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TENSIOACTIVOS Y AFINES (C.E.D.)

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TENSIOACTIVOS Y AFINES (C.E.D.)

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El Comité Español de la Detergencia, Tensioactivos y Afines (CED), es una entidad independiente sin ánimo de lucro con sede en Barcelona, que desde su fundación en el año 1957, se ha dedicado a difundir los conocimientos científicos y técnicos relacionados con la detergencia, la cosmética, las materias primas tensioactivas y otros aspectos relacionados, mediante diversas acciones:

1. La organización de Congresos, Jornadas Técnicas y Seminarios
2. Asesoramiento a entidades oficiales, emisión de informes y prestación de servicios a las empresas del sector.
3. Participación en la docencia de cursos de especialización y de postgrado, en colaboración con distintas universidades, centros de investigación y colegios profesionales
4. Relación con instituciones de intereses similares, tanto del país como del exterior: AENOR, AISE, CESIO, por ejemplo.

Desde su fundación, las actividades del CED han estado orientadas a tratar los temas de interés de las empresas del sector, los cuales han ido variando de acuerdo con la evolución de la coyuntura económica y las tecnologías empleadas en cada momento a lo largo de estos años.

Conscientes de que las necesidades de las empresas han crecido abarcando otras áreas no suficientemente cubiertas hasta ahora, el CED ha empezado una nueva etapa que incorpora los siguientes cambios:

1. La sede del comité se ha trasladado a la Facultad de Química de la Universidad de Barcelona, lo cual facilitará una mayor colaboración con el mundo académico y proporcionará mayores logros en los temas de formación y acceso a nuevos conocimientos.
2. Se propone un nuevo enfoque a las Jornadas Anuales y a las Jornadas Técnicas de manera que además de exponer temáticas técnicas sobre materias primas y productos, incorporarán nuevos aspectos, de materiales de envase y embalaje y servicios (laboratorios, consultoría…), con la intención de abarcar las diferentes áreas que cubren el desarrollo y puesta en el mercado de los productos de las empresas del sector.
3. Se incorporan nuevas modalidades de tarifas de inscripción a las Jornadas Anuales, para participantes de tipologías específicas que ahora no estaban contemplados, como visitantes, investigadores junior, y otros.
4. Se ha procurado una superior profesionalización a todo lo relativo a la organización de las Jornadas Anuales y Jornadas Técnicas, mediante su externalización a la empresa Mondial&Cititravel Congresos, especializada en organización de eventos.
5. Se están desarrollando iniciativas de formación de profesionales, mediante la organización de cursos específicos in-company, cursos on line y cursos presenciales sobre formación básica o específica en todos los ámbitos de actividad del CED, impartidos por profesionales industriales, académicos y consultores de amplia experiencia en el sector.
6. Mediante el desarrollo y potenciación de la página web de la asociación (http://www.ced.org.es) se pretende una mayor presencia mediática y visibilidad de la asociación y de sus socios en los foros virtuales, así como facilitar el acceso a la información disponible y la asistencia a jornadas y actos organizados por el CED.

Estamos convencidos que todo lo anteriormente expuesto será de gran interés para nuestros socios y dará mayor contenido y utilidad a todas las actividades organizadas por el CED.

Juan V. Robledo
PRESIDENTE C.E.D.

CONFERENCIAS/LECTURES

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A new vegetable-origin emulsifier with high versatility
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Bentonitas en los detergentes en polvo: Suavidad y perfumado
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Synthesis of superparamagnetic mixed oxide nanoparticles using the novel oil-in-water microemulsion reaction method
PEMARTIN K., AUBERY C., SANCHEZ-DOMINGUEZ M., SOLANS C. (Instituto de Química Avanzada de Cataluña (IQAC), Consejo Superior de Investigaciones Científicas (CSIC) – Barcelona, ESPAÑA)

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Hernández, R.; Draxler, A. Alpla Ibérica, S.A. Les Franqueses del Vallès, Barcelona, ESPAÑA

Los envases en el sector de detergentes: de la evolución del producto a la revolución en los envases
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Pendiente de título definitivo / Final title pending
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SORO R. (Ainia, Centro Tecnológico – Valencia, ESPAÑA)

SYNTHESIS OF MAGNETIC MIXED OXIDE NANOPARTICLES USING THE NOVEL OIL-IN-WATER MICROEMULSION REACTION METHOD

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Abstract

Recently, an oil-in-water microemulsion reaction method was developed for the preparation of nanomaterials. This novel method allowed a better control of the size and crystallinity of the obtained nanoparticles compared to other methods. The system used in this study was water, n- alkyl fatty alcohol ethoxylated surfactants and hexane. A selected microemulsion composition was used for the synthesis of 5-10 nm Mn-Zn ferrite nanoparticles which were characterized by High Resolution Transmission Electron Microscopy (HRTEM) and X-Ray Diffraction. In addition, magnetic properties of the Mn-Zn ferrite nanoparticles were assessed. Hence, magnetic nanostructured materials were synthesized in a predominantly aqueous environmentally friendly media (oil-in-water microemulsion). The properties of Mn-Zn ferrite nanoparticles were compared to those prepared using the water-in-oil microemulsion reaction method.

