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# Direct Synthesis of TiO<sub>2</sub>-Supported MoS<sub>2</sub> Nanoparticles by Reductive Coprecipitation

Lennart van Haandel,<sup>[a]</sup> John W. Geus,<sup>[b]</sup> and Thomas Weber<sup>\*[a]</sup>

Molybdenum disulfide nanoparticles supported on titania were synthesized from aqueous solutions containing Ti and Mo precursor salts by an in situ redox reaction. The synthesis involves a redox process between Ti<sup>3+</sup> and MoS<sub>4</sub><sup>2-</sup>, which proceeds readily under mild conditions in aqueous solution. Catalysts were made in a single step, yielding amorphous catalysts with high Mo content, or in two steps to obtain MoS<sub>2</sub> supported on well-defined TiO<sub>2</sub> with lower Mo content. Catalysts obtained by single-step reductive coprecipitation were highly active in the

hydrodesulfurization of dibenzothiophene, exceeding the activity of an alumina-supported Co–Mo reference. In contrast to alumina-supported catalysts, the addition of Co as promoter did not enhance the catalytic activity of MoS<sub>2</sub>/TiO<sub>2</sub> to the same extent (+30%) as for alumina-supported Co–Mo catalysts. Instead, a change in selectivity towards hydrogenolysis products at the expense of hydrogenation products was observed. It is suggested that Ti may act as a promoter for MoS<sub>2</sub> in hydrogenation reactions.

## Introduction

The synthesis of industrial heterogeneous catalysts, composed of highly dispersed active nanoparticles on a porous support, usually involves multiple steps.<sup>[1]</sup> Typically, the support is prepared and shaped first and subsequently loaded with the desired metal salt precursors. Several steps of drying, calcination, and activation are then required to obtain the catalytically active phase, each exhibiting some inherent drawbacks. For example, during drying the precursor may migrate and agglomerate at the pore mouth. Calcination can lead to incorporation of the precursor into the support and activation may lead to initial sintering of metal nanoparticles, resulting in a loss of catalytic activity and/or selectivity.<sup>[1,2]</sup> The development of synthetic routes that involve fewer steps is thus not only economically attractive, but it may also lead to a higher degree of control over materials properties.

Several one-step methodologies have been reported for the synthesis of heterogeneous catalysts containing noble<sup>[3]</sup> or non-noble<sup>[3b,4]</sup> metal nanoparticles. However, despite their simplified preparation, calcination and/or reduction may still be required to obtain the catalyst in its active state. Reduction by H<sub>2</sub> or other reducing agents such as NaBH<sub>4</sub> can be circumvented if the support facilitates reduction directly. Redox-active

supports (or their precursors) such as CeO<sub>2</sub> and TiO<sub>2</sub> are capable of reducing noble-metal salts in solution to obtain supported metallic nanoparticles directly.<sup>[5]</sup> Such an approach has not yet been demonstrated for non-noble metals, although the deposition of small amounts of MS<sub>2</sub> (M=Mo, W) on TiO<sub>2</sub> by photoreduction has suggested that a similar approach may work for transition-metal disulfides (TMS).<sup>[6]</sup>

TMS are an important class of materials that have attracted interest in a variety of fields such as catalysis and energy storage.<sup>[7]</sup> In particular, they are broadly applied in refineries to catalyze the removal of heteroatoms (S, N, O, Ni, V, etc.) from oil. Hydrotreating (HDT) catalysts are typically composed of Co- or Ni-promoted MoS<sub>2</sub> nanoparticles supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>[8]</sup> Several researchers have reported that TiO<sub>2</sub> as a support improves intrinsic hydrodesulfurization (HDS) performance by a factor of four to five.<sup>[9]</sup> Nevertheless, practical applications of TiO<sub>2</sub> as a support in HDS catalysts are limited by its maximum Mo loading, which is constrained by the lower surface area compared with Al<sub>2</sub>O<sub>3</sub>.<sup>[9a,10]</sup>

Several strategies were proposed to overcome the low Mo capacity of TiO<sub>2</sub>. These strategies include the synthesis of high-surface-area TiO<sub>2</sub>,<sup>[10]</sup> mixed supports of TiO<sub>2</sub> with other metal oxides (ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>),<sup>[11]</sup> and the synthesis of TiO<sub>2</sub>-coated Al<sub>2</sub>O<sub>3</sub>.<sup>[12]</sup> Despite the higher Mo loadings accommodated by these supports, in all cases Co and Mo were added by post-impregnation. Recently, Nguyen et al. reported a single-step synthesis of TiO<sub>2</sub>-supported Co–Mo oxide HDT catalyst precursors by a sol–gel method.<sup>[13]</sup> By this approach, the Mo loading could be varied up to 30 wt.%. A drawback of this method was that part of the Mo was incorporated in the support and remained unsulfided. Consequently, the samples prepared by the sol–gel method were less active than impregnated samples with the same Mo loading.

