Investigation of sulfur behavior on CoMo-based HDS catalysts supported on high surface area TiO$_2$ by $^{35}$S radioisotope tracer method

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Abstract

Three series of CoMo catalysts (MoO$_3$: 6, 11, 16 wt.%) with various Co/Mo molar ratios were prepared by successive incipient wetness impregnations of a titania sample previously prepared by the pH swing method, which provides a TiO$_2$ carrier with a high SSA (134 m$^2$ g$^{-1}$) and excellent mechanical properties. DBT HDS activity of the catalysts increased with addition of cobalt up to Co/Mo = 0.4 and then decreased for higher ratios, irrespective of the Mo loading. The results of a $[^{35}$S]DBT HDS method showed that $S_0$, the amount of labile sulfur atoms, increased in parallel with the activity when adding Co up to a molar ratio of 0.4. In contrast, unlike on CoMo/Al$_2$O$_3$ catalysts, only a slight increase in $k_{RE}$, the H$_2$S release rate constant, was observed upon Co addition. This was due to formation of the TiMoS phase: while formation of Ti–S–Mo bonds favorably induces an increase in sulfur mobility on Mo/TiO$_2$ catalysts, electronic density on Mo atoms increases, which limits the promoting effect of Co on mobility of $S_a$ sulfur atoms bridged between Mo and Co. Further, while the increase in HDS activity upon Co addition on a uniform MoS$_2$ monolayer on TiO$_2$ was in rather good agreement with the quantitative and kinetics data of the $^{35}$S tracer method, over MoS$_2$ slabs on TiO$_2$ this increase was larger than that expected from the results of the $^{35}$S tracer method. This was attributed to the presence of $\square$ and $\square$ CUS, i.e. catalytic sites that are not replenished with sulfur, at the steady state. A larger number of $\square$ CUS was present at low Mo wt.% or for low Co/Mo. As these particular catalytic sites are in the form of CUS at the steady state, they are not accounted by the $[^{35}$S] radiotracer method. This explains the differences observed between the experimental DBT HDS promotion and the promotion deduced from the increase in $k_{RE}$ and $S_0$.

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1. Introduction

Enhancement of the hydrodesulfurization (HDS) catalyst performances is prompted by the urgent need to improve fuel quality. Refineries must face more and more stringent environmental regulations that impose a progressive decrease in the sulfur content of commercial fuels. For example, the current norm of 50 ppm of sulfur in the light gas oils, now in effect in Japan, will be decreased to 10 ppm by 2007. Thus, actual research aims at rapidly proposing more active and selective catalyst formulations [1]. Conventional HDS catalysts consist of MoS$_2$ slabs decorated by Ni or Co atoms supported on a $\gamma$-alumina carrier. Several approaches can be envisaged to improve the HDS catalysts. First, the effect of the addition of third elements such as fluorine [2,3], phosphorus [4–12] or boron [11–19] to the Co(Ni)MoS/Al$_2$O$_3$ system can be investi-
gated. In addition, use of other active phases such as WS2 [20–24], CrS2 [25–31], noble metals [32–50], as well as other carriers such as TiO2 or mixed oxides [51–70] or carbon [71] and zeolites [72,73] can also be investigated. Among these possibilities, use of titania in replacement of the alumina support seems promising. Indeed, Mo catalysts supported on titania were 4.4 times more active than those supported on alumina for thiophene HDS [57]. However, conventional titania supports generally have a low specific surface area (70 m2 g−1) compared with alumina (∼250 m2 g−1). Moreover, the anatase phase exhibits a poor thermal stability at high temperatures [74]. Thus, TiO2–Al2O3 mixed oxides combining the advantages of the good properties of titania (high activity) and alumina (excellent texture, mechanical and thermal properties) were further proposed as HDS catalyst supports. However, use of titania-poor TiO2–Al2O3 mixed oxides did not sufficiently enhance the HDS activity; it appeared that the use of titania-rich TiO2–Al2O3 mixed oxides is essential to sufficiently benefit from the properties of TiO2. Nevertheless, contrary to the desired morphology, the surface of titania-rich sol–gel titania–alumina mixed oxides is preferentially covered by alumina. Thus, new technologies to directly synthesize high specific surface area (SSA) TiO2 are actively being developed. Recently, a titania support suitable for catalytic applications, which exhibits a high SSA of ca. 134 m2 g−1 while keeping excellent mechanical properties, was successfully synthesized by Chiyoda Corporation. This new titania support now allows the direct use of titania support in industrial catalytic applications [75,76].

The beneficial effect of titania on HDS performances of MoS2 catalysts is attributed to a better Mo dispersion [64,65] and a facilitated sulfding of the MoO3 oxide precursor into the MoS2 active phase [66]. In addition, we previously proposed that S atoms with increased mobility are formed through the creation of a TiMoS phase [52,53,67–70]. For a MoS2 non-promoted phase supported on low SSA titania (70 m2 g−1), DBT HDS activity was higher than on Mo/Al2O3 despite a limitation in the maximal Mo loading (6 wt.%) [53,70]. Optimal Mo loading could be increased to 16 wt.% by using the 134 m2 g−1 titania mentioned above, which provided a further substantial increase in global DBT HDS activity when compared to a conventional Mo/Al2O3 catalyst [70]. On the other hand, we found that, over the low SSA titania, the synergetic effect between Co and Mo was not as high as over alumina [52], in good agreement with the results of others [57].

The objective of the present work is to evaluate to what extent the addition of Co can enhance the HDS catalytic performances of Mo/TiO2 catalysts derived from the new high SSA titania (134 m2 g−1). Further, we subsequently investigated the behavior of the sulfur and the promoting effect of cobalt using a 35S-labeled dibenzothiophene (DBT) HDS method [77–80]. The results were compared to those obtained on low SSA TiO2 and Al2O3.

