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Editorial

Nanoparticles in Catalysis

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Nanoparticles (NPs) are defined as objects with dimensions ranging from 10^{-9} to 10^{-7} m [1]. Objects smaller than 2 nm are usually called clusters. NPs have been around for thousands of years, although they were not always recognized as NPs. One of the most famous ancient artifacts is the Lycurgus Cup, held in the British Museum. Its fascinating color is due to the fact that gold and silver NPs are embedded in the glasswork. Currently NPs find practical applications in a broad variety of areas, including in medicine, cosmetics, catalysis, photocatalysis, environmental protection and remediation, optics, electronics, and construction materials such as concrete, coatings, and paints. Because of their nanometer size, a substantial number of the atoms or molecules constituting these particles reside on the particle surface and interact with environment. Surface layer properties influence nanosized materials' size-dependent physical and chemical properties. The stability, solubility, and chemical and biological activity of NPs can be modified by the functionalization of the particles, which involves attaching something to their surfaces' molecules or functional groups. NPs of particular shapes, including spherical NPs, nanorods, nanosheets, nanocubes, and nanocages, exhibit shape-dependent properties. NPs containing two or more phases, like metals attached to oxides, or heterojunctions of two semiconductor NPs acquire properties which each phase, in their clear state, do not possess. The catalytic activity of metal NPs can be enhanced dramatically by ensuring attachment to a proper carrier. The high surface-to-volume ratios of NPs enable the preservation of expensive catalytic materials such as noble metals in catalyst manufacturing, thus promoting the wide spread of important technologies. The catalytic converters of modern cars with internal combustion engines reduce hydrocarbon emissions, as well as the emission of nitrous oxide and carbon monoxide. The so-called three-way catalysts of converters contain NPs based on Pt, Pd, Rh, and other metals on oxide supports. More than half of the Pd produced globally, as well as nearly half of the Pt produced globally, is used in catalytic converters.

As far as we know, the first scientific article related to catalysis by characterized NPs was published in 1941 by Rampino and Nord [2]. The authors used Pd and Pt NPs stabilized by polyvinyl alcohol to catalyze the hydrogenation of castor and fish oils at room temperature in water and water–alcohol mixtures. However, the surge in research on heterogeneous catalysis by NPs happened later, after the work of Haruta and co-workers was published [3,4]. This research group oxidized CO to CO_2 using O_2 at temperatures as low as −70 °C and a catalyst composed of 5 nm gold NPs coated with either Fe, Ni, or Co oxides. Currently, searching Google using the terms "catalysis" and "nanoparticles" returns more than 2 million records.

The works published in this Special Issue address most of the fields of application for NPs in catalysis. This Special Issue contains 11 articles, with some being research articles and others being review articles.

The emission of volatile organic compounds (VOCs) by industries causes many health problems, such as sensory stimulation, allergies, and chronic respiratory diseases. The catalytic oxidation of toluene, as a model VOC, was studied using a synthesized Pt/CeO_2-NS composite catalyst in contribution 1. Pt NPs were attached to synthesized 50–200 nm

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ceria nanospheres by the reduction of chloroplatinic acid in the presence of L-asparagine. In toluene oxidation, the synthesized Pt/CeO2-NS catalysts were superior to Pt/CeO_2 catalysts synthesized using commercial ceria. The effect of L-asparagine is ascribed to the inhibition of cerium formate formation and coordination with Pt.

The use of hydrogen as an energy carrier requires the development of efficient technologies for hydrogen production, transportation, and storage and the transformation of its chemical energy to electric power. Fuel cells with proton-conducting membranes (PEM FCs) are instruments that can be used for the efficient transformation of hydrogen's chemical energy into electricity. The propagation of hydrogen-based energy technologies, to a large extent, depends on the efficiency and stability of Pt-based electrocatalysts, which are used in the gas diffusion electrodes of fuel cells. The relatively low stability of carbon black supports of oxygen reduction catalysts can cause fuel cells to degrade. The authors of contribution 2 propose a way to increase the stability of electrocatalysts based on carbon-supported Pt. The authors synthesized a durable Pt-based electrocatalyst via depositing Pt NPs on the surfaces of carbon nanofibers. Chemically stable carbon nanofibers that could be used in high-temperature PEM FCs operational at 160–190 °C were prepared by electrospinning a polyacrylonitrile solution, followed by pyrolysis.

The use of bimetallic and multi-component NP catalysts in PEM FCs improves the activity and durability of Pt-based electrocatalysts. The authors of contribution 3 synthesized bimetallic PtM/C (M = Co, Ni, Cu, Ru) by the wet synthesis route. Special attention was paid to the adoptability of the method for electrocatalyst batch production. The activity of a PtCu/C oxygen reduction catalyst was found to be superior to that of other synthesized materials.

Chemical methods for synthesizing multi-component metal NPs usually employ toxic reagents. Green synthesis using biological reactants such as bacteria, plants, fungi, algae, waste biomass is one of the most promising methods that can be used to avoid environmental pollution and prevent the need for environment protection measures. Contribution 4 provides a perspective on the synthesis of trimetallic NPs using biological agents. The limitations of the synthesis method; the applications of and prospects for the trimetallic NPs in different areas of research, such as anticancer research; and their antimicrobial activity, drug delivery, and catalytic activity are discussed.

