Oil & Gas Science and Technology - Rev. IFP Energies nouvelles **74**, 22 (2019)
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https://doi.org/10.2516/ogst/2018094

Available online at:
ogst.ifpenergiesnouvelles.fr

PREPA12 - 12th Symposium on the Scientific Bases for the Preparation of Heterogeneous Catalysts
E. Gaigneaux, J. Martens, D. Uzio, D. Debecker, M. Devillers, S. Hermans and C. Kirschhock (Guest editors)

REGULAR ARTICLE

OPEN ACCESS

Scale-up of a NiMoP/γAl_2O_3 catalyst for the hydrotreating and mild hydrocracking of heavy gasoil

Ricardo Prada Silvy*

Chasm Advanced Materials, 2501 Technology Place, Norman, Oklahoma 73071, USA

Received: 6 June 2018 / Accepted: 30 November 2018

Abstract. This contribution shows the acquired experience during the scale-up of a NiMoP/γAl_2O_3 catalyst employed for the hydrotreating and mild hydrocracking of heavy gasoil. Three different strategies were adopted for preparing catalyst batches at pilot scale. They consisted on co-impregnation of γ-alumina extrudates with aqueous solutions containing Ni and Mo salts and phosphoric acid in one or two successive steps. The textural, chemical composition, mechanical strength, metallic surface dispersion and elemental radial distribution profile properties were influenced by the impregnation procedure employed. The co-impregnation with diluted Ni, Mo and P solutions in two successive steps is the best way to prepare the catalyst. This procedure provides a catalyst that exhibits better physico-chemical properties and catalytic activity profile than the other impregnation methods investigated. Heat and mass transfer limitations became very important when preparing catalysts in large quantities. The diffusion intra-particle and extra-particle was observed influenced by the density and viscosity properties of the metallic solution, the liquid-solid contact angle, the reactivity of phosphate, polymolybdate and phosphomolybdate species with the alumina surface hydroxyl groups, the raise of temperature produced in the solid particles during the initial impregnation step and the porosity properties of the catalyst support. It was concluded that the fine control of the metal distribution on the alumina surface during the impregnation is crucial for producing highly active uniform catalysts.

1 Introduction

The process for producing industrial catalysts involves a well-defined series of unit operations of chemical engineering and large automatized equipment combined in such ways that allow in a flexible manner the continuous manufacture of any commercial product. The catalyst industry account with professionals well-skilled in different disciplines (mainly chemists, engineers and related careers) having good understanding of the physical-chemical transformations occurring during each one of the preparation steps, many years' experience in this field and commercial know-how. Catalyst makers prefer to keep their product formulations and manufacturing processes as a trade secret, rather than disclosing sensitive information in patents that will eventually become public domain. This business strategy avoids teaching competitor companies about their technological advances and state of art. For this reason, the number of patents or literature published in this field is becoming increasingly scarce. The commercial catalysts production constitutes a perfect balanced combination between art and science [1–3].

Several years of intensive research and development works can take for developing a new catalyst with improved activity and selectivity properties, for optimizing its preparation parameters at different scales and for starting its commercial production. Some of these new developments do not become commercial products because of technical or economic limitations. According to catalyst makers, catalytic materials, also called lab prototypes, become catalysts when these materials are used in industrial processes or their scaling-up is technically and economically demonstrated.

The scaling-up is considered the critical step in the development and commercialization of a new technology. In this development stage, a potential catalytic material formulation made in the laboratory in grams quantities, is to be produced in some kilograms, hundreds of kilograms or metric tons quantities at a reasonable rate and economy. At pilot scale, which represents the intermediate step between laboratory and semi commercial production, sometimes hundreds of kilograms of material are produced. The increasing in size of catalyst production is extremely complicated to accomplish, because the physico-chemical transformations occurring during each preparation step and the heat and mass transfer limitations become more important when working with larger quantities of chemical products

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* Corresponding author: `rprada@chasmtek.com`

and larger size equipment. Special attention to details during the catalyst preparation at large scale is crucial because a small change introduced in the support impregnation, drying, or calcination processes can considerably affect the active phase dispersion and composition and the activity properties of the catalyst. Therefore, a good understanding of what is involved in terms of scaling-up, even at lab scale, greatly facilitates the process and may mean the difference between success and failure [1–6].

Few years ago, the catalyst scaling up was not considered a research priority in the academic community, perhaps because the art of catalyst scale-up was not well understood due to the limited accessibility to technical information and the lack of knowledge about the needs of the industrial sector. This situation, nowadays, is changing; in fact some university laboratories and small companies founded by professionals having industrial experience have made significant investments in pilot scale equipment of catalyst preparation and analytical capabilities to offer consulting services to the industry in this field. This has been motivating greater rapprochement between both academic and industrial sectors to work together in the development of new materials and resolution of technical problems associated with the manufacture of new catalysts [2, 4, 7–9].

