Dual Effect of H$_2$S on Volcano Curves in Hydrotreating Sulfide Catalysis

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Abstract — Dual Effect of H$_2$S on Volcano Curves in Hydrotreating Sulfide Catalysis — Recent progresses achieved by quantum molecular modeling techniques enabled the rational interpretation of catalytic trends of series of transition metal sulfide catalysts. Empirical volcano curves can be explained by microkinetic models including chemical descriptors calculated at an ab initio level. This approach was successfully applied in the field of hydrotreating catalysts utilizing the metal-sulfur bond energy descriptor. The purpose of the present work was to extend this approach by exploring the effect of reaction conditions (partial pressure of H$_2$S) on the volcano curve. On the one hand, high resolution transmission electron microscopy (HRTEM) images combined with molecular modeling of morphologies and surfaces exposed by catalysts provide an estimate of the number of potential active sites. This approach is illustrated for the relevant case of unsupported or alumina supported Co$_9$S$_8$ sulfide. On the other hand, an improved microkinetic model is proposed in order to reflect the dual effects of H$_2$S observed in the hydrogenation of toluene: an inhibiting effect for MoS$_2$, Rh$_2$S$_3$, RuS$_2$, NiMoS and a promoting effect for Cr$_2$S$_3$ and Co$_9$S$_8$. The experimental results and kinetic modeling reveal that the maximum of the volcano curve and thus the optimal sulfide catalyst depends closely on the partial pressure of H$_2$S.
INTRODUCTION

In the field of heterogeneous catalysis, volcano curves play a key role for correlating catalytic activities with intrinsic properties of catalysts such as its ability to form chemical bonds with reactants, products or intermediates [1-3]. With the tremendous progress of ab initio molecular modeling techniques within the framework of density functional theory (DFT), the origin of volcano curves can be explained by using ab initio calculated chemical descriptors directly linked to intrinsic properties of catalysts.

The experimental data and the chemical descriptors are connected with the help of Brunsted-Evans-Polanyi relationships [4, 5] and kinetic model using Langmuir-Hinshelwood (LH) formalism. This approach may offer a powerful guideline for the design of new catalysts.

Such volcano curves were obtained for hydrotreating catalysts [6], using the sulfur-metal bond energy descriptor, called E(MS), as defined in [7, 8]. A good fitting between predicted and experimental hydrodesulfurization (HDS) of dibenzothiophene (DBT) was obtained for a series of sulfides catalysts [9], with the use of a kinetic equation based on a Langmuir-Hinshelwood equation assuming that the reactant (dibenzothiophene) and H2S compete on the same catalytic site. Without any assumption on the adsorption mode of H2S and H2, this model provided a rational explanation of the origin of volcano curves in HDS catalysis.

More complex kinetic pathways including H2 and H2S dissociative activation on the catalytic sites have been proposed for the interpretation of the kinetic orders with respect to H2S determined on conventional Co(Ni)MoS catalysts [10-12]. In fact, H2S acts as an inhibitor on conventional systems based on Mo or W disulfides as also observed on unconventional sulfide active phases such as Pd, Ru, Rh [13, 14].

In contrast, recent results demonstrate that H2S may also enhance the turnover rate in toluene hydrogenation in the case of Cr2S3 catalyst [15].

In the present paper, we first show that this positive effect of H2S also occurs over unsupported and over alumina supported cobalt sulfide, pointing out the fact that sulfides with low E(MS), exhibit a specific behavior with respect to H2S. As announced in [15], we propose an improvement of the kinetic model able to explain this positive effect of H2S. At the same time, we propose an approach combining high resolution transmission electron microscopy (HRTEM) and molecular modeling of morphologies and surfaces exposed for a selected TMS series (MoS2, Rh2S3, RuS2, NiMoS, Cr2S3 and Co9S8) to estimate the number of potential active sites of the sulfides catalysts.

This approach enabling a more rigorous normalization of turnover rate will be illustrated in detail for the case of Co9S8.

