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Pavel Afanasiev

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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

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2 **Facile ambient pressure propylene carbonate solution synthesis of highly divided**
3 **CoMoS solids.**
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6 Santiago Palencia-Ruiz ^a, Dorothée Laurenti ^a, Denis Uzio ^b, Christelle Legens^b, Pavel
7 Afanasiev*^a
8

9 ^a Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne,
10 France.
11

12 ^bIFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, BP 3, F-69360 Solaize,
13 France.
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18 **Abstract**
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20 One-pot synthesis of highly dispersed Co-Mo-S materials is achieved in propylene carbonate
21 solutions by means of ambient pressure reflux of elemental sulfur, ammonium
22 heptamolybdate and cobalt nitrate mixtures. The solids were characterized and compared with
23 benchmark references in thiophene hydrodesulfurization (HDS). The sequence of reactants
24 addition is important: simultaneous addition of Co and Mo precursors or reaction of Mo
25 followed by addition of Co salt give higher surface areas and better HDS activity than starting
26 the reaction with Co salt and then adding Mo precursor.
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36 **Keywords:** cobalt molybdenum sulfide; propylene carbonate; hydrodesulfurization;
37 nanoparticles; porous materials
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42 **Introduction**
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44 Nanodispersed transition metals sulfides are important for different fields, including photo-
45 and electro catalysts [1,2], batteries [3,4], lubricants [5], hydrotreating catalysis [6,7] and
46 many other applications. Nanodispersed sulfides of different metals including molybdenum
47 and tungsten have been studied for HDS [8]. Versatile methods have been applied to prepare
48 mixed sulfides such as hydrothermal [9], precursor decomposition [10] or polymer-assisted
49 synthesis [11]. Even if CoMo sulfides are well-established catalysts, novel techniques are
50 pursued for their preparation aiming at the improvement of properties, such as HDS
51 selectivity [12].
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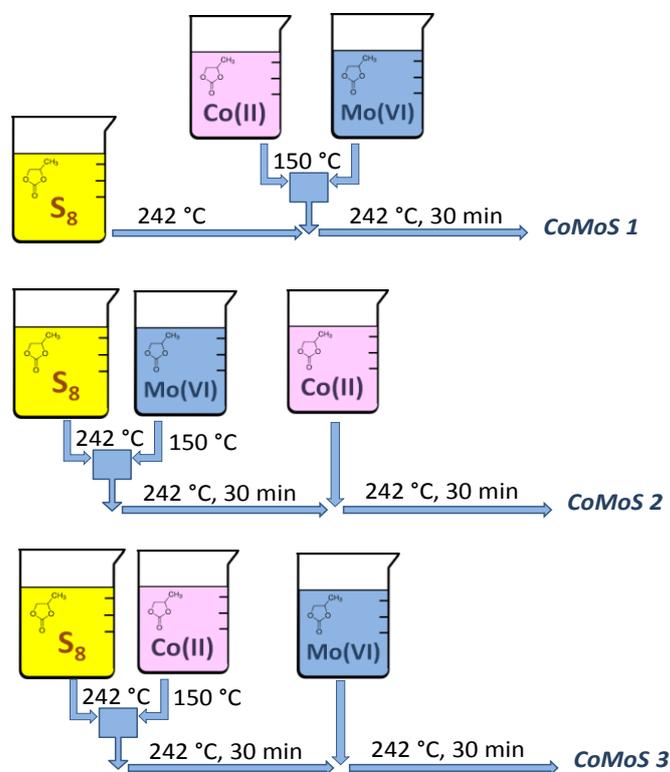
Syntheses in highly boiling polar solvents allow preparation of finely divided sulfides at ambient pressure using simple equipment. Elemental sulfur is used for sulfidation, which makes the preparations safe, easy and inexpensive. Ethylene glycol was applied previously to prepare MoS₂ [13,14] and Co-Mo-S 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 S₈ (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.

1 Simultaneously, 363 mg (0.00125 mol. Co) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 450 mg (0.0025 mol. Mo)
2 of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in 15 ml of PEC each, upon stirring at 150°C . Then
3 both Co and Mo precursors were simultaneously added to the sulfur solution and reflux was
4 continued for 30 min (method 1). Otherwise one of the two Co or Mo solutions was added to
5 the sulfur solution, the mixture being refluxed for 30 min, then the second solution was added
6 and reflux was continued for another 30 min (methods 2, 3). The solids were separated by
7 centrifugation washed with acetone to remove non-reacted sulfur and dried at room
8 temperature under nitrogen. The corresponding solids are designated as CoMoS-1, CoMoS-2
9 and CoMoS-3 respectively (Fig. 1). The solids were activated under 15% vol. $\text{H}_2\text{S}/\text{H}_2$ flow at
10 400°C , for 1h. Monometallic MoS_2 sulfide ($\text{MoS}_2\text{-PEC}$) was prepared by reflux in PEC [16].
11 Reference MoS_2 ($S_{\text{sp}}=55 \text{ m}^2/\text{g}$) ATM- MoS_2 was prepared by decomposition of $(\text{NH}_4)_2\text{MoS}_4$.
12 Last generation industrial CoMo/ Al_2O_3 catalyst CoMo-Ind (ca. 15 %wt. Mo and 3 % wt. Co)
13 was also used as a reference.
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27 *2.3. Thiophene HDS*

28 Thiophene HDS tests were carried out at atmospheric pressure in a glass plug-flow
29 microreactor. Partial pressure of thiophene was 2.7 kPa; hydrogen flow 50 mL/min. After
30 stabilization for 16 h on-stream at 320°C , steady-state activity was determined at several
31 temperatures from 300 to 340°C . The products were analyzed by on-line gas chromatography
32 and the reaction rate determined from thiophene conversion using pseudo-first rate equation
33 [14, 15]. The overall thiophene conversion was below 15%.
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41 *2.4. Characterizations*

42 Transmission Electron Microscopy (TEM) was performed on a JEOL 2010 device at 200 keV
43 accelerating voltage. The samples were dispersed in ethanol onto a lacey carbon sample
44 holder. Powder X-ray diffraction (XRD) patterns were obtained on a Bruker device with Cu
45 $\text{K}\alpha$ emission and analyzed using standard ICDD files. Textural properties were studied by
46 low-temperature nitrogen adsorption and calculated using BET and BJH equations.
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55 **3. Results and discussion**

56 Transparent yellow solution was formed upon mixing 50 mL PEC with 1.6 g of S_8 and
57 heating at 242°C . Cobalt nitrate gives pink solution, stable up to $180\text{-}200^\circ\text{C}$. Ammonium
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1 heptamolybdate (AHM) at 150°C forms a yellow cloudy suspension. When mixed with sulfur
2 solution, both metals salts solutions became black in several seconds.
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4 Earlier preparations used ethylene glycol (EG) at 196°C to obtain MoS_x dispersions of 10 nm
5 size scale. But to reach that size, a seed as 5-10 nm-size particles of ZnS or CoS should be
6 introduced into the reaction mixture [13,14,17]. Without a seed, EG preparations of MoS_x
7 lead to 200-300 nm spheres [18]. By contrast, reflux of AHM and sulfur in PEC provided 10-
8 20 nm size MoS_x particles without the need of any seed [15]. Unlike other solvents applied to
9 prepare sulfides, e.g. oleic acid [19] or oleylamine [20], PEC is a small polar molecule, easily
10 removable from the final materials by washing with water or organics.
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13 For bimetallic systems one may introduce Co and Mo precursors simultaneously or
14 sequentially. Indeed, one of the metals salts could react providing smaller nuclei so the
15 corresponding mixed solid could have advantageous morphology.
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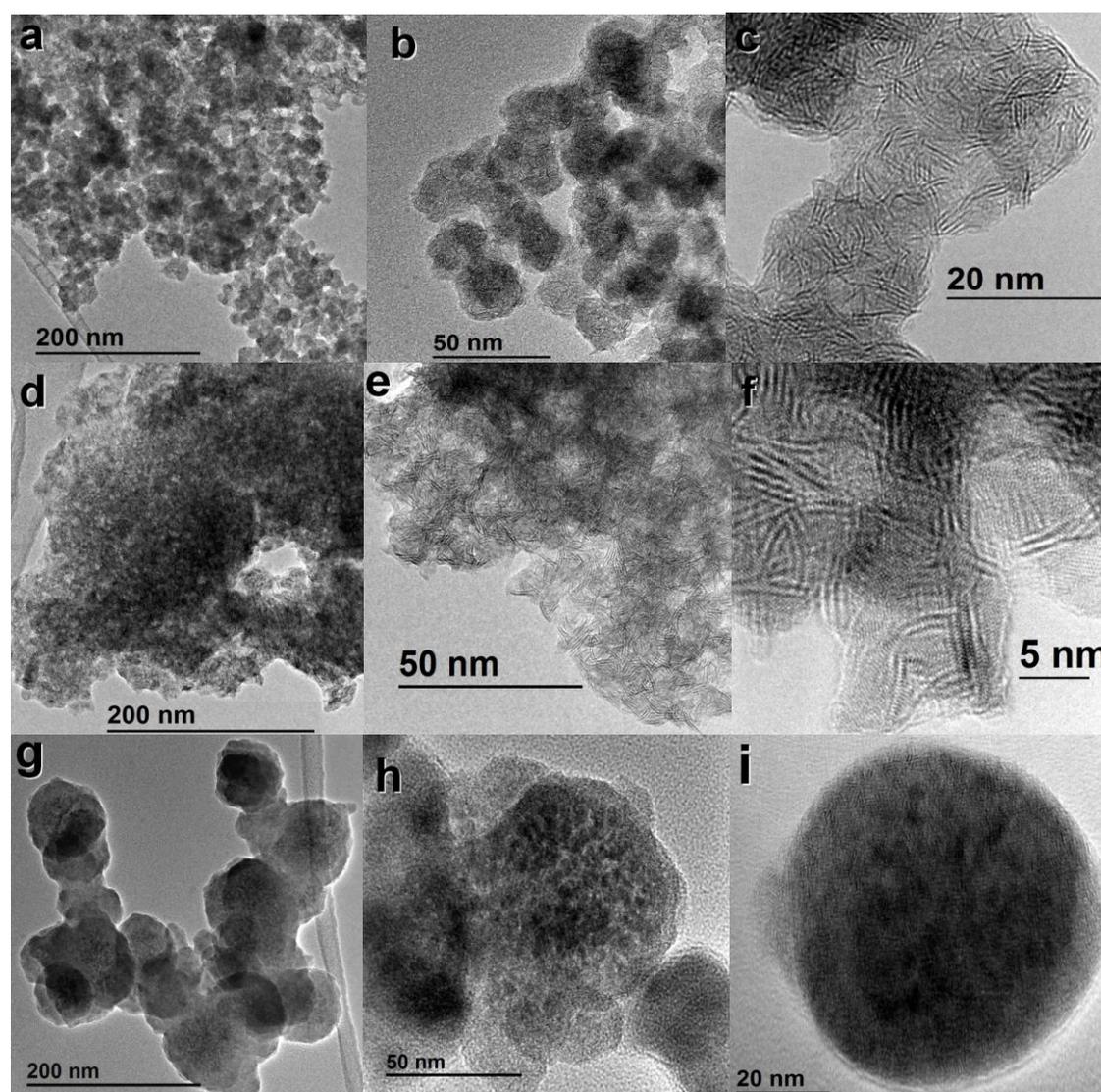


Fig. 2. TEM images for the CoMoS solids prepared with methods 1 (a-c), 2 (d-f) and 3 (g-i).

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 MoS₂ 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-S₈ 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 MoS₂ as the main phase for all samples. Highly dispersed CoS₂ phase is present in freshly prepared CoMoS-3 (Fig. 3a). Activation at 400°C with H₂/H₂S leads to crystallization of CoS and Co₉S₈ 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).

