

## The heterogeneous SCF processes for catalysis and related areas – in the focus of Russian R&D institutions

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Historically the SCF attracts a lot of attention of Soviet (Russian) R&D institutions working in very different areas. The increase in the accuracy of the experimental techniques, precise quantification of the gravitational phenomenon and the influence of impurities existing in the system showed principal role of the fluctuations in the vicinity of critical points.

In 1964 Alexander Patashinski from Siberian Branch of Soviet Academy of Science was the first who suggested describing the second order phase transition via long-wave fluctuations of small amplitude but of large dimensions [1]. This gave impetus to a number of theoretical and experimental studies of coolants, heat-transfer agents, inert gases, CO<sub>2</sub>, hydrocarbons, water etc. including supercritical fluids (SCF). In 1978, Kenneth Wilson receiving Nobel Prize acknowledged Pokrovsky and Patashinsky [2] for their ideas, which actually formed the basis of subsequent achievements.

Later in the 80-es the special attention was paid to the behavior of water at elevated temperature and pressure. Following the ideas of Patashinski and J. Frenkel [3], Prof. Gorbatyi investigated the local structure of pressurized [4] and supercritical [5] water and has been found a strong structural inhomogeneity come from fluctuations of the entropy and density. It leads to a complicated shape of the distribution of the intermolecular distances in the first coordination sphere. At the same time the energetically favorable molecular configurations are appeared to depend on anisotropic character of local intermolecular interaction (e.g. hydrogen bonding in case of water). Using X-ray scattering Yurii Gorbaty found [6] that the peak corresponding to the isotopic part of intermolecular interaction increases with the pressure growth that display the changes of molecules fraction coupled via hydrogen bonds. Those results attracted the attention to the local phenomena of intermolecular interactions that determine the properties of SCW and other fluids.

Largely due to the success in understanding of the behavior of the SCF at the atomic and molecular scale the SCF technologies were developing that time in USSR and later in Russia. In particular, the supercritical water (SCW) was considered as perspective media for different technological processes: hydrothermal synthesis, processing of low-grade fuels, destruction of different wastes including chemical weapons, as heat-transfer agent for the nuclear power plants etc.

Supercritical water takes part in many geological processes determining the formation of various deposits. In this line the control of intermolecular interactions made it possible to choose the desired parameters for biomimatic processes. While developing technologies to obtain optically-transparent crystals for lasers the Siberian scientists in 70-80-ies first suggested the method known as "horizontal directional crystallization method (STC)" to produce a wide range of artificial crystals, which can compete even with natural gemstones. The essence of the method was in the recrystallization of crashed low grade and cheap crystals in batch reactor under control temperature gradient on seeds placed in the upper part of the reactor. Nowadays well-known international company Thairus is the world's largest producer of hydrothermal so-called "created" emerald, ruby, sapphire and others which are used worldwide in jewelry.

Russian specialist suggested and developed the appropriate and economically feasible technologies to use SCW as heat-transfer agent for the nuclear power plants based on fast neutron

reactors. The SCW allows one to decrease of thermal losses, increase the heat transfer efficiency that leads to the increase of the actual efficiency of nuclear plants with a closed fuel cycle. Great efforts were spent that time to find materials and special alloys that are stable under SCW and constant neutrons irradiation. Also a lot of the projects concerning destruction of different wastes including chemical weapons were realized in former SU and Russia including those fulfilled within International Science and Technology Center.

Another example worthy of attention is the application of SCF for the sensitive chemical analysis including high-speed multicapillary chromatography. In eighties of last century Boreskov Institute of Catalysis (BIC) developed SCF chromatography for the analysis of polyaromatic and polysiloxane compounds [7,8]. Later the ultra-high speed chromatography based on original multicapillary columns was suggested in BIC. The usage of a package of thousand equaled capillaries of 10 microns in diameter leads to the absence of a pressure drop providing a large amount of the sample to be introduced making the separation process sensitive, fast and precise. One can form different layers on the inner surface of the capillary sensitive to the target substances. The technology developed is still unique and used for on-line analysis.

Nowadays more than 90 % of all worldwide chemical technologies somehow use catalysts and catalytic processes, providing products of more than \$5 trillion. For example the contribution of catalytic technologies to the material component of US GDP is around 35%. The number of countries producing a full range of catalysts for strategically important oil refining and chemical processes is less than the number of countries owning the technology for producing nuclear weapons. The largest worldwide companies spend a lot of efforts to find more efficient and stable catalysts as well as original catalytic processes based on SCF.

Considering the list of catalytic reaction for organic synthesis realized under SC condition in Russian R&D institutions one can find rearrangements of monoterpene hydrocarbons [9,10,11], catalytic Michael addition to  $\alpha$ -nitroalkenes [12], Suzuki-Miyaura cross-coupling reaction in SC-CO<sub>2</sub> [13], addition of SC CO<sub>2</sub> to organic epoxides [14,15], hydrogen transfer reaction [16], different amination and alkylation reactions [17,18] and many others.

