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Kinetic study of the hydrodesulfurization of dibenzothiophene over molybdenum carbides supported on functionalized carbon black composite

Influence of indole

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Abstract

Different carbon black composite (CBC) supported molybdenum carbides were synthesized. The support was functionalized with nitric acid at different pH of the impregnation solution (pH 5.2; 0), in order to improve the active phase dispersion. After characterization of these supported catalysts, the kinetic study of the hydrodesulfurization (HDS) of dibenzothiophene (DBT) was for the first time performed over functionalized CBC supported molybdenum carbides. It was found that the HDS of DBT proceeds via the two classical parallel routes: the hydrogenation route (HYD) leading to cyclohexylbenzene and bicyclohexyl and the direct desulfurization route (DDS) leading to biphenyl. In all cases the DDS route was more favored than the HYD route, as well as more inhibited by indole. A global kinetic model suitable for all catalysts is proposed. It could describe all experimental data, and global rate constants were calculated for the HDS of DBT. The corresponding detailed kinetics of the HDS of DBT was also put forward, considering two types of active sites and expressions for the global rate constant could be determined. Furthermore, when the CBC support was preoxidized with HNO_3, the dispersion of the molybdenum carbide active phase was improved and a higher HDS activity was observed both in the absence or in the presence of indole.

Keywords: Hydrodesulfurization; Dibenzothiophene; Hydrodenitrogenation; Indole; Molybdenum carbide; Carbon support; Oxidative treatment; Kinetics; Modelization

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1. Introduction

In order to decrease sulfur content from 50 ppm down to 10 ppm in diesel fuels by 2009 (Directive 2003/17/EC), ultra deep hydrodesulfurization (HDS) of petroleum feed stocks must still be improved. The conventional HDS commercial catalysts (alumina supported sulfided Co(Ni)Mo) cannot proceed to ultra-deep HDS at low cost and highly refractory sulfur containing molecules still remain after a classical hydrotreating (HDT) process. Approaches to ultra-deep HDS might include several options such as: designing new catalysts, developing new processes and optimizing new reactors as very well reviewed by Song and Ma [1]. Our proposal is to design a new catalyst which could be used as a finish catalyst in a two-stage HDT process.

Among potential candidates able to proceed to ultra-deep HDS, molybdenum carbide has been considered in the present paper. It possesses hydrogenating properties similar to noble metals ones [2] and was found to be sulfur-tolerant in the presence of low sulfur content [3,4]. The first studies of HDS over such materials [5–8], have reported that they could exhibit similar or higher HDS activity than sulfided Mo/Al_2O_3 or $Co(Ni)Mo/Al_2O_3$. However, most of these early works dealt with low molecular weight model molecule such as thiophene

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and in presence of very high amounts of sulfur, leading most of the time to the sulfidation of the carbide phase. These two parameters had to be re-evaluated. Indeed, heavier compounds such as DBT or alkylated DBT (mainly 4–6 DBT) should be used as model molecules as they are more representative of refractory sulfur containing molecules [9] using conventional HDT catalysts in classical operating conditions. Furthermore, only low amounts of these model molecules are needed in order to simulate the sulfur amount of a gasoil after a first-stage HDT process (50 ppm S since 2005 in Western Europe). In such operating conditions, molybdenum carbide has been reconsidered as an interesting HDT active phase. In 2001, Da Costa et al. [3], performed tetralin hydrogenation over alumina-supported molybdenum carbide. The catalytic activity was shown to be identical in the presence or in the absence of 200 ppm of sulfur. Furthermore, slabs of MoS_2 were never observed on the supported catalysts using HRTEM techniques. They suggested that molybdenum carbide was stable and tolerant to sulfur during hydrogenation of tetraline in the presence of low levels of H_2S. More recently, Szymanska-Kolasa et al. [4] studied the HDN of carbazole (refractory N-containing molecule) over bulk Mo_2C in the presence of 50 ppm of sulfur. They also did not observed any slabs of MOS_2 on the catalyst after test.

