Chapter 4

Microemulsion Route for the Synthesis of Nano-Structured Catalytic Materials

Tajamal Hussain and Rabia Batool

Additional information is available at the end of the chapter

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Abstract

Owing to their unique properties, use of microemulsion-based synthetic techniques for the generation of shape-controlled nanocatalyst is an area of great current interest. Nanocatalysts of any specific shape, morphology, surface area, size, geometry, homogeneity and composition are widely being prepared using the soft techniques of microemulsion. Easy handling, inexpensive equipment and mild reaction conditions make microemulsion an attractive reaction medium. Herein, a nanosized precursor reactant can be incorporated, leading to the formulation of a highly monodispersed metal nanoagglomerate with controlled size, shape and composition. Several factors such as presence of electrolyte, molar ratio of water to surfactant, nature and concentration of surfactant and solvent, size of water droplets and concentration of reducing agents influence the size of the nanoparticles. The reverse micelle method can be used for the fabrication of several nanosized catalysts with a diverse variety of suitable materials including silica, alumina, metals (e.g. Au, Pd, Rh, Pt), metal oxides, etc. The morphology, size distribution and shape of the nanocatalysts make them useable for a wide range of applications, for example, fuel cells, electrocatalysis, photocatalysis, environmental protection, etc. The recovery of nanoparticles from the reaction mixture is a challenge for the researchers. This chapter discusses the preparation of nanoparticles using microemulsion techniques, widely being used for the synthesis of nanocatalysts from a wide range of materials.

Keywords: microemulsion, nanoparticles, catalyst, synthesis, nanoagglomerate

1. Introduction

A single-phase system formed by the addition of a surfactant to a mixture of two immiscible liquids in large amounts, which is homogeneous macroscopically but heterogeneous microscopically, have been fascinating the world of science and technology due to their unique properties such as ability to solubilize both oil- and water-soluble compounds, low viscosity, decreased interfacial tension, optical clarity, etc. [1–3]. Unlike, normal emulsions, they exhibit a high thermodynamic stability as proposed by Ruckenstein [4]. These isotropic systems, consisting of oil droplets dispersed in water (O/W) or water droplets dispersed in oil medium (W/O) or a bicontinuous phase of these two components were termed as 'microemulsions' in 1959 by Schulman [5, 6].

A microemulsion basically consists of a hydrocarbon, water and a surfactant (a molecule having a hydrophobic tail and hydrophilic head ends) [7, 8]. After a specific concentration of surfactant (critical micelle concentration), aggregation of molecules takes place and micelles are formed. In case of W/O microemulsion, where formation of micelles takes place in an organic medium, whose hydrophobic (nonpolar) tail is outside the core and interact with the hydrocarbons, whereas its hydrophilic (polar) head is in the core; the aggregates are referred to as 'reversed micelles'. The core of W/O microemulsion, an active candidate as a nanoreactor in which several chemical reactions can be carried out, is of great interest [9]. Sometimes, a cosurfactant, mostly a medium-chain alcohol, is also used in addition to the surfactant, which enhances the system's stability and entropy by increasing the fluidity and decreasing the interfacial tension between water and oil molecules, thus easing the microemulsion formation [10]. The stability of a microemulsion can also be enhanced by changing the reaction parameters such as pressure, temperature or concentration of reagents or by the addition of a salt [11].

Depending on the ratio of individual constituents of a microemulsion, it is highly sensitive to a slight change in temperature [12]. Microemulsions are a subject of extensive research due to their wide range of applications in several fields, including cosmetics [13], lubricants [14], as pesticides in agrochemicals [14, 15], textile industry as finishing and dyeing materials, electrocatalytic, organic and photochemical reactions [16, 17], liquid membranes, fuels, detoxification of environment [18, 19], pharmaceutical industry [15, 20, 21], corrosion inhibitors [14], detergents [2], as oil flavors in the food industry [2, 22], bio-separation [23], oil recovery [24], etc. Nanoparticles having unique properties, finding their potential use in homogeneous and heterogeneous electrocatalysis, fluorescence probes, thermoelectric transport, bioassays, optical nanosensors, biotechnology, bio-imaging, aerosols, etc. are also extensively being synthesized using microemulsion technique. This chapter presents an overview of different microemulsion techniques used for the synthesis of nanocatalytic materials, factors affecting the reaction rate as well as the nanoparticle size and their applications in various fields.

2. Synthesis of nano-catalysts

In 1972, Gault and coworkers employed microemulsions, a novel technique for the synthesis of catalytic materials for the very first time. Owing to its thermal stability, specific composition and structure, very small droplet size and transparency, microemulsion, being a suitable medium for the preparation of metal-based nanocatalysts are also reported for the formation of bimetallic nanoparticles of any desired composition and controlled particle size. Metal nanoparticles stabilized in a microemulsion medium were first reported by Boutonnet [16].