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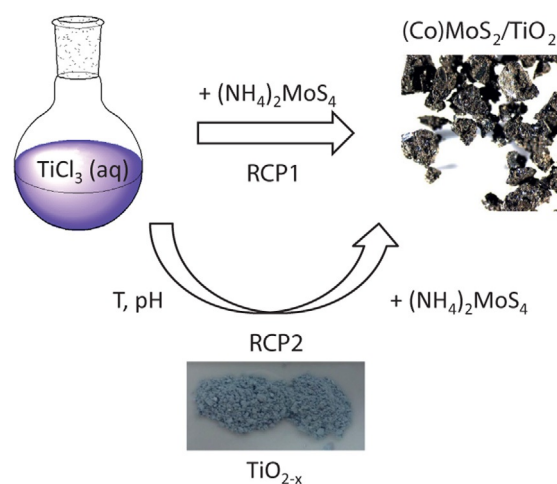
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In this work we report the direct synthesis of nonpromoted and Co-promoted MoS<sub>2</sub> nanoparticles supported on TiO<sub>2</sub> (MoS<sub>2</sub>/TiO<sub>2</sub> and Co-MoS<sub>2</sub>/TiO<sub>2</sub>, respectively) by reductive coprecipitation (RCP). The synthesis involves a redox reaction between Ti<sup>3+</sup> and MoS<sub>4</sub><sup>2-</sup> in aqueous solution and proceeds readily under mild conditions. To our knowledge, this is the first example of simultaneous formation of support and metal sulfide nanoparticles in a single step. Furthermore, unlike in the sol-gel method, we did not find evidence that coprecipitation leads to encapsulation of active MoS<sub>2</sub> particles by the support. The catalysts proved to be highly active in the HDS of dibenzothiophene (DBT) under mild conditions (40 bar, 245 °C), even in the absence of Co. The remarkable activity of the unpromoted catalyst, which is competitive with a commercial alumina-supported Co-Mo reference, can be attributed to an increased hydrogenation activity. This suggests that Ti (TiO<sub>2</sub>) may act as a promoter for MoS<sub>2</sub> in hydrogenation reactions. The as-synthesized catalysts were characterized by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray fluorescence (XRF), and X-ray photoelectron spectroscopy (XPS).

## Results and Discussion

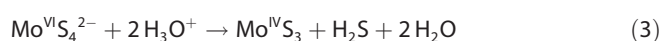
TiO<sub>2</sub>-supported MoS<sub>2</sub> catalysts were synthesized from aqueous solutions of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> and TiCl<sub>3</sub> by reductive coprecipitation (RCP). The method involves hydrolysis and oxidation of TiCl<sub>3</sub> and simultaneous reduction and decomposition of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> to MoS<sub>2</sub> (Figure 1). The involved redox process is formally described by the following half-reactions:



**Figure 1.** Schematic representation of the one-step (RCP1) and two-step (RCP2) reductive coprecipitation processes. In RCP1 the product forms directly in an aqueous solution of the precursor salts, whereas RCP2 involves preparation of TiO<sub>2-x</sub> and subsequent loading with MoS<sub>2</sub>.

Genesis of the supported catalysts is likely an interplay between redox, hydrolysis, and condensation reactions. TiCl<sub>3</sub> is hydrolyzed, and subsequently it condensates to form a gel-like structure, similarly to the early stage of TiO<sub>2</sub> synthesis from TiCl<sub>4</sub>.<sup>[14]</sup> Simultaneously, Ti<sup>3+</sup> is oxidized by MoS<sub>4</sub><sup>2-</sup>, yielding MoS<sub>2</sub>. We found that reduction of MoS<sub>4</sub><sup>2-</sup> proceeds readily under mild acidic or neutral conditions. MoS<sub>2</sub> spontaneously precipitates upon addition of a neutral solution of Ti<sup>3+</sup>, chelated by nitrilotriacetic acid, to a neutral solution of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> (see the Supporting Information and Figure S1). However, under alkaline conditions Ti<sup>3+</sup> is rapidly oxidized by water or hydroxyl anions to Ti<sup>4+</sup>. Consequently, MoS<sub>2</sub> does not form under these conditions.

