Efficiency of supported and incorporated W-SBA15 catalytic systems for oxidative desulfurization of sulfur model molecules, model fuels and LGO

Carole Lamonier,[a]* Georgette Estephane,[a] Christine Lancelot,[a] Pascal Blanchard,[a] Joumana Toufaily,[b] Tayssir Hamieh,[b] Véronique Dufaud[c]

[a]*Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France*
[b]*MCEMA, Lebanese University, Faculty of Science, Rafic Hariri University Campus, Hadath, Lebanon*
[c]*C2P2. CPE Lyon 43 Bd du 11 Nov. 1918 69616 Villeurbanne cedex. FRANCE*
**Corresponding author: Fax number, E-mail address*

Abstract:
W-SBA15 catalysts with variable contents in tungsten were synthesized by dry impregnation of a SBA15 with a phosphotungstic acid (HPW) solution and by one-pot synthesis allowing HPW incorporation. The mesoporous structure of SBA15 is maintained after HPW introduction preserved even after calcination. Supported and incorporated catalysts presented high textural properties. Catalysts were evaluated in the oxidative desulfurization (ODS) reaction of model charge and LGO diesel. All catalysts are more efficient than the classical W silica supported catalyst. The most efficient catalyst is the 25W/SBA15 allowing simultaneous oxidation of the sulfur compounds of LGO diesel (50ppmS) in 3 minutes.
Keywords: Oxidative desulfurization, HPW, SBA15.

1. Introduction

Keggin-type heteropolyacid (HPA) exhibited high catalytic performance in the oxidation of sulfur compounds[1]. However, their catalytic activities are greatly limited by their very low specific surface areas (1–10 m^2/g). Mesoporous silica materials such as SBA-15 are appropriate candidates for their use as support in catalysis due to their high specific surface area, and large pore size allowing a good diffusion and dispersion of the active phase. In the present work, oxidative desulfurization catalysts HPW-SBA15 are prepared by impregnation of $H_3PW_{12}O_{40}$ (HPW) on the mesoporous SBA-15. Leaching of the active phase is often reported in the literature during ODS reactions[2] and in order to immobilize the HPW species, a one-pot synthesis allowing their incorporation into SBA15 matrix has been used [3]. The catalytic performances of the samples are evaluated in the ODS reaction of model molecules and LGO diesel.

2. Experimental

2.1. Synthesis of W-SBA-15 catalysts

- SBA-15 support is synthesized based on the method developed by Zhao *et al*.[4]
- Impregnated catalysts named xW/SBA-15 are synthesized by dry impregnation: Support+ HPW solution → maturation→ drying→ calcination (500°C)→ ***xW/SBA-15*** (x:6,14,25)
- Incorporated catalyst are synthesized according to the synthesis protocol described by Silva *et al*. [3] with pre-hydrolysis of TEOS in a acidified mixed template solution before the direct addition of the HPW in the reaction medium. After a hydrothermal treatment, the solids were recovered by filtration, washing, drying and calcination. The obtained samples are named ***xWSBA-15***(x= 5, 10 and 19)

For both synthesis methods, x is the tungsten content expressed as WO_3 wt %.

2.2. Catalytic reaction

The ODS reaction was performed in batch reactor at 75°C with model solution with sulfur contents ranging from 50 to 1500 ppm and with a LGO diesel with 50 ppm of sulfur. *Tert*-butyl hydroperoxide (TBHP) was used as oxidant (with O/S molar ratio=2.3 and 25 for model solutions and LGO diesel, respectively). After reaction, solutions are analyzed by gas chromatography coupled with a SCD detector in order to obtain the conversion value.

3. Results and discussion

3.1. Characterization of the catalysts

Small and wide angle XRD catalysts analysis showed the preservation of the organized mesoporous structure without W based phase crystallization. In Raman spectra the characteristic lines of HPW are observed for all catalysts indicating its preservation even after calcination. Catalysts textural analyzes showed very well preserved textural properties with high specific surface areas (>700 m^2/g), pore volume (>1.2 cm^3/g) and average pore diameter (>7.0 nm).

