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CoMo/Al₂O₃ hydrotreating catalysts prepared by flame synthesis

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Introduction

Liquid fed flame spray pyrolysis (FSP) is a novel one-step synthesis method for nano-sized particles [1]. Typically, organo metallic compounds are dissolved in an organic solvent and the precursor solution is sprayed with high velocity oxygen and ignited with a small premixed methane-oxygen flame [2]. The solvent and metal organic precursors evaporate and combust to form atomically dispersed vapours, which nucleate to form clusters when reaching cooler parts of the flame. The formed clusters grow by surface growth and coalescence, accompanied by sintering [3]. This result in non-porous nanoparticles which coagulate and sinter to form agglomerates and aggregates with high inter particle porosity [1].

Hydrotreating is performed at oil refineries in order to remove sulphur and nitrogen from the heterocyclic compounds in which these elements typically occur in crude oil [4]. Industrial hydrotreating catalysts contain cobalt or nickel promoted molybdenum(IV)sulphide as active phase, on an alumina support [4]. The transition metal sulphide phase is obtained after sulfiding an oxide precursor, which can be prepared by FSP [5].

Experimental

Cobalt 2-ethylhexanoate, molybdenum 2-ethylhexanoate and aluminium acetylacetonate dissolved in toluene to metal concentration of 0.4 M were used as FSP precursors. The solutions were sprayed at 3 ml/min with 7 Nl/min oxygen dispersion gas at 2 bar. The specific surface areas were measured by 6 point BET ($p/p_0 = 0.05 - 0.25$), UV-vis reflectance using an integration sphere and Kubelka-Munk analysis and XRD using Ni filtered Cu K_α radiation. Bright field TEM images were recorded on a Technai T20 microscope. Catalytic activity was measured using liquid feed 0.5 ml/min of 3.0 wt.% dibenzothiophene, 0.5 wt.% indole, 1.0 wt.% naphthalene, 2.5 wt.% DMDS and 0.5 wt.% n-nonane dissolved in *n*-heptane. The catalyst activity was measured at: Temperature 350 °C, pressure $p(\text{total}) = 50$ atm and $p(\text{H}_2) = 38$ atm, H₂ flow rate 250 Nml/min and 300 mg catalyst.

Results/Discussion

Seven CoMo/Al₂O₃ samples were synthesized by one flame FSP. Four samples contained 8, 16, 24 and 32 wt.% Mo with a Co/Mo atomic ratio of 1/3 (alumina balance), and two samples 16 wt.% Mo with Co/Mo atomic ratio 2/3 and 1/1 and finally one unsupported reference sample

with Co/Mo atomic ratio 1/3. The catalysts had specific surface areas between 221 and 90 m²/g, with decreasing surface area with increasing transition metal content. This corresponds to average primary particle sizes of 7 to 13 nm, showing that nanoparticles were the product of the flame synthesis.

The activities of the catalysts for removal of heterocyclic sulphur and nitrogen were measured after sulfidation. The best catalysts contained 16 wt.% Mo (atomic ratio Co/Mo = 1/3). With approximately 75% of the activity of a commercial alumina supported CoMo catalyst this is strikingly good. Increasing the Co content in the FSP material caused a small drop in activity, while increasing or decreasing the Mo content resulted in significantly lower activity. TEM images of the FSP made oxides confirmed that the primary particles were nano-sized and images of the sulfided catalysts showed a significant increase in MoS₂ particles size with increasing Mo content, explaining the lower activity of the high Mo loaded catalysts (Fig. 1).

X-ray diffraction (XRD) and UV-vis reflectance spectroscopy revealed that the oxide precursor contained γ -Al₂O₃ with some CoAl₂O₄ spinel, while MoO₃ was XRD amorphous. The CoAl₂O₄ spinel is unwanted since the cobalt does not promote the MoS₂ active phase. Experiments of suppressing this phase are under way.

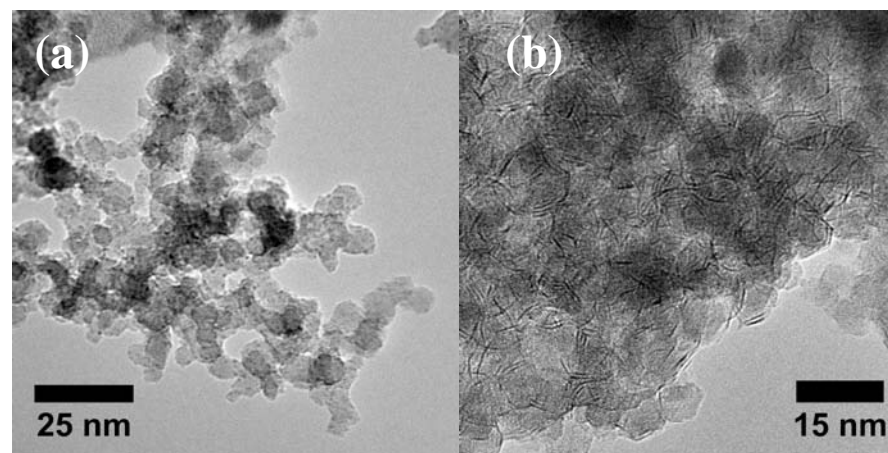


Figure 1: TEM images of 16 wt.% Mo (Co/Mo = 1/3) oxide (a) and sulfide (b).

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