

# Innovative preparations of heterogeneous catalysts for the production of (bio)fuels

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**Abstract:** The tightening of liquid fuels' specifications and the use of lower quality crude oils call for a constant effort to develop more efficient catalysts. In this context, the goal of this work was to prepare hydrotreatment (HDT) catalysts using the simpler and shorter method of co-mixing of the metal precursor with an alumina precursor. Four non-promoted molybdenum catalysts with a metal loading of 10% MoO<sub>3</sub> (w/w<sub>cata</sub>) were produced by co-mixing of two different alumina precursors (boehmite) with heptamolybdate and molybdenum trioxide plus phosphoric acid. Calcination was skipped to avoid metal sintering and stable oxide formation. Thus the dried boehmite extrudates were characterized and tested for toluene hydrogenation. These samples showed a lower activity than the reference catalyst, which can be attributed mainly to having a boehmite (not alumina) support. The co-mixing catalysts present a classic Mo sulphidation after sulphidation at 350°C.

Keywords: hydrotreatment, catalyst, co-mixing, molybdenum

## Introduction

The tightening of liquid fuels' specifications and the use of lower quality crude oils call for a constant effort to develop more efficient hydrotreatment (HDT) catalysts that remove heteroatoms (S, N, O) from refinery streams. Hydrotreatment uses mono-functional supported catalysts, typically of Mo or W with Ni or Co as promoters over gamma alumina. [1] The catalyst is active when the metals are in sulphide form, MoS<sub>2</sub> or Ni-Mo-S slabs for example, thus being called catalysis by Transition Metal Sulphides. [2]

Traditionally, these catalysts are prepared by incipient dryness impregnation of an alumina support with polyoxometalates (iso or heteropolyanions) of Mo or W and Ni or Co salts, followed by maturation and possible calcination. The active phase is formed during sulphidation that can be performed *in situ* or *ex situ*. The properties of the active phase slabs are greatly influenced by the nature of the metal precursors deposited in the support. With impregnation, there is little control of what compounds are actually deposited on the support surface, which will many times differ from the one in the impregnating solution. This is due to various interactions and pH effects that may occur in the pores of the support during impregnation, causing various metal species to form. Also, after calcination very stable oxides that are difficult to sulphide usually form, such as MoO<sub>3</sub>, and metal sintering may occur, which negatively impacts the quality of the active phase. [2]

The alumina support to be impregnated is prepared by a shaping process in which an alumina precursor, boehmite, is subjected to a mixing step using acid and basic solutions to form a paste

that can be extruded into the desired shape. After drying, the extrudates are calcined to have the topotatic transformation from boehmite to gamma alumina. Since the catalyst support essentially defines its macroscopic shape and overall textural properties such as porosity and surface area, it is the mixing step that allows some control over the texture of the final support. The acid solution used should cause the peptization, which is creating a positive net charge on the surface of the boehmite crystallites preventing them from coalescing or settling by electrostatic repulsion. A higher peptization degree may be expected to eliminate macroporosity and provide a slender pore size distribution on the mesoporous area. [3]

In this work an alternative procedure, co-mixing, was used with the aim of preparing hydrotreatment catalysts that at least perform like conventional ones and that have adequate textural properties. Co-mixing consists of the adding the metal precursor during the production of the support. This reduces the total number of steps in the catalyst preparation process, avoids the disadvantages of impregnation and may allow for higher metal loading if used in combination with impregnation. There are some works describing co-mixing procedures to produce HDT catalysts with high metal loadings and improved catalytic activity, however they show no gain in process simplicity [4] [5] [6].

Here, four non-promoted HDT catalysts with 10% MoO<sub>3</sub> (w/w<sub>cata</sub>) metal loading were prepared by co-mixing of two alumina precursors: 1) Pural SB3, a commercial high purity boehmite; 2) Powder X, the name given to a boehmite used industrially in catalyst production; with two traditional Mo precursors: 1) ammonium heptamolybdate, one of the first widely used metal precursors; 2) molybdenum trioxide and phosphoric acid, which should originate a Strandberg type heteropolyanion. The catalyst samples were characterized by Hg Porosimetry, N<sub>2</sub> Physisorption, XRD, Raman spectroscopy and XPS and catalytically tested using the model reaction of toluene hydrogenation.

