



Hierarchical TS-1 zeolite as an efficient catalyst for oxidative desulphurization of hydrocarbon fractions

D.P. Serrano^{a,b,*}, R. Sanz^a, P. Pizarro^{a,b}, I. Moreno^a, S. Medina^a

^a Department of Chemical and Energy Technology, Universidad Rey Juan Carlos, c/ Tulipán s/n, 28933 Móstoles, Madrid, Spain

^b IMDEA Energy Institute, Avda. Ramón de la Sagra, 3, 28935 Móstoles, Madrid, Spain

ARTICLE INFO

Article history:

Received 30 October 2012

Received in revised form 5 May 2013

Accepted 12 May 2013

Available online 18 May 2013

Keywords:

Oxidative desulphurization

Hierarchical TS-1

Hydrogen peroxide

Tert-butylhydroperoxide

ABSTRACT

The catalytic oxidative desulphurization (ODS) of S-containing aromatic compounds has been investigated over a hierarchical TS-1 zeolite prepared from silanized protozeolitic units, characterized by having, additionally to the zeolitic micropores, a secondary porosity within the supermicro/mesopore region. A standard TS-1 sample has been employed as reference catalyst. The influence of both the solvent (*n*-heptane and acetonitrile) and the oxidizing agent (hydrogen peroxide and tert-butylhydroperoxide, TBHP) was first studied using dibenzothiophene (DBT) as model substrate. In all cases, the catalytic activity exhibited by the hierarchical TS-1 was much higher than that obtained with the conventional TS-1 as a consequence of the improved accessibility caused by the presence of the secondary porosity. A very high desulphurization activity was obtained with the combination of heptane and TBHP, as solvent and oxidant, respectively, leading to an almost total DBT conversion. This fact has been attributed to the fully miscibility of the oxidant solution (TBHP in decane) in the organic reaction medium. Moreover, it is noteworthy that, in these conditions, the oxidation product (sulphone) is insoluble in the reaction medium, which facilitates its removal by filtration or centrifugation. Additionally, the oxidation of different aromatic organosulphur compounds [benzothiophene (BT), 2-methylbenzothiophene (2-MBT), 2,5-dimethylthiophene (2,5-DMT) and dibenzothiophene (DBT)] was investigated using the hierarchical TS-1 catalyst. The trend in the conversion values obtained was 2,5-DMT < BT < 2-MBT < DBT. These results indicate that the oxidation conversion is determined by the nucleophilic character of the sulphur atom, and not by the molecular size of the S-containing compound, provided that the steric and diffusional limitations are overcome by the presence of the hierarchical TS-1 porosity.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The presence of sulphur-containing organic compounds in liquid fuels is one of the most important sources of atmospheric pollution, since after combustion, they lead to SO_x emissions, which causes important health problems and are precursors of the acid rain. Likewise, the presence of sulphur in fuels provokes corrosion of refining equipment and combustion engines. For that reasons, and in order to minimize the negative health and environmental effects, the legislations currently in force establish that the sulphur concentrations in transport fuels should be lower than 10 ppm [1–5].

Hydrodesulphurization (HDS) is the conventional process for the elimination of organosulphur compounds from liquid fuels, by converting them into hydrogen sulphide. The HDS process is usually conducted over sulphided CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts, whose activity not only depends on the properties of the catalyst, but also on the reaction conditions (temperature, and H₂ partial pressure), reactor type, process design and nature and concentration of the organosulphur compounds present in the feed stream [6]. Crude oil fractions with low boiling points contain mostly aliphatic organosulphur compounds: mercaptans, sulphides and disulphides, which are very reactive in conventional hydrotreating processes, being easily removed from fuel. However, in heavier oil fractions like diesel, thiophenes, benzothiophenes and their alkylated derivatives are predominant. These compounds are more difficult to be removed by HDS than mercaptans and sulphides, demanding higher hydrogen pressures, temperatures and/or contact times to achieve sulphur concentrations in fuels below 10 ppm [2].

