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Microspherical ReS_2 as a High-Performance Hydrodesulfurization Catalyst

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Abstract An unsupported microspherical ReS_2 catalyst, consisting in self-assembled nano-layers, was evaluated in the hydrodesulfurization (HDS) of 3-methylthiophene showing an excellent catalytic activity. The samples were characterized by X-ray diffraction, scanning electron microscopy, high resolution electron microscopy, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. These techniques revealed that the rhenium disulfide layers are confined to a 3D hierarchical structure with different stacking, slab size and bending, according to the annealing temperature (400 or 800 °C). The presence of a defect-rich structure in the microspheres, with short and randomly-orientated ReS_2 slabs, results in the exposure of additional edge sites, which improve the catalytic performance of this material. This microspherical ReS_2 composite, with good HDS performance, is a promising catalyst for the desulfurization of fuel oils; the solvothermal reaction conditions are also useful to tune and create exotic morphologies for the design of new ReS_2 catalysts.

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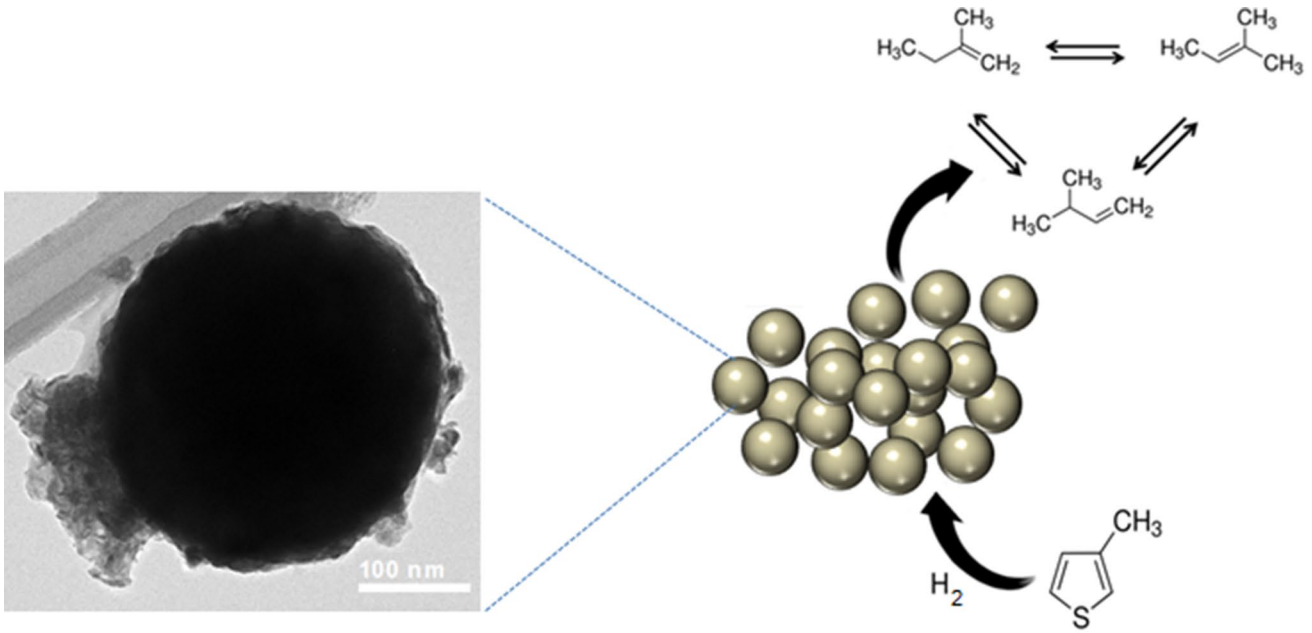
Graphical Abstract



Keywords Rhenium disulfide · Hidrodesulfurization · Heterogeneous catalysis · Solvothermal synthesis

1 Introduction

There is a great interest in the research on the catalytic applications of ReS_2-based materials for hydrotreating and water splitting reactions, as alternatives to classical MoS_2-based catalysts [1–3]. This is in part due to the structural similarity between both sulfides, and the unique combination of physical and chemical properties of rhenium and its alloys, making them highly attractive for preparation of novel materials and catalysts [4–6]. Generally, unsupported ReS_2 catalysts show intermediate hydrodesulfurization (HDS) activity in comparison to the sulfides of the group VI and VIII [7, 8]; a similar trend is observed in the Hydrogen Evolution Reaction for this dichalcogenide in comparison to its layered transition metal analogues (MoS_2 and WS_2) [9]. The differences in the catalytic behavior of the ReS_2 compared with other typical layered transition metal sulfides has been explained by considering the different crystalline structure and electronic properties among these catalysts [9, 10]. ReS_2 has a layered graphite-like structure, where the S–Re–S layers are stacked and held together in the direction perpendicular to their basal plane, joined by van der Waals forces [11]. In particular, the electronic and vibrational behavior of ReS_2 in bulk has been shown to resemble that of the single layer [12].

