Chapter 9

Preparation of Deep Hydrodesulfurzation Catalysts for Diesel Fuel using Organic Matrix Decomposition Method

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ABSTRACT

In this work, a series of supported CoMo or NiMo HDS catalysts have been prepared based on the organic-metal matrix decomposition method and tested for diesel deep HDS with minimum hydrogen consumption under relatively low hydrogen partial pressure conditions. The aim is to develop a HDS catalyst which can reduce sulphur in diesel fuel from 5000ppm down to 50 ppm in a single pass with minimum hydrogen consumption under the conditions of 340oC, 35 bar, LHSV 1.2 h-1 with low H2/oil ratio. The catalysts preparation process was monitored and the resultant catalyst samples before and after the HDS performance test have been characterised, some interesting results have been obtained. The presence of citric acid as organic additive/dispersing agent/chelating agent in the impregnation solution improved HDS activity compared to the equivalent CoMo catalyst prepared without citric acid, The order of activity of the cobalt precursors is Co citrate > Co acetate > Co nitrate.

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1. BACKGROUND

Diesel is extensively and increasingly used as a main fuel for transportation systems due to its higher fuel-efficiency and longer mileage (Abro 2014; Chen, Wang, 2010; Ismagilov., 2009; Wasserscheid, 2003). However, the extensive use of diesel has caused increasing emissions of particulate, NO**x** and SO**x**, which are harmful to human health and also resulting in more eco-problems such as acid rain and smog. Sulfur, a natural part of the crude oil from which diesel fuel is derived, is one of the key causes of particulates or soot in diesel. Legislative regulations in many countries call for the production and use of more environmentally friendly transportation fuels with the lower contents of sulfur, nitrogen and aromatics, and indeed, since 2000s, many countries around the world has ordered to reduce the sulfur content of diesel fuel to ultra low levels (10–15 ppm) with the intention of lowering diesel engine's harmful exhaust emissions and improving air quality. The environmental issues related to sulfur in diesel, current and future diesel fuel would be the continuous focus in various countries around the world.

It is known that change from ordinary to ultra deep desulfurization is very complicated and problematic process for refinery given a built up reactor system, where there have been very limited space for revamp. The catalysts, origin of the fuel, reactor configuration, hydrogen availability and pressure all have significant effect on the sulphur removal during the hydrotreatment process. Some sulfur compounds that contain alkyl side chains in the 4- and 6-positions in the dibenzothiophene molecule close to the sulfur atom (e.g. 4, 6-dimethyl dibenzothiophene; 4-methyl, 6-ethyl dibenzothiophene) are difficult to desulfurize under conventional desulfurization conditions.

In recent years, researches on the fuels upgrading, including hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and dearomatization, have become increasingly important, especially in the development of ULSD catalyst development. Our statistics of HDS catalyst survey shows that there had very few publications on diesel deep HDS work before 1992, but sharply increased to 25 publications in 1999, and 45 publications in 2004. These data were collected from the Scifinder data base searched by the keywords of diesel, deep HDS and catalysts. (Ali, 2014; Maity, 2004; Fujikawa, 2009; Kimura, Kiriyama,2006; Gao, 2011; Ho, 2004; Wan., 2010) Most of these studies have focused on exploring effective ways for the desulfurization of the least reactive sterically hindered alkyl DBTs. The role of catalysts and other key factors, such as feed quality, inhibition effects, process variables, kinetic and thermodynamic effects, reactor internals and feed distribution effects, influencing the desulfurization of the least reactive sulfur species have received increasing attention in recent years.

However, overviewing the catalysts for diesel deep HDS, the commercial available catalysts are either bulk metal oxide based catalyst (Chen, 2014) such as nebula or supported catalyst with ultrahigh metal loading (Wang, 2009), the catalyst has strength problem or the preparation process is very complex. These catalyst based on conventional impregnation gives more inert phase, which make the catalyst less active. In this work, we have developed a new catalyst preparation method, e.g., the organic-metal matrix decomposition method, which can easily control the active component loading, and adjust the active component interaction with the support. Also there have been little emission during the catalyst preparation., Series of CoMo and NiMo catalyst supported over various Al_2O_3 supports have been prepared and developed for diesel HDS.

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