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Reactivity characteristics of Pt-encapsulated zeolite catalysts for hydrogenation and hydrodesulfurization

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ABSTRACT

Noble metal catalysts are commonly used in hydrogenation processes. They are more effective than base metal catalysts such as Mo, Ni, or Co catalysts. However, noble metal catalysts are generally used in environments with sulfur concentrations below 10 ppm since they are susceptible to sulfur poisoning. This paper presents a noble metal catalyst specially prepared by using a Pt-encapsulated zeolite material. A set of pilot plant tests were conducted with naphthalene as a model hydrogenation compound and dibenzothiophene as a model sulfur compound. Based on catalyst evaluation with the noble metal catalyst and a base catalyst using novel 2-dimensional GC × GC analysis, it was observed that the Pt-encapsulated noble metal catalyst behaved differently from what is normally expected. When exposed to a high sulfur concentration of ~600 ppm, the Pt-encapsulated catalyst gave almost the same naphthalene conversion as the Mo-Ni catalyst at 360 °C. Furthermore, both the Pt and Mo-Ni catalysts yielded a primary hydrogenation product tetralin instead of the secondary hydrogenation product decalin. The Pt-encapsulated catalyst also showed selectivity toward the direct desulfurization pathway instead of the hydrogenation–desulfurization pathway that is expected for desulfurization with noble metal catalysts.
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1. Introduction

As conventional petroleum reserves decline, refineries have to process increasing volumes of heavier crudes and feedstocks from unconventional resources. The high sulfur, nitrogen, and aromatic contents in these feedstocks are a serious challenge for the production of clean and high-quality transportation fuels. Aromatics in diesel fuels have been identified as a primary source of environmental pollution due to incomplete combustion and the formation of soot particles [1]. Ultra-low-sulfur diesel (ULSD), with sulfur content of less than 15 ppm and enhanced cetane number and other properties, has become a common target product for refineries, particularly as rigorous specifications on sulfur and aromatic contents of diesel fuels are proposed and implemented [2]. Therefore, new catalysts and processes with improved aromatic saturation and ring opening capabilities, which do not sacrifice sulfur and nitrogen removal activities, are needed for middle distillate hydroprocessing. Increasing the severity of operating conditions for hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrogenation (HYD) processes is not always possible since higher pressures and temperatures can cause problems such as high operating costs and energy consumption, increased catalyst deactivation, and reduced unit run time.

One critical solution to the increased severity of industrial hydrodesulfurization processes is to develop new catalysts with high activity and selectivity [3,4]. Noble metal catalysts are commonly used in hydrogenation processes and can be prepared by incorporating Pt and/or Pd on various oxide supports [5–8] or zeolite-containing materials [9–11]. Noble metal catalysts have better hydrogenation effectiveness than base metal catalysts such as Mo, Ni, and Co catalysts. However, noble metal catalysts are generally used in low-sulfur environments [12–14] containing less than 50 ppm sulfur or even less than 10 ppm sulfur. Therefore, noble metal catalysts are generally used in the second stage of a two-stage hydrotreating process for which the feed has already been largely desulfurized in the first stage using sulfided base metal catalysts.

Although various approaches have been proposed to improve the sulfur resistance of noble metal catalysts [15–17], no effective sulfur-resistant noble metal catalysts are available commercially so far. A bi-functional catalyst with a bimodal pore size distribution in zeolites, and having two different types of active sites in the pore, has shown the potential to improve the stability of noble metal active components in hydrodesulfurization processes [18,19]. Based on this concept, a Pt-zeolite catalyst with an appropriately selected noble metal precursor and loading (1.0–1.8 wt%) was prepared to maximize the catalytic activity for dibenzothiophene (DBT) hydrodesulfurization and benzene hydrogenation using a deeply desulfurized light cycle oil (LCO) spiked with DBT at 50 ppm sulfur [20]. Instead of dual noble metal catalyst, Pawelec et al. [21] prepared a ternary Au-Pt-Pd catalyst, the sulfur

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