ReS_2 can be synthesized in several structures; including crystalline layered [13] and inorganic fullerene-like materials [14], colloidal nanoparticles [15, 16], as layered compounds supported onto carbon nanotubes [17] and as solid microspheres [18, 19], among others. The extremely weak van der Waals coupling and anisotropy of ReS_2 might explain the extreme morphological effect of the disordered lattice structure of this compound in comparison with all the LTMS [10, 20, 21]. Synthetic methods which lead to the formation of disordered, poorly stacked and small-sized layers (including sonochemical and solvothermal syntheses) have shown improvement in the catalytical performance of these materials [22, 23]. These methods also promote the formation of curved or strained layers, which might create new active sites on the basal planes, influencing the HDS activity and selectivity [24, 25].

In this work we tested the catalytic performance of a ReS_2 microspherical material, which was synthesized by a solvothermal process, with the aim to obtain poorly stacked layers with some degree of curvature and a high proportion of edge sites. The as-prepared microspherical ReS_2 catalyst was annealed at 400 and 800 °C, in order to evaluate the effects of temperature over the different layer arrangements and of the crystallinity of the compounds. The catalyst performances of the annealed samples were also compared against a commercial supported Mo/γ–Al_2O_3 sulfide catalyst.

2 Experimental

2.1 Catalysts Preparation

In order to obtain ReS_2 microspheres, 0.3 mmol of analytically pure $Re_2(CO)_{10}$, 6.0 mmol of sulfur powder (excess)

and about 2.5 mL of toluene were put into a Teflon-lined 3 mL stainless steel autoclave and heated in an electrical oven for 24 h at 180 °C. The mixture was then cooled down naturally, giving a black powder. The product was washed twice with both the reaction solvent and diethyl ether, and then was filtered and dried in vacuum for 10 h. The annealing of the sample was carried out by heating it at a rate of 2 °C per min in a conventional tube furnace under Ar flow (20 mL min^{-1}) up to 400 °C, and then maintained at this temperature for 1 h. The same annealing procedure was followed for the sample annealed at 800 °C.

2.2 Characterization and Activity Measurements

X-ray diffraction (XRD) measurements of the samples were gathered in a Philips spectrometer model X'pert using the Cu Kα radiation (40 kV, 30 mA) with wavelength of 0.154 nm. Scanning Electron Microscopy (SEM) micrographs were obtained in a SEM LEO 1420VP, Oxford Instruments, equipped with an energy-dispersive X-ray spectroscopy (EDS) system. HRTEM analyses were performed by means of a JEOL 2010 (200 kV) microscope. X-ray photoelectron spectra (XPS) were carried out in a SPECS custom made system using a PHOIBOS 150 WAL hemispherical analyzer and a μ-FOCUS 500 X-Ray source. Charge referencing was done against adventitious carbon (C 1s 284.8 eV). Re 4f and S 2p energy regions were scanned with several sweeps until a good signal-to-noise ratio was observed.

Hydrodesulfurization of 3-methyl-thiophene was carried out in vapor phase using a home-made fixed bed micro flow reactor (15 mm ID) housed in a furnace. The reactor was loaded with 100 mg of catalyst (particle size between 80 and 120 mesh) diluted with 1 g of SiC. Prior to the catalytic test, the catalyst were dried under a N_2 flow of 50 mL min^{-1} at 150 °C for 0.5 h to eliminate the moisture, which could be adsorbed on the catalyst surface. The reaction was carried out in atmospheric pressure, and at different temperatures between 280 and 340 °C. Meanwhile, the saturation of hydrogen with 3-methyl-thiophene was obtained by bubbling hydrogen (70 mL min^{-1}) through a saturator containing liquid 3-methyl-thiophene at 20 °C (reaching the mole concentration typical to 3-methyl-thiophene saturated to 0 °C). For each catalyst studied, steady state conditions were reached after 1 h of time on-stream reaction. Reaction products were analyzed using an online gas chromatograph (Agilent-7820, FID) equipped with a DB-1 column (30 m length).

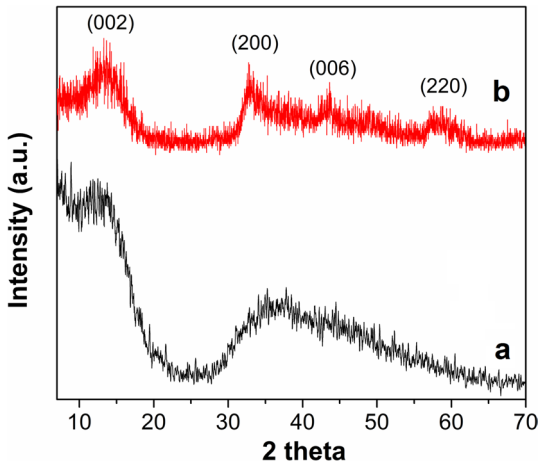


Fig. 1 XRD patterns of rhenium sulfide microspheres annealed at 400 °C (**a**) and at 800 °C (**b**)for 1 h under argon atmosphere