* Corresponding author at: Department of Chemical and Energy Technology, Universidad Rey Juan Carlos, c/ Tulipán s/n, 28933 Móstoles, Madrid, Spain. Tel.: +34 91 664 74 50; fax: +34 91 488 70 68.

E-mail address: david.serrano@urjc.es (D.P. Serrano).

Oxidative desulphurization (ODS) is considered one of the most promising methods for fuel deep desulphurization. In comparison to conventional HDS, ODS can be carried out under mild conditions, employing temperatures lower than 100 °C and atmospheric pressure [7]. Through this technology, sulphur compounds such as thiophene, benzothiophene and their derivatives can be oxidized into the corresponding sulphones by the electrophilic addition of oxygen. Sulphones are highly polarized compounds, which can be removed from oil fractions by simple liquid–liquid extraction using a polar solvent [8]. The oxidation of thiophenic and benzothiophenic compounds with hydrogen peroxide (H₂O₂) has been reported using formic acid [9], acetic acid [10] polyoxometalate [11], molybdenum supported on alumina [12] and titanium microporous molecular sieves [5,13] as catalysts. However, these materials exhibit some drawbacks: formic acid reduces the quality of the liquid fuels, polyoxometalate is difficult to be recovered and regenerated and molybdenum supported catalyst are not very stable, since molybdenum tends to be leached into the reaction medium [14]. The use of titanium-containing zeolites is also limited in ODS due to the restricted access of the bulky sulphur compounds into the zeolitic micropores. In this sense, the oxidation of thiophene and benzothiophene derivatives has been investigated over different micro and mesotitanosilicates using hydrogen peroxide [5,15]. It was found that ordered mesoporous materials such as Ti-MCM-41 and Ti-HSM are very active for the oxidation of bulky sulphur compounds, while TS-1 zeolite was almost inactive, due to the steric and diffusion limitations derived from its microporous nature. However, ordered mesoporous materials suffer from limited hydrothermal stability due to the amorphous nature of their walls, which strongly limits their durability and commercial application [16–18].

In this context, the development of Ti-containing hierarchical zeolites can overcome the limitations presented by single micro- or mesoporous materials. This new type of materials, characterized by having bimodal pore architecture, may combine the catalytic properties and hydrothermal stability of the zeolitic active sites and the enhanced accessibility provided by an additional mesoporosity [19]. The synthesis of Ti-containing hierarchical zeolitic materials, mainly TS-1 zeolite, has been reported following different strategies. Thus, hierarchical TS-1 materials have been obtained by acid and alkaline post-synthesis treatments [20] or using hard-templates such as carbon black, CMK-3 or carbons obtained from sucrose carbonization [21–23]. Likewise, the use of organosilane compounds as soft-templates has been found as a successful strategy to obtain hierarchical TS-1 zeolitic materials [24,25].

In this work, we report the application of hierarchical TS-1 zeolite, synthesized from silanized protozeolitic units, in the oxidation of thiophenic and benzothiophenic organic compounds. The hierarchical TS-1 zeolites so obtained are formed by zeolitic nanounits aggregates, showing a secondary porosity in the supermicro- and mesopore range, additionally to the microporosity typical of MFI-type materials, which provides them with enhanced BET and external/mesopore surface areas. These nanounits are not independent and isolated units, since they present significant intergrowth, providing hierarchical TS-1 with high thermal and mechanical stability, as it was shown in a previous work [26].

Firstly, the effect of the solvent nature (*n*-heptane and acetonitrile) and of the oxidant type (H₂O₂, TBHP) has been explored. In these experiments, dibenzothiophene (DBT) was used as organosulphur model compound. For comparison, the results obtained for a conventional TS-1 zeolite are also shown. Likewise, in order to study the influence of the organosulphur compound nature, the oxidation of different S-containing substrates has been investigated (benzothiophene (BT), dibenzothiophene (DBT), 2-methylbenzothiophene (2-MBT) and 2,5-dimethylthiophene (2,5-DMT)).