## **Experimental part**

### *1) Preparation of catalysts by co-mixing*

Mixing of the alumina precursors and metal precursor solutions was performed in an Brabender Mixer in two stages: 1) acid mixing – the metal precursor solution (my contain nitric acid) was added in two minutes using a mixing speed of 16 rpm and the paste thus formed is mixed for 30 minutes more at 30 rpm; 2) neutralization – a basic ammonia solution was added at once and the paste is mixed for 15 minutes at 30 rpm. The quantity of water to be used in the solutions is empirically defined as the mass of water needed to form a paste with the adequate rheological properties. The paste was then extruded in an MTS vertical piston extruder at a speed of 1 cm/min using a cylindrical die plate of 2 mm in diameter. The extrudates are dried in a Binder oven at 80°C for at least 12h, typically overnight. The catalysts were not calcined to avoid metal sintering and stable oxide formation, so the catalyst support is boehmite.

For mixing with Pural SB3 boehmite, a high purity product of Sasol with a LOI=29,4%, the solution for acid mixing contained nitric acid so that 0,63 mmol HNO<sub>3</sub>/g Al<sub>2</sub>O<sub>3</sub> were used and the basic

solution for neutralisation was prepared so that 0,25 mmol  $\text{NH}_3/\text{g Al}_2\text{O}_3$  were used. The catalysts prepared by co-mixing with Pural SB3 are referred to as: *Mo7+Pural SB3* (co-mixing with heptamolybdate) and *MoP+Pural SB3* (co-mixing with  $\text{MoO}_3$  and  $\text{H}_3\text{PO}_4$ ).

For mixing with Powder X boehmite, with a LOI=28,0% and nitric acid already in its composition corresponding to 0,48 mmol  $\text{HNO}_3/\text{g Al}_2\text{O}_3$ , the acid mixing solution was prepared without nitric acid and the neutralization solution was prepared so as to have 0,38 mmol  $\text{NH}_3/\text{g Al}_2\text{O}_3$ . The catalysts prepared by co-mixing with Powder X are referred to as: *Mo7+Powder X* (co-mixing with heptamolybdate) and *MoP+Powder X* (co-mixing with  $\text{MoO}_3$  and  $\text{H}_3\text{PO}_4$ ).

The metal precursor solutions were prepared using: a)  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  from Merck and molar mass of 1238,86 g/mol and  $\text{H}_2\text{O}_2$  30%(w/w) solution from Sigma-Aldrich, so that  $\text{H}_2\text{O}_2/\text{MoO}_3=0,5$  (molar ratio); b)  $\text{MoO}_3$  from Axens with a molar mass of 143,95g/mol and a phosphoric acid solution at 85%(w/w) from VWR Chemicals, so that molar ratio of P/Mo=0,45 is achieved.

#### 2) Preparation of the reference catalyst by impregnation

A reference catalyst with 10%  $\text{MoO}_3$  ( $w/w_{\text{cata}}$ ) metal loading was prepared by incipient wetness impregnation of a Powder X support with heptamolybdate, referred to as *Mo7/Powder X*. The support was prepared by mixing with the same procedure above mentioned with the exception of no metal precursor being used in that step. The dried support extrudates were calcined in a Naberthern muffle furnace at 540°C for 4h. The impregnating solution was prepared using  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  from Merck and molar mass of 1238,86 g/mol and  $\text{H}_2\text{O}_2$  30%(w/w) solution from Sigma-Aldrich, so that  $\text{H}_2\text{O}_2/\text{MoO}_3=0,5$  (molar ratio). After impregnation, maturation took place overnight in a Binder oven at 23°C and 95% humidity followed by drying at 120°C for 24h in a Pol-Eko-Aparatura ventilated oven.

#### 3) Preparation of calcined and of sulphided catalysts for characterization proposes

A sample of each of the co-mixing catalysts was calcined in a Naberthern muffle furnace at 540°C for 4h. Another sample of the co-mixing catalysts was sulphided *ex situ* in a sulphidation cell at atmospheric pressure. After an argon purge, the cell is heated up to 350°C at a rate of 5°C/min under a 2 L/h/ $g_{\text{cat}}$  flow of an  $\text{H}_2/\text{H}_2\text{S}$  mixture containing 15%(v/v) of  $\text{H}_2\text{S}$  from Air Liquide. After 2h at 350°C the cell is purged with argon and cooled to 250°C, with a 2h plateau at that temperature. Still under argon the cell is cooled to room temperature, put under vacuum and sealed.

