



Oxidative desulfurization of diesel using promising heterogeneous tungsten catalysts and hydrogen peroxide



José Luis García-Gutiérrez^{a,*}, Georgina C. Laredo^a, Ponciano García-Gutiérrez^{b,*}, Federico Jiménez-Cruz^a

^a Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México, D.F., Mexico

^b Universidad Autónoma Metropolitana-Iztapalapa, 09340 México, D.F., Mexico

HIGHLIGHTS

- Supported anions with Keggin- and Dawson-type structure catalyze OD using H₂O₂.
- Titania-supported tungsten catalysts show the best activity for the OD of diesel fuel.
- A mechanism via monoperoxo tungsten species is proposed for the OD process using H₂O₂.

ARTICLE INFO

Article history:

Received 5 April 2014

Received in revised form 16 July 2014

Accepted 18 July 2014

Available online 30 July 2014

Keywords:

Oxidative desulfurization

Hydrogen peroxide

Catalysis

Tungsten

4,6-Dimethyldibenzothiophene

ABSTRACT

Tungsten supported catalysts were evaluated in the oxidative desulfurization (OD) of diesel fuel (320 ppmw S) using hydrogen peroxide as oxidizing agent. These catalysts were prepared by equilibrium adsorption of tungsten from solution of tungsten (VI) oxide, tungstic acid, ammonium tungstate, ammonium metatungstate and phosphotungstic acid in supports such as alumina, silica, titania, titania-alumina and zirconia. The sulfur removal from diesel fuel was achieved up to 93.8 ppmw (70.7%) by oxidation under mild reaction conditions followed by acetonitrile extraction. The effects of the tungsten precursor, support, and solution concentration of tungsten used to prepare catalysts were evaluated. According to the results obtained a mechanistic proposal for this reaction is described.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

It is well known that the sulfur and nitrogen impurities present in the fuels are an important source of air pollution, that is, the acid rain caused by NO_x and SO_x generated during combustion in vehicle engines and their detrimental effects on catalytic converters and sensors. In order to decrease pollution, ultra-low sulfur specifications for fuels have been established worldwide. Thus, refiners required to produce fuels with sulfur levels below 10 ppmw [1,2].

In this context, hydrodesulfurization (HDS) is the conventional process for reducing organosulfur compounds in gasoline, diesel and other intermediate distillates. This process is highly efficient in removing thiols, sulfides, disulfides, and some thiophene derivatives. However, it is less effective in the case of highly substituted thiophenic compounds and dibenzothiophene (DBT) derivatives with steric hindrance on the sulfur atom (refractory organosulfur compounds), such as 4,6-dimethyldibenzothiophene (4,6-DMDBT).

These types of compounds are present in diesel fuel with concentrations in the order of 400 ppmw as sulfur [3,4]. It is possible to increase the effectiveness of the HDS toward refractory compounds by using higher temperatures and pressures, more active catalysts or longer residence times [5]. However, these alternatives are costly to refineries and may have an impact upon the global selectivity of the process. This fact has stimulated research in deep HDS, as well as the development of alternative or complementary desulfurization technologies for the production of clean fuels [6–9].

An interesting alternative technology to meet these lower sulfur specifications in fuels is the oxidation process, also called oxidative desulfurization (OD), conversion/extraction desulfurization (CED) or oxidesulfurization (ODS). The literature in this area is extensive due to the amount of research performed in the last years [7]. In this process, the organosulfur compounds, particularly the refractory compounds, are oxidized to their corresponding sulfones, and these products are removed by extraction, adsorption, distillation or decomposition [10–15]. The OD reactivity of organosulfur compounds is increased with the increase of electron density on the sulfur atom. Thus, the reactivity of DBT derivatives is

* Corresponding authors. Tel.: +52 55 9175 6607; fax: +52 55 9175 8429.

E-mail address: garciajl@imp.mx (J.L. García-Gutiérrez).

influenced by the electron donation of substituted alkyl groups. Therefore, the reactivity decrease in the order of 4,6-DMDBT > 4-methyldibenzothiophene (4-MDBT) > dibenzothiophene (DBT), just the opposite order of HDS reactivity [16,17]. Nowadays, the best oxidant option for organosulfur compounds is the hydrogen peroxide because it is cheap, nonpolluting and commercially available, but other oxidants like O₂ also are used [7]. Overall, these oxidants require a catalyst for their activation [18], e.g., H₂O₂ can be used in presence of carboxylic acids [19].

