Development of a recovery mass for trapping arsenic containing compounds from hydrocarbon feeds

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Abstract

The aim of this work was to study the solids efficiency to trap organo-arsenic compounds. For that purpose, catalyst preparation methods were applied, by dry impregnation using different metal precursors and thermal treatments (calcination). All prepared catalysts were characterized by Nitrogen Adsorption-desorption, Mercury Porosimetry, X-Ray Diffraction and X-Ray Fluorescence in order to determine textural properties and metal contents. To activate the catalysts, sulphurization was done.

Standard and reproducible catalytic tests were performed in a Grignard reactor at 250˚C and 35 bar of hydrogen pressure, using two different natures of organo-arsenic diluted feeds: triethylarsine or triphenylarsine in toluene. The mass trapping of this feeds increases with the dispersion of the metal on the catalyst. In general, the conversions are 2 times higher for $AsPh_3$ and Nickel is the most efficient metal precursor to trap both feeds, presenting conversions of 47% for $AsEt_3$ and 100% for $AsPh_3$ and kinetic constants of 4.0×10^{-3} min^{-1} and 1.3×10^{-1} min^{-1}, respectively. Even for other metals, with low concentrations of arsenic (215.5 ppm) in form of $AsPh_3$ the conversions are 100% but the trapping rate are higher for nickel ($k = 1.3\times10^{-1}$ min^{-1}) followed by cobalt ($k = 6.4\times10^{-2}$ min^{-1}) and iron ($k = 5.3\times10^{-4}$ min^{-1}). Catalysts that have molybdenum in their composition demonstrate higher conversions for high concentrations of arsenic (2155 ppm), increasing this conversion 3 times.

Tests with a concentrated feed of arsenic and sulphur were performed, proving that the conversion for arsenic is higher than for sulphur, 100% and 75% respectively, with a selectivity for arsenic of 6.4.

Key words: arsenic trapping; triethylarsine; triphenylarsine; metallic catalysts; kinetic constants; selectivity

1 Introduction

The evolution of refineries is related to the petroleum products demand, in other words, this evolution has been driven by market trends but also by improving the quality of products (increase of RON for gasoline and cetane number for diesel). Currently, the demand for light products and middle distillates increases instead of the demand for heavy products which is decreasing.

The FCC gasoline produced has a very high octane number, especially for paraffinic and naphthenic loads, but must be desulphurized without reduction of RON. This desulphurization is carried out by HDS units, which use bimetallic catalysts, in the oxide form, of Mo/W, Co/Ni and Co/Mo. To activate the catalyst is necessary to sulfurize these metal oxides.

Unfortunately, arsenic compounds, present in some feeds at trace levels, are responsible for poisoning, reducing the catalyst activity due to the formation of intermetallic phases.

The aim of this work is to develop a recovery mass, composed by transition metals deposited on a support such as alumina, which can eliminate such organo-arsenic compounds from the feeds to be treated. The main objectives are to develop a methodology for the catalytic tests, synthetize trapping mass catalysts and evaluate the performance of the catalysts.

2 Literature Review

Catalytic hydrodesulphurization process of gasoline allows to decrease the sulfur content down to the maximum limit, 10 ppm. Unfortunately, some of these feeds can also contain organo-arsenic compounds, at trace levels, 10-100 ppb, which can be poisons for these catalysts.

The catalysts responsible for the dearsenification of feeds are similar to the ones used in hydrotreatment. According to the literature [1], the activity of HDS catalysts is highly conditioned by the presence of arsenic compounds.
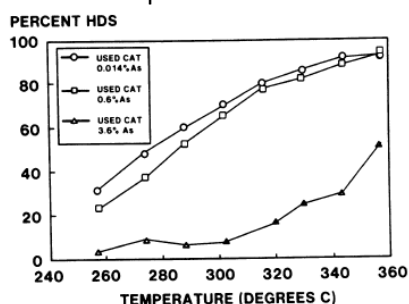

Figure 1 - HDS activity of poisoned plant catalysts [1].

A detailed understanding of the deactivation of CoMo and NiMo hydrotreating catalysts used for desulfurization of hydrocarbon feeds is important to optimize the process parameters in the refineries and to rationalize catalyst research [2]. It's possible to classify this deactivation into four different categories [3]:

1. Blocking of catalyst pores by coke formation, making the active centers unavailable for reactants;
2. Sintering of MoS_2 slabs;
3. Poisoning of active sites by strongly absorbing species, which are usually present as N-heterocyclic compounds in the middle and heavier feeds;
4. Poisoning by deposition of metals, predominantly present in resid feeds, on the active sites.

Exposure of CoMo or NiMo hydrotreating catalysts to arsenic containing feedstocks has been recognized to have a dramatic influence on the catalyst activity [4]. Owing to this problem, an arsenic trap material is installed in many hydrotreating reactors in order to prevent any arsenic coming in contact with the hydrotreating catalyst. This "arsenic guard" is usually a supported transition metal (Mo, Co, Ni) oxide/sulfide with a high tendency to chemisorb largely all the arsenic present in a hydrocarbon stream.

