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# Study of the Individual Reactions of Hydrodesulphurization of Dibenzothiophene and Hydrogenation of 2-Methylnaphthalene on ZnNiMo/$\gamma$-Alumina Catalysts

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**Abstract** A series of ZnNiMo/$\gamma$-alumina catalysts with variable Zn/(Ni + Zn) ratio were synthesized. These catalysts were characterized by chemical analysis, temperature programmed reduction (TPR) and BET surface area. After that, these catalysts were tested in the individual reactions of hydrodesulphurization (HDS) of dibenzothiophene (DBT) and hydrogenation (HYD) of 2-methylnaphthalene (2MN). The results showed an increment of the catalytic activity, for both reactions, when the catalysts were doubly promoted with Ni and Zn in comparison to those mono-promoted catalysts.

**Keywords** Dibenzothiophene · 2-Methylnaphthalene · Hydrotreating

## 1 Introduction

Generally, the combustibles pool contains undesirable compounds as sulfur and nitrogen. Some of them can be refractory and difficult to remove them from crude oil fraction as diesel. So, sulfur and nitrogen compounds, upon combustion, are converted to $SO_x$ and $NO_x$ which produce the acid rain; while the reduction of aromatic compounds improves combustion characteristics of diesel by increasing the cetane number [1–5]. Much effort has been carried out to eliminate these heteroelements in order to satisfy the environmental regulations. Hydrotreating (HDT) reactions are usually employed because they are very effectives and their technology is very well known. However, the quality of oil crude is more and more poor, and their refinement is much more difficult. New catalysts must be employed to obtain high conversions and selectivities, but several of them, can be very expensive or difficult to synthesize them. In that way, traditional catalysts (Co or Ni (Mo)/$\gamma$-alumina) have been promoted with a third metal as Zn, Sn, Ti, Cr, V, Zr, Fe, etc. [6]. Some of them have an electronic effect and other a geometric effect, as for instance Zn [7, 8]. Zn has been used as a structural promoter on Co(Ni)Mo/$\gamma$-alumina catalysts, and it has reported a markedly synergetic effect in hydrodesulphurization (HDS) reactions. The partial addition of Zn to traditional catalysts (CoMo/$\gamma$-alumina and NiMo/$\gamma$-alumina) is an easy way to synthesize catalysts cheaper (due to partial substitution of Ni or Co by Zn) and to improve successfully catalytic behavior of them. Zn can occupy the tetrahedral sites of alumina diminishing the amount of tetrahedral $Ni^{2+}$ or $Co^{2+}$ which are inactive in hydrotreating reactions [9–12].

Likewise, we have successfully recovered Ni from cellular phone batteries, and have used it in the synthesis of HDT ZnNiMo/$\gamma$-alumina catalysts. Reactions such as HDS of thiophene or vanadyl octaethyl porphirine hydrodeporphyrinization (HDP) showed an important synergetic effect [13].

Then, in this paper, we have expanded our results toward individual reactions of HDS of DBT and HYD of 2-methylnaphthalene (2MN) which are more refractory molecules and consequently more difficult to convert them.

## 2 Experimental

Catalysts were synthesized according to the literature [13]. Ni was recovered by manually separating the black

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particles (Ni) from the white ones (Cd) from previously opened Ni–Cd cellular phone batteries. Then, the Ni was dissolved in hot 10 M $HNO_3$ and filtered off, and $NH_4OH$ (35% solution) was added until the ammonium blue complex of Ni was formed. In similar way, a Zn solution in $NH_4OH$ from sulfate (Merk, 99%) was prepared. At the same time, $\gamma$-alumina (200 $m^2/g$) was impregnated by the incipient wetness method, with a solution of ammonium heptamolibdate, in order to get 15% $MoO_3$ in the final catalyst. These catalysts were calcined (500 °C) in flowing air for 4 h. This solid was then co-impregnated with the previously prepared Ni and Zn solutions, also by the incipient wetness impregnation method. The atomic Mo/(Zn + Ni) atomic ratio was kept constant and equal to 3, while Zn/(Zn + Ni) atomic ratio was varied as: 0, 0.29, 0.38, 0.47, and 1.0. After impregnation with Zn and/or Ni, the solids were dried at 100 ° C, and calcined again, to get the final catalysts. Temperature programmed reduction (TPR) analyses were carried out in a Chemisorb Analizer 2,900 from Micromeritics. The samples were heated up to 950 °C under flowing $H_2$/Ar (10/90 v/v). Surface area determinations (BET) were done in a Beckman Coulter SA Plus instrument. Chemical analyses of Ni, Cd, and Mo were performed, on samples dissolved in aqua regia, using ICP-plasma.

