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The functionalities of Pt/γ-Al_2O_3 catalysts in simultaneous HDS and HDA reactions

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Abstract

A Pt/γ-Al_2O_3 catalyst was tested in simultaneous hydrodesulfurization (HDS) of dibenzothiophene and hydrodearomatization (HDA) of naphthalene reactions. Samples of it were subjected to different pretreatments: reduction, reduction–sulfidation, sulfidation with pure H_2S and non-activation. The reduced catalyst presented the best performance, even comparable to that of Co(Ni)Mo catalysts. All catalyst samples were selective to the HDS reaction over HDA, and to the direct desulfurization pathway of dibenzothiophene HDS over the hydrogenation reaction pathway of HDS. The effect of H_2S partial pressure on the functionalities of the reduced Pt/γ-Al_2O_3 catalyst was studied. The results showed that an increase in H_2S partial pressure does not cause poisoning, but an inhibition effect, without changing the catalyst selectivity. Accordingly, the activity trends were ascribed to adsorption differences between the different reactive molecules over the same catalytic active site. TPR characterization along with a thermodynamics analysis showed that the active phase of reduced Pt/γ-Al_2O_3 is constituted by Pt^0 particles. However, presulfidation of the catalyst leads to a mixture of PtS and Pt^0 which has a negative effect on the catalytic performance without changing catalyst functionalities.

Keywords: HDS; HDA; HYD pathway; Pt/γ-Al_2O_3; Activation procedure

1. Introduction

Pt/γ-Al_2O_3 is a known reforming catalyst and much of its interaction with sulfur is understood up to date. Essentially, sulfur can modify the functionalities of reforming Pt/γ-Al_2O_3 catalysts by adsorption over the catalyst hydrogenolysis sites [1–7], therefore, changing catalyst selectivity in competitive reactions of olefins, where isomerization is favored over hydrogenation and hydrocracking reactions [5]. This effect is reversible because sulfur can be almost completely removed by hydrogen treatment, however, the remaining *irreversibly held sulfur* causes poisoning [1–7]. Besides their wide use in naphtha reforming, Pt catalysts were recognized a long time ago as effective desulfurizing catalysts [8]. Chianelli and co-workers [9,10] found that unsupported *platinum metals sulfides* (PtS, PdS, RuS_2 etc.) are more active than MoS_2. They attributed this behavior to electronic effects and supported their conclusions on the Sabatier principle [11]. In particular, the outstanding hydrogenating capacity of platinum makes it a potential catalyst for deep HDS and HDA. In deep HDS, the development of the hydrogenating function of the catalyst is crucial because a previous hydrogenation of the refractory sulfur containing molecules can reduce steric effects that impede the direct elimination of the sulfur heteroatom (DDS pathway) [12,13]. Conventional CoMo and NiMo sulfides mainly perform hydrodesulfurization via DDS, which makes them ineffective for deep HDS [14]. In the case of deep HDA the main challenge remains in achieving a selective hydrogenation and ring-opening of aromatic molecules [15,16]. Pt based catalysts are one of the main candidates to accomplish deep HDA, in spite

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of the known poisoning effect caused by the presence of sulfur compounds in the reactor feed [15,17]. An increase in the support acidity and/or the combination of Pt with other transition metals have been proposed to overcome this problem [15,16,18–24]. The combination Pt–Pd supported on acidic materials has been found to be very effective for HDA reactions in the presence of sulfur [18–24]. Nevertheless, the higher thiotolerance exhibited by Pt–Pd catalysts is not only restricted to the use of acidic supports [25]. The catalytic properties of Pt–Pd based systems have also started to attract interest for deep HDS [23,26–30]. Though some aspects related to the interactions between Pt and Pd have begun to be understood [21], few reports are devoted to the study of the catalytic functionalities of each metal within the bimetallic system [29,31]. One of the significant findings of these studies is that Pd can provide hydrogenation sites in HDS [31], whereas Pt supplies hydrogenolysis sites [29].

Within this context, the present contribution explores the catalytic functionalities of $Pt/\gamma\text{-}Al_2O_3$ in simultaneous HDS and HDA reactions as a function of different activation procedures; reduction, reduction–sulfidation, sulfidation with pure H_2S, and non-activation. The activated catalysts were characterized by TPR before and after maintaining them under a simulated reaction environment.

