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Subcritical and supercritical water: a universal medium for chemical reactions

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Abstract. The results of studies on the properties of subcritical and supercritical water are generalised. The possibility of using such water as a solvent, a reagent or a catalyst in chemical reactions is considered. Primary attention is paid to specific features of experimental research under hydrothermal conditions. Prospects for use of subcritical and supercritical water in heterogeneous catalysis for the preparation of nanocrystalline materials with predictable properties and for solving environmental problems are discussed. The bibliography includes 208 references.

I. Introduction

Over billions of years subcritical and supercritical water has been involved in the formation of ores and minerals in Earth's depths.[1] The beginning of research on supercritical fluids dates back to 1822. At that time, experiments with different solvents at high temperatures and pressures were first carried out by Cagniard de la Tour who discovered the critical points of substances.[2] The supercritical state of a substance is a state characterised by the disappearance of distinctions between the liquid and gaseous phases. In the nineteenth century, the development of chemistry of supercritical fluids was not so rapid. It was not until 1896 that Villard reported the first detailed review concerning the properties of a group of substances in the supercritical state.[2] In the twentieth century, environmental safety problems and improvement of the efficiency of chemical plants became topical. Because of this, interest increased in studying the properties of substances in the supercritical state. At present, the unique physicochemical properties of supercritical fluids are widely used in extraction and chromatographic separation of substances, in production of various materials and detoxification of liquid waste.[2–4] In addition, intensive research has been carried out on the possibility of using supercritical fluids in organic and inorganic synthesis and in homogeneous and heterogeneous catalysis.[5–9] Table 1 lists the critical parameters, *viz*., the critical temperature (T), pressure (P) and density (ρ) of the most widely used solvents. The scatter of the numerical values of these parameters for different substances is rather large, from nearly 282 K and 5 MPa for ethylene to almost 647 K and 22 MPa for water.

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Table 1. Critical point parameters of solvents.[5, 10]

Solvent	T /K	P /MPa	ρ /kg m^{-3}
C_2H_4	282.1	5.041	214
Xe	289.5	5.840	1110
CO_2	303.9	7.375	468
C_2H_6	305.2	4.884	203
N_2O	309.4	7.255	452
NH_3	405.3	11.350	235
C_2H_5OH	513.7	6.137	276
H_2O	646.9	22.060	322

Chemistry of subcritical and supercritical fluids belongs to the most rapidly progressing fields of chemical science. To date, a great body of experimental data on the properties of tens of substances at near-critical temperatures and pressures has been accumulated. Research on the properties of subcritical and supercritical water and on processes involving this substance occupies a particular place. It should be noted that supercritical water is still of limited use due to the high critical point parameters (see Table 1). However, one should keep in mind that water is the most abundant, cheap, safe and environmentally pure solvent. Because of this, water seems to be of crucial importance for further development of the chemistry of supercritical fluids.

This review summarises the available results obtained in basic and applied studies on the properties of subcritical and supercritical water and corresponding chemical processes. We present a consistent treatment of the physicochemical properties of water at elevated temperatures and pressures, experimental features and problems posed when using subcritical and supercritical water and the possibilities of using subcritical and supercritical water as a solvent, reagent and catalyst of inorganic and organic chemical reactions. The emphasis is placed on the prospects for application of subcritical and supercritical water in heterogeneous catalysis, in the fabrication of nanocrystalline materials with predictable properties and in solving the environmental pollution problem, which belongs to the most important problems of modern times.

II. Physicochemical properties of subcritical and supercritical water

At a temperature of 295 K and a pressure of 0.1 MPa, water is a polar solvent with a density of 1000 kg m^{-3}, a dielectric constant, ε, of 79.73 and an ionic product, K_w, of 10^{-14} (see Ref. 11). Raising the temperature and pressure causes significant changes in the properties of water and aqueous solutions. Changes in the thermodynamic parameters are reflected in the phase diagrams of water and corresponding multicomponent systems. The properties of water, as a solvent, vary owing to variation of its dielectric constant, conductivity, ionic product and the structure of the H bond network. Changes in the viscosity, heat capacity, diffusion coefficients and density influence the transport characteristics of aqueous solutions.

It should be noted that the physicochemical properties of water at the critical point are changed continuously rather than in stepwise manner. The characteristics of supercritical water are intermediate between those of the liquid and gas (Table 2).

Table 2. Characteristics of water under different conditions.

Characteristic	Water under normal conditions	Supercritical water	Superheated steam
T /K	298	723	723
P /MPa	0.1	27.2	1.4
ρ /kg m^{-3}	998	128	4.19
D /m^2 s^{-1} (see [a])	7.74×10^{-8}	7.67×10^{-6}	1.79×10^{-5}
Thiele modulus	2.82	0.0284	0.0122
ε	78	1.8	1.0
$-\log K_w$	14	21	41
Solubility of O_2/C_xH_y /kg m^{-3}	8×10^{-3}/?	∞/∞	∞/?

[a] Diffusion coefficient.

1. The density

At subcritical temperatures and pressures, water can exist in the liquid and gaseous states (Fig. 1). Under isothermal conditions, the density of water changes continuously in both phases; a density jump occurs only at the gas–liquid interface. At the critical point, this interface disappears and the density of water becomes equal to nearly 300 kg m^{-3}. However, in the near-critical region water is characterised by an infinite compressibility, which allows the density of water to be changed over a very wide range by (only slightly) varying the temperature and pressure. For instance, the density of water is halved as the temperature increases by only 6 K at a pressure of 22 MPa.[12] A supercritical water density of 1000 kg m^{-3} can also be achieved; however, this requires a pressure of 750 MPa to be applied at 673 K.[13]

Carrying out chemical reactions in aqueous solutions usually requires control of the reagent concentrations, temperature and pressure. On going to subcritical and supercritical water one should also control the density of the medium because minor variations of this parameter can significantly influence the rate constants for reactions and the distribution of reaction products.[10, 14] The reason is that some characteristics of water, *e.g.*, the dielectric constant, ionic product, viscosity and thermal conductivity change in parallel with the density. Using controllable variation of the density of subcritical and supercritical water, one can vary the properties of water, as a solvent, and control the physicochemical processes proceeding in the medium.

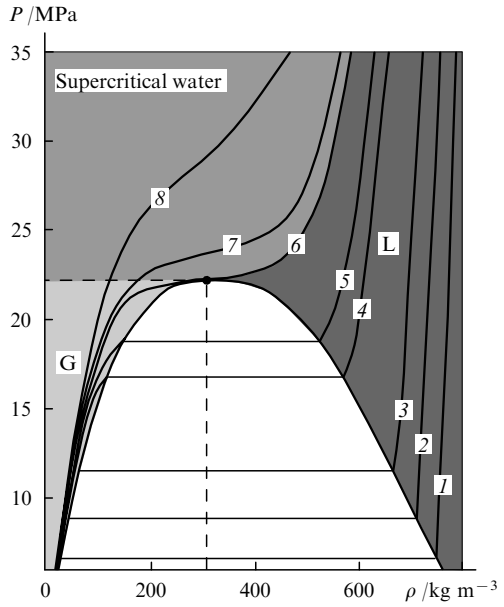


Figure 1. Phase diagram of water at elevated temperatures and pressures. T/ K: 553 (*1*), 573 (*2*), 593 (*3*), 623 (*4*), 633 (*5*), 647 (*6*), 653 (*7*) and 673 (*8*); G is gas and L is liquid.

2. The dielectric constant and ionic product

The temperature dependence of the ionic product of water measured at a constant pressure exhibits an extremum (Fig. 2). In the subcritical region the ionisation constant of H_2O reaches a maximum value, which is three orders of magnitude higher than the value typical of normal conditions. Therefore, subcritical water is a rich source of H^+ and OH^- ions (see Ref. 15); in other words, it can serve not only as a polar solvent but also as a self-neutralising acid–base catalyst. This offers great prospects for carrying out various catalytic reactions and hydrolysis in the subcritical region. As the critical point is approached, the parameter $\log K_w$ abruptly decreases and then monotonically decreases in the supercritical region (see Fig. 2).

The dielectric constant of water measured at a constant pressure continuously decreases as the temperature increases. At $T = 573$ K and a density of 700 kg m^{-3}, the dielectric constant of water is four times lower than that of acetone.[10] Supercritical water can be treated as a non-polar 'organic' solvent because its dielectric constant approaches a value of six.[16]

It should be noted that the subcritical and supercritical states of water are usually attained in various units of steam and nuclear power plants. Corresponding technological processes are thoroughly controlled. Therefore, a great body of experimental data on the properties of water at elevated temperatures and pressures was accumulated. Treatment of these data allowed the equations

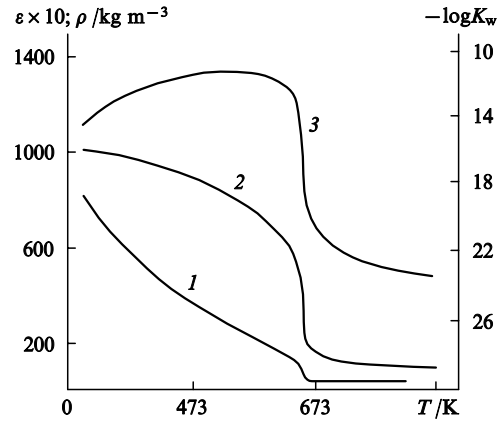


Figure 2. Temperature dependences of the dielectric constant (*1*), density (*2*) and ionic product of water (*3*) at a pressure of 24 MPa.

for calculation of the ionic product and dielectric constant of water over wide ranges of temperature and pressure to be derived.[17, 18]

3. Hydrogen bonds

Under normal conditions all water molecules are interconnected by a network of hydrogen bonds. This provides an explanation for many physicochemical properties of water. Association of water molecules leading to formation of hydrogen bonds can be described by the following reaction:

$$(H_2O)_i + H_2O \overset{K_i(T)}{\rightleftharpoons} (H_2O)_{i+1},$$

where $i = 1, 2, \ldots, \infty$ and K_i is the equilibrium constant for association.

