

On the interaction between Co- and Mo-complexes in impregnation solutions used for the preparation of Al₂O₃-supported HDS catalysts: A combined Raman/UV–vis–NIR spectroscopy study

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Abstract

Research has been carried out on the formation of cobalt (Co) and molybdenum (Mo) complexes in CoMo-solutions, which are used for the preparation of Al₂O₃-supported hydrodesulphurization (HDS) catalysts. Aim of this study was to obtain more insight into possible Co–Mo interactions and their implications for the impregnation process. For this purpose, Raman and UV–vis–NIR spectroscopy has been carried out on different impregnation solutions at various pH. In addition, multivariate curve resolution (MCR) of the Raman spectra has been applied to obtain information on the molecular structure and speciation of the different complexes present in solution. Furthermore, Raman microscopy and SEM-EDX were applied on Al₂O₃ extrudates after impregnation, to obtain information on the distribution of the different metal-ions into the catalyst body as a function of time. It is demonstrated that an interaction between Co(II)-cations and different molybdate anions is indeed present in CoMo-solutions. Two different CoMo-complexes are proposed in which Co²⁺-cations are bound to the outside of H_xMo₇O₂₄^{(6-x)-} complexes, resulting in a simultaneous transport of the Co and Mo metal–precursor complexes. Since Co acts as a promotor, a close interaction between Co and Mo in the final catalyst is of major importance for the catalytic activity. As such, the interaction should also be taken into account in the preparation of supported CoMo–HDS catalysts.

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1. Introduction

Understanding the interaction between a metal-ion precursor and a support surface is a prerequisite for a controlled preparation of supported catalysts [1–3]. Especially in the field of supported (Co/Ni)Mo hydrodesulphurization catalysts, this interaction has a large influence on the nature and dispersion of the (Co/Ni)MoS₂-phase and hence on the activity of the final catalyst. It is therefore of prime importance to know the speciation of metal-ion complexes in impregnation solutions. The classical precursor salt for the synthesis of Mo(VI)-containing impregnation solutions is (NH₄)₆Mo₇O₂₄ (AHM). For that reason, the speciation of Mo(VI)-complexes in AHM-solutions has been extensively studied and well established [4–8]. Potentiometric titrations and spectroscopic techniques

have been applied to derive formation constants of the different anions that can be present in aqueous solution. It was found that tetrahedral MoO₄²⁻ anions are present at low Mo-concentrations and high pH. The formation of isopolyanions takes place at higher concentrations in acidic solutions, while H_xMo₇O₂₄^{(6-x)-} complexes are found to be dominant in solutions of pH 3–6. At lower pH the formation of larger clusters, such as H_xMo₈O₂₆^{(4-x)-} has been reported as well. Furthermore, Mo-isopolyanions are known to react with various cations in solution to form so-called heteropolyanions. The complexation of trivalent cations, such as Al³⁺ [8,9], Cr³⁺ [10] and Co³⁺ [11] by Mo-anions has been demonstrated to result in the formation of Anderson-type complexes in acidic environment. Murase et al. reported on the formation of complexes with NiMo₆ stoichiometry in acidic NiMo solutions, for which they propose a similar structure [6]. In view of these findings, it is a logical step to study a possible interaction between Co²⁺-cations and Mo-anions in CoMo-solutions in the absence of complexing agents.

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This paper describes the results of a characterization study to determine the formation of Mo(VI)-complexes in AHM and AHM/Co(NO₃)₂ solutions as a function of pH, using UV–vis–NIR and Raman spectroscopy. The speciation of the different isopolymolybdate complexes and their reference spectra have been derived by means of multivariate curve resolution (MCR). In addition, SEM-EDX and Raman microscopy have been used to evaluate the effect of the interaction between Co²⁺-cations and Mo-anions on the transport rate of these complexes inside Al₂O₃ extrudates after impregnation, since these spatially resolved techniques are known to be useful to elucidate the chemical and physical processes that play a role during the preparation of supported catalyst bodies [12–14].