2. Experimental

2.1. Preparation of the catalysts

A 2 wt% $Pt/\gamma\text{-}Al_2O_3$ catalyst was prepared by pore filling with an aqueous solution of hydrogen hexachloroplatinate IV ($H_2PtCl_6 \cdot 4H_2O$) (Sigma). *Procatalyse* alumina was employed. The support was crushed and sieved up to a particle size between 0.3 and 0.6 mm, then, it was calcined at 673 K (heating rate 5 K/min) ($A_{BET} = 220\ m^2/g$; $V_p = 0.62\ cm^3/g$; $D_p = 11.6$ nm). The aqueous solution of $H_2PtCl_6 \cdot 4H_2O$ was kept in contact with the carrier until pH stabilization. The excess water was vacuum evaporated at 318 K in a rotary evaporator. The impregnated solid was dried under air flow at 393 K for 12 h and calcined in air at 773 K for 4 h (heating rate 5 K/min). Conventional CoMo (15 wt% MoO_3, 3 wt% CoO) and NiMo (9 wt% MoO_3, 4.5 wt% NiO) catalysts were prepared using the procedure described by Portela et al. [32].

2.2. Activation procedure

Catalysts were activated *in situ* (TPR apparatus or catatest). For the catalytic tests, samples of 0.5 g of the catalyst were dried at 393 K under N_2 flow for 1 h. Then, they were activated with a flow (170 ml/min) of different activating agents at 673 K (heating rate 10 K/min) for 2 h. After finishing the activation step, the system was allowed to cool down to reaction temperature. Compositions of the activating mixtures were pure H_2, 15 vol% H_2S in H_2, and pure H_2S. Activating mixtures were designated with the marks H, S15, and S, respectively. These marks were used to label the different samples of $Pt/\gamma\text{-}Al_2O_3$ and the conventional CoMo and NiMo catalysts; the latter ones were only activated with the S15 mixture. The non-activated sample of $Pt/\gamma\text{-}Al_2O_3$ was labeled with the letter N. A complete list of all sample codes is presented in Table 1.

2.3. TPR experiments

Samples of 10 mg of the catalyst were placed into a U-shaped quartz reactor and dried in N_2 flow at 393 K for 2 h. Then, they were activated under the same conditions as described in Section 2.2. The system was cooled down to 298 K under the corresponding activation mixture and then it was flushed with N_2 (100 ml/min) for 30 min. Under these conditions, TPR patterns were recorded registering the H_2S production. An additional set of experiments were performed as follows: the *in situ* activated samples were cooled down to the temperature used in the catalytic tests (583 K) and then, they were maintained under an H_2S–H_2 atmosphere with the same composition as that observed in the catalytic tests, under steady state conditions (see Table 1), during a time period equal to the time on stream of the catalytic test. This procedure was marked as SRE (SRE = simulated reaction environment). For these samples, the brand –SRE was added. All TPR patterns were registered by heating the samples from 298 K to 1123 K

Table 1
Activity and selectivity of $Pt/\gamma\text{-}Al_2O_3$ (activated with different agents), CoMo, and NiMo catalysts in simultaneous HDS of dibenzothiophene and HDA of naphthalene

Catalyst code[a]	Activity				Selectivity		H_2/H_2S ratio[c]
	$\%C_{HDS}$	$\%C_{HDA}$	$\%C_{BP}$	$\%C_{CHB}$	k_{HDS}/k_{HDA}	k_{DDS}/k_{HYD}[b]	
Pt^N	76	31	67	9	3.9	11.3	297
Pt^H	80	41	70	10	3.1	11.4	279
Pt^{S15}	61	25	55	6	3.3	12.6	366
Pt^S	50	18	45	5	3.5	11.6	354
$NiMo^{S15}$	87	55	68	19	2.6	5.3	–
$CoMo^{S15}$	78	40	59	19	3.0	4.3	–

[a] Indexes are referred to the type of activating mixture: H = pure H_2; S15 = 15 vol% H_2S in H_2; S = pure H_2S; and N = non-activated.

[b] DBT reaction pathway.

[c] Used for the TPR-SRE experiments. Reaction conditions: $T = 583$ K; $P = 5$ MPa; liquid flow rate = 30 ml/h; H_2/liquid charge volume ratio = 500 Nl/l.