### 2.1 Catalytic Tests

The individual reactions of HDS of DBT and HYD of 2MN were carried out on a continuous flow reactor working at 10 Bar and 300 °C. Catalysts were pre-sulfided prior to catalytic tests using a $CS_2$/heptane (10 v/v%) solution and $H_2$ stream at 400 °C, 10 Bar pressure and 4 h time on stream. The $H_2S$ was produced by decomposition of $CS_2$ in situ. Then, the reaction was performed on 100 mg of catalyst mixed with alumina (1:3). The liquid feed was composed of $1.10^{-3}$ M of DBT or 2MN containing $CS_2$ in *n*-heptane (2 v/v%, 10.5 mL/h), and $H_2$ (1.5 mL/s). The reaction products were injected ever 30 min to a Perkin–Elmer (AutoSystem XL) gas chromatograph equipped with a flame ionization detector and a capillary column [5% biphenyl (BP) and 95% dimethylsilane] of 30 m length and 0.250 mm internal diameter.

## 3 Results and Discussion

### 3.1 Characterization of Catalysts

Chemical analyses and surface area measurements, for the catalysts before sulfidation, are presented on Table 1. Chemical analyses revealed the presence of a small amount of Cd in the catalysts (<0.5 wt%). This metal is associated to the Ni extracted from the Ni–Cd cellular phone batteries. According to these results, the separation of Ni from Cd was fairly effective. As expected, the amount of Cd is slightly higher for the catalysts with higher amount of Ni. On the other hand, surface area decreases as the catalysts are impregnated with the metals (Mo, Ni, and Zn). For Ni–Zn catalysts, it is observed that the higher the amount of Zn the lower the surface area, which could be due to the formation of Zn spinel or bulk Zn oxide [14, 15]. Both effects could cause the surface area decrease. However, Zn spinel or ZnO could not be detected by XRD, which is an indication that Zn is very well dispersed.

**Table 1** Chemical analyses and surface area for ZnNiMo/$\gamma$-alumina catalysts

| Catalysts | Zn/(Zn + Ni) experimental ratios | Cd (%) | Surface area ($m^2/g$) |
|---|---|---|---|
| $Mo/Al_2O_3$ | – | 0.04 | 181 |
| $NiMo/Al_2O_3$ | 0 | 0.47 | 129 |
| $ZnMo/Al_2O_3$ | 1 | 0.03 | 146 |
| $ZnNiMo/Al_2O_3$ (0.29) | 0.29 | 0.43 | 145 |
| $ZnNiMo/Al_2O_3$ (0.38) | 0.38 | 0.41 | 133 |
| $ZnNiMo/Al_2O_3$ (0.47) | 0.47 | 0.12 | 110 |

TPR analyses are presented in Fig. 1 and Table 2. For $Mo/Al_2O_3$, two reduction peaks were observed. The first one (signal a) is well defined in the range of 430–500 °C, which, according to the literature is assigned to monocrystalline polymeric species of Mo in octahedral sites, where Mo is reduced from $Mo^{6+}$ to $Mo^{4+}$, and a second broader one (signal b) starts at 600 °C and goes up to 900 °C, which could correspond to Mo species more

