Nature of support and its effect on hydrodesulfurization of dibenzothiophene

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Abstract

Different alumina-titania and alumina-zeolite supported catalysts were evaluated for hydrodesulfurization of dibenzotiophene (DBT) in a batch reactor at 340°C, 4 MPa of hydrogen pressure and 700 rpm of stirring rate. The influence of the support preparation and the composition in the conversion of DBT was estimated for Al_2O_3-TiO_2 and Al_2O_3-zeolite CoMo supported catalysts. The effect of support composition on HDS and its reaction product selectivities are the content of the full manuscript.

1. Introduction

Hydrotreating is an important process for upgrading petroleum by removing heteroelements such as metals and sulfur. However, the problem that refiners face nowadays is the increasingly production of heavy crudes by which it is necessary to increase the operating conditions or change the catalysts/supports properties. Regarding to this, mixed oxides are useful to reach this goal [1]. In the case of the incorporation of TiO_2 to alumina good results have been obtained with model molecules but problems are associated to this support due to its low SSA and pore volume. To improve the heavy and extra heavy crudes it is necessary to increase the acidity of the support by using zeolites which improve the activity towards cracking favoring the selectivity to light distillates so that the new challenges involve high production of valuable liquids with high removal of heterolements.

2. Experimental

Six Al_2O_3-TiO_2 supports were prepared by using different Ti precursor, different method of incorporation into the alumina matrix [2]. On the other hand, different amount of zeolite (US-Y zeolite) was added into the commercial alumina (Puralox TH 50wt% and Pural SB 25 wt%) in order to generate different acidity of the support by using dry extrusion of Al_2O_3-zeolite having nitric acid (4 vol. %) as peptizing agent. The composition of TiO_2 in the support kept at around 10 wt. % due to its commercial importance as well as moderate acidity generated at this composition.

The CoMo supported catalysts were prepared by using sequential incipient wetness impregnation method. TiO_2-Al_2O_3 supported catalyst were named as CoMo/TA (number reported as different preparation method), while zeolite based catalyst are reported as CoMo/AlZeo (number report as zeolite composition). The catalyst activity test were carried out in a batch reactor with DBT having 1000 wppm sulfur dissolved in a solvent of decalin and using an internal reference decane (0.05 mol) to calculate the mass balance.

Table 1. Textural properties of catalysts

Catalyst	SSA, m²/g	PV, cc/g	APD, nm
CoMo/TA-1	230	0.4372	7.4
CoMo /TA-2	255	0.4100	6.8
CoMo /TA-3	260	0.3319	5.5
CoMo /TA-4	206	0.3200	5.8
CoMo /TA-5	232	0.3426	5.7
CoMo /TA-6	231	0.3085	4.1
CoMo /AlZeo	157	0.4378	5.6
NiMo/AlZeo	172	0.4569	5.3
NiW/AlZeo	145	0.3709	5.1

3. Results and discussion

The textural properties of catalysts are shown in **Table 1,** which indicated that all catalyst are meso-porous in nature, but the catalyst preparation method and catalyst composition notably vary the properties. An effect of support on the hydrodesulfurization is shown in the **Figure 1,** Ti-Al supported catalyst are less active than the zeolite-based catalyst, which has more stronger acid site that play a promoting role to the catalytic sites. Futher more, the conversion of DBT is significantly affected by the presence of zeolite composition that increases with increasing zeolite content in the catalyst as shown in **Figure 2.** Apart from the conversion Al_2O_3-TiO_2 supported

Fig. 1. Effect of support and active metal on DBT conversion

Fig. 2. Effect of zeolite content in the support on DBT conversion
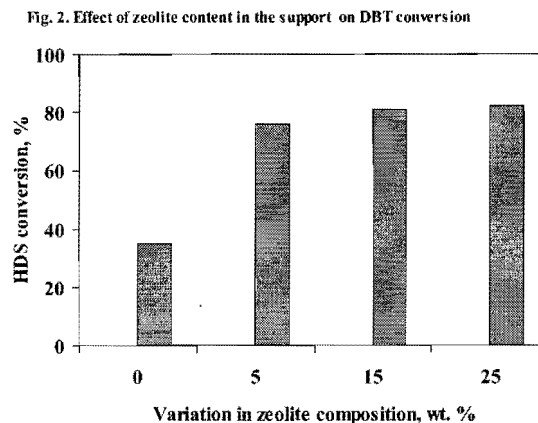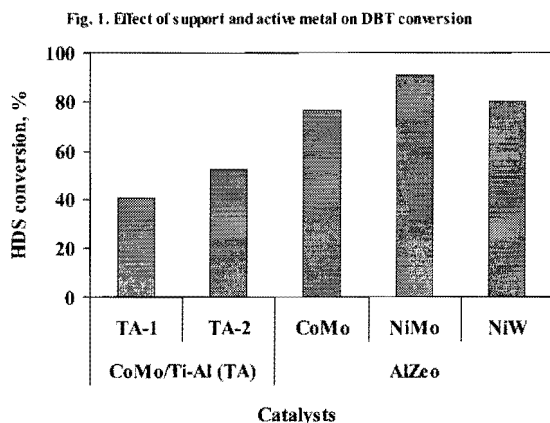
catalysts enhance the hydrogenolysis of the C-S bond showing principal product of biphenyl (BP), which is further hydrogenated to cyclohexilbenzene (CHB) and finally to bicyclohexil (BCH).

It can be observed that the CoMo/Ti-Al catalyst favors a higher selectivity toward BCH with respect to BP. Zeolite-based catalysts also enhance the hydrogenolysis mainly (cracking reactions) and compared to alumina-titania supported catalysts they are less selective to hydrogenation so that the major product is CHB in spite of using metals for hydrogenation such as Ni or W. Conversion is relatively higher and the most active one to HDS is NiMo followed by NiW and CoMo catalysts. Zeolite-based catalysts have strong Brønsted acid sites which are responsible for cracking reactions and for this reason direct desulfurization of DBT is the preferred route. Conversion with zeolite-alumina supported catalysts is in some cases twice higher than titania-alumina supported catalysts. However, selectivity of CHB-to-BP remains almost the same with both types of supports. The difference in conversion and selectivity is likely due to that hydrogenolysis and hydrogenation are taking place in different catalytic sites.

In conclusion, the method of synthesis for titania-alumina supports influences on the hydrogenolysis and the preferred path for both catalysts was the direct desulfurization; however, titania-alumina supports showed lower conversion but higher hydrogenation of intermediate compounds.

References
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