2. Experimental

2.1. Catalysts

The TiO2 support (anatase) used in this study was a solid with a surface area of 134 m2 g−1 supplied by Chiyoda Corporation. The CoMo/TiO2 catalysts were prepared by successive incipient wetness impregnations of molybdenum and cobalt. First, a series of Mo/TiO2 catalysts was prepared: titania was impregnated with an aqueous solution containing the desired amount of ammonium heptamolybdate, followed by drying at 120 °C for 3 h and calcining in air at 500 °C for 15 h. The obtained Mo/TiO2 catalysts were named MT6, MT11, MT16, in which the numerical values indicate the MoO3 content, i.e. 6, 11 and 16 wt.% MoO3, respectively. Then, the CoMo/TiO2 catalysts were prepared by a step-by-step incipient wetness impregnation on this series of catalysts. The Mo/TiO2 solids underwent successive impregnations with an aqueous solution containing a given amount of cobalt nitrate hexahydrate. For each step, an amount of Co equivalent to a Co/Mo molar ratio of 0.1 was impregnated and the procedure was repeated until the desired Co/Mo ratio was reached. After each impregnation step, the obtained solids were dried at 120 °C for 3 h and then calcined in air at 500 °C for 15 h. The CoMo/TiO2 catalysts were named CMTX(0.2), CMTX(0.4) and CMTX(0.6), where X is the Mo loading, and the values in parentheses indicate the Co/Mo molar ratio, corresponding for instance to a loading of 1.7, 3.2 or 4.8 wt.% in Co for the CMT16 catalysts.

Amounts of deposited molybdenum and cobalt were checked by X-ray fluorescence measurements with an EDX-800 spectrometer (Shimadzu).

2.2. Apparatus and procedure

The catalysts were packed in a reactor and presulfided under a flow of 5% H2S/95% H2 (51 h−1, 0.1 MPa). After presulfiding, the reactor was cooled to room temperature and then pressurized with hydrogen. The reactant solution (DBT dissolved in decalin) was fed into the reactor pre-heated at the desired reaction temperature using a high-pressure liquid pump (Kyowa Seimitsu KHD-16). Typical HDS reaction conditions were as follows: H2 flow rate 25.1 h−1, WHSV 28 h−1, reaction pressure 5 MPa, and concentration of DBT in decalin 1.0 wt.% . The liquid products were collected every 15 min and analyzed using a gas chromatograph equipped with a FID detector (Shimadzu-17A, Shimadzu Co. Ltd.) and a commercial capillary column (DB-1). The same reaction conditions were used to characterize the solid catalyst properties with the 35SDBT radioisotope tracer method described elsewhere [77–80]; Fig. 1 presents the result obtained on CMT11(0.4) at 300 °C. Details of the methodology used for the interpretation of the results can be found elsewhere [79,80].
The rate constants ($k_{\text{HDS}}$) of the pseudo-first-order reactions of HDS of DBT were determined using the following equation:

$$k_{\text{HDS}} = -\frac{F}{W} \ln(1 - x)$$  \hspace{1cm} (1)

where $k_{\text{HDS}}$ is the rate constant of HDS (mol h$^{-1}$ g$^{-1}$), $x$ the conversion of DBT, $F$ the feed rate of the reactant (mol h$^{-1}$), and $W$ is the weight of catalyst (g). Similarly, formation of cyclohexylbenzene (CHB) was used to describe the hydrogenation (HYD) reaction of DBT. The rate constants ($k_{\text{HYD}}$) of the pseudo-first-order reaction of hydrogenation of DBT were determined from the formation of CHB.

3. Results

$S_0$, the number of sulfur atoms per gram of catalyst (corresponding to the light gray area in Fig. 1 [79,80]), and $k_{\text{RE}}$, the H$_2$S release rate constant, were determined for all the catalysts at 300, 320 and 360 °C from the results of the $[^{35}\text{S}]$DBT HDS experiments using a method precisely described elsewhere [80].

First, the effect of the Co/Mo ratio on the sulfur behavior was investigated on the series of CMT16 catalysts at 300 °C. Note that 16 wt.% was the optimal MoO$_3$ loading for non-promoted catalysts supported on the high SSA titania [70].

Table 1

<table>
<thead>
<tr>
<th>Co/Mo (atom atom$^{-1}$)</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (%)</td>
<td>57.0</td>
<td>78.9</td>
<td>82.0</td>
<td>64.5</td>
</tr>
<tr>
<td>Selectivity CHB$^a$ (%)</td>
<td>71.4</td>
<td>34.6</td>
<td>26.8</td>
<td>29.0</td>
</tr>
<tr>
<td>$S_0$ (mg g-cat.$^{-1}$)</td>
<td>7.29</td>
<td>8.28</td>
<td>9.20</td>
<td>7.49</td>
</tr>
<tr>
<td>$k_{\text{RE}}$ (10$^{-2}$ min$^{-1}$)</td>
<td>3.69</td>
<td>4.13</td>
<td>4.32</td>
<td>3.96</td>
</tr>
<tr>
<td>$k_{\text{HDS}}$ (10$^{-7}$ mol h$^{-1}$ g$^{-1}$)</td>
<td>12.9</td>
<td>23.8</td>
<td>26.2</td>
<td>15.7</td>
</tr>
<tr>
<td>$k_{\text{HYD}}$ (10$^{-7}$ mol h$^{-1}$ g$^{-1}$)</td>
<td>7.99</td>
<td>4.87</td>
<td>3.80</td>
<td>3.15</td>
</tr>
</tbody>
</table>

$^a$ Selectivity of cyclohexylbenzene (CHB).
$^b$ Amount of labile sulfur.
$^c$ Release constant of $[^{35}\text{S}]$H$_2$S.
$^d$ Rate constant of pseudo-first-order reaction for hydrodesulfurization.
$^e$ Rate constant of pseudo-first-order reaction for hydrogenation.