#### 4) Catalytic testing

The catalyst's performance was evaluated by the model reaction of toluene hydrogenation (HYD) in Avantium's 16 fixed bed reactor unit *Flowrence* that operates at 60 bar in gaseous phase. The catalyst is sulphided *in situ* and the same feedstock is used for the sulphidation and reaction stages: dimethyl disulphide (5,88%(w/w)), toluene (20%(w/w)) and cyclohexane (74,12%(w/w)). The sulphidation stage starts at room temperature with heating at 2°C/min up to 350°C the liquid hourly space velocity (LHSV) is  $4\text{h}^{-1}$ . For the catalytic test, also at 350°C, the LHSV changes to  $2\text{h}^{-1}$ . The  $\text{H}_2/\text{HC}$  ratio is constant for the two stages and equal to 450 L/L. The reaction products

are analysed by gas chromatography (GC) to give the intrinsic toluene hydrogenation rate (vHYD) in converted toluene molecules per Mo atom per hour.

### 5) Characterization

The co-mixing catalysts (dried only extrudates) were characterized by Raman Spectroscopy (Renishaw inVia Raman Microscope). The calcined samples of the co-mixing catalysts were characterized texture wise by Hg Poro. (Micromeritics Autopore IV) and N<sub>2</sub> Phys. (Micromeritics ASAP 2420) and by Raman Spectroscopy. The ex situ sulphided samples of co-mixing catalysts were characterized by XRD (PANalytical XPert Pro diffractometer) and one of them was also characterized by XPS (Esca Kratos Axis Ultra spectrometer). The reference impregnated catalyst was characterized by Raman Spectroscopy.

## Results and Discussion

### 1) Textural Properties

Since the mixing influences the final support texture, the calcined samples of the co-mixing catalysts were compared to an alumina support prepared in equivalent conditions (same boehmite powder, same solutions used in mixing) texture wise. The considered parameters are presented in Table 1. Both Pural SB3 and Powder X co-mixing catalyst are mesoporous solids with a mono population of pores with an average diameter around 10 nm, such as the reference supports. The co-mixing samples present two main differences from the reference supports: 1) they have a higher surface area, which is consistent with other work [7] where that effect was explained by the formation of slit shaped pores and by inhibition of alumina sintering during calcination by the molybdenum; 2) they have a lower pore volume. In all, an effective peptization seems to have happened in co-mixing and the synthesized samples have adequate textural properties for HDT. Their main disadvantage should be the lower pore volume, if incipient wetness impregnation is to be performed in combination with co-mixing.

*Table 1 – Textural parameters of the calcined samples of the co-mixing catalysts compared with the reference supports, given by Hg Poro. ( $D(V_{meso/2})$ ,  $V_{meso}$ ,  $V_{macro}$ ) and by N<sub>2</sub> Phys. ( $V$  at  $P/P_0$  max, Surface SET)*

	<b>Support Pural SB3</b>	<b>Mo<sub>7</sub>+Pural SB3</b>	<b>MoP+Pural SB3</b>
Calcination Temp. (°C)	700	540	540
$D(V_{meso/2})$ (nm)	10,37	10,20	8,41
$V_{meso}$ (mL/g)	0,66	0,53	0,48
$V_{macro}$ (mL/g)	0,01	0,01	0
$V$ at $P/P_0$ max (mL/g)	0,743	0,607	0,548
Surface BET (m <sup>2</sup> /g)	225	296	301
	<b>Support Powder X</b>	<b>Mo<sub>7</sub>+Powder X</b>	<b>MoP+Powder X</b>
Calcination Temp. (°C)	540	540	540
$D(V_{meso/2})$ (nm)	11,15	10,79	10,10
$V_{meso}$ (mL/g)	0,77	0,67	0,64
$V_{macro}$ (mL/g)	0,02	0,01	0

V at P/P0 max (mL/g)	-	0,752	0,731
Surface BET (m <sup>2</sup> /g)	291	334	329

### 2) XRD on co-mixing catalyst ex situ sulphided samples

The samples sulphided at 350°C were suspected of being composed of a mixture of boehmite and alumina and were analysed by XRD to quantify the quantity of these two phases. The XRD analysis on these extrudates show the presence of boehmite,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MoS<sub>2</sub>. Since the co-mixing catalysts are dried only and so composed of boehmite, this result shows that the transition to gamma alumina starts during the sulphidation.