Under acidic conditions, the reduction of MoS<sub>4</sub><sup>2-</sup> by Ti<sup>3+</sup> is in competition with its hydrolysis to MoS<sub>3</sub> [Eq. (3)], an amorphous Mo<sup>IV</sup> solid, which cannot take part in the redox process anymore.<sup>[15]</sup>



The formation of MoS<sub>3</sub> was suppressed by addition of a chelating agent (ethylenediaminetetraacetic acid, EDTA; or citric acid). The chelating agent stabilized Ti<sup>3+</sup> ions in solution, allowing the reaction between Ti<sup>3+</sup> and MoS<sub>4</sub><sup>2-</sup> to proceed in acidic media. The optimum pH for synthesis was between 3 and 4, resulting in a nearly stoichiometric ratio of TiO<sub>2</sub> and MoS<sub>2</sub> (Table 1, entry 1).

**Table 1.** Properties of the as-synthesized catalysts.

Entry	Material	Mo [wt. %] <sup>[a]</sup>	S/Mo ratio <sup>[b]</sup>	Mo/Ti ratio <sup>[b]</sup>	SSA [m <sup>2</sup> g <sup>-1</sup> ]
1	MoS <sub>2</sub> /TiO <sub>2</sub> -RCP1	13.3	2.1	0.30	117
2	Co-MoS <sub>2</sub> /TiO <sub>2</sub> -RCP1	13.9	n.m.	n.m.	n.m.
3	MoS <sub>2</sub> /TiO <sub>2</sub> -RCP2-T	5.9	n.m.	n.m.	96
4	MoS <sub>2</sub> /TiO <sub>2</sub> -RCP2-H	3.2	2.5	0.04	129

[a] Sample 1 and 4 determined by XRF, sample 2 and 3 determined by ICP-OES. [b] molar ratio, n.m. = not measured.

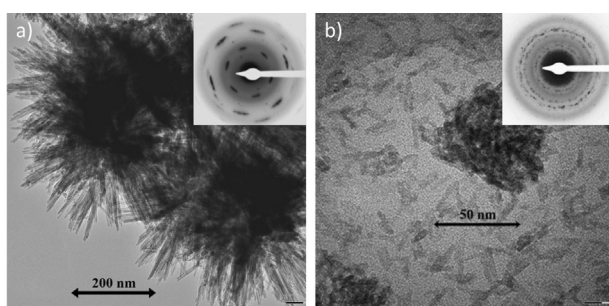
### Synthesis and characterization of TiO<sub>2-x</sub> support

The supported catalysts were synthesized in a single step, either directly from a solution of the respective metal salts (RCP1) or from a dispersion of TiO<sub>2-x</sub> support precursor in a solution of (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> (RCP2). The TiO<sub>2-x</sub> support precursor was prepared prior to the introduction of the (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> salt. The advantage of this approach (RCP2) is that the morphology of the TiO<sub>2-x</sub> support precursor can be modified by adjusting synthesis parameters (*T*, *pH*) without affecting the redox reaction between Ti<sup>3+</sup> and MoS<sub>4</sub><sup>2-</sup>, thus preventing unwanted side reactions.

Two methods were employed to synthesize TiO<sub>2-x</sub> support precursors, thermolysis and hydrolysis. In the first method, thermolysis, TiO<sub>2-x</sub> was synthesized overnight from an acidic TiCl<sub>3</sub> solution at 100 °C. In the second method, hydrolysis,

aqueous  $\text{TiCl}_3$  was hydrolyzed by adding a base (1 M NaOH solution) and subsequently kept overnight at  $60^\circ\text{C}$  to obtain  $\text{TiO}_{2-x}$ . Both methods yielded suspensions of fine blue  $\text{TiO}_{2-x}$  particles, which oxidized within one hour to  $\text{TiO}_2$  when exposed to air. As such, it was important to keep  $\text{TiO}_{2-x}$  under inert atmosphere prior to reaction with thiomolybdate.

TEM images of  $\text{TiO}_2$  particles obtained by thermolysis and hydrolysis are shown in Figure 2. Thermolysis yielded nano-sized rods of approximately 200 nm in length that tended to form spherical aggregates. Electron diffraction (ED) confirmed that the particles were crystalline and were composed of the rutile polymorph, which was also confirmed by XRD spectroscopy (Figure S2).  $\text{TiO}_2$  nanoparticles obtained by hydrolysis were approximately 25 nm in length and were polycrystalline. Both rutile and brookite were identified by their electron diffraction patterns, however, the presence of anatase could not be excluded.

