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One pot synthesis of menthol from (±)-citronellal on nickel sulfated zirconia catalysts

César Barrales Cortés, Victoria Tamayo Galván, Smid Santiago Pedro, Tomás Viveros García*

Universidad Autónoma Metropolitana-Iztapalapa, División de Ciencias Básicas e Ingeniería, Av. Rafael Atlixco 186, Col. Vicentina, 09340 México DF, Mexico

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ABSTRACT

The one-pot synthesis of menthol from (±)-citronellal was carried out using two catalysts: nickel supported on sol–gel sulfated zirconia (Ni/ZrS) and nickel added during the synthesis of sulfated zirconia (NiZrS). The supported catalyst was prepared by impregnation of nickel on the sulfated zirconia support, whereas NiZrS was prepared by the co-gellation of nickel and the sulfated zirconia by the sol–gel method. Two sets of catalytic tests were carried out. In both tests the catalysts were previously treated in He stream. First, the liquid phase cyclization of (±)-citronellal was carried out with both ZrS and NiZrS catalysts. The results showed that both ZrS and NiZrS catalysts are highly active and selective towards isopulegols (100% of selectivity) and highly stereoselective towards (±)-isopulegol (~70% of selectivity). A second reaction test was the synthesis of menthol. The catalysts were evaluated in a batch reactor at 1.4 MPa of H_2 and 100 °C. The results showed that the catalysts allow to obtain a high catalytic activity and selectivity towards stereoisomers of menthol (100% selectivity of menthols) and a high selectivity towards (−)-menthol.

1. Introduction

(−)-Menthol is an important compound in pharmaceutical, flavor and fragrance industries because of its organoleptic properties and mainly to its intense menthe flavor. Since 80s of last century, the Takasago process has provided for the increased demand for menthol in industry. The above mentioned process consists of several steps of synthesis, which uses myrcene as a main reactant. Compounds such as $ZnBr_2$, H_2SO_4 and Rh-organometallic compounds are used homogeneous catalysts [1]. This process implies the use of difficult to handle compounds which in some cases are harmful to the environment.

Recently, routes for synthesis of menthol from compounds such as citral and citronellal employing heterogeneous catalysts have been proposed [2–4]. The one-pot synthesis of menthol from citronellal (CAL) implies two steps, CAL cyclization to produce 8 enantiomers of isopulegol (Fig. 1) and the hydrogenation of isopulegols to menthols. Catalytic materials with acidic properties such as Zr-Beta, MCM-41, ZrOH, ZrO_2–PO_4, ZrO_2–SO_4 have been employed for CAL cyclization [2–6]. In the case of sulfated zirconia, synthesized by precipitation of zirconium salts and further acidification with H_2SO_4, it has been shown that it possesses and acid strength comparable to H_2SO_4 ($H_0 = -16.03$), so that it has been considered a superacid material. Its performance in the citronellal cyclization shows a very high activity but the selectivity to isopulegol is low due to the presence of compounds produced by etherification and dehydration of isopulegol and the cracking of these products [5].

For the second reaction, the hydrogenation of isopulegol to produce menthol, Ni, Pd, Ru and Pt supported on acidic materials have been employed [2,4,6,7]. With the aim to achieve an acidic and metallic bifunctionality effect for the cyclization and hydrogenation steps, active metals such as Ni, Pd, Ru, Pt have been supported on acidic materials. Research reports show the limitations in selectivity due to the presence of products of direct hydrogenation of citronellal such as citronellol and dihydrocitronellal (COL and DHCAL), and consecutive hydrogenation to produce 3,7-dimethyl-1-octanol (DMOCTOL) as seen in Fig. 1. Therefore, a limiting factor for obtaining high selectivity for menthol from citronellal is the presence of products of direct hydrogenation of citronellal; these compounds are typically obtained with Pd or Ni catalysts in metallic state using SiO_2, Al_2O_3 or carbon felt supports [4]. In a previous study [8], the liquid-phase hydrogenation of citral with Ni/SiO_2 catalyst was carried out and a high selectivity towards CAL was observed at short time of reaction, followed by the formation of the consecutive hydrogenation products such as CAL, DHCAL and DMOCTOL and the presence of isopulegol and menthol was also observed. It was concluded that there are NiO cationic surface sites that function as Lewis acid sites and these sites can promote the cyclization of CAL and to promote adsorption of ISOL and hydrogen to produce menthol.

