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Highly Active (Co)MoS_2/Al_2O_3 Hydrodesulfurization Catalysts Prepared in Aqueous Solution

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Reduction of $(NH_4)_2MoS_4$ with N_2H_4 in aqueous solution in the presence of alumina suspension leads to the formation of a highly dispersed MoS_2 supported on the surface of Al_2O_3. In the model thiophene desulfurization reaction, these MoS_2/Al_2O_3 catalysts show a linear increase of catalytic activity as a function of Mo content up to 22 wt% of molybdenum. This preparation method makes it possible to efficiently disperse amounts of the active sulfide phase on alumina much higher than those of conventional systems prepared by impregnation. Promoted by Co, these materials exhibit a HDS catalytic activity much higher than that of a commercial CoMo/Al_2O_3 catalyst used as a reference.

Key Words: **hydrotreating; hydrodesulfurization; supported catalysts; molybdenum disulfide.**

INTRODUCTION

The refining industry is facing a great challenge in the stringent limitation of sulfur content in gasoline and diesel fuels. The improved environmental performance of hydrotreating processes is mostly based on an update of catalyst formulations (1). Several possible ways for improving the catalysts activity, including the use of new supports, novel active phases, or optimizing the preparation procedure, were envisaged. Introduction of various additives such as phosphate or fluoride, the modification of the sulfidation procedure, or the promoter distribution by use of complexing agents is also applied to improve hydrotreating catalysts (2). An alternative approach utilizing nonoxidic catalyst precursors could also be envisaged. Highly active catalysts were prepared by the deposition of molybdenum sulfide from aqueous solutions (3, 4) or by decomposition of alumina-supported cluster compound $(NH_4)_2[Mo_3S_{13}]$ (5).

New soft aqueous preparation of MoS_2 developed in our previous works made it possible to prepare highly dispersed unsupported molybdenum disulfide in aqueous solution (6, 7). The present work reports the first results of the catalytic properties of pure and promoted MoS_2/Al_2O_3 catalysts synthesized by this route.

EXPERIMENTAL

Ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$, ATTM) was prepared by reaction between aqueous solutions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $(NH_4)_2S$ (∼20 wt%). The catalysts were synthesized from solution containing 0.03 mol/L ATTM and 0.12 mol/L N_2H_4 at pH 7.7. For example, to prepare the solid containing 10 wt% of molybdenum, 0.5 ml of $N_2H_4 \cdot H_2O$ (Aldrich, high purity) was dissolved in 30 ml water, the pH of solution was adjusted to 7.7 with a concentrated HCl solution, and a solution of 0.65 g ATTM in 50 ml water was added to the above mixture. Then 2 g of γ-Al_2O_3 (Procatalyse, $S_{BET} = 230$ m^2/g) was suspended in the solution and the mixture was heated at 90°C under stirring until the end of a gas production (∼4 h). The resulting solids were thoroughly washed with water and dried in an Ar flow at 100°C for 12 h. Nomenclature and properties of the prepared samples are given in Table 1.

In order to allow a correct comparison between the samples, they were all activated in 15% H_2S/H_2 flow at 350°C for 2 h prior to the catalytic test. To prepare the Co-promoted catalysts, the MoS_2/Al_2O_3 samples were impregnated with a solution of $Co(NO_3)_2 \cdot 6H_2O$ (Co/Mo atomic ratio = 0.5), dried at room temperature, and resulfided under 15% H_2S/H_2 flow at 350°C for 2 h.

Catalytic activity was measured in the hydrodesulfurization of thiophene at atmospheric pressure in a fixed-bed flow microreactor. The test conditions were chosen to provide a total thiophene conversion below 15%. The specific rate was determined after 15 h on stream at a pseudostationary state.

X-Ray photoelectron spectra (XPS) were measured on a VG ESCALAB 200R using Al$K\alpha$ radiation. Transmission electron microscopy (TEM) images were obtained on a JEOL 2010 microscope (point-to-point resolution 0.19 nm).

