Influence of the preparation method on the hydrodesulphurization activity of MoS_2/Al_2O_3 extrudates: A Raman micro-spectroscopy study on the genesis of the active phase

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Introduction

For the industrial preparation of MoS_2/Al_2O_3 hydrodesulphurization (HDS) catalysts, a solution containing Mo(VI)-complexes is generally applied to mm-sized Al_2O_3 bodies, after which drying, calcination and sulphidation is carried out to yield the active material. A homogeneous distribution of metal-complexes over the catalyst bodies is generally desired for optimal efficiency of the final catalyst [1]. Furthermore, the activity of the MoS_2 phase, achieved after sulphidation, is dependent on the nature of the Mo-oxide phase on the Al_2O_3 support obtained after calcination. The application of Raman microscopy makes it possible to monitor both the distribution and the nature of Mo-oxo-complexes during the preparation of these Mo/Al_2O_3 catalyst bodies [2,3]. In this way, the physicochemical processes that occur during the preparation of these oxidic precursors can be studied in great detail [4].

Materials and Methods

Pore volume impregnation was carried out on cylindrical Al_2O_3 extrudates (∅ 1.5 mm, SA 200 m^2/g, PV 0.7 ml/g) with aqueous solution solutions containing different Mo(VI)-complexes. Raman micro-spectroscopy was carried out on bisected catalyst bodies, as schematically depicted in Fig. 1. The activity of the catalysts was evaluated in the HDS of an industrial light gas oil fraction.

Results and Discussion

The deposition of an $Al(OH)_6Mo_6O_{18}^{3-}$ salt was detected on the external surface of the extrudates, when impregnation was carried out with an ordinary $(NH_4)_6Mo_7O_{24}$ (AHM) solution. Using in-situ Raman microscopy, the transformation of this crystalline phase into bulk MoO_3 during calcination was observed. The formation of $Al(OH)_6Mo_6O_{18}^{3-}$ could be prevented by using basic Mo(VI)-solutions. However, the poor interaction between the MoO_4^{2-} and the Al_2O_3 surface lead to a non-homogeneous distribution of Mo-complexes after drying. As a result, crystalline Mo-oxide phases were formed near the outer surface of the extrudates during calcination. None of these problems were encountered when impregnation was carried out with Mo-citrate solutions. In this case a well-dispersed Mo-oxide phase was formed on the support and a homogeneous distribution of the active phase over the catalyst bodies was observed. The amount of crystalline MoO_3 formed in these systems could be estimated by quantitative Raman measurements on powdered extrudates.

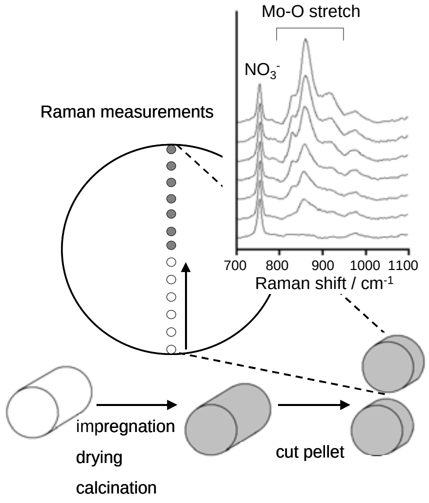

Figure 1. *Layout of a Raman micro-spectroscopy measurements on bisected catalyst extrudates.*

The relation between the dispersion of the Mo-oxide and the active MoS_2 phase was studied through the application of STEM on sulfided catalyst extrudates. The formation of crystalline Mo-oxide material resulted in the formation of a poorly dispersed MoS_2 phase after sulphidation. Furthermore, a direct relationship was found between the dispersion of the Mo-phase in the oxidic precursor and the HDS-activity of the final catalysts. The catalysts prepared from Mo-citrate solutions therefore showed superior activity

Significance

Raman micro-spectroscopy provides a way of studying the nature and distribution of metal-ion complexes in supported catalyst extrudates in all the stages of their preparation. Since the formation of crystalline material is generally to be avoided in the preparation of supported metal-oxide catalysts, its inherent sensitivity for the detection of these phases provides an opportunity for the application of the technique in quality control systems.

References

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