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Effect of catalyst precursor and its pretreatment on the amount of β-Pd hydride phase and HDS activity of Pd-Pt/silica-alumina

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ABSTRACT

The effect of catalyst precursor and pretreatment on the content of β-Pd hydride (PdH_x) and activity of the reduced bimetallic Pd-Pt catalysts in hydrodesulfurization (HDS) of thiophene and benzothiophene was studied. The catalysts prepared by co-impregnation of mesoporous silica–alumina (MSA) by different metal compounds were characterized by nitrogen, hydrogen, CO adsorption, chemical analyses, electron-probe microanalysis (EPMA) and temperature-programmed hydride decomposition (TPHD). It was found that metal precursor and its pretreatment greatly affected the properties of the catalysts. The most active catalysts were prepared from Pd acetate and $Pt(NH_3)_4(OH)_2$. Strong Brønsted acidity of the support led to the highly active and sulfur tolerant catalysts. About 20% of the active phase surface remained in the metallic state after thiophene HDS. The reduced Pd-Pt/MSA catalysts absorbed hydrogen in the form of PdH_x phase. Its amount was greatly affected by the precursor, its pretreatment and overall metal dispersion. A relation between thiophene HDS activity and the amount of hydrogen present in the PdH_x was observed within the whole series of Pd-Pt catalysts. This shows that the hydrogen accumulated in the bulk of Pd participated in the reaction along with the hydrogen activated on the catalyst surface and positively contributed to the overall thiophene transformation over Pd-Pt/MSA catalysts.

1. Introduction

Bimetallic catalysts containing Pd and Pt have primarily been studied for the purposes of hydrodearomatization of industrial feeds and hydrogenation (HYD) of aromatic model compounds in the presence of sulfur [1–6]. Parallel to this research, some studies have also been devoted to their evaluation in hydrodesulfurization (HDS) reactions of simple model compounds such as thiophene or dibenzothiophene [7,8] and for the deep HDS of substituted dibenzothiophenes [4,8,9]. This is because these catalysts show high HYD activity which allows via HYD route the easier transformation of refractory sulfur molecules. Metallic Pd-Pt phase is usually deposited on acidic supports, mostly USY zeolite and amorphous silica–alumina, favorable for the higher electron-deficiency of the noble metals which reflects in the better sulfur tolerance and catalysts activity. These catalysts are often prepared from simple metal chlorides or different complexes of Pd and Pt by co-impregnation, mostly followed by calcination in air and reduction by hydrogen at 300–500 °C.

Recently, we have studied monometallic Pt catalysts [10] as well as monometallic Pd and bimetallic Pd-Pt catalysts [11] in HDS of thiophene and benzothiophene. In both cases, catalysts supports were mesoporous silica-aluminas (MSA) with acidities enhanced by the post-syntheses acid leaching. Such modified supports impregnated with suitable noble metal compounds gave very active monometallic catalysts. The highest thiophene activities were achieved with Pt and Pd catalysts prepared from $Pt(NH_3)_4(OH)_2$ and Pd acetate, respectively. In the next, co-impregnation of modified MSA by these compounds resulted in a highly active bimetallic Pd-Pt/MSA catalyst that showed significant synergetic effect and exceeded in thiophene and benzothiophene transformations the activities of a conventional sulfide CoMo/alumina catalyst. An interesting property of the reduced Pd-Pt/MSA catalyst was a considerable amount of hydrogen present in the form of β-Pd hydride (PdH_x). This was revealed during characterization of this catalyst by TPD technique and led us to assume that the high activity of this sample could be in a relation to the absorbed hydrogen [11].

There are several examples of the catalytic role of the hydrogen absorbed in the bulk of Pd. Positive effects of the PdH_x in a metallic Pd and a reduced Pd/alumina catalyst on the rate of HYD of acetylene, ethene, and butadiene have been found by different research groups [12–14]. Hydrodechlorination of chlorofluorocarbons over

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Pd(1 1 1) crystal proceeded even in the absence of gaseous hydrogen and was ascribed to the participation of solid state hydrogen [15]. Similarly, the participation of a subsurface hydrogen in HYD of 1-pentene and 1-pentyne over Pd black was described by Teschner et al. [16] and the influence of Pd hydride on the selectivity of HYD of benzonitrile was confirmed by Bakker et al. [17]. However, all these studies concerned only Pd and to our best knowledge, there are not analogous studies concerning bimetallic Pd-Pt system or a similar study related to HDS reaction.

It is well known that the formation of PdH_x in supported Pd catalysts is strongly affected by the size of the metal particles [18–20]. Metal dispersion in Pd/silica catalysts can be influenced by thermal pretreatment of the catalyst precursors in different gas atmosphere (He, H_2, O_2) [21,22]. In addition, annealing at temperatures above 400 °C, may lead to the interaction of Pd with SiO_2 forming Pd silicide that hinders the formation of PdH_x [23]. In order to check a possible role of PdH_x in our Pd-Pt/MSA samples, we made use of the above findings and pretreated the catalyst precursors in different ways so as to obtain a broader series of catalysts with different content of PdH_x. This should make it easier to see whether the activity changes could be compared with the hydrogen content in the catalysts.

Two main goals of this work can be summarized as follows. The first, from an application point of view it seemed useful to find if the activity of Pd-Pt/MSA catalyst prepared from Pd acetate and $Pt(NH_3)_4(OH)_2$ can further be improved by some simple way, for example by the different pretreatment of its precursor. The second aim was an attempt to find if there is a relation between HDS activity of the catalysts and the hydrogen content in PdH_x phase. Because both noble metal compounds mentioned above are not the most frequently used, also other catalyst precursors, prepared from commonly used $PdCl_2$ and H_2PtCl_6 were included for comparison.