Basically, the catalytic ability of a metal-based nanocatalyst depends on the size of precursor metal particles; smaller the particle size, higher will be the activity, as the surface area of the metal particles is increased due to increasing number of atoms on its surface. Microemulsion is a promising method leading to the synthesis of catalysts at nanoscale with a narrow size distribution. Varying the size of reversed micelles leads to control over the size of catalytic particles, ranging from 1–100 nm. The composition of nanocatalysts as prepared by this technique corresponds to the initial concentration of metal precursor used for their synthesis. In contrast with the conventional methods, which require a high temperature for the synthesis of nanoparticles, reverse micelle method can be carried out at room temperature with a more précised size of nanocatalysts. Water in oil microemulsion is of higher interest in this regard. In W/O microemulsion, water droplets are dispersed in oil. The surfactant molecules surround the water particles with their polar ends facing the water particles and nonpolar ends towards the oil phase. Metal precursors are present as electrolytes in the form of metal salts in the water core of the aggregations. Either this system can be mixed with another microemulsion containing precipitating or reducing agents (hydrogen, sodium borohydride, hydrazine, etc.), or a precipitating agent can be separately added to this microemulsion system [7]. This scheme is represented in **Figure 1**. A homogeneous dispersion of precipitating agent is achieved in the former method. Nucleation reaction takes place by the collision of these agents with the precursor metal particles. Nuclei formed in this process grow to form the final form of nanocatalyst. Since oil is a continuous phase, yield of resulting catalyst can be increased by increasing the amount of oil in the system [25]. Eastoe and coworkers [25] introduced the use of environment-friendly supercritical carbon dioxide instead of oil as a continuous phase.

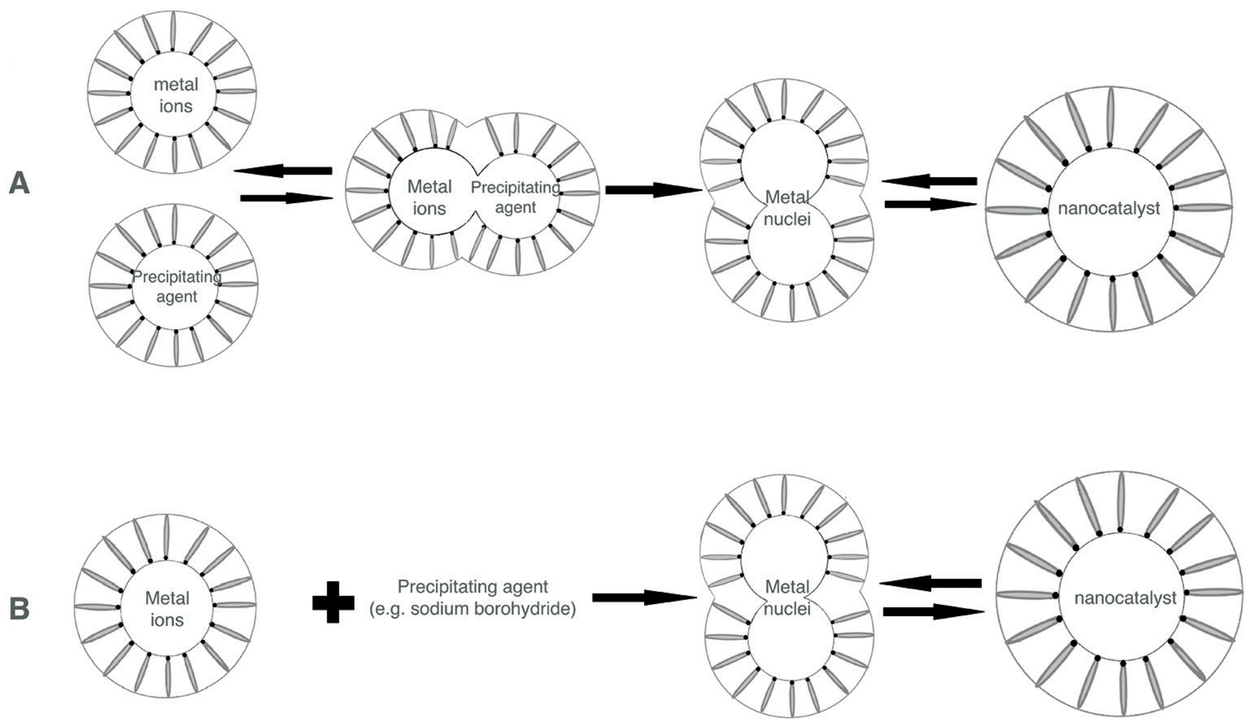

Figure 1. Nanocatalyst synthesis in microemulsion medium: (A) Mixing of two microemulsions; (B) addition of precipitating to microemulsion.