The results are summarized in Table 1 and plotted in Fig. 2. The HDS reaction rate constant $k_{\text{HDS}}$ increased with the addition of cobalt up to a Co/Mo molar ratio of 0.4 and then decreased above this ratio. A similar trend was observed for the amount of labile sulfur atoms, which increased almost linearly with the Co addition up to a Co/Mo molar ratio of 0.4 and then decreased for further Co addition. In contrast $k_{\text{RE}}$, the H$_2$S release rate constant, did not significantly vary with a value of $\sim 4.1 \times 10^{-2} \pm 0.2 \times 10^{-2}$ min$^{-1}$, irrespective of the Co/Mo ratio. Further, $k_{\text{RE}}$ values of the Co-promoted catalysts were only a little higher than that of the corresponding non-promoted catalyst at the same temperature ($3.69 \times 10^{-2}$ min$^{-1}$ for the Co-free catalyst and $3.96-4.32 \times 10^{-2}$ min$^{-1}$ for the promoted ones). In addition, $k_{\text{HYD}}$ decreased significantly with increasing the Co/Mo molar ratio for the TiO$_2$-supported CoMo catalysts (Table 1). This result shows that, contrary to the case of Al$_2$O$_3$-supported Mo-based catalysts [81], the addition of cobalt to TiO$_2$-supported Mo catalysts does not have a positive effect on the HYD performances.

Subsequently, we checked about the effect of the Co/Mo ratio on the sulfur behavior of the series of CMT16 catalysts at 320 °C and on the series of CMT11 catalysts at 300 °C. The results are summarized in Tables 2 and 3. Similarly to the CMT16-based catalysts, $k_{\text{HDS}}$ values obtained for each series of CoMo catalysts increased with the addition of cobalt up to a Co/Mo molar ratio of 0.4 and then slightly increased.

Table 2

<table>
<thead>
<tr>
<th>Co/Mo (atom atom$^{-1}$)</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (%)</td>
<td>39.4</td>
<td>67.2</td>
<td>84.6</td>
<td>65.7</td>
<td>50.0</td>
</tr>
<tr>
<td>Selectivity CHB$^a$ (%)</td>
<td>43.2</td>
<td>22.9</td>
<td>21.6</td>
<td>14.5</td>
<td>24.3</td>
</tr>
<tr>
<td>$S_0$ (mg g-cat.$^{-1}$)</td>
<td>4.13</td>
<td>6.69</td>
<td>7.83</td>
<td>6.13</td>
<td>4.79</td>
</tr>
<tr>
<td>$k_{\text{RE}}$ (10$^{-2}$ min$^{-1}$)</td>
<td>4.80</td>
<td>5.07</td>
<td>5.23</td>
<td>5.38</td>
<td>4.97</td>
</tr>
<tr>
<td>$k_{\text{HDS}}$ (10$^{-4}$ mol h$^{-1}$ g$^{-1}$)</td>
<td>7.31</td>
<td>17.1</td>
<td>28.6</td>
<td>16.4</td>
<td>10.6</td>
</tr>
<tr>
<td>$k_{\text{HYD}}$ (10$^{-4}$ mol h$^{-1}$ g$^{-1}$)</td>
<td>3.44</td>
<td>2.56</td>
<td>3.09</td>
<td>1.53</td>
<td>1.98</td>
</tr>
</tbody>
</table>

$^a$ Selectivity of cyclohexylbenzene (CHB).
$^b$ Amount of labile sulfur.
$^c$ Release constant of $[^{35}\text{S}]$H$_2$S.
$^d$ Rate constant of pseudo-first-order reaction for hydrodesulfurization.
$^e$ Rate constant of pseudo-first-order reaction for hydrogenation.
Table 3
Kinetic parameters at 300 °C for CoMo/TiO2 (MoO3: 11 wt.%) catalysts

<table>
<thead>
<tr>
<th>Co/Mo (atom atom⁻¹)</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (%)</td>
<td>28.5</td>
<td>29.5</td>
<td>63.2</td>
<td>50.6</td>
</tr>
<tr>
<td>Selectivity CHB (%)</td>
<td>93.3</td>
<td>96.8</td>
<td>89.7</td>
<td>88.8</td>
</tr>
<tr>
<td>k_C (10⁻² min⁻¹)</td>
<td>5.2</td>
<td>5.0</td>
<td>3.9</td>
<td>3.6</td>
</tr>
<tr>
<td>k_H2S (10⁻⁴ mol h⁻¹ g⁻¹)</td>
<td>5.13</td>
<td>3.35</td>
<td>15.3</td>
<td>10.8</td>
</tr>
<tr>
<td>k_H2O (10⁻⁴ mol h⁻¹ g⁻¹)</td>
<td>2.52</td>
<td>1.62</td>
<td>8.4</td>
<td>4.3</td>
</tr>
</tbody>
</table>

- Selectivity of cyclohexylbenzene (CHB).
- Amount of labile sulfur.
- Release constant of [³⁵S]H₂S.
- Rate constant of pseudo-first-order reaction for hydrogenation.
- Rate constant of pseudo-first-order reaction for hydrodesulfurization.

