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Insight into sulphur compounds and promoter effects on Molybdenum-based catalysts for selective HDS of FCC gasoline

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ABSTRACT

The effect of the nature of sulphur compounds (H_2S and 2-methylthiophene) over unsupported molybdenum-based sulphide catalysts (promoted or not by nickel or cobalt) for the transformation of a model FCC feed (hydrodesulphurisation of 2-methylthiophene and hydrogenation of 2,3-dimethylbut-2-ene) was investigated. The activities of the various catalysts were compared between each reactant alone and the full model mixture. The promoting effect of Co and Ni is found for both hydrodesulphurisation (HDS) and hydrogenation of olefins (HYD) reactions. However, the hydrogenation activity strongly depends on the amount of sulphur compound present in the feed. Nickel, used as a promoter, seems more sensitive than cobalt, particularly for the hydrogenation reaction. The presence of 2-methylthiophene in the feed induces a stronger inhibiting effect than H_2S on HYD reaction. This result highlights the different adsorption constant ratio between olefins and sulphur molecules depending on the sulphur compounds. Even though an impact of H_2S can be observed on the NiMo and CoMo catalysts, no major modification occurs on the volcano-shaped curves obtained in previous work, in terms of activity or selectivity, as a function of the metal–sulphur bond energy. Whatever the amount of H_2S added, NiMo and CoMo catalysts fit into the curve, NiMo being the most active and the most selective under these conditions.

1. Introduction

In order to meet the always more severe European regulations regarding the amount of sulphur in gasoline [1], hydrotreating catalysts must achieve a deep hydrodesulphurisation (HDS) with a minimum of olefins hydrogenation (HYD), *i.e.* get to a better selectivity (hydrodesulphurisation/olefins hydrogenation: HDS/HYD) criteria. There has been many studies dealing with HDS and focusing on the understanding of the various phenomenon involved in this reaction, in order to improve the selectivity [2–5]. To achieve such a goal, the optimisation of conventional catalysts or the elaboration of new ones are required. Processes and catalysts allowing the removal of sulphur must be more and more efficient.

Commercial gasoline is composed of different fractions coming from reforming, isomerisation and fluid catalytic cracking (FCC) units. The gasoline fraction produced from the FCC process represents 30–50% of the commercialised motor fuel but it contains up to 85–95% of the sulphur impurities. It is mainly composed of aromatics (30 vol.%), isoalkenes (20–40 vol.%) and sulphur compounds such as alkylthiophenes (max. 5000 wt ppm) [6–9]. The nature of sulphur compounds is now well-known and has been reviewed by Brunet et al. [2]: mainly benzothiophenes, alkylthiophenes, thiols and sulphides. Besides, the olefins amount is high (20–40 vol.%) and helps to improve the octane number. Therefore, it is important to remove the sulphur compounds while limiting the olefins hydrogenation in order to keep a high octane number (selective HDS). Conventional operating conditions are quite mild in terms of temperature and pressure.

Catalysts used for such hydrotreating reactions are transition metal sulphides (TMS), supported or not [10]. Brunet et al. [2] have reviewed the different parameters influencing the activity and the selectivity such as the presence of a promoter, the reactions and mechanisms involved in HDS reactions. It is known that there is a competitive competition between the sulphur and the olefin compounds on the catalyst depending on the catalyst nature, which could modify the activity and the selectivity. Daudin et al. [11] and Miller et al. [12] showed that mixed unsupported sulphides (NiMo and CoMo) had a much better HDS activity and HDS/HYD selectivity than the non-promoted catalyst MoS_2 under model conditions.

Recently, experimental results were coupled with theoretical models (mainly DFT calculations) in order to explain more precisely the mechanisms involved in HDS reactions [3,13–16]. Daudin et al.

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[11,14] have shown that there was a relation between the *ab initio* calculated metal–sulphur bond energy (E(MS)) of unsupported transition metal sulphides and their activity for the HDS and HYD reactions. They generalised the volcano-shaped curve to unsupported transition metal catalysts, showing that the maximum of activity (HDS and HYD) or selectivity (HDS/HYD) could be obtained for intermediate E(MS).

For supported catalysts, it has been shown that a more basic support would account for a higher selectivity [2,16,17]. For example, Mey et al. [16] showed a decrease in HYD on a CoMo supported catalyst doped with potassium. Another way of improving the selectivity was also to selectively poison the hydrogenation sites [4,5]. When the hydrogenation activity was inhibited by carbon deposition or adsorption of basic nitrogen compounds such as pyridine, the activity of the catalyst for the HYD reaction was more affected than the HDS, thus increasing the selectivity. Indeed, HDS/HYD selectivity is the key parameter for an efficient gasoline hydrotreating catalyst. As explained above, selectivity can be influenced by many parameters (nature of the active phase, acidic–basic properties of the support, use of selective poison) but might also depend on the amount of H_2S in the feed.

The influence of H_2S in the feed has been the subject of numerous works as it is obtained as a by-product in HDS reactions [2,18]. In particular the influence of H_2S has been studied on diesel HDS [18], olefins hydrogenation reaction [19] and very recently on model FCC feeds [16,20]. It has been admitted that Mo-based catalysts promoted by Ni are more affected by the presence of H_2S than catalysts promoted by Co while studying the HDS of dibenzothiophene or 4,6-dimethyldibenzothiophene, but the results depended on the experimental conditions [18]. Dos Santos et al. [21] used a commercial $CoMo/Al_2O_3$ catalyst under mild conditions of temperature and pressure with a model FCC feed (3-methylthiophene and hex-1-ene diluted in n-heptane), and showed that there was an inhibiting effect of H_2S on both HDS and HYD reactions and an effect of P_{H_2S} on the selectivity explained by a variation in the rate determining step.