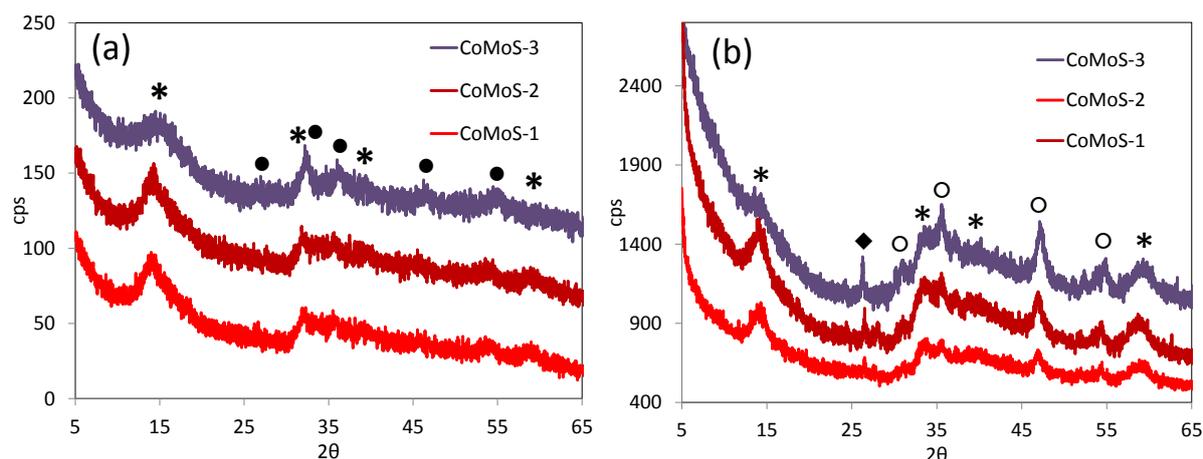


Fig. 3 XRD patterns of CoMoS1-3 solids as synthesized (a) and after activation (b). Peaks marks: * - 2H-MoS₂ (02-0132); ○ – CoS (03-065-3418); ● – CoS₂ (01-089-3056); ◆ - Co₉S₈ (02-1459).

After activation, CoMoS materials exhibit high specific surface areas up to 132 m²/g and mesopores volume up to 0.34 cm³/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.

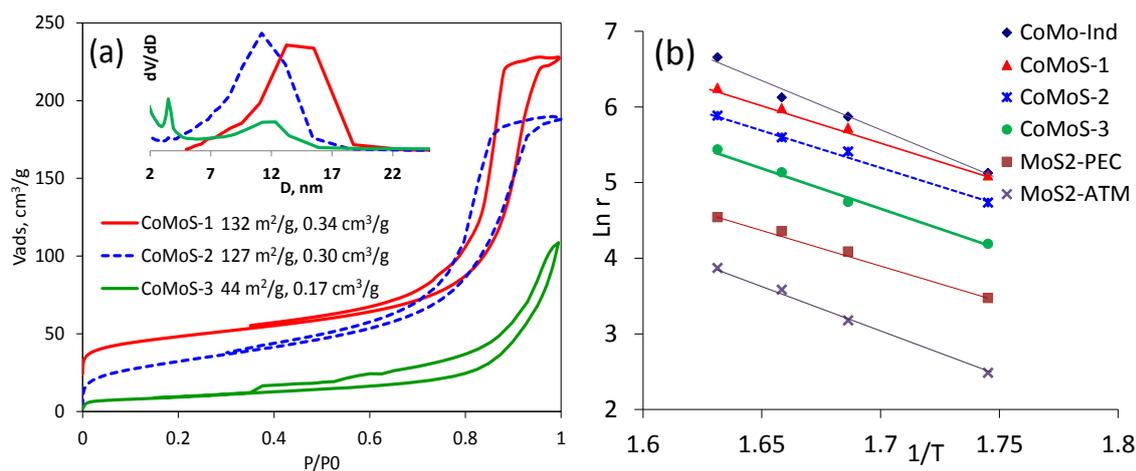


Fig. 4 (a) Nitrogen adsorption isotherms with BJH Pore Size Distribution; (b) Arrhenius plots of thiophene HDS rate for the CoMoS-1-3 and reference catalysts.

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 ($175 \times 10^{-8} \text{ mol g}^{-1} \text{ s}^{-1}$ at 300°C) close to the performance of latest-generation CoMo-Ind system, which is remarkable for a bulk MoS₂ 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 MoS₂ 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 MoS₂ species strongly improve the catalytic properties as compared

1
2 with sole MoS₂. These materials might be interesting not only as HDS catalysts but for other
3 applications (lithium batteries, pseudocapacitors) for which similar requirements exist of high
4 specific surface area and porosity.
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8 9 **References**

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