4. Discussion

The [³⁵S]DBT method is useful to describe promoting and/or synergetic effects over HDS catalysts in terms of variation in sulfur mobility through determination of k_RE, the H₂S release rate constant, as well as in terms of variation in number of active sites through determination of S₀, which represents the number of labile atoms on catalysts under working conditions. Accordingly, the next discussion is first divided into two parts dealing respectively with these two effects. Then, a third part gives a synthetic view of the results and a detailed comparison with other catalytic systems (CoMo catalysts supported on low SSA TiO₂ and on alumina).

4.1. Sulfur mobility over CoMo catalysts supported on high SSA TiO₂

The results of the [³⁵S]DBT experiments showed that the k_RE values for all the Co-promoted catalysts were only slightly higher (less than 20% higher) than those of the corresponding non-promoted catalysts at the same temperature (Tables 1–3). This is different from the results observed over Mo catalysts supported on Al₂O₃, for which the introduction of cobalt induces increasing in k_RE values by a factor larger than 3 [81]. This suggests that there is a limit in the promoting effect of cobalt on the mobility of sulfur atoms over CoMo/TiO₂ catalysts, which was also observed over low SSA titania [52] with a maximum increase in k_RE inferior to 10% at 320 °C. In contrast, the significant increase in k_RE values in the case of Co-promoted Mo catalysts supported on alumina [81] indicated that sulfur is significantly more mobile over CoMo/Al₂O₃ than over Mo/Al₂O₃. This was in good agreement with the formation of an active phase presenting an enhanced intrinsic activity, i.e. the so-called CoMoS phase previously evidenced by Topsøe et al. [82,83].

Similarly, we have previously described the promoting effect of TiO₂ on the MoS₂ phase by the formation of a ‘TiMoS’ phase (see Fig. 3). Unlike the Al₂O₃ supports, the TiO₂ supports are more or less extensively sulfided during the catalyst pre-sulfiding procedure [53,68] (Fig. 3(a)). Then, the sulfided Ti species are further reduced into Ti³⁺ species under H₂ atmosphere (Fig. 3(b)). This reduction involves the formation of sulfur anion vacancies with electrons trapped inside [68,69]. A structural model depicting the structure of the sulfided Mo/TiO₂ catalysts was accordingly proposed [52,53]. In this model, it was considered that the structure of MoS₂ is a deformed tetrahedral structure, similarly to the case over Al₂O₃ support. Due to the formation of sulfur anion vacancies and according to the possibility of an electron transfer from Ti(III) to Mo, the S⁺ sulfurs in the vicinity of the formed sulfur anion vacancy might be weakly bonded with the two neighboring Ti atoms (Fig. 3(c)). This leads to the formation of a new ‘TiMoS’ active phase in which the Mo–S⁺ bond strength is weakened making the S⁺ sulfur more labile [53,70], which in good agreement with the results of the radiotracer method. Indeed, over a 70 m² g⁻¹ TiO₂ support loaded with 6 wt. % MoO₃, k Ré was 8.93 × 10⁻² min⁻¹ at 360 °C, while it was 4.61 × 10⁻² min⁻¹ at the same temperature over a 256 m² g⁻¹ alumina loaded with 6 wt. % MoO₃ [53]. Further, over the 134 m² g⁻¹ titania, k Ré was 4.62 × 10⁻² min⁻¹ at 320 °C for MT11, while it was 2.63 × 10⁻² min⁻¹ at the same temperature over a catalyst consisting of 12 wt. % MoO₃ loaded on alumina [70]. This showed that the mobility of sulfur is increased by a factor of approx. 2 over the TiMoS phase compared to conventional MoS₂/Al₂O₃ system, irrespective of the TiO₂ support SSA. Addition of Co to the catalysts of the present

Fig. 3. Schematics of the structure of the TiMoS phase (adapted from Ref. [52]).
In contrast, we previously showed that addition of Co to Mo/Al2O3 catalysts induces an increase in sulfur mobility by a factor ~3.4 [81]. This suggests that the promotion effect on MoS2 induced by the TiO2 carrier is similar (increase in kRE) to the promotion effect induced by Co addition to Mo/Al2O3 catalysts, with formation of TiMoS and CoMoS phases, respectively. Then, it is possible to explain why the increase in sulfur mobility observed upon Co addition on the TiMoS phase is insignificant compared to that observed when promoting MoS2/Al2O3 catalysts with Co. Fig. 4 represents a schematic of the Co-promoted TiMoS phase under a reductive atmosphere [52]. In the non-promoted catalyst (equivalent to Fig. 3(c)), the S* sulfur atom is shared by Mo and Ti atoms, which induces weakening of the Mo–S* bonds. Thus, mobility of the S* atom is enhanced. In the Co-promoted catalyst (Fig. 4), due to the presence of Mo–S* bonds together with electronic interaction between S* and Ti atoms, electronic density on Mo atoms is increased (injection of electrons from formed Ti3+ species in the Mo 4d conduction band). Thus, the expected promoting effect of Co on mobility of created S* sulfur atoms in Fig. 4 is lowered. In addition, S* and Sa sulfur atoms in Fig. 4 are supposedly both stable but if S* and Sa atoms of a same pyramidal structure are removed at the same time, the structure presented in Fig. 4 is destroyed, which might be also an important reason for the observation of a promoting effect that is much lower than expected.

In brief, while sulfur atoms are more mobile over Mo/TiO2 catalysts than over Mo/Al2O3 catalysts, addition of cobalt reverses this tendency. The higher mobility of sulfur on the non-promoted Mo/TiO2 catalysts is due to the creation of a TiMoS phase in which the mobility of particular sulfur atoms (S* sulfur atoms) is increased when compared to the case on MoS2/Al2O3. On the other hand, the presence of Ti–S*–Mo bonds has the consequence of increasing the electron density on the molybdenum atoms. Then, the beneficial effect of Co on the mobility of sulfur atoms shared by Co and Mo (Sa sulfur atoms) is drastically lowered compared to CoMo/Al2O3 formulations. Moreover, the concomitant lability of Sa and S* sulfur atoms belonging to the same catalytic unit structure (Fig. 4) might lead to possible dislocation of this structure.

