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EFFECT OF SURFACTANT IN THE SYNTHESIS OF $\text{CoMo}/\text{Al}_2\text{O}_3$ CATALYSTS OBTAINED BY REVERSE MICROEMULSION FOR DIBENZOTHIOPHENE HYDRODESULFURIZATION

EFFECTO DEL TENSOACTIVO EN LA SÍNTESIS DE CATALIZADORES $\text{CoMo}/\text{Al}_2\text{O}_3$ OBTENIDOS POR MICROEMULSIÓN INVERSA PARA LA HIDRODESULFURACIÓN DE DIBENZOTIOFENO

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Abstract

Two series of microemulsions, water/1-butanol/surfactant (five samples per series) were studied; one series was prepared with cetyltrimethylammonium bromide (CTAB, cationic) and another with sodium dodecyl sulfate (SDS, anionic). For both series of microemulsions the effect of the type of surfactant on: the water in oil ratio; droplet size; amount of surfactant required and stability of the microemulsions was studied. The microemulsions employing SDS form larger drops, although require lower amount of surfactant. Microemulsions formed were stable for up to thirty days. Two $\text{CoMo}/\text{Al}_2\text{O}_3$ catalysts with the same metal composition were prepared using either surfactant, and were used in the hydrodesulfurization of dibenzothiophene. The catalyst prepared with CTAB presented a greater surface area and catalytic activity, than that prepared with SDS in the microemulsions. Product distribution in HDS followed the trend biphenyl > cyclohexylbenzene > bicyclohexyl for both catalysts suggesting the direct desulfurization route. The study suggests that the layer formed by the surfactant and organic agent, around the micelles, plays a role that determines the properties of the catalyst. The results allowed to suggest the mechanism of formation of the catalyst prepared by reverse microemulsion using CTAB as surfactant.

Keywords: microemulsion, CTAB and SDS surfactants, $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst, hydrodesulfurization.

Resumen

Se estudiaron y compararon dos series de microemulsiones agua/butanol/tensoactivo (5 muestras por serie), una con bromuro de cetiltrimetilamonio (BCTA, catiónico) y otra con dodecilsulfato sódico (DSS, aniónico). Para ambas series de microemulsiones se evaluó el efecto del tipo de tensoactivo sobre: la relación agua/orgánico requerida para formar la microemulsión; el tamaño de gota; cantidad de tensoactivo requerido y la estabilidad de la microemulsión. Las microemulsiones que emplean DSS forman gotas de mayor tamaño aun cuando requieren menor cantidad de tensoactivo. Las microemulsiones formadas mostraron alta estabilidad. Se prepararon dos catalizadores de $\text{CoMo}/\text{Al}_2\text{O}_3$ de la misma composición metálica, empleando ambos tensoactivos, los cuales fueron usados en la hidrodesulfuración de dibenzotiofeno. El catalizador preparado con el uso de BCTA presentó una mayor área superficial y actividad catalítica que el preparado con el uso de DSS en las microemulsiones. Con ambos catalizadores se observó la formación de productos por la vía de desulfuración directa, en el siguiente orden: bifenil > ciclohexilbenceno > biciclohexil. El estudio sugiere que la capa formada por el tensoactivo y agente orgánico, alrededor de las micelas, juega un rol que determina las propiedades del catalizador. Lo anterior permitió sugerir el mecanismo de formación del catalizador por microemulsión inversa, utilizando BCTA como tensoactivo.

Palabras clave: microemulsión, tensoactivos BCTA y DSS, catalizador $\text{CoMo}/\text{Al}_2\text{O}_3$, hidrodesulfuración, actividad catalítica.

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1 Introduction

Regulations of sulfur content in diesel fuels have forced the development of new catalysts with increased activities, using new methods and preparation techniques, for which Co(Ni)Mo/Al₂O₃ system is the basis, wherein the active phase MoS₂ promoted by Co or Ni atoms, has been widely investigated (Topsoe *et al.*, 1981; Topsoe *et al.*, 1996). Generally, the method of preparation used is the impregnation of the support (alumina), with cobalt and molybdenum species in solution (Choi *et al.*, 2004), in a wide pH range. The studies provide evidence, that after impregnation, drying and calcination, for the formation of a monolayer of MoO₃ species on the support and subsequent deposition of CoO species (Wang *et al.*, 1982; Spanos *et al.*, 1990; Vakros *et al.*, 2007; Bergwerff *et al.*, 2008). The main objective is the formation of highly dispersed active sites (CoMoS phase), to carry out the hydrodesulfurization of refractory compounds as dibenzothiophene and 4, 6-dimethyl dibenzothiophene (Topsoe *et al.*, 1996; Choi *et al.*, 2003). To achieve this, various impregnation techniques have been developed, including the use of different supports (Reardon *et al.*, 1998; Soukup *et al.*, 2015) and the synthesis of nano-sized catalytic particles (Choi *et al.*, 2004). Recently, it has been reported the preparation of bimetallic catalysts of Co(Ni)Mo using the microemulsion technique by precipitation (Scott *et al.*, 2015). The authors report the catalysts were less active in the hydrodesulfurization reaction, in comparison with a reference CoMo/Al₂O₃ catalyst, indicating that one of the reasons for the lower activity was the high segregation of the promoter. Erickson *et al.* (2004) have shown the potential of the reverse microemulsion method for obtaining nanoparticles used in heterogeneous catalysis. In general, the reverse microemulsion technique consists of a system composed of an aqueous phase, an organic phase and a surfactant, wherein the water phase/organic phase ratio, is equal to or less than unity (Guveli *et al.*, 1979; Patist *et al.*, 1998). The reverse microemulsions systems have as its main feature, the formation of water nanodroplets, surrounded by a layer of surfactant and dispersed in the organic phase, these systems being transparent or translucent (Sidim & Acar, 2013; Cavazos-Garduño *et al.*, 2014). The concentration of surfactant needed to initiate micelle formation, is called the critical micelle concentration (cmc), condition that can generally be determined by the electrical conductivity parameter