Several recent studies have demonstrated that on a Ni/Al_2O_3 catalyst, deactivation proceeds via a stepwise process by the initial population of surface arsenic atoms, the diffusion of these arsenic atoms into the supported nickel particles to form intermetallic Ni_xAs_y phases, and the final formation of crystalline NiAs [5, 6]. Additionally, studies using nickel reforming catalysts have also discussed the formation of Ni_5As_2 and NiAs nickeline alloy phases [7]. However, information regarding the mechanism and chemical state of arsenic after deposition on a NiMoS hydrotreating catalyst is scarce.
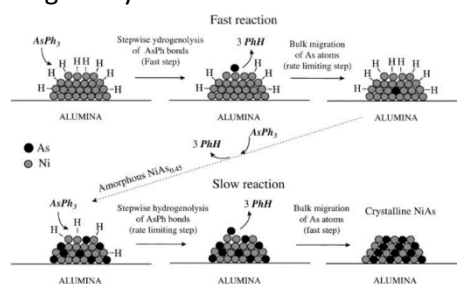

Figure 2 - Catalyst deactivation due to arsenic atoms [8].

According to the literature [9], studies about the hydrogenolysis of triphenylarsine with alumina-supported nickel catalysts with various particle sizes were done, under hydrogen pressure and at temperatures ranging from 303 to 443 K. The reaction initially takes place selectively on the surface of the nickel particles and leads to the successive hydrogenolysis of –As–Ph bonds with benzene and cyclohexane formation. At 303 K, the reaction stops when the Ni particles are completely covered with grafted –As–Ph fragments. The quantity of fixed arsenic increases with the dispersion of the metal particles. It is proposed that more As–Ph fragments (per metallic atom) are grafted onto edge atoms than onto face atoms of the Ni particles. When the reaction is performed at higher temperature, the As atoms migrate inside the nickel particles easily and form an intermetallic compound. At 373 K, the Ni_5As_2 phase, very poorly crystallized, is obtained. At 443 K, the reaction leads to a well-crystallized phase NiAs.
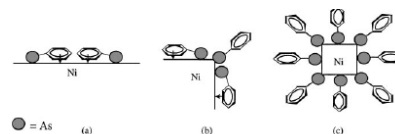

Figure 3- Models for the adsorption of $AsPh_3$ on Ni/Al_2O_3: (a) on the faces of the Ni particles, (b) on the edges, and (c) on a very small particle [9].

3 Methodology

3.1 Preparation of the trapping mass

Catalysts prepared in this study were supported metal catalysts. In order to test the reactivity of different metals (zinc, copper, nickel, cobalt and iron), were prepared solutions with the metal precursors, applying the preparation method of dry impregnation, the thermal treatment of calcination and the activation by sulphurization. Two different supports were used to prepare the catalysts: a commercial alumina (AAS: Activated Alumina Support) and a HDS catalyst from *Axens* (composed by cobalt and molybdenum on alumina support).

3.1.1 Dry Impregnation

The preparation of aqueous or organic solution with an active metal precursor is the beginning for synthesize heterogeneous catalysts. Thus, five different metal nitrates were chosen: zinc nitrate hexahydrate, copper nitrate trihydrate, nickel nitrate hexahydrate, cobalt nitrate hexahydrate and iron nitrate nonahydrate. Thirteen solutions were prepared, the first three by using just water and the metal precursor and the other ones where a dispersion agent was added (citric acid).

Dry impregnation consisted of a metal support where the glass recipient is placed with the catalyst support, which was rotating due to a stirring motor at a velocity of 60 rpm. The precursor solution present in a buret was introduced dropwise, mixing the catalyst and the solution with the aid of a metal spatula.

In order to obtain a homogeneous distribution of the precursor solution over the support, the impregnation step was performed in around 40 minutes for the alumina support and 25 minutes for the HDS catalyst.

After impregnation, the catalyst was subjected to drying in order to eliminate the excess solvent (usually water) present in the solid pore, putting the impregnated catalyst in the oven for 3 hours at 90°C.

3.1.2 Calcination

Calcination was performed with an HSV of 1500 h^{-1}, under an air flow of 139 NL/h for the catalysts supported by alumina and with 112 NL/h for the catalysts from *Axens*, in a tubular four equipped with a glass reactor which had a porous plant, controlled by an electronic system where is introduced the air flow and the temperature evolution, according to the Figure 4.
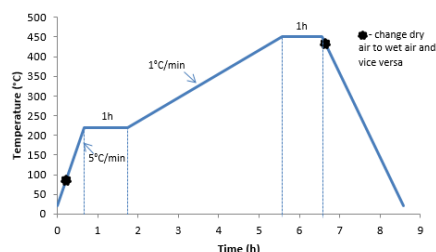

Figure 4 - Calcination profile used for all catalysts.

This program of calcination was applied to all catalysts.

3.1.3 Sulphurization

In order to activate the metal phase of the catalyst, sulphurization was performed using 3g of each catalyst. A pressure of 2 bar was used in this step.