Developing the SCF technology in catalysis it is necessary to remember that viable catalytic processes implies the solution of many problems including not just efficient chemical reaction, but also selectivity, mass and heat transfer issue (especially in case of heterogeneous catalysis), the stability of the catalysts, target products separation and purification, catalyst regeneration, the potential to use by-products, and many others. In this regards only the comprehensive analysis of fluid properties can give us a new 'brand'. The trick here is that especially combination of SCF properties including the low viscosity, high mass and heat transfer, high diffusion rate and the absence of mass transfer slowdown through the interfaces, increasing solubility of gases etc. can provide a 'new quality' for different processes.

Good example of the SCF potential in the heterogeneous catalysis is the high-selective catalytic hydrogenation. Under normal conditions, to reach the catalyst surface and react, the gas reagents should diffuse through the gas/liquid interface, then through the liquid including stagnant region near the surface of the solid catalyst, then diffuse into its porous structure, react, desorb and repeat all the way back. Under SC conditions, the stages associated with mass transfer through the interfaces are practically eliminated, diffusion resistance sharply decreases, the concentration of hydrogen over catalyst surface increases by more than order of magnitude that results to the high product yield and selectivity.

Another interesting example concerns coupling of CO<sub>2</sub> and epoxides to produce cyclic carbonates catalyzed by metal-organic frameworks (MOF) [14,15]. It was found that propylene carbonate can be synthesis by cycloaddition of CO<sub>2</sub> to propylene oxide using Cr containing MOF MIL-101 as catalyst to get 82% yield at 91% conversion after 24 h. The presence of tetrabutylammonium bromide as co-catalyst allows us to get cyclic carbonates directly from SC CO<sub>2</sub> and olefins with reasonable yield.

Usually we consider the averaged characteristics of SCF: increased solubility, diffusion, low viscosity, and so on. At the same time as it was mentioned above these properties originate from

specific intermolecular interactions which result to significant differences in the local density, local concentration and other local characteristics of SCF as compare to the conventional liquids. The relatively weak forces under SC condition can move molecules and ions into an energetically favorable position resulting in the inhomogeneous spatial distribution of molecules especially in a multicomponent system.

The local concentration phenomenon is very important issue for heterogeneous catalysis. As a rule a number of competing reactions occur in the system in parallel. The rate of each reaction depends on the pressure, temperature and also the local concentration of reagents. Using the language of kinetics theory, the rate constant of elementary reaction depends on the volume of activated complex (the difference between the molar volume of the transition complex and the sum of the volumes of corresponding reagents). This value can be order of magnitude larger for SCF as compared to the corresponding value for liquids. In case of competing reactions the variation in local concentration can change the reaction mechanism. The local concentration phenomena can be observed via some spectroscopic or resonance techniques *in situ* (Raman, FTIR, NMR or ESR) even in SC water [19].

One can change the local concentration ‘in the right place and at the right time’ changing pressure or temperature. The controllable changes in the chemical composition during the reaction can also lead to the changes of local concentration of some molecules around the others, accelerating some reactions that can lead to the increase of selectivity of the catalytic process. As an example concerning heterogeneous catalysis one can remember the disproportionation of toluene to benzene and xylene on the zeolite catalyst [20]. Para-xylene easier diffuses into pore structure of zeolite in contrast to ortho- and meta-xylene and therefore dominates in this reaction. Unfortunately the selectivity of para-xylene formation can decrease due to the secondary isomerization on the outer surface of the catalyst. However, the author found the condition to increase the local concentration of toluene molecules around. It prevents adsorption of p-xylene molecules on the outer surface of the catalyst and undesirable reaction.

The local concentration phenomena in SCF should naturally appear at the fluid/solid interface as a consequence of the difference in interaction strength (enthalpy of adsorption) of dissolved molecules and solvent molecules with the solid surface of heterogeneous catalysts. While considering the heterogeneous process the local phenomena can lead to significant changes in the rate of elementary reactions and certain physicochemical processes that can affect the direction and selectivity of the process or even erase the boundary between homogeneous and heterogeneous catalysis at all.