(Sidim & Acar, 2013). These systems have been reported to be thermodynamically stable and isotropic (Silas & Kaler, 2001). Microemulsions systems are used in various fields, some of them are in foods, and to synthesize catalytic nanoparticles, the latter are materials obtained with high surface areas and specific physico-chemical properties. (Wu *et al.*, 2001; Flores-Miranda *et al.*, 2015). In addition, it has been made clear that for each nanoparticle synthesis, the selection of the organic phase and surfactant is important because these can affect nanoparticles morphology (Pileni, 2003; Eriksson *et al.*, 2004). Some of the surfactants as cetyltrimethylammonium bromide (CTAB) cationic surfactant and sodium dodecyl sulfate (SDS) anionic surfactant, have been used in reverse microemulsion systems (Guveli *et al.*, 1979; Patist *et al.*, 1998; Pileni, 2003; Eriksson *et al.*, 2004) and its effect has been observed in nanoparticles synthesis. Sicard *et al.* (2003) reported that for the synthesis of alumina the effect of presence of CTAB and SDS was compared, and after calcination it was determined that the polar part of SDS ends within the network of alumina. On the other hand an improvement in the network structure of alumina was observed, determining a greater surface area with the use of CTAB. In other studies, CuO-ZrO₂ catalyst prepared by reverse microemulsion, used to produce hydrogen from methanol, it was determined that the use of CTAB yielded more uniform and less agglomerated nanoparticles, compared with SDS from which a higher aggregation of micelles during the preparation was observed, producing larger particles (Vahidshad *et al.*, 2010). The effect of micelles made with different surfactants, including SDS and CTAB, used as catalysts for the synthesis of quinoxaline, allowed to determine the catalytic potential in the following order: nonionic > anionic > Brønsted acids > cationic, suggesting that surfactants are better suited as catalytic aids to promote organic reactions in water (Kumar *et al.*, 2013). The present work aimed to analyze and compare two sets of reverse microemulsions, each set with a surfactant of different ionic nature (CTAB and SDS) and the same organic phase (1-butanol). For both sets, a formulation was selected, to synthesize a CoMo/Al₂O₃ catalyst with the same composition in both microemulsions. The catalysts were analyzed and compared with different characterization techniques, in order to determine the effect of surfactants on the properties of the synthesized materials, and their performance in the dibenzothiophene hydrodesulfurization.

Table 1. Composition of the microemulsions

Series 1 microemulsions					Series 2 microemulsions				
Water (wt. %)	Water (ml)	1-Butanol (wt. %)	CTAB (wt. %)	CTAB (g)	Water (wt. %)	Water (ml)	1-Butanol (wt. %)	SDS (wt. %)	SDS (g)
23.9	8	72.7	3.4	1.1	24.1	8	73.3	2.6	0.8
30.7	12	62.0	7.3	2.8	31.7	12	64.2	4.1	1.6
36.4	16	55.2	8.4	3.7	37.8	16	57.3	4.9	2.1
41.3	20	50.1	8.6	4.2	42.7	20	51.9	5.4	2.5
45.5	24	46.0	8.5	4.4	47.1	24	47.6	5.3	2.7

2 Materials and methods

2.1 Materials

To prepare reverse microemulsions, Milli-Q purified water formed the disperse phase, while 1-butanol (J. T. Baker, 99% purity) made up the continuous phase of the microemulsions. Cetyl trimethyl ammonium bromide (CTAB, $\text{CH}_3(\text{CH}_2)_{15}\text{NBr}(\text{CH}_3)_3$) cationic surfactant (Sigma-Aldrich) and sodium dodecyl sulfate (SDS, $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$) anionic surfactant (Sigma-Aldrich), were used as surfactants.

For the catalysts, cobalt nitrate 6-hydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ammonium heptamolybdate tetrahydrate (AHM, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) and aluminum nitrate 9-hydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), all were reagent grade (J. T. Baker) were used.

Butylamine ($\text{CH}_3\text{C}_3\text{H}_6\text{NH}_2$) to adjust the pH of the microemulsions (Sigma-Aldrich) was used.

2.2 Methods

Two sets of reverse microemulsions (five samples per set) were prepared, the first series was prepared with water/n-butanol/CTAB and the second set was obtained by using water/1-butanol/SDS, as shown in Table 1. Additionally, in Table 1 are shown the amount of water used and the corresponding mass fractions. 1-butanol mass fractions correspond to 30 ml in each sample. The water/1-butanol mass ratio was less than unity to ensure the formation of reverse microemulsions. During microemulsion formation, CTAB and SDS surfactants were added slowly, with continuous stirring until the mixture turned from turbid to transparent. This change was determined by the critical micelle concentration (cmc), following the electric conductivity (k), that was continuously monitored with a LabPro Vernier (model CON-BTA), coupled to a conductivity probe with a sensitivity of ± 0.001 S/m. Measurements were conducted at a constant temperature of 25 ± 0.1 °C.

The hydrodynamic diameter of the nanodroplets, was determined by means of dynamic light scattering (DLS) using Malvern Zetasizer Nano (Malvern Instruments Ltd., Malvern, Worcestershire, UK). Measurements were done at constant temperature, 25 ± 0.1 °C.