As can be seen in Figure 5, the sulphurization process is composed by 5 steps:

- It begins with a temperature ramp from the room temperature to 350°C, under H_2S/H_2 (15%H_2S) flow of 1 nL/h/g_{cat} **(1)**;
- Then this temperature is maintained in order to produce the sulfide form of the catalyst **(2)**;
- After that there is a temperature decreasing to 200°C, under H_2 flow of 1 nL/h/g_{cat} **(3)**;
- The temperature is maintained in order to reduce the catalyst and remove the reactive sulfur species (S^{2-},SH^-,S_2^{2-}) [38] **(4)**;
- To finish, the temperature is decreased until the room temperature, under Ar flow **(5)**;
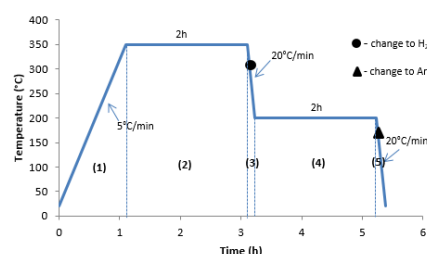

Figure 5- Sulphurization profile used for all catalysts.

This classical profile of sulphurization for HDS catalysts was adopted, not being the purpose of this subject the study of different profiles or conditions of sulphurization.

3

3.2 Characterization Methods

Different analysis were performed in order to describe the structure of the catalysts and their precursors, allowing the identification of the active sites activate and revealing possible ways to improve the catalyst structure [10]. The characterization methods used were: N_2 adsorption-desorption, mercury porosimetry, X-ray diffraction (XRD) and X-ray fluorescence (XRF).

3.2.1 N_2 adsorption-desorption at 77 K

Nitrogen adsorption-desorption is a characterization technique used to study the textural properties of catalyst supports in the micro (less than 2 nm) and mesopore range (between 2 and 50 nm), following the adsorption phenomenon.

The results obtained for alumina support by this method are presented in the next table.

Table 1 - Nitrogen adsorption-desorption results.

Catalyst	S_{BET} (m²/g)	Total porous volume (cm³/g)
Nickel	108±5.4	0.516±0.010
Cobalt	115±5.8	0.556±0.011
Iron	136±6.8	0.527±0.011
Zinc+	124±6.2	0.625±0.013
Copper+	124±6.2	0.620±0.012
Nickel+	134±6.7	0.556±0.012
Iron+	136±6.8	0.582±0.012

+ prepared with an aqueous solution with citric acid

The use of the dispersion agent increases 24% the specific surface area for nickel catalysts in relation to the catalyst prepared without citric acid. The total porous volume increases too for this catalyst but also for the iron catalyst: an increase of 8% for nickel and 10% for iron.

The average specific surface area of alumina impregnated only with a solution of metal precursor is 120 m²/g and for alumina impregnated with the solution with citric acid is 131 m²/g. The total porous volume is 0.533 cm³/g and 0.597 cm³/g, respectively. These average values are typical values for the commercial alumina AAS.

3.2.2 Mercury porosimetry

Mercury porosimetry also allows the textural characterization of catalysts with the determination of the specific surface area and pore size distribution. As opposed to nitrogen adsorption-

desorption, this technique is generally applied for macroporous samples and for the upper range of mesoporous (3,5-50 nm) [11].

The pore diameters and pore volumes for alumina support are presented in Table 2.

Table 2 - Important results from mercury porosimetry.

Catalyst	Pore Vol. for d < 7 μm (cm³/g)	Pore d at max dV/dD (nm)	Macropore vol. (cm³/g)	Mesopore vol. (cm³/g)
Nickel	0.85±0.02	13.8	0.35±0.04	0.48±0.02
Cobalt	0.86±0.02	12.8	0.35±0.04	0.48±0.02
Iron	0.86±0.02	13.4	0.36±0.04	0.49±0.02
Zinc+	1.02±0.02	11.6	0.42±0.04	0.57±0.03
Copper+	0.98±0.02	13.7	0.42±0.04	0.54±0.03
Nickel+	1.00±0.02	10.6	0.43±0.04	0.54±0.03
Iron+	1.02±0.02	10.8	0.43±0.04	0.55±0.03

+ prepared with an aqueous solution with citric acid

Comparing the influence of the dispersion agent, the pore volume of the catalysts (for a diameter less than 7 μm) increases 18%, the pore diameter at maximum dV/dD decreases around 21%, the macropore volume increases 20% and the mesopore volume increases 13%, in relation to the catalysts prepared without citric acid. The pore diameter at maximum dV/dD decreases around 21%.

The average pore volume (for a diameter less than 7 μm) of alumina impregnated only with a solution of metal precursor is 0.86 cm³/g and for alumina impregnated with the solution with citric acid is 1.01 cm³/g. The pore diameter at maximum dv/dD is 13.3 nm and 11.7 nm, the macropore volume is 0.35 cm³/g and 0.43 cm³/g and the mesopore volume is 0.48 cm³/g and 0.55 cm³/g, respectively.