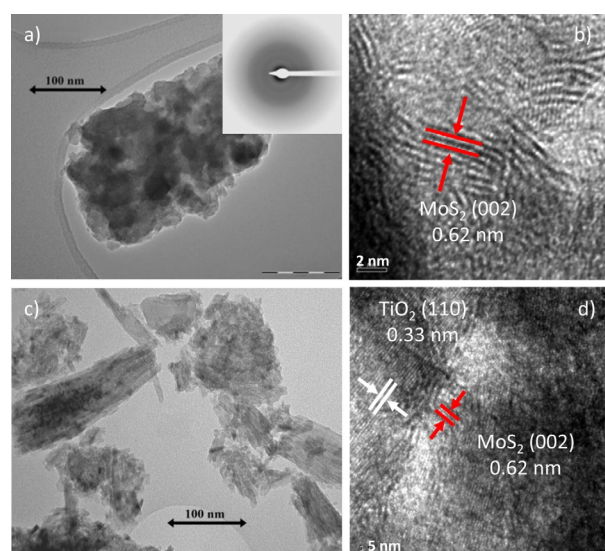


**Figure 2.** TEM images of  $\text{TiO}_2$  prepared by a) thermolysis and b) hydrolysis. Insets: ED patterns.

### Synthesis and characterization of $\text{MoS}_2/\text{TiO}_2$ catalysts

Four catalysts were prepared by the two RCP routes; their compositions are listed in Table 1. An unpromoted and a Co-promoted catalyst with high Mo loadings were prepared in a single step from aqueous solution by RCP1. The addition of Co during synthesis did not affect the redox process between  $\text{Ti}^{3+}$  and  $\text{MoS}_4^{2-}$  and yielded similar materials as far as the states of Ti and Mo are concerned. We will therefore only discuss the characterization of the unpromoted catalyst samples in the following paragraphs.

For RCP2 catalysts,  $\text{TiO}_{2-x}$  support precursors were synthesized either by thermolysis (RCP2-T) or hydrolysis (RCP2-H). Next, a solution of thiomolybdate was introduced, which was immediately reduced by the  $\text{TiO}_{2-x}$  phase to form  $\text{MoS}_2$  nanoparticles on a  $\text{TiO}_2$  surface. This procedure yielded catalysts with low Mo loadings, likely owing to the limited availability of  $\text{Ti}^{3+}$  on the  $\text{TiO}_{2-x}$  surface as indicated by the light blue color of the material. The specific surface areas (SSA) of catalysts prepared by RCP1 and RCP2 were comparable ( $100\text{--}130\text{ m}^2\text{g}^{-1}$ , Table 1). The SSA data were obtained with  $\text{MoS}_2$ -loaded samples, which suggests that the SSA of  $\text{TiO}_2$  synthesized by RCP is substantially higher than that of a typical  $\text{TiO}_2$  support ( $\text{P25}$ ,  $\text{SSA} = 50\text{ m}^2\text{g}^{-1}$ ).



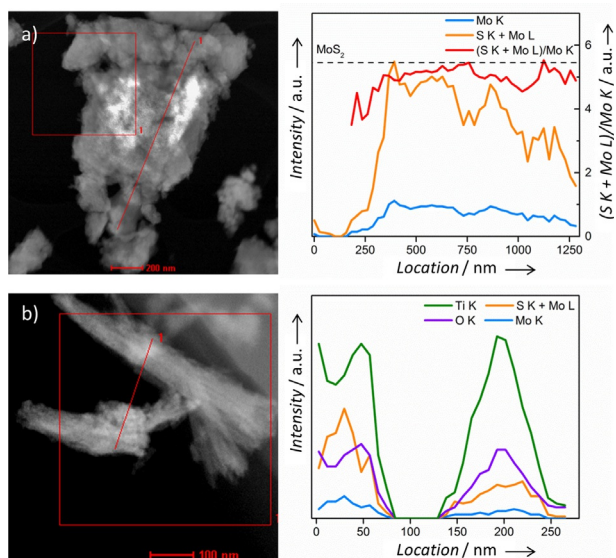
**Figure 3.** TEM images of a)  $\text{MoS}_2/\text{TiO}_2$  prepared by RCP1 in water. Inset: ED pattern. b) HRTEM image of the same sample. The red lines indicate  $\text{MoS}_2$  crystal lattice. c)  $\text{MoS}_2/\text{TiO}_2$ -RCP2-T. d) HRTEM image of the same sample. The (110) crystal lattice of rutile  $\text{TiO}_2$  and stacked  $\text{MoS}_2$  particles are indicated in white and red, respectively.