4.2. Number of active sites over CoMo catalysts supported on high SSA TiO2

In Section 4.1, we saw that promotion of MoS2/TiO2 catalysts by Co atoms has only a limited effect on the enhancement of the sulfur mobility. In Section 4.2, we will determine to what extent the use of high SSA TiO2 allows an increase in the number of active sites.

On non-promoted catalyst, at same temperature and Mo loading, S0 is similar over alumina- and titania-supported Mo catalysts. For example, at 320 °C, S0 is 6.84 mg g-cat⁻¹ over an alumina loaded with 12 wt.% MoO3 and is 7.82 mg g-cat⁻¹ over high SSA titania loaded with 11 wt.% MoO3 [70]. Further, S0 is also similar over the high SSA TiO2 and the high SSA TiO2, with respective values of 4.3 mg g-cat⁻¹ [52] and 4.13 mg g-cat⁻¹ (Table 2) for 6 wt.% MoO3 at 320 °C.

Over alumina, addition of Co induces an increase in S0 by a factor of approx. 5 [81]. In contrast, increase in S0 in the present study was lower, with an increase factor between 1.3 (for 16 wt.% MoO3) and 1.9 (for 6 wt.% MoO3) (see Tables 1–3), which is also globally lower than the S0 increase factor observed over low SSA-supported Mo titania upon Co addition, with a value of approx. 2 [52]. As in the case of kRE, compared to Al2O3 the lower increase in S0 over TiO2 upon Co addition can be explained using the model proposed in Fig. 4. Indeed, the presence of Ti–S*–Mo bonds limits the promoting effect of Co on the Sa atoms by increasing the electronic density on Mo and thus lowering the mobility of Sa sulfur atoms. Then, upon Co addition, creation of coordinatively unsaturated sites (CUS) on CoMo/TiO2 catalysts is not as promoted as on CoMo/Al2O3 catalysts, on which CUS creation is significantly facilitated [84].

Nevertheless, in a previous paper [70], we reported an increase in optimal MoO3 loading from 6 to 16 wt.% by using the high SSA TiO2 instead of the low SSA TiO2 carrier. This was accompanied with an increase in S0 of about 2.35 times at 320 °C, which was slightly lower than the increase in MoO3 loading (ca. 2.7 times). Upon Co addition, S0 increased by a factor of about 2 at 320 °C over the low SSA TiO2 with optimal MoO3 loading of 6 wt.% (see Table 4) and by a factor of about 1.3 on the high SSA titania with optimal MoO3 loading of 16 wt.% at 300 °C, for the respective optimal MoO3 loadings of 6 and 16 wt.%. Thus, considering the effect of the Co promotion and the difference in optimal Mo loading, one can obtain a global increase in S0 of about 2.35 × 1.3/2 ~ 1.5, despite an increase in optimal MoO3.

Fig. 4. Schematics of the structure of Co-promoted TiMoS phase in a reductive atmosphere (adapted from Ref. [52]).
loading of ca. 2.7 times between the low and the high SSA titania.

4.3. Comparison between experimental DBT HDS promotion factor and promotion factor deduced from $^{[35}S]DBT$ HDS experiments

4.3.1. Promotion factor due to Co addition obtained for optimal catalysts supported on alumina, high SSA titania and low SSA titania

Table 4 sums up various aspects of the extent of the promoting effect of Co addition on Mo catalysts supported on Al2O3, low SSA TiO2 and high SSA TiO2, each containing an optimal MoO3 loading and an optimal Co/Mo ratio (i.e. 0.4–0.6). The S0 increase factor is noted as $\alpha$, which is defined as the ratio between $S_0$ obtained for a catalyst promoted with Co with the optimum Co/Mo ratio (best DBT HDS activity) to $S_0$ obtained for the equivalent non-promoted Mo catalyst. The value of $\alpha$ is quite high on alumina, with values of 5.8 and 5.1 for 260 and 280 °C, respectively. In contrast, a significantly lower $\alpha$ is obtained for the titania-supported catalysts, with values of 2.0 and 1.3 over the low and the high SSA titania, respectively.

Similarly, $\beta$, the $k_{RE}$ increase factor is defined as the ratio between $k_{RE}$ obtained for a catalyst promoted with Co with the optimum Co/Mo ratio (best DBT HDS activity) to $k_{RE}$ obtained for the equivalent non-promoted Mo catalyst. The value of $\beta$ is higher over alumina, with respective values of 3.6 and 3.4 at 260 and 280 °C, than over the low and the high SSA titania, with respective values of 1.05 and 1.2. As discussed in Sections 4.1 and 4.2, we attributed the lower promotion effect of Co on titania-supported catalysts to the presence of Ti= S2–Mo bonds that increase the electron density on Mo atoms through the injection of electrons of Ti3+ species to the Mo 4d conduction band.

Further, we calculated the value of $\alpha \times \beta$, which represents the expected combined promotion effect of increase in mobility of sulfur and increase in number of sulfur vacancies upon Co addition (Table 4). The values of $\alpha \times \beta$ are compared to the values of $\chi$, which represents the effective experimental promotion effect on DBT HDS ($=(k_{HDS})_{CoMo}/(k_{HDS})_{Mo}$) (Table 4). For CoMo/Al2O3, $\chi$ and $\alpha \times \beta$ are in quite good agreement at 260 °C, with respective values of 24 and 21. While on high SSA titania, $\chi$ and $\alpha \times \beta$ are also in quite good agreement, with respective values of 2.0 and 1.6, on low SSA titania a difference of a factor of roughly 2 is observed with respective values of 4.6 and 2.1. In brief, on optimal catalysts (optimal Mo loading and optimal Co/Mo ratio), $\chi$ and $\alpha \times \beta$ are in rather good agreement on Al2O3 and high SSA TiO2 carrier. In contrast, on low SSA titania the experimentally observed increase in HDS is clearly superior to that expected from the increase in $S_0$ and $k_{RE}$ upon Co addition.