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* Corresponding author. Fax: +52 55 58 04 49 00.
E-mail address: tvig@xanum.uam.mx (T.V. García).

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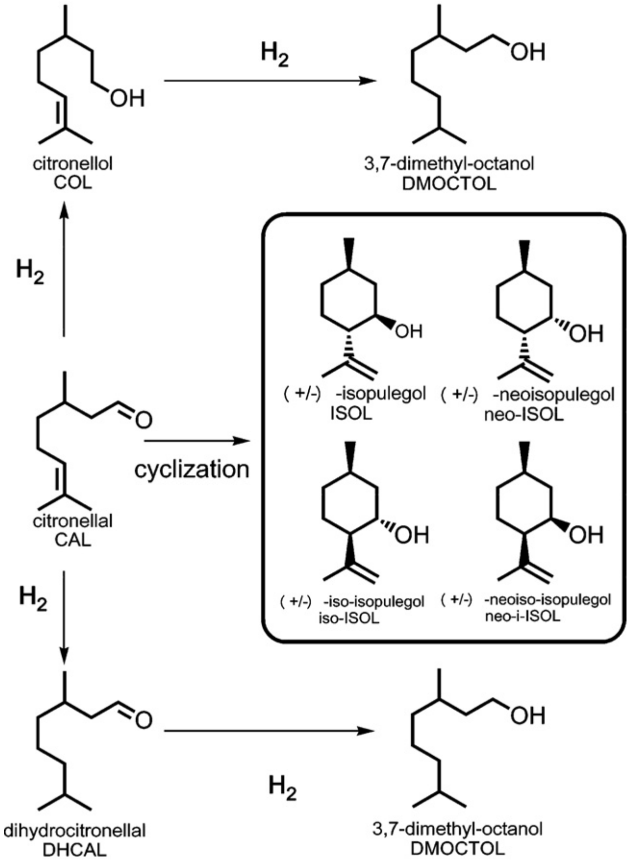

Fig. 1. Reaction scheme in the hydrogenation and cyclization of citronellal.

In this work, we report the preparation of novel bifunctional catalysts of Ni supported on sulfated zirconia synthesized by the sol–gel method with hydrogenating and acid properties to be used in the synthesis of menthol from citronellal in a one-step process. We compare the performance of two different preparations of the nickel catalyst: a nickel impregnated on ZrS and a NiZrS with nickel added during the preparation of the zirconia support. Two reacting systems were employed, the cyclization of (±)-citronellal and the one-pot synthesis of menthol from (±)-citronellal.

2. Experimental

2.1. Catalyst preparation

Sulfated zirconia (ZrS) and nickel-sulfated zirconia (NiZrS) were synthesized by the sol–gel method. The hydrolysis and condensation of zirconium *i*-propoxide (Aldrich) was carried using sulfuric acid (Aldrich) as both synthesis catalyst and sulfation agent, and using 2-propanol (J.T. Baker) as solvent. The synthesis procedure consisted in the preparation of a solution of 2-propanol, H_2SO_4 and zirconium isopropoxide at room temperature with stirring for 30 min. Then, an alcohol–water solution was added dropwise under stirring until gelation occurred. The resulting gel was aged for 24 h at room temperature, and after that the solids were dried at 100 °C. Reactants were used in the following ratios: H^+/alkoxide = 0.2, water/alkoxide = 8.0 and solvent/alkoxide = 10.0 [9]. In the NiZrS synthesis nickel was added in situ as a $Ni(NO_3)_2 \cdot 6H_2O$ (J.T. Baker) solution in order to obtain 3 wt % nickel. On the other hand, nickel supported on SiO_2 and ZrS was obtained by incipient-wetness impregnation at room temperature, using a $Ni(NO_3)_2 \cdot 6H_2O$ solution in order to obtain 3% wt. of Ni/SiO_2 and Ni/ZrS. The samples were calcined at 450 °C for 4 h on static air.