To evaluate the stability of microemulsions, the viscosity and droplet size of each system in an initial time $t=0$ and subsequently after 30 days was determined. The viscosity was evaluated to shear rates of 60 to 1×10^{-3} s^{-1} , using a rheometer (Physica, model MCR 300, Stuttgart, Germany) with a cylindrical geometry of double-gap at a temperature of 25 ± 0.01 °C controlled by a Peltier system.

From each set a microemulsion formulation was selected to synthesize a CoMo/Al₂O₃ catalyst. For this synthesis, the organic phase was 1-Butanol, the aqueous phase was a saline solution with 9.21 mM of cobalt (II) species, 23.96 mM of molybdenum (VI) species and 125.52 mM of aluminum (III) species. The CTAB and SDS surfactants in each case were added slowly, to obtain the microemulsion systems. Subsequently, microemulsion systems were adjusted to pH 10 using butylamine, to generate the required species in solution. These microemulsion systems were allowed to dry for 48 hours. The dried samples were calcined with a ramp of 2 °C / min to 500 °C, maintaining this temperature for 6 hours with an air flow of 20 ml / min, to obtain catalysts in their oxide state. Once the catalysts were obtained, were characterized as show below.

The nitrogen physisorption analysis was done in an Autosorb 1 gas sorption system (Quantachrome). Samples were outgassed at 204 °C under vacuum for six hours, the nitrogen physisorption was performed at - 196 °C. The surface area determination, volume and pore diameter was carried out using the BET equation and the BJH method.

The crystalline phases were identified using a Siemens D-500 Kristalloflex Diffractometer, with a $\text{CuK}\alpha$ radiation, $\lambda = 0.15406$ nm, with primary and

secondary beam monochromator. The equipment was operated at 35 kV, 20 mA with a time interval of 1 s and scan rate of 0.03°/s.

The hydrodesulfurization of dibenzothiophene (DBT) was carried out in a batch reactor (Parr) for 6 h. The HDS conditions were as follows: weight of catalyst 0.2 g, pressure 800 psi, temperature 320 °C, RPM 1000, solvent 100 mL hexadecane, weight of DBT 0.3 g. The catalyst was previously sulfided in an H₂S (15%)/H₂ flow at 400 °C for two hours. Products of the HDS reactions were analyzed by GC (Perkin Elmer XL Autosystem). HDS kinetic constants k_{DBT} were calculated assuming pseudo-first order kinetics referred to DBT concentration (Escobar *et al.*, 2005).

3 Results and discussion

3.1 Synthesis of reverse microemulsions

In this study the effect of two surfactants in the formation of reverse microemulsion and in the synthesis of catalysts was evaluated. As shown in Table 1, to obtain a microemulsion the mass of each surfactant required to disperse a given volume of water is different. Figure 1 shows that with increasing volume of water, the surfactant/water ratio reaches a maximum, then decreases. Specifically, for the case of microemulsions formed with SDS, less surfactant is required compared to CTAB to disperse equal water volumes. This indicates that for the water volumes tested, the amount of SDS used is 25% to 40% lower than that of CTAB. The behavior described above can be attributed to the lower cmc and lower aggregation number for SDS, compared with for CTAB (Li *et al.*, 1996; Li & Kunieda, 2003; Shafiq Ullah, 2007).

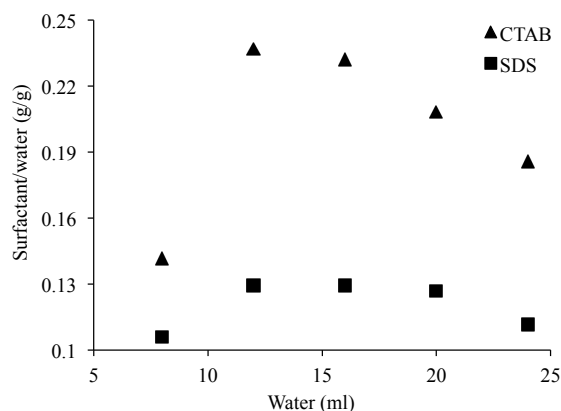


Fig. 1. Surfactant-water relationship in microemulsion systems formed with anionic and cationic surfactants.

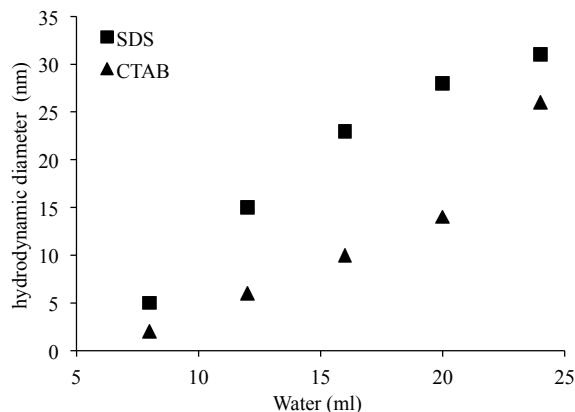


Fig. 2. Hydrodynamic diameter behavior as a function of water content.

