NMR imaging as a non-invasive technique to study the preparation of supported catalyst bodies

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Introduction

Supported catalysts are generally prepared by impregnation of a porous support with a metal-precursor solution, followed by drying and further processing to obtain the desired active phase. The efficiency of the final catalyst is strongly dependent on the nature and distribution of the active component. Both properties are influenced by the conditions in the impregnation procedure and the drying stage. Therefore, control of the preparation process is essential. Recently, micro-spectroscopy methods were developed to study the physico-chemical processes during the preparation of supported catalyst bodies. Information is obtained through analysis of bisected catalyst bodies at different stages of the preparation [1,2]. In this paper, magnetic resonance imaging (MRI) is presented a promising technique for the *in situ* study of supported catalyst preparation [3].

Materials and Methods

Pore volume impregnation was carried out on cylindrical Al_2O_3 extrudates (∅ 3.8 mm, length 10 mm, SA 150 m^2/g, PV 0.38 ml/g) with aqueous solution solutions containing different metal salts such as $Co(NO_3)_2$, $Ni(NO_3)_2$, $(NH_4)_6Mo_7O_{24}$ and H_2PtCl_6 and additives such as citrate and phosphate. ^{1}H, ^{13}C and ^{31}P images were recorded on these system in the cause of the ageing process using a Bruker Avance DRX 300 MHz wide bore spectrometer with imaging accessories.

Results and Discussion

Multinuclear NMR imaging has been employed to study the distribution of the active components and additives inside catalyst extrudates during the preparation of (Co)Mo/γ-Al_2O_3 hydrotreating catalyst. The influence of various parameters in the impregnation procedure (pH, concentrations, presence of additives in the impregnation solution) has been studied. The technique was applied to characterize both wet extrudates after impregnation and dried samples.

^{1}H NMR imaging can be used to monitor the distribution of metal-complexes inside extrudates during the preparation of (Co)Mo/γ-Al_2O_3 extrudates in an indirect manner. The paramagnetic influence of Co^{2+} ions and the diamagnetic influence of $Mo_7O_{24}^{4-}$ ions on the relaxation times of water protons were used to study the transport of these components in support bodies after dry impregnation. Citric acid was added to the impregnation solution to control the transport rate of metal-complexes inside the extrudate and the distribution of the active component after drying. On the basis NMR imaging and UV-VIS micro-spectroscopy data, the influence of citrate concentration and pH on the transport of cobalt-complexes was explained. As an example, Fig. 1 shows the distribution of Co^{2+} inside extrudates at several points in time after impregnation with a $Co(NO_3)_2$/citric acid solution. It can be seen that the addition of citric acid leads to the formation of an egg-yolk type catalyst due to competitive adsorption of citrate to the Al_2O_3 surface. The same indirect NMR imaging method was used to study the distribution of the active components (Co, Mo) inside dried catalyst bodies.

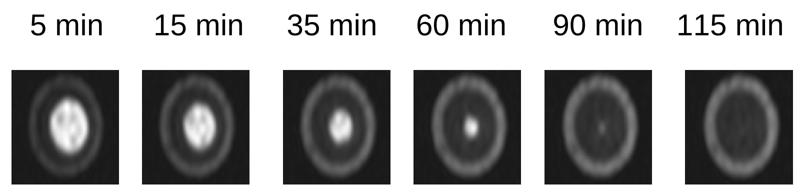

Figure 1. *^{1}H images recorded on Al_2O_3 pellets after impregnation with a 0.2 M $Co(NO_3)_2$, 0.4 M citric acid solution. The dark areas in these images represent the presence of Co^{2+} ions*

The ^{31}P NMR signal of phosphate and the ^{13}C NMR-signal of (^{13}C labeled) citrate were detected after the impregnation of support bodies in order to follow the transport of these industrially relevant additives in a direct manner.

Significance

MRI provides a way of studying the dynamics of pore volume impregnation in great detail without disturbing the processes under study. This yield interesting opportunities for fundamental studies into the preparation of supported catalyst bodies.

References

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