The nanocatalysts formed through microemulsion route are then passed through after-treatments such as reduction, washing, stabilization, calcination, etc. depending on the fields in which they are to be used [26]. The main hindrance, which prevents the approach of reactants to the surface of catalyst, is the presence of surfactant molecules. So, it must be removed from the reaction medium. Removal of nonionic surfactant molecules from the medium is easier compared to ionic surfactant. Thus, for the catalysts which are destined to be used at low as well as high-temperature liquid phase catalysis, surfactant should be removed; this can be achieved through calcination and washing. However, in some cases, presence of surfactant molecules on the surface of metal-based nanocatalyst particles may improve its selectivity. Moreover, if microemulsion-prepared metal nanocatalysts come in contact with air, they may get oxidized. To avoid this problem, reduction of nanocatalyst in hydrogen must be carried out before using it for a catalytic process.

Microemulsion has also been explored for synthesis of bimetallic nanocatalysts (catalysts containing two different metal particles). The addition of a second metal particle in the system improves its catalytic activity. Two different pathways can be employed for this purpose; either separate aqueous solutions of both precursors or an aqueous solution having both the precursor metals can be added to the microemulsion medium. However, the selection of route does not affect the particle size of product [27].

To increase the efficiency of a nanocatalyst, encapsulation of metal particles should be avoided to maximize the surface area of catalyst by creating them on a support [28]. A combination of microemulsion and sol-gel method can be employed for the synthesis of metal oxide catalysts coated with metal particles. Illustration of this method is given in **Figure 2**. A sol-gel technique is used to prepare a porous metal oxide via reactions between metal alkoxide and water. In microemulsion, it prevents sintering and agglomeration of precursor metal particles in the medium.

Microemulsion coupled with deposition precipitation method is also being used to support active catalysts over surface of nanomaterial. In deposition precipitation method, particles of metal deposited on the surface act as active catalysts. The surface of nanomaterials acts as a support for the metal catalyst. This will help in improving the catalytic ability as well as ther-

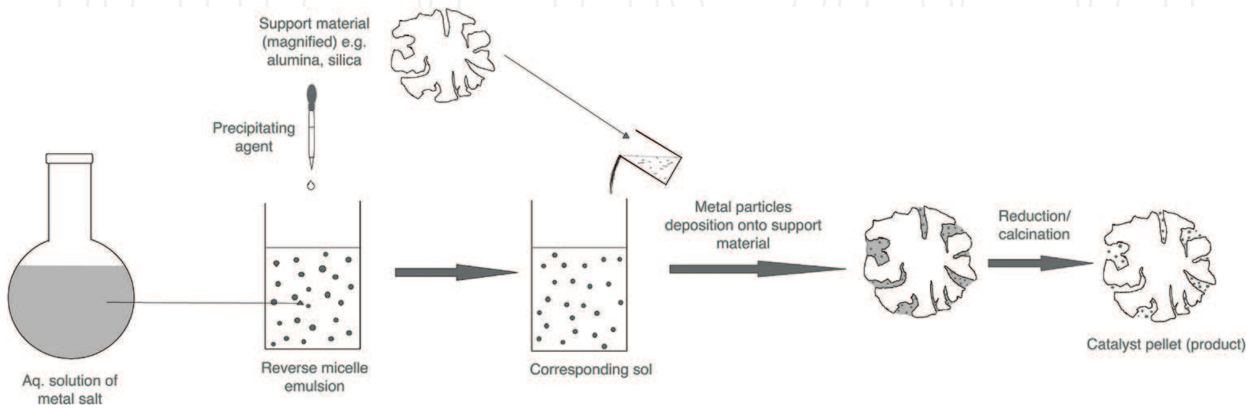

Figure 2. Microemulsion route for the synthesis of supported metal catalysts.

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mal stability of the catalyst [29]. Such a three-way catalyst (TWC) has been prepared by Shah et al. [30], who supported CuO particles on $CesZrO_2$. The doping of CuO activated the highly stable catalyst at lower temperature.

3. Factors affecting the particle size

3.1. Concentration of water

Water content in the microemulsion goes hand in hand with particle size of the catalyst. Increasing the water content increases the water-to-surfactant ratio, increasing the particle size of metal catalysts (see **Table 1**). Micellar size is decreased at lower water contents, which results in homogeneous dispersion of relatively smaller particle size. At low amount of water, the tightly packed water molecule surrounded by surfactant molecules results in the production of more stabilized and monodispersed as well as smaller catalyst particles. This means that for the synthesis of catalysts having a smaller size, amount of water in the microemulsion should be reduced [36–38]. This effect was studied by Wongwailikhit and Horwongsakul. They selected reverse micellar route for the synthesis of monodispersed, spherical iron (III) oxide nanocatalysts. Particle size of the nanocatalyst was found to be strongly dependent on molar ratio of water to surfactant. Decrease in concentration of water in the system favored the decrease in particle size, thus enhancing the catalytic activity of product [39].