1 EXPERIMENTAL

1.1 Catalysts Preparation

1.1.1 Unsupported Cobalt Sulfide

Unsupported cobalt sulfide was prepared at room temperature by addition drop by drop of Na2S in a Co(NO3)2·6H2O aqueous solution [16]. The powder obtained was filtered, washed with water and dried in a N2 flow. Then, the solid was heated in a 15% H2S/H2 flow at 713 K during 4 h. The specific surface area of the sample is 40 m²/g. Its composition according to chemical analysis (S/Co atomic ratio of 0.9) and XRD pattern corresponds to a Co9S8 phase.

1.1.2 Supported Samples

Co supported catalyst (14.8 wt% of Co) was prepared by pore-filling impregnation of a γ-Al2O3 support (surface area: 240 m²/g and pore volume: 0.61 cm³/g) with an aqueous solution of Co(NO3)2·6H2O. The catalyst was calcined overnight at room temperature and during 10 hours at 373 K. Subsequently this material was calcined at 673 K for 4 h in a flow of air (100 cc/min), then sulfided at 673 K for 4 h in a 15% H2S/H2 flow.

The Mo, Ru, Rh and Cr supported catalysts were prepared by the same method using respectively (NH4)6Mo7O24·4H2O, RuCl3, [(NH3)5Rh]Cl3 and Cr(NO3)3 precursor salts. Metal loadings of each sample are reported in Table 1. However, only Mo and Rh catalysts were calcined respectively at 673 K for 4 h and 523 K for 1 h in a flow of air. After all the catalysts were sulfided: Ru and Rh in a 15% H2S/N2 flow at 673 K for 4 h; Mo and Cr in a 15% H2S/H2 flow at 673 K for 4 h. It is important during the activation procedure to avoid a too reductive atmosphere in the case of Ru and Rh to obtain the fully sulfided state [17].

1.2 Catalysts Characterization and Modeling

1.2.1 Characterization

Several techniques such as TEM combined with EDS (Jeol 2010, point to point resolution 0.19 nm), C-S analysis (Juwe), XRD (Bruker D5005) and chemical analysis were used for the characterization of the catalysts. Particle sizes estimated from TEM and S/M ratio are reported in Table 1.

1.2.2 Molecular Modeling of Surfaces and Morphologies

Modeling of sulfide surfaces and morphologies was carried out using the “Crystal Builder” and “Surface Builder” modules of Cerius2 interface [18]. The (hkl) surfaces corresponding to the planes observed by transition electron microscopy (TEM) have been built in two steps: the sulfides crystal is created from the conventional cell with the “Crystal Builder” module, then the crystal is cleaved in the (hkl) direction with
the “Surface Builder” module. Depending on the surface orientations, there may exist non equivalent choices for the cleavage plane. Ab initio calculations of surface energies help for determining the thermodynamic stability of surface: this has been undertaken in previous studies for MoS₂, Co(Ni)MoS [19, 20] and RuS₂ surfaces [21, 22]. However, such a systematic investigation for the whole sulfide series explored in the experimental section was beyond the scope of the present work. In a first approximation, the most probable exposed surface was chosen as the one minimizing the total number of cleaved bonds (sulfur-metal, metal-metal and sulfur-sulfur). In the future, it can be expected that new ab initio results will enable a more precise determination of surfaces stability.

### TABLE 1
Characteristics of the supported TMS ordered as a function of the sulfur-metal bond descriptor, E(MS), as defined in [9]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal loading (% wt.)</th>
<th>Estimated particle size (nm)</th>
<th>S/Me atomic ratio</th>
<th>E(MS) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS₂/Al₂O₃</td>
<td>10.2</td>
<td>2</td>
<td>2.3</td>
<td>166</td>
</tr>
<tr>
<td>RuS₂/Al₂O₃</td>
<td>5.4</td>
<td>2.5</td>
<td>2.3</td>
<td>141</td>
</tr>
<tr>
<td>NiMo/Al₂O₃</td>
<td>9.3 (Mo), 2.4 (Ni)</td>
<td>2</td>
<td>1.8</td>
<td>128</td>
</tr>
<tr>
<td>Rh₂S₃/Al₂O₃</td>
<td>0.9</td>
<td>2</td>
<td>1.3</td>
<td>119</td>
</tr>
<tr>
<td>Co₉S₈/Al₂O₃</td>
<td>6.3</td>
<td>10</td>
<td>1.1</td>
<td>111</td>
</tr>
<tr>
<td>Cr₂S₃/Al₂O₃</td>
<td>3.2</td>
<td>5</td>
<td>1.3</td>
<td>97</td>
</tr>
</tbody>
</table>