This suggests that, for the low SSA titania, the activity promotion factor due to Co addition cannot be fully described by the $[35S]DBT$ HDS method, while reliable results are obtained over alumina and high SSA titania. In order to propose an explanation, we will first discuss some differences of active phase morphology among the supports.

4.3.2. Comparison of morphology of MoS2-based active phase over alumina, low SSA titania and high SSA titania

Optimal Mo density (defined as the density for which DBT HDS activity is maximal) over non-promoted catalysts is ~3.9 atom nm$^{-2}$ over alumina, 4.2 atom nm$^{-2}$ over low SSA titania and 5.2 atom nm$^{-2}$ over high SSA titania (Table 4). The difference in optimal Mo density between alumina and high SSA titania was attributed to a difference in MoS2 optimal distribution over alumina and titania [85]. Indeed, over alumina the best activity is obtained when MoS2 slabs of a proper size are dispatched on the alumina surface, because desulfurization active sites are located on the edge of MoS2 slabs, which makes the ratio edge Mo to total Mo a crucial parameter for HDS performances [86]. In contrast, over titania, formation of mobile sulfur atoms S* enabled uniform distribution of the active sites all over the surface of the MoS2 slabs, which implies that the best activity is obtained for a MoS2 monolayer over TiO2 (TiS2).

### Table 4
Comparison of kinetic and quantitative parameter variations upon Co promotion of optimal Mo-based catalysts supported on alumina, low and high SSA titania

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Alumina (256 m$^2$ g$^{-1}$)</th>
<th>Low SSA titania (70 m$^2$ g$^{-1}$)</th>
<th>High SSA titania (134 m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimal Mo density (atom nm$^{-2}$)</td>
<td>~3.9$^a$ (20 wt.% MoO3)</td>
<td>4.2 (6 wt.% MoO3)</td>
<td>5.2 (16 wt.% MoO3)</td>
</tr>
<tr>
<td>Optimal Co/Mo ratio</td>
<td>~0.6$^b$</td>
<td>~0.6$^b$</td>
<td>0.4$^c$</td>
</tr>
<tr>
<td>$\alpha = S_0$ increase factor</td>
<td>~5.8</td>
<td>~2.0</td>
<td>~1.3</td>
</tr>
<tr>
<td>$\beta = k_{RE}$ increase factor</td>
<td>~3.6</td>
<td>~1.05</td>
<td>~1.2</td>
</tr>
<tr>
<td>$\alpha \times \beta$</td>
<td>~21</td>
<td>~2.1</td>
<td>~1.6$^d$</td>
</tr>
<tr>
<td>$\chi = (k_{HDS})<em>{CoMo}/(k</em>{HDS})_{Mo}$</td>
<td>~24</td>
<td>~4.6</td>
<td>~2.0$^e$</td>
</tr>
</tbody>
</table>

$^a$ The best activity was obtained for 20 wt.% MoO3 but effective optimal MoO3 loading might be between 16 and 20 wt.%, i.e. 2.9 and 3.9 atom nm$^{-2}$ [70,84].

$^b$ Optimal Co/Mo ratio might be between 0.4 and 0.6 but catalyst with Co/Mo = 0.5 was not tested; among the tested catalysts, the best activity was obtained for Co/Mo = 0.6.

$^c$ Optimal Co/Mo ratio might be between 0.4 and 0.6.

$^d$ $\alpha$ Represents the ratio $S_0$ of a catalyst with optimal Mo loading and promoted with Co with optimal Co/Mo ratio (as reported in the third row of the present table) to $S_0$ of the non-promoted catalyst. $\beta$ Is similarly calculated but relatively to $k_{RE}$.

$^e$ $\alpha \times \beta = 2.1$ and $\chi = 3.9$ for 6 wt.% MoO3 at 320 °C; $\alpha \times \beta = 1.7$ and $\chi = 3.0$ for 11 wt.% MoO3 at 300 °C.
In good agreement, optimal Mo density over the high SSA TiO$_2$ was 5.2 atom nm$^{-2}$, which corresponds to the density of a perfect (1 0 0) MoS$_2$ plane [85]. Further, on high SSA TiO$_2$, this optimal Mo density of 5.2 atom nm$^{-2}$ was higher than on low SSA titania (4.2 atom nm$^{-2}$). This was attributed to the original preparation method, the pH-swing method [75,76,87], used to prepare the high SSA titania. Indeed, with this method a solid presenting a great homogeneity was obtained, which might favor long range regular growing of MoS$_2$ slabs over an homogeneous TiO$_2$ (TiS$_2$) surface [85]. In contrast, over low SSA titania, a uniform monolayer of MoS$_2$ is not easily obtained due to disruption of the MoS$_2$ planes, whose long-range growth might be hindered by surface asperities (TiO$_2$ surface structure might locally deviate from a uniform ideal structure, etc.). Then, an optimal Mo density of 4.2 atom nm$^{-2}$ is observed, which is lower than the optimal Mo density in a perfect MoS$_2$ surface developing as (1 0 0) MoS$_2$ plane (5.2 atom nm$^{-2}$). That is to say, the active phase structure over the so-called optimal Mo/TiO$_2$ catalysts is different over the low SSA carriers and over the high SSA carriers.