3.2. Intermicellar exchange

Microemulsion synthesis of nanocatalysts depends strongly on the intermicellar exchange. If the rate of exchange of materials between reverse micelles is slow, a few catalyst particles with relatively larger particle size are obtained. In contrast, higher exchange rate leads to the synthesis of a large number of nanoparticles having smaller particle size [40]. As

Serial #	Nano-catalyst	Water to surfactant ratio (w)	Size of nanocatalyst (nm)	Reference
1	Cu_2S	2	8.09	[31]
		3	69.2	
2	TiO_2	3	5.3	[32]
		5	6.9	
3	$MnCO_3$	6.25	71	[33]
		7.5	89	
4	$MgAl_2O_4$	2	13	[34]
		8	17	
5	CdS	5	6.2	[35]
		10	10.80	

Table 1. Effect of water-to-surfactant ratio on size of nanocatalyst.

reported by Bagwe et al. [41] who synthesized silver chloride nanoparticles in microemulsions, the intermicellar exchange further depends on the water content, choice of continuous phase and precursor metal particles in the nanodroplets. At greater water-to-surfactant molar ratio, water molecules exists in free state in the reaction medium; this increase in medium's fluidity enhances the intermicellar exchange rate and forms smaller nanocatalyst size owing to their rapid nucleation. The intermicellar exchange is also weakly affected by the size of cations. It is well known that cationic size decreases with increasing valency, reducing the distance between surfactant heads and forming a tightly packed layer of surfactant. Hence, larger cations affect the formation of nanocatalysts by reducing the intermicellar exchange. Another factor affecting materials exchange is the continuous phase (solvent) present in the microemulsion medium. The penetration of continuous (oil) phase into the surfactant tail becomes difficult as the chain length of the oil is increased; however, oil molecules align themselves parallel to the tail, decreasing the interaction between continuous phase, that is, solvent and surfactant. This deficiency of solvent molecules allows the surfactant tails to interact with each other. These two effects combine and result in an increased intermicellar exchange.

3.3. Reducing or precipitating agent

The nature and concentration of precipitating or reducing agent is a strong function of the microemulsion synthesized metal nanocatalyst size. As reported by Boutonnet et al., increase in the content of hydrazine, N_2H_4, which is an efficient reducing agent, increases the particle size of metal nanocatalysts [42]. In this work, it is reported that N_2H_4 carries out reduction more effectively and forms comparatively smaller nanoparticles as compared to when pure hydrogen is used for reduction.

A research carried out by Solanki [43] showed that nature of reducing agent in microemulsion technique affects the particle size of nanocatalysts. They used two different reductants, that is, hydrazine and sodium borohydride for the synthesis of silver (Ag) nanocatalysts keeping the water-to-surfactant ratio constant. Sodium borohydride, being a stronger reducing agent, catalyzes the nucleation and growth of particles, resulting in greater particle size. Therefore, hydrazine is more preferable for the synthesis of nanocatalysts with reduced particle size.

3.4. Nature of surfactant

Particle size of a nanocatalyst is also affected by changing the concentration of surfactant in the emulsion keeping the water and oil content constant. Ionic and van der Waals forces hold the aggregates formed in the presence of surfactant. By reducing the amount of surfactant, number of droplets also decreases. This causes an increase in ions per droplet and hence the particle size also increases. However, the catalyst particles are formed in the nuclei, not in the droplet. It is known that the dynamic microemulsion system synthesizes nanocatalyst in two steps: nucleation and aggregation. Presence of surfactant keeps the particle growth neither too slow nor too fast. Particle size is determined by the number of surfactant molecules surrounding it [44, 45].

Surfactants being used in microemulsion-mediated synthesis of nanocatalysts include different nonionic, anionic and cationic surfactants. Anionic surfactant AOT (sodium bis(2-ethylhexyl) sulfosuccinate), employed for the synthesis of monodispersed and highly stable metallic (Au, Ni, Cu) nanoparticles as well as metal oxides and sulfides catalysts with very fine particle size strongly bonded through electrostatic interactions, is the most important surfactant in this regard [46].

3.5. Addition of a cosurfactant

Providing same particle size, addition of a cosurfactant in the microemulsion reaction medium during the synthesis of a bimetallic nanocatalysts assists the complete reduction of precursor metal ions to form well-alloyed monodispersed nanoparticles with desired phase composition. The presence of a cosurfactant incorporates more amounts of metal particles in the catalyst, owing to the increased rigidity of micellar interface. The cosurfactant molecules solubilize in the tail region of surfactant, the heads of surfactant come close to each other, making no effect on the water droplet size, which determines the particle size of nanocatalysts [47]. Increasing the chain length of cosurfactant stabilizes the nanocatalyst particles formed, leading to a decreased average particle size. This effect was shown by He [48] and coworkers, studying the size of nanocatalysts with changing cosurfactant in the microemulsion medium (see **Table 2**).