Keywords: magnetism, microemulsion, nanoparticles, spinel ferrite

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1. Introduction

There is an increased interest in the development of novel and more efficient methods of nanoparticle preparation, in order to meet the needs of multidisciplinary applications in collaborative fields such as medicine, chemistry, biology, and physics. The technological advancement in such disciplines is growing constantly, increasing the potential for possible application fields. Nanoparticles can play an important role in the expectations of specific applications.
Regarding wet chemistry synthesis, nanoparticles are usually prepared by conventional methods such as co-precipitation, sol-gel and impregnation processes. The drawbacks with these methods are not only the particle size which often is larger than 20 nm but also the poor control of particle size distribution even though there have been some improvements, generally associated with complex refinement processes.[1]

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For applications such drug delivery, cancer therapies [2], data storage [3], contrast imaging, gene delivery, solar cells, fuel additives, cosmetics, sunscreens, and catalysis, amongst others, it is necessary to obtain very small particle sizes, in the order of 10 nm or less, with a high control in the particle size distribution. Thus, there has been a growing interest in the synthesis of nanoparticles by the microemulsion reaction method (MRM). This method consists in promoting reactions in nanometric droplets, in a confined fashion. Each droplet could be considered as an individual nano-reactor [4, 5]. The first synthesis of noble metal nanoparticles in water-in-oil (W/O) microemulsions was described by M. Boutonnet *et al* in 1982.[6] Many types of inorganic nanoparticles have been synthesized by this method since then [4,5] even complex mixed oxides such as spinels and perovskites.[9] Most of the works reported in the literature employ surfactants of the ionic type such as Dioctyl sodium sulfosuccinate (AOT) [7] or quaternary ammonium salts [8] to form water-in-oil microemulsions. However, complex functional species may be absorbed on the particle surface and it could interfere with its growth [5, 10], as well as with the reaction itself. Hence, some microemulsions formed with nonionic surfactant type have been used [11]. For example, Span–Tween 80, a commercial mixture of sorbitol monooleate and polysorbate 80, was used to prepare TiO_2 nanoparticles in microemulsions [12]. In addition, Polyoxyethylene 4 lauryl ether was also used to prepare Pd, Pt and Pt/Pd nanoparticles, which showed an efficient catalytic activity [13]. Triton X-100 [Polyoxyethylene(9)4-(1,1,3,3 tetramethylbutyl) phenyl ether] has been also employed in preparation of different types of nanoparticles such as CeO_2 [14], Ce–Tb mixed oxides [15], Al_2O_3 [16], and Y_2O_3:Eu^{3+} [17]. The general drawback of the water-in-oil microemulsion reaction method is the use of organic solvents as a continuous phase, which has a negative effect on the environment.
With this motivation, recently a novel method has been developed, which consists in the use of oil-in-water (o/w) microemulsions as confined reaction media [18]. CeO_2, ZrO_2, $Ce_{0.5}Zr_{0.5}O_2$, and TiO_2 nanoparticles were synthesized by this method and their use as catalyst support for CO oxidation was tested [19]. The main advantage is that the major component is water which is more environmentally friendly and less costly than organic solvents.

The aim of this investigation is to synthesize mixed metal oxide nanoparticles using the novel oil-in-water microemulsion reaction method and to characterize the obtained materials. In parallel, the comparison of properties of the nanomaterials synthesized in water-in-oil (W/O) and oil-in-water (O/W) microemulsions will be carried out. Mn-Zn ferrite nanoparticles are investigated in this study. In the biomedical field, Mn-Zn ferrite nanoparticles are of high interest due to potential superparamagnetic properties and hence possible applications as Magnetic Resonance Imaging (MRI) contrast agents. In addition, this work may set the basis for the future synthesis of a variety of nanostructured spinels which could have potential applications in the catalytic production of hydrogen [20].

