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Trends in the synthesis of metal oxide nanoparticles through reverse microemulsions in hydrocarbon media

Salambek N. Khadzhiev, Khusain M. Kadiev, Galina P. Yampolskaya, Malkan Kh. Kadieva *

Hydroconversion of heavy oil residue and crude oil Group, Chemistry of petroleum and petrochemical synthesis Laboratory (2), A.V. Topchiev Institute of Petrochemical Synthesis, RAS (TIPS RAS), 29, Leninsky prospekt, 119991, Moscow, Russian Federation

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A B S T R A C T

In recent years, more and more attention is given to production and use of nanoparticles dispersed in hydrocarbon medium and synthesized in reverse microemulsions. In this article the data and research results on synthesis of inorganic nanoparticles in reverse microemulsions are summarized. The major attention is paid to thermochemical approach for nanoparticle synthesis in reverse microemulsions with precursors of Mo, Al, Ni, Co and Fe oxides being active components of the catalysts for petroleum chemistry and refinery. A high efficiency of native crude oil surfactants for the production of catalyst nanoparticles in reverse microemulsions has been found.

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1. Introduction

Due to the depletion of light and medium oil reserves, alternative raw materials – such as natural gas, coal, heavy high-viscosity oils and natural bitumens comprising more than 90% of the world recoverable hydrocarbon reserves – become an important feed source to meet the needs in fuel and petrochemical products.

Conversion of natural gas or coal to synthetic oil is based on Fisher–Tropsh synthesis applied in industry but characterized with a low activity and selectivity of used catalysts as well as low economic efficiency.

Application of heavy high-viscosity oils and natural bitumens is limited by a high concentration of high-molecular components including asphaltic and resinous compounds, metals (vanadium, nickel, iron etc.), sulfur, nitrogen, oxygen, that makes an efficient use of traditional thermal and catalytic technologies for deep oil processing complicated or sometimes impossible. As a result, the yield of low-quality high-sulfuric products rises sharply, a fast non-reversible deactivation of catalysts of traditional process and an increase in capital and operational costs are observed.

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* Corresponding author. Tel.: +7 8 495 258 5308.
E-mail address: mkadieva@ips.ac.ru (M.Kh. Kadieva).

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Use of nanosized catalysts allows increasing sufficiently the efficiency of syngas (produced from natural gas or coal) conversion to synthetic oil by Fisher–Tropsh method, as well as hydrogenation processing of heavy oils and oil residues to motor fuels and petrochemical feedstock [1]. Nanoparticle sizes are within the range of 1 nm < D ≤ 100 nm that leads to a rise of surface area to volume ratio [2]. Dimensional parameters of nanosized particles determine the enhancement of catalytic, electronic, thermophysical, optical, photonic, magnetic and other properties along with an increase in mechanical and thermal stability [3]. Various nanoparticle synthesis methods are known: chemical vapor deposition, chemical deposition in solutions, thermal pulverization, spray pyrolysis, various methods of dispersion, photo- and radiational chemical reduction, high-temperature decomposition of solid precursors, sol–gel synthesis etc. [2,4]. However, most of the developed methods are applicable only to synthesize small amounts of nanomaterials in laboratory scale. A transfer to industrial scale of nanosized catalysts application faces problems consisting in synthesis optimization and stabilization of synthesized particles as well as development of catalyst (or precursor) introduction method to specific reaction systems. Synthesized catalysts should meet the following requirements: simple dispersion in hydrocarbon medium, chemical compatibility with hydrocarbon phase, catalytic activity and thermal stability. Most of these problems are resolved successfully by using the principle of *in situ* formation of catalytic nanoparticles in hydrocarbon reactionary medium for processes including C–C bond breaking and formation. This way of synthesis is realized by emulsion- or microemulsion-mediated approach for introduction of catalyst precursors to hydrocarbon feed. Such nanosized catalysts are used in petroleum chemistry and refinery for a relatively short time, but their significantly high activity has already been found [1,5–8]. Reactions are catalyzed with submicron or nanosized particles of metals, metal oxides and sulfides synthesized in absence of carrier *in situ* in hydrocarbon medium, which can also have a stabilizing effect, particularly in case of crude oil medium, increasing sedimentative and aggregative resistance of fine-dispersed catalytic systems. The formed area became a basis for new technologies of novel nanosized catalyst synthesis and application [1,5–11].

Chemical composition of catalyst nanoparticles synthesized in petroleum medium is similar to traditional heterogeneous catalysts, but due to higher catalytic activity the new technology allows reducing sharply catalyst concentration in the feedstock (e.g. up to 100–1000 ppm) [7,12,13].

