Russian Chemical Reviews

Volume 89 Number 12 2020

Contents

Supercritical fluids in chemistry

E.S.Alekseev,^a A.Yu.Alentiev,^b A.S.Belova,^c V.I.Bogdan,^{a,d} T.V.Bogdan,^a A.V.Bystrova,^{c, c} E.R.Gafarova,^f E.N.Golubeva,^a E.A.Grebenik,^f O.I.Gromov,^a V.A.Davankov,^c S.G.Zlotin,^d M.G.Kiselev,^g A.E.Koklin,^d Yu.N.Kononevich,^c A.E.Lazhko,^h V.V.Lunin,^a S.E.Lyubimov,^c O.N.Martvanov,ⁱ LI.Mishanin,^d A.M.Muzafarov,^{c, c} N.S.Nesterov,ⁱ A.Yu.Nikolaev,^c R.D.Oparin,^g O.O.Parenago,^h O.P.Parenago,^b Ya.A.Pokusaeva,^d I.A.Ronova,^c A.B.Solovieva,^j M.N.Temnikov,^c P.S.Timashev,^{f,j,k} O.V.Turova,^d E.V.Filatova,^d A.A.Philippov,ⁱ A.M.Chibiryaev,ⁱ A.S.Shalvginⁱ

^a Department of Chemistry, Lomonosov Moscow State University, Russia

^b A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia

^c A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia

^d N.D.Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia

^e Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, Moscow, Russia

 f Institute for Regenerative Medicine, I.M.Sechenov First Moscow State Medical University, Russia

⁸G.A.Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, Ivanovo, Russia

^h N.S.Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia ⁱ Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia

^j Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

^k Institute of Photonic Technologies, Research Center 'Crystallography and Photonics', Russian Academy of Sciences, Troitsk, Moscow, Russia

This review analyzes the rapidly developing applications of supercritical fluids, mainly supercritical carbon dioxide, in catalysis, chemistry of high-molecular-weight compounds, and medicinal chemistry in Russia and abroad. It considers the methods of catalyst preparation based on impregnation of inorganic and organic supports with metal-containing compounds, immobilization of organometallic and metal complex reagents in matrices of oxide and polymer supports, and deposition processes employing supercritical fluids. An analysis is presented of the prospects for applying CO_2 and some organic compounds, such as aliphatic alcohols, in sub- and supercritical states as reactants and (or) solvents for catalytic reactions of hydrocarbon isomerization and cracking, hydrogenation, dehydrogenation, oxidation, etc., including the asymmetric reactions. The review discusses processes of synthesizing and modifying polymer materials for various purposes, including aerogels, foams, and composites impregnated with photochromes, in a supercritical fluid medium. Special attention is paid to supercritical one-pot processes, which make the techniques of obtaining new materials simpler, less expensive, and more efficient. The work investigates the effect of supercritical CO₂ on the morphology, gas separation characteristics, and dielectric properties of polymers. One of the promising applications of supercritical fluids in medicine that is discussed in this study is their use in transplantology and pharmacology, for example, for obtaining drug polymorphs with higher bioavailability. The review also provides an overview of the recent data on the use of EPR spectroscopy for studying the properties of supercritical fluids, including those exhibited in the vicinity of the critical point and identifying the intermediates of chemical reactions in such media. Bibliography --- 1151 references.

Detonation nanodiamonds: new aspects in the theory and practice of synthesis, properties and applications

V.Yu.Dolmatov,^a* A.N.Ozerin,^b I.I.Kulakova,^c O.O.Bochechka,^d N.M.Lapchuk,^e V.Myllymäki,^f A.Vehanen^f

^a Federal State Unitary Enterprise 'Special Design and Technological Bureau 'Technolog', St. Petersburg, Russia

^b Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, Moscow, Russia ^c Department of Chemistry, Lomonosov Moscow State University, Russia

^d V.N.Bakul Institute of Superhard Materials of the National Academy of Sciences of Ukraine, Kiev, Ukraine ^e Belarusian State University, Department of Physics, Department of Physics of Semiconductors and

Nanoelectronics, Minsk, Belarus ^fCarbodeon Ltd. Oy, Vantaa, Finland

The review is devoted to the current state of research concerning detonation nanodiamonds, including production, methods of studying the properties and application prospects. The main achievements in the theory and practice of synthesis of detonation nanodiamonds over the past 15 years are addressed systematically; the influence of control factors on this process involving single or mixed explosives are discussed. A new highly economical and environmentally friendly method for chemical cleaning of nanodiamonds is described. The operational characteristics of new materials based on nanodiamonds are presented. The application prospects of nanodiamonds in traditional and new fields are demonstrated. Bibliography — 214 references.

Electrodeposition of lanthanides from ionic liquids and deep eutectic solvents

A.V.Rudnev

1337

A.N.Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia

Lanthanides belong to the most important raw materials and are highly demanded in high-tech industry. Low-temperature electrochemical deposition of lanthanides and lanthanide-based alloys for recycling and obtaining functional materials can provide a real alternative to the currently used high-temperature electrolysis of molten salts. The review summarizes the advancements in the field of electrodeposition of lanthanides from organic ionic systems, such as ionic liquids and deep eutectic solvents. The growing interest in these ionic systems is due to their excellent physicochemical properties, in particular nonvolatility, thermal and electrochemical stability. The review also discusses further prospects and potential of the electrochemical approach for obtaining lanthanide-containing advanced materials. Bibliography — 219 references.

Modern bio and chemical sensors and neuromorphic devices based on organic semiconductors

P.A.Shaposhnik,^{a,b} S.A.Zapunidi,^b M.V.Shestakov,^b E.V.Agina,^b S.A.Ponomarenko^{a,b}

^a Department of Chemistry, Lomonosov Moscow State University, Russia ^b Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, Moscow, Russia

This review summarizes and highlights the current state-of-the-art of research on chemical sensors and biosensors in liquid environment and neuromorphic devices based on electrolyte-gated organic transistors with the active semiconductor layer of organic π -conjugated materials (small molecules, oligomers and polymers). The architecture and principles of operation of electrolyte-gated organic transistors and the main advantages and drawbacks of these devices are considered in detail. The criteria for the selection of organic semiconductors for these devices are presented. The causes of degradation of semiconductor layers and ways of their elimination are discussed. Examples of the use of electrolyte-gated organic transistors as bio and chemical sensors, artificial synapses and computing devices are given. Bibliography — 132 references.

1463

1483

1428

Widely accessible 3D printing technologies in chemistry, biochemistry and pharmaceutics: applications, materials and prospects

E.G.Gordeev, V.P.Ananikov

N.D.Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia

Representative examples of application of 3D printing in organic synthesis, biochemistry, biotechnology, analytical chemistry, pharmaceutics and chemical education are considered. It is shown that additive technologies open up new prospects in the development of these fields of science. The features of widely used methods of 3D printing (fused deposition modeling and stereolithography) are discussed in the context of chemical applications. The key feature of these methods, that is, widely accessible of technologies and Bibliography 498 references.