2. Experimental part

2.1. Materials

Synperonic® 10/6 and Synperonic® 13/6.5 were a gift from Croda. Fe (III) 2-ethylhexanoate (Fe-EH), Zn 2-ethylhexanoate (Zn-EH) and Mn (II) 2-ethylhexanoate (Mn-EH) were purchased from Alfa Aesar. Iron (II) sulfate heptahydrate (puriss. p.a. ACS 99.5% min.), Manganese (II) sulfate monohydrate (puriss. p.a. ACS 99% min.), Zinc sulfate heptahydrate (puriss. p.a. ACS 99.5% min) were purchased from Sigma-Aldrich. Hexane (Suprasolv, for gas chromatography) and isooctane (Suprasolv, for Gas Chromatography) were purchased from Merck. Isopropanol was purchased from Carlo Erba and Tetramethylammonium hydroxide (TMAH, 98%) and hydrogen peroxide (purum p.a. 30% w/w min) were purchased from Fluka.

2.2. Preparation of oxide nanoparticles by the oil-in-water microemulsion reaction method

The microemulsion system studied was: Water/Synperonic® 10/6/Hexane. The microemulsion containing the organometallic precursors (Fe-EH, Zn-EH, Mn-EH) was prepared by mixing appropriate amounts of surfactant, oil component and Milli-Q water. The composition investigated in this study corresponds to a surfactant/water ratio equal to 25/75 with 20% of oil containing the metallic precursors in an atomic ratio of 2:0.5:0.5 of Fe:Mn:Zn. The obtained microemulsion was homogeneous, transparent brown, fluid and isotropic. Then, a certain amount of Tetramethylammonium Hydroxide solution, TMAH (0.5 M in aqueous phase) was added up to pH=11.5-12 under vigorous stirring at 25ºC. After 1 hour, a small amount of concentrated H_2O_2 (30% w/w) was added in the mixture. The reaction mixture was kept stirring overnight, followed by centrifugation and washing cycles and dried in the oven at 70ºC.

2.3. Preparation of oxide nanoparticles by the water-in-oil microemulsion reaction method

Two microemulsions of aqueous phase / Synperonic 13/6.5 / isooctane were prepared. The composition investigated in this study corresponds to a surfactant/oil ratio equal to 25/75 with 20% of aqueous phase. In one of the microemulsiones the aqueous phase contained the metallic precursors in an atomic ratio of 2:0.5:0.5 of Fe:Mn:Zn (Fe^{2+}, Mn^{2+}, Zn^{2+} sulfates dissolved in H_2SO_4). In the other the aqueous phase contained TMAH 0.5 M. The synthesis was carried out by adding certain amount of microemulsion containing TMAH to a microemulsion containing metal precursor salts, until pH 11.5-12 was reached; typically, the approximate weight ratio of the microemulsions to achieve this pH was 1 part of microemulsion with precursor salts to 4 parts of microemulsion with TMAH. Before mixing, both microemulsions were equilibrated to 50ºC, and the mixing was also carried out at this temperature. The reaction mixture was kept stirring at 50ºC during 1 hour. A small amount of concentrated H_2O_2 (30% w/w) was then added and the reaction mixture was left stirring at 50ºC for 30 minutes. After the synthesis was finished, the product was separated from the microemulsion by addition of absolute ethanol:water 1:1 v/v,

followed by several cycles of centrifugation and washings with absolute ethanol. Finally, the product was dried in the oven at 70ºC.

2.4. Characterization of the nanoparticles

Particle size and morphology were investigated by Transmission Electron Microscopy (TEM 300KV Philips CM30). A few milligrams of nanoparticles were sonicated in isopropanol (2 ml), and a drop of this dispersion was deposited onto a holey carbon copper grid. The grid was left drying for 30 min to ensure the complete evaporation of isopropanol. Dried powders were characterized by X-ray diffraction (XRD). The magnetic nature of the Mn-Zn ferrite nanoparticles synthesized in oil-in-water microemulsion was assessed qualitatively by observing their attraction to a magnet.

3. Results and discussion

Mn-Zn Ferrite nanoparticles were prepared under mild conditions of reaction in o/w microemulsion as described in section 2.2. By means of centrifugation the particles were isolated from the reaction mixture. The remaining liquour was a stable, transparent fluid and isotropic solution. The o/w microemulsion was stable before, during and after reaction.

Particle shape and size were determined by TEM studies (*Figure 1*). The average particle size was 10 nm for nanoparticles synthesized in oil-in-water (O/W) microemulsion and they were globular in shape. Latice planes of these nanoparticles could be observed and corresponded to a d-spacing = 2.5 Å (hkl=311). In comparison, the particle size for the nanomaterial synthesized in w/o microemulsions was smaller (3-5nm), with a globular shape as well, and less agglomerated.

