanted products; these are important points to be able to achieve environmentally friendly and sustainable catalytic processes. Self-organized nanoparticles on flat surfaces is an intermediate configuration between extended catalytic surfaces and realistic catalysts and a necessary step to better extrapolate results between model and realistic systems. We have thus extended the *di*-block copolymer method to the synthesis of bimetallic catalysts [4]. In our presentation we will deal with a PdAu system, obtained from a PS-*b*-P2VP copolymer micellar solution that we transfer by spin-coating to a surface of a SiNx electron-transparent films on dedicated microchips than are heated in Wildfire sample holder (DENS Solutions) within an objective lens aberration-corrected environmental TEM (Titan ETEM G2 80-300 kV from ThermoFisher Scientific) so that we can study in situ the behaviour of such a system in variable temperature and gas pressure. We observed the formation of the individual particles from the seeds within the core of the micelles in the presence of oxygen in variable temperature; sintering of the seeds within the micelle cores starts at 350 °C and is completed at 500 °C, temperatures that correspond, respectively, to the onset of the copolymer decomposition and to its quasi-completed decomposition [5]. We also observed that the network of nanoparticles is stable under oxygen up to 900 °C and that, above this temperature, the network is modified only by the decomposition of the nanoparticles (when we approach their melting point).

The authors acknowledge the French Microscopy and Atom probe network (METSA) and the Consortium Lyon – St-Etienne de Microscopie (CLYM) for supporting this work.

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