3.2.3 X-Ray diffraction

X-Ray diffraction is a technique used to analyze the elemental properties of a crystal, which normally allows the identification of crystallite phases and the evaluation of the crystallite sizes, according to their degree of crystallization.

An example is given for nickel oxide on alumina. The results demonstrate the presence of NiO with a measured angle for determine the crystal size of 43.3° (2θ). The crystal size obtained was 154±15 Å.
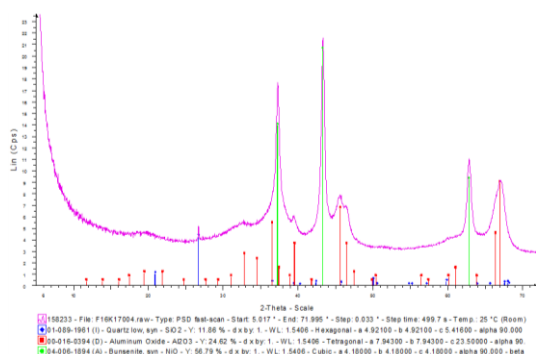
Figure 6- XRD results for nickel oxide on alumina.

3.2.4 X-Ray fluorescence

In order to determine the elemental mass loadings, X-Ray Fluorescence was used.

The results obtained for alumina support by this method are presented in the next table.

Table 3 - Metal content obtained by X-Ray Fluorescence.

Catalyst	Metal (wt. %)
Nickel	14.56±0.47
Cobalt	13.79±0.45
Iron	10.82±0.26
Zinc[+]	7.49±0.39
Copper[+]	7.48±0.39
Nickel[+]	7.34±0.26
Iron[+]	6.29±0.19

+ prepared with an aqueous solution with citric acid

3.3 Catalytic Tests

Catalytic tests for dearsenification of organo-arsenic compounds were carried out in a batch reactor. The metal catalysts previously prepared and some reference catalysts (RC1 and RC2) were tested. RC1 is composed by nickel, cobalt and molybdenum and RC2 by nickel, all of them on alumina support. A simple model feed was used in order to study the conversion of organo-arsenic compounds.

To perform the tests in the reactor, different solutions of organo-arsenic compounds were prepared. It is possible to divide them in two different groups according to the chemical compound involved: triphenylarsine and triethylarsine. To prepare this solutions, toluene was used as solvent.

The tests were performed in the Grignard reactor, closed, stirred and under hydrogen pressure. The main objective of this unit is to determine the activity and selectivity of catalysts, according to representative molecular models of a FCC gasoline. The reactor has a total volume of 500 mL and the stirring was performed at a rate of 1000 rpm. The liquid feed is stocked in the tank of 50 mL, pressurized by a line of hydrogen. The loading of the reactor was done by the introduction of the catalyst and the solvent, performed in a glove box to avoid contact with air (possibility of oxidation). The mass of catalyst introduced in the reactor was 3 g and 220 mL of solvent are used. To introduce the catalyst inside the reactor is used a basket, schematized in Figure 7.
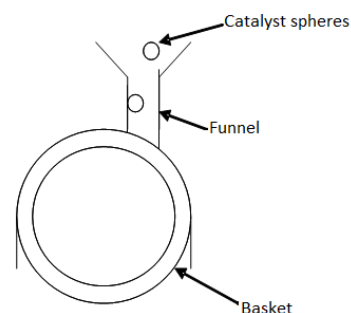

Figure 7 - Scheme of catalyst filling in the basket.

The reactional conditions were 250°C and 35 bar, using 30 mL of the concentrated feed.

The reactor liquid effluents were analyzed by gas chromatography, with data acquisition performed by the software *Galaxie*, in order to follow the concentration evolution of the arsenic compounds in the solvent, determining the conversion of the reaction. To perform this, few samples were taken with different reaction times (in minutes): at t=0 (when is introduced the concentrated feed inside the reactor); t=5; t=10; t=15; t=20; t=30; t=40; t=50; t=60; t=75; t=90; t=120. A sample of the concentrated feed was also taken in order to know the initial concentration of the arsenic compound and compare with the different concentrations over the time.

The arsenic conversion corresponds to the arsenic quantity trapped in the catalyst. The quantity of organo-arsenic compound is proportional to the peaks areas obtained by gas chromatography. The arsenic conversion was obtained from the ratio between the quantity of arsenic present at the taken samples and the initial quantity of arsenic in the concentrated feed.

4 Results and Discussion

4.1 Kinetics of Arsenic trapping

To study the influence of the catalyst type and the variation of arsenic concentration with two different organo-arsenic compounds (AsPh$_3$ and AsEt$_3$), the adsorption reaction of arsenic mass trapping is assumed as a first order reaction due to be a traditional and simple way to treat the results, the objective of this work being not to determine the order of the reaction.

$$ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

The variation of concentration with time is given by the peak areas obtained by gas chromatography of the samples taken during the reaction and, in this way, it is possible to determine not only the conversion of the reaction but also the kinetic constant of the reaction.

4.2 Reference experiments with RC1 and RC2

Two commercial trapping mass available in large quantity have been used to develop a methodology for this study. RC2 catalysts contains nickel and RC1 is composed by nickel, cobalt and molybdenum, both on alumina support.