At room temperature and atmospheric pressure, the $(H_2O)_{i+1}$ aggregates can comprise up to 100 molecules.[19] The formation of hydrogen bonds is an exothermic process; therefore, the equilibrium constant K_i decreases as the temperature increases.[10] Near the critical point the structure of water changes significantly, namely, an infinite network of hydrogen bonds is destroyed and water exists as separate clusters with a chain structure.[20] In the supercritical region, molecules within these clusters remain hydrogen bonded. At 673 K and a water density of 850 kg m^{-3}, up to 50% of the total amount of hydrogen bonds are broken.[21] A computer simulation showed that the number of water molecules in the clusters strongly depends on the density of the supercritical fluid. For instance, in the low density region ($T = 673$ K, $\rho = 167$ kg m^{-3}) water clusters comprise up to ten molecules, but as the density increases ($T = 772$ K, $\rho = 528$ kg m^{-3}), the number of molecules in certain clusters can exceed twenty. At a high density of supercritical water ($T = 680-771$ K, $\rho = 972-1284$ kg m^{-3}), all molecules are again interconnected by hydrogen bonds, but there are also a few clusters comprised of less than fifteen molecules that temporarily are not involved in the common infinite network of H bonds.[20]

It is this breakdown of hydrogen bonds on going to the critical point that is responsible for the decrease in the dielectric constant, changes in the dynamic viscosity and an increase in the self-diffusion coefficient of water.[22] Indeed, for a molecule in a liquid to be mobile, free space and weakened interactions with neighbouring molecules are needed. Water molecules not involved in the system of hydrogen bonds are more mobile; this is responsible for the increase in the self-diffusion coefficient of water.

4. Solubility of substances in subcritical and supercritical water

The solubility of inorganic and organic compounds in subcritical and supercritical water is governed by the dielectric constant of the medium. A decrease in the dielectric constant on going to the critical point causes an increase in the solubility of organic compounds and a decrease in the solubility of inorganic ionic compounds. Supercritical water can be mixed with oxygen, hydrogen and hydrocarbons in any proportion. Generally, the solubility of substances in water increases with temperature (provided a constant density of water) and with pressure (under isothermal conditions). Since slight variations of the state parameters near the critical point lead to significant changes in all physicochemical characteristics of water, even minor changes in the pressure and temperature can result in complete dissolution or, contrarily, precipitation of oxides and salts from solutions.[1, 2]

In the supercritical state, water molecules are clustered round the solute molecules; this causes local density fluctuations. On adding a substance, the density of the system near the critical point can increase to such an extent that the molar volume of the solute decreases by one or two orders of magnitude.[23]

A decrease in the dielectric constant of water at elevated temperature and pressure is responsible for significant changes in the structure of electrolyte solutions. Namely, under subcritical and supercritical conditions water molecules cannot efficiently screen ions; therefore, rearrangement of hydration shells and ion pairing occur.[24–26] For instance, nearly 50% of water molecules are lost in the first hydration shell of the Ni^{2+} ion in a nickel bromide solution at 698 K and 69 MPa.[24] If under normal (not critical) conditions nickel ions in aqueous solutions are octahedrally coordinated by water molecules (coordination number equals six), in supercritical water the H_2O molecules in the hydration shell are replaced by bromide anions and there are only 2.5 water molecules per Ni^{2+} cation. A similar 'ion dehydration' effect in supercritical water was also observed in sodium chloride[25, 27] and strontium nitrate and zinc nitrate solutions.[26, 28] A Raman spectroscopy study showed that replacement of water molecules in the hydration shells of ions under near-critical conditions leads to appreciable strengthening of cation–anion interactions and the number of ion pairs (here, cations are tightly bound to anions) increases.

A decrease in the number of water molecules surrounding an ion usually facilitates ion diffusion.[29] However, considering the conductivity of electrolyte solutions in the supercritical region, one should take into account two competing factors, *viz*., the number of water molecules in the hydration shell of the ion and the strength of the interaction between the ion and water molecules. The former factor dominates in the high-density region while the latter dominates at low density of supercritical water. Because of this, the electric conductivity plots for electrolyte solutions can exhibit extrema.[29]

5. Multicomponent systems

Efficient use of subcritical and supercritical water in various chemical and technological processes is impossible without investigating the phase diagrams of corresponding multicomponent systems. First of all, this is necessary in order to determine the temperatures, pressures and component concentrations corresponding to a monophase system. Indeed, operation with a homogeneous medium allows one to avoid the diffusion-related difficulties associated with mass transfer through the interface. For instance, the rate constant for cellulose hydrolysis increases abruptly on going from subcritical to supercritical water, thus providing an explanation for the transition from a heterogeneous to homogeneous reaction.[30]

Adding substances to water significantly complicates the water phase diagram. Phase equilibria studies in multicomponent systems near the critical point of water face some experimental problems; for this reason, computer simulation is often used.

To date, tens of phase diagrams of binary and ternary systems such as $H_2O-C_xH_y$,[13, 23, 31–33] H_2O-CO_2,[13] H_2O-O_2,[34] $H_2O-NaCl(NaOH,KCl)$,[35] $H_2O-CH_{4-x}F_x$,[36] $H_2O-Na_2SO_4$,[37] $CF_4(CHF_3)-H_2O-NaCl$[36] and $NaCl-Na_2SO_4-H_2O$[38] are available. All phase equilibria at high temperatures and pressures can be described by five schematic phase diagrams which were considered in detail in Ref. 2.

In practice, it is convenient to use projections of the $P-T-x$ diagrams on the $P-T$ plane. Figure 3 presents the critical curves (lines connecting the critical points of individual components) plotted in the $P-T$ coordinates for a number of binary systems.[13] If water and the second component have similar properties (as is the case of, *e.g*., the system H_2O-NH_3), the critical curve connecting the critical points of the two pure components in the $P-T$ diagram is continuous. If the polarity of the solute differs appreciably from that of water, the critical curve will consist of two portions. The upper portion issues from the critical point of the pure component with the higher boiling temperature and then the curve goes either to the region of high pressures and temperatures (as for the systems H_2O-Ar and H_2O-H_2) or initially to the low-temperature region and then, after passing through a minimum, to the region of high temperatures and pressures (as for the systems $H_2O-C_6H_6$ and H_2O-CO_2). Adding an electrolyte to water appreciably shifts the critical point of water.

The critical curves bound the homogeneity region of binary systems, namely, above the critical curve we deal with a mono-

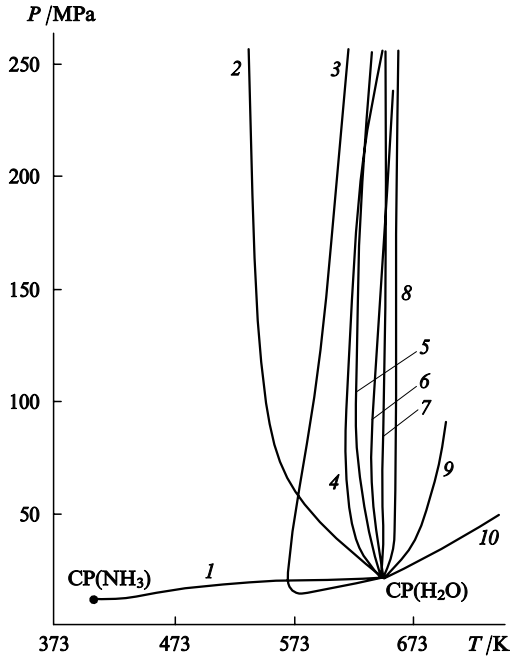


Figure 3. Critical curves for binary systems NH_3-H_2O (*1*), CO_2-H_2O (*2*), $C_6H_6-H_2O$ (*3*), $Xe-H_2O$ (*4*), CH_4-H_2O (*5*), N_2-H_2O (*6*), H_2-H_2O (*7*), $Ar-H_2O$ (*8*), $HCl-H_2O$ (*9*) and $NaCl-H_2O$ (*10*).[13]
$CP(H_2O)$ and $CP(NH_3)$ are the critical points of water and ammonia, respectively.

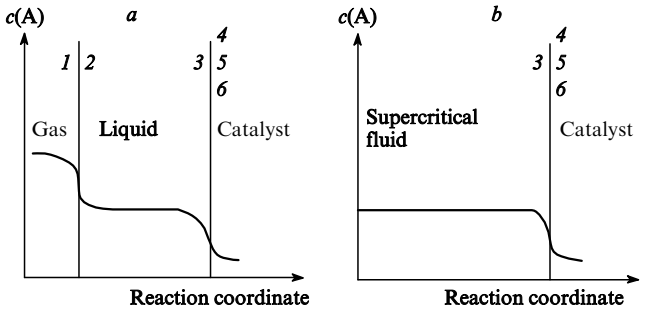


Figure 4. Concentration profiles of gas A in the course of a heterogeneous catalytic reaction carried out in water under normal conditions (*a*) and in supercritical water (*b*).[5]
Process: gas diffusion towards the gas/liquid interface (*1*), gas adsorption at the interface and gas diffusion in the bulk of the liquid (*2*), gas diffusion and liquid diffusion towards the liquid/catalyst interface (*3*), gas diffusion and liquid diffusion in the porous structure of catalyst (*4*), gas adsorption and liquid adsorption at the surface of the catalyst (*5*) and reaction between the gas and liquid molecules at the surface of the catalyst, desorption of reaction products and their diffusion in the bulk of the liquid phase (*6*).

phase system. At $T > 673$ K, all hydrocarbons, hydrogen and oxygen can be mixed with supercritical water in any proportion. In particular, adding oxygen to a water–methane (70% : 30%) mixture can lead to combustion ($T = 723$ K, $P = 100$ MPa); under these conditions, electrolysis of supercritical water can proceed without formation of the gas phase on electrodes.[13]

6. Homogeneous and heterogeneous catalysis

Among the most promising application avenues of subcritical and supercritical water are homogeneous and heterogeneous catalyses. Recently, a few reviews concerning the use of supercritical fluids in catalysis were published.[5, 9, 39] Unfortunately, subcritical and supercritical water is of limited use in the field so far. We would like to point out some advantages of the use of water in the near-critical region in various catalytic processes. Subcritical and supercritical water can serve as:

— a non-toxic solvent whose physicochemical properties can be 'tuned' in an optimised fashion to perform particular catalytic reactions;

— an efficient acid–base catalyst in homogeneous catalysis;

— a reagent and/or medium for preparing nanocrystalline heterogeneous catalysts with specified properties.