The present contribution shows the acquired experience during the scaling-up of a typical NiMoP/γAl_2O_3 catalyst used for the Hydrotreating (HDT) and Mild Hydrocracking (MHCK) of heavy gas oils. Essentially, we investigate the parameters controlling the impregnation step when employing the incipient wetness technique, a standard catalyst preparation method employed by catalyst producers. For this purpose, different strategies were adopted for the preparation of catalyst batches at pilot scale (several kilograms catalyst). The different prepared catalyst batches were characterized by using the following physico-chemical techniques of analysis: BET surface area, Bulk Crushing Strength, X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). The activity properties for the Hydrodesulfurization (HDS), Hydrodenitrogenation (HDN), Aromatic Hydrogenation (HDA) and Hydrocracking (HCK) reactions using heavy gas oil were investigated.

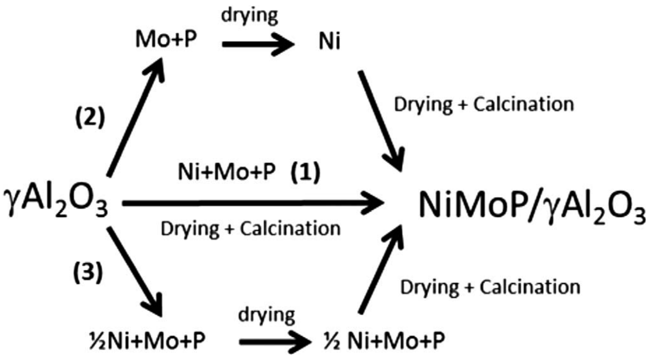
2 Experimental

2.1 Catalysts preparation conditions and scale-up strategies

The NiMoP/γAl_2O_3 catalyst developed at lab scale, denoted in the following as reference material, was prepared by wet impregnation method. About 50 g of γ-alumina extrudates having 1.4 mm diameter, 256 m^2/g BET surface area, 0.70 mL/g pore volume and 8 kg/cm^2 crush strength, were dipped into a metallic aqueous solution containing ammonium heptamolybdate, nickel nitrate and phosphoric acid in a glass container for the contact time necessary for total pore filling and metal adsorption. The impregnated material was drained, aged, and then dried at 120 °C for 4 h and calcined in air flow at 500 °C for 4 h.

The incipient wetness impregnation method, also called pore volume impregnation or dry impregnation method, was employed for the catalyst scaling-up study. This method is extensively used by catalyst makers due to its simple execution, good control of active metal composition in the finished product, safer operation, and low cost.

Three different strategies were adopted to prepare NiMoP/γAl_2O_3 catalysts batches at pilot scale. They are represented in a simplified manner in Schema 1.



Schema 1. Strategies adopted to prepare NiMoP/γAl_2O_3 catalysts at pilot scale.

A first NiMoP/γAl_2O_3 catalyst batch was prepared according to the following procedure. About five kilograms of γAl_2O_3 support was placed in rotary drum equipment and then the solid was sprinkled with a Ni, Mo and P solution by mean of a sprayer nozzle. The metallic solution contained the equivalent chemical composition of the reference catalyst. Drying and calcination steps were conducted under the same conditions as above employed. In the following, this preparation procedure will be denoted as NiMoP-1.

A second NiMoP/γAl_2O_3 catalyst batch was prepared by two successive impregnation steps. This is a standard procedure employed by catalyst makers where; molybdenum or tungsten active metals are first supported on the alumina and then the nickel or cobalt promoters in a second impregnation step. In this case, the support was co-impregnated with a Mo and P solution followed by a drying step and then the solid was impregnated with a Ni solution. Drying and calcination steps were conducted under the above described experimental conditions. In the following, this preparation procedure will be denoted as MoP->Ni.

A third NiMoP/γAl_2O_3 catalyst batch was also prepared in two successive co-impregnation steps. The initial Ni, Mo, P solution employed for the first catalyst batch preparation was split in two parts and then they were diluted with DeIonized (DI) water until completion of the pore filling volume of the alumina support. The impregnated material was dried and calcined under the same experimental conditions above described. In the following, this preparation procedure will be denoted as NiMoP-2.

2.2 Characterization

BET surface area, pore volume and diameter distribution were performed using the multipoint method by N_2 adsorption on a Micromeritics ASAP 2400. Samples were first dried at 400 °C for about 4 h under vacuum before the analysis. Pore size distribution was determined through the N_2 desorption isotherm and C_{BET} values are reported for all samples.

Bulk crushing strength was determined by using the Shell N° SMS1471 method described as follows. The samples were first dried in an oven at 300 °C during 2 h. About 20 cc of the sample was taken and placed in the cell and covered with 5 cc of steel balls diameter 3 mm, and then put on the anvil of the stress transducer. Increasing force is applied by the piston to the catalyst in stages of 3 min. The fines obtained at the different pressure stages are separated by sieving, and weighed: particles which pass through the mesh of a sieve of opening 420 μm are considered as fines. The Bulk Crushing Strength is estimated according to the following equation:

$$P = \frac{F}{A},$$

where F is the force to be applied on the catalyst in Kgf to produce 0.5% fines and A is the cross-sectional area of the sample holder in cm^2.

