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# Supported $MoO_3$ catalysts: preparation by the new "slurry impregnation" method and activity in hydrodesulphurization

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**Abstract**

A new preparation of supported $MoO_3$ is described. Slurry $MoO_3$/water is used instead of the solution $(NH_4)_6Mo_7O_{24}$. Preparation and HDS activity are illustrated for $MoO_3$ supported over $Al_2O_3$, active carbon and $ZrO_2$. Another application of the new principle is the preparation of high surface area $MoO_3$/MgO by the reaction of MgO with slurry $(NH_4)_6Mo_7O_{24}$/methanol. Texture of MgO that is deteriorated in aqueous solution of $(NH_4)_6Mo_7O_{24}$ is stable in that slurry. "Slurry impregnation" is a special case of equilibrium adsorption impregnation. It is simple and it provides monolayer dispersion of molybdena. 

*Keywords:* Supported Mo catalysts; Slurry impregnation; Hydrodesulphurization

## 1. Introduction

Supported $MoO_3$ is an important catalyst or catalyst precursor in a number of industrially relevant reactions. The present paper is related to hydrodesulphurization and the catalysts are tested in sulphided form. However, oxide or reduced form is the active form in other reactions such as oxidation, dehydrogenation, oxidative dehydrogenation, isomerization, metathesis, etc. [1].

The conventional method of preparation of the $MoO_3$/support solids is schematically described in Fig. 1. The support is impregnated with solution of common soluble molybdenum compound, ammonium heptamolybdate, AHM (the solubility is 43 g of AHM per 100 ml of water at room temperature). For the purpose of the present paper, this method can be named "solution impregnation". From the point of view of molybdenum oxide, the procedure starts with its dissolution in ammonium hydroxide. Ammonia serves as a helping ion that is firstly added to the system and then removed from it by calcination.

However, we have found that the use of the helping ammonia ion is not necessary and $MoO_3$ alone can be used as the impregnation compound (see Fig. 1). The slurry of $MoO_3$ in water is mixed with support. The solubility of $MoO_3$ is low (0.1 g $MoO_3$ per 100 ml of water at room temperature) but sufficient for gradual transport of molybdena species to the surface in pores. The dissolved species are adsorbed and another solid $MoO_3$ is dissolved. At the end of impregnation all molybdena is deposited; the original solid $MoO_3$ disappeared and the amount of molybdena present in dissolved form is negligible. The catalyst is dried and it is not necessary to calcinate it. Slurry of the impregnation compound is used instead of its solution and this impregnation method can be named "slurry impregnation".

Supported $MoO_3$ catalysts belong to the class of the so-called monolayer type catalysts (for review, see for instance [2–4]). Slurry impregnation is a special

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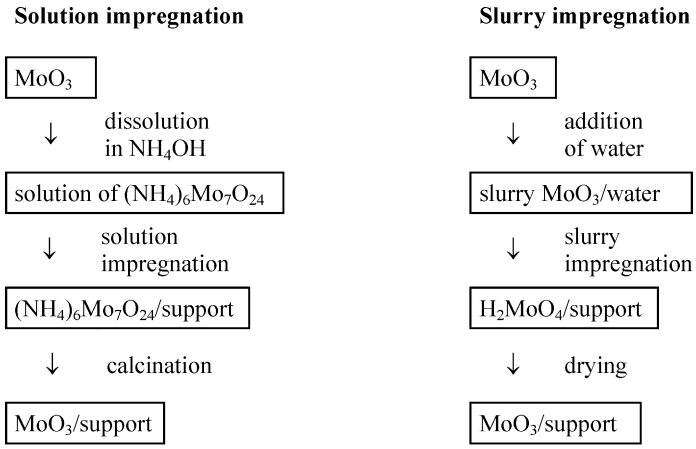


Fig. 1. Schematic comparison of the preparation of $MoO_3$/support catalysts by conventional solution impregnation and new slurry impregnation.

case of equilibrium adsorption impregnation method (for review of the equilibrium adsorption method see for instance Refs. [3,5]). The maximum amount of $MoO_3$ that can be deposited by slurry impregnation corresponds to the formation of "saturated adsorption monolayer" (for more detailed discussion see for instance Ref. [5]).