The ideal particle morphologies have been modeled using the Gibbs-Curie-Wulff law connecting surface energies and particle morphology (Equations 1 and 2).

\[
\Gamma_{\text{hkl}} = \frac{\Gamma_{\text{hkl}}}{d_{\text{hkl}}} = \frac{\Gamma_{\text{k'k''l'}}}{d_{\text{k'k''l'}}}
\]  

(1)

\[\Gamma_{\text{hkl},\text{p}} = \Gamma_{\text{hkl}} - \sum_{\text{hkl}} S_{\text{hkl}} \text{p} \]  

(2)

Γ_{hkl} surface energy of (hkl) plane exposed on the particle surface,

d_{hkl} distance between the (hkl) surface and the particle centre,

S_{hkl} area of the (hkl) plane exposed on the particle.

For MoS₂ and Co(Ni)MoS surfaces, surface energy values and morphologies are already solved by previous ab initio calculations [23, 24]. However, for other sulfides, ab initio data are not available. Without knowing the surface energy values of the surfaces exposed by the different transition metal sulfides, hypothetical morphologies have been created using the “Morphology” module of Cerius² (by varying arbitrarily Γ_{hkl}) to generate crystallites morphologies exposing the surfaces observed by HRTEM. For each morphology, we deduce the relative area of the different (hkl) surfaces which is the important insight for determining the surface density of sites.

### 1.2.3 Active Sites Counting

The analysis of the surface coordination of all atoms belonging to the surface is carried out in order to determine the number of sulfur-metal, sulfur-sulfur and metal-metal bonds. After cleavage, we considered as a potentially catalytically active site, the transition metal atoms verifying the following rules:

- the transition metal atom is a Coordinatively Unsaturated Sites (CUS) exhibiting at least one sulfur vacancy,
- the transition metal atom possesses one sulfur neighbor on the catalytic surface.

The surface concentration of potential active sites for the (hkI) surface is determined by the following relationship:

\[\left[\text{AS}\right]_{\text{hkl}} = \frac{N_{\text{hkl}}}{S_{\text{hkl}}} \]  

(3)

N_{hkl} number of potentially active sites for a define (hkl) surface by simulation cell,

S_{hkl} area of the (hkl) surface in the simulation cell.

The average number of potential active sites per particle is deduced:

\[\left[\text{AS}\right]_{p} = \sum_{\text{hkl}} S_{\text{hkl}} \left[\text{AS}\right]_{\text{hkl}} = \sum_{\text{hkl}} x_{\text{hkl}} S_{\text{p}} \left[\text{AS}\right]_{\text{hkl}}\]  

(4)

x_{hkl} proportion of the (hkI) surface for the given morphology,

S_{p} total surface area of the particle for the given morphology.

The estimate of particle sizes obtained by TEM (Table 1) is used to deduce the value of S_{p} according to 3D morphological models adapted for each sulfide. The morphologies and values of x_{hkl}, [AS]_{hkl} and [AS]_{p} are reported in Table 2 for all sulfides.

