



The functionalities of Pt–Mo catalysts in hydrotreatment reactions

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ABSTRACT

The catalytic functionalities of bimetallic Pt–Mo/ γ -Al₂O₃ catalysts in hydrotreatment were studied by performing simultaneous and independent dibenzothiophene (DBT) hydrodesulfurization (HDS) and naphthalene hydrodearomatization (HDA) reactions as a function of the activating agent and the MoO₃ content. Pt–Mo/ γ -Al₂O₃ catalysts always displayed a higher selectivity to both the direct route of desulfurization (DDS) of DBT and to HDS over HDA than the one exhibited by conventional CoMo and NiMo/ γ -Al₂O₃. It was established that for the Pt–Mo catalytic system, the selectivity DDS to the hydrogenation route of desulfurization of DBT can be indirectly described by the selectivity HDS/HDA in simultaneous HDS–HDA catalytic tests. The model of an active phase composed of separated metallic Pt particles, PtS_x species, and sulfided Mo which can either act as independent or cooperative active centers seems to be suitable to explain both the observed kinetic trends and the synergy effect between Pt and Mo.

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1. Introduction

Search of new catalytic active phases for hydrotreatment (HDT) remains a challenge for the petroleum refining industry due to stringent environmental regulations [1–3]. Specific requirements depend on the refinery cut to be treated. For example, FCC naphtha can be easily desulfurized but non-desirable hydrogenation of olefins (HYDO) must be reduced at maximum to avoid octane number loss in the final product [4,5]. Conversely, very active hydrogenating active phases are to be developed for simultaneous deep hydrodesulfurization (HDS) and hydrodearomatization (HDA) of heavy oil cuts [6–8]. It has been found that the use of small loadings of noble metals as promoters of conventional MoS₂/ γ -Al₂O₃ catalysts leads to highly active HDT catalysts [9–17]. Concerning the behavior of Pt–Mo catalytic systems in HDS, it has been established that Pt plays a double role; it acts as a promoter of the MoS₂ active phase and simultaneously possesses its own active sites [12–15,18,19]. Therefore, the interpretation of the kinetic trends registered for Pt–Mo systems in HDS is particularly complex and must differ from that normally accepted for conventional systems. Dibenzothiophene (DBT) and naphthalene (NP) are very useful model molecules to investigate the catalytic properties of a given material in HDT. It is known that the HDS of dibenzothiophene type molecules proceeds via two parallel pathways: the direct desulfurization (DDS) and hydrogenation mediated desulfurization (HYD) [20,21]. C–S–C bond breaking is often considered to occur

via the same mechanism in both DDS and HYD [20,21]. HYD implies the saturation of one of the benzene rings of DBT by π complex formation with the catalytic active sites [22–24], as in HDA [23,25]. Though two mechanisms of DDS are currently on debate [20,26]; one implying the direct hydrogenolysis of the C–S–C bond from a dihydrodibenzothiophene intermediate [20] and the other from the thiophenic ring without previous hydrogenation of the aromatic structure of DBT [26], it can be said that, in general, the selectivity in DBT desulfurization qualitatively measures the catalytic functionalities of the tested material involving hydrogenolysis – complete benzenic ring hydrogenation of the DBT molecule. This is not possible when using sterically hindered 4,6-alkyl(substituted)-DBTs as HDS model molecules, because for them DDS is not a viable route of desulfurization [24,25].

On the other hand, NP is a two-fused aromatic structure that can be bonded to the catalytic surface by π adsorption via either its olefin-type unsaturated bonds or the aromatic system depending on both the strength of its interaction with the catalytic surface and the intrinsic rate of hydrogenation [27–30]. Consequently, very interesting conclusions can be attained on the functionalities of HDT catalysts from kinetic measurements performed with DBT and NP as probe molecules. Both molecules are major constituents of ordinary refinery cuts [6].

In this work, an evaluation of the catalytic functionalities of Pt–Mo/ γ -Al₂O₃ in independent and simultaneous HDS of dibenzothiophene and naphthalene HDA reactions was performed under relevant industrial reaction conditions. The role of Pt as a promoter of the sulfided Mo phase in terms of the DDS/HYD and HDS/HDA selectivities and synergy were analyzed from the effect of the

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MoO₃ content and of different activation procedures (reduction, reduction–sulfidation, sulfidation with pure H₂S, and non-activation) on the Pt–Mo functionalities.

2. Experimental

2.1. Preparation of catalysts

Two series of catalysts were prepared: monometallic Mo/ γ -Al₂O₃ and bimetallic Pt–Mo/ γ -Al₂O₃ catalysts; wetness and the sequential wetness impregnation were used accordingly. A commercial γ -Al₂O₃ (Procatalyse) was used as support. The support was crushed and sieved up to a particle size between 0.3 and 0.6 mm. Then it was dried at 393 K (2 h) and calcined at 673 K (4 h), and its textural properties were measured. The precursors of Pt and Mo employed were hydrogen hexachloroplatinate IV (H₂PtCl₆·4H₂O, Sigma) and ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Merck), respectively. Aqueous solutions of both precursors were prepared and kept in contact with the carrier until pH stabilization. The excess water from the precursors' solutions was vacuum evaporated at 318 K in a rotavapor. Solids were dried under air flow at 393 K for 12 h and, then, calcined in air at 773 K for 4 h. For the bimetallic Pt–Mo catalysts, the molybdenum was impregnated first on the γ -Al₂O₃ support using the procedure described above. Then, platinum was impregnated in the obtained MoO₃/ γ -Al₂O₃ solid repeating the same experimental procedure as for Mo. Monometallic Mo catalysts were prepared with nominal MoO₃ contents of 2 (Mo(2)), 8 (Mo(8)), and 15 wt.% (Mo(15)), respectively. A monometallic 0.5 wt.% Pt catalyst (Pt(0.5)) was also prepared as described above. Bimetallic catalysts contained 0.5 and 2.0 wt.% of platinum and 2, 8 and 15 wt.% MoO₃. Therefore, bimetallic catalysts were labeled according to their nominal Pt and MoO₃ contents as follows: Pt(0.5)Mo(2), Pt(0.5)Mo(8), Pt(0.5)Mo(15) and Pt(2)Mo(15). Finally, two conventional γ -Al₂O₃ supported NiMo (4.5 wt.% NiO, 9 wt.% MoO₃) and CoMo (2 wt.% CoO, 10 wt.% MoO₃) catalysts were prepared as presented elsewhere [13]. All metal contents were verified by atomic absorption analysis [12,14].