The experience on three systems prepared by the slurry impregnation using slurry $MoO_3$/water will be summarized in the present paper: $MoO_3$/alumina, $MoO_3$/active carbon and $MoO_3$/zirconia.

The fourth example of the application of slurry impregnation that will be discussed is preparation of $MoO_3$/MgO catalyst by the reaction of MgO with the slurry AHM/methanol. Ammonia ions are present in that case and the idea of this application will be explained henceforward.

## 2. $MoO_3/Al_2O_3$ catalyst

Simplicity of the slurry impregnation is illustrated by the typical preparation of the 15 wt.% $MoO_3/Al_2O_3$ catalyst. The slurry of $Al_2O_3$ (surface area 280 $m^2\,g^{-1}$, particle size 0.16–0.32 mm, 15 g), $MoO_3$ (finely ground, 2.7 g) and water (60 ml) are heated at 95–100°C. The fine grey powder of $MoO_3$ disappears after about 3–5 h. The catalyst is dried and calcination is not necessary. No waste solution and no calcining nitrogenous gases are produced.

Various shapes of alumina (powder, extrudates) can be impregnated. The impregnation time depends on particle size of the support, loading and temperature. For higher loadings of about 70–100% of the saturated adsorption monolayer, it is about 3–5 days for extrudates (1.5 mm) at room temperature and about 2–3 h for the impregnation in the aqueous paste of finely ground $MoO_3$ and $Al_2O_3$ at 95–100°C. The impregnation time is shorter for lower loading.

The catalysts $MoO_3/Al_2O_3$ of various origin of the starting alumina, shape of alumina, loading, and impregnation temperature were prepared by slurry impregnation in our laboratory. They were characterized by some physico-chemical techniques and their catalytic activity in hydrodesulphurization was tested. The results were compared with the $MoO_3/Al_2O_3$ catalysts prepared by the conventional solution impregnation using AHM. It was found that the slurry impregnation is a simple, clean and reliable method to prepare the $MoO_3/Al_2O_3$ catalysts with good, monolayer type dispersion of molybdena [5–8]. The highest amount of $MoO_3$ deposited by slurry impregnation corresponded well to the formation of saturated monolayer observed in literature for samples prepared by other methods, impregnation with AHM or thermal spreading [5].

The example of catalytic data is shown in Table 1. Two alumina supports were used to prepare the 15 wt.% $MoO_3/Al_2O_3$ catalysts by the slurry impregnation and the conventional solution

Table 1
Relative rate constants of hydrodesulphurization over slurry impregnation and conventional $MoO_3/Al_2O_3$ catalysts[a]

| Preparation | Alumina support | |
|---|---|---|
| | Norton SA 6175 | Akzo HDS 000.1.5 |
| Conventional impregnation | 1.00 | 1.04 |
| Slurry impregnation, dried at 160°C | 1.24 | 1.36 |
| Slurry impregnation, calcined at 400°C | 1.00 | 1.11 |

[a] Hydrodesulphurization of thiophene at 1 MPa and 350°C. The reference point of activity is the BASF M8-30 $MoO_3/Al_2O_3$ catalyst with the relative rate constant equal to 1. The loading of all catalysts was 15 wt.% $MoO_3$.

impregnation. The commercial BASF M8-30 $MoO_3/Al_2O_3$ catalyst was chosen as the reference point of activity. The slurry impregnation samples were tested in the dried (160°C) or calcined (400°C) form. It is seen that the activity of the calcined slurry impregnation samples was about the same as activity of the conventional laboratory made samples and also of the reference commercial catalyst. However, the activity of the dried slurry impregnation samples was higher. Calcination of the slurry impregnation samples probably enhances the interaction between alumina and molybdena (for instance by the formation of molybdenum aluminate). This results in more difficult sulphidation and lower activity of the calcined catalysts as compared with the dried samples.