3.6. Addition of electrolytes

Several electrolytic species such as metal salts, which have a great impact on aggregation of micelles, the solubility and dissociative degree of the surfactant, may also be added to the microemulsion medium used for the synthesis of nanocatalysts [49]. For instance, shape of catalyst particles in water-AOT-isoctane microemulsion was altered by the addition of sodium chloride salt in the system, where cubical, cylindrical or trigonal catalytic particles were obtained [50].

3.7. Reactant concentration

The concentration of reactants in the microemulsion medium strongly affects the amount, size and shape of the nanocatalysts thus synthesized. The particle size of silver nanoparticles as prepared by Lisiecki et al. [51] was observed to decrease with decreasing concentration of reducing agent (hydrazine). An increase in reactants concentration (PbS, $NaBH_4$) increased the amount of final product, catalysts particles [52, 53].

Serial #	Co-surfactant	Size of nanocatalyst (nm)
1	1-Heptyl alcohol	47.1
2	1-Amy alcohol	51.5
3	1-Hexyl alcohol	53.8
4	1-Butyl alcohol	63.4

Table 2. Effect of surfactant on size of nanocatalyst.

An important edge a microemulsion provides is its potential to control the shape (onion-like, core shell, etc.) of the synthesized nanocatalysts by changing the initial concentration of reactants added to the system [54, 55]. Core with uniform thickness of particles can be obtained by using rigid films or introducing low concentration of reactants in the reaction mixture providing one of the reactants is in excess amount. Using stoichiometric and relatively higher amounts of reactants and addition of a second reactant to the reaction mixture produce a core-shell structure [55, 56]. Efforts are also being done for the polymer encapsulation of microemulsion synthesized nanocatalyst particles either by in situ polymerization by making use of polymerized surfactants [57] or by enfolding after the extraction of nanocatalysts [58].

4. Applications of microemulsion synthesized nanocatalysts

The nanocatalysts prepared by using microemulsion systems have been reported to be used in many catalytic processes including reforming, oxidation/hydrogenation of hydrocarbons, reduction of nitrogen oxide, fuel cells, Fischer-Tropsch method, production of hydrogen, oxidation of carbon monoxide, breaking down of organic species, etc. [26] (see **Table 3**). Details are given below.

4.1. Photocatalysis

Microemulsion technique produces better nanostructured photocatalyts. Photocatalysis is a process used for the breakdown of organic matter present in wastewaters. Titanium dioxide, being a semiconductor, is widely being employed in this process. With the absorption of photon whose energy is equal to semiconductor's band gap, the catalysis begins. Titania either accepts or donates electrons to the species present in the surrounding medium. Yan and coworkers [58] synthesized one such catalyst via microemulsion route, which enhanced its catalytic activity. Fuerte et al. [65] studied the effect of microemulsion route on photocatalytic activity of mixed oxides nanoparticles containing titanium (Ti) and tungsten (W) for degradation of toluene. In the microemulsion medium, tungsten doping leads to the formation of charge-trapping centers, leading to enhanced catalytic activity of the nanocatalyst. Another core/shell catalytic system containing ZnS and CdS are known to be applicable for the photolytic production of hydrogen from water [66].

Photocatalytic decomposition of 4-nitrophenol, a toxic compound used in pesticide production, is carried out over microemulsion-synthesized titania nanocatalysts [67]. Organic contaminants present in water can be degraded under UV/visible light using an active single-phase $LaNiO_3$ as prepared by a single reversed microemulsion process [68].

4.2. Storage of hydrogen

Microemulsion-synthesized nanosized bimetallic catalysts find their applications to enhance the reaction rate of formation of carbon nanofibers, which are used for storage of hydrogen. The nanofibers as produced by this technique show a uniform distribution of very small

Serial#	Nanocatalyst	Application	Reference
1	Pt	Oxygen reduction reaction	[49]
2	Pt-Ru	Oxidation of methanol	[50]
3	TiO_2	Photodegradation of methyl orange	[51]
4	Pd/CNT	Hydrogenation of olefins	[52]
5	Pd-Au/carbon	Electrooxidation of sodium borohydride	[53]
6	Ag/Al_2O_3	Reduction of nitro aromatic compounds	[37]
7	Barium hexaaluminate	Combustion of methane	[54]
8	Fe/Cu/La	Fischer-Tropsch catalyst	[55]
9	MoO_3-K_2O/CNT	Synthesis of higher alcohols	[56]
10	Mn-containing mixed oxides	Catalytic oxidation of toluene	[57]
11	Rh/SiO_2	CO hydrogenation	[58]
12	Pt-in-CeO_2	Water-gas shift reaction	[59]
13	Pd-Cu-O/SiO_2	Oxidative carbonylation of phenol	[60]
14	Pt-Ru-Sn/BDD	Electro-oxidation of alcohol	[61]
15	Pd-Co-Au	Oxygen reduction	[62]
16	Pt/carbon	Hydrogenation of nitro compounds	[63]
17	Ni-Fe/Al_2O_3	Hydrogen rich gas production	[64]