X-ray Photoelectron Spectra (XPS) of the catalysts were recorded using a Leybold Heraeus LHS-121 apparatus equipped with a computer system, which allows the determination of peak areas. Analysis were performed in an ultra-high vacuum system at a base pressure of 1.2×10^{-9} mbar using an Al K_α radiation ($E = 1486$ eV) of the source. All samples were previously ground and then pressed into the sample holders. Signals corresponding to C_{1s}, Al_{2s}, Mo_{3p}, Ni_{2p} and P_{2p} energy levels were recorded. The C_{1s} energy level (284.5 eV) was taken as a reference originating from adventitious carbon contamination to account for charging effects. Atomic surface dispersion ($I(e) \times 100/INi_{2p}+IMo_{3p}+IP_{2p}+IAl_{2s}$) of supported elements (e) was determined from the peak integrated areas and the sensitivity factors provided by the equipment manufacturer.

Elemental radial profile distribution in the catalyst extrudates was obtained using Scanning Electron Microscopy (SEM) technique. An ISI-60 apparatus equipped with energy dispersive X-ray analyzed (Kevex S-7000) was used for these measurements. Catalyst extrudates were mounted on an epoxy slide and then polished before scanning under the electron beam.

2.3 Catalytic testing

Catalytic properties for HDS, HDN, HDA and MHCK reactions of the different catalyst batches were evaluated in a high pressure fixed bed pilot reactor, 60 cc of catalyst loading and employing a heavy gas oil feedstock containing 1.6 wt% S, 1206 ppm N, 58 wt% aromatics and 52% of 370^+ °C distillation fractions. Hydrocracking capacity (MHCK) of the different catalysts was determined by the selective conversion of the 370 °C fraction in the heavy gas oil into middle distillates (jet fuel, diesel and kerosene) employing the simulate distillation analysis. The system was operated at a total pressure of 5.5 MPa, temperature of 380 °C, space velocity (LHSV) of 0.65 h^{-1}, H_2/HC ratio of 600 Nm^3/m^3. Results are reported under steady state reaction conditions that were reached after several hours on stream.

3 Results

The influence of the preparation procedure on the textural and mechanical properties of the NiMoP/γAl_2O_3 catalysts is shown in Table 1. Both, the reference and NiMoP-2 catalysts show similar textural and mechanical properties. However, the preparation procedures NiMoP-1 and MoP-> Ni, show lower BET surface area, pore volume and bulk crushing strength values. The C_{BET} constant value for the different analyzed samples varies in the 101–114 range. This constant is most frequent between 50 and 300 when using nitrogen at 77 K [10].

Table 2 shows the pore size distribution of the different prepared catalyst batches. For all samples, it is observed that more than 80% of the pores are in the 30–90 Å range. Both, the reference and the NiMoP-2 catalysts show similar pore size distribution profile. The micro porosity (pores <30 Å) of the NiMoP-1 catalyst slightly increased while, the MoP->Ni samples shows a larger proportion of pores having diameters >60 Å.

Chemical composition of the different NiMoP/γAl_2O_3 catalyst batches is shown in Table 3. Very small differences in MoO_3, NiO and P_2O_5 content are observed for the NiMoP-2, MoP->Ni and the reference catalyst. However, a slight loss in metallic composition can be seen for the catalyst prepared according to the NiMoP-1 procedure.

Table 4 shows the XPS results corresponding to the different NiMoP/γAl_2O_3 catalyst batches. Relative intensities $I(e)/(INi_{2p}+Mi_{3p}+P_{2p}+Al_{2s})$ are reported for all samples. Metallic surface dispersion is practically the same for both NiMoP/γAl_2O_3 reference and NiMoP-2 catalysts. Lower metallic surface dispersion values are observed for NiMoP-1 and MoP->Ni catalyst batches.

The SEM micrographs in Figure 1 show radial distribution profile of Mo, Ni and P elements through the cross section of the catalyst extrudates. The Ni radial distribution is uniform for all prepared catalysts, however significant differences in Mo and P radial distribution profile can be observed for the different prepared catalyst batches. For both, the reference and the NiMoP-2 catalysts, Mo and P are uniformly distributed through the cross section of the catalyst extrudates. For both NiMoP-1 and MoP->Ni catalysts, Mo and P show a non-uniform radial distribution profile; both elements are preferentially adsorbed at the outer surface of the extrudate showing an eggshell-type distribution profile.

