

GENERAL ARTICLE

What we need to consider for a successful development of catalysts?

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A lot of papers are regularly published in different journals and majority of them are on basic and fundamental research. They give insight information of various catalysts in their catalysis research. This has been possible on account of modern tools now available to study surface species of active metals, their crystal orientation, shape and size etc., at the atomic level. The information provides insight of catalyst but does not suggest the way to achieve them by processing in a particular way/steps. That is why it is still said that the catalyst preparation is “an art” and the basic information is used as support for the catalyst development. It is extremely important to understand the catalyst first with respect to various functions and structures before we take up the development work for commercial exploitation. Just seeing the catalyst composition, it should not be taken as a simple mixture and start preparation to achieve that. It may not be possible to cover various parameters which have to be looked into in the process of catalyst development. In addition to parameters, which govern the structure and texture of the catalysts, the following may also be studied and chosen for commercially viable formulation.

Among other parameters of catalyst development, the most important is the selection of raw materials, which may justify the claim for the development of improved and commercially viable catalyst. The following aspects are kept in mind before the project is taken up for the development of catalysts.

A. Selection of raw materials

This is the most important factor in developing a commercially viable catalyst. Any commercial catalyst should first meet the cost in addition to activity, selectivity, stability and regenerability. When we talk about the raw materials, we mean the purity, ease of handling, preparation of solutions, disposal of unwanted by-products and environment friendliness. Besides these aspects, the cost is utmost important which will have its impact on final product (catalyst) unless it is comparable or cheaper with existing catalyst in the market, may not be accepted by user industry. This consideration is to be examined at the stage of laboratory scale preparation during development. The quality and cost are to be given highest importance in selection of raw materials. Otherwise any impurity or undesirable ingredients may give rise to unwanted products which may create problem for removal, on environment and disposal of waste, resulting in a set-back for commercialization due to these factors.

B. Catalyst formulation

Next to the selection of raw materials is the formulation of catalyst using various process steps. The catalyst process steps (preparation steps) for the preparation of the catalyst should be such that the scale up and commercial production are simple and easy i.e., not involving any complex unit operations. It is also equally important to have quality control parameters of processed materials at each process steps, to check any

deviation from desired properties which may lead to a product different from one targeted.

C. Selection of equipment at each process steps

Another important aspect of the catalyst development work is to select the preparation procedure and equipment at laboratory scale, which could be easily translated in scale up units. Just to make this point clear, the precipitation step can be taken as an example. In the lab scale of preparation, generally the precipitation of support material or the catalyst components is done in a beaker and to mix the precipitated mass during precipitation, an electric stirrer or some time, glass rod is used. If the precipitated mass is quite thick, vigorous stirring is done. But when the same step is carried out at larger batch (scale-up), baffled vessel is used for proper mixing. If the first stage product is compared with this product, it is found that it differs with respect to crystallinity, crystallite size, etc., due to uneven mixing in laboratory scale operation. So, this step can not be translated in scale up. This is just a first step but similar history may repeat when we go for other preparation steps and their scale up. For example, the filtration, drying and activation steps involving lab scale units differ considerably from the bench scale/commercial scale units and their operating conditions.

Now, we will discuss the various preparation steps, which need proper controls during unit operations to emphasize the importance and the effect on product variation by any minor change in processing. The significance of raw materials is already discussed and the other preparation steps will be briefly covered by using an example of hydrodesulphurization catalyst. The objective of this paper is to highlight a few salient points to the scientists who are engaged in the

development of catalyst for commercial exploitation.

Criticality at various steps of support/catalyst preparation (HDS catalyst)

These criticalities cannot be generalized as they differ from catalyst to catalyst. For convenience and ease of discussions, HDS catalyst is taken as an example.

Step-1 Support preparation

For the preparation of a HDS catalyst, the support material is invariably γ -alumina. Other functionalities can be incorporated in the support during its preparation. For example a mild acidity function by adding P, zeolites or even amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$. It may also be noted that the support does catalyze certain reactions in catalytic processes in some of the catalysts, especially in bifunctional catalysts.

In the preparation of alumina support, different aluminium salts are taken in the form of solution and neutralized with ammonia solution at a particular temperature and pH, for example: -

- a) Aluminium nitrate solution with NH_4OH solution
- b) Aluminium sulphate solution with NH_4OH solution

Another procedure which is also practiced in Industry is by precipitating aluminium hydroxide by neutralizing NaAlO_2 solution with nitric/sulphuric acid solution. Sodium aluminate solution is prepared by digesting commercially available alumina trihydrate (gibbsite) with NaOH at higher temperature, say $100\text{-}120^\circ\text{C}$ in an autoclave.