4.2.1 Triphenylarsine (AsPh$_3$)

Four catalysts were tested in order to determine the arsenic mass trapping (conversion) for a feed containing AsPh$_3$ with low and high concentrations of arsenic.
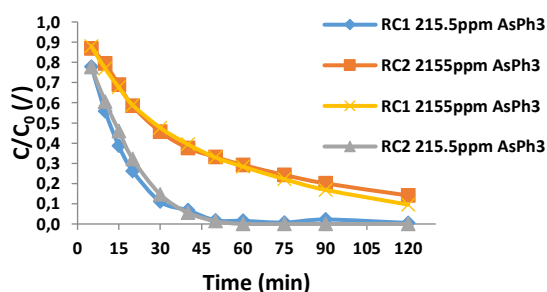

Figure 8 – Arsenic trapping of AsPh$_3$ for RC1 and RC2.

RC catalysts show high conversions, especially for low concentrations feeds of AsPh$_3$, and kinetics in the order of 10^{-2} min^{-1} (Table 4).

Table 4 – Conversion rates and kinetic constants for RC1 and RC2.

Catalyst	Arsenic concentration (ppm)	Arsenic trapped (ppm)	k (min^{-1})	Conversion (%)
RC1	2155	1940	1.9×10^{-2}	90
	215.5	214	4.5×10^{-2}	99
RC2	2155	1854	1.6×10^{-2}	86
	215.5	215.5	8.7×10^{-2}	100

4.2.2 Triethylarsine (AsEt$_3$)

The same catalysts were tested in order to determine the arsenic mass trapping (conversion) for a feed containing AsEt$_3$ with low and high concentrations of arsenic.
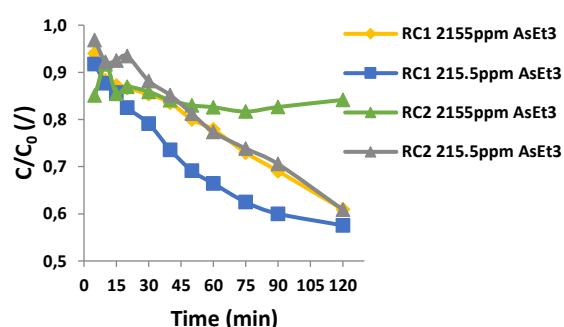

Figure 9 - Arsenic trapping of AsEt$_3$ for RC1 and RC2.

Table 5 - Conversion rates and kinetics constant for RC1 and RC2.

Catalyst	Arsenic concentration (ppm)	Arsenic trapped (ppm)	k (min^{-1})	Conversion (%)
RC1	2155	841	3×10^{-3}	39
	215.5	91	4×10^{-3}	42
RC2	2155	345	1×10^{-3}	16
	215.5	84	4×10^{-3}	39

For concentrated feeds of AsEt$_3$, RC catalysts have lower conversions compared with concentrated feeds of AsPh$_3$. The kinetics are also lower ($k=10^{-3}$ min^{-1}).

4.2.3 Reproducibility of the catalytic tests with AsPh$_3$

In order to ensure the reproducibility of the tests, two tests have been duplicated for a concentrated feed of AsPh$_3$ (2155 ppm As). The graphics show very good results, as it is possible to verify in the following figures:
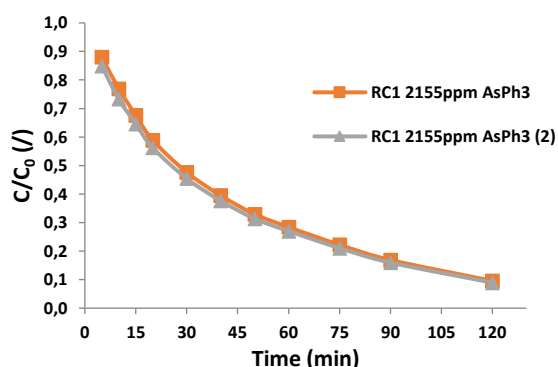
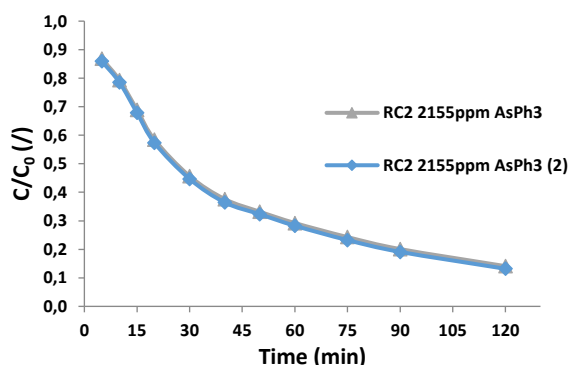**Figure 10** – Reproducibility of RC1 for high concentrations of AsPh$_3$.

Figure 11 - Reproducibility of RC2 for high concentrations of AsPh$_3$.