### 3) Assessment of present species by Raman Spectroscopy

The nature of the molybdenum species actually present in the catalysts produced and solutions used was determined by Raman Spectroscopy. For the heptamolybdate solution, prepared with hydrogen peroxide, heptamolybdate, octomolybdate and a peroxodimolybdenum species were identified. The octomolybdate is more relevant when nitric acid is added, which is in agreement with the aqueous chemistry of molybdenum that presents polymerization with pH decrease. The co-mixing catalysts prepared with heptamolybdate have mainly this compound present, with a possibility of there being also monomolybdate. No octomolybdate is present in the catalysts since it should transform into heptamolybdate during the mixing by the basic hydroxyl groups of the boehmite and/or by the ammonia solution used in the neutralisation stage.

For the molybdenum trioxide and phosphoric acid solution there is no difference with the addition of nitric acid and two compounds may be identified: the Dawson type HPA P<sub>2</sub>Mo<sub>18</sub>O<sub>62</sub><sup>n-</sup> and the Strandberg type HPA P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub><sup>6-</sup>, which was expected to form. The spectra of the co-mixing catalysts prepared with molybdenum trioxide and phosphoric acid are of more difficult interpretation, but the Strandberg type HPA could be identified.

The spectra of the calcined samples of the co-mixing catalysts show that there is no formation of the MoO<sub>3</sub> refractory species, which opens the possibility of calcination of the extrudates, to have an alumina support, without the risk of severely damaging sulphidation ability.

In the impregnated reference catalyst, heptamolybdate is the main species, however monomolybdate and the aluminium Anderson HPA, AlMo<sub>6</sub>O<sub>24</sub>H<sub>6</sub><sup>3-</sup> are also present. This illustrates a classical result of heptamolybdate impregnation.

### 4) XPS results

The catalyst prepared by co-mixing of molybdenum trioxide and phosphoric acid with Powder X MoP+Powder X was sulphided at 350°C and analysed by XPS. Only one sample was tested due to the availability of the analysis equipment. The result of 80% of sulphided Mo in relation to the total Mo is in the normal range of sulphidation in the conditions used, indicating that the possible trapping of Mo precursor in the walls of the catalyst, if existing, is not significant.

### 5) Catalytic test results

The intrinsic hydrogenation rate resulting from the toluene hydrogenation test for the catalysts is shown in Figure 1.

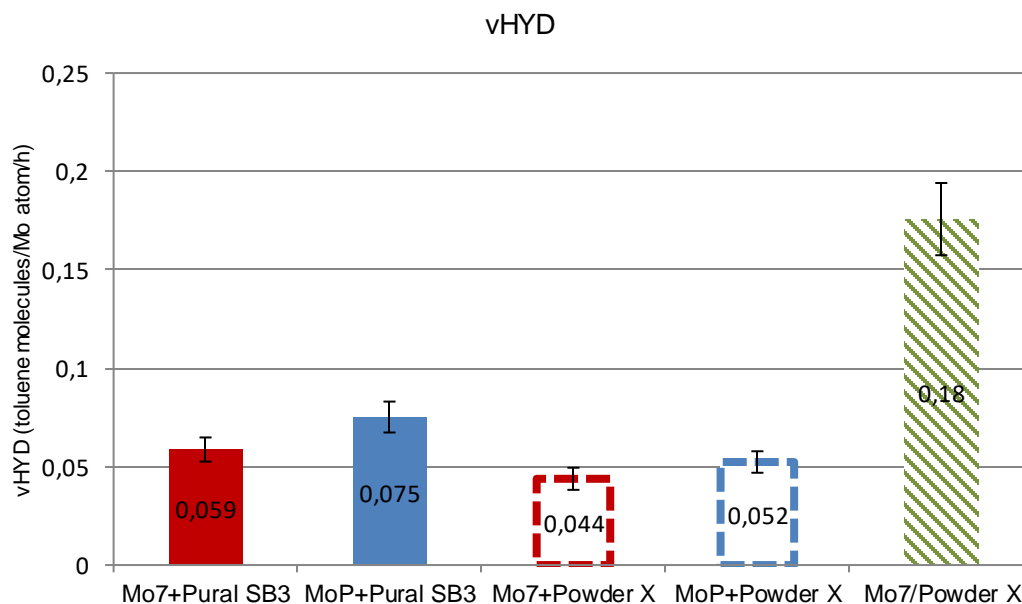


Figure 1 - Histogram of the intrinsic hydrogenation rate obtained in the catalytic testing