The TEM images in Figure 3 show catalysts synthesized by the RCP1 and RCP2 methods. The presence of crystalline  $\text{TiO}_2$  or  $\text{MoS}_2$  phases in  $\text{MoS}_2/\text{TiO}_2$ -RCP1 could not be confirmed by electron diffraction (ED, Figure 3a inset), indicating that the catalyst was mainly amorphous. A high-resolution TEM (HRTEM) image of the same particle revealed the presence of stacked  $\text{MoS}_2$  layers with a characteristic d-spacing of 0.615 nm (Figure 3b). The TEM image of  $\text{MoS}_2/\text{TiO}_2$ -RCP2-T (Figure 3c) clearly shows deposits on the  $\text{TiO}_2$  rods. Furthermore, the presence of  $\text{MoS}_2$  in the same region was identified by HR-TEM (Figure 3d). This suggests that both synthesis methods successfully yielded  $\text{MoS}_2$ . No crystalline  $\text{MoS}_2$  could be detected by XRD analysis, which may be attributed to the small particle size or disordered structure of the  $\text{MoS}_2$  phase (Figure S2).

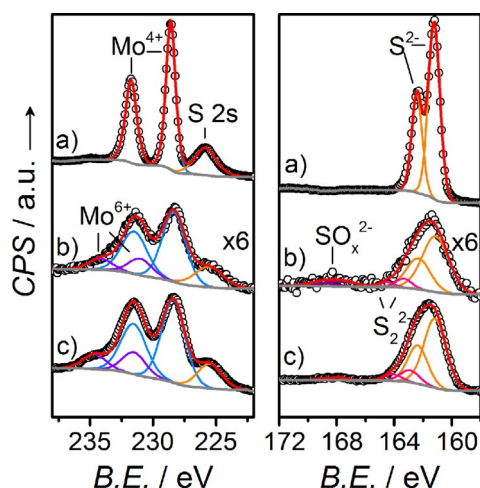
The homogeneity of  $\text{MoS}_2$  on the support was evaluated by EDX spectroscopy and is shown in Figure 4. In both samples prepared by RCP1 and RCP2, the intensity of the Mo K and Ti K fluorescence lines varied simultaneously over the length of the linescan, indicating an even loading of Mo on  $\text{TiO}_2$  (Figure 4, bottom right). The stoichiometry of S to Mo could not be determined directly by EDX analysis because the emission lines of the S K (2307 eV) and Mo L shell (2293 eV) overlapped. Instead, we compared the (S K + Mo L)/Mo K intensity ratio to that of bulk  $\text{MoS}_2$  as displayed in Figure 4a. The obtained ratios for the samples were similar to that of bulk  $\text{MoS}_2$ , pointing to a successful reduction of thiomolybdate to  $\text{MoS}_2$ .

In Figure 5, the XP spectra of  $\text{MoS}_2/\text{TiO}_2$ -RCP1 and  $\text{MoS}_2/\text{TiO}_2$ -RCP2-T are compared with that of bulk  $\text{MoS}_2$ . The Mo 3d XP spectra reveal the presence of Mo in the 4+ and 6+ oxidation states. A lower binding energy (BE) was observed for the  $\text{TiO}_2$ -supported samples with respect to the bulk  $\text{MoS}_2$  reference (Table 2). We attribute this shift in BE to electron donation from  $\text{TiO}_2$  to  $\text{MoS}_2$ , which indicates a strong TMS-support inter-





**Figure 4.** TEM-EDX linescan of a)  $\text{MoS}_2/\text{TiO}_2\text{-RCP1}$  and b)  $\text{MoS}_2/\text{TiO}_2\text{-RCP2-T}$ . The linescan started at 1 and followed the red line as indicated in the TEM image (left) and the intensities of the emission lines are plotted on the right. The black dotted line indicates the intensity ratio of (S K + Mo L)/Mo K emission lines of a bulk  $\text{MoS}_2$  reference sample.



**Figure 5.** Fitted Mo 3d (left) and S 2p (right) XP spectra of a) bulk  $\text{MoS}_2$  reference, b)  $\text{MoS}_2/\text{TiO}_2\text{-RCP2-T}$ , and c)  $\text{MoS}_2/\text{TiO}_2\text{-RCP1}$ . The data points are represented by open circles and the red lines represent the fits. The various contributions to the fit are labeled in the graphs. The spectra of  $\text{MoS}_2/\text{TiO}_2\text{-RCP2}$  were magnified six times.