4.2.4 Competition between desulfurization and dearsenification

Using toluene as solvent, a concentrated feed was prepared with low concentration of As, 215.5 ppm, in the form of AsPh$_3$ and with a concentration of 1000 ppm of sulphur, in the form of 3-methylthiophene.

To determine the kinetic parameters is used the same equation explained in **chapter 4.1**.

Comparing the results for both catalysts it is possible to verify that RC1 and RC2 reach the total conversion for arsenic, however RC1 is more efficient to trap arsenic and sulphur at the same time. Knowing that the composition of RC2 is only nickel and that RC1 is composed by nickel, cobalt and molybdenum, it is possible to conclude that nickel is responsible for the arsenic trapping (as concluded previously) and the other metals play the role to increase the reaction of desulphurization. Nevertheless, nickel is also responsible for trap sulfur as can be seen in the conversion of this compound equal to 25% for RC2.

Following the curves of dearsenification without sulphur (represented by a dashed line) it is possible to conclude that the influence of sulphur to trap arsenic can be considered negligible for both catalysts in this concentration range.
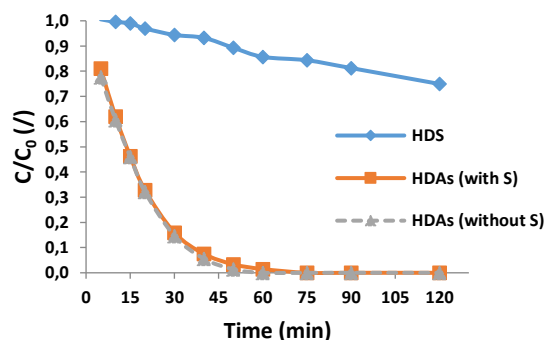

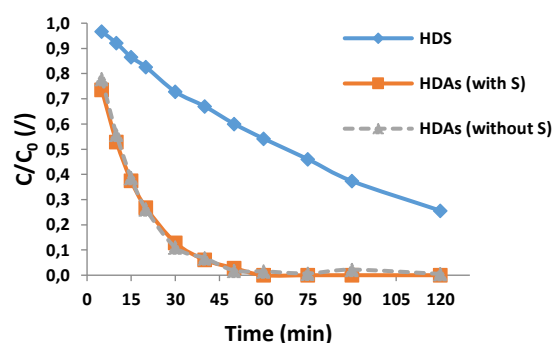**Figure 12** – Arsenic and sulphur trapping for RC2.

Figure 13 – Arsenic and sulphur trapping for RC1.

Table 6 - Arsenic and sulphur concentrations and amount of mass trapping.

Catalyst	Arsenic concentration (ppm)	Sulphur concentration (ppm)	Arsenic trapped (ppm)	Sulphur trapped (ppm)
RC2	215.5	1000	215.5	250
RC1	215.5	1000	215.5	250

Table 7 - Conversion rates, kinetic constants and selectivities for both catalysts.

Catalyst	k_{As} (min^{-1})	k_S (min^{-1})	Conversion$_{As}$ (%)	Conversion$_S$ (%)	$S_{As/S}$
RC2	7.3×10^{-2}	3.0×10^{-3}	100	25	28.2
RC1	7.3×10^{-2}	1.1×10^{-2}	100	74	6.4

4.3 Experiments with metals impregnated on alumina support

Eight catalysts were tested in order to determine the arsenic mass trapping (conversion) for a feed containing AsEt$_3$.

Metals impregnated on alumina support show a very low conversion of AsEt$_3$ with low kinetics (k≈10^{-4} min^{-1}).
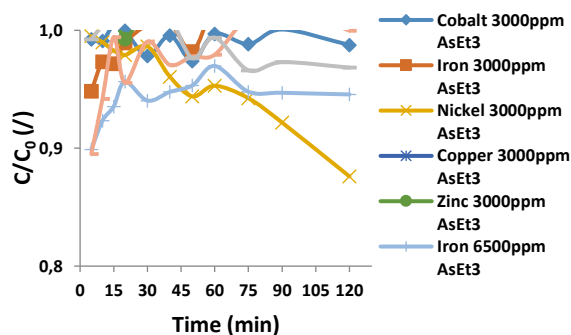
Figure 14 - Arsenic trapping of AsEt$_3$ for metals impregnated on alumina support.

Table 8 - Conversion rates and kinetics constant for metals impregnated on alumina support.

Catalyst	Arsenic concentration (ppm)	Arsenic trapped (ppm)	k (min^{-1})	Conversion (%)
Nickel	6500	195	4×10^{-4}	3
Cobalt	6500	0	0	0
Iron	6500	0	0	5
Nickel⁺	3000	360	1×10^{-3}	12
Cobalt⁺	3000	30	3×10^{-5}	1
Iron⁺	3000	0	0	0
Zinc⁺	3000	0	0	0
Copper⁺	3000	0	0	0

+ prepared with an aqueous solution with citric acid

4.4 Experiments with metals impregnated on HDS catalyst

HDS catalysts contain molybdenum and it is important to study their influence with metals impregnated, in order to compare with the other types of catalysts.

