



# Influence of support and supported phases on catalytic functionalities of hydrotreating catalysts



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## HIGHLIGHTS

- Mixed oxide supports of Al<sub>2</sub>O<sub>3</sub>–zeolite, Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> were prepared.
- The HDS activity in DBT conversion was in the order: NiMo ≥ NiW > CoMo on alumina.
- Al<sub>2</sub>O<sub>3</sub>–zeolite support was the most active in HDS of DBT.
- The most active catalyst in HDS of DBT was NiMo supported on Al<sub>2</sub>O<sub>3</sub>–zeolite.

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## ABSTRACT

Different mixed-oxide supports were synthesized using homogeneous co-precipitation methods. Alumina–silica, alumina–titania, and alumina–zeolite supports were prepared and then impregnated with Mo (or W) and Co (or Ni) in order to evaluate their behavior in the dibenzothiophene hydrodesulfurization. Supports and supported catalysts were characterized by atomic absorption and textural properties. The conversion of model compounds (tetralin, 1-methylnaphthalene, and decalin) was investigated with the aim of understanding ring opening reaction over the support in presence of hydrogen. The model test reactions for support as well supported sulfide catalysts were carried out in a batch reactor at 4 MPa and 340 °C. Conversion of cyclo-compounds showed that decalin had the highest conversion followed by 1-methylnaphthalene and tetralin when using a silica–alumina supported catalyst. The hydrodesulfurization results as a function of support variation indicated that high acidity of support has positive effect on the hydrogenolysis of C–S bond breaking. Thus, it is inferred that a balance between metal sites of hydrogenation and cracking of the support is critical in order to synthesize a bifunctional catalyst for deep hydrodesulfurization where sulfur removal as well as cetane improvement are mandatory.

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## 1. Introduction

The stringent environmental regulations for clean fuels have made that more research is being developed in hydrotreating of petroleum fractions using new catalytic materials and designing efficient processes. Sulfur elimination in fuels such as diesel and gasoline is mandatory to meet environmental specifications. However, along with low sulfur specification, other properties such as cetane number of diesel eventually have been considered to be important in order to provide efficient and clean fuel. Thus, the effect of polynuclear aromatic compounds (PNA's) on the cetane number and their negative impact, demand to open the aromatic

ring in order to improve the quality of the diesel. With the aim of developing proper catalysts, support preparation is an option to synthesize materials with increased activity of hydroprocessing catalyst improving the textural properties, selectivity, acidic nature, and optimal metal–support interaction [1]. The use of mixed oxides improves the textural properties of catalysts and modifies the interaction among active metals [2,3]. Mixed oxides preparation has been reported to be carried out using sol–gel [4], homogeneous precipitation to give meso and macro-porous materials [5], and homogeneous delayed precipitation using ammonia as precipitant [6].

The refractory sulfur compounds are usually PNA's; thus, the need for the catalyst development is based on the aromatic ring opening and content reduction of sulfur in presence of hydrogen. In general, refractory sulfur compounds in petroleum are methyl

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substituted dibenzothiophene such as 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene [7,8]. Different supports and catalysts have been used in HDS of dibenzothiophene [9–12]. In addition, reports dealing with hydrodesulfurization of dibenzothiophene have been also written [13].

The cetane number of benzene, toluene, ethyl benzene, and tetralin are determined to be 0, 7, 8, and 13, respectively, by which decreasing their concentration in fuels makes the cetane number increases. Tetralin as an example of model compound of aromatic and naphthenic fused rings undergoes ring-opening reactions, but the key step in the reaction was the isomerization reaction (ring-contraction) of the naphthenic ring of decalins, which is enhanced by the presence of Pt on bifunctional catalysts [14]. In the case of 1-methylnaphthalene (1-MN), the hydrogenation and ring-opening reactions have been reported to be carried out on Pt/USY catalysts [15], where selectivity toward C<sub>11</sub>-products increased with decreasing the number of Brønsted acidity of zeolite. The cetane number of C<sub>10</sub>-cyclo hydrocarbon significantly increases when a naphthenic ring is converted into paraffins, keeping similar C<sub>10</sub>-product molecule.

Other studies have been carried out in order to understand the naphthalene hydrogenation to *cis*- and *trans*-decalin through tetralin intermediate [16]. Naphthenics also undergo ring-opening such as decalin. In this regard, decalin conversion through ring-opening has been studied previously [17–19]. To obtain high selectivity toward the formation of ring-opening products from decalin, mildly acidic catalysts are recommended to achieve high selectivity and yield by ring-opening [20].