The emission of carbon dioxide due to fossil fuel burning is the main cause of ongoing climate change. The reduction of CO_2 to useful compounds, such as methane or methanol, is an innovative way to keep CO_2 concentrations in the atmosphere at a reasonable level. The authors of contribution 5 address issues related to the reduction of CO_2 to useful products using mono- and bimetallic nanocatalysts and other metal/metal oxide catalysts supported on biochar. Biochar, produced by the thermochemical treatment of biomass, is especially useful as a porous support for catalysts prepared by thermochemical methods. The catalytic reduction of gaseous CO_2 to methanol by the use of metal NP catalysts supported on biochar can be carried out at relatively low temperatures, specifically in the 200–500 °C range.

The authors of the contribution 6 explored the possibility of converting waste from he brewing industry, i.e., brewer's spent grain, into biochar supports for Ag-Cu NP catalysts. In this study, oxidation by hydrogen peroxide in aqueous solutions of model pollutant compounds, namely Methyl Orange and Methylene Blue, in the presence of suspended catalysts was monitored by UV-vis spectroscopy.

Another way to capture CO_2 is to photochemically reduce it to methanol. The authors of contribution 7 reduced CO_2 to methanol in an irradiated aqueous solution. Visible light was absorbed by nanoparticles of a 15% Bi_2O_3/CeO_2 photocatalyst suspended in solution. Photoexcited electron–hole pairs were separated by Bi_2O_3/CeO_2 heterojunction. The reduction of CO_2 occurred at Bi_2O_3, while water oxidation with the release of oxygen occurred at ceria.

The biodiesel manufacturing industry produces high amounts of glycerol, which is not needed in such large quantities. Glycerol can be converted to useful products

such as acrylic acid and lactic acid by mild oxidation. Oxidizing the carbon dioxide of organic pollutants dissolved in water is a method for industrial waste water treatment. Photoassisted electrochemical oxidation of methanol, ethylene glycol, glycerol, and 5,6,7,8-tetrahydro-2-naphthol was carried out in contribution 8. Organic matter oxidation was conducted on thin-film hematite photoanodes irradiated with visible light. The hematite film of the photoanodes was modified by titania.

Diesel-powered light- and heavy-duty vehicles, as well as agricultural and construction machinery, emit particulate matter, with soot making up the vast majority. Diesel particulate filters capture more than 85% of the soot in the exhaust. The soot accumulated in the filter can be removed by periodic burning using appropriate catalysts embedded in the filter. In contribution 9, CeO_2 and Co_3O_4 NP catalysts were synthesized by precipitation from solution, followed by calcination at 600 °C. Precipitation was performed by introducing microdroplets of $Ce(NO_3)_3$ or $Co(NO_3)_2$ into alkaline aqueous solutions. Oxide NPs were anchored to stainless steel or ceramic supports by colloidal cerium oxide. The catalytic activity of the synthesized materials in soot oxidation was evaluated. For this evaluation, samples containing carbon particles, which were collected from the filter of a real diesel engine, were mixed with synthesized catalyst particles and subjected to temperature-programmed oxidation.

In the context of fuels, replacing raw fossil materials with renewable materials is a way to stabilize the levels of carbon dioxide in the atmosphere. Renewable sources of hydrocarbons include products of biomass fermentation and lignin, which is a complex three-dimensional crystalline polymer contained in plant cells and some algae. Every year, 150–200 million tons of lignin waste are generated. In contribution 10, a microwave-assisted plasma catalytic process was used to convert lignin and fuel oil into hydrogen, synthesis gas, and liquid hydrocarbons in the presence of nano-sized cobalt-containing systems. The authors found that it is probable that the role of Co-containing particles in catalytic processes consists in activating the carbon bonds of lignin, which substantially increases the microwave absorption capacity of the system as a whole. The process was conducted in a CO_2 atmosphere. In the presence of cobalt-containing particles, the temperature of the reaction zone during microwave treatment reached 800 °C.

The contamination of water resources, including sea water, by salts of heavy metals can cause multiple effects that are damaging to human health. Even some sea fish contain dangerous levels of mercury ions. The maximum contaminant level for inorganic mercury in drinking water is only 2 ppb. Measuring mercury concentrations in water from many sources at so low levels requires highly sensitive, selective, and cost-effective instruments. The authors of contribution 11 devised an electrochemical sensor tailored for the detection of Hg^{2+} in water at a lower detection limit of 0.18 ppb Hg^{2+}. Using the instrument, the detection of Hg^{2+} is unaffected by other ions commonly found in environmental fluids. The voltametric sensor of the instrument is a glassy carbon electrode with attached silver NPs. The silver NPs were synthesized by the reduction of silver nitrate in the presence of xanthan gum. This instrument acts as a reducing and capping agent.

The Guest Editors greatly appreciate the scientific novelty of the articles which comprise this Special Issue. It is important to mention that all the articles in the Special Issue are focused on environmental protection. The number of environmental problems that the world is facing is only increasing. Thus, the need to develop safe, efficient, and cheap catalysts will only become more urgent.

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