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Effect of Mesostructured Zirconia Support on the Activity and Selectivity of 4,6-Dimethyldibenzothiophene Hydrodesulfurization

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Abstract: In contrast with the conventional CoMoS/alumina catalyst, the use of amorphous mesostructured ZrO2 as support for the dispersion of the CoMoS active phase in deep hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene leads to a higher promotion rate and a better sulfidation of the cobalt species. The CoMoS dispersed over mesostructured amorphous ZrO2 as catalyst also induces a modification of the main desulfurization way, in that case a shift towards direct desulfurization selectivity is observed. This result is unexpected regarding the literature. Indeed, the hydrogenated route is observed for commercial zirconia. The designed catalysts are therefore more eco-friendly since they consume less hydrogen. This implies a better use of the fossil resources.

Keywords: mesostructured zirconia; amorphous; hydrodesulfurization catalysts; 4,6-Dimethyldibenzothiophene; direct desulfurization

1. Introduction

Because it can cause health problems (cancer, etc.), air quality in cities is a major issue; the latter is affected by atmospheric pollution to which the gas emissions from vehicles contribute in a significant way, in particular by the emission of sulfur oxides. In order to limit this impact, standards have been fixed to have fuels that are more respectful of the environment. For example, in Europe since 2009 the maximum sulfur content is limited to 10 ppm [1]. Considering the increase consumption of fuels in particular in emerging countries and the diversity of the origin of the raw material (mainly from fossil material but also from lipidic or lignocellulosic biomass in a less extent), the hydrotreatment processes have a great interest. For diesel cuts, it is admitted that 4,6-dimethyldibenzothiophene (46DMDBT) is the most representative compound of the most refractory sulfated molecules [2–5]. Hydrotreating catalysis is a highly mature field and catalyst manufacturers have improved and optimized the preparation of alumina-supported, Co- or Ni-promoted MoS2 catalysts over decades. However, one aspect that has been somewhat neglected in industrial development is the important role of the support. Industrial hydroprocessing catalysts are almost exclusively supported on alumina [6].

However, because of the strong interaction between alumina and the support, the formation of the active phase during the sulfidation process is not optimal, especially when catalysts are
promoted [7]. Different activities and selectivities can be noticed when alumina is replaced by silica, titania or zirconia [8–13]. Indeed, since the interactions of the support with Mo will modify the electronic properties of the coordinately unsaturated sites (CUS) [14], which are well identified as the active phases, the support plays an important role in improving the properties of a catalyst in terms of activity, selectivity, and stability. For example, it has been reported that the intrinsic activity of MoS₂ deposited on titanium oxide is greater than that of MoS₂ supported on alumina [15,16]. In addition, studies performed in Raman spectroscopy and X photoelectron spectroscopy (XPS) reveal that molybdate anions are strongly and uniformly bound to the surface of titanium oxide. This homogeneous dispersion is related to the distribution of hydroxyl groups at the surface of TiO₂ [17]. Shimada [18] has shown that the structure of TiO₂ facilitates the formation of MoS₂ slabs, which contribute to the increase in the catalytic activity. Ishihana et al. [19] highlighted the role of Ti³⁺, which could have an electronic effect on the active phase. More recently, by comparison with conventional catalysts, we have shown that a change of selectivity for the HDS of 46DMDDBT is obtained when the active phase is dispersed on mesostructured titania [20]. This behavior has been correlated for one part to the intrinsic properties of the mesostructured titania [20].

Among the different oxides, zirconia is also of peculiar interest for hydrodesulfurization (HDS) of gazole [12,21–25]. It is reported that for the same amount of molybdenum atom per nm², the activity of the catalyst deposited on a zirconia support is three times higher than when it is deposited on alumina [24]. Regarding the promoted catalyst by Ni, due to a better promotion on ZrO₂ than on Al₂O₃, an enhancement of the NiMoS activity is noted [25]. Another study, reported by Li et al. [23] evidenced that on a zirconia support, nickel is sulfided much more easily than on alumina, making the catalyst more efficient in term of activity [23]. Therefore, ZrO₂ appears as an interesting material for the dispersion of the active phase to prepare HDS catalyst with high activity and selectivity [12]. However, the specific surface area of ZrO₂ (≈ 100 m²/g) is quite low comparing to silica or γ-alumina (≈ 250 m²/g) and it is thermally unstable. To overcome these drawbacks zirconia is usually used in mixture with alumina or silica. Since good textural properties are considered to be the most important criterion that any catalyst support should fulfill for the hydrotreating of heavy feeds [26–28], an increase in the specific surface area of zirconia could have beneficial effect on the activity of the ZrO₂-based catalyst. Thanks to their properties, mesostructured metal oxides are excellent candidates to meet the criterion required; i.e., high specific surface area, well-ordered uniform pore structure containing mesopores stable to thermal treatments, and narrow pore size distribution, for an efficient hydrotreatment catalyst support. Recently, we have reported the preparation of mesostructured amorphous zirconia with high specific surface area (> 300 m²/g) and thermal stability (> 480°C). ZrO₂ is obtained by combining the surfactant templating pathway and the sol-gel process from an EISA-derivate method [29]. Here, due to the interest of zirconia for hydrotreatment, the mesostructured amorphous zirconia has been used as support to design MoS₂/ZrO₂ catalyst promoted by cobalt, which have been tested for the hydrodesulfurization of 46DMDDBT. In particular, we have investigated the effect of the ZrO₂ on the selectivity of the catalyst. Catalytic results are compared with the ones obtained by dispersing the active phase on the conventional alumina support.

