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Oxidative desulfurization of synthetic diesel using supported catalysts Part II. Effect of oxidant and nitrogen-compounds on extraction–oxidation process

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Abstract

Oxidative desulfurization (ODS) of a synthetic diesel was carried out at mild conditions (atmospheric pressure and 60 °C) in presence of V_2O_5/Al_2O_3 and V_2O_5/TiO_2 catalysts. Two main aspects were studied: the effect of the oxidant reagent and the presence of nitrogen compounds on ODS of benzothiophenic compounds prevailing in diesel, such as benzothiophene, dibenzothiophene and alkyl substituted in positions 4 and 6. Results show that activity is improved when using hydrogen peroxide, as oxidant reagent, and V_2O_5/Al_2O_3, as catalyst. This result was attributed to the high decomposition of peroxide due to the presence of catalyst. In presence of nitrogen compounds, the ODS activity decreases in the order: quinoline > indole > carbazole. In order to explain this effect, successive chemisorption of DBT and quinoline on V_2O_5/Al_2O_3 catalyst was evaluated by FT-IR, and the results show that DBT is displaced by quinoline, occupying the adsorption sites of catalyst. N-compound effect could be explained by strong adsorption of nitrogen compounds on catalytic sites.

Keywords: Oxidant effect; Nitrogen compounds; Oxidative desulfurization; Ultra low sulfur diesel

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1. Introduction

Sulfur compounds removal from petroleum is necessary for both industrial and environmental reasons. Sulfur in petroleum products poisons catalytic converters, corrodes parts of internal combustion engines and refineries because the formation of oxyacids of sulfur and causes air pollution due to exhaust from diesel engines.

The conventional method for reducing sulfur is catalytic hydrodesulfurization (HDS). In the HDS process, hydrogen and organic sulfur compounds react together at high temperatures and pressures [1]. The effectiveness of HDS process depends on the type of sulfur compounds. The complete sulfur removal depends on reactivity of refractory HDS compounds, as dibenzothiophenes, mainly alkyl substituted in 4 and 6 positions. Other processes have been studied in order to remove these compounds [2]. Among these options, oxidesulfurization (ODS) is an attractive alternative to the HDS process [3–14].

ODS has a significant advantage over HDS, since the sulfur compounds that are the most difficult to eliminate by HDS are the most reactive on ODS [10]. Compared with traditional HDS, ODS has several advantages such as mild conditions (atmospheric pressure and temperature lower than 80 °C), high selectivity, absence of expensive hydrogen and potential for desulfurization of sterically hindered sulfides as alkyl benzothiophenes.

ODS, in presence of a solid catalyst, generally is defined in two steps: oxidation of S-compounds to sulfones and removal or extraction of oxidized S-compounds from the treated fuels [3,7]. Previous results [15] suggest that the first step is removal of sulfur compounds by extraction from the treated fuel, and the following step is their oxidation to the corresponding sulfones in the solvent phase, since having reactants in the polar phase facilitates their reaction. In these conditions, the solvent is very important in the process, the extraction of sulfur compounds took noticeable place without catalyst. By the contrast, in presence of catalyst and oxidant but without extraction solvent,

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there was no oxidation reaction of these compounds [16]. Then, total removal depends on the contribution of extraction and oxidation steps. Butyrolactone and acetonitrile were the most efficient dipolar aprotic solvents in ODS process, but oxidation to sulfone was higher with the latter. Total removal of DBT was close to 100%, but the oxidation to sulfone was only about 80%, using butyrolactone as solvent [15]. For this reason, it is important to evaluate the contribution of each step, in order to know the real activity of the catalyst.

Several oxidants have been used in ODS, such as hydrogen peroxide, tertbutyl hydroperoxide (TBHP), peracids and ozone [17]. Among these reactants, peroxides are very attractive since generally the reaction proceeds rapidly and selectively under mild conditions. The oxidant selection depends on the hydrophobic character of the catalyst, given that hydrogen peroxide produces water and it inhibits the ODS activity [16]. However, in this case, the vanadium-based catalysts showed good ODS activity for sulfur compounds prevailing in diesel, with hydrogen peroxide. Unlike the group IV–VI metal oxide based catalyst, silicates are active in diluted aqueous solutions of hydrogen peroxide, whereas anhydrous organic hydroperoxides, such as TBHP, are the oxidants of choice for the former catalysts [18]. These catalysts favor the adsorption of the organic substrates over the more polar water molecules present in the aqueous H_2O_2 solutions [19]. In this sense, the aim of the study is to evaluate the oxidative reactivities of S-compounds in presence of vanadium oxide catalysts with hydrogen peroxide and TBHP, as oxidants. Firstly, oxidation of a model diesel was carried out, using V_2O_5 supported on alumina or titania as catalysts, to evaluate their oxidative activities. Secondly, oxidation of model sulfur compounds was studied with H_2O_2 or TBHP, to analyze the oxidant effect on the activities of these sulfur compounds.