3 Results and Discussion

3.1 Characterization of Catalysts

3.1.1 X-ray Diffraction Analysis

The influence of the annealing over the as-prepared compound was evaluated using X-ray diffraction. The measured XRD patterns of ReS_2 microspheres treated at 400 and 800 °C are shown in Fig. 1; the annealed sample at 400 °C show broad diffraction peaks, which are mainly located in a low angle region (about $2\Theta = 13°$), and a broad envelope starting at $2\Theta = 30°$ and lasting out to about $2\Theta = 60°$. The ReS_2 (002) plane is broadened, indicating a low stacking of the crystallites along their basal plane, while that the broad peaks between $2\Theta = 30°$ and 60° are not well resolved, due to the small basal plane sizes and the amorphous nature of the compound [15]. The ReS_2 sample treated at 800 °C (Fig. 1b) shows an improvement in the crystallinity, indicating a growing and stacking of the rhenium disulfide layers; the broad peak between $2\Theta = 30°$–60°, observed at 400 °C, resolves into four broad low intensity peaks which correspond closely to the (200), (006) and (220) planes of triclinic ReS_2 [26]. A lattice expansion, characteristic of strained and curved layers, is also observed in the shift of the (002) reflection to a lower angle ($2\Theta = 13°$, 94°) [27].

3.1.2 HRTEM Analysis

The surface morphology and structure of the ReS_2 sample annealed at 400 and 800 °C were investigated by SEM

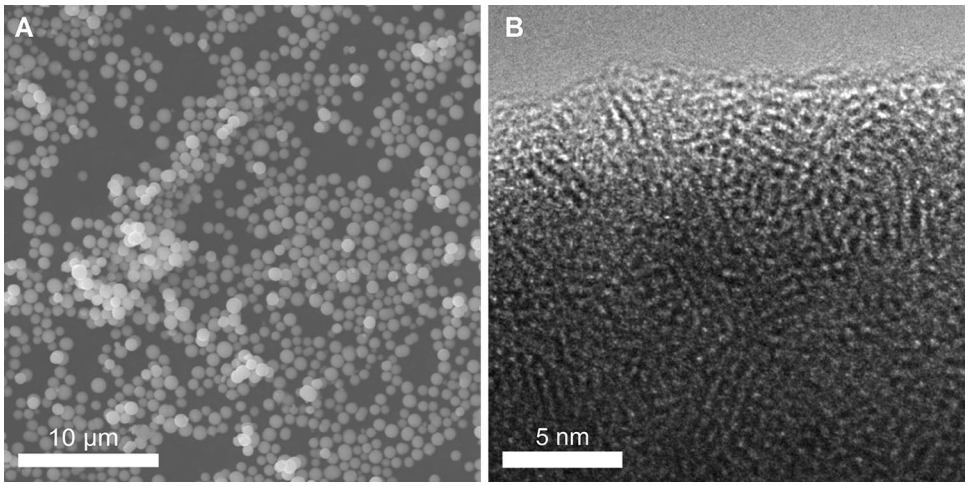


Fig. 2 SEM overview of microspheres annealed at 400 °C (**a**) and TEM details of the border of a microsphere (**b**)

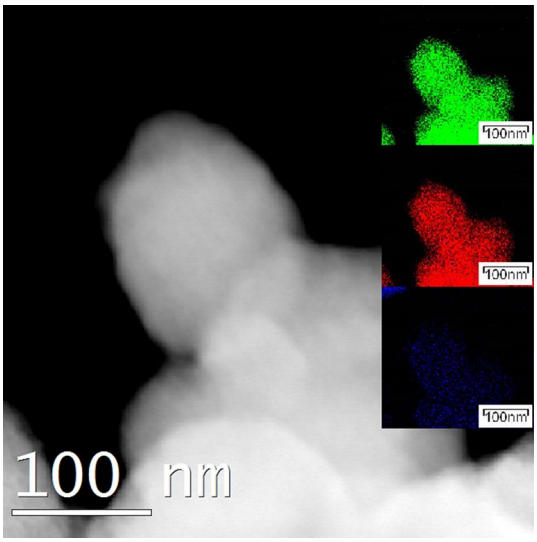


Fig. 3 Selected image for X-ray dot mapping for ReS2 microspheres annealed at 400 °C: rhenium (*green*), sulfur (*red*) and carbon (*blue*)

and by High Resolution Transmission Electron Microscopy (HRTEM). Figure 2a show an overview of the ReS_2 sample annealed at 400 °C; this sample consists in discrete and smooth microspheres with a mean diameter of 0.79 µm. The microsphere borders, observed in Fig. 2b, show unclosed shells with many open edges at their surfaces, while the interior of the microsphere is composed by a random arrangement of amorphous rhenium disulfide, in agreement with the broadened XRD pattern. EDS mapping indicates a high percentage of rhenium, sulfur, and a lower percentage of carbon, which is homogeneously distributed around the entire microsphere, scaffolding the inorganic structure (Fig. 3).