First, for the co-mixing products, there is a slight increase in activity when MoP is used in comparison to the heptamolybdate. This was expected and can be attributed to the known fact that phosphorus enhances the activity of HDT catalysts. Furthermore, for the same metal precursor used, Pural SB3 shows better results than Powder X, but again there is only a minor difference.

Secondly, the reference catalyst prepared by impregnation has an activity of more than double than that of the co-mixing catalysts. Therefore it is clear that the preparation of HDT catalysts by co-mixing of heptamolybdate and molybdenum trioxide and phosphoric acid with the boehmite powders used in conventional mixing conditions does not produce catalysts with even the same performance as catalysts prepared by the traditional protocol.

With the information available for this set of catalysts there is no way of being sure of the cause. On the one hand there could be less Mo accessible by *trapping* of molybdenum compounds in the “walls” during co-mixing, though this idea was dismissed by the XPS results. It can be also thought that some degree of sintering may occur during drying creating large Mo clusters that later sulphide forming big MoS<sub>2</sub> slabs, with a smaller *active site/slab* ratio.

On the other hand, using boehmite as the support material may impact the reaction conditions. To begin with the surface of a boehmite support is different from an alumina one, having more hydroxyl groups, which may influence not only the formation of the MoS<sub>2</sub> slabs and their interaction with the support (remember the difference between Type I and Type II CoMoS) but also the adsorption of reactants and products.

In second place, we have seen that the transition to alumina will start at 350°C during cell sulphidation, so the same thing may be expected to happen for the *in situ* sulphidation. The release of water in this transformation may cause a local dilution of the feed.

## Conclusions

Non-promoted hydrotreatment catalysts can be produced by co-mixing of heptamolybdate and of molybdate trioxide and phosphoric acid in a conventional mixing protocol comprising an acid mixing stage and neutralisation.

In comparison with alumina supports, the catalysts have higher surface area, result consistent with other work, and lower pore volume. Being mesoporous solids, the catalysts have appropriate texture for most HDT applications.

The co-mixing products have the same species on the inside and on the edge of the extrudates, being homogenous in that sense, and clusters of MoO<sub>3</sub> are not found in the calcined extrudates. This provides the opportunity of calcination after co-mixing without the formation of that refractory species that is difficult to sulphide.

Regarding the catalysts' performance concerning toluene hydrogenation, the co-mixing ones have lower activity than the reference catalyst prepared by dry impregnation. Since the XPS analysis showed a normal sulphidation of Mo, we considered that there should be no relevant amount of inaccessible molybdenum species due to the co-mixing. Thus, this result was attributed to having boehmite as the support. Boehmite has a different surface chemistry than alumina and is not thermally stable so these factors may have an impact on catalyst performance.

## Bibliography

- [1] S. Eijsbouts, "Hydrotreating Catalysts," in *Synthesis of solid catalysts*, WILEY-VCH, 2009, pp. 301-328.
- [2] H. Toulhoat e P. Raybaud, *Catalysis by Transition Metal Sulphides*, Paris: Technip, 2013.
- [3] F. Schüth, K. S. W. Sing e J. Weitkamp, Edits., *Handbook of Porous Solids*, WILEY-VCH.
- [4] D. W. Blakely, "Method for comulling metals without crystal formation". Patente US 4402865, 1983.
- [5] Kemp e Adams, "Hydrogel-derived catalysts. Laboratory results on nickel-molybdenum and cobalt-molybdenum hydrotreating catalysts," *Applied Catalysis A: General*, vol. 134, pp. 219-317, 1996.
- [6] H. D. Simpson, "Desulfurization process and catalyst". Patent US 4097413, 1978.
- [7] D. Minoux, "Préparation de catalyseurs d'hydrotraitement par comalaxage molybdène-boehmite : influence sur les propriétés texturales, structurales et catalytiques du matériau final.," 2002.