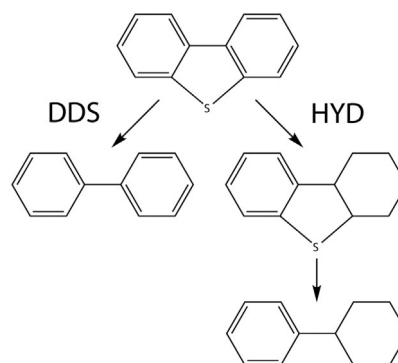
Sample	Mo <sup>4+</sup> BE [eV]	Mo <sup>6+</sup> BE [eV]	Mo <sup>4+</sup> [ <sup>a</sup> ] [%]	S/Mo <sup>[b]</sup>
$\text{MoS}_2/\text{TiO}_2\text{-RCP1}$	228.4	231.5	79	1.9
$\text{MoS}_2/\text{TiO}_2\text{-RCP2-T}$	228.4	231.2	81	2.1
$\text{MoS}_2$	228.9	–	100	2.1

[a] Calculated as  $I_{\text{Mo}^{4+}} / (I_{\text{Mo}^{4+}} + I_{\text{Mo}^{6+}})$  where  $I$  is peak intensity. [b] Calculated as  $I_{\text{S}_{\text{red}}} / I_{\text{Mo}^{4+}}$  where  $I_{\text{S}_{\text{red}}}$  is the peak intensity of sulfur excluding sulfate.

action. The S 2p XP spectra are mainly composed of  $\text{S}^{2-}$  and  $\text{S}_2^{2-}$  species.<sup>[16]</sup> A small amount of oxidized S was also identified ( $\text{SO}_x^{2-}$ ). This indicates that oxidized Mo and S species were likely formed by oxidation of  $\text{MoS}_2$  during storage under ambient conditions. The sulfidation of Ti was not observed in the as synthesized samples. The stoichiometry of reduced sulfur to molybdenum for the samples prepared by RCP is comparable to that of bulk  $\text{MoS}_2$  (Table 2), in line with the EDX results. A survey scan confirms that the as-synthesized catalysts are mainly composed of Mo, S, Ti, and O (Figure S3). Residual C and N species were also detected in the survey scan of the as-synthesized samples. In view of the low solubility of EDTA, we attribute this to the presence of EDTA in the as-synthesized materials. Nevertheless, EDTA thermally decomposes under the reaction conditions. Thus, we do not expect that it affected the catalytic properties of the materials.

### Catalytic hydrodesulfurization properties

The catalytic activity and selectivity of samples prepared by RCP1 and RCP2 were evaluated in the liquid-phase HDS of dibenzothiophene (DBT) at 4.0 MPa and 245 °C. Desulfurization of DBT can proceed by two pathways as displayed in Scheme 1. Desulfurization of DBT by hydrogenolysis (DDS) yields biphenyl (BP) as the product, whereas hydrogenation of DBT followed by sulfur extraction (HYD) yields cyclohexylbenzene that can further be hydrogenated to bicyclohexane.



**Scheme 1.** Simplified mechanism of the desulfurization of DBT by direct desulfurization (DDS) or hydrogenation (HYD).

In Table 3, the results obtained from DBT activity tests of RCP and reference samples are reported. Additional selectivity (Figure S5) and Arrhenius plots (Figure S4) are provided in the Supporting Information. The reference samples were  $\text{MoS}_2$  supported on P25 titania (65% anatase, 35% rutile) and a  $\gamma\text{-Al}_2\text{O}_3$  supported commercial Co–Mo catalyst. Highest activities were obtained for unpromoted and Co-promoted  $\text{MoS}_2/\text{TiO}_2$  prepared by RCP1, which exceeded the activity of the commercial reference with comparable metal loading. Catalysts prepared by RCP2 showed similar activity to the  $\text{MoS}_2/\text{P25}$  reference, but were significantly less active than samples prepared by RCP1.

**Table 3.** Catalytic properties of the various samples in the liquid-phase HDS of DBT at 245 °C and 20 bar H<sub>2</sub>.

Sample	$k_{\text{HDS}}^{[a]}$ [g <sub>feed</sub> g <sub>Mo</sub> <sup>-1</sup> h <sup>-1</sup> ]	$k_{\text{BP}}^{[b]} \times 10^4$ [mol <sub>BP</sub> mol <sub>Mo</sub> <sup>-1</sup> h <sup>-1</sup> ]	HYD/DDS <sup>[c]</sup>	$E_{\text{Act}}^{[d]}$ [kJ mol <sup>-1</sup> ]
MoS <sub>2</sub> /TiO <sub>2</sub> -RCP1	9.1	0.85	27.9	170
Co-MoS <sub>2</sub> /TiO <sub>2</sub> -RCP1	12.1	6.1	4.4	128
MoS <sub>2</sub> /TiO <sub>2</sub> -RCP2-T	1.0	0.73	2.7	124
MoS <sub>2</sub> /TiO <sub>2</sub> -RCP2-H	n.m.	n.m.	n.m.	128
MoS <sub>2</sub> /P25 impregnated <sup>[e]</sup>	1.3	0.55	5.4	115
commercial <sup>[f]</sup>	8.8	14.0	0.7	125

[a] Estimated error margin ± 10%. [b] Rate constant for formation of biphenyl [c] Defined as (([Products]–[BP])/[BP]). [d] Arrhenius plots are presented in Figure S4. Estimated error margin ± 10%. [e] Prepared by pore–volume impregnation, Mo loading 7.5 wt. % [f] Commercial Co–Mo/γ–Al<sub>2</sub>O<sub>3</sub> catalyst containing ≈ 15 wt. % Mo.

The high activity of MoS<sub>2</sub>/TiO<sub>2</sub>-RCP1, as compared with that of the commercial catalyst, is remarkable since it does not contain a promoter. The sample was approximately eight times more active than MoS<sub>2</sub>/TiO<sub>2</sub> prepared by impregnation or RCP2. However, the production rate constant of BP was similar for all unpromoted samples supported on TiO<sub>2</sub>. The high activity obtained by the RCP1 method can thus be attributed to increased hydrogenation activity. The higher apparent activation energy of MoS<sub>2</sub>/TiO<sub>2</sub>-RCP1 points to a different formation mechanism of this sample compared to the others. If Co was present in the catalyst (Co–MoS<sub>2</sub>/TiO<sub>2</sub>-RCP1), the selectivity towards BP increased drastically whereas the overall rate only increased by 30%. The Mo loading remained constant, indicating that active HYD sites were replaced by DDS sites.

Several researchers have reported an increased hydrogenation activity of MoS<sub>2</sub> catalysts supported on TiO<sub>2</sub> versus those on other support materials.<sup>[11b,17]</sup> It has been proposed that Ti<sup>3+</sup>, which may form under the reducing HDS conditions, could act as an electronic promoter in hydrogenation reactions over Ti–S–Mo sites.<sup>[17,18]</sup> Our results agree with this proposition, as addition of Co led to increased DDS activity at the expense of HYD activity. This suggests that Co resides at MoS<sub>2</sub> edge sites that would otherwise be promoted by Ti. Consequently, Co promotion in MoS<sub>2</sub>/TiO<sub>2</sub> catalysts does not increase the overall HDS rate to the same extent as it does in γ–Al<sub>2</sub>O<sub>3</sub>-supported catalysts.<sup>[9c,17]</sup>

Despite the similar textural properties of catalysts prepared by RCP1 and RCP2, their morphologies as observed by TEM were obviously different. RCP2 and impregnated samples, which exhibited a relatively low hydrogenation activity, were prepared by depositing MoS<sub>2</sub> on a well-defined TiO<sub>2</sub> support. On the other hand, catalysts prepared by RCP1 were composed of coprecipitated MoS<sub>2</sub> and amorphous TiO<sub>2</sub>. We anticipate that the RCP1 method yielded more Ti-promoted sites that are active in hydrogenation, which may explain the increased hydrogenation activity of these materials. Further studies in our laboratory aim to characterize the amorphous TiO<sub>2</sub> support and explore the unique activity of MoS<sub>2</sub>/TiO<sub>2</sub>-RCP catalysts in ultradeep HDS applications with real feed.