All these functions will be discussed below taking particular reactions and processes as examples.

It is convenient to consider the advantages of using supercritical water in catalysis taking a hypothetical heterogeneous reaction of gas A with liquid B on the surface of catalyst C as an example.[5] Figure 4 presents the concentration profiles of gas A for the same reaction carried out in water under normal conditions and in supercritical water. In the former case we deal with a ternary system 'gas + liquid + solid catalyst' (Fig. 4 *a*).

The concentration profile of gas A for the same reaction in supercritical water is quite different (Fig. 4 *b*). In this case, the gas and the liquid can be mixed in any proportion and we deal with a binary system 'supercritical fluid + solid catalyst'. Now, diffusion-related problems associated with mass transfer at the gas–liquid interface (processes *1* and *2*) are absent. In addition, diffusion of reagents towards the supercritical fluid/catalyst interface and in pores of the catalyst (processes *3* and *4*) proceeds much faster owing to the low viscosity of supercritical water. Thus, the catalytic reaction in the supercritical water proceeds in the kinetic region and its rate and, hence, selectivity can be controlled by varying the temperature and pressure. Probably, the poisoning and coking rates of the catalyst in supercritical water will be much lower due to the low viscosity of the medium, shorter time of contact between reagents and the surface of catalyst and high diffusion coefficients of reagents and reaction products.[40]

The activity and selectivity of heterogeneous catalysts are complex functions of their chemical compositions and the morphology and macrostructure parameters. Structure imperfection, state of the surface, nature of active centres and the concentration and distribution of impurity phases are governed by the synthesis conditions and heat treatment regime of the catalyst. The use of subcritical and supercritical water for preparing catalysts is quite promising for the design of new efficient nanocrystalline catalytic systems and for modification of the properties of traditional catalysts and supports.[41–44]

III. Specific features of experimental research using subcritical and supercritical water

Experiments with water at elevated temperatures and pressures require taking particular care and use of tailor-made equipment suitable for operation under extreme conditions. The end products of hydrothermal synthesis as well as the rates and selectivities of processes in subcritical and supercritical water are to a great extent determined by not only the properties of water but also the experimental technique, reactor material, being also dependent on the accuracy of maintenance of the specified temperature (pressure) and other parameters.

1. Batch and flow reactors

Reactions in subcritical and supercritical water can be carried out in batch and flow reactors. The simplest batch reactor is an autoclave placed inside a powerful heater and connected to temperature and pressure transducers (Fig. 5). In most cases the pressure in the batch reactor depends on the water filling degree; however, it can also be maintained using an external compressor or a pump. Reactions in these reactors can proceed both isothermally and under temperature gradient conditions .[45]

The vast majority of the studies on subcritical and supercritical media were carried out in batch reactors. However, from our point of view, this reactor design is for some reasons

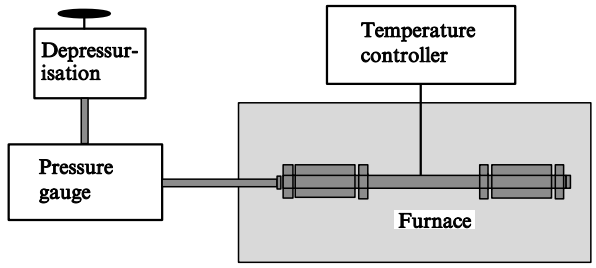


Figure 5. Scheme of a batch reactor.

inappropriate for experimental research. For instance, if a reaction is followed by a release of gaseous products, it is difficult to maintain the density of the medium at a constant level in the batch reactor. Target organic synthesis in these systems is nearly impossible because variations of the reagent and product concentrations in the course of experiments can change the mechanisms of the processes occurring in the system, thus making the interpretation of the results obtained more difficult.

Batch reactors are appropriate only for carrying out recrystallisation processes and obtaining single crystals and minerals.[46] All other experiments in subcritical and supercritical water can be more conveniently performed in highly efficient flow systems that are also easy to control. In addition, laboratory flow systems can be scaled with ease to commercial plant level.

A scheme of a typical experimental flow system for operation with subcritical and supercritical water is shown in Fig. 6. Using a high pressure pump, water is continuously supplied to the system of powerful heaters at a specified rate and is heated to the desired temperature. A solution of reagents is continuously supplied to the system using the second pump. Mixing of the two flows at the inlet of the reactor is followed by physicochemical transformations of the reagents in subcritical and supercritical water. After passage through the reactor the reaction mixture is cooled to room temperature and then collected at the system's outlet. The pressure in the reactor is maintained by a back pressure regulator. If needed, one can use additional pumps for separate supply of several reagents to the reactor. For instance, oxidation reactions of organic compounds in supercritical water can be designed in such a way that one pump will supply the organic compound and the other pump will supply the oxidiser, *e.g.*, hydrogen peroxide.

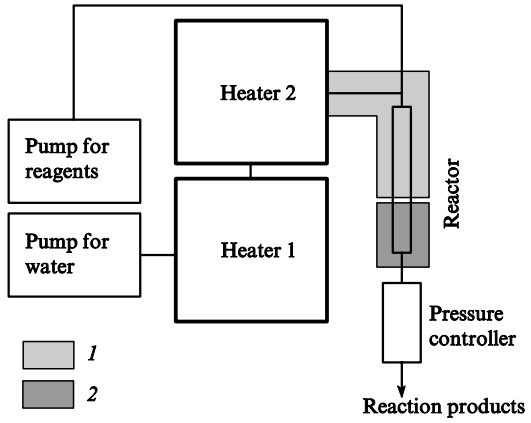


Figure 6. Scheme of an experimental flow reactor for operation with subcritical and supercritical water.
Heating zone (*1*) and cooling zone (*2*).

The duration of a reaction in a flow reactor (τ) depends on the specific volume of water under the experimental conditions (υ /m^3 kg^{-1}), on the reaction mixture consumption (M_f/kg s^{-1}) and on the volume of the reaction zone (V/m^3)

$$\tau = \frac{V}{M_f \upsilon}.$$

Typically, the duration, τ, is of the order of a few seconds for a flow reactor,[43] being much shorter than for the batch reactors.

Near the critical point the heat capacity of water tends to infinity; therefore, powerful heaters are needed to attain the supercritical state. These can be conventional electric furnaces as well as other heat sources, *e.g.*, microwave radiators.[47]

To establish the mechanisms of the reactions proceeding in subcritical and supercritical water, it is of great interest to study processes *in situ* using various spectral methods. To this end, the reactor can be equipped with a tailor-made optical cell suitable for operation under hydrothermal conditions.[7,48]

When carrying out reactions in flow systems, the possibility of reactor blockage due to precipitation of various substances (*e.g.*, inorganic salts and oxides) should be taken into account.[49] In order to avoid reactor blockage, it is appropriate to periodically pass a solvent through the reactor to remove organic and inorganic sediments.[50]

Extraction processes used in household and industrial waste management and in modification of the properties of various systems involve treatment of solid materials with subcritical and supercritical water, which can hardly be done in flow reactors. Specific pumps for operation with aqueous suspensions function only if solid particles have a particular size. To solve this problem, a system was designed with simultaneous supply of the solid phase and subcritical or supercritical water to the batch reactor.[51] After a specified time the reaction products are removed from the reactor and a new portion of reagents is supplied to the system. This design combines the advantages of the flow and batch reactors.

2. Corrosion problem

Perhaps, the most complicated problem in operating with subcritical and supercritical water is corrosion of experimental setups. Even deionised supercritical water is a highly corrosive medium, which causes destruction of the alloys the reactors are made of.[52] When performing chemical reactions involving organic and inorganic substances under hydrothermal conditions, researchers deal with oxidant, salt, acid and base solutions that are corrosive media even under normal conditions. In this connection, the search for materials that are corrosion stable at high temperatures and pressures is a topical problem in chemistry of subcritical and supercritical water.[53,54]

Corrosion studies [52,54–62] of various materials in subcritical and supercritical water showed that stainless steel, nickel alloys, titanium, tantalum, noble metals and ceramics undergo severe destruction in the presence of salts, acids or gases.[61]

The mechanism of water corrosion at high temperatures and pressures is somewhat different from the conventional water corrosion mechanism. Electrochemical corrosion usually involves two or more conjugated redox reactions on different sides of the corroding metal. The low conductivity of supercritical water hampers ion transfer between the centres of the conjugated redox reactions; therefore, in this case corrosion is a result of the one-step reaction of, *e.g.*, oxygen or HCl with the metal.[58]

The corrosion stability of many metals and alloys is due to the formation of passivating oxide films on their surfaces. However, metal oxides become reactive in supercritical water. For instance, Cr_2O_3 is dissolved to give chromic acid [57]

$$\frac{1}{2}O_2 + Cr_2O_3 + 2x\,H_2O = 2[CrO_2 \cdot x\,H_2O].$$

Because of this, chromium and some Cr-based alloys corrode in supercritical water. Only the G-30 alloy (29.4% Cr, 40.1% Ni, 14.5% Fe, 5.1% Mo, 2.9% W + Co + Cu) exhibits a high corrosion stability against aqueous solutions containing oxygen and chloride ion at 693 K and a pressure of 40 MPa.[60]

Sometimes, in order to avoid corrosion, the inside of metallic reactors is covered with ceramics. However, often this does not make the situation better, because out of more than thirty investigated ceramic materials only pure alumina and $Al_2O_3-ZrO_2$ ceramics did not severely corrode in supercritical water containing hydrogen peroxide and hydrochloric acid.[59]

IV. Hydrothermal synthesis of nanocrystalline oxide materials

Recently, interest in nanocrystalline materials has been growing increasingly because of the unique physicochemical properties of these objects. It was established that the majority of the properties of solids become size-dependent as the particle size decreases down to a few interatomic distances in one, two or three dimensions. Nanocrystalline metallic and oxide powders with specified morphologies, phase compositions and properties of the bulk phase and the surface are needed to produce a variety of new generation materials such as sensors, semiconductors, fuel cells, high-density ceramics, efficient heterogeneous catalysts and sorbents.