Activity results corresponding to the different NiMoP/γAl_2O_3 catalysts are shown in Figure 2. The NiMoP-2 catalyst shows slightly higher conversion level in HDS, HDN, HDA and MHCK than the reference catalyst. However, both MoP->Ni and NiMoP-1 procedures give catalyst with lower levels of activity, being the NiMoP-1 catalyst the less active of the prepared catalyst batches.

4 Discussion

The above results clearly showed how the textural and mechanical properties, the chemical composition, the surface active metal dispersion, and the elemental radial

Table 1. Textural and mechanical properties of the NiMoP/γAl_2O_3 prepared catalyst batches.

Sample	BET surface area (m^2/g)	Pore volume (mL/g)	C_{BET}	Bulk crushing strength (kg/cm^2)
Reference catalyst	184	0.44	110	21
NiMoP-1	160	0.38	114	15
MoP->Ni	175	0.41	103	16
NiMoP-2	189	0.46	101	20

Table 2. Pore size distribution of the different NiMoP/γAl_2O_3 prepared catalyst batches.

	<30 Å	30–60 Å	60–90 Å	90–150 Å	150–300 Å	>300 Å
Reference catalyst	0.6	52.5	34.5	5.2	2.6	4.6
NiMoP-1	5.3	55.1	26.0	7.6	1.5	4.5
MoP->Ni	0.0	37.8	43.8	13.5	1.9	3.0
NiMoP-2	1.8	50.0	35.0	6.3	2.1	4.8

Table 3. Chemical composition of the NiMoP/γAl_2O_3 prepared catalysts.

Sample	MoO_3 (wt%)	NiO (wt%)	P_2O_5 (wt%)
Reference catalyst	15.5	5.5	7.5
NiMoP-1	14.8	4.7	7.0
MoP->Ni	15.2	5.0	7.0
NiMoP-2	15.3	5.2	7.5

distribution through the cross section of the alumina extrudates are strongly influenced by the catalyst preparation procedure employed. Co-impregnation of alumina in two successive steps with Ni, Mo and P diluted solutions (NiMoP-2) gave a catalyst with the following features:

- The largest specific surface area and porous volume.
- Similar pore size distribution, mechanical strength, chemical composition and active metal surface dispersion properties than the reference NiMoP/γAl_2O_3 catalyst.
- Homogeneous Mo, Ni and P radial distribution profile.
- The higher level of conversion for the HDS, HDN, HDA and MHC reactions.

To facilitate the discussion of our results, let us first describe the observed behavior during the preparation of the catalyst by impregnation in one single step (NiMoP-1). Subsequently, we will try to explain the obtained results by taking into account fundamental studies published in the literature that deal with the chemistry of Ni, Mo and P species in solution and their mechanism of adsorption on alumina. Finally, we will examine the behavior observed during the preparation of the catalysts in two consecutive stages of impregnation (MoP->Ni and NiMoP-2 catalyst batches).

4.1 NiMoP-1 catalyst batch preparation

As mentioned before, our first strategy was to prepare a catalyst by incipient wetness impregnation method in a single step having the same chemical composition than the NiMoP/γAl_2O_3 reference material. The results of Tables 1–4 and Figure 2 clearly indicated that this procedure gave catalysts with lower specific surface area and porous volume, mechanical strength properties, chemical composition, surface dispersion and catalytic activity properties than the other catalyst preparation procedures. SEM analysis of Figure 1 revealed the formation of a reaction front where phosphate was preferentially adsorbed at the outer surface of the alumina extrudates, molybdenum radial distribution was not uniform while Ni showed a flat radial distribution profile. By breaking some catalyst extrudates in two halves, it was observed that some particles showed a light green color and others a darker color at the core of the particles confirming the heterogeneity of the impregnated material.

When the metal solution was initially sprayed on the alumina extrudates surface, it produced an increase in the temperature of approximately 55–60 °C in the solid as well as in the rotary drum walls, causing a flash drying of the metallic solution. After spraying a significant amount of solution on the solid, it was observed that the extrudates began to stick with each other which could indicate a loss of the solution uptake capacity of the alumina support. A small volume of the metal solution remained adhered to the rotary drum walls which could explain the lower chemical composition and XPS intensity ratio observed for this catalyst batch.

In view of these results, we decided to determine the factors affecting the preparation of the NiMoP-1 catalyst batch with the aim to design a new catalyst preparation strategy. For this purpose, we proceeded to determine the properties of the impregnating solution and its stability as a function of the aging time. The turbid green aspect NiMoP-1 solution showed a density of 1.55 g/cc and a viscosity of 5.39 cSt. After 24 h of aging, the precipitation of

Table 4. XPS results of the NiMoP/γAl_2O_3 prepared catalysts.

