



Study of hydrodesulfurization of 4,6-DM-DBT over Pd supported on mesoporous USY zeolite

Lei Zhang, Wenqian Fu, Qingping Ke, Shuai Zhang, Huile Jin, Jianbo Hu, Shun Wang, Tian-di Tang*

College of Chemistry and Materials Engineering, Wenzhou University, Zhejiang 325027, PR China

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ABSTRACT

Two ultra-stable Y zeolites (USY550 and USY600) with mesoporous volumes of 0.15 and 0.25 cm³/g were prepared by steam dealumination at 550 and 600 °C, respectively. Pd catalysts were supported on γ -Al₂O₃, H-forms of zeolite Y (HY), mesoporous USY for hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene (4,6-DM-DBT). The 4,6-DM-DBT conversions over Pd/USY550 (85.7%) and Pd/USY600 (76.9%) are higher than over Pd/HY (43.7%) due to the facilitated mass transfer of 4,6-DM-DBT in the mesopores USY. The better HDS performance of Pd/USY than Pd/ γ -Al₂O₃ is attributed to the stronger acidity of USY, as demonstrated by the stepwise temperature-programmed desorption of ammonia. Thermogravimetric and X-ray photoelectron spectroscopic analysis of the used catalysts showed that the poison of Pd particles over the supports by sulfur was responsible for the catalyst deactivation.

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1. Introduction

The reduction of the sulfur content in diesel fuel has been paid much attention in recent years owing to stringent environmental legislations in many countries for the sulfur level [1–3]. To meet the latest standard (less than 10 ppm), even the refractory sulfur species, such as 4,6-dimethyldibenzothiophene (4,6-DM-DBT), should be sufficiently removed. The 4,6-DM-DBT can be desulfurized to 3,3'-dimethylbiphenyl (DM-BP) by direct desulfurization pathway (DDS), and can be hydrogenated to sulfur-containing intermediates that were subsequently desulfurized (HYD) [4–6]. However, the DDS rate is low due to the steric hindrance of the methyl groups present at the 4 and 6 positions [7–9]. When the phenyl rings were hydrogenated, the molecule was distorted, resulting in the reduction of the steric hindrance, and favor the desulfurization of the sulfur species [9–11]. Therefore, the catalyst with high hydrogenation activity is desired for the deep hydrodesulfurization (HDS) of 4,6-DM-DBT.

It is well known that, compared to conventional metal sulfides (CoMo and NiMo), noble metals catalysts, such as Pd, Pt and Pd–Pt, possess higher hydrogenation activity [12–14], but they are sensitive to sulfur-containing compounds. Notably, the sulfur resistance of noble metal catalysts could be significantly enhanced by using the acidic supports such as ZSM-5, Beta and Y zeolites [15–19]. The explanation is that the strong acidic sites on the zeolite support result in electron-deficiency metal particles, which reduces their

interaction with H₂S [20–23]. Moreover, strong acidity is also helpful for spillover of hydrogen atoms from the metal particles to the aromatic sulfur-containing molecules, which could create a second hydrogenation pathway [24–26].

Nevertheless, noble metals supported on conventional zeolites cannot accomplish the deep HDS of the bulky 4,6-DM-DBT molecules due to their pore size limitation [16–19]. Recently, mesoporous zeolites such as Beta, MFI and FAU have been successfully synthesized by using hard and soft templates [19,27–35], and their supported Pd catalysts showed excellent catalytic activities in the deep HDS of 4,6-DM-DBT [16–19]. However, the industrial applications of these mesoporous zeolites are still limited owing to the complicated synthetic procedure and the high cost of the organic templates [34].

In this work, ultra-stable Y zeolites (USY) with different mesoporous volumes and acidities were tailored by steam dealumination process, and the Pd supported on USY were prepared for the deep HDS of 4,6-DM-DBT. Compared with Pd supported on γ -Al₂O₃ and H-form of zeolite Y (HY), Pd supported on acidic mesoporous USY exhibited higher catalytic activity in HDS of 4,6-DM-DBT. These results demonstrate that supports with large mesoporous surface area and high mesoporous volume as well as relatively strong acidity are desired for HDS of 4,6-DM-DBT over Pd catalysts.

2. Experimental

2.1. Materials synthesis

Zeolite NaY was synthesized from an aluminosilicate gel with molar ratios of 1.0Al₂O₃/3.4Na₂O/7.9SiO₂/150.0H₂O. In a typical

* Corresponding author. Tel.: +86 577 86689366; fax: +86 577 88373098.

E-mail address: Tangtd2006@yahoo.com.cn (T.-d. Tang).