At present, nanocrystalline materials are obtained using the sol–gel technique, codeposition, hydrolysis of alkoxides, organometallic synthesis, pyrolysis, gas-phase methods and detonation synthesis. Most of the methods mentioned above involve a number of stages and are labour-consuming, which complicates the wide use of nanocrystalline materials (even well-studied materials!) in technological processes. In this connection development of new, high-performance methods of fabrication of nanomaterials becomes topical.

Among the most promising methods of fabrication of oxide nanocrystalline materials is hydrothermal synthesis (a heterogeneous reaction in water at $T > 373$ K and $P > 0.1$ MPa).[45] When synthesising various oxides, the reaction conditions can be varied over a wide range, *i.e.*, it is possible to carry out hydrothermal synthesis both under mild conditions at moderate temperatures and pressures [47, 63] and in supercritical water.[8, 43] The hydrothermal method is used to obtain nanocrystalline oxide powders with specified particle sizes and phase compositions and well-developed specific surface area, which often cannot be attained using conventional techniques. The method also permits preparation of nanocrystalline metastable phases that cannot be synthesised under normal conditions.[64, 65]

For a long time, single crystals and minerals were mainly obtained by hydrothermal synthesis in batch reactors. The authors of most recent studies on the synthesis of nanocrystalline simple and complex oxide systems in subcritical and supercritical water [*e.g.*, solid solutions with fluorite structures $Ce_{1-x}M_xO_{2-\delta}$ (M = Eu, Sm, La, Pr, Ca, Sr, Gd, Y),[66–70] ZrO_2-CaO (see [71]) and $ZrO_2-Y_2O_3$,[72] perovskites $BaTiO_3$, $SrTiO_3$ and $(Ba_{1-x}Sr_x)TiO_3$,[73–75] simple oxides HfO_2,[76] Y_2O_3,[77] ZnO,[78] Cu_2O and CuO,[43, 79] Fe_3O_4,[80] CeO_2] also used batch reactors.[81] These nanocrystalline oxide materials often comprise a number of phases and are characterised by a nonuniform particle size distribution, which is due to the difficulties of control of the experimental conditions in batch reactors. According to published data, the synthesis can take from a few minutes [79] to several days;[72] often, no explanation is given for the choice of a certain duration of the reaction.

To the best of our knowledge, current research on the synthesis of nanocrystalline oxide materials using subcritical and supercritical water in flow reactors is carried out at three research centres, namely, at the Tohoku University (Japan),[8, 82–89] at the University of Nottingham (United Kingdom) [65, 90] and at the M V Lomonosov Moscow State University (Russia).[41–44] Here, researchers developed methods of synthesis of many simple and complex oxide systems and demonstrated the possibility of carrying out one-step syntheses of supported nanocrystalline heterogeneous catalysts in flow reactors (Table 3). The majority of systems synthesised in flow reactors are characterised by a narrow particle size distribution, a well-developed surface, and by being monophase. The synthesis takes a few seconds and the experimental conditions vary from 503 K and 25 MPa to 673 K and 35 MPa. The physicochemical properties of oxide nanosystems are governed by the synthesis conditions (temperature, pressure, duration) and by the composition and concentration of the reaction mixture.

1. Mechanism of oxide formation

A research group from Japan headed by Prof. K Arai proposed a two-step mechanism of metal oxide formation under hydrothermal conditions.[8, 83] The first reaction stage involves fast hydrolysis of the metal salt solution to give corresponding hydroxides. In the second stage, dehydration of hydroxides results in the formation of oxides.

$$ML_x + x\,H_2O \rightleftharpoons M(OH)_x + x\,HL,$$

$$M(OH)_x \rightleftharpoons MO_{x/2} + x/2\,H_2O.$$

The overall rate of oxide formation is a function of the temperature, ionic product of water and dielectric constant of the medium. The ionic product of subcritical water is high; therefore, one can expect that in this case hydrolysis will proceed at a higher rate compared to the reaction in supercritical water. At the same time, dehydration of hydroxides and nucleation of oxides require a low dielectric constant of the medium. The solubilities of inorganic compounds in subcritical water are rather high; this hampers attainment of local supersaturations which is necessary for nucleation of crystalline oxides. Owing to the high dielectric constant of the medium, dehydration of hydroxides in subcritical water proceeds at a lower rate compared to the process in supercritical water. In this connection one should choose the experimental conditions with allowance for specific features of a particular system (namely, the tendency of the precursor towards hydrolysis and the solubility of the reaction products). In most cases the maximum rate of formation of nanocrystalline metal oxides under hydrothermal conditions is achieved using supercritical water. For instance, the synthesis of nanocrystalline α-Fe_2O_3 (particle size 20 nm) from ferric nitrate in supercritical water takes less than a second.[8]

2. Choice of precursor

The properties of nanocrystalline oxides obtained by the hydrothermal method are to a great extent determined by the choice of precursor, all things being equal. For instance, hydrolysis of $Fe(NO_3)_3$, $Fe_2(SO_4)_3$ and $FeCl_2$ in supercritical water results in α-Fe_2O_3; however, the reaction carried out under identical conditions with $Fe(NH_4)_2H(C_6H_5O_7)_2$ as precursor gives mixed oxide Fe_3O_4.[8] The case in point is that in the latter case thermal decomposition of ammonium citrate leads to carbon monoxide, which reduces Fe^{3+} to Fe^{2+}.

Usually, nanocrystalline oxides are synthesised in flow reactors from true solutions of metal salts (nitrates, chlorides, sulfates, acetates). Multicomponent oxides are obtained using solutions that simultaneously contain a number of salts in stoichiometric ratios (see Table 3).

The use of solutions for the synthesis of multicomponent oxides in batch reactors is usually precluded owing to different hydrolysis rates of the salts of the metal constituents of the complex oxide because gradual heating of the autoclave leads to formation of individual simple oxides at different instants of time. Therefore, experiments in closed systems are carried out with gels or codeposited metal hydroxides as precursors. For instance, the oxides $Ce_{1-x}M_xO_{2-\delta}$ (M = Eu, Sm, La) were synthesised [66–68] in autoclaves loaded with gels prepared by coprecipitation of solutions of cerium nitrate and the second metal with ammonia at pH 10, while nanocrystalline solid solutions ZrO_2-CaO were synthesised from amorphous hydrated zirconia, freshly prepared CaO and alkali additives (LiOH or NaOH).[71] However, synthesis involving alkali and other mineral additives is undesirable because they can contaminate nanomaterials.

Table 3. Synthesis conditions and characteristics of nanocrystalline oxide systems obtained under hydrothermal conditions.

Oxide	Synthesis conditions			Precursor	Particle size /nm	Specific surface /$m^2\ g^{-1}$	Ref.
	T /K	P /MPa	τ /s				
α-Fe_2O_3	673	35	120	$Fe(NO_3)_3$	~50	–	8
	673	35	120	$Fe_2(SO_4)_3$	~50	–	8
	673	35	120	$FeCl_2$	~50	–	8
Fe_3O_4	673	35	120	$Fe(NH_4)_2H(C_6H_5O_7)_2$	~50	–	8
Co_3O_4	673	35	120	$Co(NO_3)_2$	~100	–	8
AlOOH	673	35	120	$Al(NO_3)_3$	~600	–	8
NiO	673	35	120	$Ni(NO_3)_2$	~200	–	8
ZrO_2	673	30	120	$ZrOCl_2$	~10	–	8
	653	25	4.5	$ZrO(NO_3)_2$	3–5	163–172	42
TiO_2	673	30	120	$TiCl_4$	~20	–	8
	673	35	120	$TiSO_4$	~20	–	8
	503	25	8.5	$(CH_3COO)_xTi(OPr)_{4-x}$	7–9	189–201	42
CeO_2	573	30	20	$Ce(NO_3)_3$	~300	–	84
	673	30	20	$Ce(NO_3)_3$	~18	–	84
	603	25	6.8	$(NH_4)_2Ce(NO_3)_6$	6–7	110	42
$Ce_{1-x}Zr_xO_2$ ($x = 0-1$)	573	25	5	$Zr(CH_3COO)_4$, $(NH_4)_2Ce(NO_3)_6$	3–5	180	65
$Zr_{1-x}Y_xO_2$ ($x = 0.03-0.1$)	653	25	4.5	$ZrO(NO_3)_2$, $Y(CH_3COO)_3$	4–5	147–161	42
$Zr_{1-x}In_xO_2$ ($x = 0.03-0.1$)	653	25	4.5	$ZrO(NO_3)_2$, $In(CH_3COO)_3$	4–5	135–154	42
$Ce_{0.1}Y_xZr_{0.9-x}O_2$ ($x = 0.06, 0.1$)	653	25	4.5	$ZrO(NO_3)_2$, $Y(CH_3COO)_3$ $(NH_4)_2Ce(NO_3)_6$	3–4	115–164	42
$BaO \cdot 6\,Fe_2O_3$	673	30	60	$Fe(NO_3)_3$, $Ba(NO_3)_2$	50–1000	–	85
$Al_5(Y+Tb)_3O_{12}$	653	25	4.5	$Al(NO_3)_3$, $Y(NO_3)_3$, $TbCl_3$	20–600	–	89
$LiCoO_2$	673	30	60	$LiNO_3$, $Co(NO_3)_2$	40–400	–	89
Pd–Rh/ZrO_2	653	25	4.5	$ZrO(NO_3)_2$, $Rh_2(CH_3COO)_4$ $Pd(CH_3COO)_2$	3–5	160–170	44
Pd–Rh/TiO_2	503	25	8.5	$(CH_3COO)_xTi(OPr)_{4-x}$ $Rh_2(CH_3COO)_4$ $Pd(CH_3COO)_2$	7–9	190–210	44

3. Particle size and phase composition

By varying the synthesis conditions it is possible to vary the particle size and to change the morphology of the oxides obtained. An increase in the synthesis time causes an increase in the average particle size. A similar effect is also observed with increasing the concentration of reagent solutions.