2.2. Catalyst characterization

Thermal analyses of the dried samples were performed on a NETZSCH instrument in static air with temperature rate set at 10 °C/min in the 25–1000 °C temperature range. The crystalline structures of the calcined samples were determined by X-ray diffraction (XRD) using a D-500 Siemens diffractometer using a Cu Kα radiation with $\lambda = 1.5406$ Å. BET area, total pore volume and pore size distribution were obtained by N_2 adsorption in a Quantachrom (Autosorb-1) sorptometer. FTIR pyridine thermodesorption was performed on a Nicolet 560 Magna spectrophotometer. Wafers of samples calcined at 450 °C were pretreated at 400 °C under vacuum followed by the adsorption of pyridine at 100 °C. Then excess pyridine was eliminated under vacuum and spectra were obtained in the range 50–400 °C.

2.3. Catalytic testing

2.3.1. Cyclization of citronellal

The cyclization of (±)-citronellal was carried out in a glass reactor with magnetic stirring at atmospheric pressure and hexane reflux temperature. The amount of catalysts, citronellal, and solvent loaded in the flask were 50 mg, 2 ml and 20 ml, respectively. Reaction samples were taken and analyzed with an Agilent 6890 Gas Chromatograph coupled to a mass spectrometer using a HP-5MS capillary column. The concentration of components was determined using calibration curves obtained beforehand. The citronellal conversion was determined as $X_{CAL} = (C_{CAL}^{0} - C_{CAL}^{t})/C_{CAL}^{0}$ where C_{CAL}^{0} is the CAL initial concentration and C_{CAL}^{t} is the CAL concentration at time t. Product selectivity S_i (moles of compound i/moles of consumed reactant) was calculated as $S_i = C_i/\Sigma C_i$, where ΣC_i are the total moles of products.

2.3.2. Synthesis of menthol

The one-pot synthesis of menthol from citronellal was carried out in a Parr 4843 reactor at 1.4 MPa of H_2 and 100 °C with 1000 rpm of stirring to ensure kinetic regimen. The reactor was loaded with 500 mg of catalyst and a solution CAL/solvent of 0.1 M. Before reaction, the catalyst was treated in a He stream at 300 °C to eliminating moisture. Products of reaction withdrawn of the reactor were analyzed *ex situ* in an Agilent 6890N gas chromatograph coupled to a mass spectrometer with a HP-5MS capillary column. Enantioselectivity of menthols was analyzed with an α-DEX Supelco chiral column. CAL conversion and product selectivity were calculated as indicated above.

3. Results and discussion

3.1. Catalyst characterization

Fig. 2 shows the thermochemical evolution profile of both dry non-calcined ZrS and NiZrS. Both samples show weight loss due to evaporation of solvent and physisorbed water, and to elimination of water by dehydroxylation, which corresponds with DTA endothermic signal centered at 138 °C. ZrS shows a DTA exothermic signal at 300 °C, which is associated to the combustion of organic compounds from synthesis precursors. Both ZrS and NiZrS show DTA exothermic signal at 625 and 680 °C respectively, this signal is associated with typical weight loss attributed to sulfates decomposition [9].

Fig. 3 shows XRD diffractograms of ZrS and NiZrS catalysts calcined at 450 °C. The results indicate a microcrystalline structure of both ZrS and NiZrS samples. The diffractogram obtained for a ZrO_2 sample treated at the same temperature, shown as comparison, indicates a fully crystalline sample. Hence, the insertion of sulfate ions to zirconium oxide network hinders the formation of typical