% Dispersion	Ni/Ni+Mo+P+Al	Mo/Ni+Mo+P+Al	P/Ni+Mo+P+Al
Reference catalyst	2.68	8.28	5.34
NiMoP-1	2.75	6.36	5.09
MoP->Ni	2.72	6.80	5.43
NiMoP-2	2.66	8.03	6.07

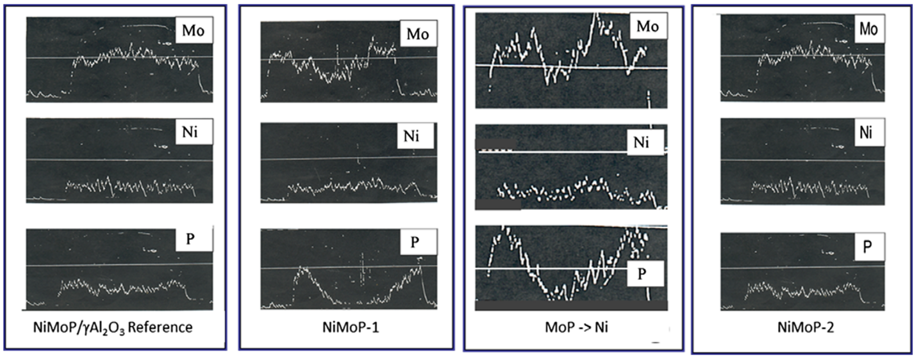


Fig. 1. Scanning electron microscopy results of NiMoP/γAl_2O_3 prepared catalysts.

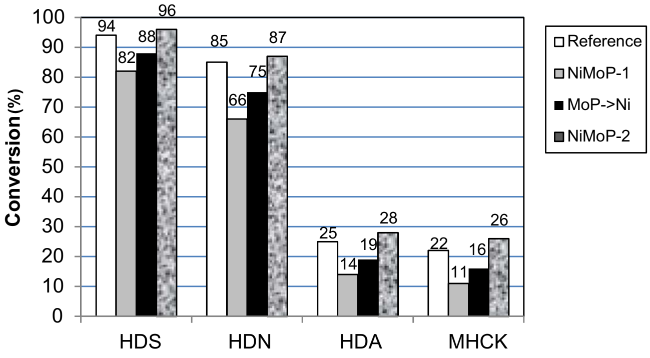


Fig. 2. Catalytic activity properties of the NiMoP/γAl_2O_3 catalysts.

small yellowish-green particles and others of white color was observed, that is clear evidence of the instability of the NiMoP-1 solution. Instable metallic solutions represent a high technical and economic risk at the moment of producing commercial catalysts. For such reasons, catalyst makers first check these properties before deciding to prepare large volumes of metallic solutions in their facilities.

Heat transfer limitations occurring during the impregnation are rarely considered in the literature, because the heat released when preparing catalysts at lab scale is very low. However, at larger production scales, heat transfer limitations become critical and this requires immediate attention in the operation to avoid modifications in textural and mechanical properties of the material, changes in the kinetics of adsorption of the metal ions in solution, metallic salts decomposition and mass transfer limitations intra-granular or extra-granular.

The rapid increase of the temperature in the solid observed at the beginning of the impregnation step can be explained by two simultaneous effects: (i) the heat released by the wetting of the alumina, which is a typical behavior of catalyst supports having large internal surface area. These supports can burst at the moment of wetting under the effect of capillary forces and (ii) the heat released by the neutralization reaction between the phosphoric acid molecules in solution and the surface basic hydroxyl groups of the alumina. The heat release due to the neutralization reaction is higher than the heat of wetting of the alumina support. If the local temperature is not well controlled during the solution addition, the porosity of the material could be affected by an increase of the pressure inside the pores.

To avoid thermal effects during the impregnation step, the practice of different techniques can be employed. The simplest technique is to spray a certain volume of DI water to introduce some moisture, paying special attention the temperature rise during addition, before starting to add the metallic solution. Some catalyst makers pretreat the alumina support with steam to reduce the tendency to burst [3]. Another technique is to pretreat the support with a wetting agent, for instance a solvent less polar (such as alcohols, pentane, cyclohexane, etc.) having lower heat adsorption capacity than water [3, 11]. Among the benefits provided by the wetting agents are: (i) it improves the solubility of the metallic salts, (ii) it modifies the solution surface tension by decreasing liquid-solid contact angle facilitating in this manner the diffusion of the liquid inside the pores and (iii) it reduces significantly the impregnation and aging times.

Other fundamental aspects to consider when producing catalysts at pilot or commercial scales are the mass transfer limitations. In porous catalyst supports diffusional limitations intra-granular (capillary diffusion) or extra-granular take place. The rate of diffusion depends on the porous structure of the support, the solution properties (density and viscosity), solution-solid contact angle, and surface ion-exchange reactions. Very often, ion exchange is very rapid, in particular when it is an acid-base exchange reaction. In such case, the rate of diffusion becomes limiting for the overall process, and a reaction front takes place at the outer surface of the extrudates [11]. For the catalyst batch prepared according to the NiMoP-1 procedure, it was evidenced by SEM analysis a reaction front between P and Mo ions with the hydroxyl sites of the alumina surface. Because the alumina surface is positively charged at acid solution pH, the repulsion forces between these surface charges with the Ni^{+2} ions makes their diffusion inside the pores easier. This satisfactorily would explain the Ni flat radial distribution profile observed by SEM analysis for all prepared catalyst batches.

