CONVERSION OF QUINOLINE ON ReS₂ CATALYSTS: EFFECT OF THE SUPPORT AND THE ADDITION OF CS₂ IN THE FEED

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ABSTRACT

The effect of supports and the addition of CS₂ in the feed were studied on hydrodenitrogenation of Quinoline in a continuous flow reactor over ReS₂/support catalysts at 300, 325 and 350 °C and 3MPa of H₂. The ReS₂ supported on TiO₂ displayed the highest activity followed by ZrO₂, γ-Al₂O₃ and SiO₂ supports. The activity trend was correlated with the Re dispersion on the support. The effect of the addition of CS₂ was increased activity until 2.5 v/v % content. At higher CS₂ content the activity decreased due to competitive adsorption between CS₂ and Quinoline on the active sites.

Keywords: Quinoline, support, Carbon sulphide.

1. INTRODUCTION

The quality of crude oil decreases with content of heavier sulphur and nitrogen organic compounds that hinder hydrotreatment processes (HT), particularly hydrodesulphurisation (HDS) and hydrodenitrogenation (HDN). Moreover, stringent environmental regulations have forced the oil industry to reduce the sulphur and nitrogen levels present in fuels. In order to meet the required standards, it is essential to find more active catalysts than the typical HT Ni(Co)-Mo/Al₂O₃ ones . In this context, several research studies have been carried out in an attempt to either improve the activity of classical sulphide catalysts or find alternative catalysts[1-3].

In recent years there have been various investigations into HDN, since the nitrogen molecules present in oil produce a poisoning of the catalysts used in other oil refining processes[4], and mainly because these molecules inhibit HDS and other HT processes[5].

In this context, Eijsbouts et al.[6] studied the reactivity of first-, second-, and third-row transition metal sulphide (TMS) supported on activated carbon in the HDN of Quinoline. They found that the first-row transition metal sulphides displayed low Quinoline conversion to hydrocarbons, while the second- and third-row TMS formed a volcanic curve with maximum at Rh/C and Ir/C catalysts, respectively. On this curve, Re/C presented intermediate activity but with high selectivity for propylbenzene. The ReS₂ catalyst has been studied rarely with HDN reactions, though a ReS₂/Al₂O₃ catalyst exhibited higher activity (1.6 times) than the Ni-Mo/Al₂O₃ catalyst in the HDS of thiophene[7].

Considering the high activity of ReS₂ in the HDS, the objectives of the present study was to analyse the effect of the support (TiO₂, ZrO₂, SiO₂ and γ-Al₂O₃) on the HDN of Quinoline using catalytic systems based on rhenium sulphide, and to evaluate the effect of adding CS₂ into the feed, due to the absence of H₂S as reaction product, to stabilize the active sites.

2. EXPERIMENTAL

2.1 Preparation of the catalysts

The rhenium catalysts supported on γ-Al₂O₃ (BASF D10-10), ZrO₂, TiO₂ (P-25 Degussa) and SiO₂ (BASF D10-11) were prepared by wet impregnation using NH₄ReO₄ (Aldrich, 99%) as the precursor salt. The ZrO₂ support was obtained by direct calcination of commercial hydrated zirconia, Zr(OH)₄ (MEL Chemicals) at 573 K for 3 hours. The nominal metal content was 2.7 at nm⁻². The impregnated catalysts were left to soak at room temperature for 24 h. They were then dried at 393 K for 12 h and finally calcined at 573 K for 0.5 h.

2.2 Characterisation of the catalysts

The BET specific surface areas (S_BET) and pore volumes of the samples were determined using Micromeritics-TriStar II 3020. X-ray powder diffraction patterns were obtained using a Rigaku diffractometer. The total acidity measurements of sulphide catalysts were carried out by potentiometric titration [8]. X-ray photoelectron spectra (XPS) of sulfide catalysts before and after reaction were recorded on a VG Escalab 200R electron spectrometer. Details of the experimental procedure have been reported in a previous work[9].