In the preparation of support material (alumina hydrate) the precipitation is carried out in a baffled vessel by controlling the following:-

- a) Concentrations of aluminium salt solution and precipitating agents
- b) Precipitation temperature and final pH
- c) Mode of addition and their rate
- d) Ageing time and temperature
- e) Filtration and nature of washing liquid
- f) Drying
- g) Extrusion (shape & size)

During these processing steps the alumina hydrate phases are developed and crystallinity and crystallite sizes grow. Depending upon the phases required i.e., boehmite, pseudo-boehmite, bayerite or gibbsite, the preparation conditions are chosen and the desired precursor hydrate is prepared. Unless the conditions are well controlled (by automation), it is very difficult to have 100% repeatability with respect to crystalline phase and crystallite sizes. These properties control the surface area, pore volume, pore size distribution, thermal stability etc. Generally, a combination of crystalline phase and amorphous alumina hydrate are formed by neutralizing Al-salt with precipitating agent and their optimum composition is maintained to meet the requirement of various catalysts. The selection of alumina hydrate phase and desired crystallite size can be obtained by an exhaustive experimental work, but still problems may be faced at commercial level. Now a days, the catalyst has so many specific features that it is difficult to achieve the desired properties but that is not impossible. In order to have a good repeatability, maximum possible parameters are controlled at each step of operation so that the reproducibility of batch is within acceptable limit. At times physical observation also becomes an important parameter.

Presently, considering the complexity in the preparation of basic alumina hydrate materials, several manufacturing agencies have come up to offer various alumina hydrate products with a combination of

crystalline and amorphous phases, suited to user's requirement. For example, the main suppliers are SASOL (Germany), ALCOA (USA), ENGLEHART (USA) etc. But here too, the catalyst scientist has to work by using various combinations of their products to achieve desired characteristics of the required support. This approach has reduced a lot of work for the preparation of alumina precursor hydrates using Al-salts and neutralizing agent and maintaining a lot of parameters to control the alumina hydrate crystalline phases and their crystallite sizes. The sizing of the product (alumina hydrates) is an additional step for processing the alumina hydrate obtained by reacting Al-salts and neutralizing agent.

Step 2 – Extrusion of precursor hydrate to shaped support.

The alumina hydrate powder having desired phases and particle size distribution is mix-mulled in a roller type mix-muller with peptizing agent and water. The following parameters are controlled to achieve consistency in the extrudate's properties: -

- 1) Loss on ignition (LOI) of alumina hydrate
- 2) Free water of precursor hydrate
- 3) Quantity and concentration of peptizing agent
- 4) Amount of water added during mix-mulling
- 5) Mix-mulling time

All these factors are standardized with respect to extruder i.e., the size of the die and the compression. An expert can tell based on his experience, at what stage the mix mulling is complete and ready for extrusion. The extrusion can be cylindrical or shaped (trilobe, quadrilobe, etc.) depending upon the process and reactor requirement. These parameters are further standardized when the scale up is done for commercial production to achieve the same physico-chemical properties, particularly the

crushing strength, pore volume, bulk density, etc.

These extrudates are dried in an oven at 110-120°C for 8-12 h, preferably in flow of dry air to remove free water and acid from the surface during drying. Here, the extent of mix-mulling, the compression in extruder and the die size are important parameters which control pore size distribution, bulk density and crushing strength, etc. both at laboratory scale and commercial production.

Step 3 – Calcination / Activation:

After drying the extrudates, it is subjected to calcination at 500 - 550°C for 4-6 h to develop surface and pore structures. The calcination in flow of dry air improves surface area and if it is done in close system like muffle furnace, a marginally lower surface area is observed and the support is subjected to some extent, hydrothermal treatment, resulting in better thermal stability of the material.

Step 4: impregnation with active metals (i.e. Co-Mo or Ni-Mo).

Please refer Table 2. There are several options to incorporate Co/Ni and Mo in the support. It can be mixed solution of Co/Ni salt and Mo or in sequence by putting first Ni/Co and then Mo or even vice versa. Organometallic complexes of Co or Mo also have been used to have high dispersion of Mo. Now a days, the maximization of site II in the catalyst formulation is given the priority which gets sulfided nearly 100% giving rise highest activity of desulphurisation. It depends on how we can maximize site II active sites in catalyst development.