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TABLE 1

Catalytic Activities in Thiophene Hydrodesulfurization

Catalyst	Mo loading, wt% of Mo	Rate of thiophene desulfurization: A_s, 10^{-8} mol · g^{-1} · s^{-1}	Rate of thiophene desulfurization: A_i, 10^{-4} molecules · atom^{-1} Mo · s^{-1}
Mo 1	4.6	11.5	2.4
Mo 2	10.2	24.4	2.3
Mo 3[a]	10.0	19.0	1.8
Mo 4	16.9	38.1	2.2
Mo 5	21.7	44.8	2.0
Mo 6	29.5	38.2	1.2
$CoMo/Al_2O_3$ commercial reference	8.3	159.3	18.4
CoMo 1[b]	4.5	128.7	27.5
CoMo 2	9.9	245.3	23.8
CoMo 4	16.0	342.1	20.5

Note. Temperature: 583 K, thiophene pressure 2400 Pa.

[a] Dry impregnation of alumina with ammonium heptamolybdate solution, calcination at 500°C in air and further sulfidation under 15% H_2S/H_2 flow at 400°C for 4 h.

[b] The promoted catalysts were prepared from the corresponding MoS_2/Al_2O_3 samples (Co/Mo atomic ratio 0.5).

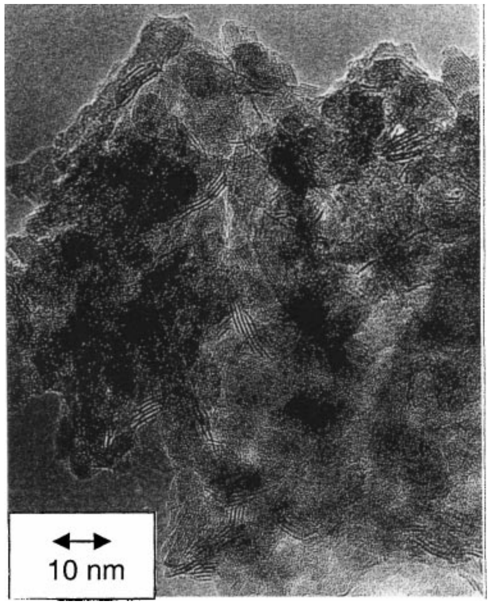

FIG. 1. TEM image of the MoS_2/Al_2O_3 catalyst prepared in aqueous solution (sample Mo 1 in Table 1).

RESULTS AND DISCUSSION

Unpromoted MoS_2/Al_2O_3 Catalysts

It was shown that the reaction between $(NH_4)_2MoS_4$ and N_2H_4 in aqueous solution results in the reduction of molybdenum and the formation of a stable aqueous suspension of poorly crystallized MoS_2 (7). The composite MoS_2–Al_2O_3 material prepared in this study can be easily separated from the reaction solution, indicating that the MoS_2 particles are indeed deposited on the surface of the alumina particles. The electronic state of molybdenum and sulfur in the deposited sulfide does not differ from that in the bulk material: the binding energies (BE) revealed by XPS analysis of the supported samples (Mo $3d_{5/2}$ BE = 228.4 eV and S $2p_{3/2}$ BE = 161.8 eV) are the same as those observed previously (7).

According to the analysis of the TEM images of the Mo 1 sample (Fig. 1), MoS_2 nanocrystals are present with an average stacking number of 2 and an average length of the particles equal to 3 nm. These values are comparable to those generally observed for alumina-supported MoS_2 (8, 9). The particle dispersion for a highly loaded sample (Mo 4, Table 1) cannot be estimated by TEM with certainty due to a significant interpenetration of MoS_2 layers.