Only a few papers are available in the literature dealing with the influence of sulphur compounds (H_2S) on the olefins alone [19,21,22]. Lamic et al. [19] showed the negative impact of H_2S on different unsupported molybdenum-based catalysts for the transformation of a model olefin (2,3-dimethylbut-2-ene), the NiMo catalyst being more inhibited than the CoMo or the MoS_2 one by small amounts of H_2S. Dos Santos et al. [21] discussed a model for the competitive reactions happening during the deep HDS of FCC gasoline, using a $CoMo/Al_2O_3$ catalyst and under model conditions, and found that there was a competitive adsorption of 3-methylthiophene and hex-1-ene on the catalyst surface as well as an inhibiting effect of H_2S on both reactions (HDS and HYD). For the HYD reaction, the authors showed that the olefin and the sulphur molecule were in competitive adsorption on the same active site, and that a strong influence of the olefin was shown on the HDS reaction.

This paper will deal with the transformation of model molecules, either alone or in mixture, representative of sulphur and olefinic compounds found in FCC gasoline. The influence of P_{H_2S} on the performances of unsupported Mo-based catalysts will be described in terms of HDS and HYD activities and HDS/HYD selectivity. The influence of the nature of the promoter, cobalt or nickel, will be particularly studied. The impact on the olefin reactivity of two sulphur compounds: H_2S, already known as an important parameter for hydrotreatment reactions, and 2-methylthiophene, one of the reactants, will be addressed. This study will be extended to previous results correlating reactivity as a function of the metal–sulphur bonding energy (E(MS)) in order to observe the impact of the sulphur compound nature on the volcano-shaped curves established for transition metal sulphides.

2. Experimental

2.1. Catalysts preparation

The preparation method of unsupported molybdenum sulphide catalysts has already been reported in previous works [11,14,19–24]. Molybdenum sulphide preparation was carried out by thermal decomposition of ammonium thiomolybdate at 673 K under H_2S/H_2 (10 mol% H_2S) during 4 h. First, the ammonium tetrathiomolybdate $(NH_4)_2MoS_4$ (ATM) was obtained by reaction between ammonium heptamolybdate $(NH_4)_6[Mo_7O_{24}]$, $4H_2O$ (4 g in 20 cm^3 of distilled water) with 50 wt% of ammonium sulphide $(NH_4)_2S$ in aqueous solution at 353 K. The ATM precursor precipitated as red crystals by cooling down the solution in iced water during 3 h. Then, the precipitated red crystals were thoroughly washed with isopropanol and dried.

Molybdenum-based materials promoted by nickel or cobalt in order to obtain NiMo and CoMo catalysts were prepared according to the method reported by Fuentes et al. [25] and are the same than those used by Lamic et al. [19]. $(NH_4)_2MoS_4$ (prepared as mentioned below) was used as a support to impregnate $Co(NO_3)_2$ or $Ni(NO_3)_2$ diluted in acetone in order to obtain an atomic ratio of Ni(Co)/(Ni(Co) + Mo) = 0.3. The bimetallic organosulphides precursors were obtained by removing the solvent at room temperature. Finally, NiMo and CoMo catalysts were prepared by thermal decomposition of the corresponding bimetallic organosulphide precursor at 673 K under H_2S/H_2 (10 mol% H_2S) flow during 4 h.

All catalysts were characterised before and after catalytic activity measurements by TEM combined with EDX (Philips CM 120 kV), X-ray diffraction (Bruker D5005), BET surface area (Micromeritics ASAP 2010) and elemental analysis (CE Instruments NA2100 Protein) at the University of Poitiers (LACCO) in order to verify the exact nature of the transition metal sulphide (TMS) and that there was no modification of the catalyst during the test, according to Lamic et al. [19,27]. XPS analyses have also been performed at IFP-Lyon and are reported elsewhere [19] and confirmed the formation of the desired sulphide catalysts.

Characterisation of the catalysts before and after catalytic test (Tables 1 and 2 [19]) showed a decrease in the S_{BET} especially for the MoS_2 catalyst (from 76 to 10 $m^2\,g^{-1}$) while the promoted catalysts were less affected (from 13 to 7 $m^2\,g^{-1}$ for CoMo and from 14 to 12 $m^2\,g^{-1}$ for NiMo). The particles size is small for all catalysts (8, 9 and 6 nm for MoS_2, NiMo and CoMo, respectively) and the size of the particles was almost not modified after catalytic test (8, 8 and 5 nm for MoS_2, NiMo and CoMo, respectively). Quantitative analyses of XPS are reminded in Table 2, showing that the ratios of Co and Ni in the mixed phase were found to be different: only 18% of Co was engaged in CoMoS phase instead of 45% for the nickel. Consequently, the NiMoS phase seems to be more favoured than CoMoS phase under sulpho-reductive conditions. It was also shown that the global sulphidation level was very high for all catalysts. For the CoMo catalyst the value was about 95% whereas it was 80% for NiMo in accordance with the NiO_x presence detected by XPS.

2.2. Activity measurements

Catalytic activity measurements were carried out in a fixed-bed reactor at 523 K under a total pressure of 2 MPa. The catalyst was presulphided at 673 K for 10 h with a mixture of 10 mol% H_2S/H_2 under atmospheric pressure and then cooled down to the reaction temperature in the presence of the sulphiding mixture. The desired reaction conditions were adjusted (T = 523 K, P = 2 MPa, H_2/feed = 360L/L) and the model feed was injected into the reactor. Three feeds were studied in order to compare the results for each reactant taken separately or in mixture: