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Hydrodesulfurization of 4,6-dimethyldibenzothiophene over Pt supported on γ-Al_2O_3, SBA-15, and HZSM-5

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Abstract

The promoting effect of an acidic support on the hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene (DMDBT) was studied by comparing the activity and selectivity of Pt/HZSM-5 with those of Pt/γ-Al_2O_3 and Pt/SBA-15. Pt/γ-Al_2O_3 and Pt/SBA-15 hydrogenated DMDBT fast to the intermediate hexahydro-4,6-dimethyldibenzothiophene and removed sulfur from DMDBT somewhat slower, giving 3,3′-dimethylbiphenyl. The dodecahydro-4,6-dimethyldibenzothiophene intermediate was not observed, indicating that it was very quickly desulfurized. The conversion of DMDBT over Pt/HZSM-5 was low, probably because of the high hydrocracking of the decane solvent and coking of the catalyst by the cracking products. Decreasing the bifunctional hydrocracking by lowering the temperature was not successful, because of a too low HDS activity. Poisoning of the acid sites by co-feeding pyridine suppressed the hydrocracking, but brought the HDS activity down to the level of Pt on a non-acidic support like SBA-15.

Keywords: Hydrodesulfurization; 4,6-Dimethyldibenzothiophene; Platinum catalysts; Alumina; SBA-15; HZSM-5

1. Introduction

To reduce the contents of sulfur in transportation fuels to a very low level also molecules with alkyl groups adjacent to the sulfur atom must be removed [1,2]. Such molecules are very difficult to desulfurize and 4,6-dimethyldibenzothiophene (which we will abbreviate with DMDBT) is therefore often used as model molecule in deep hydrodesulfurization (HDS) studies. In contrast to the HDS of dibenzothiophene, which occurs mainly by the so-called direct desulfurization (DDS) to biphenyl, the methyl groups hinder the σ adsorption of 4,6-DMDBT and its HDS occurs predominantly by hydrogenation followed by desulfurization, through the so-called hydrogenation route (HYD) [1–5].

The HDS of DMDBT is therefore dependent on the hydrogenation activity of the catalyst. Metals are good hydrogenation catalysts and might be well suited as catalysts for deep HDS. They transform into metal sulfide particles in the presence of sulfur-containing molecules and H_2S, however, and only the noble metals Pd and Pt have proved to be less sensitive to sulfur [6,7]. Their sulfur resistance is further improved by alloying [8,9]. Noble metals may thus be used in the second reactor of a two-stage hydrotreating process, where the feed first undergoes HDS in a first reactor filled with a conventional metal sulfide catalyst. After removal of H_2S formed in the first reactor, the amount of sulfur entering the second reactor may be low enough for the noble metals to keep a sufficient activity.

Not only the noble metal, but also the support can improve the HDS activity of catalysts. Acidic supports, such as amorphous silica-alumina (ASA) and zeolites, increase the conversion of DMDBT. They enable dealkylation and isomerization reactions of the alkyl substituents, which may transform refractory components into more reactive species and thus accelerate HDS [10]. Acidic supports also improve the catalytic activity of the catalyst particles by increasing their sulfur resistance [11,12] and by promoting their intrinsic activity. Several explanations have been given for the latter enhancement, such as the creation of positively charged metal particles when they are in contact with acidic sites [13,14] and the enhancement of the concentration of aromatic (basic) compounds on the support surface close to the metal particles [15].

Recently, we compared the HDS of DMDBT over Pt, Pd, and PtPd catalysts supported on γ-Al_2O_3 with that over Pt, Pd, and PtPd supported on amorphous silica-alumina to investigate the

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role of the support acidity [16–18]. Also the inhibiting effect of amines such as pyridine and piperidine on the HDS of DMDBT over these same catalysts was studied [19,20]. The more acidic ASA was found to have a very positive effect on the HDS activity and therefore we extended our studies to HZSM-5, which is even more acidic. In addition we present the HDS of DMDBT over Pt supported on SBA-15, to see how the wider pores of this support affect the catalysis. Similar to our former studies, we not only analyzed the final hydrocarbon products, but also the partially hydrogenated intermediates.

2. Experimental

2.1. Catalyst preparation

All Pt catalysts were prepared by incipient wetness impregnation. Pellets of γ-Al_2O_3 (Condea, BET surface area 220 m^2/g, total pore volume 0.4 ml/g, average pore size 5.7 nm) were milled and sieved to a particle size of 35–60 mesh (250–400 μm). Aluminium-free SBA-15 was prepared in our laboratory (BET area 811 m^2/g, pore volume 1.3 cm^3/g, pore size 7.6 nm) according to the recipe given in [21]. ZSM-5 was also synthesized in our laboratory [22], pretreated by ion exchange and then calcined to obtain HZSM-5 (Si/Al ratio 20, BET area 375 m^2/g, pore volume 0.2 cm^3/g). Prior to impregnation, all supports were dried in air at 120 °C for 4 h and calcined at 500 °C for 4 h.