4.4.1 Triphenylarsine (AsPh$_3$)

Five catalysts were tested in order to determine the arsenic mass trapping (conversion) for a feed containing AsPh$_3$.

HDS catalysts have higher conversions for AsPh$_3$ feeds, similar to the ones observed for RC catalysts. However, the kinetics are different and nickel is responsible to improve this value ($k = 10^{-4/-2}$ min^{-1} to $k = 10^{-1}$ min^{-1}).
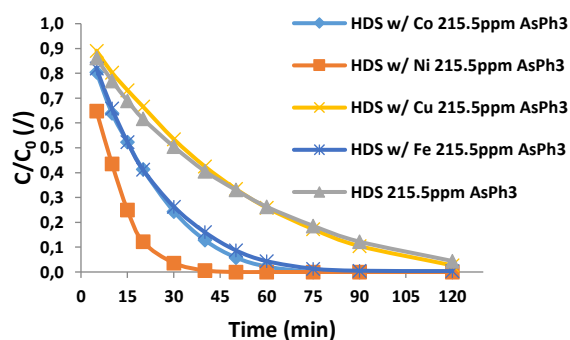

Figure 15 - Arsenic trapping of AsPh$_3$ for HDS catalysts.

Table 9 - Conversion rates and kinetics constant for HDS catalysts.

Catalyst	Arsenic concentration (ppm)	Arsenic trapped (ppm)	k (min^{-1})	Conversion (%)
HDS	215.5	207	2.5×10^{-2}	96
HDS + Cu⁺	215.5	209	2.9×10^{-4}	97
HDS + Fe⁺	215.5	215.5	5.3×10^{-4}	100
HDS + Ni⁺	215.5	215.5	1.3×10^{-1}	100
HDS + Co⁺	215.5	215.5	6.4×10^{-2}	100

+ prepared with an aqueous solution with citric acid

4.4.2 Trapping rate of AsPh$_3$

All of the HDS catalysts prepared have an arsenic trapping conversion for AsPh$_3$ around 100%, however the type of metallic precursor influences the time necessary to trap all the arsenic content.

The time required to trap all the arsenic content is inversely proportional to the kinetic constant for each catalyst, in other words, the catalyst that shows a bigger kinetic constant has a shorter required time.

Thus, knowing that the composition of the HDS catalyst is cobalt and molybdenum, the presence of nickel precursor on this catalyst increases the efficiency of mass trapping, reaching the conversion of 100% in less time.

Table 10 - Time required to trap all the arsenic content and kinetic constants.

Catalyst	Time required (min)	k (min^{-1})
HDS + Fe⁺	90	5.3×10^{-4}
HDS + Co⁺	75	6.4×10^{-2}
HDS + Ni⁺	50	1.3×10^{-1}

+ prepared with an aqueous solution with citric acid

4.5 Influence of molybdenum in the efficiency of nickel catalysts for AsEt$_3$ and AsPh$_3$

According to the results obtained in the previous chapters, the catalysts that contain nickel in their composition have higher trapping conversions. Therefore, it is interesting to study the influence of molybdenum on these type of catalysts for a concentrated feed of AsEt$_3$ and AsPh$_3$.

For both forms of concentrated feeds the influence of molybdenum is most pronounced for high concentrations of arsenic. For AsEt$_3$, the presence of molybdenum increases the conversion in around fifteen times in relation to the nickel catalyst and three times regarding the nickel catalyst prepared with citric acid (Table 11). For AsPh$_3$, the value of conversion increases 1.2 times in relation to the one prepared with citric acid.

For low concentration values, the influence of molybdenum for both feeds appears to be negligible.

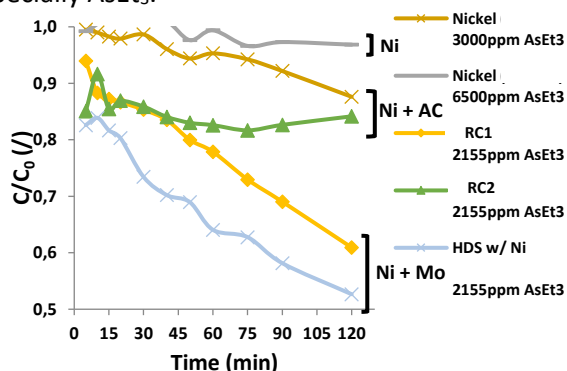Thus, molybdenum affects the trapping mass of high concentrated organo-arsenic compounds, especially AsEt$_3$.

Figure 16 - Influence of molybdenum for high and low concentrations of AsEt$_3$.

Table 11 - Influence of molybdenum for high concentration of AsEt$_3$.