2.2 Catalytic Activity

The Quinoline conversion reaction was carried out in a continuous flow micro-reactor, with the following reactor load: 0.2 g of the catalyst Re(2,7)/γ-Al₂O₃, Re(2,7)/ZrO₂, Re(2,7)/TiO₂ or Re(2,7)/SiO₂, diluted at a ratio of 1: 1 v/v with SiO₂ (BASF D11-10). The remainder of the reactor was filled with SiC. The catalysts were subjected to an in-situ pre-sulphurization treatment at 623 K for 4 hours. The catalytic reaction was then carried out under conditions similar to industry standards at reaction temperature of 573 K, with a feed of 5000 ppmv of Quinoline at a flow rate of 0.1 mL min ⁻¹ and 3MPa of H₂. The samples were analysed by GC-FID once a steady state had been reached. In order to evaluate the effect of CS₂ on the HDN of Quinoline, Re(2,7)/γ-Al₂O₃ was used as the catalyst, and the feed was altered with three concentrations of CS₂ 2.5 %, 5% and 10 % v/v.

In order to compare the results for Quinoline conversion on the different supports, the specific rate (r) was calculated using the rate integral equation assuming pseudo-first order in the quinoline, in accordance with the following equation:

$$r = k * C_o = - \frac{F_o}{m} * \ln(1 - \tau)$$

This kinetic equation is designated the first order integral equation, in which the reaction rate is in unit of mol g⁻¹ s⁻¹, τ is the level of conversion, m the mass of the catalyst (g) and F_O is the molar flow (mol s⁻¹).

The intrinsic rate, r_i, represents the molecules of quinoline transformed by the Re atoms per second (molec. at. Re⁻¹ s⁻¹), and was calculated using the following equation:

$$r_i = \frac{r}{N_{Re}} * Nav$$

Where N_{Re} are the Re atoms per gram of catalyst per nm² of support, r is the rate and Nav is Avogadro's number.

3. RESULTS AND DISCUSSION

3.1 Characterisation of the supports and catalysts

Table 1 shows the results for the textural properties of the supports and catalysts samples obtained from N₂ isotherms and the total acid strength of the sulphide catalysts. These results show a decrease in specific surface area and total pore volume with Re impregnation. This decrease is almost proportional

to the Re charge, suggesting that there is no significant pore blocking on the supports. The acidic strength was found in accordance with the criteria proposed by Cid and Pecchi[8], and follows the following trend: $ReS_2/\gamma-Al_2O_3$ > ReS_2/SiO_2 > ReS_2/TiO_2 > ReS_2/ZrO_2. For this trend, E_0 > 100 are for very strongly acidic sites, $0 < E_0 < 100$ means strongly acidic sites, $0 > E_0 > -100$ is for weakly acidic sites and $E_0 < -100$ means very weak acidic sites. Therefore, the results show that the catalyst $ReS_2/\gamma-Al_2O_3$ has weak acidic sites, while the other catalysts present very weak acidic sites.

Table 1. Composition, textural properties and acidic strength of the supports and catalysts.

Samples	Re Nominal content (at. nm^{-2})	$^a S_{BET}$ (m^{2}g^{-1})	$^b Vp$ (cm^{3}g^{-1})	Acid Strenght E_0 (mV)
$\gamma-Al_2O_3$	--	211	0.55	--
Re(2,7)/ $\gamma-Al_2O_3$	2.7	174	0.30	-93
ZrO_2	--	41	0.09	--
Re(2,7)/ ZrO_2	2.7	43	0.08	-126
SiO_2	--	187	0.31	--
Re(2,7)/ SiO_2	2.7	124	0.23	-185
TiO_2	--	54	0.09	--
Re(2,7)/TiO_2	2.7	44	0.07	-151