The influence of the annealing at 800 °C was also evaluated using HRTEM micrographs. Figure 4a shows that the growth of the ReS_2 layers collapses the microspherical structure, protruding from the borders of the microsphere; the rhenium sulfide fringes present a curved and folded structure, with longitudinal sizes < 30 nm (Fig. 4b). The

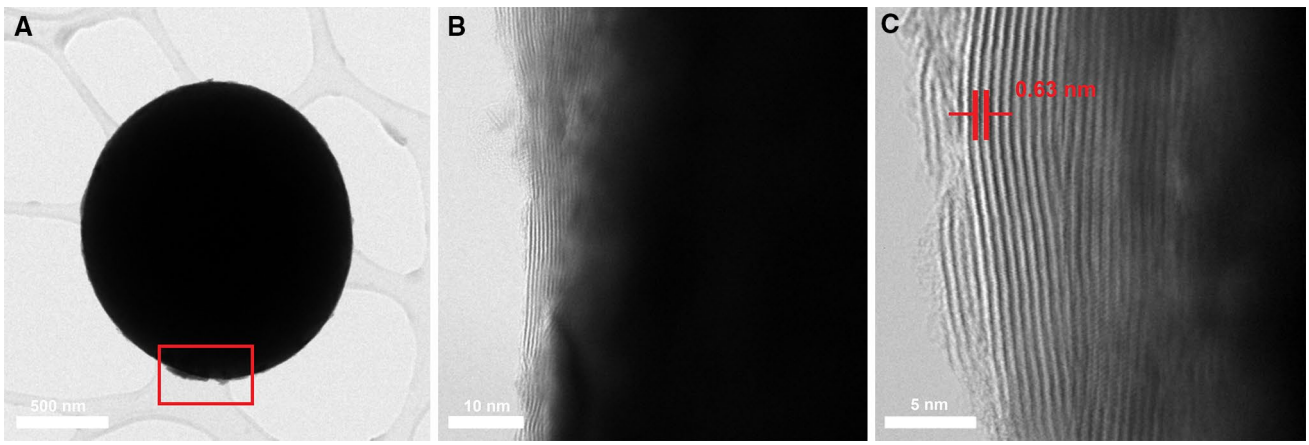


Fig. 4 TEM of ReS2 microsphere annealed at 800 °C (**a**) and details of the layers (**b, c**). The *red square* indicates defects on the microspherical structure

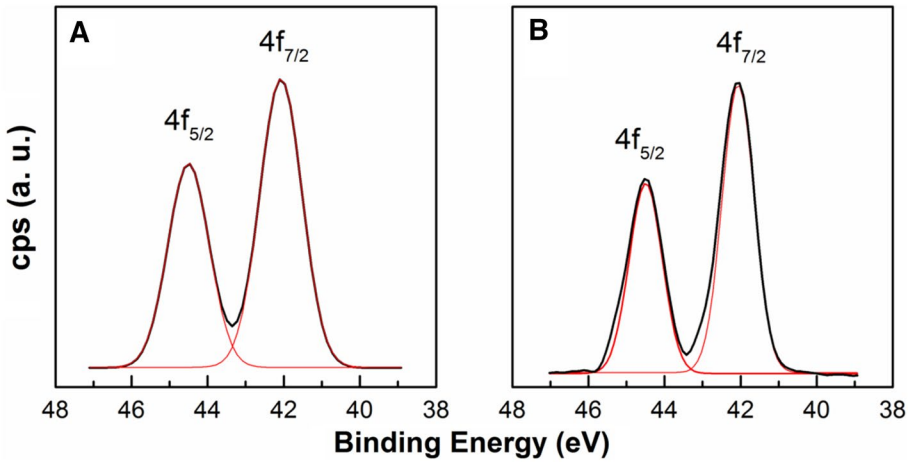


Fig. 5 Re 4f XPS spectra and component fittings of microspherical ReS2 samples annealed at **a** 400 °C and **b** 800 °C

interlayer distance match the ReS_2 (002) plane (0.64 nm) (Fig. 4c), which corresponds to the interlayer distance expansion found in the XRD diffraction pattern. The EDS analysis (Fig. S1) of the sample treated at 400 °C exhibit a S/Re atomic ratio of 2.46,which indicates an excess of sulfur in the sample; the sample treated at 800 °C shows a lower value for this ratio (2.015) close to the theoretical value which indicates the release of the sulfur excess from the structure.

3.1.3 X-ray Photoelectron Spectroscopy

The effect of annealing temperature on the chemical state and surface exposure of ReS_2 catalysts was investigated by X-ray photoelectron spectroscopy, which also corroborated the presence of ReS_2 in the sample. Figure 5a show the XPS spectrum on the region of rhenium for the sample annealed at 400 °C, where the peak at 42.1 eV correspond to the core level Re $4f_{7/2}$. XPS spectrum of the sample annealed at 800 °C is shown in Fig. 5b; the presence of Re^{+4} can be observed in the core level Re $4f_{7/2}$ peak at 42.3 eV [1]. The binding energy values of the S $2p_{3/2}$ core level of the microspherical ReS_2 annealed at 400 and 800 °C are presented in Table S1. The annealed samples have the S $2p_{3/2}$ peak at 161.8 and 161.9 eV, for the ReS_2-400 °C and ReS_2-800 °C samples respectively, which is characteristic of S^{2-} ions [1, 18]. The present solvothermal process leads to the formation of pure phases of rhenium disulfide in comparison for example to the sulfidization by H_2S/H_2 [28].

