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Improvement of HDS catalysts through the modification of the oxidic precursor with 1,5-pentanediol: Gas phase sulfidation and thiophene conversion

Amélioration d'un catalyseur d'HDS via la modification du précurseur oxyde avec du 1,5-pentanediol : sulfuration en phase gaz et conversion en HDS du thiophène

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The performance, in thiophene HDS, of a CoMo/Al_2O_3 catalyst was successfully improved through chemical modification of its oxidic precursor by impregnation with 1,5-pentanediol solution. The gas phase activation with a H_2/H_2S mixture was followed by thermogravimetric analysis coupled with a rapid chromatograph; the catalysts were characterized at different steps of the activation using X-ray photoelectron spectroscopy (XPS). It appeared that the addition of the organic agent retards the sulfidation of the supported metals, leading to a simultaneous sulfidation of Co and Mo atoms. This induces the formation of smaller MoS_2 slabs and thus an increase in the number of active CoMoS sites, directly correlated with the better HDS performance of the modified solid. The role of 1,5-pentanediol is likely to inhibit, at low temperature, the adsorption of H_2S on the solid and thus the sulfidation of the supported metals.

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R É S U M É

La performance d'un catalyseur CoMo/Al_2O_3 en HDS du thiophène a été améliorée grâce à une modification chimique du précurseur oxyde par imprégnation avec une solution de 1,5-pentanediol. L'activation en phase gazeuse avec un mélange H_2/H_2S a été suivie par analyse thermogravimétrique couplée à un chromatographe rapide en phase gaz et les solides ont été caractérisés à différentes étapes de l'activation par spectroscopie de photoélectrons induits par rayons X (XPS). L'addition de cet agent organique induit un retard de la sulfuration des métaux supportés. Ceci se traduit par une sulfuration simultanée des atomes Co et Mo, conduisant à une taille inférieure des feuillets de MoS_2 et donc à une augmentation du nombre de sites actifs CoMoS. Cette augmentation est directement

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corrélée aux meilleures performances en HDS du solide modifié. Le rôle du 1,5-pentanediol semble donc être d'inhiber l'adsorption d'H_2S sur le solide à basse température, et en conséquence la sulfuration des métaux.

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1. Introduction

The severe environmental regulations concerning the reduction of sulfur content in diesel oil demand a drastic efficiency of the hydrodesulfurization (HDS) of petroleum feedstock, which is a catalytic process most generally performed on $CoMo/Al_2O_3$ catalysts. The active phase of these catalysts is the so-called CoMoS phase that consists of well dispersed MoS_2 nanocrystallites decorated with Co promotor atoms located at the edges and corners of the MoS_2 slabs [1]. This active phase is obtained by sulfiding an oxidic precursor, generally prepared by incipient wetness impregnation of an alumina support with an aqueous solution containing the elements to be deposited (Co and Mo), followed by a drying and a calcination step. New methods of preparation of the oxidic precursors have been developed in order to improve catalytic performance. Among them the use of Keggin or Anderson based heteropolyanions was proposed several years ago to prepare impregnating solutions instead of the classical ammonium heptamolybdate precursor [2,3]. Improvements have also been obtained through the addition of organic agents to the impregnating solution prepared with [4,5] or without [6] heteropolyanions. More recently the modification of dried or calcined oxidic precursors by organic molecules was shown to improve HDS catalytic performances [7–10]. Whatever the approach, various organic agents that have been used can be divided in two families: the chelating agents allowing complexation with metallic ions and the non-chelating agents. Among the chelating molecules, EDTA (ethylenediaminetetraacetic acid) [11], En (ethylenediamine) [12,13], CyDTA (cyclohexanediaminetetraacetic acid), NTA (nitrilotriacetic acid), TA (tartaric acid) [5] or saccharose [14] were considered. In our laboratory TGA (thioglycolic acid) [7,8], also described as a sulfiding agent [15], was used to impregnate a commercial $CoMo/Al_2O_3$ oxidic precursor. Recently due to its low cost and availability, citric acid has attracted much attention for the preparation of fresh catalysts [4,6,11]. Through the formation of Mo and/or Co complexes with the chelating agents, the improved HDS catalytic activities have been ascribed to (i) a decrease of the interaction between metals and the support [16–21] and/or to a lower formation of cobalt aluminate [2], (ii) an improvement of the Mo and/or Co dispersion [2,12,13,22–26], and (iii) the modification of the sulfidation of Co and Mo atoms (delay of Co sulfidation) [7,8,27–35].

Researchers have also developed modifications with non-complexing agents. Among them the glycol-type agents have been largely employed [9,20,21,36]. In these cases the beneficial effect cannot be related to metal complexation. According to Nicosia and Prins [21] introduction of TEG (triethyleneglycol) into the impregnating solution containing phosphorus restrains interaction between metals and the support and facilitates Co interaction with phosphomolybdate species in solution while according to Iwamoto et al. [25,26] the role of PEG (polyethyleneglycol) with a high molecular weight was to prevent Co and Mo aggregation facilitating their dispersion on the support surface. Gonzalez-Cortes et al. [37] have proposed a “urea-organic matrix” method with addition of urea to the impregnating solution to prepare modified HDS CoMo catalysts in order to improve the dispersion of Co and Mo species and to increase the MoS_2 slab stacking for better HDS performance.

Recently we have shown that the use of the non-complexing 1,5-pentanediol for the modification of $CoMoP/Al_2O_3$ oxidic precursors led to a drastic increase of the performance in SRGO HDS [10]. To understand the role of this type of agent, we investigate here its effect on the gas phase sulfidation and on thiophene HDS performance. A detailed characterization of the genesis of the active phase monitored by XPS together with thermogravimetric analysis allows us to describe the exact role of the pentanediol modifying molecule.

2. Experimental

2.1. Preparation of the oxidic precursor

The $CoMo/Al_2O_3$ solid used in this work is a commercial catalyst containing 17.3 wt% of MoO_3, 3.5 wt% of CoO and 0.08 wt% of P. This oxidic precursor will be denoted hereafter by CoMoRef. Its presents a surface area of 260 m^2 and a water pore volume of 0.9 cm^3 per g of catalyst.

2.2. Preparation of the modified oxidic precursors

The CoMoRef was pore volume impregnated with an aqueous solution containing the desired amount of 1,5-pentanediol (C_5diol) to have a C_5diol/Mo molar ratio equal to 1. After 2 h of ageing, the modified solid was dried at 80 °C under N_2 for 15 h. The CoMo modified solid is denoted by CoMo1C_5diol.

2.3. Sulfided catalysts

For characterizations the oxidic precursors were sulfided for 3 h (otherwise specified) at temperatures ranging from 50 to 350 °C. Prior to sulfidation no additional pretreatment, neither drying nor calcination, was performed on the CoMoRef or CoMo1C_5diol solids. The sulfidation took place at atmospheric pressure with a flow (100 mL/min) of a H_2/H_2S (90/10) mixture in a glass reactor. The sulfidation

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