(a) (b)

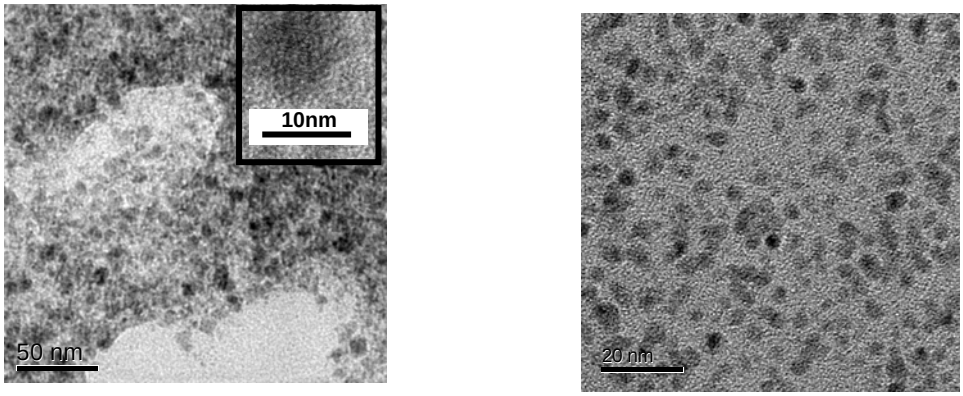

Figure 1: TEM micrograph of $Fe_2Mn_{0.5}Zn_{0.5}O_4$ nanoparticles synthesized with 20 wt% dispersed phase in a) oil-in-water microemulsion – b) water-in-oil microemulsion.

X-ray diffraction revealed a crystalline spinel structure for the Mn-Zn ferrite nanoparticles obtained by both o/w and w/o microemulsion reaction methods (*Figure 2 a and b*); this is an important result as in most studies a calcination step becomes necessary in order to attain such crystalline structure. It is worth noting that XRD of the as-prepared nanoparticles in O/W microemulsion presented better defined peaks in comparison with those from W/O microemulsion. This could be explained by the size difference of nanoparticles.

By using the Debye- Scherrer equation, the approximate crystallite size of $Fe_2Mn_{0.5}Zn_{0.5}O_4$ nanoparticles was calculated to be about 11 nm for the material obtained in O/W microemulsion, while for nanoparticles obtained by W/O microemulsions it was about 3.1 nm.

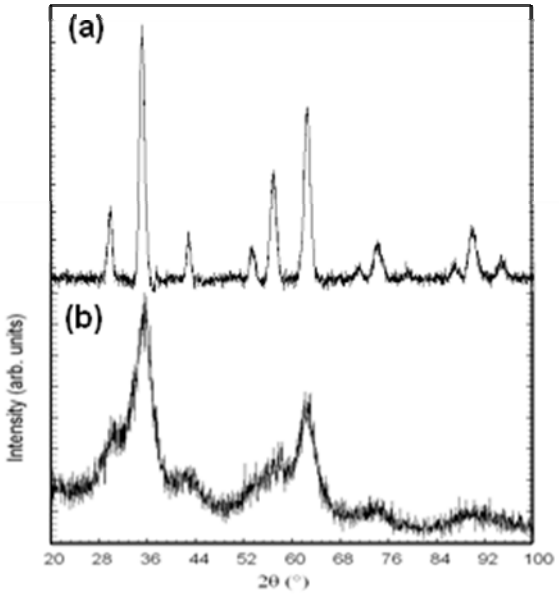

Figure 2: X-Ray diffractogram of dried Mn-Zn Ferrite nanoparticles prepared using 20 wt% of dispersed phase and a surfactant : continuous phase ratio of 25:75. (a) prepared in oil-in-water microemulsion; (b) prepared in water-in-oil microemulsion

As a conclusion, comparing the intensity of peaks from the XR diffractogram (Figure 2) nanoparticles from O/W microemulsion were more crystalline than those from W/O microemulsion.

The magnetic nature of the nanoparticles was assessed in a qualitative fashion by looking at their interaction with a Neodimium magnet.. The approach was to put a magnet near the flask containing the nanoparticles from oil-in-water microemulsion. As showed in figure 3, nanoparticles prepared in O/W microemulsions were attracted to the magnet and remained on the wall of the flask. Using this experiment, magnetic properties of Mn-Zn ferrite nanoparticles, which could have a high interest in applications, were qualitatively highlighted. Detailed magnetization studies as a function of magnetic field and temperature are underway in order to confirm their superparamagnetic behaviour.

Figure 3: Magnetic behaviour of Mn-Zn Ferrite nanoparticles synthesized with 20% of dispersed phase in O/W microemulsion

4. Conclusion

A novel oil-in-water microemulsion reaction approach has been used for the synthesis of nanocrystalline mixed oxides with spinel structure, particle size below 10 nm and magnetic properties. Nanoparticles from O/W microemulsion are slightly larger and have better crystallinty than those obtained from W/O microemulsion. The new O/W microemulsion reaction process is potentially more environmentally friendly since the continuous phase is water and the nanoparticles are obtained by one-pot synthesis.

5. Aknowledgements

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