### 1.3 Catalytic Tests

Hydrogenation (HYD) of toluene is used as a model reaction to determine the catalytic activities of the catalysts. The test was performed under dynamic conditions with various H₂S partial pressures, obtained by dilution of H₂S/H₂ standard mixtures, in the following conditions: P_{total} = 3.5 \times 10³ kPa, Total flow rate = 80 mL/min, P_{Toluene} = 5.6 kPa and T_{reaction} = 623 K. Specific activity was measured, according to first-order kinetics, after 15 h on stream when the steady state is reached. Activities are accurate to within 10%. Different relevant levels of H₂S partial pressures were chosen in the range of 0.52 to 12 kPa. The procedure was described in detail in [15].

### 2 RESULTS AND DISCUSSION

#### 2.1 Effect of H₂S on the Catalytic Activity

In our previous study [15], we observed a positive kinetic order with respect to H₂S for Cr₂S₃ which is localized on the ascending branch of the volcano curve corresponding to low
Effect of \( H_2S \) partial pressure on the catalytic conversion of toluene on \( Al_2O_3 \) supported and non supported \( Cr_2S_3 \) and \( Co_9S_8 \) catalysts.

Table 2: Analysis of the morphology and site density for the supported sulfide catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Morphology</th>
<th>Surfaces (hkl): proportion</th>
<th>Density of sites ([AS]_{hkl}) (per nm² of (hkl) surface)</th>
<th>Active sites (mol per g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Co_9S_8/Al_2O_3 )</td>
<td><img src="image" alt="Co9S8" /></td>
<td>( \langle 0\overline{2}2 \rangle : 25% ) ( \langle 4\overline{2}2 \rangle : 25% ) ( \langle 1\overline{3}1 \rangle : 25% ) ( \langle 1\overline{1}1 \rangle : 25% )</td>
<td>2.9 ( \times 10^{-20} ) ( 3.3 ) ( 3.5^* ) ( 5.9 ) ( 2.0 )</td>
<td>0.5 ( \times 10^{20} )</td>
</tr>
<tr>
<td>( RuS_2/Al_2O_3 )</td>
<td><img src="image" alt="RuS2" /></td>
<td>( \langle 1\overline{1}1 \rangle : 25% ) ( \langle 0\overline{1}0 \rangle : 25% ) ( \langle 1\overline{0}2 \rangle : 25% ) ( \langle 1\overline{1}0 \rangle : 25% )</td>
<td>6.3 ( \times 10^{-20} ) ( 6.3 ) ( 5.7 )</td>
<td>1.1 ( \times 10^{20} )</td>
</tr>
<tr>
<td>( RhS_2/Al_2O_3 )</td>
<td><img src="image" alt="RhS2" /></td>
<td>( \langle 211 \rangle : 59% ) ( \langle 1\overline{2}3 \rangle : 38% ) ( \langle 1\overline{3}1 \rangle : 3% )</td>
<td>5.8 ( \times 10^{-20} ) ( 5.8 ) ( 5.8 )</td>
<td>0.5 ( \times 10^{20} )</td>
</tr>
<tr>
<td>( Cr_2S_3/Al_2O_3 )</td>
<td><img src="image" alt="Cr2S3" /></td>
<td>( \langle 0\overline{0}2 \rangle : 93% ) ( \langle 1\overline{1}0 \rangle : 3.5% ) ( \langle 1\overline{1}0 \rangle : 3.5% )</td>
<td>1.4 ( \times 10^{-20} ) ( 6.9 ) ( 1.7 )</td>
<td>4.5 ( \times 10^{20} )</td>
</tr>
<tr>
<td>( MoS_2/Al_2O_3 )</td>
<td><img src="image" alt="MoS2" /></td>
<td>( \langle 1\overline{0}1\overline{0} \rangle : 48% ) ( \langle 0\overline{1}0 \rangle : 4% )</td>
<td>2.5 ( \times 10^{-20} ) ( 2.5 ) ( 2.4 )</td>
<td>2.0 ( \times 10^{20} )</td>
</tr>
</tbody>
</table>

* \([AS]_{hkl}\): average number of site density (expressed per nm² of particle).