2. Results and Discussion

2.1. Characterization of the Mesostructured ZrO₂-based Catalyst

Before sulfidation to get the active phase, the support has been impregnated with cobalt and molybdenum precursors. At each step materials have been characterized. The SAXS (Small Angle X-ray Scattering) pattern of the bare zirconia exhibits one broad peak centered at around 8.1 nm (Figure 1a), meaning that the mesopore network adopts a wormhole-like structure analogous to the one reported for the silica MSU (Michigan State University) materials [30], which presents a lack of long-range crystallographic order. The position of the broad peak corresponds to the sum of the pore diameter and the wall thickness. A type IV isotherm, characteristic of mesoporous material according to the IUPAC (International Union of Pure and Applied Chemistry) classification [31] is
obtained by nitrogen adoption-desorption analysis (Figure 1b). The values of the specific surface area and of the pore volume are equal to 420 m²/g and 0.43 cm³/g, respectively. The mesopore size distribution is homogeneous with a maximum at 4.6 nm. The wall thickness is thus around 3.5 nm. After impregnation the wormhole-like mesostructure is preserved as confirmed by the presence of a broad peak centered at 7.2 nm (Figure 1a). According the broadness of the peaks the difference in the maxima before and after impregnation is not significant and one can conclude that the structural properties are barely influenced by the wet impregnation. The shapes of the isotherm and of the mesopore size distribution are not modified neither (Figure 1b and 1c). However, comparing with the bare ZrO₂, lower quantity of adsorbed nitrogen (Figure 1b) and lower dV/dD values (Figure 1c) are noticed. These decreases can be correlated to the drop of the BET (Brunauer, Emmett et Teller) specific surface area to 255 m²/g, pore volume to 0.25 cm³/g and pore diameter to 3.9 nm. The variation of textural characteristics is mainly due to the mesopores filling by the molybdenum and cobalt species. Moreover, the similitude in the shape of both N₂ sorption and pore size distribution shape reflects a homogeneous dispersion of Mo and Co species.

![Figure 1](image.png)

**Figure 1.** SAXS pattern (a), nitrogen adsorption-desorption isotherms (b) and mesopores size distribution (c) of the bare and of the impregnated amorphous mesostructured ZrO₂.

The acidity properties of the impregnated zirconia material have been investigated by pyridine adsorption followed by Infra-red (Figure 2). Obtained spectra are in accordance with those reported in literature [32–35]. The intensities of the band at around 1540 and 1447–1452 cm⁻¹ are used to quantify the Lewis and Brønsted acidity. From Figure 2, no significant Brønsted site is detected and the Lewis acidity of CoMo/ZrO₂ (0.90 µmol.m⁻²) is similar to the one measured for the impregnated alumina (≈ 1.1 µmol.m⁻²), which will be used as the benchmark catalyst for HDS.
Figure 2. Infrared spectra of pyridine adsorbed on CoMo/Al$_2$O$_3$ and CoMo/ZrO$_2$.