3.2 Activity and Selectivity of Catalysts

3.2.1 Hydrodesulfurization Activity

The comparison of the catalysts HDS activities upon steady-state conditions is shown in Fig. 6; all catalysts exhibit an increase of activity as a function of reaction temperature. At a reaction temperature of 340 °C, the

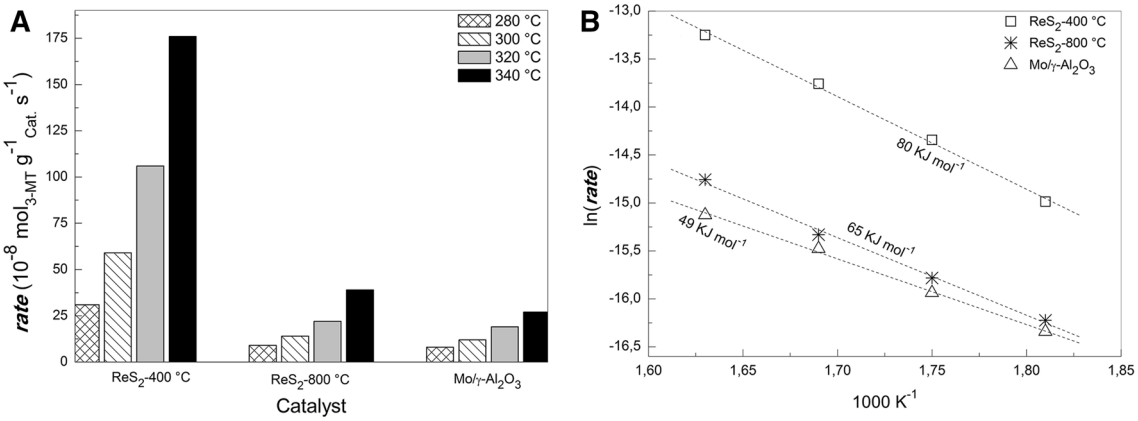


Fig. 6 HDS of 3-methyl-thiophene over sulfide catalysts (a flow reactor, a steady-state; atmospheric pressure, T = 280, 300, 320, 340 °C and conversions between 15–20%) (**a**), Arrhenius plots of the temperature dependent studies of the HDS of 3-methyl-thiophene over ReS2 and reference sample (**b**)