## 3. $MoO_3$/active carbon catalyst

Adsorption of molybdena species from the slurry $MoO_3$/water is very easy for this support; it is faster than over alumina and the saturated adsorption loading for typical active carbons of surface area of about 1000 $m^2\,g^{-1}$ is high, of about 30 wt.% $MoO_3$. It is an important advantage for this support that calcination is not included in the slurry impregnation because oxidative degradation of active carbon impregnated by molybdena starts at relatively low temperature of about 250°C during calcination on air.

Several $MoO_3$/active carbon samples were prepared and it was found that hydrodesulphurization activity of these catalysts was the same as that of the catalysts prepared by conventional solution impregnation using AHM [7,9]. This is illustrated by the example of catalytic data shown in Fig. 2.

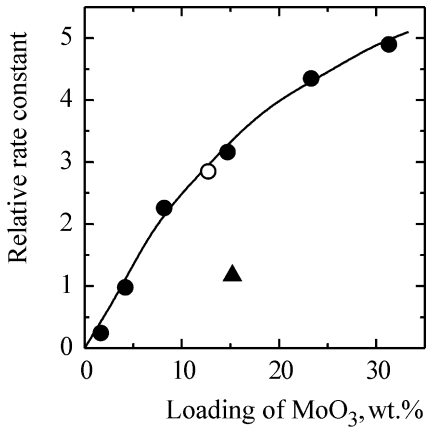


Fig. 2. Comparison of the activity of the $MoO_3$/active carbon catalysts prepared by the conventional solution impregnation and new slurry impregnation method in hydrodesulphurization of thiophene at 1.6 MPa and 350°C [9]: (●) Mo/active carbon, slurry impregnation; (○) Mo/active carbon, conventional solution impregnation; (▲) reference $MoO_3/Al_2O_3$ catalyst BASF M8-30.

## 4. $MoO_3/ZrO_2$ catalyst

The support $ZrO_2$ is commonly prepared by calcination of $Zr(OH)_4$. However, it is well known in literature that sintering of finely dispersed zirconia is easy and surface area of the resulting $ZrO_2$ decreases rather sharply with increasing temperature of calcination [10–14]. This is also illustrated by data from our laboratory in Fig. 3 obtained with samples provided by MEL Chemicals. For the application in catalysis over sulphides, the support should be calcined at the temperature of about 400–500°C. The conventional preparation of $MoO_3/ZrO_2$ by impregnation of the calcined $ZrO_2$ by solution of AHM provides the catalyst of about the same surface area as that of the starting $ZrO_2$ and it is usually not very high.

However, it is well known in literature that sintering of zirconia during calcination can be inhibited by the addition of oxides of various elements such as La, Si, Al, S, etc. [11,13,14]. This is illustrated by our data in Fig. 3 obtained with samples provided by MEL Chemicals; $Al_2O_3$ added to the extrudates not only serves as binder but it also stabilises their texture during

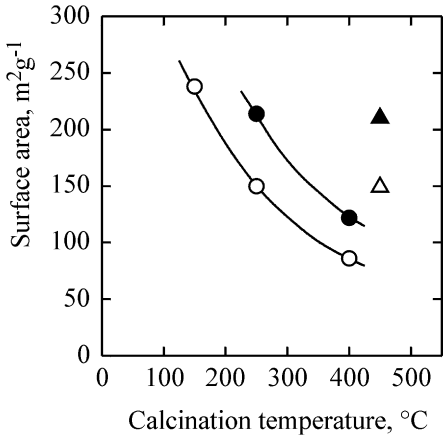


Fig. 3. Dependence of surface area on the temperature of calcination: (○) undoped $Zr(OH)_4$ (MEL Chemicals), (△) extrudates of $Zr(OH)_4$ containing 15 wt.% $Al_2O_3$ as a binder (MEL Chemicals); (●) 12 wt.% $MoO_3/Zr(OH)_4$ prepared from pure $Zr(OH)_4$ by slurry impregnation; (▲) 9 wt.% $MoO_3/Zr(OH)_4$ prepared from $Zr(OH)_4$ extrudates by slurry impregnation.

calcination as compared with pure $Zr(OH)_4$. However, the additives also strongly influence chemical character of the surface and this might be a complication for catalytic application.