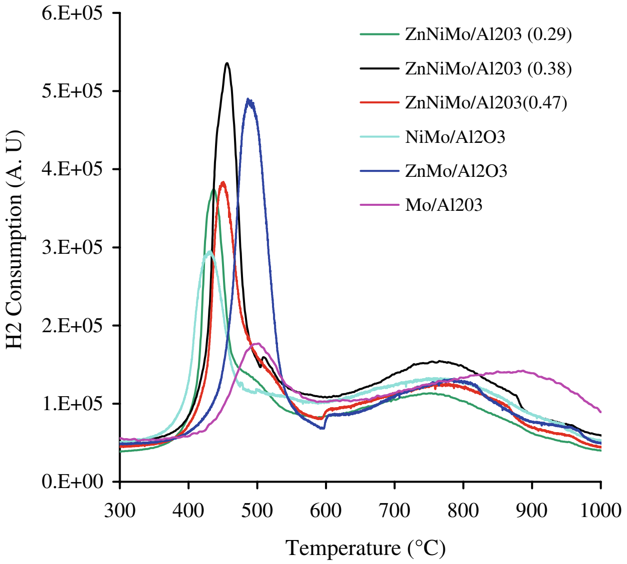

**Fig. 1** TPR analysis for ZnNiMo/$\gamma$-alumina catalysts with variable Zn/(Ni + Zn) ratio

**Table 2** TPR results for ZnNiMo/$\gamma$-alumina catalysts with variable Zn/(Ni + Zn) ratio

| Catalysts | Temperature a peak maximum (°C) | | a/b heights ratio |
|---|---|---|---|
| | Signal a | Signal b | |
| $Mo/Al_2O_3$ | 500 | 880 | 1.25 |
| $NiMo/Al_2O_3$ | 433 | 750 | 2.19 |
| $ZnMo/Al_2O_3$ | 500 | 800 | 4.16 |
| $ZnNiMo/Al_2O_3$ (0.29) | 438 | 760 | 3.31 |
| $ZnNiMo/Al_2O_3$ (0.38) | 458 | 770 | 3.46 |
| $ZnNiMo/Al_2O_3$ (0.47) | 453 | 770 | 2.94 |

difficult to reduce in tetrahedral sites or the reduction of $Mo^{4+}$ to metallic Mo [16–18]. Both signals are present in all Mo containing catalysts. For the catalysts where the second metal (Ni or Zn) is added to Mo, the reduction peaks of each one of the second metal tend to be overlapped with Mo signals, making difficult any assignation to Zn or Ni reduction temperatures. However, some differences in the intensities of the peaks are observed. Thus, for the $ZnMo/Al_2O_3$ catalysts intensity ratio between first and second peak is almost four times higher than for the Mo catalysts. This increase in the intensity ratio could be due to the overlapping of the signals, and/or to the occupancy of the tetrahedral sites of the alumina by $Zn^{2+}$, which reduces the amount of Mo that can occupy this type of sites. Thus the peak at around 800 °C, which is assigned to Mo in tetrahedral coordination (Mo(t)) or metallic Mo, decreases in favor of the peak at 500 °C which is due to Mo in octahedral coordination (Mo(o)). It is important to point out that the addition of Zn does not significantly change the position of the Mo peaks but their intensities are changed, indicating that Zn does not change the reducibility of Mo but the amount of Mo in tetrahedral and octahedral coordination.

For $NiMo/Al_2O_3$ reduction peaks appear at lower temperatures than for $Mo/Al_2O_3$ (Fig. 1; Table 2). In this case, Ni increases the reducibility of Mo. At the same time, there is also an increase in the intensity ratio between the first and second Mo reduction peaks, as compare to $Mo/Al_2O_3$, but to a lesser proportion than in the case where the Mo catalyst is only promoted by Zn. It is well known that Ni can also occupy alumina tetrahedral sites, then it can hinder some of the Mo from occupying tetrahedral sites, hence Ni could also increase the amount of Mo(o) and then increase the intensity of the first Mo reduction peak.

When the catalysts are doubly promoted by Zn and Ni, both effects are observed, that is, there is and increased in the reducibility of Mo and its amount in octahedral coordination. Thus, the ratio between Mo(o) and Mo(t), reduction peaks, increases from 1.1 for the mono-promoted catalysts to 3.2 for the promoted ones, and the temperature at peak maximum decreases, in average, 50 and 113 °C, for Mo(o) and Mo(t), respectively. A similar effect was reported by Fierro et al. [8] for gravimetric reductions of ZnCoMo catalysts at 450 °C. It was found that the reducibility of the catalysts increases when Mo is doubly promoted by Zn and Co.

The dual effect, observed in our case, is due, on one hand to the interaction of the Zn with the alumina support occupying tetrahedral sites which does not allow Ni and Mo to go to this kind of sites, so there is more Ni in interaction with Mo instead of with the alumina; and on the other hand, to the increase in the amount of Ni which is not forming the spinel with alumina and promotes the reduction of Mo, may be by a spillover effect. The first effect is supported by the reported fact that Zn easily occupies tetrahedral sites of the alumina [8, 13].

### *3.1.1 HDS of Dibenzothiophene*

The results from the dibenzothiophene HDS catalytic activity and its selectivity are given in Fig. 2 and Table 3. Final conversion dates were reported when steady-state operation conditions were reached (210 min, Table 3). As can see, all catalysts showed conversion toward HDS reaction. Figure 2 shows, for all essayed catalysts, except for $Mo/Al_2O_3$ catalyst where a slightly deactivation was observed, that the conversion is increased as time on stream is increased until 210 min time on stream where the steady-state is reached. Possibly, these results could be related with the generation of new active sites which were produced during the running-in time by the sulfurization [19]. The conversion values lowest were found for ZnMo and Mo catalysts (Table 3). $MoS_2$ is generally the active phase determined in the HDS catalysts but it is well know that some interactions could be occur between the support