2. Experimental

2.1. Synthesis of hierarchical TS-1 zeolite

The hierarchical TS-1 zeolite (h-TS-1) was prepared according to the protozeolitic units silanization method previously reported by our group [24,26]. Firstly, a synthesis gel, with molar composition of 1SiO₂:0.0163 TiO₂:0.44 TPAOH:28.5 H₂O, was prepared following the original recipe developed by Taramasso and co-workers [27]. After that, in order to promote the protozeolitic units generation, this solution was precrystallized in a reflux system under stirring conditions at 90 °C for 24 h. Then, the silanization agent (phenylaminopropyltrimethoxysilane, PHAPTMS, Aldrich) was added with a loading of 8 mol% in regard to the total silica content in the gel, and the mixture was stirred at 90 °C for 6 h. Finally, the crystallization treatment was carried out at 170 °C for 8 h in a Teflon vessel under autogenous pressure using microwave heating radiation. During this last crystallization step, the silanization agent, anchored over the surface of the protozeolitic units, disrupts the crystal growth, hindering partially the zeolitic units aggregation. Additionally, a conventional TS-1 zeolite was also prepared following the synthesis procedure previously described but omitting the precrystallization and silanization steps. In both cases, the solid products obtained after the crystallization treatment were recovered by centrifugation, washed several times with distilled water, dried overnight at 110 °C and calcined in air at 550 °C under static air conditions.

2.2. Characterization of the catalyst samples

XRD analyses were performed using CuK α radiation with a Philips X'PERT MPD diffractometer using a step size and a counting time of 0.02° and 10 s, respectively. DR UV–vis spectra were collected on a CARY-500 spectrophotometer equipped with a diffuse reflectance accessory. Titanium content of the calcined samples was estimated by means of atomic emission spectroscopy with induced coupled plasma (ICP–AES) analyses using a Varian Vista AX instrument. Ar adsorption–desorption isotherms at 87.3 K were measured with an Autosorb-1 analyzer from Quantachrome instruments, degassing the samples at 573 K for 5 h prior to the analysis. The total surface area was estimated according to the BET method, whereas the pore size distribution and the cumulative volume curve were calculated by applying the NL-DFT model assuming cylindrical pore geometry and employing argon–zeolite as adsorbate–adsorbent kernel in the adsorption branch [28]. Finally, TEM images were taken in a PHILIPS TECHNAI 20 electron microscope operating at 200 kV and 2.7 Å resolutions. Previously, the sample was dispersed in acetone and a droplet of the suspension was deposited onto a carbon-coated copper grid.

2.3. Catalytic tests

The catalytic behaviour of the TS-1 zeolite samples was evaluated in oxidative desulphurization process using benzothiophene (BT, 95%, Aldrich), dibenzothiophene (DBT, 98%, Aldrich), 2-methylbenzothiophene (2-MBT, 97% Aldrich), and 2,5-dimethylthiophene (2,5-DMT, 98%, Aldrich) as model sulphur compounds. The catalytic experiments were carried out at atmospheric pressure in a 50 ml round bottom flask immersed in an oil-heating bath and equipped with a magnetic stirrer. Typically, 5 g of solvent, acetonitrile (99%, Alfa) or *n*-heptane (99%, Sharlau), 0.3 mmol of sulphur-containing organic compound and 12.5 mg of catalyst were put in contact at 80 °C. Then, the oxidizing agent, hydrogen peroxide (H₂O₂, 30%, Sharlab) or tert-butylhydroperoxide (TBHP, 5.5 M in decane, Aldrich) was added using an oxidant/S-organic compound molar ratio of 2. The catalytic tests were carried out at reaction times between 0 and 60 min.

Download English Version:

<https://daneshyari.com/en/article/45180>

Download Persian Version:

<https://daneshyari.com/article/45180>

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