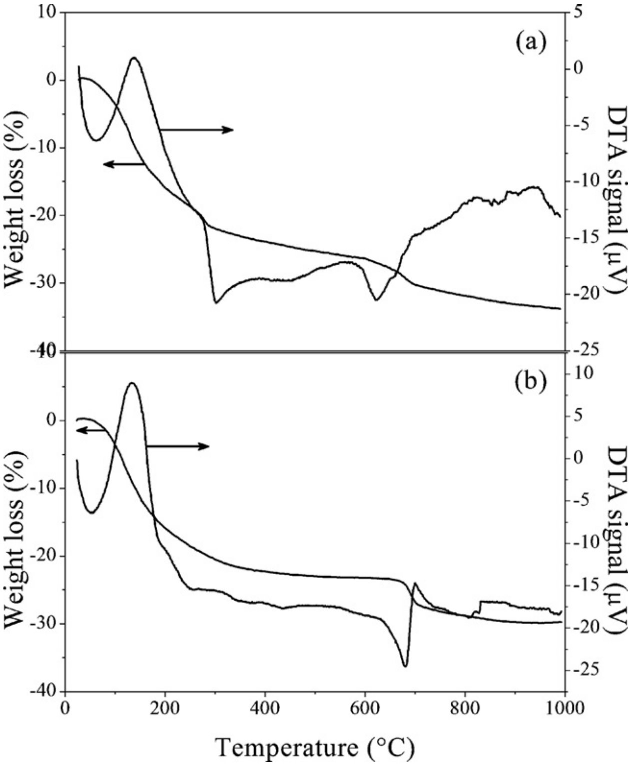

Fig. 2. TGA and DTA of catalytic precursors: (a) ZrS and (b) NiZrS.

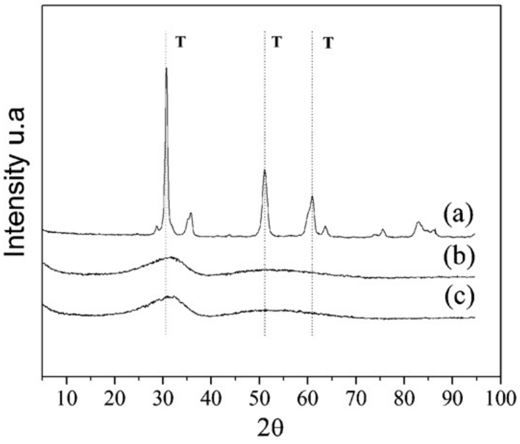

Fig. 3. X-ray diffraction patterns of: (a) ZrO_2, (b) ZrS and (c) NiZrS. T indicates the tetragonal phase.

crystalline phases of non-sulfated ZrO_2 (tetragonal, cubic and monoclinic) after treatment at 450 °C, a result which is in agreement with previous reports in the literature [9,10,13].

Table 1 give the results obtained of nitrogen physisorption of both ZrS and NiZrS catalysts. These catalysts show BET area values in agreement with those reported for sulfated-zirconia obtained by sol–gel method [9,10]. On the other hand, the insertion of nickel cation during the materials synthesis produces a decrease of BET area in comparison to the ZrS catalyst; the average pore diameter, however, remains unchanged and both catalysts present values in the range of mesopores. The results found in the literature do not show a clear trend. Some authors report the decrease in surface area with the insertion of nickel [10–12] using the sol–gel method for the preparation of the zirconia samples. Ozkan et al. [13] show first and increase then a decrease in surface areas depending upon the amount of metal (Pd) added. The results are evidently affected by the variations in the synthesis conditions and temperature of treatment, which are important effects when the sol–gel method is used. SiO_2 textural properties are also given for comparison. As expected, the values show the surface area is higher than those presented by the zirconia-based systems.

Table 1
Textural properties obtained by N_2 physisorption.

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)
ZrS	115	0.24	85
NiZrS	85	0.17	83
SiO_2	640	0.18	65

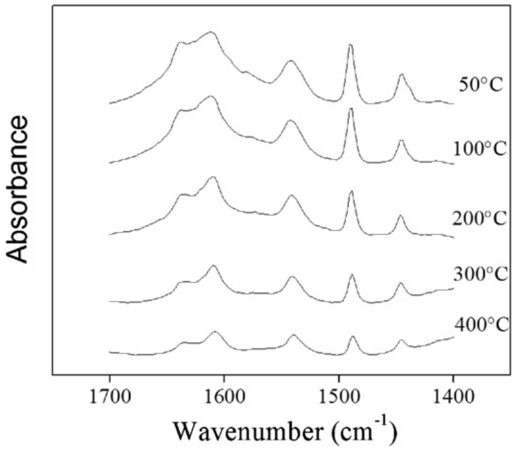

Fig. 4. Pyridine IR spectra on ZrS after evacuation at 50, 100, 200, 300 and 400 °C.