There is no consensus of opinion as to the influence of the temperature of hydrothermal synthesis on the particle size. Taking TiO_2 as an example, it was shown that an increase in the reaction temperature from 503 to 653 K causes an increase in the particle size from 7–9 to 16–18 nm, respectively, and a decrease in the specific surface area of titania from 200 to 50 $m^2\ g^{-1}$, respectively (see Ref. 43). The reverse was observed for ceria, *viz*., the CeO_2 particle size is 300 nm at 573 K and 18 nm at 673 K (see Ref. 84). Probably, these results could be explained with allowance for specific features of precursors and the ratio of the rates of hydrolysis, dehydration and crystal growth at various temperatures.

In spite of the short times for the synthesis of oxides in flow reactors, these substances are characterised by a high degree of crystallinity. Sometimes hydrothermal treatment leads to stabilisation of phases that are metastable under normal conditions. For instance, hydrolysis of zirconium nitrate in subcritical water results in a mixture of monoclinic and tetragonal ZrO_2 polymorphs.[65] The formation of the metastable tetragonal polymorph is most probably due to the size effect, namely, a decrease in the particle size to a certain critical size causes preferred formation of the phases with higher symmetry of the crystal lattice.[65,91]

Depending on the composition of the solution used in the hydrothermal synthesis of the oxides $Zr_{1-x}M_xO_2$ (M = Ce, Y, In), it is possible to obtain systems with specified ratios of the monoclinic, tetragonal and cubic polymorphs. For instance, as the indium content in the system $Zr_{1-x}In_xO_2$ increases, the tetragonal-to-monoclinic ratio of ZrO_2 phases increases; nanocrystalline solid solutions $Ce_{0.5}Zr_{0.5}O_2$ and $Ce_{0.1}Y_{0.1}Zr_{0.8}O_2$ obtained in supercritical water have cubic lattices.[43]

4. Control of the oxidation states of elements

Hydrolysis of metal acetates, formates and oxalates in supercritical water involves partial decomposition of acids formed to CO. At supercritical temperatures and pressures, carbon monoxide can be mixed with water in any proportion, thus forming a homogeneous reducing medium. By varying the experimental conditions one can control the oxidation states of the elements in nanocrystalline oxides and thus obtain systems with specified ratios of the phases containing the same element in different oxidation states.

In supercritical water ($T = 658$ K, $P = 35$ MPa) copper hydroxycarbonate decomposes into copper(II) oxide and oxalic acid decomposes into carbon monoxide. Carrying out these two reactions simultaneously in a batch reactor results in metallic copper, a mixture of copper and copper(I) oxide or a mixture of

copper(I) oxide and copper(II) oxide.[43] The content of each phase is governed by the amount of oxalic acid added and can be controlled with ease. This technique seems to be promising for the preparation of catalysts and magnetic materials with preset concentrations of paramagnetic centres.

Hydrocarbon ligands can also favour the formation of reduced nanocrystalline systems in supercritical water. In particular, hydrothermal treatment of copper(II) nitrate in the presence of hexane-1-thiol affords metallic copper with particle sizes lying between 1.5 and 30 nm (see Ref. 79).

The oxidation states of elements can also be controlled in the course of fabrication of nanocrystalline materials in subcritical and supercritical water using hydrogen, oxygen and hydrogen peroxide. For instance, hydrolysis of cobalt(II) salts under hydrothermal conditions in the presence of H_2O_2 involves oxidation of Co^{2+} to Co^{3+}, which allows phases containing cobalt(III), *e.g.*, $LiCoO_2$ to be synthesised.[89]

It should be noted that subcritical and supercritical water can be successfully used for the synthesis of not only oxides but also other nanocrystalline materials. For instance, carbon nanotubes can be obtained by hydrothermal treatment of amorphous carbon at a temperature of 1073 K and a pressure of 100 MPa.[92] The nanotubes are a few hundred nanometres long, have an outer diameter of 10 to 50 nm and contain no amorphous carbon impurities.

Nanomaterials can also be formed under hydrothermal conditions by the rapid expansion of supercritical water containing dissolved oxides and hydroxides (RESS process).[93] Nearly instantaneous transition from supercritical fluid to gas ($< 10^{-5}$ s) causes the formation of nanocrystalline oxides. However, this is a low-performance technology because of the low solubility of inorganic substances in supercritical water. For instance, the solubility of $Co(OH)_2$ and $Ni(OH)_2$ in water at 653 K is only 10^{-6} and 10^{-8} mol kg^{-1}, respectively.[94] In this connection the RESS process is of limited use.

V. Organic reactions in subcritical and supercritical water

To date, wide experience in carrying out various organic reactions under hydrothermal conditions has been accumulated.[6, 95–97] Unfortunately, most studies are concerned with deep oxidation of organic substances in subcritical and supercritical water. These studies are undoubtedly of importance for solving problems of treatment of toxic industrial and municipal waste. However, water at elevated temperatures and pressures is first of all of interest as a unique solvent and reagent for fine organic synthesis.

Carrying out many organic reactions is preceded by the routine procedure of choosing a solvent with optimum physicochemical characteristics. Many solvents are toxic, fire-hazardous and explosive, which present severe problems for the industrial application of these compounds. In the case of reactions involving subcritical and supercritical water the choice of solvent is replaced by 'tuning' the temperature and pressure in such a way that the properties of the medium (density, ionic product, dielectric constant, viscosity, *etc.*) be optimised for performing a particular organic reaction.

Differences between the physical properties of subcritical and supercritical water are responsible for the fundamentally different mechanisms of organic reactions proceeding in these media. Typically, acidic and basic catalyses involving charged intermediates proceed in subcritical water while free-radical processes proceed in supercritical water.[98] In the latter case the reactions are initiated by hydrogen atoms and hydroxyl radicals that form in the homolytic decomposition of water molecules. Primary free radicals can also be formed in the system by collisions between the reagent and solvent molecules or as a result of the reactions with O_2 and NO_2 molecules having unpaired electrons.

Generally, the organic reactions possible in subcritical and supercritical water are as follows: hydrolysis; hydration/dehydration; various rearrangements; elimination; formation and cleavage of carbon–carbon bonds; hydrogenation/dehydrogenation and oxidation.

Many of these reactions can proceed under hydrothermal conditions at rather high rates and yields in the absence of catalysts. As to other types of reactions, subcritical water is an efficient acid-base catalyst, which excludes the necessity of neutralisation of large amounts of salts traditionally used as Lewis acids in, *e.g.*, alkylation reactions.[14] Conventional oxide and metallic heterogeneous catalysts can also be employed; however, in this case particular attention should be paid to the stability of catalytic systems in subcritical and supercritical water.[99]

Below we will consider a number of organic reactions that proceed under hydrothermal conditions, are of greatest value for practical use and provide an idea of the features of transformations of organic compounds in subcritical and supercritical water.

1. Methanol oxidation

Methanol oxidation is one of the best studied reactions in supercritical water.[100–108] At present, most studies in the field are concerned with analysis of the available experimental data.

Methanol oxidation in supercritical water results in water and carbon dioxide as end products. A detailed kinetic model[100] for this reaction is in good agreement with the experimental data. The model includes one hundred and forty-eight reversible elementary radical stages and twenty-two types of reactive particles. Among the primary products of methanol oxidation is formaldehyde, which is more reactive than methanol under the reaction conditions (773–862 K, 24.6 MPa); therefore, eventually the yield of formaldehyde is at most 24%.[101] Kinetic studies revealed that methanol oxidation is a pseudo-first order reaction with respect to methanol and zero order reaction with respect to oxygen and has an activation energy of 328 ± 84 kJ mol^{-1}.

Later,[102] it was shown that the kinetics of methanol oxidation in supercritical water can be correctly described using seventeen fastest radical reactions and fourteen types of reactive particles. The calculated overall rate constant for the reaction and the yields of various oxidation products were in agreement with those obtained using the more complex model (see Ref. 100).

Methanol oxidation under hydrothermal conditions can also be described using the ideal gas model.[101, 102] However, near the critical point of water the equation of ideal gas state is inapplicable owing to the infinite compressibility of the medium. The compressibility of supercritical water can be taken into account using, *e.g.*, the Peng–Robinson semiempirical cubic equation.[103]

2. Reactions involving hydrocarbons

The high stability of hydrocarbons at temperatures and pressures near the critical point of water opens great prospects for carrying out target organic synthesis under hydrothermal conditions. Here, methane oxidation reaction has been best studied (Refs 100, 106, 107, 109–112). Most studies were concerned with deep oxidation of methane in supercritical water to carbon oxides and water. The process is characterised by an activation energy of about 180 kJ mol^{-1} at $T = 288–923$ K and $P = 24.6$ MPa, being a first order reaction with respect to methane and a 2/3 order reaction with respect to oxygen.[109]

Methane oxidation in an excess of oxygen can be theoretically described using both traditional combustion models corrected for high pressure and the ideal gas model. In the latter case the inclusion of reactions involving the $HO_2^{\bullet}$ radical (probably, the main oxidant under supercritical conditions) has the strongest effect on the results of calculations.[100, 110]

Partial methane oxidation into methanol in subcritical and supercritical water is also possible.[112, 113] Methane conversion in a batch reactor ($T = 622–754$ K, $\rho = 150–350$ kg m^{-3}) at a $[CH_4]:[O_2]$ ratio of 10 : 26 is at most 6%, the greatest selectivity of methanol formation (75%) being attained at low methane conversions.[112] The maximum selectivity of methanol formation in a flow system in the temperature range 673–683 K at a pressure

of 25 MPa is 35%.[113] Among other oxidation products are carbon oxides and hydrogen. Raising the temperature and an increase in oxygen conversion reduces the selectivity. The activation energy for methane oxidation is 400 kJ mol^{-1}, the process being a 1.3 order reaction with respect to methane and a 0.3 order reaction with respect to oxygen.