^{a} Specific area, BET Method ^{b} Total pore Volume

The XRD are summarised in Figure 1 and shows the X-ray diffraction patterns for the ReOx catalysts along with the supports. It shows the presence of ReO_3 and ReO_4^- for the rhenium catalysts on SiO_2 and $\gamma-Al_2O_3$. Figure 1 also shows that no diffraction peaks attributed to ReO_3 and ReO_4^- are found with the ReOx catalyst on ZrO_2, suggesting that there is a high degree of dispersion of ReOx on the ZrO_2. For the case of ReOx/TiO_2, only the species ReO_4^- was detected, and were published previously[9].
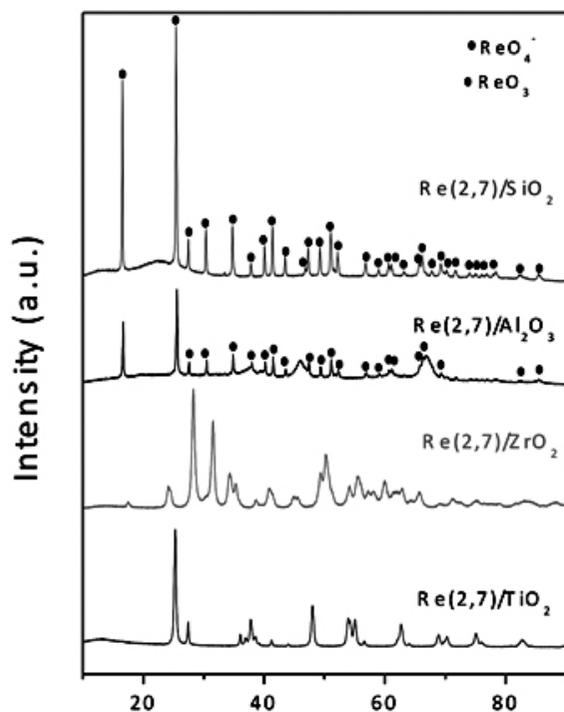
Figura 1: X-ray diffraction of : ReOx/SiO_2, ReOx/$\gamma-Al_2O_3$, ReOx/ZrO_2 y ReOx/TiO_2 catalysts. (ReO_4^- (JCPDS: 2101669 and ReO_3 (JCPDS: 00-24-1009)

Figure 2 shows the XPS results for the sulphide catalysts. For the catalysts supported on SiO_2 and TiO_2, a single fold containing Re 4f $_{7/2}$ and Re 4f $_{5/2}$ can be seen. This was assigned to species of ReS_2[9]. For the catalysts supported on Al_2O_3 and ZrO_2, two overlapping folds are seen; one assigned to ReS_2 and the other the Re oxysulphide species[10,11]. The binding energy values are summarised in Table 2. The results indicate that the sulphurization of Re was slightly incomplete on Al_2O_3 and ZrO_2 (close to 90 %). The results also suggest strong interaction between the ReOx and the supports. The Re/M atomic ratio values (M= Si, Ti, Al and Zr) obtained by XPS, shows that the catalyst ReS_2/TiO_2 has the highest Re/M atomic ratio, followed by $ReS_2/\gamma-Al_2O_3$, ReS_2/SiO_2 and finally ReS_2/ZrO_2. This trend suggests that ReS_2 is more dispersed over the TiO_2 support in agreement with XRD, while the ReS_2 dispersion is low over the ZrO_2; a similar result was observed previously[12]. The lowest dispersion showed by XPS for ReS_2/ZrO_2 catalyst is in opposite to the results obtained from XRD. These result suggested that the high Re dispersion obtained by XRD was modified in the sulphurization process leading to the formation of ReS_2 aggregates.
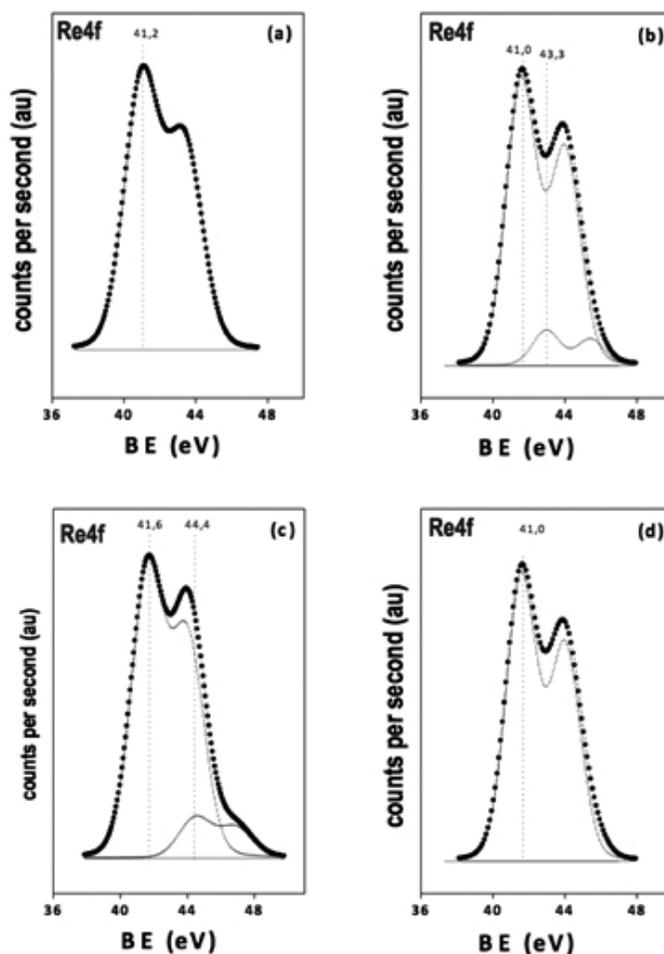
Figure 2: XPS of sulfides: a) Re/SiO_2, b) Re/$\gamma-Al_2O_3$, c) Re/ZrO_2 and d) Re/TiO_2 catalysts.