Fig. 4 shows the FTIR spectra of pyridine (Py) thermodesorption of ZrS sample. The results show the presence of Bronsted acid sites at 1540 cm^{-1}, Lewis acid sites at 1440 cm^{-1} and total acidity (Lewis and Bronsted) at 1490 cm^{-1} [14]. The spectra show a decrease of total acid sites as the temperature is increased in the 50–400 °C, observing the presence of strong Lewis and Bronsted sites at the highest temperature. For the Ni/ZrS and NiZrS samples pyridine is almost completely desorbed at 300 °C. Table 2 shows the results of Py adsorbed at 100 °C for ZrS, Ni/ZrS and NiZrS, and indicate that the addition of nickel hinders the amount of Py adsorbed in comparison to that obtained on ZrS, in agreement with results reported in the literature [10]. Also, the type and density of acid sites are affected by the presence of nickel and the method of preparation: ZrS sample shows a Bronsted to Lewis ratio (B/L) = 3.0, whereas for the sample Ni/ZrS, (B/L) = 0.6 and for NiZrS, (B/L) = 0.9. It is important to notice an increase of Lewis acid sites when Ni is impregnated on the ZrS support, with an amount of Lewis acid sites higher than that present on the ZrS support. In this sense it is possible that nickel as NiO_x species act as Lewis acids [15].

3.2. *Cyclization of citronellal*

The cyclization of citronelal was studied on the ZrS, Ni/ZrS and NiZrS materials using hexane as solvent. The results can be

Table 2
Amount of adsorbed pyridine of catalysts after evacuation at 100 °C.

Catalyst	Amount of adsorbed pyridine (μmol/g)			
	Bronsted 1540 cm^{-1}	Lewis 1440 cm^{-1}	Total acidity 1490 cm^{-1}	B/L[a]
ZrS	114	40	154	3.0
Ni/ZrS	34	61	95	0.6
NiZrS	14	16	30	0.9

[a] Bronsted/Lewis ratio.

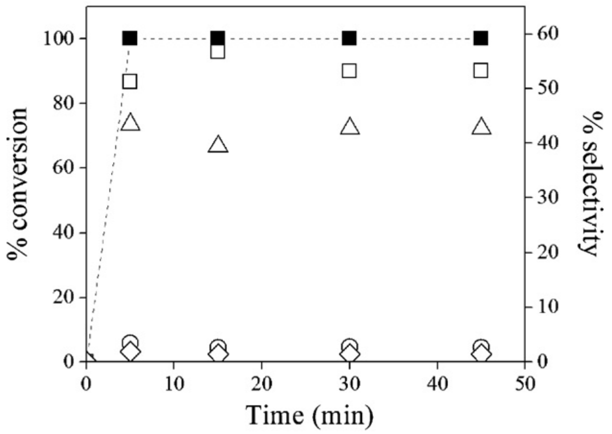

Fig. 5. Conversion and distribution of products in the cyclization of CAL on ZrS. (■) Citronellal conversion (X_{CAL}); selectivity to (□) ISOL, (△) neo ISOL, (○) neo *i*-ISOL and (◊) iso *i*-ISOL.