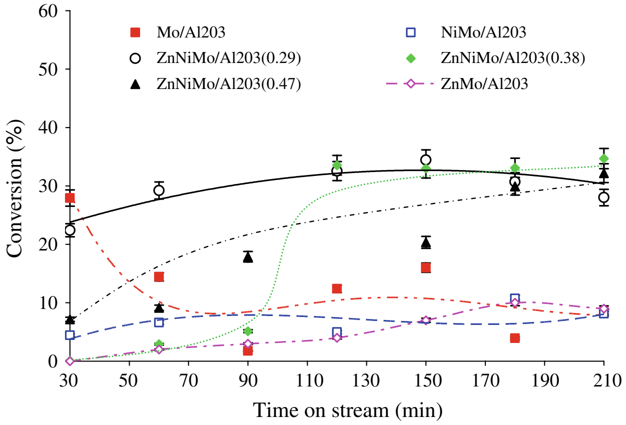

**Fig. 2** HDS of DBT as a function of time on stream for ZnNiMo/$\gamma$-alumina catalysts with variable Zn/(Ni + Zn) ratio

**Table 3** Conversion (%) and selectivity (%) of HDS of DBT and HYD of 2MN for ZnNiMo/γ-alumina catalysts with variable Zn/(Ni + Zn) ratio

| Catalysts | Conv. | Selectivity | | | Conv. | Selectivity | | |
|---|---|---|---|---|---|---|---|---|
| | HDS (%) | BF (%) | CHB (%) | BF/CHB | HYD (%) | 6MT (%) | 2MT (%) | 6MT/2MT |
| $Mo/Al_2O_3$ | 8.1 | 92 | 8 | 11.5 | 2 | – | – | – |
| $Zn/Al_2O_3$ | 9.0 | – | – | – | 1 | – | – | – |
| $NiMo/Al_2O_3$ | 9.5 | 82 | 18 | 4.6 | 8 | 75 | 25 | 3.0 |
| $ZnNiMo/Al_2O_3$ (0.29) | 28.0 | 90 | 10 | 9.0 | 8 | 70 | 30 | 2.3 |
| $ZnNiMo/Al_2O_3$ (0.38) | 35.0 | 91 | 9 | 10.1 | 11 | 62 | 38 | 1.6 |
| $ZnNiMo/Al_2O_3$ (0.47) | 32.0 | 90 | 10 | 9.0 | 17 | 70 | 30 | 2.3 |