Figure 2 shows the hydrodynamic diameter of micelles as a function of water volume. The hydrodynamic diameter is of the same order of magnitude in both series of microemulsions, but a greater hydrodynamic diameter is observed for SDS formulations than for CTAB microemulsions. This behavior is explained by taking into account the following: there is a greater contribution of electrostatic repulsion between the charged heads of the SDS surfactant, as compared to CTAB (Patist *et al.*, 1998; Zakharova *et al.*, 2003). This, in turn produces that a greater number of molecules of 1-butanol can be transported to the interface (Guveli *et al.*, 1979; Mathew & Juang, 2007), so that alcohol molecules with different carbon chain behave as cosurfactants. Shiao *et al.* (1997), further reported that when organic molecules are transported to the interface, a marked decrease of the water/organic interfacial tension occurs, producing an increase in microemulsions stability. In other studies, the authors comment that the SDS has a carbon chain smaller, which also allows further migration of 1-butanol molecules to the interface, justifying a lower aggregation number of SDS over the CTAB (Li *et al.*, 1996; Feng *et al.*, 2005; Samakande *et al.*, 2008).

With these results, it is possible to select two appropriate systems, one per series of microemulsions within the composition intervals used, to synthesize catalytic materials within the nanodroplets. Additional experiments (not shown here) indicated that when aqueous phase/organic phase ratio is very close to unity, microemulsions tend to lose their transparent appearance, and bicontinuous microemulsions are formed. Also, in the lower limit of water content the droplets are small and may not be appropriate for the formation of the materials, since this allows

the precipitation of the solid particles formed inside the micelles (Pileni, 2003). The selection of the appropriate systems ensures the generation of micelles with the hydrodynamic diameters capable of containing solid particles.

3.2 Stability of microemulsion systems

In Table 2, viscosity values in an interval of 0 to 30 days are shown. In column 1, the water content corresponds to the percentages of Table 1. Columns 2 and 4 correspond to the microemulsions prepared with SDS, whereas columns 3 and 5 to the microemulsions prepared with CTAB. As observed, viscosity remains unchanged in the time interval analyzed. Also, the average droplet size did not change significantly (results not shown). This indicated that the micelles formed at time $t = 0$ remain stable. Paul *et al.* (2000) in their review indicate that the viscosity is dependent on the components of the microemulsion and the preparation conditions. Additionally, for each system the fluidity plays an important role, which determines the material properties to synthesize. In our case, all of the microemulsions showed Newtonian behavior in the experimental shear rate interval used, indicating Brownian free motion of micelles (high mobility).

3.3 Synthesis of $\text{CoMo}/\text{Al}_2\text{O}_3$ catalysts

Based on the composition for all microemulsions given above, in Table 3, the percentages in mass of the microemulsion systems selected (one per series) are given. As observed, the microemulsions selected correspond to the preparations in the middle range. The selection prevents possible effects on droplet size,

either by the formation of bicontinuous systems (high concentration of aqueous phase) or by the formation of very small droplets.

The aqueous phase was used to prepare a solution with the precursor salts, later the two microemulsion systems were formed, as described. The hydrodynamic diameter of the droplets of microemulsion was 5.3 nm using CTAB and 12.5 nm with SDS. These values were lower with respect to the hydrodynamic diameters (10 nm with CTAB and 22.7 nm with SDS) observed without the presence of salts. The reduction in size of the micelles is due to the presence of electrolytes in the aqueous phase, which significantly reduce the repulsive forces of the polar part of the surfactant; a greater packaging is produced, which results in a decreased hydrodynamic diameter (Ayyub *et al.*, 1993; Paul & Moulik, 2000). Once formed, both microemulsions were adjusted to pH=10 to obtain the formation of the following species: $\text{Co}(\text{OH})_2$, MoO_4^{2-} and $\text{Al}(\text{OH})_3$ inside the micelles. As has been reported, these species are appropriate to prepare active HDS catalysts (Wang & Hall, 1982; Inamura *et al.*, 1997; Parida *et al.*, 2009).

Table 4 shows the nominal composition, surface area and pore volume of the calcined materials. Both materials were mesoporous; the catalyst synthesized with CTAB resulted with higher surface area than that obtained with SDS, with significant differences. Compared to $\text{CoMo}/\text{Al}_2\text{O}_3$ catalysts prepared by diverse impregnation techniques, the surface areas found are within the range reported for similar materials (Papadopoulou *et al.*, 2004; Escobar *et al.*, 2005). On the other hand, Pérez De la Rosa *et al.* (2004), reported an area of 227 m^2/g for a DSD-14 industrial catalyst.

Table 2. Viscosities of microemulsion systems

Water ml	Viscosity SDS mPa (t = 0 days)	Viscosity CTAB mPa (t=0 days)	Viscosity SDS mPa (t=30 days)	Viscosity CTAB mPa (t=30 days)
24	8.143	8.169	8.145	8.171
20	8.120	8.039	8.122	8.042
16	8.019	7.840	8.016	7.835
12	7.914	7.568	7.900	7.563
8	7.846	7.121	7.850	7.196

Table 3. Microemulsion systems composition for the catalysts synthesis

Microemulsion	Water (wt. %)	1-Butanol (wt. %)	SDS (wt. %)	CTAB (wt. %)
Series 1	36.4	55.2	-	8.4
Series 2	37.8	57.3	4.9	-

Table 4. Nominal composition of the catalysts CoMo/Al₂O₃ (wt. %) and textural properties

Catalysts	CoO (wt. %)	MoO ₃ (wt. %)	Al ₂ O ₃ (wt. %)	Area BET (m ² /g)	Pore Vol. (cm ³ /g)
CoMo/Al ₂ O ₃ (CTAB)	3.5	14.7	81.8	261	0.41
CoMo/Al ₂ O ₃ (SDS)	3.5	14.7	81.8	124	0.62

Sicard *et al* (2003) observed the effect of the addition of surfactants during alumina preparation. They reported that the addition of SDS had an adverse effect on the alumina properties, obtaining low surface areas, but the addition of CTAB produced alumina with high surface areas.