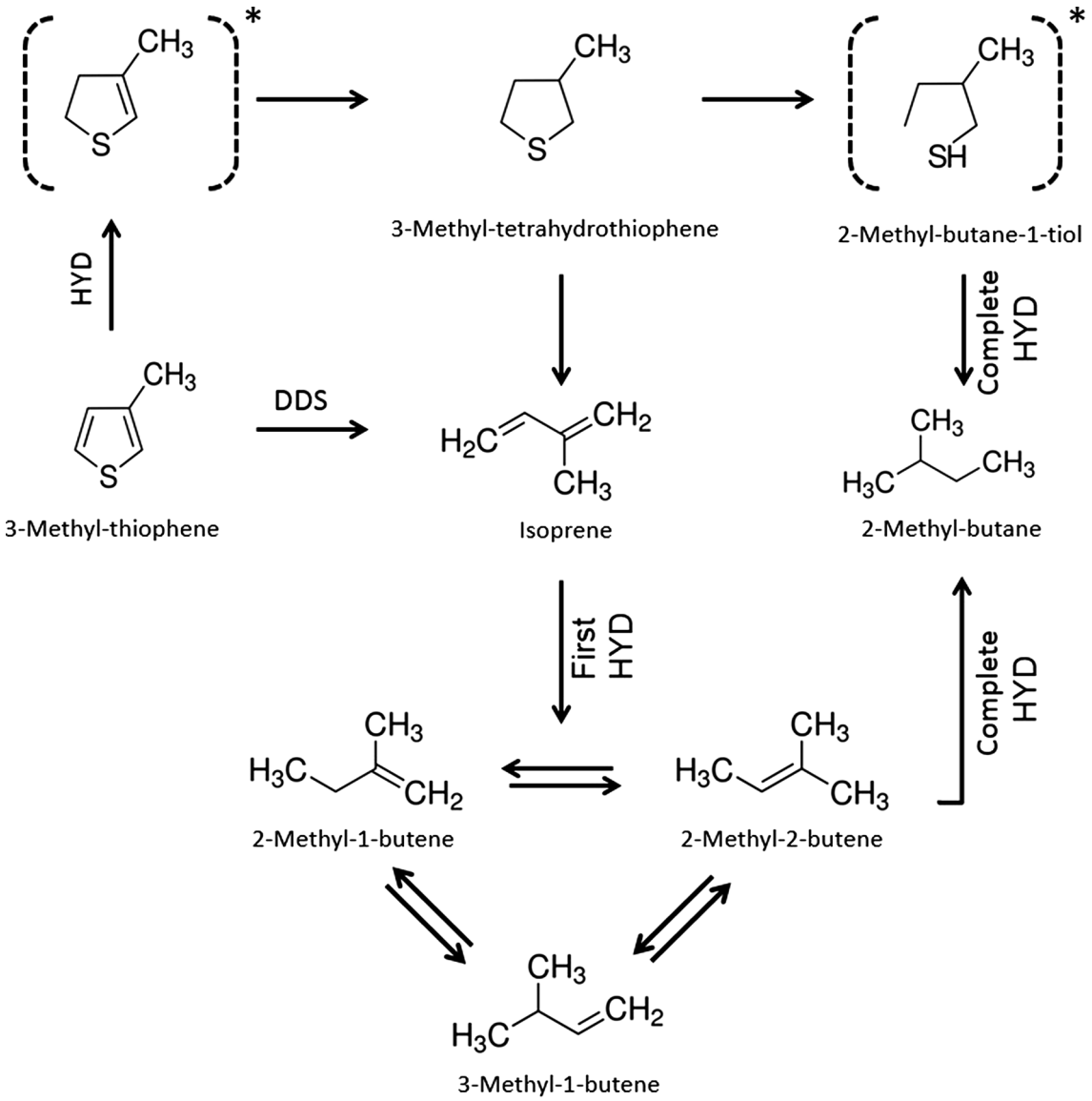


Fig. 7 Reaction path network for the 3-methyl-thiophene hydrodesulfurization

catalyst activity follows the trend: ReS_2-400 °C >> ReS_2-800 °C > Mo/γ–Al_2O_3 (Fig. 6a).The Arrhenius plots and the calculations of the apparent activation energy (E_{ap}) for the catalytic reaction are shown in Fig. 6b; the E_{ap} follow the trend: ReS_2-400 °C (80 KJ mol^{-1}) > ReS_2-800 °C (65 KJ mol^{-1}) >> Mo/γ–Al_2O_3 (49 KJ mol^{-1}). Thus, surprisingly, the ReS_2-400 °C exhibit the higher activity and higher apparent activation energy than ReS_2-800 °C counterpart. The same paradoxical behavior reported for ReS_2 catalysts occurs when the reaction temperatures employed is higher than the isokinetic temperature of the target reaction [29, 30].

3.2.2 *Selectivity*

Under the reaction conditions employed in this work, the reaction products identified were 3-methyl-tetrahydrothiophene (3MTHT), 2-methyl-1,3-butadiene (Isoprene), 3-methyl-1-butene (3M1B), 2-methyl-1-butene (2M1B), 2-methyl-2-butene (2M2B), 2-methyl-butane (2MB), 1-pentene (1P) and mixture (cis- and trans-) 2-pentene (2P). The reaction path network proposed in this work for the HDS of 3-methyl-thiophene (3MT) is shown in Fig. 7, and their possible reactions mechanisms in Fig. S2. Taking into account the products detected, the 3MT transformation over all the studied catalysts proceeds via hydrogenation