\( E(MS) \) values. \( Co_9S_8 \) also belongs to this region of the volcano curve according to the sulfur-metal bond energy descriptor [7-9]. As shown in Figure 1, the supported Co sulfide catalyst slightly increases its catalytic activity when \( H_2S \) partial pressure increases even if it is to a lesser extent than for \( Cr_2S_3 \). The kinetic order with respect to sulfur is 0.13. Unsupported \( Co_9S_8 \) showed also the same trend (kinetic order 0.18) evidencing that it is an intrinsic property of this cobalt sulfide phase.

For Mo, Ru and Rh sulfides supported over alumina, the inhibiting effect of \( H_2S \) has been reported [10, 15] and was found to vary in the following order \( Mo < Ru < Rh \). These previous data will be used for comparison with the cobalt catalyst.

### 2.2 Morphology of Sulfide Particles

In order to investigate the crystallographic surfaces involved in the catalytic reaction, HRTEM was performed on the different catalysts. In what follows, we focus on the case of cobalt sulfides. A similar approach was used for all other sulfides.
For unsupported Co$_9$S$_8$ several atomic resolution images were obtained as illustrated in Figure 2. Statistical analysis on the particle size, average description of zone axis and surface planes were combined with the modeling of the active surface and morphology description of the particles. Thus, the geometrical model of an active particle can be obtained and the surface concentration of potentially active sites numbered as illustrated in Figure 3.

This systematic approach was also performed on the supported cobalt catalyst, and example of HRTEM image obtained is illustrated in Figure 4. For this sample, only one zone axis [211] was observed suggesting that a preferential orientation exits through an orientation relationship (400) of Al$_2$O$_3$ and (422) of Co$_9$S$_8$ with a small lattice misfit between the two planes (0.202 nm and 0.1985 nm respectively). This epitaxial effect gives rise to a different morphology for the supported Co$_9$S$_8$ particles as illustrated in Figure 5.

This crystallographic analysis was extended to all the supported samples and allowed us to determine for each system the morphology representative for the different exposed surfaces and the concentration of active sites. Table 2 reports all information for the morphology and surface site counting. It can be noticed that all supported TMS exhibit the same range of active site concentration (when expressed per gram of catalyst). In contrast, catalytic activities are observed to change from 1 to 3 orders of magnitude depending on the active phase which suggests that the activity is not only related to the number of CUS. More complex factors involving the nature of the active sites influencing the relative stability of reactants, intermediates and transition states must be considered. It can also be observed that surface site concentrations remain comprised between 1.4 and 5.8 sites/nm$^2$ which may also explain why volcano curves have been reported in the literature by expressing activities by surface area.
Figure 3

Figure 4
HRTEM image of Co₉S₈ alumina supported catalyst a) and his Fourier transform b).
2.3 Microkinetic Modeling

For hydrogenation and hydrodesulfurization reactions over sulfide catalysts, many kinetic studies have been carried out in the literature so far [11, 12, 25-29]. In the same spirit as [10, 25, 27], we have tested several relevant models and determined the model able to reproduce at best the experimental catalytic results obtained previously. In [15], we have applied a first model within the Langmuir-Hinshelwood formalism, which considers molecular adsorption for all species. H₂S is regarded as a pure inhibitor of the toluene hydrogenation reaction. A similar microkinetic model was already used in a previous work [9], putting forward a volcano curve relationship between HDS of DBT and $E(MS)$, the ab initio calculated sulfur-metal bond energies of the sulfide catalysts [7-9]. $E(MS)$ appeared thus as a good chemical descriptor of the catalyst for recovering such a volcano. A second and more refined model (also called model 6b in [10]), is a one site model within the Langmuir-Hinshelwood formalism and assumes that H₂S and H₂ adsorb dissociatively at the surface. In this case, the sulfhydryl groups engendered by H₂S dissociation may also take part to the elementary steps of the reaction as earlier proposed by Kastzelan [10, 27]. In what follows we will focus on this microkinetic model to underline its improvement for the description of the toluene hydrogenation reaction. This model is optimized by expressing the adsorption constants and activation energies as a linear relationship of the sulfur-metal bond energies calculated by DFT in previous work [7-9]. It must be noticed that we have tested all other models reported in [10], however the one described in what follows appears as the best one.