It is well known that the main drawback for industrial application of the homogeneous catalysts is the difficulty of their recovery from the reaction medium; therefore, the use of solid catalysts in the OD process has been researched in recent years. In general, the published results show that heterogeneous tungsten-based catalysts are more active for the OD process than the rest of the metal-based catalysts [10]; however, heterogeneous tungsten-based catalysts show low activity and selectivity to organosulfur compounds in fuel oils as compared to homogeneous tungsten-based catalysts. Thus, for example, Torres et al. [20] prepared a 30 wt.% W/ZrO₂ catalyst by solid impregnation of ZrO_{2-x}(OH)_{2x} with ammonium metatungstate solution under controlled pH, which was evaluated in the OD of diesel fuel with 320 ppmw sulfur using H₂O₂ and γ -butyrolactone at 333 K and atmospheric pressure, the sulfur elimination was 72%. Likewise, Yazu et al. [21] reported the use of phosphotungstic acid with Keggin-type heteropolyacids encapsulated in a SiO₂ framework as the catalyst for OD of diesel fuel. The desulfurization of diesel was carried out with H₂O₂ as the oxidant and acetonitrile as the extraction agent in the temperature range 323–353 K. The sulfur content in diesel was reduced to as low as 48–86 ppm from an initial level of 438 ppm. Similarly, it was reported that an immobilized 12-tungstophosphoric acid on an anion exchange resin [22]. This material catalyzed the OD of diesel oil containing 330 ppmw of total sulfur using H₂O₂ and acetonitrile, the sulfur content in diesel oil was reduced to below 50 ppmw.

Thus, the solid catalysts with high activity and selectivity are highly desirable in heterogeneous OD system; in the case of heterogeneous tungsten-based catalysts, robust research about the effect of tungsten precursor, supports and preparation methods is needed.

Continuing with our research in oxidation coupled with liquid extraction process [16,19,23], we describe here our results in the evaluation of some supported tungsten catalysts and hydrogen peroxide in OD of diesel fuel (Scheme 1) by exploring the effect

of tungsten precursors in five different supports and mechanistic aspects thereof.

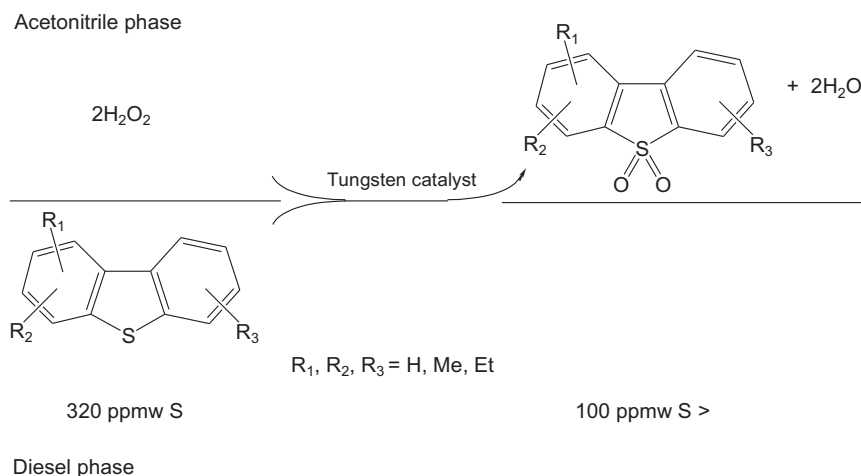
2. Experimental section

2.1. General comments and materials

Unless otherwise stated, all chemicals were obtained from Aldrich and used without purification. In the preparation of the catalysts we used as tungsten precursors: Tungsten (VI) oxide, 99 + % (WO₃); tungstic acid, \geq 99% (H₂WO₄); ammonium tungstate, 99.99% ((NH₄)₁₀W₁₂O₄₁); ammonium metatungstate, 99.99% ((NH₄)₆W₁₂O₃₉·xH₂O); and phosphotungstic acid, 99 + % (12WO₃H₃PO₄·xH₂O). The evaluated supports were: alumina (Criterion; surface area: 357 m²/g, pore volume: 0.83 cm³/g, pore size: 89.7 Å), silica (surface area: 321 m²/g, pore volume: 1.11 cm³/g, pore size: 138.4 Å), titania (UCI Co.; surface area: 54 m²/g, pore volume: 0.28 cm³/g, pore size: 202.9 Å), titania-alumina (UCI Co.; surface area: 98 m²/g, pore volume: 0.36 cm³/g, pore size: 146.0 Å), and zirconia (Mel Chemicals; surface area: 156 m²/g, pore volume: 0.26 cm³/g, pore size: 58.8 Å). The sulfur compounds evaluated were: dibenzothiophene (99%) and 4,6-dimethyldibenzothiophene (97%). Methanol (99.95%), heptane (99%), acetonitrile (99.93%) and hydrogen peroxide (30%) were purchased from Tecisquim. The fuel tested was a commercial Mexican diesel fuel with 320 ppmw of total sulfur and their properties are shown in Table 1.

Table 1
Properties of the diesel fuel.

Total Sulfur (ppmw)	320
Total aromatics (wt.%)	34.0
Total nitrogen (ppmw)	29
Basic nitrogen (ppmw)	15
Specific weight 20/4 °C	0.8435
<i>Atmospheric distillation</i>	
Volume (%)	Temperature (K)
IBP	426.75
5	507.55
20	551.85
40	566.95
60	580.35
80	595.95
95	617.55
FBP	630.95



Scheme 1. OD process of diesel fuel using tungsten-based catalysts and hydrogen peroxide.

Download English Version:

<https://daneshyari.com/en/article/206004>

Download Persian Version:

<https://daneshyari.com/article/206004>

[Daneshyari.com](https://daneshyari.com)