Table 2: XPS binding energies (eV) and surface atomic ratios of sulphided catalysts.

Catalysts	M 2p (Si, Al, Zr, Ti) (e.V.)	Re4f$_{7/2}$ (e.V.)	S2p (e.V.)	Re/M (Si, Al, Zr or Ti)
ReS$_2$(2.7)/SiO$_2$	103.4	41.3	161.6	0.068
ReS$_2$(2.7)/γ-Al$_2$O$_3$	74.5	41.2 (90) 42.3 (10)	161.9	0.090
ReS$_2$(2.7)/ZrO$_2$	182.2	41.7 (89) 43.8 (11)	162.2	0.053
ReS$_2$(2.7)/TiO$_2$	458.6	41.5	161.9	0.310

3.2   Catalytic activity

Figure 3 shows the distribution of the products in steady state as a function of the Re (2,7) catalysts/support. It can be seen that for all catalysts, the quinoline is converted into 1,4-tetrahydroquinoline (1,4-THQ), decahydroquinoline (DHQ), orthopropylaniline (OPA), propylbenzene (PB) and propylcyclohexane (PCH).
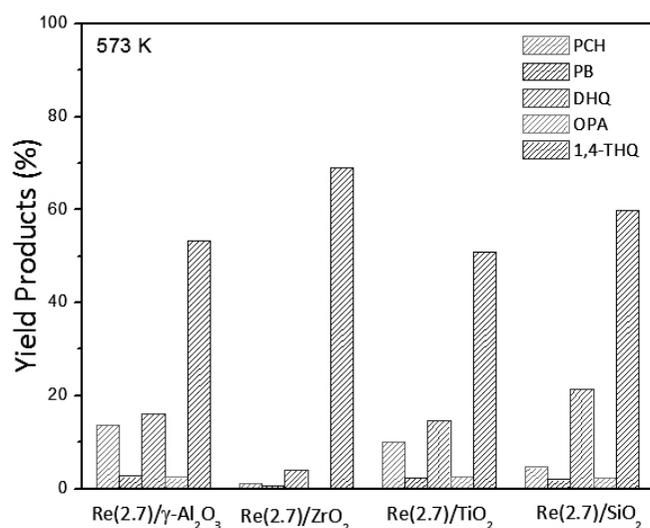
Figure 3: % Formation of products using ReS$_2$ on different supports.