2.3.1 Elementary Steps of the Mechanism

Equations (E1) to (E7) describe the relevant elementary steps of the mechanism involved in the one site ($M'$) microkinetic model of toluene hydrogenation.

\[
M'^* + H₂S \xrightleftharpoons{k_1} MS + H₂
\]  (E1)

\[
MS + M'^* + H₂ \xrightleftharpoons{k_{56}} MSH + MH
\]  (E2)
Step (E1) is the creation of MS species required for hydrogen and H₂S activation. This equation is also related to the sulfidation state of the catalytic surface depending on the sulfo-reductive conditions as revealed by DFT calculations [19, 20, 23, 24]. We cannot exclude that this state changes in various reaction conditions. Hydrogen and H₂S are both activated through heterolytic dissociation through steps (E2) and (E3). Step (E4) stands for the adsorption of toluene (labelled \( R \)) on the active sites. Step (E5) is the first hydrogen transfer from the sulfhydryl group to the adsorbed toluene and is assumed to be rate determining. Step (E6) is the second hydrogenation from MH group. In the models tested (not described here), this step was also supposed as being rate determining. However, this assumption does not provide a good fit of the experimental data. Subsequent elementary steps leading to methyl-cyclohexane occur as follows:

\[
\begin{align*}
MS + M^* + H_2S & \rightarrow 2MSH \quad (E3) \\
M^* + R & \rightarrow MR \quad (E4) \\
MR + MSH & \rightarrow MRH + MS \quad (E5) \\
MRH + MH & \rightarrow MRH_2 + M^* \quad (E6)
\end{align*}
\]

These elementary steps ensure simultaneously the alcan formation and the partial regeneration of \( M^* \) sites. In order to equilibrate the global reaction scheme (full \( M^* \) recovery, avoiding \( H_2S \) over-consumption), the following final steps (occurring two times) are proposed:

\[
\begin{align*}
2M^* + H_2 & \rightarrow 2MH \quad (E7) \\
MRH_2 + MSH & \rightarrow MRH_3 + MS \quad (E8) \\
MRH_3 + MH & \rightarrow MRH_4 + M^* \quad (E9) \\
MRH_4 + MSH & \rightarrow MRH_5 + M \quad (E10) \\
MRH_5 + MH & \rightarrow MRH_6 + M^* \quad (E11) \\
MRH_6 & \rightarrow RH_6 + M^* \quad (E12)
\end{align*}
\]

These elementary steps lead to methyl-cyclohexane occur as follows:

\[
\begin{align*}
2M^* + H_2 & \rightarrow 2MH \quad (E13-E14) \\
2MH + MS & \rightarrow 3M^* + H_2S \quad (E15-E16)
\end{align*}
\]

As a consequence, \( H_2S \) takes part to the reaction by producing the MS and MSH species at the surface and is regenerated at the end of the catalytic cycle so that it does not appear in the global reaction.

### 2.3.2 Equation Rates and Brønsted-Evans-Polanyi Relationships

Within the proposed mechanism, steps (E1) to (E4) are assumed to be equilibrated, whereas step (E5), corresponding to the addition of the first hydrogen from the sulphydryl group, is rate determining. Many other assumptions (such as listed in [10]) have been checked: they all lead to less satisfactory results.

The equation of site conservation is written as follows:

\[
0^* + 0_S + 0_{SH} + 0_H + 0_R = 1
\]  

The reaction rate is finally expressed as:

\[
r(T, p_{H_2S}, p_{H_2}) = k_{SH} \Theta H_{SH} \frac{\alpha_p G_S^{1/2} G_{HS}^{1/2}}{(1 + \alpha_S + \alpha_H + \alpha_{HS} G_S^{1/2} G_{HS}^{1/2} + \alpha_{HSH} G_S^{1/2} G_{HS}^{1/2})^2}
\]

with \( \alpha_S = \frac{p_{H_2S}}{K_S p_{H_2}} \) and \( \alpha_H = K_H \frac{p_H}{p} \).