observed in Figs. 5 and 6 and the conversion and selectivity are given in Table 3. All catalysts show 100% conversion but at different reaction times, being the ZrS catalyst the most active and the Ni/ZrS catalyst the less active. Lower activity of Ni/ZrS and NiZrS can be attributable to the lower acidity of the samples due to the presence of Ni species that block active sites originally present on the sulfated zirconia, and to the lower surface area. Chua et al. [5] obtained a very active catalyst for citronellal cyclization using sulfated zirconias, but the sample was so strongly acidic that the yield to isopulegol decreased with reaction time due to the presence of side reactions such as dehydration, cracking and etherification [5]. In our case all the materials are highly selective towards isopulegols (100% of selectivity). Regarding the product distribution, all catalysts present higher selectivity towards isopulegol stereoisomers than neo-isopulegol stereoisomers (ZrS: 55% ISOL, 42% neo ISOL; Ni/ZrS: 58% ISOL, 35% neo ISOL; NiZrS: 60% ISOL, 35% neo-ISOL). The similar results obtained for the isopulegols/neo-isopulegols distribution on the three samples indicate there is no effect of the Bronsted/Lewis acidity distribution, unlike the results reported by Trasarti et al. [2] and Chua et al. [5] who reported the effect of Bronsted and Lewis acidities on the isopulegols and neo-isopulegols distribution. In this work the results show that ZrS, Ni/ZrS and NiZrS catalysts effectively promote the cyclization of citronelal without presenting other reaction products related to the acid character of the catalytic materials [5,16].

Table 3
Conversion and selectivity of cyclization of citronellal and one-pot synthesis of menthol from citronellal.

Catalyst	$\%X_{CAL}$/time (min)	% Selectivity		
		ISOLS[c]	MTOLS[d]	MTOL[e]
ZrS[a]	100/5	100	–	–
NiZrS[a]	100/90	100	–	–
Ni/ZrS[a]	100/180	100	–	–
Ni/ZrS[b]	100/30	0	100	70
NiZrS[b]	100/150	0	100	60
Ni/SiO_2[b]	55/120	90	10	n.d.

[a] Activity in cyclization of citronellal.
[b] Activity in one-pot synthesis of menthol from citronellal.
[c] Total selectivity of isopulegol stereoisomers at final reaction time.
[d] Total selectivity of menthol stereoisomers at final reaction time.
[e] Estereoselectivity of (±)-menthol.

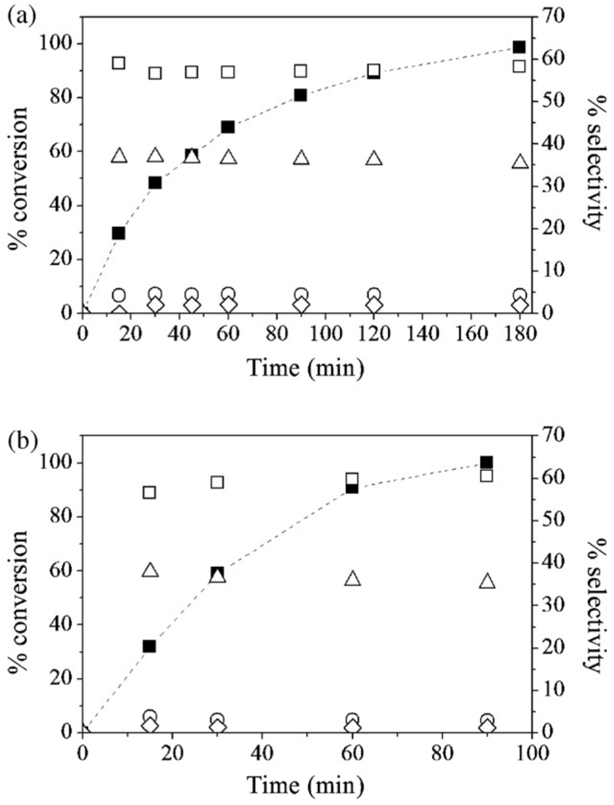

Fig. 6. Conversion and distribution of products in the cyclization of CAL on: (a) Ni/ZrS and (b) NiZrS. (■) Citronellal conversion (X_{CAL}); selectivity to (□) ISOL, (△) neo ISOL, (○) neo *i*-ISOL and (◊) iso *i*-ISOL.