3.2. Catalytic evaluation of the catalysts

For ODS of dibenzothiophene in dodecane (50 ppmS), all catalysts presented high conversions between 93 and 100%. Using successive additions of DBT (500 ppmS) impregnated catalysts showed higher conversions of DBT compared to the incorporated ones (Figure 1-A).This can be related to the location of the active species which are dispersed on the surface for impregnated catalysts while their accessibility in incorporated catalysts can be affected by precipitation of sulfones into the pores during reaction process. In ODS of model mixtures solutions, the order of reactivity is DBT > 4,6-DMDBT>> C1-BT showing that the oxidation reaction depends on the one hand on the electron density on the sulfur atom and on the other hand, on the steric hindrance caused by the methyl substituents near the sulfur, in agreement with literature data [4].

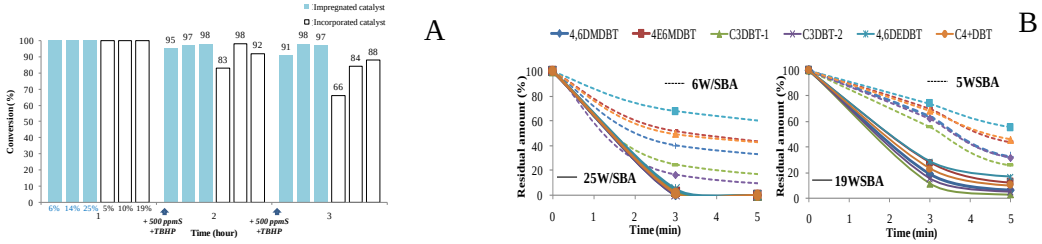

Figure 1. Conversion rates in simulation of dynamic test (A), Evolution of residual amounts of Cx-DBTs in LGO50 (B)

During ODS reaction of LGO (50 ppmS) containing only alkyl-dibenzothiophenes (Cx-DBTs) being the most refractory compounds to HDS, the concentration of six selected sulfur molecules: 4,6-DMDBT, 4E6MDBT, C3-DBT-1, C3-DBT-2, 4,6-DEDBT and C4+DBT has been followed. As reported in Figure 1-B, better performances are obtained for 25W/SBA and 19WSBA with high W content compared to low W content catalysts. With low oxidation rate as noted on 6W/SBA differences in reactivity of the Cx-DBTs were observed. Indeed, alkyl-DBTs such as 4,6-DEDBT and 4E6MDBT with alkyl groups around the sulfur atom and C4+DBT appear to be less reactive than C3-DBTs. These results indicate that reactivity depends on the steric hindrance as well as the number of methyl substituents. However, 25W/SBA catalyst, which is the most efficient, simultaneously oxidizes the six sulfur-containing molecules in 3 minutes.

4. Conclusions

In summary, HPW-SBA-15 catalysts presented good performances in ODS of model solutions and also LGO diesel. The order of reactivity in our catalytic system is DBT> 4,6-DMDBT>> C1-BT. The impregnated 25W/SBA catalyst was the most efficient; it can oxidize simultaneously sulfur compounds in LGO diesel in just 3 minutes. Therefore, the HPW-SBA-15 materials prepared in the present work are promising and efficient catalysts for the ODS of the fuel oils.

References

[1]Li B, Ma W, Liu J, Han C, Zuo S, Li X. Catal Commun. 13(2011) 101-105.

[2]Chica A., Corma, A. & Domine, M. J. Catal. 242(2006) 299–308

[3]S. Silva, A. Chaumonnot, A. Bonduelle-Skrzypczak, F. Lefebvre, S. Loridant, V. Dufaud. ChemCatChem. 6 (2014) 464–467.

[4]D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024 – 6036.