Table 3. Applications of microemulsion-synthesized nanocatalysts.

particle size. A Fe-Cu nanocatalyst was synthesized by Marella et al. [69] to study the formation of nanofibers through the decomposition of ethylene.

4.3. Aquathermolysis reaction

The limited use of heavy oils due to their high viscosity can be improved by reducing its viscosity. For this purpose, aquathermolysis, physiochemical reactions of oil with water or steam at temperature range between 200 to 300°C is an important reaction [70]. However, a major problem observed in this reaction was the formation of large molecules by Van der Waals or hydrogen-bonded hetero-atoms (O, N, S) present in the heavy oil [71]. To overcome this difficulty, a catalyst can be used which catalyzes the breakdown of large oil particles into smaller ones, increasing the amount of saturates and decreasing the concentration of resins and asphaltenes in the oil [72]. The enhanced catalytic activity of microemulsion-synthesized nanocatalysts due to their smaller particle size makes them an interesting candidate to be used in this viscosity reduction method [73].

4.4. Reduction of nitrogen oxides

In the presence of excess oxygen, mixed metal nanocatalysts such as perovskites [74] are generally used for the reduction of nitrogen oxides (Eq. (1)). Microemulsion synthesis enhances the activity of nanocatalysts by decreasing their particle size and increasing their surface area. Homogeneously mixed precursor metal particles in the microemulsion medium lead to the formation of nanocatalysts at elevated temperatures:

$$2NO + O_2 \xrightarrow{CaTiO_3} 2\,NO_2 \tag{1}$$

Reduction of nitric oxide by carbon monoxide using Lanthanum-based nanocatalysts [75] synthesized in microemulsion medium is also reported. The activity was compared with the conventionally prepared nanocatalysts. The enhanced surface area of microemulsion-synthesized nanocatalysts increased the rate at which oxidation reaction occurred.

In gas turbines, nitrogen oxide formation should be minimized by reducing the temperature at which catalytic combustion is carried out. For this purpose, hexaaluminate can be used as a catalyst. This catalyst having a higher surface area, when prepared via microemulsion technique, is an active candidate to be used at low temperatures [76].

4.5. Water-gas shift reaction

In water-gas shift (WGS) reactions, carbon dioxide and hydrogen are produced by reacting carbon monoxide with water. These reactions take place in industries to increase the amount of hydrogen in syngas (a fuel gas produced as a result of partial oxidation of hydrocarbons). These reactions can be catalyzed using ceria (CeO_2) encapsulated Pt nanoparticles synthesized in microemulsion medium (Eq. (2)) [77]:

$$CO + H_2O \xrightarrow{CeO_2} H_2 + CO_2 \tag{2}$$

4.6. Fischer-Tropsch synthesis

Use of nanocatalysts based on metal prepared through microemulsion technique in Fischer-Tropsch (FT) synthesis (conversion of hydrogen and carbon monoxide mixture into liquid hydrocarbon, Eq. (3)) is of great interest. Due to their low cost, selectivity and activity towards FT synthesis, low deactivation rate, supported cobalt catalysts are highly recommended to be used in FT synthesis [78]. Re supported Co catalysts were synthesized and deposited on titania. Using microemulsion method, smaller particle size of these catalysts was obtained whose catalytic activity in FT reactions was very much higher as compared to those prepared by other methods. Carbon nanotubes (CNT), when used as a catalyst carrier-support for Co nanoparticles, provides a higher reproducibility and higher degree of dispersion of catalyst [79]. Moreover, the catalytic activity of Co in FTS depends on its size distribution [80]:

$$(2n+1)H_2 + nCO \xrightarrow{Co} C_nH_{2n+2} + n\,H_2O \tag{3}$$

4.7. Electrocatalysis

Metal particles dispersed on carbon electrode are most widely used catalysts for electrolytic reactions. Xiong and He [81] reported the use of tungsten oxide and tungsten nanoparticles in electrocatalysis. They reported that surfactant must be removed from the surface of catalysts to make them useable at elevated temperatures. Iron-based nanocatalysts prepared in microemulsion medium found application in the electrocatalytic reduction of hydrogen peroxide (Eq. (4)) [82]. Cathodic catalysts to be used in fuel cells are also reported to be synthesized via microemulsion route [83]. Yet, the microemulsion-synthesized nanocatalysts exhibit unsatisfactory long-term stability [84]:

$$H_2O_2 + 2\,H^+ \overset{Fe}{\Leftrightarrow} 2\,H_2O \tag{4}$$

4.8. Combustion/oxidation/hydrogenation of hydrocarbons

Hexaaluminate is a catalyst used widely for catalytic combustion of methane. To enhance the activity of a catalyst, it is highly recommended to increase its surface area. Microemulsion route is proven to be a confirmed way to increase surface area of catalysts by decreasing their particle size [85]. The homogeneity of particles in microemulsion medium is increased, leading to the formation of catalyst at elevated temperatures, hence increasing its surface area. Hydrothermal treatment of microemulsion during synthesis of catalyst affects the effective surface area of catalyst. Particles having a smaller size over the range of approximately 2 nm ignite the process of reaction [86]. Silica- and alumina-coated metal particles such as platinum and nickel particles are also known to be used for complete and partial catalytic oxidation of methane (Eq. (5)); the high selectivity of this reaction lies in diffusion of methane particles to the catalyst surface through the silica coating [87–89]. The coating prevents the detachment of precursor metal particles from the support material, growth of carbon fibers and conversion of metal particles into their oxides and makes the nanocatalysts more stable and reactive. Synthesizing these catalysts in microemulsion route minimizes the size of particles rendering their activity high:

$$CH_4 + 2\,O_2 \xrightarrow{Pt/Ni} CO_2 + 2\,H_2O \tag{5}$$

Trimetallic nanocatalysts [90] prepared in microemulsion are more effective as compared to bimetallic catalysts for the oxidation of methanol as well as ethanol. Microemulsion synthesis overcomes the problems faced in the oxidation process, that is, poisoning by carbon monoxide, slow process of oxygen reduction [91, 88]. Carbon nanotube supported Pd, Rh and bimetallic (Pd/Rh) nanocatalysts are also employed as very effective catalysts for hydrogenation of olefins (Eq. (6)) [59]:

$$RCH = CH_2 + H_2 \xrightarrow{Pd/CNT} RCH_2CH_3 \tag{6}$$

A microemulsion based on a less toxic solvent, super critical CO_2, is employed by Meric and coworkers [89] for synthesis of palladium nanocatalysts. Due to capacity of this solvent to dissolve hydrogen and oxygen gases, it is highly recommended to be used in liquid-phase reactions as a medium. It also enhances the rate at which the reaction proceeds. The effect of Pd nanocatalysts on citral (3,7-dimethyl-2,6-octadienal) hydrogenation was studied by Meric. Using nanocatalysts dispersed and stabilized in microemulsion, approximately 68% unsaturated aldehyde (citeranol) was obtained. However, saturated aldehyde was gained as a main product in liquid or vapor phase reactions. This difference lies in the presence of palladium enclosed by micelle particles. Hydrogenation of α,β-unsaturated citral molecule forms the basis of certain reactions carried out in perfumery industry [26].

4.9. Oxidation of toluene

Mixed metal oxide nanoparticles containing noble metals (Au, Ag, Pt, etc.) can be used in oxidative catalysis of toluene. In a recent research, a cheaper non-noble metal manganese (Mn) is reported to be used in this process (equation 7) [64]. A comparison between Mn nanocatalysts prepared via microemulsion and precipitation techniques showed that surface area of the former was much greater and hence the catalytic activity was also higher. This activity was approximately the same as that of a conventionally prepared palladium-based nanocatalyst. Therefore, a cheaper nanocatalyst with improved efficiency can be prepared using microemulsion technique:

$$CH_3 - C_6H_5 \xrightarrow{Mn} C_6H_5 - COOH \tag{7}$$

4.10. Catalytic reforming

Nanocatalysts synthesized in microemulsion medium are applicable in certain reforming process, such as bi-functional reforming of naphtha. These catalysts have greater number of active sites on their surface, thus enhancing their activity. The deactivation of such catalysts is comparatively much slow. They also increase the yield of main product, that is, toluene and benzene, and decrease the yield of unwanted by-products [92].

