Synthesis and Characterization of (ZrO_2-TiO_2)/Al_2O_3 Ternary Oxides as Hydrodesulfurization Catalyst Carrier

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Introduction

The production of ultra-clean oil-derived fuels of very low S content have encouraged numerous investigations focused in improving currently available refining processes. More efficient catalytic hydrotreatment (HDT) operations are key to getting the aforementioned goal. One of the strategies followed to improve HDT catalysts consists in developing novel carriers that could contribute to obtain enhanced activity, selectivity or stability of supported sulfided CoMo or NiMo active phases. Recently [1-4], our group has reported on the suitability of wide-pore ZrO_2-TiO_2 (obtained through solvo-thermal post-treatments during sol-gel processing) as support for sulfided CoMo or NiMo catalysts applied in dibenzothiophene hydrodesulfurization (HDS). Considering the interesting properties of ZrO_2-TiO_2 oxides as catalyst carrier we tried to obtain materials of improved extrudability and mechanical strength. To this end, we prepared zirconia-titania-alumina materials at various compositions by depositing ZrO_2 and TiO_2 over an Al_2O_3 matrix. These ternary systems were used as supports for CoMo-based sulfided catalysts applied in HDS of both dibenzothiophene (DBT) or 4,6-dimethyl-dibenzothiophene (4,6-DM-DBT) in *n*-dodecane.

Materials and Methods

Zirconia (from $ZrOCl_2$) and titania (from $TiCl_4$) were precipitated (NH_2-CO-NH_2 thermal decomposition) over a powdered commercial alumina matrix (S_g= 397 m^2/g, V_p=0.95 cm^3/g, D_p ~9.6 nm). Ternary formulations at various compositions were prepared where Al_2O_3 molar fraction was varied (0.9, 0.8, 0.7, 0.6, 0.4 and 0.2) meanwhile titania(T)/zirconia(Z) molar ratio was kept constant at T/Z=60/40. After zirconia-titania precipitation materials were filtered, then water-washed until total Cl^- anions elimination. Further processing of these hybrid supports included drying at 120 ºC (10 h) and calcining at 500 ºC (5 h). A reference zirconia-titania material containing no alumina was also synthesized. Pore-filling impregnation was used for Mo deposition (from ammonium heptamolybdate). Impregnated samples (at 2.8 Mo atoms/nm^2) were then dried and calcined under N_2 (at 120 and 400 ºC, respectively). Cobalt (from $Co(NO_3)_2$) was added at Co/(Co+Mo)=0.3 over a series of non-calcined Mo-impregnated precursors. Further processing included drying and calcining under inert atmosphere (at 120 and 400 ºC, respectively). Materials characterization included N_2 physisorption, X-ray diffraction, thermal analysis, UV-vis and Raman spectroscopies, temperature-programmed reduction and transmission electron microscopy. Final sulfided catalysts were obtained by submitting calcined impregnated solids to an H_2S/H_2 flow (at 10/90 mol/mol, 4 l/h) at 400 ºC (2 h). HDS tests (DBT or 4,6-DM-DBT in *n*-dodecane) were carried out in a batch reactor operating at 320 ºC and 800 psi. Analysis of liquid samples taken at various reaction times was carried out by gas chromatography (FID).

Results and Discussion

Deposition of increasing zirconia-titania amounts progressively decreased average pore diameter and pore volume of alumina substrate suggesting some degree of pore-plugging. However, surface area was much less affected where the original value for Al_2O_3 matrix diminished by about 15-18% even in the case of ternary oxides of high ZrO_2-TiO_2 content (≥40 mol%). This fact pointed out to deposition of porous zirconia-titania domains contributing to total surface area of composite materials. No crystalline patches of either zirconia or titania where identified (XRD) indicating strong interaction among these components. Also, by differential thermal analysis it was observed that exothermal crystallization to $ZrTiO_4$ [1], shifted to higher temperature suggesting chemical interaction between deposited zirconia-titania and the alumina substrate.

According to reaction tests (DBT HDS), the material with ternary carrier with 20% mol of zirconia-titania (20TZ/A) had the highest pseudo first order kinetic constant (*k*). Thus, that solid was chosen to be promoted by cobalt and further tested in the HDS of both DBT and 4,6-DM-DBT. The corresponding *k* values are shown in Table 1 where alumina and zirconia-titania supported catalysts are also included as reference.

Table 1. Pseudo first order kinetic constants in HDS of DBT (k_1) and 4,6-DM-DBT (k_2) for various catalysts prepared. Solvent: *n*-dodecane, batch reactor, T=320 ºC, P=800 psi. [1]In the DBT HDS; [2]In the 4,6-DM-DBT HDS.

Catalyst	k_1 ×10^{-5} (m^3 $kg_{cat}^{-1}s^{-1}$)	HYD/DDS[1]	k_2 ×10^{-6} (m^3 $kg_{cat}^{-1}s^{-1}$)	HYD/DDS[2]
CoMo/A	3.7	0.04	4.2	0.68
CoMo/(20TZ/A)	11.5	~0.0	12.8	0.60
CoMo/ZT	2.0	0.11	4.7	1.31

It could be observed that the Co-promoted catalyst with ternary oxide with 80% mol alumina as carrier had much better hydrodesulfurizating properties that the corresponding materials supported on either Al_2O_3 or ZrO_2-TiO_2. This suggested that the 20TZ/A composite combined, in a single formulation, some of the surface properties of ZrO_2-TiO_2 with the good textural properties of Al_2O_3 substrate. Regarding the ratio of products from hydrogenation (HYD) to that of direct desulfurization (DDS), all tested materials strongly favored biphenyl formation (DBT HDS). As expected, the trend was the opposite in the 4,6-DM-DBT desulfurization where the catalysts with ternary carrier had the best hydrogenating properties.

Significance

Zirconia-titania-alumina ternary oxides appeared to be promising supports for CoMo-based HDS catalysts aimed to obtaining oil-derived middle distillates of ultra-low sulfur content.

References

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