Alumina is the current support for commercial hydrotreating catalysts. However, the full sulfidation of the oxide precursor is difficult to complete because of the alumina–oxide precursor interactions [10–12]. Substituting alumina support by carbon, which is a more inert material during the impregnation steps, led to promising results. For example, Duchet et al. [13] and Arnoldy et al. [14] have shown that sulfided Mo activities for thiophene HDS increased in the trend: sulfided Mo/Al_2O_3 < sulfided Mo/SiO_3 < sulfided Mo/C. This trend has been also observed with sulfided rhenium [14], tungsten [13], Ni(Co)Mo [15–17]. Moreover, according to Mordenti et al. [18], the use of a carbon support could drastically simplify the synthesis of the transition metal carbide (TMC). Indeed, carburization could be carried out in pure H_2, as the carburizing agent is formed by reaction between the carbon support and the hydrogen carrier gas. Such a protocol, *avoided the formation of polymeric carbon on the surface of* Mo_2C [18]. On the contrary, the classical method of TMC synthesis (temperature programmed reaction "TPR" between an oxide precursor and a mixture of hydrogen and carbon-containing gases such as CH_4, C_2H_6, ...), leads to a surface polymeric carbon contaminating TMCs [19]. However, these carbon materials supports [13–18], mainly activated carbons, are deficient for commercialization as they possess low mechanical strength as well as a high volume of micropores, inaccessible to large molecules present in HDT.

In the present work, molybdenum carbide was chosen as the active phase and was supported over a mesoporous carbon material such as a carbon black composite (CBC) possessing a high mechanical strength [20]. Following the patent of Schmitt et al. [21], the CBC was prepared by conglomeration of carbon black particles (soot). The CBC mesoporosity was mainly due to the CBC intergranular space between the spherical soot particles [21]. The CBC was functionalized with nitric acid in order to optimize the dispersion of the active phase during the impregnation step [22–26]. Indeed, such oxidative treatments create anchoring sites on the carbon surface, in the form of oxygen surface groups which can superficially interact with the oxide precursor as shown in a previous publication [23]. The impregnated supports were carburized according to the protocol of Mordenti et al. [18].

In the present investigation, the effects of support functionalization on one hand, and of the pH acidity of the impregnation solution, on the other hand, towards the dispersion of the active phase were studied. The HDS of dibenzothiophene with or without indole was performed over all prepared catalysts. Indole as well as any nitrogen containing compounds, usually present in oils, are known to be inhibitors of the HDS process [28–34]. A global kinetic study as well as its simulation have been investigated in order to first determine global reaction orders. Furthermore, a detailed kinetic study of the HDS of DBT over the different supported catalysts was put forward considering two types of active sites.

2. Experimental

2.1. Catalyst preparation

The CBC support was prepared according to Schmitt et al. [21], from the mixture of soot (carbon black Printex 90, DEGUSSA) and a binder (polyfurfurylic alcohol). The CBC (denoted C) was oxidized in boiling concentrated HNO_3 (65 wt.%) for 0.5 h, washed with distilled water and then dried at 393 K. The resulting nitric acid treated support was denoted C-NA Then, C and C-NA supports were impregnated by ammonium heptamolybdate dissolved in a 10 vol.% acetone/H_2O mixture (pH 5.2), using the incipient wetness impregnation method. The impregnation of 10 wt.% Mo was carried out in one step and followed by drying at 383 K for 16 h. A third sample was prepared, where the C-NA support was impregnated with 6 wt.% Mo in four steps, with the same ammonium heptamolybdate solution described above, but at pH 0.

The three impregnated supports were next carburized according to Mordenti et al. [18]. Temperature was raised from room temperature to 973 K at a rate of 33 K h^{-1} and then left for 2 h at 973 K under a flow of hydrogen of 20 L h^{-1} g^{-1} [18]. The samples were finally quenched in hydrogen down to room temperature. C and C-NA supported molybdenum carbides whose impregnation was done at pH 5.2 will be denoted Mo_2C/C and Mo_2C/C-NA, respectively. Their PZC were determined following the procedure of Noh and Schwartz [34]. The values of PZC were 8.4 and 2.4 for the samples C and C-NA, respectively. To avoid misunderstanding, the C-NA supported molybdenum carbide whose impregnation was performed at lower pH (pH 0) will be denoted (Mo_2C/C-NA)ac.

2.2. Catalysts characterizations

The three catalysts were characterized by X-ray diffraction (XRD), nitrogen physisorption at 77 K, elemental analyses,