It was reported in literature that inhibition of sintering can also be achieved by the addition of molybdena to $ZrO_2$ precursor before calcination. Molybdena stabilises the texture of the $ZrO_2$ arising during decomposition of the precursor by calcination. One method of this type is "molten salt method" (for review see Refs. [14,15]). The melt of $KNO_3$, $NaNO_3$, $(NH_4)_6Mo_7O_{24}$ and $ZrOCl_2$ is decomposed at temperatures of 300–550°C and the resulting solid is washed with water and calcined. This method is effective for obtaining high surface area catalysts but it is rather complicated and it produces nitrogenous gases and waste solutions. Another method of this type is impregnation by solution of AHM of wet or dried $Zr(OH)_4$ instead of calcined $ZrO_2$. The calcination of the obtained $(NH_4)_6Mo_7O_{24}/Zr(OH)_4$ provides higher surface area $MoO_3/ZrO_2$ catalyst as compared with the calcination of $(NH_4)_6Mo_7O_{24}/ZrO_2$ [14,16,17].

It was found in our laboratory that this latter method can be further simplified by application of the principle of slurry impregnation. Molybdenum oxide reacts with zirconium hydroxide in aqueous slurry. The deposited molybdena stabilises texture of $ZrO_2$ emerging during calcination. This is illustrated by the data in Fig. 3. The stabilising effect of molybdena was found both for pure $Zr(OH)_4$ and for the $Zr(OH)_4$ extrudates containing alumina binder.

## 5. $MoO_3$/MgO catalyst

High surface area $MoO_3$/MgO (surface area 200–300 $m^2\,g^{-1}$) might be an interesting catalyst or catalyst precursor for a number of industrially relevant reactions including hydrodesulphurization. Conventional impregnation using aqueous solution of AHM has been commonly used for the preparation of $MoO_3$/MgO in literature (for instance [18–22]). However, magnesia is unique among the supports since it reacts easily with water (see, for instance [23–29]). High surface area MgO is transformed to low surface area $Mg(OH)_2$ in aqueous solutions even at room temperature. A part of the support might dissolve at natural pH of the AHM impregnation solution [21].

It was found in our laboratory that this complication can be overcome using methanol instead of water [30]. The conventional "solution impregnation" using solution of AHM in methanol is not feasible because AHM is practically insoluble in this solvent. However, it was found that it is possible to use the slurry of AHM in methanol instead of its solution. Such method can be classified as "slurry impregnation".

The slurry of AHM in methanol is mixed with MgO support. The solubility of AHM is very low. However, the dissolved AHM is continually removed from the solution by the reaction with MgO surface in pores; molybdena species are deposited and ammonia is evolved. Another AHM is gradually dissolved and consumed by the reaction at MgO surface. At the end of the impregnation the surface of MgO is saturated by molybdena species. The texture of the starting support is stable in the methanol slurry.

The first example illustrating the method is shown in Fig. 4. The reaction of laboratory made MgO extrudates (surface area 250 $m^2\,g^{-1}$) with the impregnation slurry AHM/methanol at room temperature was followed by electron microprobe analysis. The impregnated extrudates were dried in rotary vacuum evaporator at 95–100°C and were not calcined. Surface area of the impregnated extrudates was about the same (±10%) as that of the starting support. The molyb-

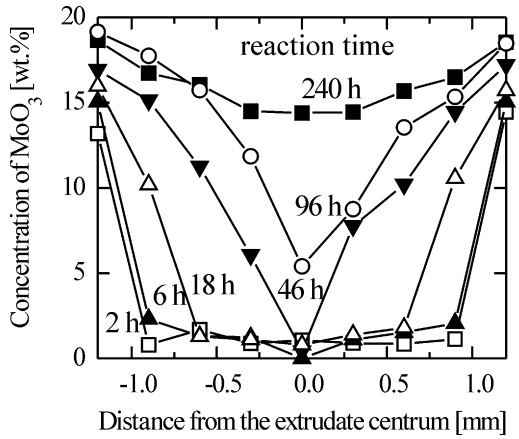


Fig. 4. Profiles of $MoO_3$ concentration in MgO extrudates (2.5 mm) impregnated by the reaction with the slurry ammonium heptamolybdate/methanol at room temperature and various reaction times. Nominal loading was 15 wt.% $MoO_3$ and the profiles were measured by electron microprobe analysis.