In the same spirit as firstly proposed by Kasztelan [30], or more recently revisited by Toulhoat and Raybaud [9], we express the adsorption constant, \( K_i \), and activation energy as a function of a relevant intrinsic parameter of the sulfide catalyst, the sulfur-metal bond energy, \( E(MS) \), as defined in [7-9]. Similar approaches within the framework of ammonia synthesis on metal catalysts have been proposed recently [5, 31].

The adsorption constants, \( K_i \), and the kinetic constant \( k_{SH} \) are thus written as:

\[
K_i = e^{\Delta S_i / R - \Delta H_i / RT} = e^{\Delta S_i / R} \left( \frac{\alpha_p G_S^{1/2} G_{HS}^{1/2}}{1 + \alpha_S + \alpha_H + \alpha_{HS} G_S^{1/2} G_{HS}^{1/2} + \alpha_{HSH} G_S^{1/2} G_{HS}^{1/2}} \right)
\]

\[
k_{SH} = k_B T e^{-\Delta G_{\text{SH}} / RT} = k_B T e^{\left( \Delta G_{\text{SH}} + \gamma_{\text{SH}} E(MS) \right) / RT}
\]

where \( k_B \) and \( h \) are the Boltzmann and Planck’s constants respectively.

If a linear relationship holds between the internal energy variation (resp. activation energy) and \( E(MS) \), resulting from Brønsted-Evans-Polanyi (BEP) relationship [32-34], \( K_i \) and \( k_{SH} \) depend on the catalyst via \( E(MS) \) and the BEP parameters, \( \beta \) and \( \gamma_{\text{SH}} \). We thus obtain an expression of \( r \) as a function of \( T, p_{H_2S}, p_{H_2}, E(MS) \).

The BEP linear relationships used for the kinetic modelling are plotted in Figure 6. All adsorption energies are exothermic. The higher \( E(MS) \), the stronger the interaction of the active free site \( M^* \) with toluene, -S, -SH is.
2.3.3 Volcano Curves and Surface Coverage

In Figure 7, it can be observed that the volcano curve as already proposed for DBT HDS in [7-9] is recovered for the toluene hydrogenation on the six tested sulfides catalysts. In our previous work [15], such a volcano was also obtained with a more simple model where the molecular adsorption of H2 and H2S was assumed. However, as found in [15], this model is not able to render the subtle promoting effect of H2S on Cr2S3 and Co9S8 catalysts. We confirm that the optimal catalysts (Rh2S3 and NiMoS) are found for intermediate value of E(\(MS\)). This result can be interpreted again within the framework of the Sabatier principle [1,8]. A careful analysis of the species coverages (Fig. 8) as a function of E(\(MS\)) reveals that for high E(\(MS\)) the surface is saturated by MSH species. For low E(\(MS\)), the surface is fully covered by MH species. In these two regions, the number of toluene molecules adsorbed on the surface is extremely low, and the rate law decreases abruptly (as expected from the rate equation (6) for very low \(\theta_R\) value). For intermediate E(\(MS\)), the toluene coverage reaches a maximum. Furthermore, the sulfhydryl species coverage is simultaneously high at the surface which maximizes the product \(\theta_{SH}\theta_R\) and explains why the maximum of the hydrogenation rate law is reached close to the E(\(MS\)) value of Rh2S3. It can be noticed that, in this region, MH species occupy a non negligible fraction of catalytic sites. Hence, the optimal distribution of toluene, MSH and MH species for intermediate sulfur-metal bond strength explains why this region is optimal for catalysis as suggested earlier by Kasztelan [25].