These ideas were used for the hydrogenation of low-grade fuels in SC H<sub>2</sub>O in the flow regime in the presence of metals for example Zn and Al. This excellent approach was realized by researches from the Institute of Thermophysics [21, 22]. It is well known that the oxidation of aluminum in water under normal conditions stops fast due to the formation of the alumina film on the metal surface. The transition into SC state results in the situation then active ions can intensify the oxidation process and extend it into the bulk of the metal. As a result one can get H<sub>2</sub> *in situ* which is solubilized effectively in the SCF leading to the high concentration necessary for the conversion of low-grade fuels. The process can be fine-tuned by the additions of SC CO<sub>2</sub> that slowdown the H<sub>2</sub> production. The combined effect of hydrogen generation and heat release during the oxidation of metal in SCW leads to the changes of the reaction mechanism and different composition of the products. In particular, it has been shown that the addition of Zn and Al leads to the increase of the yield of light hydrocarbons in several times, gases – up to 10 times, and the decrease of the residue content by a factor of 2-4. Addition of metals leads to a decrease in the characteristic mass of n-alkanes and an increase in the content of aromatic compounds in liquid products of bitumen and coal conversion. A strong effect of Zn additives on the amount of sulfur in the products and the residue of conversion of fuels was found.

SCW is rather harsh environment [23]. Lower alcohols in SC state can be also considered as perspective media for hydrogen transfer reactions. In homogeneous case the highest yield of hexane-soluble fraction is observed in SC EtOH and PrOH [24]. Ni-based catalyst allows us

completely transform asphaltenes into a hexane or benzene soluble fraction while no residue is observed.

It appeared that reactivity and local concentration of MeOH molecules around silica surface at elevated temperature and pressure is enough to destroy siloxane bonds. This is important for catalysis because methanol takes part in many processes realized in SCF where catalysts are based on silica supports [17]. Silica is usually considered as chemically inert support. Careful study showed that silica indeed slowly reacts with SC methanol. In 5 hours 4 wt% of silica gel goes into SC fluid. It's not much but noticeable. It's well-known that silica at moderate temperature chemisorbs alcohol molecules well and produce alkoxylation of the surface but without its destroying. At elevated temperature and pressure the methanol has enough reactivity to disrupt silicon-oxygen bond in contrast to other lower alcohols. Mostly TMOS (tetramethyl orthosilicate) are formed during this reaction. The following oligomerization leads to the decrease of apparent silicon quantity in the solution. The situation is reversible and subsequent heating to 350 °C leads to the TMOS formation.

It appeared that tetramethyl orthosilicate (TMOS) catalyze the methylation of indole in supercritical methanol leading to the high selectivity and conversion [25]. So one can simply generate the enough homogeneous catalyst (TMOS in this case) in the system comprising quartz, indole and SC-methanol and afterwards remove silica from the system and get almost the same conversion of indole and yield of 3-methylindole. It leads to the mixing mode of catalytic process, high selectivity and actually blurs the borderline between homogeneous and heterogeneous catalysis at elevated temperature and pressure.

Catalysis at elevated temperatures and pressures is not only a 'chemical reaction', but also catalysts, adsorbents, supports and composites that should function and evolve in SCF environments. Therefore the functional material in catalysis should be synthesized for the certain process. We can remember a couple examples from BIC experience. Large attention is paid nowadays to the metal-organic frameworks (MOF) as they are unique material for different processes. At the same time so far there are no processes based of MOF implemented into the large industry. The problem is that MOF is mostly obtained in the form of fine powder which extremely difficult to pack into pellets. It blocks the development and implementation of any efficient processes in flow regime and blanks the most advantages and unique properties of the MOFs.

BIC has great experience in the production of aerogels for the needs of physics as one of the largest producer of aerogels for the Cherenkov detectors [26,27]. At the same time in spite all capabilities there is still no application of aerogels in the real catalytic processes. Recently we suggested the way to synthesize MOF composite using aerogel as a matrix [28]. An original method was developed which allowed us to disperse MOF in aerogel matrix preserving structure and unique properties of MOF as well as availability of active centers. It was demonstrated for the first time that composite obtained can work in flow type processes as catalyst [29] or highly efficient stationary phase for conventional liquid chromatographic separation of organic molecules.

There is another popular approach for the synthesis of functional materials using supercritical fluids - supercritical antisolvent system (SAS). There are few outstanding examples of how SAS can give us catalysts with unique activity and selectivity. However so far SAS was applied to prepare oxide catalysts only with relatively low specific surface area and was not used for the synthesis of metal based catalysts. Recently we suggested an original method to disperse the catalyst precursors together with the oxide sols, which form matrix needed for stabilization of metal nanoparticles [30]. As a result, we get high metal loading simultaneously with high dispersion of the supported metal phase, the availability of active sites for the reagents, no phase separation in case of bimetallic particles and thermal stability of the system [31]. It was shown that this approach allows us to get stable and more active catalyst for example for deoxygenation of biofuels.

In conclusion, to use efficiently SCF for heterogeneous catalysis, synthesis the catalysts and related materials it's necessary to start from the catalytic processes, analyze its peculiarities at atomic and molecular level that implies the application of physical methods *in situ*.

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