In the course of catalytic cyclotrimerisation of alkynes under supercritical conditions water behaves as a conventional organic solvent.[114, 115] Hydration of hydrocarbons to give ketones proceeds only in the presence of acids.[114] In particular, treatment of hex-1-yne at pH 6 affords nearly 10% – 14% yields of hexan-2-one in accord with Markovnikov's rule. In the case of salt catalysed ketone hydrolysis the product yields correlate with the acidity of the cation aqua complexes, namely, no hydrolysis proceeds in the presence of NaCl and $CaCl_2$ and a 100% selectivity of hexan-2-one formation is achieved in the presence of $CuCl_2$ and $SnCl_2$.

Subcritical water (573 – 628 K) is suitable for selective oxidation of alkylaromatic hydrocarbons with molecular oxygen to the corresponding aromatic acids and carbonyl compounds in the presence of catalysts.[116] The best results were obtained using $MnBr_2$ and $CoBr_2$ as catalysts. Reactions in the presence of other salts or in the absence of catalysts are characterised by severe charring and formation of dimerisation products.

3. Dehydration of alcohols

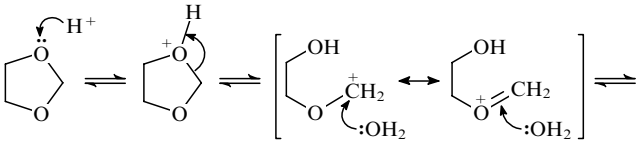
Dehydration of alcohols to give alkenes in subcritical water proceeds at high rates even in the absence of catalysts.[6, 117] In the supercritical region, the reaction significantly slows down and the process can be accelerated only by adding mineral acids.[98] As a consequence, the selectivity decreases due to the reactions between the catalyst and alcohols. Formation of carbon oxides, methane and ethane in the ethanol dehydration in supercritical water points to a radical character of the reaction.

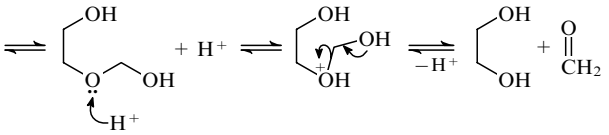
Subcritical water is a protic solvent; therefore, dehydration under subcritical conditions proceeds following the E2 mechanism with high selectivity.[117] The appearance of small amounts of by-products is due to alkene protonation to give carbocations that undergo rearrangements followed by isomerisation. For instance, dehydration of cyclohexanol results in cyclohexene, 1-methylcyclopentene and 3-methylcyclopentene.

4. Ether transformations

Supercritical water possesses no ionic properties; however, reactions catalysed by bases or acids that were added (or formed in the course of reaction) can proceed in this medium at high pressures and moderate temperatures. In particular, diphenyl ether decomposes into typical radical condensation products, diphenyl and phenoxydiphenyl, at a density of water of less than 300 kg m^{-3} in the temperature interval 688 – 753 K.[118] However, as the critical density of water ($\sim$300 kg m^{-3}) is attained, the conversion of diphenyl ether increases dramatically and only phenol is formed, a product of ether hydrolysis by the S_N1 cationic mechanism. The reaction is catalysed by protons that appear during heterolytic dissociation of phenol; therefore, the process accelerates with time.

Hydrolysis of ethers in subcritical water has been well studied.[98, 119 – 122] Note that in this case water can act as an efficient acid-base catalyst owing to a high dissociation constant.[6, 14] For instance, hydrolysis of 1,3-dioxolane at 623 K and 34.5 MPa proceeds by the following acid-base mechanism:[98]





The degree of conversion is 99.8% and the end products are formaldehyde and ethylene glycol.

Decomposition of dibenzyl ether in supercritical water at 936 – 961 K and a density of water of 347 kg m^{-3} results in benzyl alcohol, benzaldehyde, toluene and a number of by-products.[123] The proposed mechanism of the process includes eight main stages and is in good agreement with experimental data. The rate constant for pyrolysis of dibenzyl ether in supercritical water exceeds the rate constant for hydrolysis of this compound.

5. Acetic acid oxidation

The limiting stage of decomposition of various organic substances in supercritical water is oxidation of an intermediate product, acetic acid. Therefore, particular attention is paid to acetic acid oxidation under hydrothermal conditions.[108, 124 – 130]

Depending on the reaction conditions, various products can be formed. For instance, oxidation with oxygen at 698 – 873 K and a pressure of 24.6 MPa (100% conversion at a residence time of 8 s) leads to the formation of carbon oxides, methane, hydrogen and trace amounts of propionic acid.[124] Oxidation in a batch reactor at long residence times results in carbon dioxide and water; however, in this case the conversion of acetic acid is at most 64% even in a five-fold excess of oxygen.[125] Hydrogen peroxide is a more efficient oxidant; here, the acid conversion increases to 97.7%.

Addition of transition metal cations favours the formation of large amounts of hydroxyl radicals and enhances the oxidising ability of H_2O_2. The efficiency of acetic acid oxidants in supercritical water (T = 673 – 733 K, P = 27.5 – 35.0 MPa) decreases as follows:[126] $Cu-H_2O_2 > Fe-H_2O_2 > MnSO_4-H_2O_2 > H_2O_2 > O_2$. In this case, the strongest acetic acid oxidant is potassium permanganate; however, its activity decreases in subcritical water.

Acetic acid oxidation reaction in a flow reactor is $\sim 1/3$ order with respect to oxygen and nearly first order with respect to acetic acid,[124, 128] with an activation energy of about 180 kJ mol^{-1}.

Acetic acid remains rather stable in supercritical water in the absence of oxidants, namely, the conversion of AcOH at 873 K and 24.6 MPa and a residence time of 8 s is only 35%.[124]

6. Phenol oxidation

The chemistry of phenol in supercritical media is interesting in regard to both the utilisation of toxic industrial waste and target organic synthesis, because phenolic type fragments are present in the structures of many organic molecules. A great body of experimental data and results of theoretical studies concerned with phenol transformations under hydrothermal conditions are available.[131 – 140] However, all of them were obtained for phenol oxidation only. At the same time phenol is rather stable in supercritical water in the absence of oxygen.[135] This suggests the possibility of carrying out more complex reactions involving phenol, such as formylation, sulfonation, amination, *etc*. under hydrothermal conditions.

The majority of the experimental data on phenol oxidation are consistent. The activation energy for this reaction is 100 – 125 kJ mol^{-1} (see Refs 135 and 136). The rate of the reaction in supercritical water is proportional to the phenol concentration [133 – 137] and oxygen concentration to the 0.4 – 0.5 power.[133, 136] It was experimentally proved that the rate of phenol oxidation is independent of the total pressure in the system, being dependent on the reagent concentrations [135]

$$\frac{d[PhOH]}{dt} = -k\frac{[PhOH][H_2O]^{1.38}\chi}{2.89+\chi},$$

where

$$\chi = \frac{[O_2]}{[PhOH]}.$$

It is assumed that the mechanism of phenol oxidation involves two parallel reactions, ring opening and dimerisation.[140] The reaction results in carbon oxides as the end products; chain branching in the course of decomposition of an aromatic hydroperoxide and bimolecular initiation have the strongest effect on the kinetics of phenol oxidation. However, the reaction order with respect to oxygen, the activation energy and the rate constant for the reaction calculated using this model are overestimated compared to the experimental data.

More complex kinetic models include the possibility for water to participate in the phenol oxidation as a reagent.[135, 138] Initially, the reaction system contains only phenol, oxygen and water; therefore, the oxidation can be initiated by three monomolecular and two bimolecular reactions [138]

$$PhOH \longrightarrow PhO^{\bullet} + H^{\bullet},$$

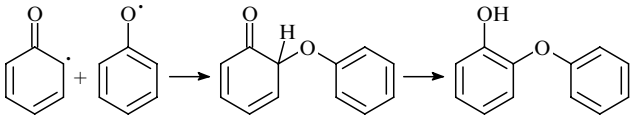
$$O_2 \longrightarrow 2O^{\bullet},$$

$$H_2O \longrightarrow OH^{\bullet} + H^{\bullet},$$

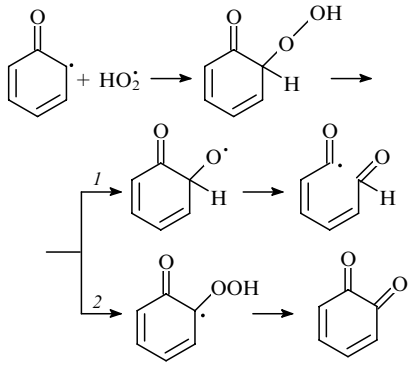
$$PhOH + O_2 \longrightarrow PhO^{\bullet} + HO_2^{\bullet},$$

$$H_2O + O_2 \longrightarrow HO_2^{\bullet} + OH^{\bullet}.$$

The phenoxyl radical formed in the reaction can then undergo dimerisation, hydroxylation to give cresols and ring opening. Dimerisation leads to 2-phenoxyphenol, dibenzofuran, 4-phenoxyphenol and 2,2′-diphenol as the major products.[138] As an example, we will consider the formation of 2-phenoxyphenol.



Ring opening of the phenoxyl radical can proceed as follows:[138]



Only route *1* resulting in a substituted vinyl radical is possible for the radical bearing the unpaired electron in the *para*-position to the oxygen atom. Phenol dimers can also undergo similar transformations to give formic, glyoxylic, propionic, oxalic, succinic, maleic and acetic acids.[136, 138] Further oxidation of these carboxylic acids results in water and carbon dioxide.

7. Reduction of aldehydes and ketones

Reduction of the carbonyl group provides an example of a selective, environmentally safe reaction in subcritical water. Sodium formate reduces aldehydes and a number of ketones in the absence of catalysts and toxic solvents at 523 – 573 K and a pressure of 7.5 MPa.[141] Environmentally friendly carbon dioxide is produced as a by-product of the reaction. The selectivity of the reaction can be controlled by varying the reaction conditions. An increase in temperature gives higher yields of primary alcohols. In most cases the reduction proceeds with high yield (up to 74%); only for acyclic ketones does the conversion remain low even at long residence times.