The catalytic properties of the solids are summarized in Table 1 (A_s, specific activity; A_i, intrinsic activity). A remarkable feature of the prepared series of catalysts is the nearly linear increase of the catalytic activity up to about 22 wt% of molybdenum (Fig. 2). It is well known that the activity of conventional HDT catalysts vs molybdenum loading is saturated for a loading exceeding ~12 wt% of Mo (2). This effect was explained by the distribution of molybdenum in the oxide precursor. The value of 12 wt% of Mo corresponds approximately to a monolayer dispersion of molybdenum oxide species on the surface of γ-Al_2O_3, and at a higher loading of particles of bulk MoO_3 begin to appear (8, 10). After sulfidation these MoO_3 crystallites yield poorly dispersed MoS_2 and have consequently a lower catalytic activity.

In contrast, in the aqueous synthesis presented here, the MoS_2 particles grow in the solution, so their size depends only on the reaction conditions (pH and hydrazine concentration) and should remain the same regardless of

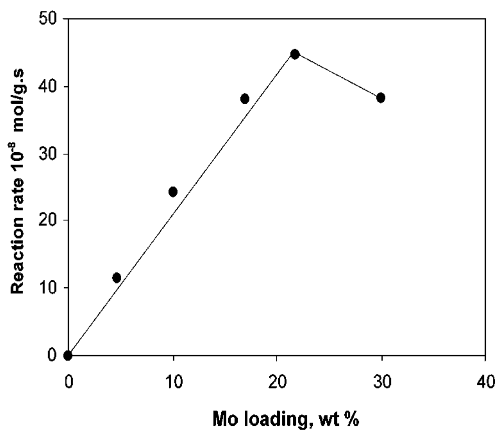

FIG. 2. Dependence of the thiophene hydrodesulfurization rate on the Mo loading.

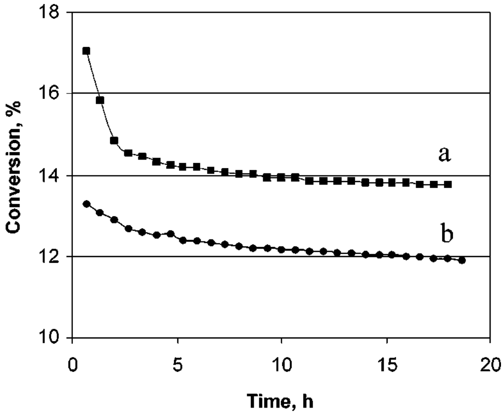

FIG. 3. Thiophene conversion versus time for $CoMo/Al_2O_3$ sulfide catalysts at 310°C: (a) sample CoMo 4 and (b) commercial reference catalyst.

the loading. Thus in this case the proportion of the edges in the whole surface is the same for all samples, which leads to a nearly constant intrinsic activity (Table 1). However, for the highest loading (29.5 wt% of Mo, sample Mo 6) MoS_2 represent about half of the solid and can be considered as a bulk material rather than a supported one, which explains the observed decrease of activity.

Promoted $CoMo/Al_2O_3$ Sulfide Catalysts

The promotion of the Mo samples with cobalt results in the expected significant increase of the catalytic activity. Impregnation of the sample containing supported MoS_2 with cobalt nitrate followed by sulfidation results in a catalyst having a catalytic activity considerably higher than that of the $CoMo/Al_2O_3$ commercial reference with the same loading of cobalt and molybdenum. This effect was observed earlier (11) and may be due to the fact that the existence of the MoS_2 particles allows a more facile formation of the CoMoS phase and prevents the loss of the promoter in side processes leading to other phases like Co_9S_8 or $CoAl_2O_4$.

Surface "overpopulation" in highly loaded catalysts could make sintering and deactivation in such systems more pronounced. As shown in Fig. 3 no drastic deactivation has been noted for these catalysts in our tests.

It seems that the technique described above provides a simple aqueous way of preparing highly loaded sulfide catalysts with enhanced activity. Optimization of the promotion procedure for $CoMo/Al_2O_3$ and preparation of sulfides on supports such as silica and zirconia are envisaged in future work.

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