Chapter 8
Trimetallic Sulfide Catalysts for Hydrodesulfurization

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ABSTRACT

The more stringent environmental regulations enacted throughout the world have increased the need of more active hydrotreating (HDT) catalysts, in the petroleum refining industry. Usually, the catalysts used for diesel oil hydrotreatment are γ-Al$_2$O$_3$ supported molybdenum or tungsten sulfides promoted with cobalt or nickel. Current strategies for the design of novel HDS catalysts often include variations in the support formulation, catalyst preparation method and active phase formulation. In this sense, the new generations of catalysts, such as NEBULA®, are based on a totally different concept of bulk-like. In this chapter, we present recent research related to the synthesis, characterization and performance of trimetallic sulfide nanocatalysts for hydrodesulfurization. The present chapter analyses the state of art of the ternary sulfide hydrotreating catalysts.

1. INTRODUCTION

Traditionally, in the early 1990s, sulfur used to be removed from petroleum-derived feedstocks by a hydrodesulphurization (HDS) process using γ-Al$_2$O$_3$-supported Mo or W sulfide catalysts promoted by Co or Ni (Topsøe *et al.,* 1996; Ho, 2004 and 2008). However, because the thermodynamic limitations of bimetallic Co(Ni)Mo(W)/Al$_2$O$_3$ catalyst formulation to perform deep HDS reactions at high temperature, it was impossible to satisfy stringent legislative requirements for ultra-low sulfur transport fuels using

those catalysts. After many efforts in the design novel catalyst formulations, supports and new preparation procedures, the recent catalyst developments and technologies allow production of ultra-low sulfur diesel (ULSD) (Soled *et al.,* 2000; Topsøe *et al.,* 1996). However, the determination that catalyst could be used depends on the specific refinery configuration, feedstock blends employed, and it might be a simple matter of economics (Topsøe *et al.,* 2005).

The S-containing refractory compounds, which should be removed from the feedstock's, are dibenzothiophene (DBT) and alkyl-substituted DBT. For those molecules, the HDS reaction occurs mainly *via* hydrogenation (HYD) and direct desulfurization (DDS) pathways. For the HDS of DBT reaction (see Box 1), direct desulfurization pathway (DDS) leads to formation of biphenyl (BP), whereas hydrogenation pathway (HYD) leads to formation of tetrahydrodibenzothiophene (THDBT), cyclohexylbenzene (CHB) and dicyclohexyl (DCH) (Ho, 2004 and 2008). It is well established that DDS route of this reaction is favored for the Co-promoted catalysts whereas Ni-promoted ones exhibit enhanced HYD route of DBT transformation, as it was confirmed for the all catalysts studied in this chapter. The presence of alkyl groups in the highly refractory 4,6-dimethyldibenzothiophene (4,6-DMDBT) hardly affects the hydrogenation (HYD) pathway whereas the DDS pathway is severely inhibited. The hindrance of the C-S bond cleavage in the THDBT was claimed to be the most probably reason for the low reactivity of 4,6-DMDBT (Ho, 2004 and 2008). To overcome this problem, novel HDS catalysts exhibit enhanced hydrogenation function.

Actually, many refineries used a BRIM™ hydroprocessing technology developed by Haldor Topsøe (Topsøe *et al.,* 2005) whereas others successfully employed unsupported catalysts called NEBULA (Soled *et al.,* 2000; Plantenga *et al.*, 2003). The Ni-Mo/Al$_2$O$_3$ catalysts based on the BRIM™ hydroprocessing technology possess Mo(W)S$_2$ phases having a large amount of "*brim sites*". Owing their metallic character, those catalysts exhibit enhanced hydrogenation function, and in consequence, display superior hydrodesulphurization activity and excellent stability (Lauritsen *et al.* 2004a, b).

Box 1. General reaction scheme for the hydrodesulfurization of dibenzothiophene over unsupported and supported trimetallic catalysts
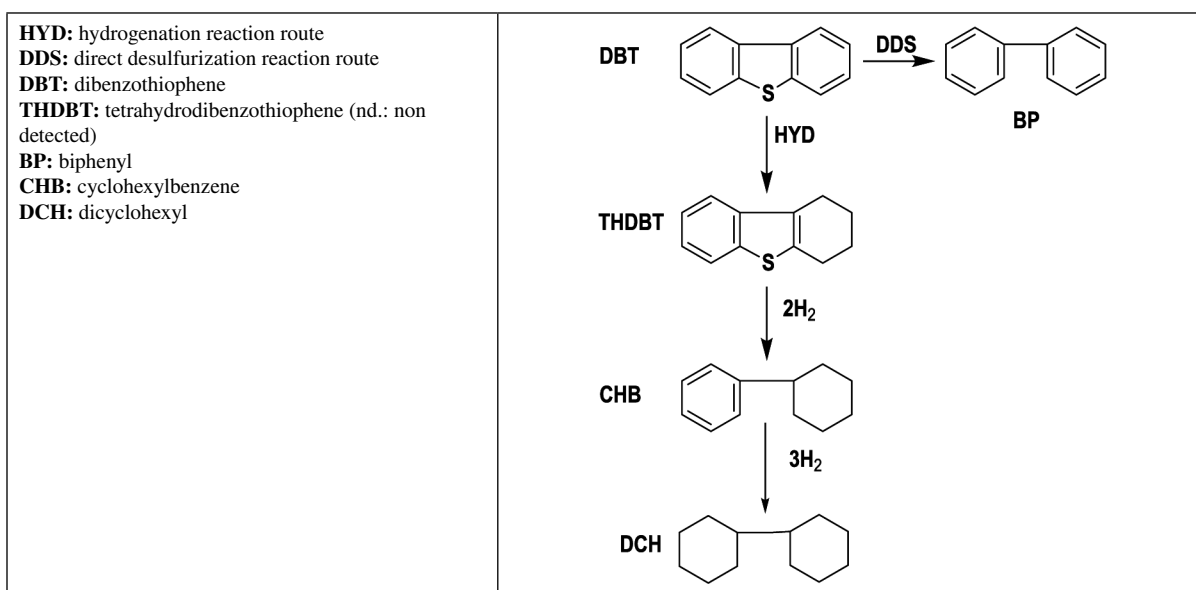
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