3.4 X-ray diffraction (XRD)

In Figure 3, the diffractogram of the catalyst synthesized with the microemulsion using CTAB is presented. The result shows an amorphous material, indicating that the cobalt and molybdenum oxides are highly dispersed on the Al₂O₃ support (Haruta *et al*, 1984). Xin *et al* (2004), analyzed aluminas synthesized by microemulsion method, using CTAB as surfactant, and reported mesostructured alumina, observing a similar XRD pattern to that shown in Figure 3.

In Figure 4, the diffractogram of the catalyst synthesized in the microemulsion formed with SDS is shown. In the diffractogram, the reflections shown correspond to sodium sulfate, which is still present after calcination.

Choi *et al* (2004) reported a CoMo/Al₂O₃ catalyst prepared by spray pyrolysis to obtain spheres that consisted of primary particles of nanometric size. XRD analysis of these samples showed the presence of molybdates (MoO₄ and Al₂(MoO₄)₃), for all samples containing a large amount of MoO₃. Sicard *et al* (2003) reported that during the synthesis of aluminas, the presence of surfactants (CTAB) at basic pH does not affect the porosity. However, traces of bromide and sodium ions were detected, showing a direct interaction between the surfactants and alumina. And in the case of SDS, occlusion of the sulfate group head in the alumina framework was determined. In contrast to Sicard *et al.* (2003), in our work no bromide ions were detected and the presence of sulfate ions was observed by XRD.

3.5 HDS of DBT

The catalytic activity in terms of DBT conversion is shown in Figure 5 for both catalysts. The catalyst prepared with CTAB had a conversion of 93%, whereas for the SDS-prepared catalyst the conversion

was only 24%. The kinetic constants for the initial reaction rate, showed a value of 3.02×10^{-4} m³/kg_{metal}s, for catalyst synthesized using CTAB, being sixfold more active, with respect to catalyst synthesized using SDS, whose value was 0.54×10^{-4} m³/kg_{metal}s. It is noticeable the huge difference between both catalysts having the same formulation. Comparing both it appears as if the SDS-formulated sample deactivate reaching a constant low conversion after 5 hours of reaction. XRD results suggest that the remaining sulfate present in the catalyst after calcination is the cause of this behavior.

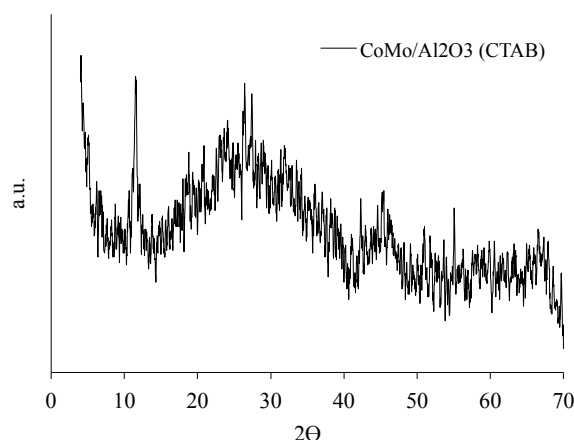


Fig. 3. X-ray diffractogram of calcined CoMo/Al₂O₃ catalyst prepared with CTAB

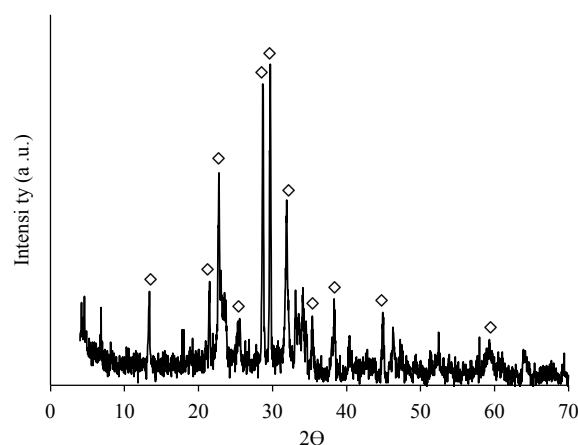


Fig. 4. XRD pattern for calcined CoMo/Al₂O₃ prepared with SDS. ◊: sodium sulfate

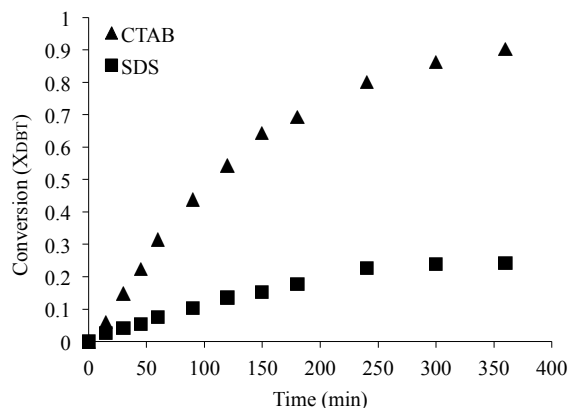


Fig. 5. DBT conversion for the two CoMo/Al₂O₃ catalysts prepared.

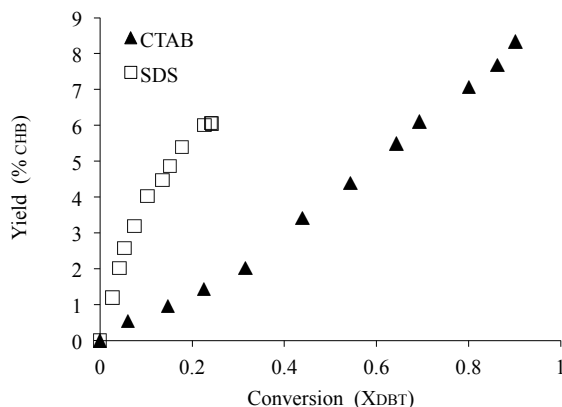


Fig. 7. Cyclohexylbenzene yield as a function of DBT Conversion.