After sulfidation two peaks located at 182.1 eV and 184.5 eV are observed on the XPS Zr 3d spectrum (Figure 3a). They are characteristic of ZrO$_2$ [36]. XPS also evidences the success of the sulfidation process (Figure 3). Indeed, on the molybdenum spectrum we can observe at 231.9 (Mo 3d$_{3/2}$) and 228.8 eV (Mo 3d$_{5/2}$) the +IV oxidation state of Mo bonded with the sulfur atoms (Figure 3b). Three peaks at 778.7, 778.0 and 780.8 eV with the associated satellites are detected on the Co 2p$_{3/2}$ spectrum. They are due to CoMoS, Co$_9$S$_8$ and CoOx, respectively [37]. The formation of the active phase is also supported by the presence of the peak S 2p$_{1/2}$ and S 2p$_{3/2}$ located around 162.7 and 161.2 eV (Figure 3d). In a sake of comparison, the impregnated commercial Al$_2$O$_3$ was sulfided under the same conditions than the mesostructured zirconia. No significant difference in the formation of the various phases is noted between ZrO$_2$ and Al$_2$O$_3$ after sulfidation (Table 1). However, the proportion of CoMoS obtained on ZrO$_2$ (33%) is slightly higher than the one observed on Al$_2$O$_3$ (26%), suggesting a better sulfidation of cobalt on mesostructured zirconia.
Figure 3. Zr 3d (a), Mo 3d (b), Co 2p (c) and S 2p (d) XPS spectra of the CoMoS/ZrO₂ catalyst.

Table 1. Percentage obtained by XPS analysis of the phases formed after sulfidation.

| Oxide        | Mo distribution (at.%) | Co distribution (at.%) | S distribution (at.%) |
|--------------|------------------------|------------------------|-----------------------|
|              | Mo⁹⁺ | MoO₅ | CoMoS | Co₉S₈ | CoO | Sulfur | Sulfates |
| ZrO₂         | 65   | 20   | 16    | 33.0  | 48.7 | 18.3   | 90.7     | 9.3      |
| Al₂O₃*       | 70   | 15   | 15    | 25.7  | 52.3 | 22     | 100      | 0        |

*used as reference for 46DMDBT hydrodesulfurization.

From Table 1, data characterizing the active phase have been determined from the relations reported in reference [21].

The obtained values are given in Table 2. The sulfidation degree of Mo is similar for both supports since the amount of MoS₂ obtained at the surface of alumina (70%) and mesostructured zirconia (65%) are very closed, suggesting that interactions between Mo and Zr are in the same range of order than the ones between Mo and Al [38]. The better sulfidation of the cobalt species on mesostructured ZrO₂ is also reflected by a higher value of the promotion ratio and of the promotion rate (0.3 and 33%, respectively, against 0.1 and 26% for the alumina support).

Table 2. Parameters characterizing the active.

| Oxide        | TSMo (%) | TSG (%) | PR (%) | S/Mo | Co/Mo | (Co/Mo)slabs |
|--------------|----------|---------|--------|------|-------|--------------|
| ZrO₂         | 65       | 56      | 33     | 1.6  | 0.6   | 0.3          |
| Al₂O₃*       | 70       | 53      | 26     | 1.5  | 0.3   | 0.1          |

*used as reference for 46DMDBT hydrodesulfurization.

2.2. Catalytic Activity for Hydrodesulfurization of 46DMDBT HDS

The obtained catalysts have been tested for the hydrodesulfurization of 46DMDBT, which is the model molecule representative of the most refractory ones contained in gazole cuts. According to literature [5], it is well established that the transformation of 46DMDBT converts via three pathways: the hydrogenation (HYD), the direct desulfurization (DDS) and the acidic ways (Figure 4). Acidic route is observed for catalysts such as zeolites, which present Bronsted acid sites at their surface [40,41].

Activities of CoMoS/Al₂O₃ and of CoMoS/mesostructured ZrO₂ catalysts are given in Table 3. We can consider that the total activity is in the same range of order for both catalysts: 0.73 and 0.61 mmol.h⁻¹.g⁻¹ for CoMoS/Al₂O₃ and CoMoS/ZrO₂, respectively. The conventional alumina-based catalyst is highly selective (75%) for the hydrogenated route. This result is in good accordance with literature [6]. The situation is quite different when mesostructured amorphous zirconia is used as
support. Indeed, in that case the contribution of the HYD pathway to the total activity falls to 41%. The direct desulfurization pathway predominates (59%). A detailed analysis of the DDS activity highlights that the direct C-S bond rupture (green route in Figure 4) mainly contributes to the total DDS activity (85%). We note also a slight participation (15%) of the acidic way blue pathway in Figure 4 (dismutation and isomerization), which is unexpected regarding the acidic properties of the CoMo impregnated ZrO$_2$. Indeed, as mentioned above CoMo/ZrO$_2$ exhibits only Lewis acidity similar to the one of CoMo/Al$_2$O$_3$.

