Influence of oxidation and precursor on the morphology and catalytic properties of CoMoS/Al2O3-TiO2 for HDS.

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Abstract

Alumina supported molybdenum and tungsten sulfides promoted by cobalt or nickel are commonly used as commercial hydrotreating catalysts. One way to develop better catalysts for hydrodesulfurization (HDS) is to look for other supports. In this respect, have reported that titania induces very good dispersion of molybdenum disulfide [1-3]. In this study, mixed aluminum and titanium oxide (Al_2O_3-TiO_2, 10% TiO_2) prepared by the sol-gel method were used as a support for HDS catalytic systems. The Mo content is 18 wt% with an atomic ratio R = Co/(Co+Mo) = 0.3. The Mo and Co were incorporated by incipient wetness impregnation of the support with an aqueous solution of metallic salts. Calcination at 500°C resulted in a catalytic support with high surface area (131.3-220.2 m^2/g) and good thermal stability. MoS_2 catalysts promoted by Co and supported on this Al_2O_3-TiO_2 support were evaluated in the reaction of hydrodesulfurization of dibenzothiophene (DBT).

Catalysts were obtained in two sets; with or without pre-oxidation treatment in air flow at 500 C. Both sets of catalysts were activated following two different routes: 1) *ex situ* activation under a H_2/H_2S flow (15% H_2S v/v) at 400°C, and 2) *in-situ* activation directly performed during the HDS of DBT. Two precursors of MoS_2 were used, ammonium thiomolybdate (ATM) and tetramethyl-ammonium thiomolybdate, (TMTMA). The catalysts when pre-oxidized were labeled with "O", those *ex situ* as

"C" and the ones *in situ* as "P". Finally, catalysts from TMTMA were labeled as "C1". Thus, the catalysts obtained were LP, LC, LC1P, LOP, LOC, LC1OP, LC1C, and LC1OC. Catalysts were characterized by XRD, SEM, and nitrogen adsorption.

Results and Discussion

Figure 1 shows x-ray diffraction patterns for $Co/MoS_2/Al_2O_3-TiO_2$ catalysts. Poorly crystalline structures are obtained suggesting that a good distribution of the active phase on the $Al_2O_3-TiO_2$ support. The MoS_2 diffraction lines are more hardly discernible for the non oxidized solids that for the pre-oxidized catalyst. The pre-oxidation treatment appeared new peaks due to MoO_3. Nitrogen adsorption measurements are shown in Table 1 indicate that surface area depends on the treatment, non oxidized catalysts show higher surface area than catalysts treated with air. Also, *in situ* activation gave greater surface area than *ex situ* activation and the catalysts from TMTMA exhibited higher surface area than those from ATM. The catalytic activity in the HDS test (Table 1) does not show a behavior as function of the oxidation treatment. However, the activity is better when the catalyst is obtained from TMTMA and *ex situ* activated than when is obtained from TMA and *in situ* activated.

The characteristic morphology of the catalysts (Figure 2) is as irregular agglomerated particles, like a sponged solid. Finally, this support allows a good dispersion of the active phase and high activity for HDS.
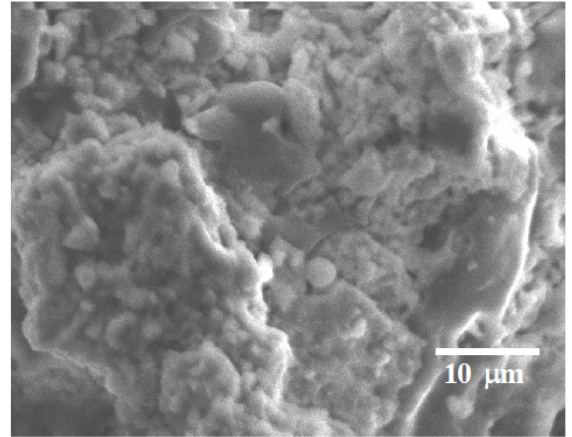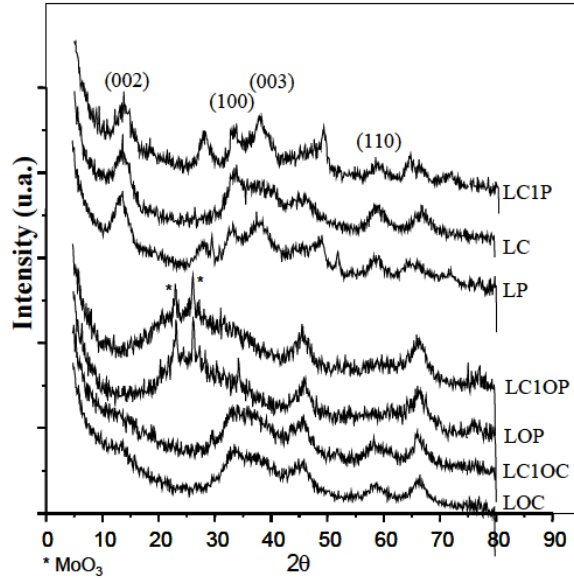
Figure 1: XRD patterns of non-oxidized catalysts and pre-oxidized catalysts after HDS test.

Figure 2. Micrograph of LC1P catalyst.

Table 1 Surface area (S.A.), catalytic activity and selectivity in HDS test.

Pre-Oxidation				Non oxidation			
Sample	S. A. (m^2/g)	K X10^7 (mol/g.s)	HYD/ HDS	Sample	S. A. (m^2/g)	K X10^7 (mol/g.s)	HYD/ HDS
LOP	141.1	6.7	0.30	LP	171	7.8	0.24
LOC	131.3	11	0.24	LC	164	10.1	0.02
LC1OP	178.1	7.5	0.04	LC1P	220.6	14	0.28
LC1OC	144.4	15.5	0.20	LC1C	203.1	8.4	0.17