Let us now examine some works published in the literature dealing with the behavior of the chemistry of the Ni, Mo and P species in solution and their proposed adsorption mechanism on alumina.

When phosphoric acid is added to a solution containing ammonium heptamolybdate; pentamolybdodiphosphate complex ($P_2Mo_5O_{23}^{6-}$) is formed [12, 13]. In these compounds, two phosphate groups in tetrahedral coordination with oxygen atoms are located above and below the planar of 5-members ring of MoO_6 octahedral. The phosphate groups in pentamolybdodiphosphate complex, to differences of other types of P–Mo heteropolycompounds, are accessible to interact with the alumina surface. At low solution pH, the predominant phosphomolybdate species is the protonated form [14, 15].

$$16H^+ + 5Mo_7O_{24}^{2-} + 14H_2PO_4^- \Longleftrightarrow 7H_2P_2Mo_5O_{24}^{4-} + 15\,H_2O \tag{1}$$

According to equation (1), the decomposition of phosphomolybdate complex into molybdate and phosphate is favored by a rise of solution pH, which would shift the chemical equilibrium to the left. In a solution containing the stoichiometric P/Mo molar ratio of 0.4; Cheng and Luthra [12] observed by NMR technique that a small amount of phosphorus remains in form of phosphate, which suggests the existence of a chemical equilibrium between phosphate and molybdate ions in solution. These researchers also observed that pentamolybdodiphosphate complex decomposes to phosphate and molybdate upon contact with alumina [11]. Equilibrium between heptamolybdate ions ($Mo_7O_{24}^{6-}$) and molybdate ions (MoO_4^{2-}) is also affected by rise in pH (Eq. (2)) [15, 16].

$$Mo_7O_{24}^{6-} + 4H_2O \Longleftrightarrow 7MoO_4^{2-} + 8H^+ \tag{2}$$

When $H_2P_2Mo_5O_{24}^{4-}$ complex decompose by contact with alumina surface, competition between phosphate and molybdate ions takes place for the same adsorption sites. Since phosphate ions interact more strongly with the alumina surface than molybdate ions, phosphate ions are preferentially adsorbed at the outer surface of the alumina while molybdate ions diffuse and adsorb inside the extrudates [17].

The adsorption mechanism of phosphate species on alumina was investigated by Morales *et al.* [18]. When phosphorus is adsorbed on the alumina surface, the authors observed similar effects to that showed in Table 1 where the surface area and pore volume decreased significantly. Two explanations were proposed; (i) phosphorous might behave as a corrosive agent breaking some micropores of the support with a consequent increase in macroporosity. The results of the MoP->Ni catalyst batch of Table 2 showed a larger proportion of pores having diameters >60 Å and (ii) phosphorus species can be directly adsorbed at the pore mouth blocking the support micropores. The thermal effects produced during the initial addition of the metal solution on the alumina extrudates could amplify some physico-chemical processes, not observable when preparing catalysts at laboratory scale. For instance; the rise in temperature in the solid during impregnation could favor; (i) the decomposition of phosphomolybdate complex on the alumina surface accelerating in this manner the kinetics of adsorption of phosphate ions, (ii) the pore blockage by phosphate adsorbed species can inhibit other ions to enter inside the pores and therefore the solution uptake capacity of the support can be affected, (iii) the digestion of some alumina particles could take place by contact with the hot strong acid solution. The results of Table 2 indicated a significant decrease in the percentage of pores having 60–90 Å diameter and simultaneous increase in pores having <60 Å diameter for the NiMoP-1 sample, relative to the reference and NiMoP-2 catalysts. In this case, the preferential deposition of phosphate in the pore mouth reduces the pore diameters while creating a slight increase (~5%) in microporosity.

In summary, the preparation of the NiMoP-1 batch represents a typical example where the rate of capillary diffusion intra-granular and extra-granular is limiting the overall process. The identified factors that caused a non-homogeneous metal distribution and significant changes in textural properties of the catalyst support are related to: (i) the high density and viscosity of the metallic solution, (ii) high liquid-solid contact angle and (iii) the rise of the temperature during the initial impregnation step which facilitated the decomposition of the phosphomolybdate complex and increased the reactivity between the phosphate species and the alumina surface causing a reaction front. These identified factors made the preparation of the NiMoP/γAl_2O_3 by one step impregnation procedure a failure.