The formation of these reaction products can be explained using the reaction scheme shown in Figure 4[13]. In general, all ReS$_2$ catalysts showed low yields for dehydrogenated products (PCH and PB). Re(2,7)/SiO$_2$ showed the highest level of formation of DHQ, suggesting that it has a highly hydrogenating nature. This was suggested previously by Sepulveda *et al.*[14] in the HDS of 4,6-Dimethyldibenzothiophene and was attributed to the formation of Re with an oxidation between $0 < x < 4$ under reaction conditions. The Re(2,7)/Al$_2$O$_3$ showed the highest degree of formation of PCH, which may be attributed to the higher acidic strength associated with this catalyst. The ReS$_2$/ZrO$_2$ showed the lowest yield for PCH and PB, with no OPA formation observed.
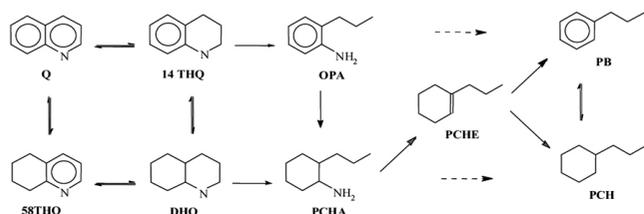
Figure 4: Reaction scheme for HDN of quinoline[13].

This may be attributed to the lower acidic strength of the catalysts, as shown in Table 3. However, it can also be related to the effect of the particle size of ReS$_2$, in accordance with the XPS results, which showed that Re(2,7)/ZrO$_2$ had

the lowest Re/Zr atomic ratio. Unfortunately, measurements of HRTEM could not be taken on these catalysts, since under the beam of electrons the ReS$_2$ sheets decompose into spherical structures[12].

Figure 5 shows the intrinsic rates calculated in steady state for the Re(2,7)/ supports. In this figure it can be seen that the activity depends on the support used and it increases in the following order: Re(2,7)/SiO$_2$ < Re(2,7)/γ-Al$_2$O$_3$ < Re(2,7)/ZrO$_2$ < Re(2,7)/TiO$_2$. The higher activity may be attributed to a higher Re/M surface ratio (Si, Al, Zr and Ti) obtained by XPS for the Re(2,7)/TiO$_2$. However, the trend obtained for the other catalysts cannot be correlated with the dispersion measurements relative to Re obtained by XPS, the degree of sulphurization of the ReS$_2$ and the acidic strength of the catalysts, suggesting that the support is modifying the electron properties of the ReS$_2$.
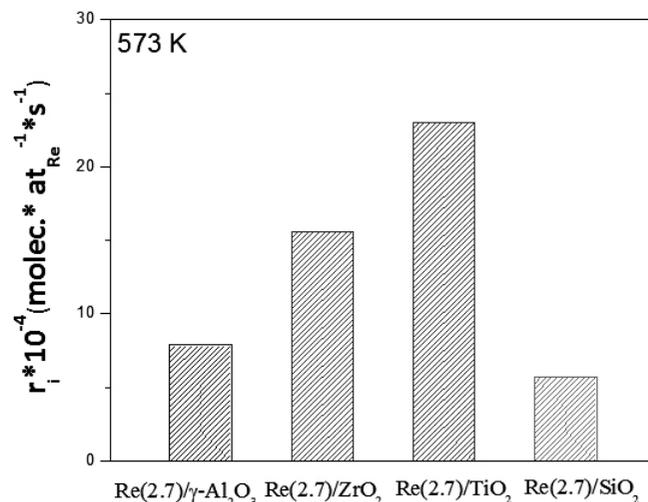
Figure 5: Catalytic intrinsic activity of ReS$_2$ on the different supports