Impregnation solutions were prepared by dissolving the appropriate amount of $Pt(NH_3)_4(NO_3)_2$ (Aldrich, 99%) in water. In order to achieve a high metal dispersion and inhibit agglomeration of the salt during the evaporization of the solvent, the total volume of the solution was equal to that of the used pore volume of the support. After impregnation, the catalysts were dried overnight in air at ambient temperature, then 4 h at 120 °C, and finally calcined at 500 °C for 4 h to get the 0.5% Pt/γ-Al_2O_3, 0.5% Pt/SBA-15, and 0.5% Pt/HZSM-5 catalysts.

2.2. Acidity test reaction

The acidity of the catalyst supports was investigated by means of the isomerization of 2-methyl-2-pentene (2M2P), by passing the gaseous alkene over 0.1 g of the support in a quartz tube reactor. The support was pretreated in flowing helium for 1 h at 450 °C before use. The isomerization reaction was first conducted at 200 °C for 1 h, while flowing 15 ml/min of 7% 2M2P in helium at atmospheric pressure over the support. Then the feed was stopped and the support allowed cooling to 150 °C while being flushed with helium. At this temperature the reactant was reintroduced into the reactor. After a reaction time of 10 min, the next measurement was made. Products were analyzed online on an Agilent 6890 GC with an FID detector using a 50 m HP5 packed column.

2.3. HDS reaction

All experiments were conducted at 300 °C and 5 MPa(G) total pressure in a continuous down-flow fixed-bed reactor (Inconel 718) over 50 mg fresh Pt catalyst diluted with SiC, to improve the thermal conductivity. Before the HDS experiments, the Pt catalysts were activated by in situ reduction at 300 °C and 0.5 MPa(G) with a 50 Nml/min hydrogen flow for 2 h. Then the total pressure was increased to the reaction pressure of 5 MPa(G) and the liquid reactants were preheated and fed to the reactor. The gas-phase feed consisted of 130 kPa decane (as solvent and also to simulate the existence of other chemicals in the industrial feedstock), 8 kPa dodecane (as internal standard), 1 kPa DMDBT, and 4.85 MPa(G) hydrogen. In order to stabilize the fresh catalyst, the reaction was continued for at least 15 h (overnight) under these conditions.

To diminish a possible influence of catalyst deactivation, all experiments were started at the highest weight time (i.e. lowest flow rate), and then the weight time was decreased step by step till reaching the lowest weight time. Two samples were taken at each measuring point and each sample was analyzed twice. The interval between samplings was long enough to make sure that the reaction was steadily going on and that the results were reliable. The liquid reaction products were collected in a condenser, separated from the gas phase, and analyzed off-line with a Varian CP-3800 gas chromatograph equipped with a DB-5 fused silica capillary column (J&W Scientific, 30 m, inner diameter 0.25 mm, film thickness 0.25 μm) and a flame ionization detector. A Turbochrom Workstation was used to collect and analyze the data.

3. Results and discussion

3.1. Support acidity

NH_3-TPD is often used to quantify the total number of acid sites and IR-pyridine to measure the acidity amount and to recognize the acidity types, Brønsted or Lewis. The isomerization of 2-methyl-2-pentene (2M2P) is a good probe reaction to evaluate the acidity of solid acids [23]. The molar ratio of *trans*-3-methyl-2-pentene (t-3M2P) (obtained by methyl shift from 2M2P) to *trans*- and *cis*-4-methyl-2-pentene (t-4M2P and c-4M2P) (obtained by a H shift) reflects the acidity of solid acids. The methyl shift needs stronger acid sites than the H shift and, as a consequence, the higher the molar ratio is, the stronger the acidity. HZSM-5 had a higher conversion in the isomerization of 2-methyl-2-pentene (80%) than γ-Al_2O_3 (25%) and SBA-15 (23%). Moreover, HZSM-5 gave a much higher t-3M2P/(t-4M2P + c-4M2P) molar ratio (1.8) than γ-Al_2O_3 (0.1) and SBA-15 (0.2), demonstrating that HZSM-5 possesses a much stronger acidity than the other two supports. Based on the test results, γ-Al_2O_3 and SBA-15 had a similar number of acid sites and a similar acid strength.

3.2. HDS over Pt/γ-Al_2O_3

Fig. 1 shows the results of the HDS of DMDBT over 0.5% Pt/γ-Al_2O_3, which was used for comparison with Pt/SBA-15 and Pt/HZSM-5. The vertical axis indicates the relative partial pressures of reagent and products, based on the total DMDBT pressure. In this way, the conversion of DMDBT is equal to