8. Diels – Alder reaction

The Diels – Alder reaction is a conventional method of synthesis of organic compounds containing six-membered rings in the chemical structure. However, a significant drawback of this reaction is its low rate. Sometimes, the reaction can take a few days. Raising the temperature accelerates the process; here, subcritical and supercritical water are excellent solvents.

It was established that the non-catalytic reaction of diethyl maleate with cyclopentadiene under hydrothermal conditions at 648 K results in a mixture of 2,3-diethoxycarbonyl-5-norbornene isomers in 86% yield.[142] The reaction time is at most one hour (*cf.* a few hours to a few days for the process in organic solvents under normal conditions).

Not only the rate but also the selectivity of the Diels – Alder reaction changes under hydrothermal conditions. In particular, the reaction of ethyl acrylate with cyclopentadiene in supercritical water results in a mixture of *endo*- and *exo*-isomers of 2-ethoxycarbonyl-5-norbornene in an equimolar ratio. Under normal conditions in the presence of the catalyst $LiClO_4$ the yield of the *endo*-isomer is eight times higher. The change in the selectivity is associated with a weakening of hydrophobic interactions in supercritical water.[143]

VI. Use of subcritical and supercritical water for solving environmental problems

Development of efficient and environmentally safe technologies for treatment of increasing amounts of various toxic inorganic and organic waste (products of anthropogenic activity) is among the most important problems of modern times. A possible way of solving this problem could be the use of subcritical and supercritical water for detoxification of these products. Being an environmentally safe solvent, water can be mixed with oxygen and organic compounds in any proportion near the critical point, it dissolves organic solid substances (but not inorganic salts), has high diffusion and mass transfer coefficients, is of low viscosity and zero surface tension.[144] It is these properties that must be possessed by a solvent appropriate for efficient treatment of industrial wastes.

Traditionally, organic waste detoxification methods involve combustion, liquid-phase oxidation or biodegradation.[145] Each technology has certain drawbacks and can only be used for particular concentration ranges of organic substances. For instance, combustion of highly concentrated organic waste produces toxic substances, *e.g.*, CO, NO_x, dioxins and polyaromatic compounds that should be neutralised. Liquid-phase oxidation technology is applicable to moderate concentrations of organic waste. The process is limited by mass transfer phenomena and the solutions formed contain high concentrations of carboxylic acids and ammonia. Biodegradation is only used for neutralisation of waste containing up to 1 mass% of organic substances. This is a rather slow process and simultaneous biodegradation of large amounts of wastewater requires large surface areas.

The expedience of the use of supercritical water for detoxification of organic waste was assessed taking catalytic oxidation of pyridine as an example and this treatment technology was found to be efficient.[145] According to calculations, the amount of investment necessary to build a waste-disposal plant for treatment of pyridine-containing solutions in supercritical water is 1 650 000 US dollars. Building waste-disposal plants for combustion and liquid-phase oxidation treatment requires 1 920 000 and 2 350 000 US dollars, respectively. A plant for catalytic oxidation of pyridine in supercritical water is also cheaper than those employing combustion and liquid-phase oxidation treatment. In addition, supercritical water oxidation imposes almost no limitations on the concentration of the pyridine-containing solutions.

Thus, treatment of organic waste with subcritical and supercritical water could be an alternative to traditional methods.

Studies on the use of subcritical and supercritical water for the detoxification of waste were concerned with dechlorination and dearomatisation of organic solutions,[53, 55, 131, 135, 146–162] treatment of polymers and plastics,[30, 144, 163–167] oxidation of municipal and food waste,[51, 168–173] gasification of biomass,[174–176] oxidation of toxic naval waste,[177] hydrolysis of cellulose and lignin,[3, 178–182] treatment of industrial waste [183] and extraction of heavy-metal compounds from waste water.[30, 49, 184–186] A number of processes are considered below.

1. Phenol and heterocyclic compounds

Every year chemical and petroleum industries produce millions of tons of liquid waste containing aromatic and heterocyclic organic compounds and their halogenated derivatives. These substances are highly toxic and are often carcinogenic; however, they are irreplaceable in the production of various pharmaceuticals, vitamins, herbicides and pesticides. Here, dearomatisation, dechlorination and removal of heterocyclic compounds from waste water can be performed using subcritical and supercritical water.

The efficiency of hydrothermal detoxification of pyridine- and phenol-containing waste substantially increases when using heterogeneous catalysts.[131, 151, 152, 159, 187–189] For instance, a 99% conversion is reached in supercritical water oxidation of pyridine in the presence of catalyst (0.5% Pt/Al_2O_3).[187] The process is limited by the diffusion of reagents in the pores of the catalyst; it results in CO_2, N_2O and nitrate as the major oxidation products.

The use of CuO/Al_2O_3 catalyst in supercritical water oxidation of phenol permits not only acceleration of the reaction but also reduction of the yield of undesirable polycyclic by-products.[131] Carbon-supported catalysts are more reactive in the phenol oxidations.[151] By reducing the partial pressure of oxygen down to 0.2 MPa it is possible to decrease the oxidation rate of this catalyst in the reaction medium. The use of catalytic systems MnO_2/CeO_2, V_2O_5/Al_2O_3, Cr_2O_3/Al_2O_3 and V_2O_5 in supercritical water oxidation of phenol provides 100% conversion of PhOH to carbon dioxide, the formation of by-products being suppressed.[152, 153] It should be noted that hydrothermal phenol oxidation is also possible at lower temperatures (308–338 K) in the presence of a bimetallic catalyst (20% Pt–5% Ru)/C with a high content of noble metals.[156] The rate of hydrothermal phenol oxidation depends on the temperature and reagent concentrations, being at the same time independent of the pressure in the system.[135]

2. Chlorinated organic compounds

Dechlorination in supercritical water is a promising environmentally safe method of decomposition of chlorinated organic compounds.[53] The efficiency of catalytic neutralisation of liquid waste containing chlorophenols increases in the presence of alkali metal and iron cations.[154, 158, 190] The presence of these metals favours chlorine fixation and suppresses the formation of by-products (*e.g.*, trichlorophenols, dibenzo-*p*-dioxin and polycyclic aromatic hydrocarbons).

Zeolite catalysts used for the supercritical water decomposition of chlorophenols do not react with the chlorine released; this was confirmed by X-ray photoelectron spectroscopy data.[149] The highest efficiency of the process is achieved using the CuO/ZSM-48 catalyst.[149, 158] Due to its two-dimensional channel structure, the catalyst ZSM-48 zeolite (in contrast to the ZSM-5 and Y zeolites) suppresses the formation of undesired by-products. Hydrothermal hydrodechlorination and hydroaromatisation of thirteen various chlorophenols under mild conditions (T = 298–353 K, P = 0.3–0.5 MPa) in the presence of industrial catalyst Ru/C was performed.[146] The complete conversion of contaminants into nontoxic cyclohexanol and sodium chloride was achieved.

3-Chlorodiphenol oxidation in supercritical water results in carbon dioxide, water and HCl.[157] Reactions carried out under similar conditions (T = 673 K, P = 30 MPa, reaction time 72.7–101.7 s) with hydrogen peroxide and molecular oxygen as oxidants were characterised by substantially different conversions, 99.999% in the former and 14.3% in the latter case. The efficiency of hydrodechlorination of polychlorinated diphenyls considerably increases in the presence of methanol,[161] which initiates a radical decomposition of intermediate chlorine-containing products with the formation of diphenyl.

Methylene chloride decomposition in subcritical and supercritical water involves two stages. Initially, hydrolysis of methylene chloride yields hydrogen chloride, formaldehyde and methanol.[55] Then, HCHO and CH_3OH are oxidised with oxygen to CO and CO_2. A 99.9% conversion of methylene chloride is achieved if the reaction is carried out in the temperature range 723–873 K at a pressure of 24.6 MPa and residence times of 4 to 9 s. Here, hydrolysis is a first order reaction with respect to methylene chloride, being also the limiting stage. The decomposition rate of methylene chloride increases only slightly in the presence of sodium chloride and does not depend on the amount of oxygen added.[160]

3. Polymers and plastics

Production of polymers and plastics is increasing worldwide annually. The amount of polymeric and plastic waste also increases; therefore, the search for new utilisation methods is topical. Nearly 100 000 tons per year of printed circuit board waste are to be disposed of in Taiwan.[144] High bromine content in these wastes hampers utilisation by conventional methods. In supercritical water (T = 793 K, P = 24 MPa, τ = 600 s) the material printed circuits are made of is oxidised with hydrogen peroxide to water and CO_2. The degree of conversion is 90% and the bromine released is efficiently bound by sodium cations.

Subcritical and supercritical water can also be used for treatment of other polymers. In particular, polyethylene terephthalate decomposes in supercritical water producing oligomers, ethylene glycol and terephthalic acid.[30] Hydrolysis of polycarbonate in the temperature range 503–703 K results in the formation of phenol, bisphenol A, *p*-isopropenylphenol and *p*-isopropylphenol.[165] Decomposition of polyethylene in supercritical water is characterised by higher conversion and the formation of hydrocarbons with shorter chains compared to pyrolysis in argon.[164] At the same time polyethylene degradation in supercritical water proceeds more slowly than thermal pyrolysis; however, the yield of liquid decomposition products in the former case is higher.[166]

4. Municipal and industrial wastes

Efficient treatment of excretory waste and biomass is a severe problem, especially in megalopolises. It could also be solved using subcritical and supercritical water. For instance, a flow reactor for oxidation of excretory and alcohol production waste with hydrogen peroxide in supercritical water (473–873 K) was designed.[168] Two major intermediate oxidation products are acetic acid and ammonia. Further oxidation of ammonia requires a higher temperature compared to the oxidation of acetic acid. The efficiency of ammonia oxidation to nitrogen can be significantly enhanced using heterogeneous catalysts, *e.g.*, MnO_2/CeO_2.[191]

Biomass and organic wastes can also be gasified under hydrothermal conditions to produce fuel gas.[174] At T = 873 K and P = 25 MPa, biomass is completely gasified in the presence of KOH and K_2CO_3, forming a hydrogen-rich gas containing CO_2 as the main carbon compound. Concentrations of CO, CH_4 and C_2-C_4 hydrocarbons in the product gas are <1 vol.%, ~ 3 vol.% and <1 vol.%, respectively.