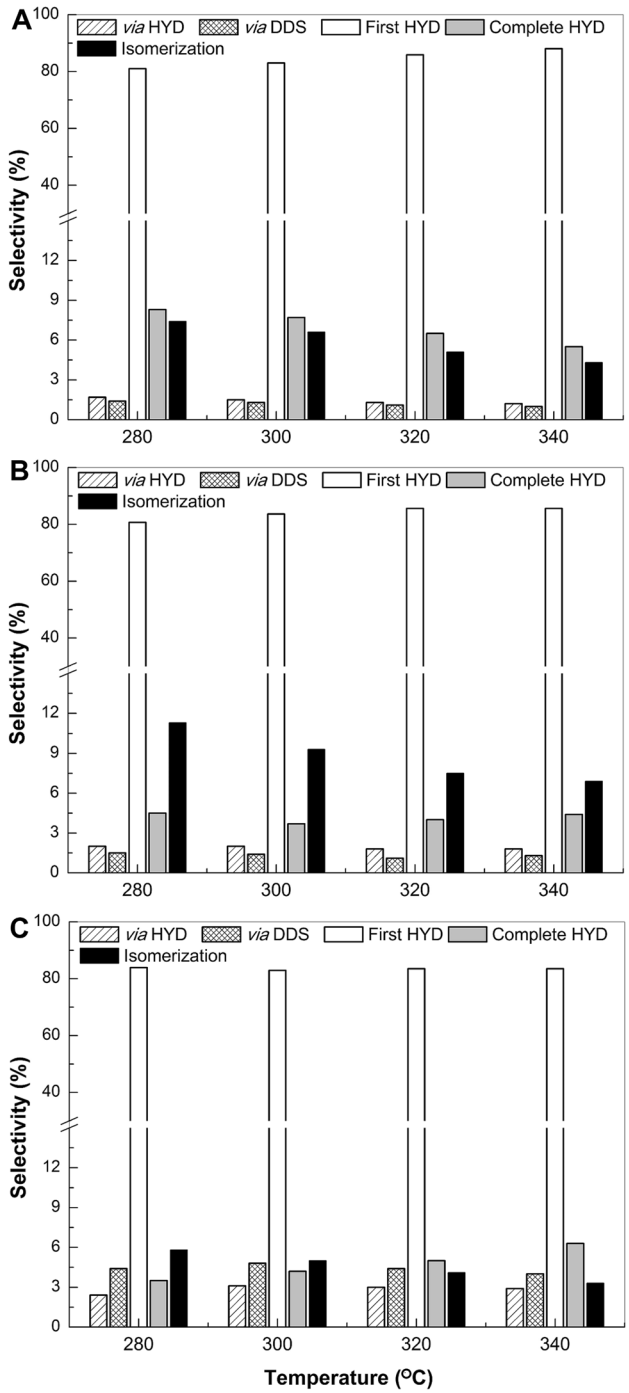


Fig. 8 Selectivity taken to 20–25% of 3-methyl-thiophene conversion of the ReS2 samples annealed at 400 °C (**a**), 800 °C (**b**) and Mo/γ–Al2O3 (**c**)

(HYD) and direct desulfurization (DDS) reaction pathways. The HYD reaction route led to formation of 3MTHT, isoprene and 2-methyl-butane (2MB). However, isoprene could be formed also via the direct desulfurization reaction route.

Considering the selectivity towards the S-containing product (3MTHT), the catalyst ability for sulfur removal follows the trend: ReS_2-400 °C > ReS_2-800 °C > Mo/γ-Al_2O_3.The hydrogenation of this compound led to the formation of the mixture of olefins: 3-methyl-1-butene, 2-methyl-2-butene and 2-methyl-1-butene. Their further isomerization led to the formation of 1-pentene and a mixture of cis- and trans-2-pentenes. For all catalysts studied, the main reaction products were olefins (3M1B, 2M1B and 2M2B). However, the catalysts exhibit a difference in the selectivity towards the formation of complete hydrogenation and isomerization products, including the path of the reaction (DDS and HYD).

The influence of the reaction temperature on the product selectivity (at 3-methyl-thiophene conversion of 20–25%) is shown in Fig. 8. In order to clarify the discussion of the catalytic selectivity results, the DDS and HYD selectivity are defined as selectivity toward isoprene and 3MTHT, respectively, whereas that the olefin mixture (3M1B, 2M1B and 2M2B) were considered as products of the first hydrogenation of their intermediary (isoprene) product. Total hydrogenation was defined considering the selectivity towards 2-methyl butane (2 MB). Finally, to evaluate the contribution of the isomerization reaction pathway, the sum of 1-pentene and mixture of 2-trans(cis)-pentenes was taken into account. By comparing the activity and selectivity of the ReS_2 samples annealed at 400 °C and 800 °C, it is clear that the annealing treatment influences on both the catalytic activity and the selectivity (Fig. 8a, b). Although the selectivity towards the first hydrogenation products and the hydrodesulfurization via HYD and DDS is comparable in both samples, the sample annealed at 800 °C displayed higher formation of isomerization products and lower complete hydrogenation products than the sample annealed at 400 °C. Although the catalytic activity of the sample annealed at 800 °C is several times lower than its counterpart annealed at 400 °C, its lower hydrogenation ability and higher isomerization properties are attractive characteristics for the production of gasoline. The Mo/γ-Al_2O_3 sulfided sample (Fig. 8c) exhibited higher selectivity towards 3MTHT and isoprene than both ReS_2 samples. Also, the selectivity to the isomerization path was the lowest among the samples, while the selectivity towards the complete hydrogenate products was similar than the ReS_2 sample annealed at 800 °C. The selectivity results showed improved HDS activity of the ReS_2 samples, in comparison with the traditional Mo/γ–Al_2O_3 sulfided catalyst.

3.2.3 Isomerization/Hydrogenation Selectivity's Ratios

In order to obtain more precise information about the isomerization and hydrogenation properties of the catalysts studied, 2 MB/olefin and isomerization/olefin selectivity's