Further, these differences imply that the location of the Co promotor on the active phase might be slightly different between alumina and titania. In the case of alumina it is now well admitted that Co decorates the edge Mo atoms of MoS$_2$ slabs [88]; further, a model describing the localization of the Co promotor in a millerite-type structure possessing sulfur atoms that are labile under hydrogen atmosphere was subsequently proposed [89,90]. In the case of the optimal catalyst supported on the high SSA titania, a uniform layer of MoS$_2$ is formed. Thus, as slabs are supposedly not present, the Co promotor is likely to be distributed all over the MoS$_2$ monolayer. Note that MoS$_2$ slabs are obviously present for Mo loadings inferior to the optimal one over the high SSA TiO$_2$ carrier, and also over the low SSA TiO$_2$ carrier over which the MoS$_2$ layer is parceled out. This means that edge Co atoms are also present in these latter cases.

Differences in MoS$_2$ distribution (uniform monolayer or distributed slabs) over the various supports might be responsible for differences in catalytic behavior. Similarly, any difference in Mo loading (i.e. any difference in MoS$_2$ slab size) must have also an influence on the activity promotion factor of MoS$_2$/TiO$_2$ catalysts with Co. This is discussed in the next part.

4.3.3. Variation of promotion factor due to Co addition as a function of Mo loading on various supports

We plotted $\chi$ and $\alpha \times \beta$ as a function of MoO$_3$ loading for the low and the high SSA titania (Fig. 5). On the high SSA titania, for MoO$_3$ loadings inferior to the monolayer (16 wt.%), MoS$_2$ slabs supposedly grow in an homothetic manner when MoO$_3$ loading increases, as described elsewhere [86]. It is remarkable that $\chi$ and $\alpha \times \beta$ exhibit the same trend, i.e. a decrease when MoO$_3$ loading increases (Fig. 5). In other words, over TiO$_2$ the more the size of the MoS$_2$ slabs increases, the more the theoretical factor of Co promotion and the experimental factor of Co promotion on DBT HDS activity decrease. Note that, for 6 wt.% MoO$_3$, $\chi$ and $\alpha \times \beta$ are similar for both low SSA and high SSA titania. Further, over the high SSA titania, when MoO$_3$ loading increases, the difference between $\chi$ and $\alpha \times \beta$ is progressively minimized (Fig. 5); for 16 wt.% MoO$_3$ this difference is rather low, as observed in the case of CoMo catalyst supported on alumina (Table 4). This is further illustrated in Fig. 6, in which we plotted the ratio $\chi/(\alpha \times \beta)$ as a function of MoO$_3$ loading. In Fig. 6, $\chi/(\alpha \times \beta)$ ratio of 1 means that the DBT HDS activity increase upon addition of optimal quantity of Co can be fully described in terms of variations in number of active sites and in sulfur mobility, as determined using the $[^{35}S]$DBT method. Fig. 6 shows that,

![Fig. 5. $\chi$ and $\alpha \times \beta$ as a function of MoO$_3$ loading for optimal Co/Mo ratio on high SSA TiO$_2$ and low SSA TiO$_2$ (see Table 4). Definitions of $\chi$, $\alpha$ and $\beta$ can be found in Table 4.](image)

![Fig. 6. Ratio $\chi/(\alpha \times \beta)$ as a function of MoO$_3$ loading for optimal Co/Mo ratio on high SSA TiO$_2$, low SSA TiO$_2$ (calculated from results of Ref. [52]) and conventional alumina. For alumina carrier, the result for 16 wt.% MoO$_3$ is calculated from results of Ref. [81] at 260 °C, and the result for 12.5 wt.% MoO$_3$ is calculated from results of Ref. [91] at 300 °C. Definitions of $\chi$, $\alpha$ and $\beta$ can be found in Table 4.](image)
4.3.4. Nature of the active sites over CoMo catalysts supported on alumina and titania

4.3.4.1. Active sites on CoMo/Al₂O₃. The good agreement obtained between χ and α × β for the catalysts supported on alumina originates in the fact that the MoS₂ (CoMoS) structure is stable over alumina under experimental conditions. On the working catalysts, sulfur atoms easily replenish catalytic sites (CUS), which means that at the steady state sulfur atoms are present in the catalytic sites. Then, the [³⁵S]DBT HDS method gives reliable results.

4.3.4.2. Active sites on CoMo/TiO₂. We have to take into account that, over non-promoted Mo/TiO₂ catalysts, the activity of the MoS₂ phase is enhanced by the formation of S⁺ sulfur atoms exhibiting a high mobility (Fig. 3). Over the promoted catalysts, mobile S⁺ atoms are still present, together with newly formed S₄ labile sulfur atoms (Fig. 4). Due to the electronic interactions discussed in Section 4.1, these S₄ atoms are not as mobile as they should be, when compared with the CoMoS phase supported on alumina (Mo–S₄ bound strength is not sufficiently weakened due to the electronic influence of Ti³⁺ atoms). Then, on promoted catalysts mobile sulfur atoms S⁺ from the TiMoS phase and sulfur atoms S₄ of a CoMoS phase with so to speak comparatively ‘lowered’ performances coexist.

The DBT HDS mechanism is represented in Fig. 7 in the case of catalytic sites derived from S₄ sulfur atoms (in the case of conversion of DBT into BP). An equivalent general mechanism can be similarly proposed in the case of the S⁺ sites (with creation of □⁺ CUS). In the case of Ru-based catalysts, we have previously shown that the catalyst steady state involves the presence of CUS [41], in contrast with (Co)Mo/Al₂O₃ catalysts for which catalytic sites are replenished with S atoms at the steady state. As at the steady state the active sites on the Ru-based catalysts are not replenished with sulfur atoms, these active sites work in the metallic state and are therefore not detected by the [³⁵S] radiotracer method. The results of Fig. 6 for the CoMo/TiO₂ catalysts can be interpreted in the same way, i.e. the catalytic phase exhibits a certain number of CUS at the steady state (like in Fig. 7(d) or (a)).