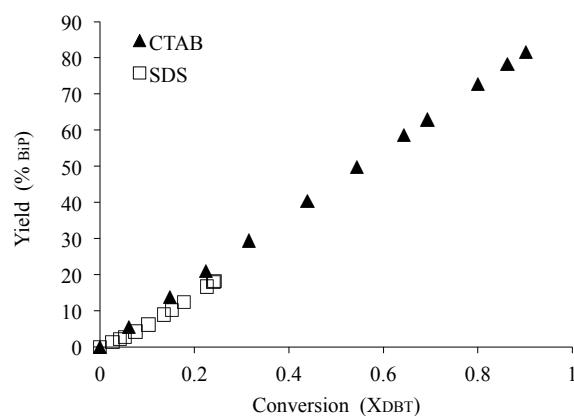


Fig. 6. Biphenyl yield as a function of DBT Conversion

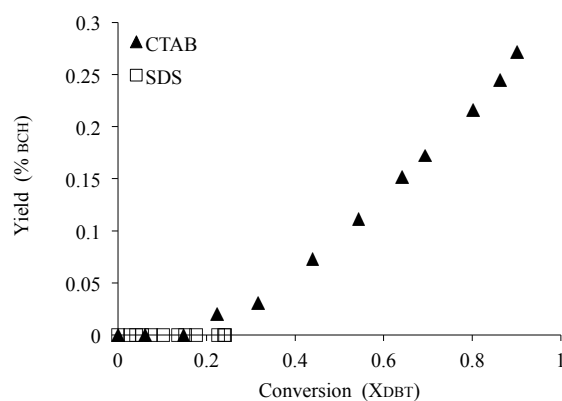


Fig. 8. Bicyclohexyl yield as a function of DBT Conversion.

Products distributions of dibenzothiophene hydrodesulfurization are given in Figures 6, 7 and 8, where the yields are presented in terms of DBT conversion. The products were: biphenyl (BiP), cyclohexylbenzene (CHB) and bicyclohexil (BCH). Higher yields were obtained for the catalyst synthesized using CTAB, due to higher DBT conversion. In both catalysts the main product was BiP. 81.6 % of DBT was converted to BiP when using CTAB and only 18.2 % when the catalysts was prepared with SDS. Regarding CHB, 8.3 % of the DBT was converted using CTAB, and only 6.0 % when using SDS. The conversion to CHB was very small when using both catalysts.

It is well known that the hydrodesulfurization of DBT occurs following two pathways (Houalla *et al.*, 1980); one pathway is the hydrogenation and the second pathway, indicates direct desulfurization

(DSD). DSD involves the breaking of C-S bonds, preserving the aromaticity of the rings to produce biphenyl (BiP) as the first product. Once formed the biphenyl, the hydrogenation of one of the aromatic rings occurs producing cyclohexylbenzene (CHB). A subsequent hydrogenation of the second ring produces bicyclohexil (BCH). It is clear that under the conditions used the main product is biphenyl, which means that the hydrogenation steps are slower than the elimination of sulphur. Several reports (Houalla *et al* 1980; Bataille *et al* 2001) have indicated that in cobalt catalysts this pathway is favored for the HDS of DBT. It is also known that in the DSD pathway the desulfurization is faster than in the hydrogenation pathway, about three orders of magnitude (Houalla *et al.*, 1980). In this study the results obtained indicate for both CoMo/Al₂O₃ catalysts that the direct desulfurization route is followed.

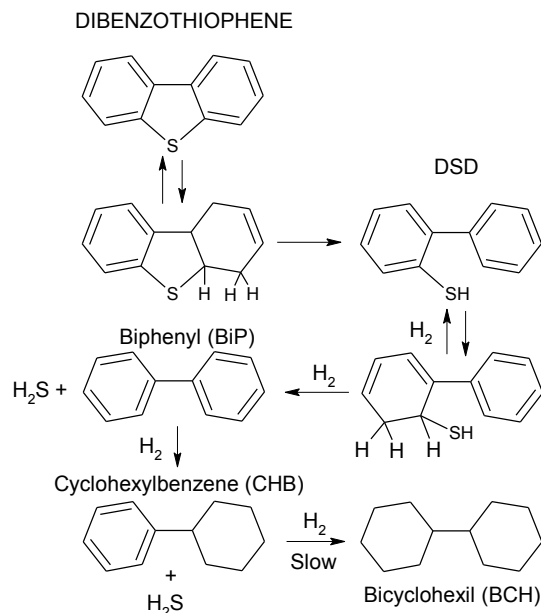


Fig. 9. Direct desulfurization route for DBT.

Conclusions

This work compares the microemulsion characteristics using two different surfactants, one anionic and one cationic. The amount of surfactant needed to form the microemulsion and the micelles sizes indicate the influence of the ionicity of surfactant, although both sets are highly stable. Larger droplets are formed with CTAB suggesting the possibility to manage larger concentrations of materials precursors and to avoid precipitation. To synthesize the catalysts a value in the middle of the region tested was used to prevent the formation of bicontinuous systems or the formation of very small droplets. Materials prepared with CTAB present larger surface areas and greater activity in the hydrodesulfurization of DTB. In fact catalyst prepared with SDS had a very low activity and after 5 hours the catalyst deactivated completely. In agreement with the literature for CoMo catalysts the preferred route to eliminate sulfur is the direct desulfurization

We have demonstrated that with the use of reverse microemulsions, complex catalysts such as CoMo/Al₂O₃ used in hydrodesulfurization can be obtained, and that the surfactant, its ionicity and chemical composition used for the synthesis have a tremendous impact in the catalyst performance.