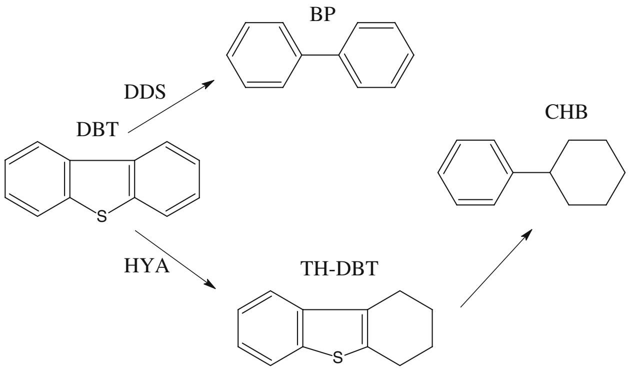

**Fig. 3** Reaction scheme of HDS of DBT [10]

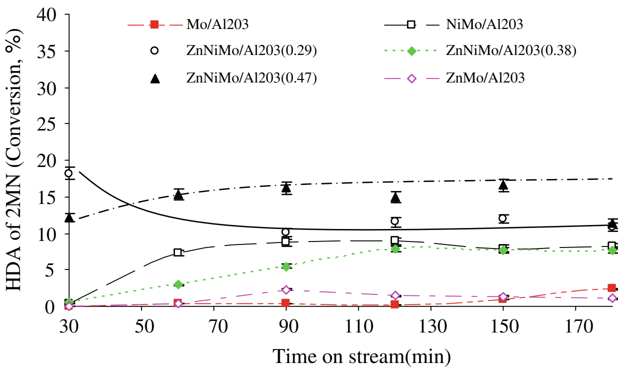

**Fig. 4** HYD of 2MN as a function of time on stream for ZnNiMo/γ-alumina catalysts with variable Zn/(Ni + Zn) ratio

(γ-alumina) and Mo species which induce a low reducibility of Mo atoms, such as was confirmed by TPR studies. The presence of Zn in the Mo catalyst did not substantially improve the conversion values. Zn can occupy the tetrahedral sites of the alumina but does not improve the reducibility of Mo atoms as was explained above. The catalytic activity presented by Mo/γ-alumina was quite similar to that reported by ZnMo/γ-alumina. The Mo/γ-alumina impregnation with Ni improves slightly the DBT HDS conversion. Ni increase the reducibility of Mo and a new active phase is probably formed (NiMoS). However, much higher conversions are obtained when Mo catalysts are promoted with along Zn and Ni. The addition of Zn to NiMo/γ-alumina catalysts allows a higher interaction of the $Zn^{2+}$ cations with alumina support occupying tetrahedral sites which does not allow that Ni and Mo going to this kind of sites. So, the NiMo interactions can widely be improved and Ni can easily reduce the Mo species. The maximum conversion is reached when the Zn/(Zn + Ni) ratio in the NiMo catalyst is 0.38. So, this catalyst was four time more active than the catalyst promoted only by Ni. This result is according with those reported by Fierro et al. [8] and Linares et al. [13] when ZnCoMo/γ-alumina or ZnNiMo/γ-alumina catalysts were used in the reaction of thiophene HDS.

Table 3 also shows the selectivity products of the DBT HDS reaction at same conversion (10%). DBT undergo HDS via two parallel pathways: (i) direct desulfurization (DDS) or hydrogenolysis leading to the formation of biphenyls and (ii) hydrogenation (HYD) followed by desulfuration to give tetrahydro- and hexahydrodibenzothiophenes (TH-DBT), which are further desulfurized to cyclohexylbenzene (CHB) and bicyclohexyls [20, 21] (Fig. 3). We only detected BP and CHB as main products. Other products were no detected, probably because of their fast conversion and thus low concentration. According to our results, the DDS route is much easier than the HYD route. The formation of BP was almost nine times higher than the formation of CHB for all catalysts, except for NiMo/γ-alumina catalyst where ratio of biphenyl/cyclohexilbencene was 5. Zn, as was mentioned, avoids the formation of Ni (or Co) spinel [8]. The incorporation Zn to the catalysts, does not affect the selectivity among the catalysts with Zn but increases direct desulfuration route of HDS of DBT in comparison with the NiMo catalyst.

### *3.1.2 HDY of 2-methylnaphthalene*

Table 3 and Fig. 4 show catalytic activity and selectivity of the reaction of HDY of 2-methylnaphthalene. For this reaction, the final catalytic activity was determined at 180 min when the steady-state was reached. During this

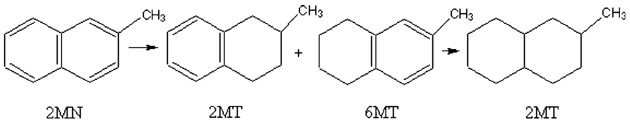

**Fig. 5** Reaction scheme of HYD of 2MN [3]

process, 2-methylnaphtalene is previously hydrogenated to 2-methyl tetraline (2MT) and 6-methyl tetraline (6MT). The total hydrogenation of the 2-methylnaphthalene rings conduct to the formation of 2-methyldecaline (2MD) [3, 22] (Fig. 5). In our case, this last product cannot be found probably to the low $H_2$ pressure used. The behavior of catalysts related to their conversion, show tendencies similar to those reported in the DBT HDS reaction. So, Mo, and Zn catalysts showed the lowest conversion. The addiction of Ni improved the conversion, due to electronic effects presented by this promoter. However, those catalysts impregnated with Zn and Ni, the catalytic conversion is widely improved, especially in those catalysts where the Zn content was higher. Zn, as we mentioned, occupy the tetrahedral site of alumina support, allowing Ni can successfully interact with the active phase. Conversion results showed that HDS reaction was higher that HYD reaction due principally to complexity of 2MN molecule which is more impeded than the DBT molecule.

Also, on Table 3 reports selectivity for 2-methyl naphthalene reaction at same conversion (10%). As can see, 6MT/2MT molar ration was 2.0 approximately for all catalysts series. This result is related to the steric impediments associated to the substituted ring which avoids its hydrogenation [23].

## 4 Conclusion

It was possible the synthesis of ZnNiMo catalysts with variable Zn/(Zn + Ni) ratios. These catalysts were actives for HDT and HYA reactions and they showed an increment of the catalytic activity when these catalysts were doubly promoted. The addition of Zn to NiMo/$\gamma$-alumina catalysts to allow a higher interaction of the $Zn^{2+}$ with alumina support occupying tetrahedral sites which does not allow that Ni and Mo going to this kind of sites.

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