![Figure 4](image)

**Figure 4.** Transformation ways of 46DMDBT (HYD: Hydrogenation route, DDS: Direct desulfurization route, sulf: sulfide phase, acid: acid properties, Dism: Dismutation, Isom: Isomerization. 4,6-DMDBT: 4,6-dimethyldibenzothiophene, MCHMB: methylcyclohexylmethylbenzene, MBPh: methylbiphenyl, DMDBT: dimethyldibenzothiophene, DMBPh: dimethylbiphenyl, TMDBT: trimethylbiphenyl, MBP: methylbiphenyl).

![Diagram](image)

**Table 3.** 46DMDBT HDS activities (A mmol.h$^{-1}$.g$^{-1}$) and selectivity (%) obtained for CoMoS/Al$_2$O$_3$ and CoMoS/ZrO$_2$ materials (T = 340°C, P = 40 bars, H$_2$/feed = 475 NL/L).

| Materials       | $A_{total}$ | $A_{acid}$ | $A_{HYD}$  | $A_{total DDS}$ | $A_{HYD}/A_{DDS}$ |
|-----------------|-------------|------------|------------|-----------------|-------------------|
| CoMoS/Al$_2$O$_3$ | 0.73        | 0.00       | 0.55(75%)  | 0.18(25%)       | 3.1               |
| CoMoS/ZrO$_2$   | 0.61        | 0.17       | 0.18(41%)  | 0.26(59%)       | 0.7               |

$A_{total}$ represents the total activity. $A_{acid}$, $A_{HYD}$ and $A_{total DDS}$ stand for the activity obtained from the acidic, the hydrogenated and the direct desulfurization routes, respectively.

To explain the appearance of the desulfurization products through the dismutation and isomerization reactions, we can assume that during the sulfidation and/or HDS reaction a part of the amorphous phase is transformed into monoclinic structure. Indeed, in a paper dealing with the surface characterization of zirconia polymorphs, by infrared analysis after pyridine adsorption, Sun et al. [41] have shown that Lewis acid sites are present on amorphous, monoclinic and tetragonal ZrO$_2$ with a variation of their intensity in the order amorphous ZrO$_2$ > monoclinic ZrO$_2$ > tetragonal ZrO$_2$. By contrast, using this probe Brønsted sites are detected only for the monoclinic zirconia. Tao et al. [42] have also reported similar conclusions in a study concerning a comparison of the surface acidic properties of tetragonal and monoclinic nanostructured zirconia. Moreover, a higher amount of Lewis acid sites is obtained for the monoclinic ZrO$_2$ [43].

The inversion of selectivity observed for the CoMoS/ZrO$_2$ catalyst is quite unexpected regarding the literature. For example, for HDS of 46DMDBT Ninh et al. [44] have obtained a
HYD/DDS ratio of 1.43 and 0.60 for CoMoS dispersed on ZrO$_2$ and Al$_2$O$_3$, respectively. In their study the authors used a commercial monoclinic ZrO$_2$ ($S_{\text{BET}} = 96 \text{ m}^2/\text{g}$) as support. Orozco et al. have reported that the HYD activity of MoS$_2$ deposited on ZrO$_2$ is twice the one of MoS$_2$ dispersed on Al$_2$O$_3$ [45]. In our case, even if the acidic route contributes to the DDS pathway, the change of selectivity cannot be explained only by this contribution. Indeed, in that case the main contribution arises from the direct cleavage of the C-S bond. From Table 4, it can be seen that for the zirconia-based catalyst, the activity per m$^2$ is lower. This could be expected since the amorphous ZrO$_2$ has a higher specific surface area than Al$_2$O$_3$. However, the same tendency is noted for the activity per atom of Mo, we can thus assume that the difference in activity and selectivity may be due to a modification of the active sites which are the molybdenum atoms. This involves different interactions with the support because of the presence of amorphous phase, which will lead to modifications of the electronic properties as already observed with TiO$_2$ [20]. Indeed, in a recent study [29], we have shown that the prepared amorphous mesostructured ZrO$_2$ exhibit a high thermal stability up to 400°C, so we can assume that the change in selectivity is mainly due to the presence of this amorphous phase, which likely modifies the intermediates of reaction by favoring the ones involved in the direct rupture of the C-S bond [5] and/or by modifying the properties of the active phase.

| Materials       | $A_{\text{total}}$ | $A_{\text{acid}}$ | $A_{\text{HYD}}$ | $A_{\text{total DDS}}$ |
|-----------------|---------------------|-------------------|------------------|------------------------|
| CoMoS/Al$_2$O$_3$ | 2.5                 | 0.9               | 0.68             | 0.72                   |
| CoMoS/ZrO$_2$   | 6                   | 2                 | 0.68             | 0.72                   |

$A_{\text{total}}$: represents the total activity. $A_{\text{acid}}$, $A_{\text{HYD}}$ and $A_{\text{total DDS}}$ stand for the activity obtained from the acidic, the hydrogenated and the direct desulfurization routes, respectively.