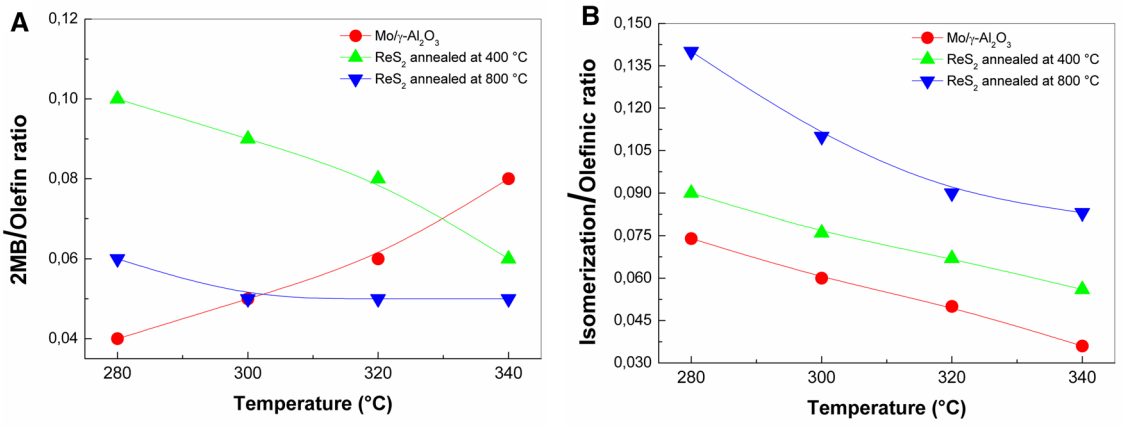


Fig. 9 **a** 2MB/olefin ratio versus reaction temperature and **b** isomerization/olefin ratio versus reaction temperature

ratios were calculated for the same 3-methylthiophene conversion (20–25%). The total hydrogenation (HYD) was defined considering the selectivity toward 2-methyl butane (2MB) whereas the isomerization reaction pathway was defined as the sum of 1-pentene and mixture of 2-trans(cis)-pentenes.

Figure 9a, b shows the isomerization/olefin and 2MB/olefin selectivity´s ratios versus the reaction temperature, respectively. As seen in Fig. 9a, on the contrary to both ReS_2 samples, for the Mo-based catalyst the 2MB/olefin ratio increases with an increase of the reaction temperature. At the highest reaction temperature studied (340 °C), the paraffin/olefin ratio follows the trend: $MoS/\gamma\text{-}Al_2O_3 > ReS_2\text{-}400\,°C \approx ReS_2\text{-}800\,°C$. This is a very interesting observation because this situation indicates that, by using ReS_2-based catalysts for the processing of FCC gasoline, the total olefin hydrogenation to paraffin should be avoided. Finally, for all catalysts studied, the isomerization/olefin ratio decreased with an increase of the reaction temperature (Fig. 9b). The ReS_2 sample annealed at 800 °C showed the superior isomerization ability (highest isomerization/olefin ratio), in comparison with the others samples.

Summarizing, taking into account that the catalysts for hydrotreating of FCC gasoline must promote the desulfurization reaction instead of the hydrogenation of olefins, their high HDS activity, low hydrogenation of olefins to paraffins (2-methyl-butane was formed only), and a large isomerization of olefins, the microspherical ReS_2 catalysts are promising catalysts for hydrotreating of FCC gasoline.

3.2.4 Factors Influencing on Catalyst Activity

The outstanding HDS activity of the rhenium disulfide annealed at 400 °C can be attributed to the crystalline structure confined into the microsphere, where the amorphous ReS_2 generates an open surface structure with many reactive edge sites. This sample presents preference for complete hydrogenation reactions, which commonly are associated to edge sites [24]. On the other hand, the sample annealed at 800 °C leads to a significant decrease in activity due to the formation of stacked and longer slabs, which implies a lower proportion of edge sites. With the increase of annealing temperature the ReS_2 layers grow forming an external shielding; the nature of the shield is similar to onion-type structures, but present much more defects derived from the folded and curved layers [14]. The disordered atomic arrangement of the amorphous phase leads to the breakage of the basal plane during the annealing at higher temperatures, resulting in the formation of the additional edges. It is important to known that the catalytic results show that the microspheres annealed at 800 °C present more ability to the isomerization reaction than the 400 °C annealed microspheres. This is probably due to the highly bended structure of the microspheres annealed at 800 °C, considering that the differences in the isomerization reactions have been related with the presence of acidic sites on the surfaces of basal planes [1, 22]. Thus, in terms of both catalyst characterizations, the lower activity and different selectivity of the ReS_2-800 °C respect to its ReS_2-400 °C counterpart can be explained due to the superposition of the positive effect of structural defects originated on the basal planes of bended layers, and to the negative effect of their higher stacking and longer length. A similar effect has been reported indicating the negative effect of the bending $Mo(W)S_2$ layers for the HDS performance [32].

4 Conclusions

In this paper we evaluate the use of a new microspherical ReS_2 catalyst for the hydrodesulfurization of

3-methylthiophene. The ReS_2 microspherical catalyst was successfully synthesized through a simple solvothermal route using elemental sulfur, $Re_2(CO)_{10}$ and toluene as solvent. The subsequent annealing process at different temperatures plays an important role in the conformation and characteristics of the self-assembled ReS_2 in the microspherical hierarchical structure, and in their further catalytic properties. ReS_2 microspheres annealed at 400 °C are composed by an amorphous arrangement of nano-layers, while those of the sample annealed at 800 °C exhibit larger basal planes with bended and more stacked layers. The amorphous and defect-rich ReS_2 layers on the microsphere results in the exposure of additional edge sites, leading to an outstanding catalytic performance for the hydrodesulfurization of 3-methylthiophene. The present work indicates that the solvothermal synthesis of microspherical ReS_2 can be a useful pathway for the preparation of ReS_2 HDS catalysts.

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