After impregnation of metals (Co-Mo or Ni-Mo) using special technique the catalyst is expected to have the following physico-chemical properties (Table 1).

Table 1

Item	Value
Surface area m²/g	240-250 Co-Mo 215-230 Ni-Mo-P
Pore volume ml/g	0.35-0.45 Pores in the range 6 and 10 nm)
Bulk density g/ml	065-0.70
Size nm	1.2-1.8
Shape	Cylindrical for Naphtha/KeroHDS Trilobe/Triax for Gasoil and VGO HDS
Metal loading	
wt% MoO₃	15-20
Wt% CoO/NiO	3.5-4.5
For Naphtha/kero	
Wt% MoO₃	13-15
Wt% CoO	3.5-4.0
For gasoil/VGO	
Wt% MoO₃	13-15
Wt% CoO/NiO	3.5-4.0
Metal Dispersion %	>20

The selection of promoter depends upon the feed composition. Ni-Mo combination is chosen when feed contains basic nitrogen compounds and or refractory sulfur compounds. In absence of these compounds, Co-Mo combination is preferred due to its higher desulphurisation activity. Phosphorous, modified Y-zeolite and amorphous silica-alumina are also incorporated in Ni-Mo active metals combination to take care of nitrogenous compounds and to impart some isomerisation activity to isomerise refractory sulfur compounds so as to avoid steric hindrance of S compounds (shifting of CH₃ group to another position) on adsorption to CoMoS active sites.

Now, depending upon the requirement of product specifications, the composition of catalyst is chosen i.e. Co-Mo or Ni-Mo. The alumina support is then impregnated with the salt solutions; a few options can be employed with any of the following technique for impregnations:

- 1) By dipping in excess solution
- 2) Incipient impregnation
- 3) Spraying the solutions on the support

The volume of the solution for impregnation of the support in case (2) and (3) should be equivalent to the total pore volume of the solution. Another aspect is that the mix solution, if used, should be homogeneous without any turbidity or precipitation of any metal component. In case the concentration of metals in solution is high and some turbidity or precipitation is observed, the impregnation can be done in two stages. The impregnation with metals one after the other is also reported. The sequence has to be studied for meeting the required activity. Another alternative to incorporate higher metal loading is that a metal solution partly can be added into support at mix-mulling stage, at the time of support preparation, extrusion and the balance can be added by impregnation. There are several ways to incorporate metals on any support, but merit/demerit is to be studied before deciding the catalyst preparation with high activity and stability. As mentioned earlier, P or zeolitic components are some times added to Ni-Mo formulation for feed containing nitrogen compounds and refractory sulfur compounds as well as poly nuclear S and N compounds. The component can also be added at mix-mulling stage at the time of support preparation. The addition of zeolite improves the surface area of the catalyst whereas phosphorous causes reduction in surface area.

It is also important to note that on metals impregnation, there is reduction in surface

area as well as pore volume in the final catalyst (product) particularly in case of higher metals loading. Hence, care is to be taken to choose the support which on metals impregnation results in properties as targeted. A support with reasonable high surface area and pore volume may be selected to get the desired physico-chemical properties of the catalyst after impregnation and calcination.

After impregnation of the support with metals solution, the catalyst is dried at 120°C for 12-16 h and then calcined at 500°C for 4-6 h similar to the conditions for support drying and calcination.

The catalyst with higher metals loading can also be prepared by co-precipitation of support material and metals solutions by using suitable precipitating agent.

Some claims have been made for using organometallic compounds as source for metals (Co/Ni or Mo) for loading on alumina support, as already mentioned earlier in order to get higher activity of the catalyst. But the author feels that the use of organometallic compounds may result in higher production cost and may not be compatible in price with the catalysts already available in the market. Even the stability of the catalyst is likely to be poor due to non-existence of proper interaction between the metals and the support. These aspects are to be first studied before taking up the catalyst development using organometallic compounds for metals incorporation.

The catalyst prepared by any of the above techniques are evaluated for their physico-chemical properties and compared with the targeted values. High surface area, pore size distribution, bulk density and metal dispersion are the main criteria for a successful development. In recent past, it

has been also emphasized that the catalyst should have maximum MoS₂ Type II sites in order to have very high activity (Fig 1). These MoS₂ Type II sites get sulfided easily and 100% sulfidation takes place if the catalyst contains Type II sites. The catalyst preparation method has to be tailored in such a way that Type II sites are predominant and to achieve this, specific methodology has to be developed for the preparation.