Another important factor in ODS process is to evaluate the effect of other compounds present in the oil fractions. Otsuki et al. [20] studied the effect of nitrogen-model compounds, olefins, aliphatic and aromatic hydrocarbons, found in light gas oil, on oxidation of DBT. This study shows that the conversion of DBT was not influenced by the addition of *n*-pentadecane or by addition of xylene, indicating that aliphatic and aromatic compounds did not affect the oxidation of DBT. In contrast, the addition of diisobutylene and indole retarded the oxidation reaction. These results were attributed to a higher reactivity of these compounds compared to that of DBT, in conditions of the oxidation reaction. Ishihara et al. [21] reported that denitrogenation performance of N-containing compounds in oxidation process is possible. Denitrogenation activity order of model compounds was: indole > quinoline > acridine > carbazole. However, while the oxidation products of N-compounds were not fully identified, they suggested the presence of polymeric compounds. Since sulfur compounds are removed quantitatively from fuels by physical extraction without oxidation reaction [15], then the N-compounds could be removed only by extraction. In order to analyze the effect of nitrogen compounds on ODS reactions, in this work we also study the ODS of synthetic diesel in presence of several N-compounds, such as indole, carbazole or quinoline.

2. Experimental

2.1. Materials

All compounds were purchased from Sigma–Aldrich and used without further treatment. Benzothiophenes, which represent sulfur species in diesel, were selected to evaluate the reactivity in ODS reaction. Hexadecane (99.8%) was used as solvent of model compounds: benzothiophene (BT, 98%), dibenzothiophene (DBT, 98%), 4-methyl dibenzothiophene (4-MDBT, 96%) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT, 97%). This synthetic diesel was prepared with 936 S ppmw: 308 of BT, 224 of DBT, 209 of 4-MDBT and 195 of 4,6-DMDBT. Acetonitrile (99.9%) was used as extraction solvent. Indole (99%), carbazole (96%) and quinoline (98%) were used as the model N-compounds.

2.2. Catalysts and characterization

V_2O_5/Al_2O_3 and V_2O_5/TiO_2 catalysts were obtained by thermal spreading at 500 °C during 5 h in air [22,23]. Catalyst represents a physical mixture of the support (alumina with 175 m^2/g or TiO_2 with 120 m^2/g) and V_2O_5 (99.6%, Aldrich) obtained through intensive manual milling. Each catalyst was prepared with a V_2O_5 loading equivalent to a monolayer coverage [24,25], 17 wt.% for V_2O_5/Al_2O_3 (V/Al) and 11 wt.% for V_2O_5/TiO_2 (V/Ti).

Catalysts were characterized by: X-ray diffraction (XRD) using a Siemens D500 powder diffractometer with Cu Kα radiation. Textural properties were obtained by N_2 adsorption–desorption isotherms of the samples, with a Tristar Micromeritics apparatus. Nitrogen physisorption isotherms were analyzed using the BJH method. Prior to the textural analysis, the samples were outgassed for 8 h in vacuum at 350 °C. Elemental composition was determined by SEM-EDX in a Jeol JSM-5900 LV microscope equipped with an energy dispersive X-ray (EDX) elemental analysis system. The FT-Raman spectra of catalysts were performed in a Nicolet FT-Raman 950 spectrometer with a resolution of 4 cm^{-1} and 500 scans. Before the analysis, the samples were pretreated at 100 °C during 12 h in static air. A conventional temperature programmed reduction (TPR) apparatus was used for the study of the reducibility of the catalysts. TPR of the catalysts was performed using a flow of H_2/Ar mixture (30% H_2, v/v, 25 cm^3/min) at atmospheric pressure, 0.25 g of sample and a heating rate of 10 °C/min from room temperature to 1000 °C. The IR spectra were performed on a Nicolet Magna 760 Fourier Transform Spectrometer with a resolution of 2 cm^{-1} and 100 scans. For IR experiments, wafers of the pure catalyst were made (∼20 mg) and outgassed under vacuum in a special IR cell at 250 °C during 1 h to physically remove adsorbed impurities from the catalyst sample. After that, a pulse of the probe molecules was introduced and a spectrum was taken. Finally, the cell was outgassed at room temperature and a