3.3. Synthesis of menthol

The one-pot synthesis of menthol from citronellal was carried out with Ni/ZrS, NiZrS and Ni/SiO_2 as catalytic materials and using hexane as a solvent. The results of the liquid phase hydrogenation of citronellal with Ni/SiO_2 as catalyst can be observed in Fig. 7 and also in Table 3. As mentioned in the experimental section all catalysts were treated in He previous to reaction. The results show a conversion of 55% of CAL at 120 min of reaction and selectivity of 90% to isopulegols and 10% of menthols; no other products of hydrogenation of CAL were observed. The absence of other hydrogenation products is an indication of the lack of Ni^0 species, which are assumed to adsorb and reduce both C═O and C═C bonds of CAL [17]. As mentioned in the introduction, previous results have showed the presence of menthols in the liquid phase hydrogena-

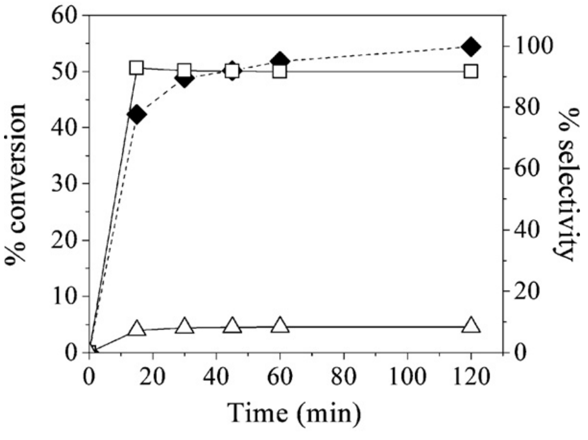

Fig. 7. Conversion and distribution of products in the cyclization and hydrogenation of CAL with Ni/SiO_2 catalyst. (♦) Citronellal conversion (X_{CAL}); selectivity to (□) ISOL and (△) MTOL.

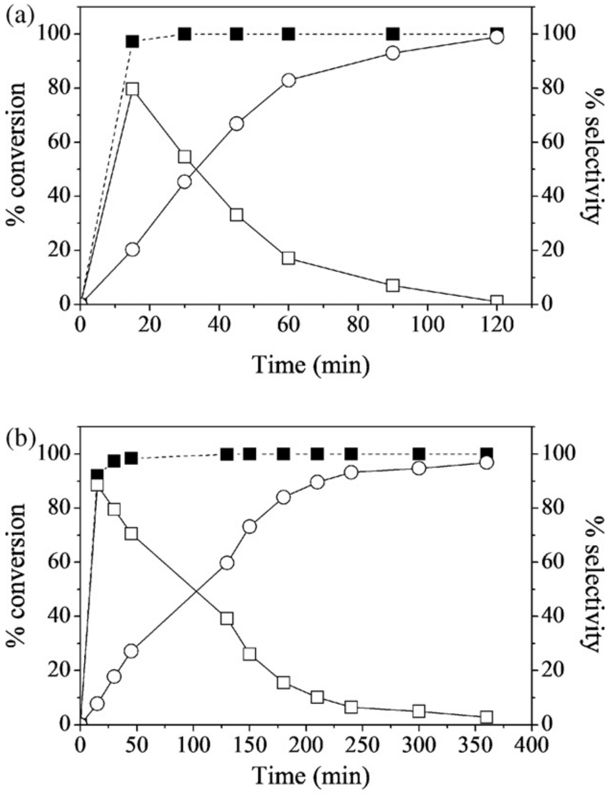

Fig. 8. Conversion and distribution of products of one-pot synthesis of menthol from CAL: (a) Ni/ZrS and (b) NiZrS. (■) Citronellal conversion (X_{CAL}); selectivity to (□) ISOL and (○) MTOL.