Figure 6 shows the effect of adding CS$_2$ on the quinoline conversion using the ReS$_2$ catalysts supported on γ-Al$_2$O$_3$. It can be seen that the addition of CS$_2$ at a concentration of 2.5 % v/v increases the activity in comparison to the absence of CS$_2$ in the feed. This may be because the carbon sulphide avoids the deactivation of the active sites. However, at the higher concentration of CS$_2$, the quinoline conversions decrease, as observed previously in the conversion of guaiacol[15]. This can be explained by the fact that the H$_2$S formed from the CS$_2$ leads to competitive adsorption with the quinoline on the active sites of the catalyst, thus decreasing the sites accessible for quinoline conversion.
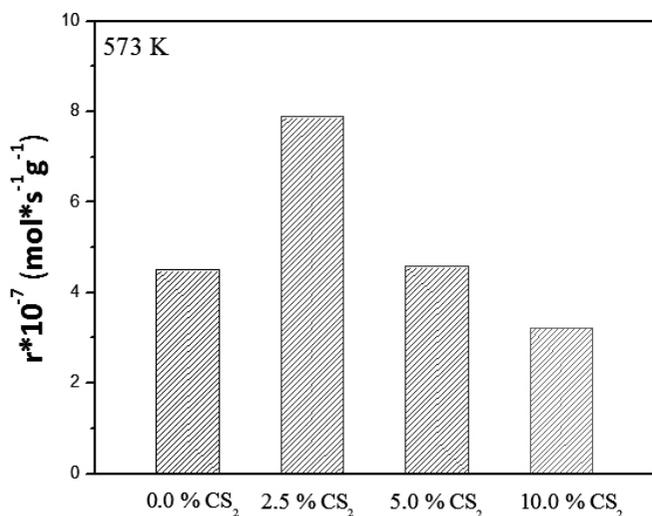
Figure 6: Catalytic activity obtained using ReS_2/γ-Al_2O_3, and feed modified with the addition of: 0.0% CS_2, 2.5% CS_2, 5% CS_2 and 10 % CS_2.

Figure 7 shows the distribution of reaction products at different CS_2 content on the ReS_2/TiO_2. It can be seen that by adding CS_2 to the feed, the yield of denitrogenated products (PCH and PB) increases considerably and it is not proportional to the change in conversion.
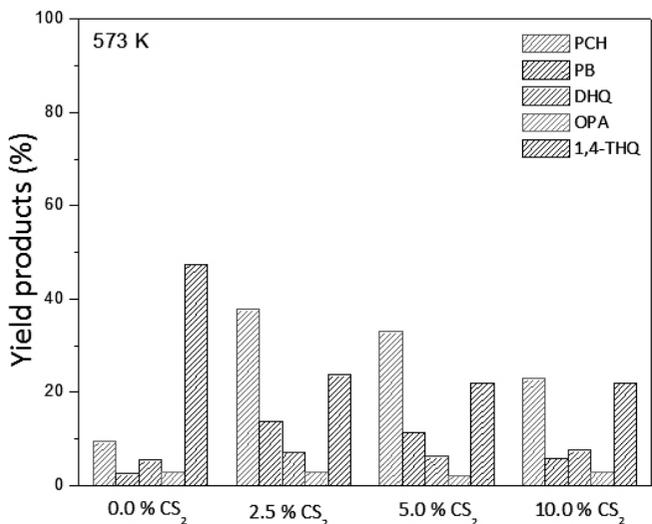
Figure 7: Product formation using ReS_2/γ-Al_2O_3, and a feed modified with the addition of: 0.0% CS_2, 2.5% CS_2, 5% CS_2 and 10 % CS_2.

This change in the distribution suggests that the H_2S may be modifying the active sites on the ReS_2, decreasing the hydrogenation sites and favouring hydrogenolysis sites. However, Vrinat *et al.*[16] demonstrated the existence of a single type of active site on sulphide catalysts. Therefore, the increase in N-free products in the presence of H_2S on ReS_2 may be attributed to the fact that H_2S is decreasing the metal nature of ReS_2, diminishing its hydrogenating nature. In other words, in the absence of CS_2 the ReS_2 tends to form Re species with oxidation status of $0 < x < 4$, thus favouring hydrogenation sites, while in the presence of CS_2, the stability of ReS_2 is favoured, leading to a higher percentage of denitrogenated products.

CONCLUSIONS

The results of this study show that the support affects the catalytic activity of ReS_2. The highest activity was obtained on TiO_2 and was attributed to the highest ReS_2 dispersion. For the activity on the other supports, no direct correlation was found with the structural properties of the ReS_2. The addition of 2.5% v/v CS_2 increased the quinoline conversion. This increase was attributed to the improved stability of the ReS_2. The distribution of the products suggests that quinoline conversion in the presence of H_2S has a different reaction mechanism than in the absence of H_2S. The effect of H_2S shows that high concentrations inhibit the reaction due to adsorption competition with the quinoline.

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