

Facile ambient pressure propylene carbonate solution synthesis of highly divided CoMoS solids

Santiago Palencia-Ruiz, Dorothée Laurenti, Denis Uzio, Christelle Legens, Pavel Afanasiev

▶ **To cite this version:**

Santiago Palencia-Ruiz, Dorothée Laurenti, Denis Uzio, Christelle Legens, Pavel Afanasiev. Facile ambient pressure propylene carbonate solution synthesis of highly divided CoMoS solids. Materials Letters, 2020, 277, pp.128296. 10.1016/j.matlet.2020.128296 . hal-02956115

HAL Id: hal-02956115
https://ifp.hal.science/hal-02956115

Submitted on 2 Oct 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

*Manuscript
Click here to view linked References

Facile ambient pressure propylene carbonate solution synthesis of highly divided CoMoS solids.

Santiago Palencia-Ruiz [a], Dorothée Laurenti [a], Denis Uzio [b], Christelle Legens[b], Pavel Afanasiev*[a]

[a] Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne, France.

[b]IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, BP 3, F-69360 Solaize, France.

Abstract

One-pot synthesis of highly dispersed Co-Mo-S materials is achieved in propylene carbonate solutions by means of ambient pressure reflux of elemental sulfur, ammonium heptamolybdate and cobalt nitrate mixtures. The solids were characterized and compared with benchmark references in thiophene hydrodesulfurization (HDS). The sequence of reactants addition is important: simultaneous addition of Co and Mo precursors or reaction of Mo followed by addition of Co salt give higher surface areas and better HDS activity than starting the reaction with Co salt and then adding Mo precursor.

Keywords: cobalt molybdenum sulfide; propylene carbonate; hydrodesulfurization; nanoparticles; porous materials

Introduction

Nanodispersed transition metals sulfides are important for different fields, including photo- and electro catalysts [1,2], batteries [3,4], lubricants [5], hydrotreating catalysis [6,7] and many other applications. Nanodispersed sulfides of different metals including molybdenum and tungsten have been studied for HDS [8]. Versatile methods have been applied to prepare mixed sulfides such as hydrothermal [9], precursor decomposition [10] or polymer-assisted synthesis [11]. Even if CoMo sulfides are well-established catalysts, novel techniques are pursued for their preparation aiming at the improvement of properties, such as HDS selectivity [12].

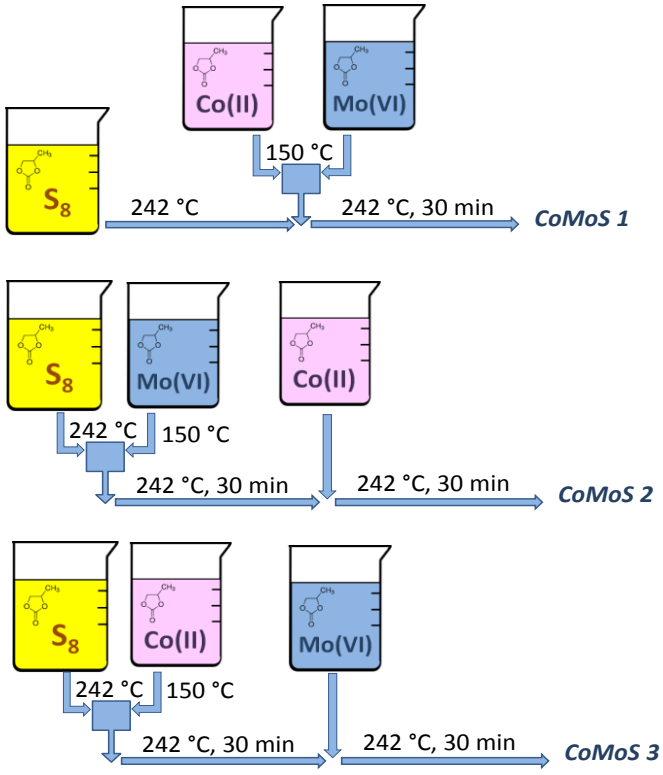
Syntheses in highly boiling polar solvents allow preparation of finely divided sulfides at ambient pressure using simple equipment. Elemental sulfur is used for sulfidation, which makes the preparations safe, easy and inexpensive. Ethylene glycol was applied previously to prepare MoS_2 [13,14] and Co-Mo-S solids [15].

Recently, propylene carbonate (PEC) was applied to prepare individual molybdenum sulfide. 20 nm-size MoS_x nanoparticles were prepared in PEC by short-time reflux. PEC combines high boiling temperature with significant sulfur solubility, which makes it a convenient reaction medium for the preparation of nanodispersed sulfides. This work firstly reports on PEC synthesis of Co-Mo-S solids.

2. Experimental

2.1. Catalysts preparation

In all the preparations, high purity grade chemicals were used, purchased from Sigma Aldrich. Three synthesis routes have been applied, differing by the order of reactants addition (Scheme 1). In all cases, 1.6 g S_8 (0.05 mol. S) was first dissolved in 50 ml of PEC upon stirring at PEC boiling temperature 242°C.



Scheme 1. Schematic illustration of the three methods used to prepare Co-Mo-S materials.

Simultaneously, 363 mg (0.00125 mol. Co) of $Co(NO_3)_2.6H_2O$ and 450 mg (0.0025 mol. Mo) of $(NH_4)_6Mo_7O_{24}.4H_2O$ were dissolved in 15 ml of PEC each, upon stirring at 150°C. Then both Co and Mo precursors were simultaneously added to the sulfur solution and reflux was continued for 30 min (method 1). Otherwise one of the two Co or Mo solutions was added to the sulfur solution, the mixture being refluxed for 30 min, then the second solution was added and reflux was continued for another 30 min (methods 2, 3). The solids were separated by centrifugation washed with acetone to remove non-reacted sulfur and dried at room temperature under nitrogen. The corresponding solids are designated as CoMoS-1, CoMoS-2 and CoMoS-3 respectively (Fig. 1). The solids were activated under 15% vol. H_2S/H_2 flow at 400°C, for 1h. Monometallic MoS_2 sulfide (MoS_2–PEC) was prepared by reflux in PEC [16]. Reference MoS_2 (S_{sp}=55 m^2/g) ATM-MoS_2 was prepared by decomposition of $(NH_4)_2MoS_4$. Last generation industrial $CoMo/Al_2O_3$ catalyst CoMo–Ind (ca. 15 %wt. Mo and 3 % wt. Co) was also used as a reference.

2.3. Thiophene HDS

Thiophene HDS tests were carried out at atmospheric pressure in a glass plug-flow microreactor. Partial pressure of thiophene was 2.7 kPa; hydrogen flow 50 mL/min. After stabilization for 16 h on-stream at 320°C, steady-state activity was determined at several temperatures from 300 to 340°C. The products were analyzed by on-line gas chromatography and the reaction rate determined from thiophene conversion using pseudo-first rate equation [14, 15]. The overall thiophene conversion was below 15%.

2.4. Characterizations

Transmission Electron Microscopy (TEM) was performed on a JEOL 2010 device at 200 keV accelerating voltage. The samples were dispersed in ethanol onto a lacey carbon sample holder. Powder X-ray diffraction (XRD) patterns were obtained on a Bruker device with Cu Kα emission and analyzed using standard ICDD files. Textural properties were studied by low-temperature nitrogen adsorption and calculated using BET and BJH equations.

3. Results and discussion

Transparent yellow solution was formed upon mixing 50 mL PEC with 1.6 g of S_8 and heating at 242°C. Cobalt nitrate gives pink solution, stable up to 180-200°C. Ammonium

heptamolybdate (AHM) at 150°C forms a yellow cloudy suspension. When mixed with sulfur solution, both metals salts solutions became black in several seconds.

Earlier preparations used ethylene glycol (EG) at 196°C to obtain MoS_x dispersions of 10 nm size scale. But to reach that size, a seed as 5-10 nm-size particles of ZnS or CoS should be introduced into the reaction mixture [13,14,17]. Without a seed, EG preparations of MoS_x lead to 200-300 nm spheres [18]. By contrast, reflux of AHM and sulfur in PEC provided 10-20 nm size MoS_x particles without the need of any seed [15]. Unlike other solvents applied to prepare sulfides, e.g. oleic acid [19] or oleylamine [20], PEC is a small polar molecule, easily removable from the final materials by washing with water or organics.

For bimetallic systems one may introduce Co and Mo precursors simultaneously or sequentially. Indeed, one of the metals salts could react providing smaller nuclei so the corresponding mixed solid could have advantageous morphology.

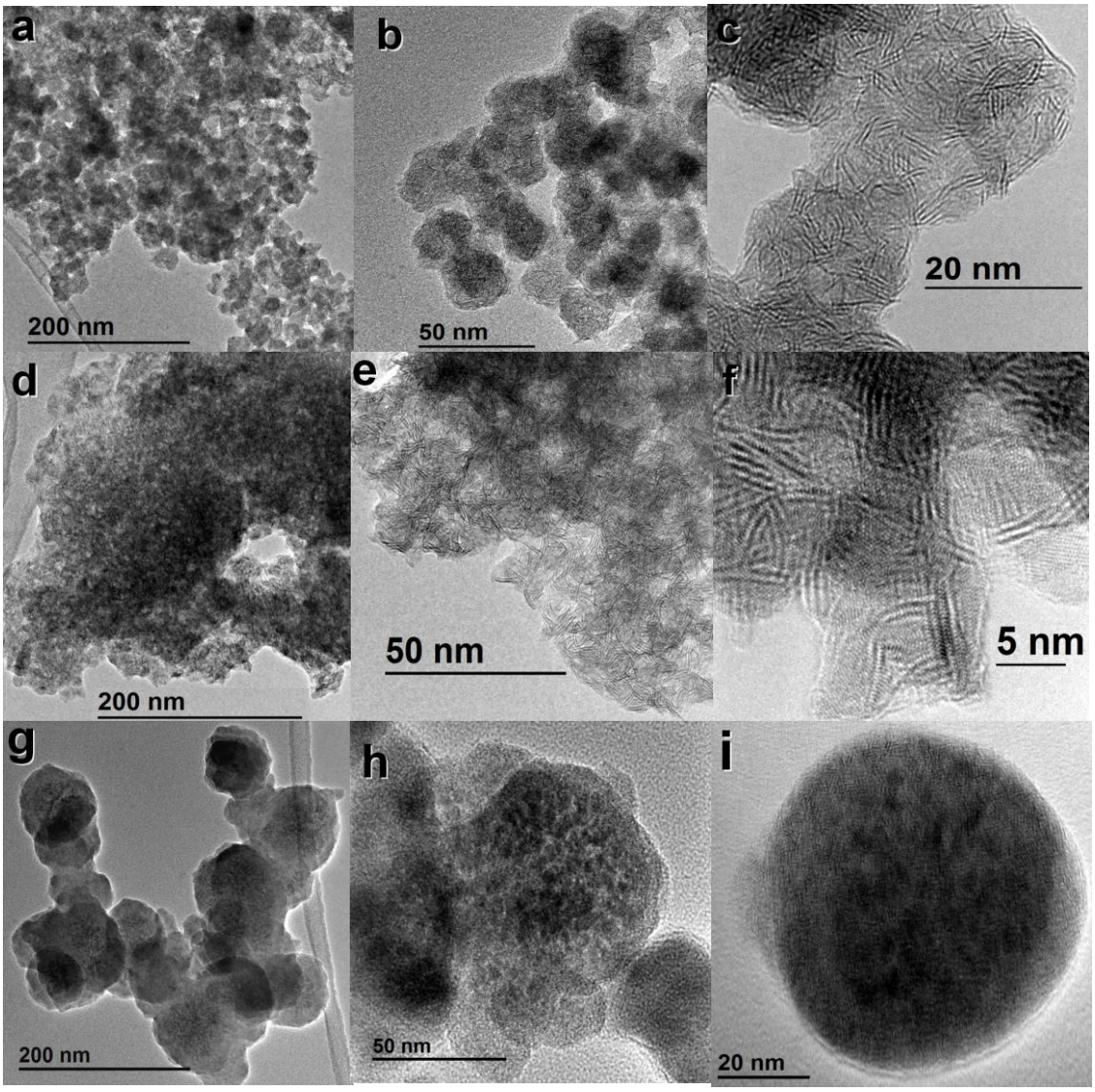


Fig. 2. TEM images for the CoMoS solids prepared with methods 1 (a-c), 2 (d-f) and 3 (g-i).

TEM attests considerable difference of morphology between the three methods. CoMoS-1 shows 20-30 nm spherical particles containing weakly stacked 3-5 nm length MoS_2 fringes (Fig.2a-c). For CoMoS-2 the structure is more agglomerated, but at high resolution the slabs are similar to CoMoS-1. Method 3 leads to 50-100 nm spherical particles (Fig 2 g-i). The reaction product for sole Co after 30 min reflux in PEC-S_8 mixture contains 50-100 nm-size CoS_x particles. Therefore, in Method 3 large CoS_x particles are first formed and then covered with MoS_x.

XRD shows highly dispersed MoS_2 as the main phase for all samples. Highly dispersed CoS_2 phase is present in freshly prepared CoMoS-3 (Fig. 3a). Activation at 400°C with H_2/H_2S leads to crystallization of CoS and Co_9S_8 sulfide phases. XRD peaks intensity of CoS_x phases indicates that phase homogeneity changes in the sequence CoMoS-1 > CoMoS-2 > CoMoS-3 (Fig. 3b).

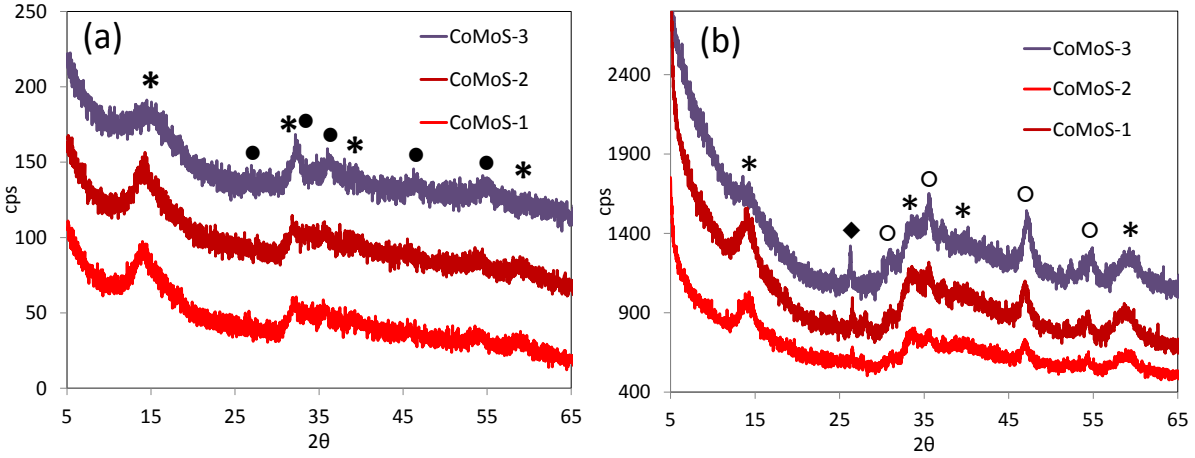


Fig. 3 XRD patterns of CoMoS1-3 solids as synthesized (a) and after activation (b). Peaks marks: * - 2H-MoS_2 (02-0132); ○ – CoS (03-065-3418); ● – CoS_2 (01-089-3056); ◆ - Co_9S_8 (02-1459).

After activation, CoMoS materials exhibit high specific surface areas up to 132 m^2/g and mesopores volume up to 0.34 cm^3/g. Nitrogen adsorption isotherms show significant difference of textural properties. The highest mesopores volume and specific surface area was observed for CoMoS-1 (Fig. 4a). CoMoS-3 has the lowest surface area and considerably smaller porosity, probably because it is composed of compact dense spheres (Fig. 2g-i) with a poor access to the interior surface.

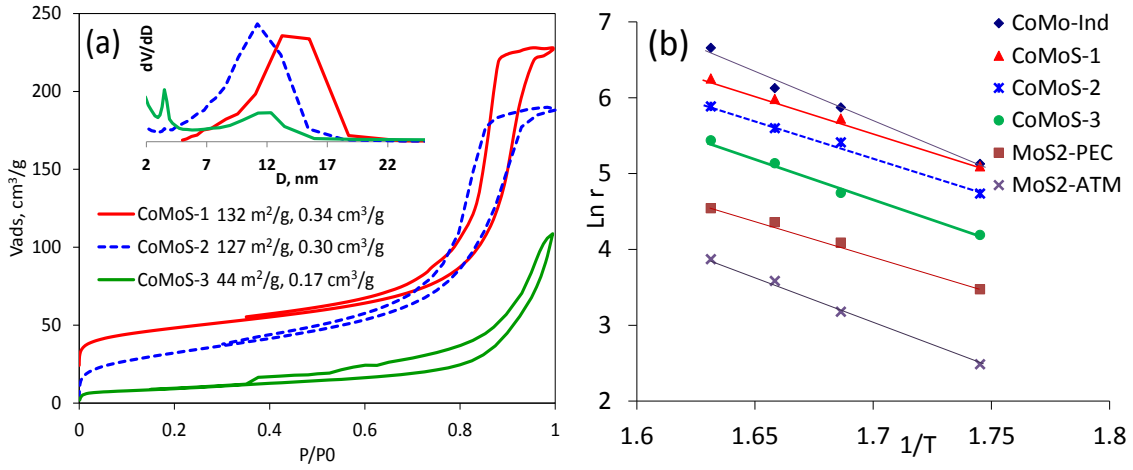


Fig. 4 (a) Nitrogen adsorption isotherms with BJH Pore Size Distribution; (b) Arrhenius plots of thiophene HDS rate for the CoMoS-1-3 and reference catalysts.

Fig 4b shows steady-state Arrhenius plots HDS rates vs. the inverse of temperature (1/K) for CoMoS-1-3 solids and benchmark references, including industrial catalyst CoMo-Ind. For all catalysts HDS activation energy was around 80 kJ mol^{-1}, attesting the kinetic regime. Among the prepared catalysts, CoMoS-1 showed the highest HDS activity (175×10^{-8} mol g^{-1} s^{-1} at 300°C) close to the performance of latest-generation CoMo-Ind system, which is remarkable for a bulk MoS_2 catalyst. The HDS activity varies in the sequence CoMoS-1 > CoMoS-2 > CoMoS-3, in step with the sequence of textural properties and the degree of phase homogeneity, suggested by XRD. High degree of promotion for CoMoS solids is obvious from comparison with the HDS rates on non-promoted MoS_2 references (Fig. 4b), the preparation method 1 being optimal.

Conclusion

A simple and scalable method has been developed for one-step solution preparation of CoMoS nanoparticles. The method is environmentally friendly and uses cheap and relatively non-toxic reagents. The order of reactants mixing is important for the products properties. Advantageous textural properties and phase homogeneity lead to high performance of the CoMoS solids as HDS catalysts. Due to highest surface area, mesoporosity and phase homogeneity simultaneous mixing of solutions lead to the best HDS performance. Synergistic effects between CoS and MoS_2 species strongly improve the catalytic properties as compared

with sole MoS_2. These materials might be interesting not only as HDS catalysts but for other applications (lithium batteries, pseudocapacitors) for which similar requirements exist of high specific surface area and porosity.

References

1 F. Raza, D. Yim, J.H. Park, H.I. Kim, S.J. Jeon, J.H. Kim, J. Am. Chem. Soc. 2017, 139, 14767–14774.

2 Q. Lin, J. Liang, J. Liu, Q. Zhang, W. Peng, Y. Li, F. Zhang, X. Fan, Ind. Eng. Chem. Res. 58 (2019) 23093-23098.

3 K. Yang, T. Mei, Z. Chen, M. Xiong, X. Wang, J. Wang, J. Li, L. Yu, J. Qian and X. Wang, Nanoscale, 2020, Advance Article , DOI: 10.1039/C9NR09260A

4 Y.C. Tang, Z.B. Zhao, Y.W. Wang, Y.F. Dong, Y. Liu, X.Z. Wang, J.S. Qiu, ACS Appl. Mater. Interfaces 2016, 8, 32324– 32332.

5 I. Lahouij, B. Vacher, J.-M. Martin, F. Dassenoy, Wear, 296 (2012) 558-567.

6 J.N. Díaz de León, C. Ramesh Kumar, J. Antúnez-García, S. Fuentes-Moyado, Catalysts 9 (2019) 87.

7 R. Singh, S. Arora, D. Kunzru, S. Sivakumar. Energy & Fuels 34 (2020) 749-757.

8 T.A. Zepeda, B. Pawelec, J.N. Díaz de León, J.A. de los Reyes, A. Olivas, Appl. Catal. B Environ. 111–112 (2012) 10–19.

9 B. Yoosuk, C. Song, J.H. Kim, C. Ngamcharussrivichai, P. Prasassarakich, Catal. Today **2010**, 149, 52–61.

10 Y.E. Armenta, J.C. Reyes, F.P. Delgado, M.D. Valle, M.D.; Alonso, G.; Fuentes, S.; Rivera, R.R. Appl. Catal. A Gen. 486 (2014) 62–68.

11 V Hetier, D Pena, A Carvalho, L Courthéoux, V Flaud, E Girard, D Uzio, S Brunet, P Lacroix-Desmazes, A Pradel, Catalysts 9 (2019) 793

12 J. Xu, Y. Guo, T. Huang, Y. Fan, Appl. Catal. B: Env. 244 (2019) 385-395.

13 P. Afanasiev, C. Geantet, I. Llorens, O. Proux, J. Mater. Chem. 22 (2012) 9731-9737.

14 E. Blanco, D. Uzio, G. Berhault, P. Afanasiev, J. Mater. Chem. A 2 (2014) 3325–3331.

15 A.H. Aissa, F. Dassenoy, C. Geantet, P. Afanasiev, Catal. Sci. Technol. 6 (2016) 4901–4909.

16 P. Afanasiev, J. Solid State Chem. 213 (2014) 158-164.

17 P. Njiwa, A. Hadj-Aïssa, P. Afanasiev, C. Geantet, F. Bosselet, B. Vacher, M. Belin, T. Le Mogne, F. Dassenoy
Tribology Lett. 55 (2014) 473-481.

18 P. Rabaso, F. Ville, F. Dassenoy, M. Diaby, P. Afanasiev, J. Cavoret, B. Vacher, T. Le Mogne, Wear 320 (2014) 161-178.

19 J.C. Park, H. Song, Chem. Mater. 19 (2007) 2706-2708.

20 C. Altavilla, M. Sarno, P. Ciambelli, Chem. Mater. 23 (2011) 3879-3885.