It may be noted here that the example given for the preparation of hydrodesulphurisation catalyst is just an indication for the formulations of catalyst but each step needs proper control to monitor the structural and textural properties. Any modification of the procedure or even an additional step is meant to achieve the required specifications of final catalyst.

Similarly, other catalysts can be made by selecting proper process steps and then evaluate to match the targeted properties. Each catalyst has one or two specific properties other than normal characteristics like surface area, pore volume and their distribution, bulk density, shape and size, crushing strength and chemical composition. But it must be kept in mind that the best catalyst is the one that gives excellent performance, stability, selectivity and regenerability. Any conclusion can be drawn only after the performance test.

Conclusion

The objective of this write up is to convey with simple illustration to a researcher that a simple combination of catalytically active metallic components with support material may not be considered as the development of catalyst after finding the characteristics and testing for a reaction. Presently, the new generation catalysts meet the demand of very high activity, selectivity and life, in many applications. These developments are only possible by proper monitoring and

structural studies using surface characterization techniques to understand the catalyst systems with respect to their textural and structural properties. All these inputs are needed for any better catalyst development for industrial application. In this competitive world, there are several factors which will decide about the discovery of better catalyst. For example, the catalyst has to be very active and selective with no or minimum by-products formation. Energy-saving process conditions, tolerance towards poisons, long life and ease of regenerability are built into such catalysts. The most important is the simplicity in scale up from laboratory scale to commercial level and the total cost of the catalyst (raw materials, processing, overheads, etc.). Unless these factors are met, no vendor/manufacturer will take up any new or improved formulation for production and subsequent commercial exploitation.

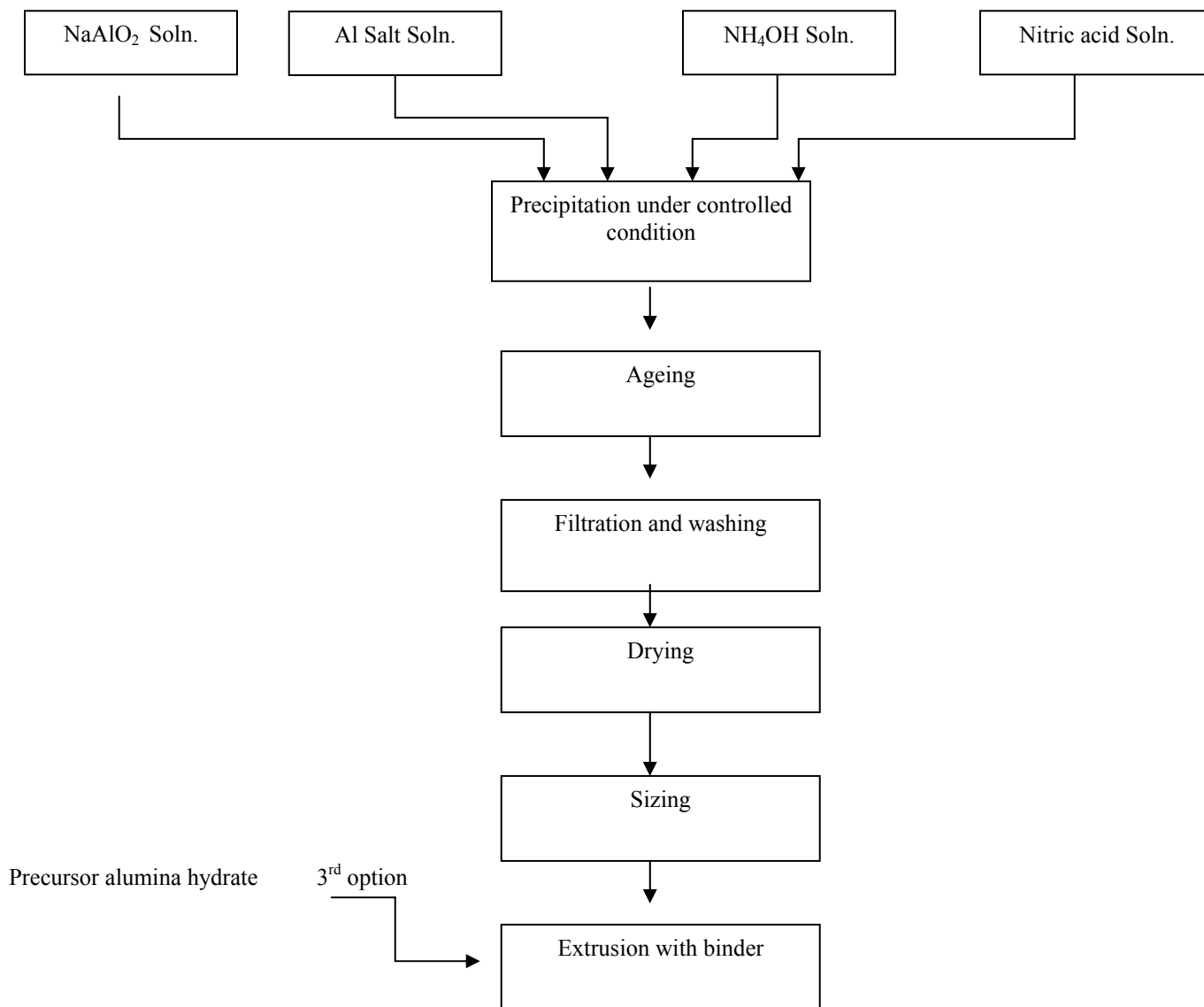
Reference:

1. John N. Armour "Do you really have a better catalyst", Applied Catalysis A: General, **282** (2005) 1-4.
2. Salvatore Torrisi, Jr, and P. Michael Gunter "Fundamentals of ULSD production" Petroleum Technology Quarterly, Summer 2004.

FLOW SHEET –1 - PREPARATION OF SUPPORT (ALUMINA)

Route 1 – NaAlO₂ soln. and Nitric acid soln.

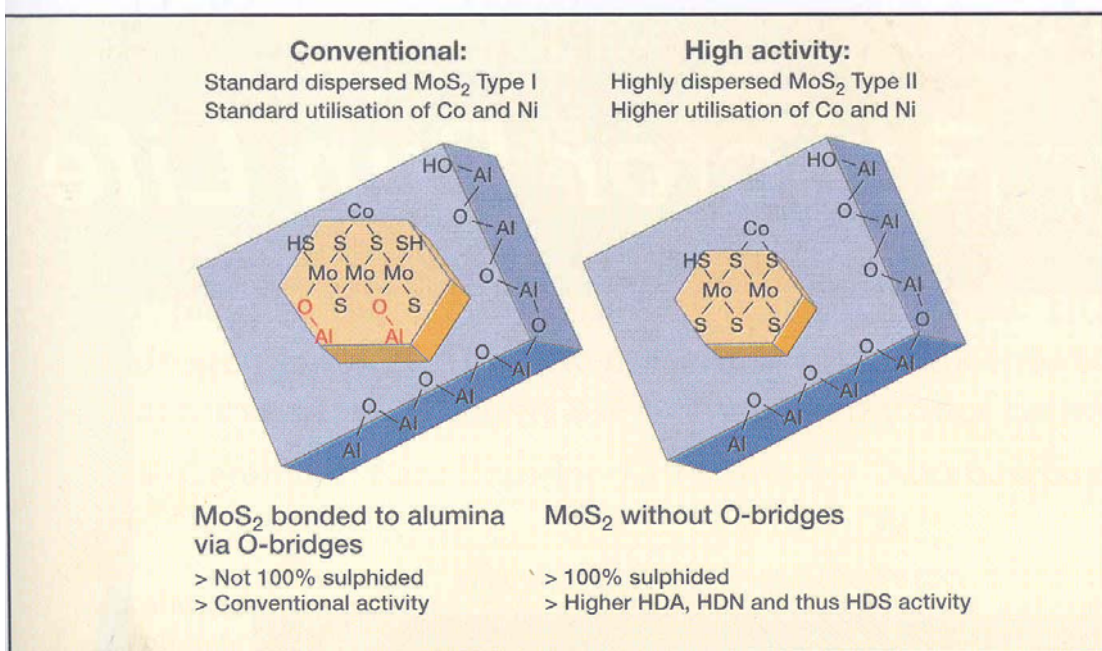
Route 2 – Al. salt soln. and NH₄OH Soln.