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References

- Ayyub, P., Maitra, A., & Oshah, D. O. (1993). Microstructure of the CTAB-Butanol-Octane-Water microemulsion system: effect of dissolved salts. *Journal of the Chemical Society, Faraday Transactions 89*, 3585-3589.
- Bataille, F., Lemberon, J. L., Pérot, G., Lyrit, P., Cseri, T., Marchal, N., & Kasztelan, S. (2001). Sulfided Mo and CoMo supported on zeolite as hydrodesulfurization catalysts: transformation of dibenzothiophene and 4,6-dimethyldibenzothiophene. *Applied Catalysis A: General*, 220, 191-205.
- Bergwerff, J. A., Visser, T., & Weckhuysen, B. M. (2008). On the interaction between Co- and Mo-complexes in impregnation solutions used for the preparation of Al₂O₃-supported HDS catalysts: A combined Raman/UV-vis-NIR spectroscopy study. *Catalysis Today* 130, 117-125.
- Cavazos-Garduño, A., Ochoa Florez, A. A., Serrano-Niño, J. C., Beristain, C. I., & García, H. S. (2014). Operating and compositional variables for preparation of betulinic acid nanoemulsions. *Revista Mexicana de Ingeniería Química* 13, 689-703.
- Choi, K.-H., Korai, Y., & Mochida, I. (2004). Preparation and characterization of nano-sized CoMo/Al₂O₃ catalyst for hydrodesulfurization. *Applied Catalysis A: General* 260, 229-236.
- Choi, K.-H., Kunisada, N., Korai, Y., Mochida, I., & Nakano, K. (2003). Facile ultra-deep desulfurization of gas oil through two-stage or -layer catalyst bed. *Catalysis Today* 86, 277-286.
- Eriksson, S., Nylen, U., Rojas, S., & Boutonnet, M. (2004). Preparation of catalysts from microemulsions and their applications in heterogenous catalysis. *Applied Catalysis* 265, 207-219.

- Escobar, J., Toledo, J. A., Cortés, M. A., Mosqueira, M. L., Pérez, V., Ferrat, G., Torres-García, E. (2005). Highly active sulfided CoMo catalysts on nano-structured TiO₂. *Catalysis Today* 106, 222-226.
- Feng, Z., Yukou, D., Ping, Y., Xingchang, L., & Ji'an, T. (2005). Adsorption behavior of hexadecyltrimethylammonium bromide (CTAB) to mica substrates as observed by atomic force microscopy. *Science in China Series B Chemistry* 48, 101-106.
- Flores-Miranda, G. A., Valencia del Toro, G., & Yáñez-Fernández, J. (2015). Stability evaluation of β -carotene nanoemulsions prepared by homogenization-emulsification process using stearic acid as oil phase. *Revista Mexicana de Ingeniería Química* 14, 667-680.
- Guveli, D. E., Kayes, J. B., & Davis, S. S. (1979). Hydrodynamic studies of micellar systems of alkyltrimethylammonium bromides and the effect of added 1-alkanols. *Journal of Colloid and Interface Science* 72, 130-139.
- Haruta, M., Lemaitre, J., Delannay, F., & Delmon, B. (1984). Preparation and properties of colloidal spherical particles of molybdenum and cobalt sulfides. *Journal of Colloid and Interface Science* 101, 59-71.
- Houalla, M., Broderick, D. H., Sapre, A. V., Nag, N. K., de Beer, D. H., Gates, B. C., & Kwart, H. (1980). Hydrodesulfurization of methyl-substituted dibenzothiophenes catalyzed by sulfided Co-Mo/Al₂O₃. *Journal of Catalysis* 61, 523-527.
- Inamura, K., Uchikawa, K., Matsuda, S., & Akai, Y. (1997). Preparation of active HDS catalysts by controlling the dispersion of active species. *Applied Surface Science* 121-122, 468-475.
- Kumar, D., Seth, K., Kommi, D. N., Bhagat, S., & Asit, K. C. (2013). Surfactant micelles as microreactors for the synthesis of quinoxalines in water: scope and limitations of surfactant catalysis. *RSC Advances* 3, 15157-15168.
- Li, X., & Kunieda, H. (2003). Catanionic surfactants: microemulsion formation and solubilization. *Current Opinion in Colloid and Interface Science* 8, 327-336.
- Li, X., Lin, E., Zhao, G., & Xiao, T. (1996). Microemulsion formation and phase behavior of anionic and cationic surfactants with sodium dodecyl sulfate and cetyltrimethylammonium bromide. *Journal of Colloid and Interface Science* 184, 20-30.
- Mathew, D. S., & Juang, R.-S. (2007). Role of alcohols in the formation of inverse microemulsions and back extraction of proteins/enzymes in a reverse micellar system. *Separation and Purification Technology* 53, 199-215.
- Papadopoulou, C., Vakros, J., Matralis, H. K., Voyiatzis, G. A., & Kordulis, C. (2004). Preparation, characterization, and catalytic activity of CoMo/ γ -Al₂O₃ catalysts prepared by equilibrium deposition filtration and conventional impregnation techniques. *Journal of Colloid and Interface Science* 274, 159-166.
- Parida, K. M., Pradhan, A. C., & Sahu, N. (2009). Synthesis and characterization of nano-sized porous gamma-alumina by control precipitation method. *Materials Chemistry and Physics* 113, 244-248.
- Parida, K. M., Pradhan, A. C., & Sahu, N. (2009). Synthesis and characterization of nano-sized porous gamma-alumina by control precipitation method. *Materials Chemistry and Physics* 13, 244-248.
- Patist, A., Axelberd, T., & Shah, D. O. (1998). Effect of long chain alcohol on micellar relaxation time and foaming properties of sodium dodecyl sulfate solutions. *Journal of Colloid and Interface Science* 208, 259-265.
- Paul, B. K., & Moulik, S. P. (2000). The viscosity behaviours of microemulsions: an overview. *PINSA* 5, 499-519.
- Pérez De la Rosa, M., Texier, S., Berhault, G., Camacho, A., Yacamán, M. J., Mehta, A., Chianelli, R. R. (2004). Structural studies of catalytically stabilized model and industrial-supported hydrodesulfurization catalysts. *Journal of Catalysis* 225, 288-299.
- Pileni, M.-P. (2003). The role of softcolloidal templates in controlling the size and shape of inorganic nanocrystals. *Nature Materials* 2, 145-150.