4.2 MoP->Ni and NiMoP-2 catalyst batches

Metallic solutions containing both nickel or cobalt and molybdate salts are unstable, thus $NiMoO_4$ or $CoMoO_4$ phases start to precipitate when the solution pH is higher than 3.0 [3]. For such reasons, sequential impregnations are used in the practice where the alumina support is first impregnated with the molybdenum solution and then the nickel or cobalt promoter is supported. Additives such as phosphoric acid, citric acid, hydrogen peroxide, chelating agents, etc. prevent the precipitation of nickel molybdate or cobalt molybdate mixed phases when both metals are in the same solution.

In previous work, we have investigated the effect of the impregnation sequence on the texture, surface acidity and metal dispersion in MoP/γAl_2O_3 catalysts. We concluded that co-impregnation procedure gives catalysts with improved textural properties, surface acidity, mechanical strength, metal dispersion and homogeneous elemental radial distribution profile than sequential impregnation method [17]. As discussed above, co-impregnation procedure leads to the Mo-P heteropoly-compound formation, while sequential impregnations with phosphorus induce to the formation of bulk MoO_3 species. Jian and Prins [15] and Chadwick *et al.* [19], also observed that molybdenum dispersion improved when Mo and P are co-impregnated. Lopez Cordero *et al.* [20] by using sequential impregnation in the preparation of MoP catalysts, concluded that phosphorus leads to the formation of poorly dispersed molybdate species such as; multilayered molybdate, bulk MoO_3 and $Al_2(MoO_4)_3$.

Supported by previous investigation conducted in our laboratories together with the results obtained by other researchers on the preparation of MoP/γAl_2O_3 catalysts by co-impregnation method [14, 15, 17, 19], a second NiMoP/γAl_2O_3 catalyst batch was prepared where MoP was first impregnated and then Ni (MoP->Ni procedure). The density and viscosity values of the MoP solution were in this case lower than the NiMoP-1 solution (1.36 g/cc and 2.44 cSt, respectively). The colorless MoP solution remained stable for several days. In this case, the spraying of the metallic solution into the alumina extrudates was controlled to avoid an excessive temperature rise. In spite of this, the temperature in the solid increased to approximately 45–50 °C.

As the results of Tables 1–3 indicated, the textural properties and chemical composition of this new NiMoP/γAl_2O_3 catalyst batch were comparable with the reference catalyst. However, this catalyst showed lower mechanical strength and metal surface dispersion values. SEM images of Figure 1, showed a substantial improvement of the elemental radial distribution profile as compared with the NiMoP-1 catalyst. Both Ni and Mo showed uniform radial distribution profile, while P still showed some heterogeneities.

The catalytic properties of the MoP->Ni catalyst batch significantly improved regarding the NiMoP-1 catalyst batch, but this catalyst batch is still less active than the reference material (Fig. 2). However, in spite of the improvements achieved in the physico-chemical and catalytic properties when the catalyst was prepared by the MoP->Ni procedure, it is believed in this case, that the rate of diffusion intra-granular and extra-granular is still limiting the overall process. The MoP solution density and viscosity and the phosphorus reactivity with the alumina surface are still high.

The results obtained with the previous NiMoP/γAl_2O_3 catalyst batches allow us to design a new preparation strategy. According to our observations, there is high probability to minimize the impact over the metals diffusion inside the particles produced by the high solution density and viscosity and the high reactivity of the phosphate species if the alumina is co-impregnated with diluted metallic solutions (NiMoP-2 procedure). The aspect of this solution was translucent green color; it remained stable for several days, its density and viscosity were 1.25 g/cc and 1.31 cSt respectively. A good solution uptake capacity was observed during the impregnation. The rise of temperature in the rotary drum remained lower, in this case, than in previous catalyst batches preparations ($\leq$45 °C).

Our hypothesis can be confirmed by the results of Tables 1–4 and Figure 1, where the NiMoP-2 preparation procedure gave a catalyst with improved physico-chemical, surface, and catalytic properties. When phosphorus is uniformly distributed through the cross section of the alumina extrudates, the beneficial effect of this additive for improving the mechanical properties of the catalyst support becomes more noticeable.