2. Experimental

2.1. Preparation of the support and catalysts

Mesoporous silica-alumina (MSA) modified by post-synthesis extraction by nitric acid was used in the form of 0.16–0.315 mm particles as a catalyst support. The acid extraction eliminated the originally present extra-framework non-acidic Al_{oct} forms and the modified support was thus substantially enriched by Al_{tet} species. It contained 91 wt.% SiO_2, 9 wt.% Al_2O_3 and possessed the BET surface area of 643 m^2/g. Extraction led to enhancement of strong Brønsted acidity, proven by catalytic tests in skeletal isomerization of cyclohexene and cracking of cumene [11].

Two catalyst precursors were prepared by co-impregnation of the modified MSA with solutions of Pd acetate + $Pt(NH_3)_4(OH)_2$ and Pd acetate + H_2PtCl_6. Acetone solution of Pd acetate was mixed with aqueous solution of $Pt(NH_3)_4(OH)_2$ (or H_2PtCl_6,) giving a mixture (1:1). The third precursor was prepared similarly from aqueous solution of $PdCl_2 + H_2PtCl_6$. In these solutions, we assume the presence of non-dissociated Pd acetate, while cationic $Pt(NH_3)_4{}^{2+}$ species and $PtCl_6{}^{2-}$ and $PdCl_4{}^{2-}$ anions. The three combinations used gave homogeneous solutions and no precipitation was observed.

The slurries were evaporated to dryness at 60 °C under vacuum in a rotary evaporator and the solids were dried at 120 °C on air. They were either directly reduced by hydrogen (symbol H) or calcined in helium or air (symbols He and Ox, respectively) at 300–600 °C prior to their reduction in hydrogen. The symbols PdA, PdC, PtO and PtC stand for Pd acetate, $PdCl_2$, $Pt(NH_3)_4(OH)_2$ and H_2PtCl_6, respectively. The bimetallic catalyst precursors are denoted accordingly, as PdA-PtO, PdA-PtC and PdC-PtC. The pretreatment temperature is given by a number behind the symbol for gas.

2.2. Characterization of the catalysts

The chemical composition of the catalysts was determined by inductively coupled plasma-atomic absorption spectroscopy (ICP/AAS). BET surface areas and pore-size distributions of the samples degassed at 400 °C were determined by nitrogen adsorption with an ASAP2010 M instrument (Micromeritics). Metal dispersions were determined by pulse hydrogen adsorption at 22 °C in an apparatus equipped with thermal conductivity detector (TCD) [24]. The catalyst (40–80 mg) was reduced by hydrogen at 300 or 400 °C for 1 h, purged by nitrogen at the same temperature for 0.5 h, and cooled to 22 °C. Then it was titrated by 10 μl pulses of hydrogen. The H:Pd = 1:1 and H:Pt = 1:1 stoichiometries were adopted for the calculation of Pd and Pt dispersions according to Anderson and Pratt [25]. In addition, the metal dispersions of two samples were determined by CO adsorption on a commercial Autochem 2920 instrument (Micromeritics). 40 mg of a catalyst sample was reduced by 5% hydrogen in argon at 300 or 400 °C, purged by helium at the same temperature for 1 h and cooled to 0 °C in helium. The catalysts were then titrated by pulses of 5% CO in helium. The CO:Pd = 1:2 and the CO:Pt = 1:1 stoichiometries were adopted for the calculation of Pd and Pt dispersions, respectively [18,20,25,27]. The overall dispersion of the Pd-Pt catalysts was calculated by using the above stoichiometries and taking into account the molar fractions of the metals in the catalysts. The dispersion was expressed by H/(Pd + Pt) or CO/(Pd + Pt) atomic ratios. The sulfur coverage of the active metal phase is usually calculated as $\Theta_S = (D_R - D_S)/D_R$, where D_R and D_S are dispersions or gas uptakes (CO, hydrogen) on the reduced and sulfided metals, respectively [4,26]. In the present work, D_r and D_S mean the dispersions prior to and after thiophene HDS test, respectively.

The amount of the hydrogen absorbed in PdH_x was evaluated by temperature-programmed hydride decomposition (TPHD) by a procedure analogous to that used by Pinna et al. [18]. TPHD was carried out in the same apparatus as used for hydrogen adsorption. The catalysts (60–200 mg) were in situ re-reduced by hydrogen at 300 or 400 °C for 0.5 h, cooled in hydrogen to room temperature and purged with a mixture of 5% H_2 in argon (35 ml/min) for 0.5 h. Then the temperature was raised to 140 °C (ramp 15 °C/min) in a hydrogen/argon mixture and the amount of desorbed hydrogen was monitored by TCD. The amounts of hydrogen released between 55 °C and 95 °C were taken as corresponding to the PdH_x decomposition [19].

The electron probe micro-analysis (EPMA) was performed on a SX-100 Instrument (Cameca, France). The reduced catalysts particles were mounted on a 1-inch epoxy disc, polished to expose their cross-section area and coated with thin layer of gold. The W cathode at 15 kV and back-scattered electron mode was used during measurements. Several images and point analyses were taken for each catalyst sample.

2.3. Catalytic tests

2.3.1. Thiophene HDS

The activity of the catalysts in HDS of thiophene (TH) was evaluated in a flow microreactor with a fixed catalyst bed at 280 °C and 2 MPa, as described in detail previously [11]. The feed contained 240 ppm of TH in hydrogen (150 ml/min). The flow rate F_{TH} was constant (9.7×10^{-5} mol_{TH}/h) and the catalyst amount W was close to 10 mg. The catalysts were in situ re-activated by hydrogen reduction at 300 or 400 °C for 1 h before reaction, which was usually carried out 4–6 h on stream. The on-line analyses were carried out on a GC HP 5890 equipped with FID detector and a 3.5 m packed