## Conclusions

Unpromoted and cobalt-promoted molybdenum disulfide nanoparticles supported on titania were synthesized from

aqueous solutions containing Ti and Mo precursor salts by an in situ redox reaction. The synthesis method, reductive coprecipitation (RCP), is simple and proceeds under mild conditions. Moreover, catalysts prepared by this way have higher Mo loading than those prepared by impregnation and their performance is comparable to that of commercial catalysts. Analysis by energy-dispersive X-ray spectroscopy indicated that the samples were composed of homogeneously dispersed MoS<sub>2</sub> nanoparticles on amorphous TiO<sub>2</sub>. The morphology of TiO<sub>2</sub> could be controlled by synthesis of TiO<sub>2-x</sub> prior to MoS<sub>2</sub> deposition, but this was at the expense of a lower Mo loading. Highest activities were obtained for the promoted RCP1 samples, which exceeded the performance of a commercial reference in hydrodesulfurization of dibenzothiophene. The addition of Co as a promoter did not enhance the catalytic activity of MoS<sub>2</sub>/TiO<sub>2</sub> to the same extent (+30%) as for Al<sub>2</sub>O<sub>3</sub>-supported Co–Mo catalysts. However, the promoter changed the selectivity towards hydrogenolysis products at the expense of hydrogenation products. These results point to the substitution of Ti-promoted sites by Co-promoted sites upon addition of Co.

## Experimental Section

### Materials preparation

A detailed description of the materials synthesis is provided in the Supporting Information. Key aspects of the synthesis are given below. The RCP synthesis procedure was modified from Xie et al.<sup>[5a]</sup> MoS<sub>2</sub>/TiO<sub>2</sub>-RCP1 was synthesized from aqueous solutions of TiCl<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> at 100 °C. The promoted material, Co–MoS<sub>2</sub>/TiO<sub>2</sub>-RCP1, was synthesized by the same procedure with Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O added to the TiCl<sub>3</sub> solution. For the preparation of RCP2 materials, TiO<sub>2-x</sub> was synthesized first by thermolysis (T) or hydrolysis (H). In thermolysis, TiO<sub>2-x</sub> was formed overnight at 60 °C from an aqueous solution of TiCl<sub>3</sub> in HCl, stabilized by NaCl. In hydrolysis, TiO<sub>2-x</sub> was formed overnight at 60 °C by basification of acidic TiCl<sub>3</sub> solution with NaOH (1 M). TiO<sub>2-x</sub> was filtered and washed and redispersed in water. MoS<sub>2</sub>/TiO<sub>2</sub>-RCP2 materials were then synthesized by addition of an aqueous (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> solution to the suspension of TiO<sub>2-x</sub> under inert conditions.

### Characterization

N<sub>2</sub> adsorption isotherms were measured at –196 °C on a Micromeritics Tristar II. Prior to analysis, samples were heated at 160 °C for

4 h under flowing N<sub>2</sub>. Specific surface areas were determined by the BET method. TEM measurements were made with a Tecnai-20F microscope operated at 200 kV and equipped with a field-emission gun. EDX spectroscopy was performed on the same microscope, utilizing an EDAX analyzer with TIA software. XRD patterns were recorded with a PANalytical X'pert PRO powder diffractometer equipped with a sealed Cu anode tube, operated at 45 kV and 40 mA. Samples were ground with a mortar and pestle prior to analysis. XPS was performed with a Kratos AXIS Ultra spectrometer, equipped with a monochromatic X-ray source and a delay-line detector. Spectra were obtained by using the aluminium anode (Al<sub>Kα</sub> = 1486.6 eV). Survey scans were measured at a constant pass energy of 160 eV and region scans at 40 eV. The background pressure was 2 × 10<sup>-9</sup> mbar. Energy correction was performed by using the C 1s peak at 284.6 eV as a reference. X-ray fluorescence (XRF) was recorded with a PANalytical spectrometer equipped with a MagiX Pro (PW2440). Samples were mixed with Al<sub>2</sub>O<sub>3</sub> and a glass bead was sintered for analysis.

### Catalytic hydrodesulfurization activity

The catalytic activity was determined by means of DBT HDS in a fixed-bed high-pressure tubular reactor with a down-flow (trickle flow) of gas and liquid feed (40 bar, H<sub>2</sub> flow of 2.25 mL min<sup>-1</sup>, weight hourly space velocity of 1.4 h<sup>-1</sup>). The reactor, 240 mm in length and 4 mm in diameter (ID), was packed with 30–80 mesh catalyst particles (400 mg) sandwiched between two ZrO<sub>2</sub> layers. The catalysts were pretreated with *n*-hexadecane (Sigma-Aldrich) spiked with 5.2% tetranonyl pentasulfide (Sigma-Aldrich) at 280 °C for 5 h and subsequently at 340 °C for 24 h. Afterwards, the temperature was lowered to 200 °C for 8 h. Then, the feed was switched to the reaction feed (5 wt.% DBT, 2 wt.% adamantane in *n*-hexadecane). After equilibration for 2 h, the temperature was increased to the desired reaction temperature (245 °C). Steady-state activity was measured after 24 h of reaction by offline GC-FID.

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