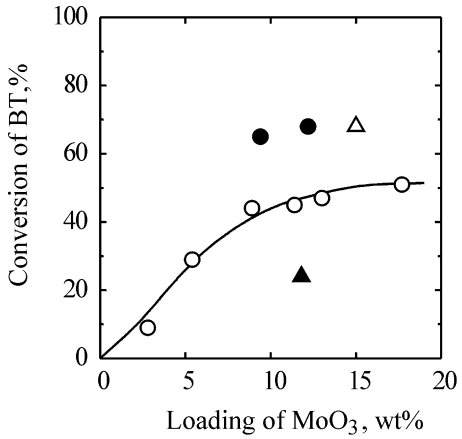


Fig. 5. Relative activity of $MoO_3$/MgO catalysts prepared by slurry impregnation in the slurry $MoO_3$/methanol. Model reaction was hydrodesulphurization of benzothiophene in the gas phase at 1.6 MPa and 330°C (for details of testing see [30]). (○) $MoO_3$/MgO catalysts prepared with impregnation time of 10 days at room temperature; (●) $MoO_3$/MgO catalysts prepared with impregnation time of 5 h at 65°C; (△) reference industrial $MoO_3/Al_2O_3$ catalyst BASF M8-30; (▲) reference industrial $MoO_3/Al_2O_3$ catalyst Cherox 33-00.

denum concentration wave gradually moved into the extrudates with increasing impregnation time. After 10 days, almost uniform distribution of molybdena across the extrudates was achieved and the deposited loading of $MoO_3$ corresponded within the experimental error to the nominal loading of 15 wt.% $MoO_3$.

The second example illustrating the method is shown in Fig. 5. Magnesia particles of the size fraction 0.16–0.32 mm impregnated with various loading and under various conditions are shown in Fig. 5. The hydrodesulphurization activity of the catalysts was tested in hydrodesulphurization of benzothiophene in fixed bed flow reactor. The feed was solution of benzothiophene in decane, pressure was 1.6 MPa and the temperature was 330°C. Two industrial alumina supported molybdenum catalysts served as reference points of activity. The industrial application of the BASF M8-30 catalyst is the hydrorefining of crude benzene by the BASF-Scholven process. The catalyst Cherox 3500 (Chemopetrol Litvínov, Czech Republic) is a robust pelleted catalyst intended for aromatisation of gasoline fractions and general hydrotreating (it was probably prepared by coprecipitation and it is out of production at present). It is seen in Fig. 5 that using the slurry impregnation it is possible to prepare magnesia supported catalysts with high activity similar to the activity of the reference alumina supported samples.

## 6. Conclusions

The new slurry impregnation method of preparation of supported molybdenum catalysts is a simple and clean alternative to the conventional preparation using solutions of ammonium heptamolybdate. Support is impregnated in the slurry $MoO_3$/water. Solubility of $MoO_3$ is low but sufficient for transport of molybdena species to the surface where they are adsorbed. The method belongs to the equilibrium adsorption methods and the maximum amount of deposited $MoO_3$ corresponds to saturated monolayer. Calcination is not necessary and no waste solutions and calcining nitrogenous gases are formed and well-defined monolayer type catalysts are obtained. Various catalysts supported on alumina and active carbon were prepared by the slurry impregnation and were tested in hydrodesulphurization. Slurry impregnation of $Zr(OH)_4$ is a simple interesting way to $MoO_3/ZrO_2$ catalyst with improved surface area as compared to the conventional impregnation of $ZrO_2$. High surface area $MoO_3$/MgO is prepared by the reaction of the support with the slurry ammonium heptamolybdate/methanol. This approach overcomes

the problem of instability of high surface area MgO in aqueous impregnation solutions and provides $MoO_3$/MgO catalysts with high hydrodesulphurization activity.

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