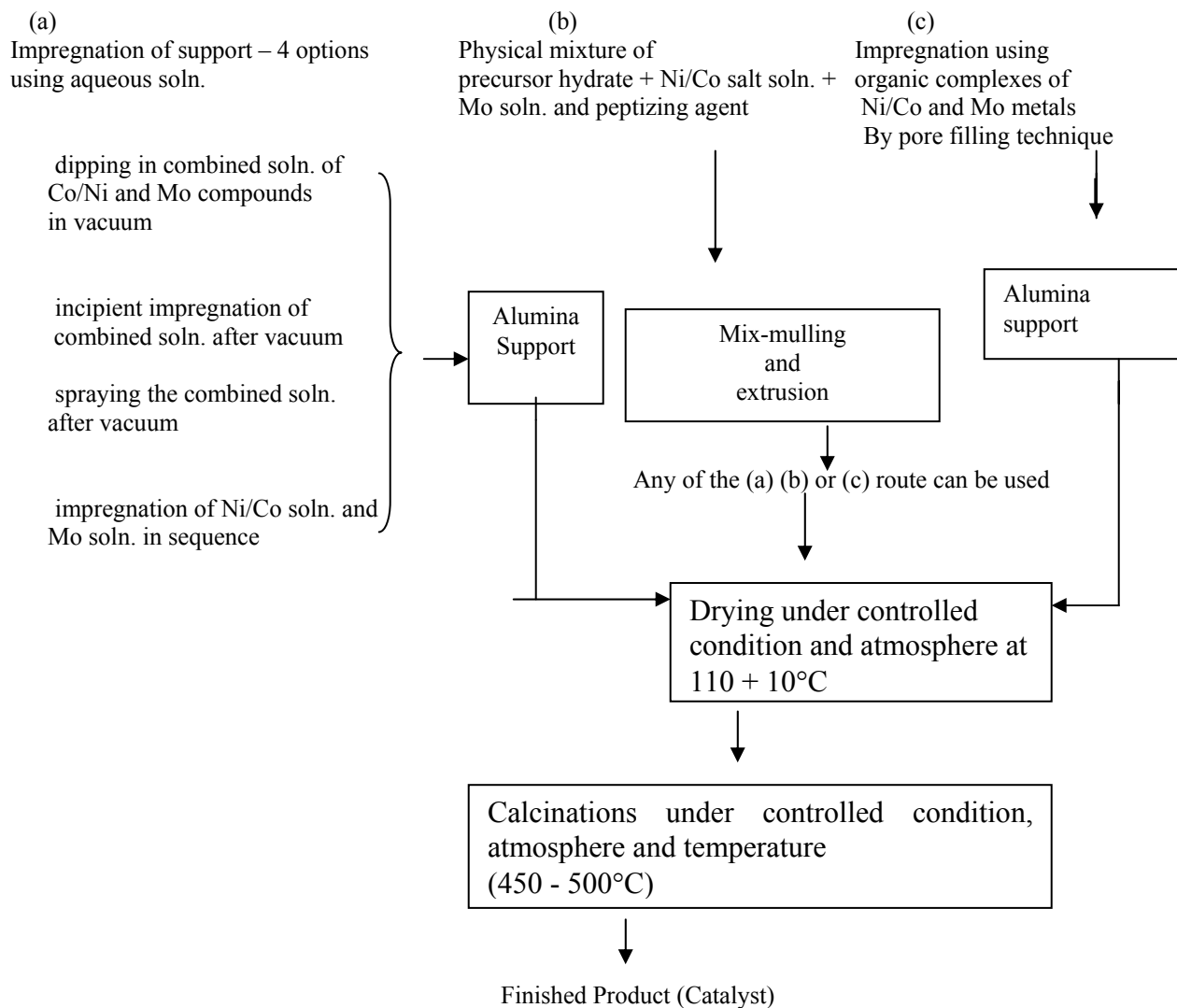
B. Selection of commercially available supports (for other applications).

- Precursor alumina hydrate from variety of precursor hydrates of different crystalline phases with a particular alumina hydrate phase and particle size distribution.
- Zeolytic support from various zeolites by selecting proper zeolite with their pore dimensions, silica/alumina ratio, crystallinity and crystallite size.
- Silica/alumina amorphous support with a particular silica to alumina ratio or any particular clay with specific composition and properties.

Figure 1 Structural composition of metals active sites for conventional and high activity HDS catalysts



Flow Sheet 2 – Metals incorporation in alumina support



A combination of steps from (a), (b) and (c) can also be considered to achieve the target of high activity catalyst for hydrodesulphurisation.