2.3.4 Effect of \(p_{H2S}\)

Figure 7 shows that for E(\(MS\)) values greater than 115 kJ/mol, the increase of the partial pressure of H2S from 3.2 kPa to 12 kPa decreases the reaction rate. This inhibiting effect of H2S was observed experimentally on many sulfides such as MoS2 [10]. However, as we pointed out in the previous section, for Cr and Co sulfides, H2S has a promoting effect on the hydrogenation activity. After exploring many different possible mechanisms, we conclude that the positive effect of H2S can only be recovered when the hydrogenation step involving H transfer from sulfhydryl groups (engendered...
The effect of H$_2$S is also to shift the position of the optimal catalyst. More precisely, an increase of the partial pressure of H$_2$S implies a slight displacement of the volcano maximum towards weaker sulfur-metal bond energies. This displacement is explained by the impact of H$_2$S partial pressure on the surface coverages, as visualized in Figure 8. An increase of $p_{H_2S}$ implies a shift of the maximum of the toluene surface coverage towards low $E(\text{MS})$. At the same time, the crossing point of the MSH and MH species is also displaced towards lower $E(\text{MS})$. The combination of both trends induces the shift of the volcano’s maximum. This effect reveals that the optimal catalyst depends on the reaction conditions and tends to counteract the effect of $p_{H_2S}$. Furthermore, at low $E(\text{MS})$ increasing leads to higher SH surface coverages, whereas $\theta_R$ is moderately affected. This analysis explains why for higher $p_{H_2S}$, the HDS activity is enhanced on catalysts such as chromium and cobalt sulfides. Such an impact of the reaction conditions on the periodic trends of catalytic properties was proposed by Kasztelan in [25] who noticed that “the nature of the optimum solid will depend on the reactions conditions”. Results obtained in the current work give a more quantitative and rational basis for understanding this trend.

CONCLUSIONS

HRTEM combined with molecular modeling was used to describe the sizes and morphologies of unsupported and supported Co$_9$S$_8$ as well as for Cr$_2$S$_3$, Rh$_2$S$_3$, RuS$_2$ and MoS$_2$ transition metal sulfides. γ-alumina support was found to interact strongly with the cobalt sulfide providing a preferential orientation. This HRTEM and molecular modeling approach provided an estimate of the number of potential active sites present on the various supported catalysts and furnished a more rigorous way for determining normalized turnover rates in hydrogenation of toluene. It was shown that the variation of the number of active sites is not able to account for the change in 3 orders of magnitude of turnover rates measured. This complete description of the morphology of the TMS is also the primary step required for further modeling of the reactivity and the understanding of the structure sensitivity of TMS surfaces.

The hydrogenation of toluene on unsupported and alumina supported catalysts was found to be slightly promoted by an increase of H$_2$S partial pressure for cobalt and chromium sulfides. The analysis of this peculiar effect of H$_2$S on the catalytic activity of the TMS series was performed by combining a LH approach and BEP relationships using the sulfur-metal bond energy $E(\text{MS})$ descriptor. From the various selected LH equations, the best volcano curve correlation was obtained by using a model based on the heterolytic dissociation of H$_2$ and H$_2$S, and the first toluene monohydrogenation from MSH group as the rate determining step of the reaction. The promoter effect of H$_2$S is explained by the increase of SH concentration for catalysts with low $E(\text{MS})$ values such as Co$_9$S$_8$ and Cr$_2$S$_3$. This positive effect of H$_2$S can only be recovered when the hydrogenation step involving H transfer from sulfhydryl groups (engendered by H$_2$S dissociative adsorption) is rate determining. In contrast, this effect cannot be observed with mechanisms where the rate determining step is the hydrogenation through MH species. The second effect of $p_{H_2S}$ is to displace the position of the volcano curve’s maximum. This maximum moves in direction of catalysts with $E(\text{MS})$ values counteracting the effect of $p_{H_2S}$. This result puts forward that the optimal catalyst for toluene hydrogenation depends on the reaction conditions.

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18 Surface Builder Crystal builder, Morphology modules distributed within the Cerius² (release 4.8.1) and Materials Studio (release 4.0) package by Accelrys (http://www.accelrys.com).