Surfactant concentrations in waste water can be rather high. These compounds are oxidised with hydrogen peroxide in supercritical water to low-molecular-mass fatty acids (formic acid and acetic acid), sulfur-containing aromatic substances and sulfates.[192]

Phenol-containing olive oil production waste water can be efficiently neutralised in the presence of oxygen or hydrogen

peroxide in the temperature range 653–773 K at a pressure of 25 MPa.[171] The major oxidation products are water and carbon dioxide.

Utilisation of municipal waste in supercritical water can be combined with liquefaction of low-rank coals to produce liquid fuel.[175] The use of organic solvents for liquefaction is inefficient because of the high cost. The physicochemical properties of supercritical water are similar to those of nonpolar organic solvents. Supercritical water can be mixed with liquefaction products in any proportion and provides an efficient separation from liquid fuel on cooling. However, liquefaction of coals in supercritical water produces fuel with high oxygen content compounds, which reduces the heat of combustion. This problem can be solved by adding a source of hydrogen (*e.g.*, excretory waste or cellulose) to water.

In megalopolises solid municipal waste is usually burned out. In the atmosphere, components of the ash formed produce up to 50% of all dioxin-containing contaminants. Ash treatment with supercritical water in the presence of hydrogen peroxide ($T = 673$ K, $P = 30$ MPa, $\tau = 1800$ s) permits oxidation of up to 99.7% of all dioxins to produce non-toxic chemical compounds.[173]

As mentioned above, inorganic compounds are insoluble in supercritical water owing to the low dielectric constant of the medium. This property can be used successfully for detoxification of liquid waste containing inorganic substances. For instance, 96% of sulfates and chlorides are removed from waste at $T > 773$ K and $P = 29.8$ MPa.[184] Cobalt and other metals can also be extracted from low-level radioactive nuclear power plant waste under similar conditions.[30, 185, 186]

The possibility of simultaneous neutralisation of several components of industrial waste and waste water using subcritical and supercritical water should be pointed out. For instance, a compact plant was built for the oxidation of toxic naval waste simultaneously containing fuel, hydraulic liquids, lubricants, coolants, dyes and photographic materials.[177] The oxidant used was air; oxidation products obtained at $T = 870$ K and $P = 22.5$ MPa were CO_2, water, oxides and mineral acids. The plant is compact and can be placed on a ship's board.

5. Food waste

Oxidation of food waste (beef suet and carrots) with hydrogen peroxide in supercritical water involves two stages.[169] Fast hydrolysis of polysaccharides with the formation of glucose (in the case of carrots) or glycerides to give glycerol and carboxylic acids (in the case of beef suet) is followed by slow oxidation of the intermediates formed.

Hydrothermal treatment of various types of food waste can be combined with the production of valuable chemicals, *e.g.*, amino acids.[51, 172] For instance, shrimp shells usually contain 17% of chitin and 42% of proteins. Treatment with subcritical water permits extraction of up to 70 mg of valuable amino acids per gramme of dry shrimp shells.[172]

6. Cellulose and lignin

Cellulose is one of the most important organic substances on the Earth. At the same time large amounts of cellulose-containing waste have not been treated efficiently. Hydrolysis of various cellulose sources in supercritical water ($T = 773$ K, $P = 35$ MPa, $\tau = 3–105$ s) allows one to obtain glucose and its derivatives.[179] The degree of cellulose conversion achieved is as high as in the treatment of corn starch under similar conditions. This result deserves particular attention because the time taken to attain the same conversion in the case of enzymic hydrolysis of cellulose is three orders of magnitude longer than in the case of corn starch. Probably, the water present in the structure of cellulose microfibres goes to a supercritical state at high temperatures and pressure, which appreciably accelerates hydrolysis.[179]

The rates of cellulose hydrolysis in subcritical and supercritical water were compared [180] with the rates of further decomposition of glucose, fructose and various oligomers formed. Near the critical point the rate of cellulose hydrolysis abruptly increases by more than an order of magnitude; therefore, hydrolysis in supercritical water produces much higher yields of products compared to the process in subcritical water. At temperatures and pressures below the critical point parameters, saccharide decompositions dominate hydrolysis of cellulose. Hence, by varying the temperature and pressure it is possible either to obtain saccharides from cellulose (in supercritical water) or perform a deep treatment of cellulose waste (in subcritical water).

The mechanisms of cellobiose (a cellulose model compound) pyrolysis and hydrolysis in subcritical and supercritical water have been studied in detail.[182] Pyrolysis products are glycosylerythrose and glycosylglycol aldehyde, whereas hydrolysis gives glucose, erythrose and glycolaldehyde.

Gasification of a lignin–cellulose mixture in water at $T = 623$ K and $P = 25$ MPa produces hydrogen, methane and carbon dioxide.[193] The amount and composition of the product gas strongly depends on the lignin content; probably, cellulose is a hydrogen donor for lignin hydrogenation, which causes changes in the composition of the gas produced depending on the lignin/cellulose ratio.

7. Extraction processes

Such properties of supercritical fluids as low viscosity and zero surface tension open great prospects for the use of these substances in the extraction and impregnation of various materials. At elevated temperatures and pressures, water can be used instead of many toxic solvents such as dichloromethane and acetone traditionally used for the extraction of organics from various matrices. Subcritical and supercritical water was employed in extraction of toxic contaminants from soil,[194–199] sorbent regeneration,[200] impurity desorption from the surface of materials [201] and fuel quality improvement.[202–204]

Usually, detoxification of compounds in soil requires preextraction. Petrochemicals, chlorophenols, chloroanilines and methylanilines, nitrotoluene, alkylbenzenes, polychlorinated diphenyls, phosphonium acids and pesticides can be efficiently extracted from natural matrices with subcritical and supercritical water. Subcritical water extraction of polar contaminants (phenols and amines) proceeds at lower temperatures compared to nonpolar contaminants (polycyclic aromatic hydrocarbons).[205] By adding anionic surfactants to water it is possible to substantially shorten the hydrocarbon extraction time.[196]

The solubility of dioxins in subcritical water is 340 times higher than in water under normal conditions.[199] At 523 K, 30% to 100% of dioxins are extracted from soils depending on the type of the matrix; raising the temperature favours an increase in the extent of extraction.

Pesticides are nonpolar compounds well extractable with supercritical water, *i.e.*, at high temperature and pressure.[195] However, the addition of ethanol and some other solvents causes a substantial decrease in the polarity of subcritical water, which permits extraction of pesticides from soils under milder conditions.

In microelectronics, various contaminants must be removed from the surface of silicon. Compounds traditionally used to this end are acidic and basic solutions; as a consequence, utilisation of corrosive waste is required. Subcritical water is a good solvent for ionic inorganic compounds at temperatures below 373 K and for carbonaceous substances at higher temperatures.[201] Thus, subcritical water can be used instead of the corrosive solvents traditionally employed for cleaning the surface of silicon. Adding small amounts of carbon dioxide to water allows (at $T = 373–443$ K and $P = 1.03–13.8$ MPa) not only a silica film and hydrocarbons but also amorphous carbon insoluble in pure subcritical water to be removed from the surface of silicon.

Extraction of gaseous contaminants from air and treatment of waste water and drinking water are usually performed using activated carbon. This sorbent efficiently absorbs even very low

concentrations of toxic substances. However, the rather high cost of activated carbon requires its regeneration. In the case of thermal regeneration the loss of carbon is 5% – 10%, bioregeneration is only applicable to biodegradable substances and chemical regeneration is too expensive a process.[200] Treatment of activated carbon with subcritical water (T = 573 K, P = 12 MPa) allows the adsorption properties of the material to be completely regenerated. The process is accompanied by removal of phenol, dyes and pesticides. The properties of carbon do not deteriorate after a few regeneration cycles.[200] Under more severe conditions (T = 873 – 923 K, P = 25.5 – 34.5 MPa) carbon reacts with water to give carbon monoxide and hydrogen; however, short-term gasification favours an increase in the specific surface area and improvement of the adsorption characteristics of activated carbon.[206]

Modified subcritical water can be used to improve fuel quality. For instance, treatment of coal with subcritical water containing nitric acid (4 vol.%) causes extraction of Al, Ca, Mg, Na, K and other ash-forming elements.[207] Subcritical water containing HNO_3 and KCl can also be used for metal extraction from used industrial oils. After treatment of oil for 270 s up to 90% of Cu, V, Pb, Ni, Cd and Cr goes to the aqueous phase.

It should be noted that though traditional extraction techniques are much simpler to use compared to subcritical and supercritical water extraction, they are often of low selectivity. Extraction under hydrothermal conditions requires the use of complex equipment; however, in this case the process selectivity can be controlled by varying the temperature and pressure.[208]

VII. Conclusion

Subcritical and supercritical water is finding increasing use as a reagent, acid-base catalyst and a unique environmentally safe solvent whose physicochemical properties can be varied over a wide range. In this review we have tried to demonstrate the possibilities and advantages of the use of subcritical and supercritical water for the synthesis of nanocrystalline materials, in organic synthesis and for solution of environmental problems.

Successful practical application of subcritical and supercritical water requires a deep insight into all features of the physicochemical interactions occurring under hydrothermal conditions on the molecular level. Production of efficient industrial plants requires the design of new materials that are corrosion stable under extreme conditions. Systematic basic and applied research on the possibility of use of subcritical and supercritical water for target organic synthesis and in heterogeneous catalysis should be carried out. In the latter case water at high temperatures and pressures should be considered not only as a medium appropriate for performing catalytic reactions but also as a reagent for the one-step synthesis of multicomponent nanocrystalline heterogeneous catalysts with specified properties. One shoud expect that, in contrast to traditional systems, catalytic systems prepared under nonequilibrium subcritical and supercritical conditions will be sufficiently stable for the operation in supercritical media.

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