### 3. Materials and Methods

#### 3.1. Materials Preparation

Amorphous mesostructured ZrO$_2$ was prepared according the procedure described in reference [29] and wet impregnated using CoN$_2$O$_6$, 6H$_2$O, 99.00% Si (Sigma-Aldrich Chemie S.a.r.l., Saint-Quentin Fallavier, France) and (NH$_4$)$_6$Mo$_7$O$_{24}$, 6H$_2$O, 99.98% (Sigma-Aldrich Chemie S.a.r.l., Saint-Quentin Fallavier, France) precursors under the same conditions than the ones reported in reference [20].

As reported in previous papers [20], the catalyst is sulfided in situ before the catalytic reaction in the presence of hydrogen by the hydrogen sulfide resulting from the decomposition of dimethyl disulfide (DMDS). The sulfurizing charge consists of a mixture of n-heptane and DMDS (5 by weight). The sulfurizing feed and hydrogen flow rates are respectively 8 mL/h and 4.7 L/h for an H$_2$/feed ratio of 587 NL/L. The sulfurizing charge is injected at 150°C. After 1 h of sulfidation at 150°C, the temperature is raised to 350°C at a rate of 5 °C/min then maintained at 350°C for 14 h. After this plateau, the temperature is lowered to 340°C.

#### 3.2. Characterization

SAXS measurements were carried out using on a SAXSess mc$^2$ (Anton Paar, Vienna, Austria), equipped with a classical tube ($\lambda$ Cu, K$_\alpha = 0.1542$ nm) operating at 40 kV and 50 mA. Textural properties were evaluated from Micromeritics (Company, Merignac, France) TRISTAR 3000 sorptometer. The BET the BJH (Barrett, Joyner et Halenda) equations were applied to determine the specific surface area and the repartition of the mesopores diameters.
XPS spectra were collected on a Kratos Axis Ultra (Kratos Analytical, Manchester, United Kingdom) spectrometer with a hemispherical energy analyzer and using a monochromatic Al Ka source (1486.6 eV). The peak at 284.6 eV is taken as reference for the bending energies.

3.3. Catalytic Tests

The transformation of 4.6DMDBT was studied under HDS conditions of a diesel cut at a temperature of 340 °C under a total pressure of 4.0 MPa while maintaining the H2/HC ratio constant and equal to 475 NL/L. The model charge, containing 1% by weight of sulfur, consists of 500 ppm S from (4.6DMDBT) and 9500 ppm S of H2S generated by dimethyl disulfide (DMDS) diluted in n-heptane. The transformation of 46DMDBT was measured for a conversion of 25%, which corresponds to liquid feed and hydrogen flow rates of 48 mL/h and 22.8 L/h, respectively while keeping the H2/HC ratio constant (equal to 475 NL/L). Organic products are analyzed by gas chromatography (Varian 3400 GC, Agilent, Paris, France), using a flame ionization detector (FID). The different products were separated on a non-polar DB 1 type capillary column (Agilent, Paris, France) 30 m in length, with an internal diameter of 0.32 mm and a film thickness of 5 μm. The experiment conditions are as follows: a plateau of 30 s at 50°C, followed by a rise in temperature at 2 °C/min up to 60°C, then at 7 °C/min to end at a temperature of 250°C which is maintained for 18 min. The temperatures of the injector and the detector were set at 320°C. The samples taken over time are injected (2 μL) into the chromatograph using a micro-syringe.

4. Conclusions

Mesostructured amorphous ZrO2 have been wet impregnated and sulfided to prepared catalyst for the 46DMDBT hydrodesulfurization.

Comparing with the conventional alumina support, a higher promotion rate and an enhancement of the sulfidation of Co species is observed.

Compared to CoMoS supported over conventional Al2O3 a similar total activity was measured but the direct desulfurization pathway predominates over the hydrogenated route when amorphous mesostructured zirconia is used as support. This result is unexpected since according to literature commercial zirconia favors the hydrogenated route. This study emphasis the role of the amorphous phase on the selectivity.

Author Contributions: I.N.: Investigation; L.M.: Investigation; J.D.C.: Investigation; S.R.: Investigation; M.B.: Investigation; C.M.: Formal analysis; S.B.: Resources, Formal analysis; B.L.: Resources, Supervision; J.B.: Writing - Original Draft, Supervision.

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Conflicts of Interest: The authors declare that they have no competing interests

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