2.2. Activation procedure

Catalysts were activated *in situ* (temperature programmed reduction (TPR) apparatus or catatest). Previous to activation, calcined catalysts (0.5 g) were dried at 393 K under N₂ flow (1 h) and, then, contacted with the corresponding activating mixture at 673 K (10 K/min) for 3 h. The flow of the activating gaseous mixture was maintained until reaching the temperature required for either the catalytic tests or the TPR analysis. Activating agents were pure H₂ (H), 15 vol.% H₂S in H₂ (S15), 40 vol.% H₂S in H₂ (S40), and pure H₂S (S). A test without activation (N) was also performed to evaluate the effect of catalyst sulfidation due to the H₂S generated from the HDS reaction. The catalysts were labeled with a super-index according to the corresponding activating agent used.

2.3. Characterization of the catalysts

TPR experiments were carried out in a ChemBET3000 TPR/TPD apparatus (Quantachrome) provided with a TCD. Samples of 0.1 g of the calcined catalyst were placed into a U-shaped quartz reactor and dried in N₂ 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, flushed with N₂ (100 ml/min) for 30 min. Under these conditions, the TPR patterns were recorded registering the H₂ consumption. An additional set of experiments was performed

as follows: the *in situ* activated samples were cooled down to the temperature used in the catalytic tests (583 K) and, then, maintained under an H₂S–H₂ atmosphere with the same composition as the one observed in the catalytic tests under steady state conditions, during a time period equal to the time on stream of the catalytic test. This procedure was marked as TPR–SRE (SRE = simulated reaction environment). For these samples, the brand – SRE was added. All TPR patterns were registered during heating of the samples from 298 K to 1123 K (heating rate 10 K/min) in a flow (30 ml/min) of highly pure H₂. A TCD detector was used to measure either the H₂ consumption (TPR) or H₂S production (TPR–SRE experiments). For TPR, a trap at 207 K, consisting of a steel pipe submerged in an ethanol–solid CO₂ bath, was placed before the TCD to capture both the H₂S and H₂O produced during the reduction process. For the TPR–SRE experiments, such trap consisted of a solid–liquid mixture of NaCl–saturated water at 260 K to condense any trace of water.

2.4. Catalytic tests

Catalysts were tested in a continuous-flow high-pressure fixed-bed reactor at 5 MPa, feed liquid flow rate of 30 ml/h and a H₂/liquid feed ratio of 500. Kinetic tests performed consisted of simultaneous DBT hydrodesulfurization and naphthalene HDA reactions at 583 K. As references, two additional catalytic tests were performed over the Pt(0.5)Mo(2) catalyst: naphthalene HDA under an H₂S atmosphere (concentration c.a. 4074 ppm, which corresponds to the H₂S concentration obtained at a molar DBT conversion of c.a. 60%) at 563 K, and DBT hydrodesulfurization at 583 K. The composition of the model charge (liquid charge) was 2 wt.% DBT (Acros, 99 wt.%) and/or 3 wt.% NP (commercial) dissolved in cyclohexane (commercial). Hexadecane (2 wt.%) was used as an internal standard for the GC analysis. For all tests, 0.5 g of the catalyst were diluted in glass spheres (1 mm diameter). The absence of any diffusion limitations was previously verified. Liquid products were analyzed using a HP 6890 GC equipped with FID, a capillary column (HP-5 Crosslinked 5% PH ME Silicone) of 30 m, and a split injector. A FPD was used to determine the H₂S concentration in the effluent gas from the reactor.

Reaction conditions for the test of the non-activated catalyst were reached under a N₂ atmosphere. Catalytic activity was expressed as the specific rate constant (k_i , L/s g) considering pseudo-first order kinetics [31], DDS selectivity (S_{DDS}) was defined as the $k_{\text{BP}}/(1 - k_{\text{BP}})$ ratio, where BP stands for biphenyl; the desulfurized product from DDS. For the bimetallic Pt–Mo catalysts, the synergy intensity percentage (%SI) was defined as the percent of the conversion difference between experimental and theoretical conversions with respect to the theoretical one; the latter is defined as the algebraic sum of the monometallic catalysts conversions corresponding to the composition of the bimetallic catalysts [12,14].

3. Results and discussion

3.1. Functionalities of the Pt–Mo system in the HDS of dibenzothiophene and naphthalene HDA

Reaction products detected in the HDS of dibenzothiophene were mainly BP and cyclohexylbenzene (CHB). Non quantitative traces of the partially hydrogenated tetrahydro-dibenzothiophene intermediate were detected during the independent HDS reaction performed over Pt(0.5)Mo(2). Tetralin was the only product in the HDA of naphthalene.

Table 1 shows the steady-state catalytic activity of two selected Pt(0.5)Mo(2)^{S15} and Pt(2)Mo(15)^{S15} catalysts and the conventional

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