Further, addition of Co to the TiMoS phase leads to the creation of pyramidal structures such as that represented in Fig. 4, with the consequence of more or less sterically hindering the mobility of the S⁺ sulfur atoms of the TiMoS phase located below. This is especially the case for a uniform monolayer of TiMoS phase promoted with the stoichiometric ratio Co/Mo ~ 0.5. In other cases (non-stoichiometric Co/Mo ratio or MoS₂ slabs distributed on the TiO₂ surface), some S⁺ sulfur atoms (not topped by pyramidal structures or located on the edges of Co-promoted MoS₂ (TiMoS) slabs) are not (or are only limitedly) sterically hindered. Note that the mobility of S⁺ sulfur atoms present on the edge (less hindered S⁺ atoms) of MoS₂ slabs might be increased by the presence of Co (promoting effect of Co on edge S⁺). For low Mo loadings, the proportion of non-hindered S⁺ sulfur atoms is higher (because the Mo/S₄/Mo ratio is larger for smaller slabs). Then, the more pronounced difference between χ and α × β for low Mo loadings is supposedly due to a larger number of □⁺ at the steady state. When the Mo loading increases, i.e. when the proportion of sterically hindered S⁺ atoms increases, the difference between χ and α × β is diminished but is still higher than in the case of CoMo/Al₂O₃ catalysts (Fig. 6). For 16 wt.% MoO₃ and Co/Mo = 0.4 (monolayer of TiMoS promoted with Co near the stoichiometric ratio) χ/(α × β) is about equal to 1.4, while it is about 1.1 in the case of CoMo/Al₂O₃ (Fig. 6). This suggests that, at the steady state, □⁺ CUS might be also present.

Further, in good agreement, the value of kHYD of the CoMo/TiO₂ catalyst with 16 wt.% Mo decreased with the addition of Co (Table 1). In other words, when S⁺ atoms were progressively covered with Co pyramidal structures, their HYD properties were hindered. This suggests that H₂S⁺ formation was made more difficult. Then, the steady state for S⁺ sites was supposedly shifted from that like in Fig. 7(a) (□⁺ CUS) to that like in Fig. 7(c) (sites replenished with S⁺ sulfur atoms) when Co loading increased. This is different from the case of 6 wt.% (Table 2) and 11 wt.% Mo catalysts (Table 3), for which catalysts with an optimal ratio Co/Mo of 0.4 exhibited a maximum in kHYD. This might be due to the presence at the steady state of a larger number of □⁺ (edge) sites with enhanced HYD properties (due to the presence of Co atoms), which is also in good agreement with the high value observed for χ/(α × β) in Fig. 6.
5. Conclusions

(1) HDS activity of the CoMo catalysts supported on the high SSA TiO2 increased with the addition of cobalt up to a Co/Mo molar ratio of 0.4 but decreased above this value, irrespective of the MoO3 loading. The amount of labile sulfur ($S_0$) increased also with the addition of cobalt up to a Co/Mo ratio of 0.4. In contrast, only a negligible increase in the H2S release rate constant ($k_{RE}$) was observed after Co promotion. The promoting effect of Co on catalytic performances was relatively poor when compared with Al2O3-based systems. This was explained by the presence of a ‘TiMoS’ phase behaving like the ‘CoMoS’ phase. While this phase promotes mobility of sulfur atoms through the creation of Ti–S*–Mo bonds in the case of non-promoted catalysts, the presence of these bonds induces an increase in the electronic density on molybdenum, which limits the cobalt promotion by decreasing the mobility of sulfur atoms $S_a$ located in bridging positions between cobalt and molybdenum.

(2) While the expected increase in DBT HDS activity upon Co addition, as evaluated from the combined effect of the increase in $k_{RE}$, the H2S release rate constant, and the increase in $S_0$, the number of labile sulfur atoms, was in good agreement with the experimental results for the optimal MoO3 loading, for lower MoO3 loadings the observed DBT HDS activity was significantly higher than expected from the increase of these two parameters. We supposed that at the steady state a certain number of $\square^+ \text{CUS}$ from the TiMoS phase as well as $\square_a \text{CUS}$ of the CoMoS phase created over the TiMoS phase by addition of Co are present. Addition of Co to the TiMoS phase sterically hinders the lability of $S^-$ sulfur atoms. This progressively shifts the steady state of the TiMoS layer from $\square^+ \text{CUS}$ to sulfur-replenished $S^*$ sites. Nevertheless, the sterical hindrance might be lower for $S^*$ atoms on the edges of the TiMoS phase. Then, for low molybdenum loadings for which a large number of mobile edge $S^*$ atoms are present, a larger number of $\square^+ \text{CUS}$ are present at the steady state. In contrast, for high Mo loadings, TiMoS slabs are larger and contain then a larger proportion of basal $S^*$ atoms compared to the proportion of edge $S^*$ atoms; the number of non-sulfur-replenished $\square^+ \text{CUS}$ at the steady state thus decreases. The active sites non-replenished with sulfur at the steady state ($\square^+ \text{CUS}$ and $\square_a \text{CUS}$) are not counted by the [$^{35}\text{S}$] radiotracer method, explaining the difference observed between the experimental HDS promotion and the HDS promotion calculated from $S_0$ and $k_{RE}$ values, which is larger for low Mo loadings.

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