Catalyst	Conversion (%)
Ni	3
Ni + AC	14
Ni + Mo	43

5 Conclusions and Future Work

The aim of this work was to study the solids efficiency to trap organo-arsenic compounds. For that purpose, catalyst preparation methods were applied, by dry impregnation using different metal precursors on two supports (AAS and HDS catalyst) and thermal treatments (calcination). By Nitrogen

Adsorption-desorption, it was possible to obtain the values for the specific surface area and porous volume and to conclude that are typical values for the commercial alumina AAS (125 m^2/g and 0.57 cm^3/g, respectively). The use of the dispersion agent during the impregnation increases the specific surface area for nickel catalysts as well as the total porous volume (24% and 8%, respectively). Mercury Porosimetry results show that the pores can be considered as mesopores (3,5-50 nm) and the use of the dispersion agent increases the pore volume of the catalysts in around 18%. X-Ray Diffraction was performed in order to determine the crystal size of the metal oxides and X-Ray Fluorescence to obtain the metal contents. To activate the catalysts, sulphurization was done with an excess of H$_2$S comparatively with the amount of metal present in the catalysts, to ensure that the sulphurization was complete.

Catalytic tests were performed in a Grignard reactor at 250°C and 35 bar of hydrogen pressure, in order to determine the conversion of the dearsenification reaction and the kinetics of As mass trapping. The metal catalysts prepared and some catalysts from *Axens* (RC1 and RC2) were tested, using a model feed composed by toluene as solvent and two different natures of organo-arsenic concentrated feeds: triethylarsine and triphenylarsine. For all the tests done, the conversions are higher for a concentrated feed of AsPh$_3$. The catalyst that shows a higher conversion even for low and high concentrations of arsenic (for both types of feeds) is RC1, composed by nickel, cobalt and molybdenum (with 90% and 39% for high concentrations of AsPh$_3$ and AsEt$_3$, respectively, and 99% and 42% for low concentrations of AsPh$_3$ and AsEt$_3$, respectively). For RC catalysts was analyzed the reproducibility of the tests and the results demonstrate very good results. The mass trapping of this feeds increases with the dispersion of the metal on the catalyst. In general, the conversions are 2 times higher for AsPh$_3$ and Nickel is the most efficient metal precursor to trap both feeds, presenting conversions of 47% for AsEt$_3$ and 100% for AsPh$_3$ and kinetic constants of 4.0×10^{-3} min^{-1} and 1.3×10^{-1} min^{-1}, respectively. Even for other metals, with low concentrations of arsenic (215.5 ppm) in form of AsPh$_3$ the conversions are 100% but the trapping rate are higher for nickel ($k = 1.3 \times 10^{-1}$ min^{-1}) followed by cobalt ($k = 6.4 \times 10^{-2}$ min^{-1}) and iron ($k = 5.3 \times 10^{-4}$ min^{-1}). With these values it is possible to conclude that for both feeds the conversions are

higher for low concentrations of arsenic. A possible explanation for these results is the excess of metal on the catalysts compared with the total amount of arsenic present in the concentrated feed. Due to that, all the active sites are more available to trap arsenic, resulting in a higher and more rapid conversion. The presence of molybdenum on the catalysts increases the conversions for high concentrations of arsenic (2155 ppm) in 3 times, especially for a concentrated feed of $AsEt_3$.

Tests with a concentrated feed of arsenic ($AsPh_3$) and sulphur (3-Me-Thi) were performed with RC catalysts, with a relative concentration similar to the observed in a real gasoline, proving that RC1 is more efficient to trap arsenic and sulphur at the same time. The conversion for arsenic is higher than for sulphur, 100% and 75% respectively, with a selectivity for arsenic of 6.4. It is also possible to conclude that nickel is more responsible to promote the reaction of dearsenification, as concluded with the previous catalytic tests, and cobalt and molybdenum to increase the reactions of desulphurization. Comparing the dearsenification reaction with and without sulphur for RC catalysts, the presence of this compound can be considered insignificant in the concentration range used. However, it is not possible to ensure that these results have the same trends than for the real gasoline.

Regarding the perspectives of this work, six important points should be studied:

- <u>Test HDS catalysts with $AsEt_3$</u>: the HDS catalysts showed similar conversions observed for the ACT catalysts with a concentrated feed of $AsPh_3$. Thus, it is interesting to discover if this type of catalysts have similar conversions for a concentrated feed of $AsEt_3$;
- <u>Change the experimental conditions of the reactor for a $AsEt_3$ feed</u>: modifying the temperature and pressure of the reaction, increasing this value, may lead to higher conversions of arsenic;
- <u>Perform catalytic tests with 3-Me-Thi using RC catalysts</u>: determine the conversion of sulphur and compare with the value obtained for a concentrated feed constituted by an organo-arsenic compound and sulphur, in order to study the influence of arsenic in the reaction of desulphurization;
- <u>Perform competition tests of dearsenification and desulphurization with HDS catalysts</u>: as explained in the first topic, it is interesting to compare the conversions, kinetics and selectivity between RC and HDS catalysts;
- <u>Test the competitivity of $AsEt_3$ and 3-Me-Thi</u>: the competition between $AsPh_3$ and 3-Me-Thi was studied and it is important to compare these results but with a feed composed by $AsEt_3$;
- <u>Do the same catalytic tests but with a feed composed by an olefin, an organo-arsenic compound ($AsPh_3$ and $AsEt_3$) and sulphur (3-Me-Thi)</u>: study the competition between all these compounds, determining the conversions, kinetics and selectivity of each compound.

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