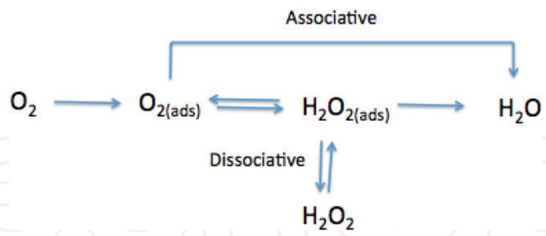
4.11. Oxidative coupling of methane

Oxidative coupling of methane is an effective method, which makes use of natural gas (CH_4) as an industrial feed stock. He and coworkers [93] utilized microemulsion technique to synthesize CeO_2/ZnO nanocatalysts for this purpose (Eq. (8)). They reported that the methane coupling over this specific catalyst prepared in microemulsion medium was much higher than the catalysts prepared by other techniques:

$$2\,CH_4 + O_2 \xrightarrow{CeO_2/ZnO} C_2H_4 + 2\,H_2O \tag{8}$$

4.12. Oxygen reduction reaction

Microemulsion route is also explored for the preparation of nanoparticles, which can be employed as catalyst in oxygen reduction reactions (ORRs) (most important reaction in life processes, Eq. 9). For instance, PtFe nanocatalysts supported on carbon are reported to be used in ORR. Using another metal such as Fe with Pt reduces the cost of electro catalyst. A major problem in ORR is the presence of adsorbed hydroxide [94]



(9)

which blocks the active sites on the surface of the catalysts; this problem is overcome by using bimetallic nanocatalysts prepared in microemulsion. These catalysts can be made cathode in proton exchange membrane fuel cell (PEMFC), improving the performance of fuel cell. PEMFC in return is an important candidate for portable and vehicle applications [95].

4.13. Environmental application

The emission of air pollution into the atmosphere from automobile engines can be reduced by the use of TWCs. It can be introduced in engines as an after treatment system. Incorporation of zirconium ions in CeO_2 increases its surface area and thermal stability. Use of this catalyst enhances the activity of TWCs. However, copper can also be included in the system, which catalyzes the oxidation process of organic compounds and carbon monoxide [31, 96]. For this synthesis, microemulsion technique combined with deposition precipitation technique can be employed [31].

An important reaction in environmental protection is hydrogenation of benzene to cyclohexane [97]. Ruthenium nanocatalysts supported on alumina are applicable to catalyze the hydrogenation process (Eq. (10)). However, owing to their better tolerance towards sulfur poisoning, recycled catalysts exhibit better performance [98].

$$C_6H_6 + 3H_2 \xrightarrow{Ru/Al_2O_3} C_6H_{12} \qquad (10)$$

5. Challenges in microemulsion synthesis of nanocatalysts

Although microemulsion is found to be a novel route for the preparation of nanocatalysts applicable in several fields, the recycling and separation of the organic solvents and nanocatalyst particles from the microemulsion medium is still a challenge for scientists. Traditional separation methods such as addition of a solvent, solvent evaporation, ultracentrifugation, and so on are used for this purpose. Addition of an anti-solvent (e.g. supercritical carbon dioxide, having a relatively low dielectric constant), along with a stabilizing agent such as carboxylate perfluoropolyether surfactant, being an innocuous and cheaper method, can be applied to control the stability of the catalysts effectively [11]. Making use of a photo-destructible surfactant, actuating de-stabilization of nanocatalyst particles from the microemulsion is also an interesting method for this purpose [99]. However, the shape of the nanocatalysts separated using destabilizing agents is irregular [100]. Regardless of their successful utilization in several important reactions, use of microemulsion for nanocatalyst synthesis is not much appreciated due to the lack of any industrial technique for this purpose. The cost for the synthesis of nanoparticles is relatively higher as expensive metals (Rh, Pt, etc.) are being used for the reaction. If microemulsion-based catalysts are managed to be produced at industrial scale, it is by far much better than other cheaper techniques [26]. So in the present scenario, a chemically clean and inexpensive microemulsion-synthesized nanocatalyst having desired particle size with a narrow size distribution is a real challenge [26, 101].

6. Conclusion

Microemulsion synthesis is a powerful and feasible technique for the preparation of several metal-based unimetallic, bimetallic (supported catalysts) as well as three way nanocatalysts, showing very interesting properties in certain chemical reactions. Dispersion of precursor metal particles in the nanosized droplets of microemulsion allows controlling the size, shape, morphology and size distribution of the as-prepared product depending on factors such as the initial concentration of reactants, surfactant, cosurfactant, addition of an electrolyte, and so on. The enhanced thermal stability, high catalytic activity and selectivity of the catalysts enables their use in wide range of reactions (e.g. aquathermolysis reaction, catalytic reforming, oxygen reduction reaction, photocatalysis, electrocatalysis, etc.), important in different fields such as perfumery industry, gas turbines, fuel cells, environmental protection, and so on. Despite the fact that microemulsion route synthesizes highly catalytic nanoparticles of any desired size, the process involving noble metal particles, becomes a very expensive method. This problem can be overcome by finding out an industrial way to utilize the microemulsion route for the synthesis of nanocatalysts. Moreover, the clean recovery of synthesized nanocatalysts from the reaction mixture is still a challenge.

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Author details

Tajamal Hussain* and Rabia Batool

*Address all correspondence to: tajamalhussain.chem@ou.edu.pk

Institute of Chemistry University of the Punjab, Lahore, Pakistan

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