- Reardon, J., Datye, A. K., & Sault, A. G. (1998). Tailoring Alumina Surface Chemistry for Efficient Use of Supported MoS₂. *Journal of Catalysis* 173, 145-156.
- Samakande, A., Chaghi, R., Derrien, G., Charnay, C., & Hartmann, P. C. (2008). Aqueous behaviour of cationic surfactants containing a cleavable group. *Journal of Colloid Interface Science* 320, 315-320.
- Scott, C. E., Pérez-Zurita, M. J., Carbognani, L. A., Molero, H., Vitale, G., Guzman, H. J., & Pereira-Almao, P. (2015). Preparation of NiMoS nanoparticles for hydrotreating. *Catalysis Today* 250, 21-27.
- Shafiq Ullah, A. K. (2007). SANS analysis on CTAB (cetyltrimethyl ammonium bromide micellar solution). *BRAC University Journal* 4, 59-62.
- Shiao, S. Y., Patist, A., Free, M. L., Chhabra, V., Huibers, P. D., Gregory, A., Shah, D. O. (1997). The importance of sub-angstrom distances in mixed surfactant systems for technological processes. *Colloids and Surfaces* 128, 197-208.
- Sicard, L., Lebeau, B., Patarin, J., & Kolenda, F. (2003). Synthesis of mesostructured or mesoporous aluminas in the presence of surfactants. Comprehension of the mechanisms of formation. *Oil & Gas Science and Technology* 58, 557-569.
- Sidim, T., & Acar, G. (2013). Alcohols effect on Critic Micelle Concentration of Polysorbate 20 and Cetyl Trimethyl Ammonium Bromine Mixed Solutions. *Journal of Surfactants and Detergents*, 16(4), 601-607.
- Silas, J. A., & Kaler, E. W. (2001). Effect of Dodecyldimethylammonium Bromide on the Phase Behavior of nonionic surfactant-silicone oil microemulsions. *Langmuir* 17, 4534-4539.
- Soukup, K., Procházka, M., & Kaluza, L. (2015). Microstructural Properties and HDS Activity of CoMo Catalysts Supported on Activated Carbon Al₂O₃, ZrO₂, TiO₂. *Chemical Engineering Transactions* 43, 841-846.
- Spanos, N., Vordonis, L., Kordulis, C., & Lycourghiotis, A. (1990). Molybdenum-oxo species deposited on alumina by adsorption. *Journal of Catalysis* 124, 310-314.
- Topsoe, H., Clausen, B. S., & Massoth, F. E. (1996). Hydrotreating catalysis. *Fuel Science and Technology International* 14(10).
- Topsoe, H., Clausen, B. S., Candia, R., Wivel, C., & Morup, S. (1981). In situ Mössbauer emission spectroscopy studies of unsupported and supported sulfided CoMo hydrodesulfurization catalysts: Evidence for and nature of a CoMoS phase. *Journal of Catalysis* 68, 433-452.
- Vahidshad, Y., Abdizadeh, H., Baseri, M. A., & Baharvandi, H. R. (2010). Size-controlled synthesis of CuO-ZrO₂ nanoparticles prepared through reverse micelle method. *Journal of Sol-Gel Science and Technology* 53, 263-271.
- Vakros, J., Papadopoulou, C., Voyiatzis, G. A., Lycourghiotis, A., & Kordulis, C. (2007). Modification of the preparation procedure for increasing the hydrodesulfurisation activity of the CoMo/Al₂O₃ catalysts. *Catalysis Today* 127, 85-91.
- Wang, L., & Hall, W. K. (1982). The preparation and genesis of molybdena-alumina and related catalyst systems. *Journal of Catalysis* 77, 232-241.
- Wu, M.-L., Chen, D.-H., & Huang, T.-C. (2001). Synthesis of Au/Pd bimetallic nanoparticles in reverse micelles. *Langmuir* 17, 3877-3883.
- Xin, Z., Feng, Z., & Kwong-Yu, C. (2004). The synthesis of large mesopores alumina by microemulsion templating, their characterization and properties as catalyst support. *Materials Letters* 58, 2872-2877.
- Zakharova, L., Valeeva, F., Zakharov, A., Ibragimova, A., Kudryavtseva, L., & Harlampidi, H. (2003). Micellization and catalytic activity of the cetyltrimethylammonium bromide-Brij 97-water mixed micellar system. *Journal of Colloid and Interface Science* 263, 597-605.