ODS of dibenzothiopene with titanium-modified SBA-16

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1. Introduction

Over the past, oxidative desulfurization (ODS) has drawn considerable interest as a new alternative method for deep sulfur elimination from light oils. This can be attributed to its attractive properties, including lower temperature and pressure conditions and lower operating cost [1-3] than conventional hydrodesulfurization (HDS) process. Oxidation of organosulfur compounds results in the formation of sulfoxides/sulfones, highly polar and hence easily removed by both extraction into polar solvents or by adsorption. Due to their low reactivity, dibenzothiophene derivatives (DBTs) are the most refractory species to be eliminated from oils. Hence, the ODS process through which DBTs are converted to their corresponding sulfones involves great interest at present [4-6]. We recently reported a good performance of this support in hydrotreating processes [7]. In this work, we describe the preparation and characterization of new mesoporous catalytic materials based on Ti-containing SBA-16. We study here, the effect of the preparation method of titania-modified SBA-16 (characteristics of the active Ti and/or TiO_2 species) and the effect of the different operation conditions in ODS of DBT under mild conditions in order to find the best performance. TiO_2-modified mesoporous SBA-16 and titanium-substituted mesoporous SBA-16 were developed and tested in the oxidative desulfurization (ODS) of dibenzothiophene prevailing in liquid fuel. We assessed the impact exerted on performance of different reaction variables, including (nature and amount of the active catalytic species, phase system, molar ratio of oxidant H_2O_2 and DBT, reaction temperature, nature of the substrate and reuse of catalysts).

2. Experimental Section

2.1 Synthesis of the catalyst

Mesoporous silica materials with cubic Im3m structure SBA-16 were synthesized and modified with titanium according to [7].

2.2 Catalytic activity

The catalytic activity was measured in a batch reactor, fitted with condenser and magnetic stirrer at 60°C. Oxidant (hydrogen peroxide (30 wt. %)) and catalyst (100 mg) were then introduced into the reactor with vigorous stirring. The products were identified with a GC HP 5890 Series II with a HP-5 column and connected to FID and PFPD detectors. The model feed consisted of 0.2 wt.% of DBT (98.5% FLUKA) in acetonitrile.

3. Results and discussion

The titania-based catalysts were characterized by chemical analysis, XRD, EDX and TEM. The titanium state as tetrahedral (in Ti-SBA-16 sample) or octahedral (in TiO_2/SBA-16 sample) coordination surrounding in the silicate matrix was determined by XPS, UV-vis DRS, FTIR, Raman and XANES. Figure 1 shows the catalytic results from the ODS of DBT using the different synthesized catalysts (TiO_2, TiO_2/SBA-16 and Ti-SBA-16) in a liquid-solid (L–S) and in a liquid-liquid-solid (L-L-S) phase system. DBT was oxidized to it sulfone (100% yields). From the Figure, we can note that TiO_2/SBA-16 displays a DBT conversion 20% higher than that of Ti-SBA-16, and 4 times higher than that of TiO_2. The effect of mass transfer was studied comparing two different phase systems. In the three phase system, the catalytic oxidation of DBT occurs by simultaneous extraction/oxidation of dibenzothiophene in acetonitrile solution, wherein are the catalyst and H_2O_2. Ti surface sites in the catalysts are capable of interacting with H_2O_2 to produce large amounts of superoxide radical. These radical species can oxidize the DBT molecules in acetonitrile phase to their corresponding sulfones, and hence polar sulfones do not migrate into the oil phase. A better conversion was obtained in the L-S phase system for all the samples, probing the existence of mass transfer limitation.

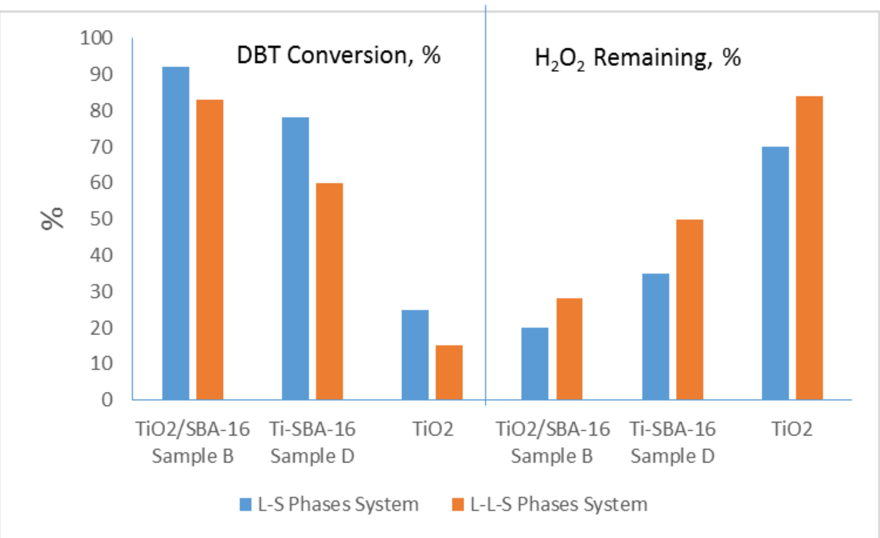

Fig. 1. DBT conversion (left) and H_2O_2 remaining (right) after ODS reaction, with TiO_2/SBA-16, Ti-SBA-16 and TiO_2 in L–S phase system (acetonitrile) and in L–L–S phases system (acetonitrile and dodecane). Molar ratio H_2O_2/DBT=5, g DBT/g cat=1, T=60°C. Reaction time= 60 min.

4. Conclusions

We achieved 90% of S removal from a 0.2 wt.% dibenzothiophene solution at 60°C in less than 1 h of reaction. The best catalytic results are obtained with high exposed surface of nanometric TiO_2 species of TiO_2/SBA-16 sample. The activated catalyst is very active in ODS reaction and can be reused four times with no loss in activity.

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