For the formation of nanosized catalytic particles *in situ* in hydrocarbon medium, microemulsion systems are perspective, which allow varying properties (dispersity, structure) of target nanophase in a wide range [14–17]. Highly dispersed systems "*water solution of precursor–petroleum feedstock*" have approved themselves particularly for *in situ* synthesis of nanosized catalyst for hydroconversion of high-molecular petroleum components.

Recent intensive research development in field of microemulsions was determined by their potential use to increase crude oil recovery [18]. Microemulsions turned out to be ideal cleaners, detergents and cosmetics, containers for drug delivery, microreactors for chemical and biological reactions [19]. Reactions in microemulsions are conducted in limited volume of nanodroplet. Thus, catalyst nanophases for fuel components [20,21], olefin dechloridation [22] and novel nanofluids [2] have been synthesized. Microemulsions are perspective for controlled synthesis of various-nature nanoparticles (inorganic, organic, including polymers of certain structure).

The article contains analysis and classification of the research results on the formation of nanosized catalyst particles in reverse microemulsions containing metal salts (precursors) in water phase. The main attention is paid to the methods based on thermal initiation of chemical transformation of precursor in reverse microemulsion medium. Precursor transformations result in formation of nanosized metal oxide particles (Mo, Al, Ni, Co, Fe). Such approach to the catalyst nanoparticle synthesis is the most perspective due to relatively simple realization.

2. Formation and properties of microemulsions

Microemulsions (ME) are multicomponent isotropic, optically transparent, thermodynamically stable nanosized dispersions consisting of at least three components: dispersed polar (water) and continuous non-polar (hydrocarbon) liquid phases, and a surfactant. Concerning rheological properties ME relate to Newtonian fluids with the viscosity similar to that of continuous phase even at high dispersed phase concentration (nanodroplets of water in reverse or water-in-oil ME, nanodroplets of oil — in oil-in-water ME). To produce reverse ME with inorganic salts in dispersed phase different types of surfactants are used (Fig. 1) and also hydrocarbons (as the non-polar phase), and co-surfactants (short-chain aliphatic alcohols) are generally added. Surfactants are represented as amphiphilic molecules consisting of non-polar hydrophobic part (straight or branched hydrocarbon chain with 8–18 carbon atoms) and polar or ionic part (hydrophilic). The hydrocarbon chains interact weakly with water, whereas the polar or ionic groups interact strongly with water molecules [23]. Table 1 shows some examples.

ME differ principally from emulsions and cannot be considered as emulsions with small-size droplets. Emulsions are thermodynamically unstable systems and inevitably break down to macrophases after the processes reducing free surface energy. ME are thermodynamically stable systems and form spontaneously with structure and propertied independent from method of preparation. ME are characterized with ultralow interphase tensions (specific interfacial free energy), which consists a basis of description of thermodynamic stability. Comparison of microemulsion and emulsion properties is given in Table 2 [19,24].

ME are homogeneous on macroscopic level and represent microheterogeneous systems on microscopic scales consisting of oil-in-water (O/W) or water-in-oil droplets (W/O) or form bicontinual structures of similar water and oil domains bound on macroscopic scale. ME interphase borders are stabilized by surfactant and co-surfactant monolayers. Spontaneous formation of ME occurs due to ultralow interphase tensions ~ 10^{-3}–10^{-4} mN/m, and type of formed ME (O/W, reverse or bicontinual) depends on conjugated parameters that characterize properties of the surfactant interphase layers [25–28]. ME droplet size is generally 100 times smaller than in traditional emulsions and varies from 1 to 100 nm (Table 3), which is equivalent to specific interphase surface within the range of 300–30 m^2/g. To study ME microstructure optical methods, small-angle X-ray and neutron scattering, electron microscopy (TEM, SEM), rheological measurements, electron paramagnetic resonance (EPR), infrared (IR) spectroscopy, nuclear magnetic resonance (NMR), ellipsometry and electrical conductivity are used [23,29–34].

2.1. Surfactant micelle formation in hydrocarbon medium

Usually reversed microemulsions are considered as systems with reverse micelles, which provide additional mobile or free water in cores [35]. Generally formation of normal or reverse micelles in microemulsions is determined with strong hydrophobic interaction between non-polar surfactant chains (normal micelles) and hydrophilic interactions of polar surfactant groups (reverse micelles) (Fig. 2).

In the first instance aggregation numbers are generally large, while aggregation of polar surfactant groups in non-polar medium is complicated and do not lead to large aggregation numbers (usually less than 20) [36]. Thus, the transition from molecular solution of surfactant to micellar one is gradual, and for some cationic and nonionic surfactants the critical micelle concentration (CMC) cannot be determined at all. Anionic surfactants are characterized with the largest aggregation numbers (25–30) in reverse micelles, and CMC is determined more or less reliably. For conventional surfactants association in non-polar medium is characterized with sequence and leads to formation of small and polydisperse aggregates. However, in presence of traces of water (e.g. atmospheric) the formation of reverse micelles is