Some relevant studies from the literature concerning the stability of phosphomolybdate species during their surface adsorption on different catalyst supports may help in the interpretation of our results. The stability of phosphomolybdate by contact with alumina was investigated by several researchers [14–17, 21, 22]. Cheng and Luthra [16] investigated the adsorption of different phosphomolybdate compounds on γAl_2O_3 and SiO_2 spheres using the NMR technique. These compounds were supported by incipient wetness impregnation method. The pentamolybdodiphosphate complex decomposes slowly upon contact with alumina surface into phosphate and molybdate species giving a catalyst phosphorus-rich shell and a molybdenum-rich core. The authors concluded that an excess of phosphorus inhibits the decomposition of pentamolybdodiphosphate complex. They also observed that 12-molybdophosphate and the dimeric 9-molybdophosphate adsorbs on the alumina intact. Prada Silvy *et al.* [17], also obtained uniform Mo and P distribution profile in alumina extrudates when adding an excess of phosphoric acid in the MoP co-impregnating solution. Jian and Prins [15], observed that controlling the solution pH by addition of nitric acid and the phosphorus content, phosphomolybdates compounds interact less strongly with alumina and then they can diffuse inside the particles attaining an uniform Mo and P distribution. Atanasova and Halachev [21], investigated by IR spectroscopy the different phases present in NiMoP/γAl_2O_3 catalysts prepared by co-impregnation. The authors observed signals corresponding to $AlPO_4$ and Ni-Mo-P heteropolycompounds. We also observed by IR spectroscopy of NiMoP/γAl_2O_3 and CoMoP/γAl_2O_3 calcined catalysts the presence of a band at about 1055 cm^{-1} that correspond to P-O-Mo vibrations in phosphomolybdate compounds [17]. Contrary to Lopez Cordero *et al.* [20], bulk MoO_3 and $Al_2(MoO_4)_3$ phases were not detected in the samples. High phosphorus loading leads to an increase in degree of molybdenum polymerization and to changes in the ratio between the different types of heteropolycompounds, Ni-Mo-P/Al-Mo ratio increases with increasing phosphorus loading.

Table 5. Surface tension, liquid-solid contact angle and capillary pressure.

Impregnating solution	Surface tension (γ) (mN/m)	Contact angle (θ) (°)	Δp (N/m^2)10^7
DI water	73.5	50.2	2.02
NiMoP-1	70.9	69.9	1.08
MoP	76.7	65.8	1.40
NiMoP-2	75.3	58.9	1.73

Taking into account our results together with those of the literature, we can propose that for the NiMoP-2 catalysts preparation procedure, phosphomolybdate complex remained stable during impregnation. In this case, the rate of diffusion intra-granular and extra-granular is faster than the rate of adsorption of phosphomolybdate complex on the alumina surface. The adsorption strength of these compounds would be different from that of phosphate and molybdate. Consequently, Mo and P attain a uniform distribution profile.

Because the uptake of metallic solution into the pores occurs due to capillary diffusion, we have estimated the capillary pressure (Δp) by using Young-Laplace correlation represented by equation (3) [23]:

$$\Delta \mathrm{p} = (2\gamma / r_{\mathrm{p}}) \cos \theta \tag{3}$$

where γ is the interfacial surface tension, r_{p} is the pore radius and θ is the liquid-solid contact angle. It is clear that the pressure difference depends inversely on the pore size, so the liquid is preferentially sucked up by the smaller pores.

Interfacial surface tension (γ) of the different impregnating solutions were determined using the Wilhelmy plate method [24]. Solution-solid contact angle was determined by using tablets of mesoporous γ-alumina support having about 2.0 cm diameter and NiMoP solutions droplets of about 4.5 μL volume. The contact angle values are the average of five independent measurements. The mean pore diameter of the γ-alumina support obtained by BET method is 9.0 nm.

The results of capillary pressure for the different impregnating solutions are shown in Table 5. As it can be seen, the surface tension values did not vary significantly among the different metallic solution. However, the capillary pressure decreased by a factor of 2, with respect to the Δp value obtained for DI water, for the NiMoP-1 solution. In this case, the liquid-solid contact angle is the main parameter influencing on the solution diffusion inside the pores. Higher is the liquid-solid contact angle, lower is the pressure difference, therefore the metal solution diffusion inside the pores will be lower.

We have also investigated the effect of the aging time and drying conditions on the elemental radial distribution and chemical composition of the NiMoP-2 catalyst. When the impregnated material was not aged, we observed that both Mo and P did not reach the core of the alumina extrudate. This is another important parameter to consider at the moment of producing catalysts at large scale. These results will be published elsewhere [25].

5 Conclusions

The following conclusions emerging from this study are:

The co-impregnation with diluted Ni, Mo and P solutions in two consecutive steps is the more appropriate procedure for producing the NiMoP/γAl$_2$O$_3$ catalyst at large scale. This procedure gives a catalyst with the largest specific surface area and pore volume, higher mechanical strength, metallic surface dispersion, homogeneous elemental radial distribution profile and catalytic activity which demonstrates the success of the scale-up.

Heat and mass transfer limitations became important when preparing catalysts at large scale. The rate of diffusion intra-particle and extra-particle was observed limited by the features of the impregnating solution (density, viscosity and liquid-solid contact angle), the reactivity of the phosphate, molybdate and phosphomolybdate species with the alumina surface, the rise of the temperature occurred during the initial impregnation step, and the porosity of the catalyst support.

The fine control of the metal deposition profile during the catalyst preparation by incipient wetness impregnation method is crucial for producing uniform metal distribution and highly active catalysts.

Acknowledgments. The author wants to dedicate with all gratitude this work to Professors Bernard Delmon and Paul Grange who have had a great influence on his professional career.

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