tion of citral with nickel catalysts supported on silica, this being attributed to the presence of partially oxidized nickel species acting as Lewis acid sites, carrying out the cyclization of citronellal, and consecutively producing menthols. The isomerization of CAL to produce ISOLs due to the presence of Lewis acid sites in partially oxidized NiO_x species has been proposed [15]. On the other hand, Chuah et al. [3] showed that Ni^0 metalic species are not functional for citronellal cyclization when using Ni/MCM-41 catalysts without H_2 in the reacting mixture. With H_2 present they only obtained citronellal hydrogenation products. In the case of Ni/ZrS and NiZrS, these catalysts were highly active and selective in the one-step synthesis of menthol from CAL as seen in Fig. 8. Both catalysts showed 100% conversion, being more active Ni/ZrS (100% of conversion of CAL at 30 min) than NiZrS (100% of conversion of CAL at 150 min). As in the case of Ni/SiO_2 catalyst, the pretreatment in He stream, avoids the formation of products of direct hydrogenation of CAL due to lack of Ni^0 surface species, producing only the cyclization of CAL by the acid sites present on sulfated zirconia. The complete transformation of isopulegols to menthols can be due to presence of NiO in catalytic surface, which could catalyze C=C-containing species, to carry out its hydrogenation as has been mentioned in the literature [18]. In the case of NiZrS and Ni/ZrS catalysts the results are very interesting since the activity is high, there is a complete conversion of citronellal and the only final product is menthol. In fact when comparing the behavior of silica and sulfated zirconia samples it is evident that as ISOLs disappear MTOLs appear, and at 120 min reaction time in the silica based catalyst the amount of menthol is only 10%, whereas is 100% for the sulfated zirconia samples. Moreover, no other compounds from etherification, dehydration or hydrogenation reactions were observed. Table 3 compares the stereoselectivity towards isopulegols and menthols over Ni/ZrS and NiZrS catalysts. For both Ni/ZrS and NiZrS, it was observed, by gas-chromatography with a chiral column, an enantioselectivity of 88% towards (−)-menthol, a fact of great importance since (±)-citronellal was used as a reactant. In the production of (−)-menthol, conventional processes use (+)-citronellal to produce (−)-menthol reaching 95% of selectivity [1].

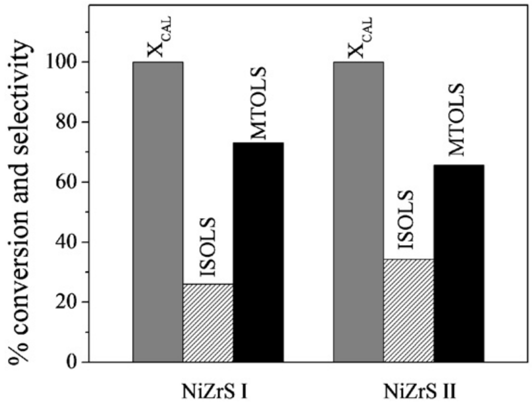

Fig. 9. Conversion and selectivity in the one-pot synthesis of menthol from CAL at 150 min reaction time for fresh catalyst NiZrS I and re-used catalyst NiZrS II.

In order to test the possibility of sulfate elution from the catalyst during the liquid phase reaction, an experiment was carried out, using a catalyst from a previous catalytic test. After reaction, the NiZrS catalyst was washed, dried and calcined at 450 °C, and used in a subsequent test. The results are presented in Fig. 9, in which the activity and selectivity at 150 min reaction time are given for the fresh and used samples. It is outstanding to see the same activity and almost the same selectivity. A small reduction in hydrogenating power was obtained. From this result we can see that the sample retains its catalytic performance, with the same acidic and metallic functionalities.

4. Conclusions

In the present work sulfated zirconia catalysts by sol–gel method were synthesized. These catalysts were impregnated or cogeled with nickel solutions with the aim to carry out the one-pot synthesis of menthol from (±)-citronellal. The use of Ni catalysts without H_2 pretreatment before reaction avoids producing compounds from the direct hydrogenation of CAL. In the cyclization of CAL, ZrS and NiZrS catalysts showed high catalytic activity allowing total conversion of CAL at short time of reaction. Added Nickel in situ over ZrS during the synthesis caused a decreased in catalytic activity because of blockage of acid sites that allow the cyclization of CAL. Products distribution was not affected by the addition of nickel being obtained a selectivity of 60% towards isopulegol stereoisomers. In the one-pot synthesis of menthol, both Ni/ZrS and NiZrS catalysts showed a bifunctional character that allows the production of menthols effectively, obtaining (−)-menthol selectively. The only hydrogenation product was menthol, and no other reactions products were observed. The catalysts were proved to be stable maintaining their catalytic performance in subsequent reaction tests.

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