Usually, alumina-based supported catalysts are used to removal of polynuclear aromatics, which have limitations in order to open aromatic ring. Thus, it has been considered to improve the acidity of supports to facilitate the opening of one of the polyaromatic molecules, increasing the cetane number in the molecule. However, strong cracking function may carry unselective cracking, which will increase the lighter fraction yield. Therefore, limited acidic function catalyst to ring opening could result in a high-cetane product without the loss of reactant molecular weight. The heavy petroleum model compound fractions were investigated with the purpose of understanding ring opening reaction over the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support while the effect of support and active metals composition were investigated for the HDS of dibenzothiophene. The investigation inferred that a critical balance between active sites of hydrogenation and cracking is required in order to obtain active bifunctional catalysts.

The aim of this work is to synthesize different supports and catalysts to study their influence of support on dibenzothiophene hydrodesulfurization. The acidic nature of supports and catalysts was also evaluated in the ring-opening and ring-contraction of tetralin, 1-methylnaphthalene, and decalin.

## 2. Experimental

### 2.1. Synthesis of supports

Different supports were synthesized in order to vary their acid–base properties. Supports prepared were silica–alumina, titania–alumina, and zeolite–alumina.

#### 2.1.1. Alumina–silica (AS) support

Sol–gel technique was used to prepare alumina–silica supports. Tetraethyl orthosilicate (TEOS) and aluminum nitrate were used as support precursors in the presence of polyethylene oxide referred as PEO in acid medium (nitric acid 60 vol.%). The required amount of Al(NO<sub>3</sub>)<sub>3</sub> and TEOS were used as precursors in order to obtain Si/(Si + Al) weight ratio equal to 0.25. Solution was aged, filtered,

washed, and then extrudates were obtained, which were dried at 120 °C and calcined at 550 °C during 5 h.

#### 2.1.2. Alumina–titania (AT) supports

Various Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (AT) supports were prepared by using different methods (indicated by 1, 2, 3, 4, 5, and 6) which were discussed in detail elsewhere [21] and due to the commercial importance the composition of TiO<sub>2</sub> in the support was kept low (i.e., 10 wt.%). Supports named as AT-1 and AT-2 were synthesized by hydrolysis of urea and ammonia. Precipitation was carried out using TiCl<sub>4</sub> and Al(NO<sub>3</sub>)<sub>3</sub>. Support identified as AT-3 was similarly synthesized as AT-1 and AT-2, but using titanium isopropoxide instead of TiCl<sub>4</sub>. AT-4 was prepared by impregnation of titanium isopropoxide on  $\gamma$ -alumina. AT-5 was synthesized by impregnation of titanium isopropoxide over boehmite. AT-6 was prepared using urea hydrolysis delayed precipitation of TiO<sub>2</sub>, where aluminum nitrate was firstly precipitated and subsequently titanium iso-propoxide, considering that titania precipitates on the surface of the alumina particle. The wet extrudates of AT supports were prepared, which were dried at 120 °C and calcined at 550 °C for 5 h.

#### 2.1.3. Alumina–zeolite (AZ)

The dry extrudates of commercial alumina boehmite (Puralox TH and Pural SB, 50 and 25 wt.%, respectively) and ultra-stable-Y zeolite (CBV-712: SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio = 12.0) support were prepared by using physical mixing with 5% (v/v) HNO<sub>3</sub> in H<sub>2</sub>O as peptizing of alumina. In this case, the amount of zeolite in the alumina support was also varied with 5, 15, and 25 wt.% of zeolite indicated by AZ-5, AZ-15 and AZ-25, respectively. The extrudates were subsequently dried and calcined at 550 °C for 5 h.

### 2.2. Preparation of catalysts

AS, AT, and AZ supports were impregnated by incipient wetness method. Ammonium heptamolybdate and nickel nitrate were used as metal precursors to give a final composition of MoO<sub>3</sub> and NiO (CoO) of 12 wt.% and 3 wt.%, respectively. However, the loading of NiW (NiO = 3 wt.%; WO<sub>3</sub> = 21 wt.%) was also performed by the incipient wetness method using a co-impregnation solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>6</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]. After impregnation, the catalysts were dried in air at 120 °C for 12 h, followed by calcination at 450 °C for 5 h.

The physical properties of the supports and supported catalysts were determined using the N<sub>2</sub> isotherm measured on a Quantachrome Nova 4000 system at –196 °C. The surface area was calculated by the BET equation while pore volume and pore size distribution were calculated by the BJH equation. Previously, solid material was degassed at 300 °C for 3 h. Table 1 shows the textural properties of the catalysts. Atomic absorption was also employed to determine the metal content in each catalyst.

### 2.3. Catalyst activation

Sulfidation *ex situ* was carried out in a glass tubular reactor where around 1 g of catalyst is loaded. Hydrogen flows at 50 mL/min in a container having carbon disulfide saturator at room temperature where H<sub>2</sub> acts as carrier for CS<sub>2</sub> vapor, which is fed to the reactor at 400 °C during 3 h to complete the sulfidation reaction. Then, the catalyst is cooled at room temperature and nitrogen is passed through the catalyst in order to keep an inert atmosphere. Finally the catalyst is transferred to a batch reactor to be tested.

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