2. Experimental

The compositions of the solutions used for spectroscopic studies are listed in Table 1. (NH₄)₆Mo₇O₂₄ (Acros, p.a.) and Co(NO₃)₂·6H₂O (Acros, p.a.) were used for the preparation of these solutions. For Raman measurements on Mo-solutions, NH₄NO₃ (Acros, p.a.) was added to serve as an internal standard. Concentrated NaOH (Merck, p.a.) and HCl (Merck, p.a.) solutions were used for pH adjustment. Care was taken that the concentration of the components under study was not altered during measurements.

Raman spectra were recorded on the different solutions using a Kaiser RXN spectrometer equipped with a 70 mW, 532 nm diode laser for excitation. The data point resolution in these spectra, which were subject to baseline correction before analysis, is 2 cm⁻¹. The NO₃⁻ peak at 1044 cm⁻¹ was used as an internal standard and spectra were scaled to this band. UV–vis–NIR measurements (250–1100 nm) were carried out on the solutions in series 2 using a Varian Cary 50 spectrophotometer equipped with a Hellma immersion probe. UV–vis–NIR spectra were recorded on the solutions in series 3 in the spectral range of 200–1350 nm on a Varian Cary 500 spectrophotometer with water as the reference. The data point resolution of the UV–vis–NIR measurements was 1 nm. All measurements were carried out under ambient conditions (298 K).

Impregnation was carried out on cylindrical Al₂O₃ extrudates of 1.5 mm diameter and an average length of 10 mm. The pore volume of this material was 0.80 ml/g and its surface area was 300 m²/g. Impregnation was carried out on 20 g batches of extrudates with a 1.0 M Mo/0.2 M Co solution prepared from AHM and Co(NO₃)₂. Care was taken that the extrudates were completely wetted by the solution. Drying was carried out by passing hot air onto the wet extrudates. Drying

Table 1
Composition of Mo- and CoMo-solutions used for spectroscopic studies

[Mo] (M)	[Co] (M)	[NO ₃ ⁻] (M)	pH	<i>n</i>	Technique
0.1	–	0.1	2.11–8.24	26	Raman
0.1	0.1	0.1	2.00–5.96	19	Raman
					UV–vis–NIR
0–0.40	0.04	0.08	5.0	8	UV–vis–NIR

The concentration (*M*), the pH range, the technique applied and the number of spectra (*n*) that were recorded in each titration series are included.

was regarded to be complete when the temperature of the catalyst bed had reached 120 °C. One batch of material was dried 5 min after impregnation, while another batch was allowed to age in a closed container for 3 h before drying. Scanning electron microscopy was performed in combination with energy-dispersive analysis of X-rays (EDX). Samples were embedded in Castoglas and polished on SiC paper with 2-propanol. Samples were then carbon-coated and line scans were recorded across the cross-section of bisected extrudates with a step-size of 10 μm at a 20 kV acceleration voltage. For comparison, extrudates were also impregnated with a 1.0 M Mo AHM-solution and a 0.2 M Co(NO₃)₂ solution. Raman spectra were recorded on bisected dried extrudates using a Kaiser RXN spectrometer equipped with a 785 nm diode laser in combination with a Hololab 500 Raman microscope. A 10× objective was used for beam focusing and collection of scattered radiation, resulting in a spot size on the sample of approximately 50 μm diameter. The extrudates were calcined at 500 °C for 1 h in static air. Upon calcination the color of the samples containing Co changes from pink to blue, which made it easier to observe the distribution of this metal-ion in bisected extrudates.

3. Results and discussion

3.1. Mo-solutions

In industrial catalyst preparation, impregnation solutions with high Mo-concentrations (typically exceeding 1.0 M Mo) are used to obtain high Mo-loadings in the final catalyst. However, at these concentrations, formation of larger Mo(VI)-clusters at low pH results in the precipitation of Mo(VI)-salts. Hence, for the spectroscopic investigations described in this section, 0.10 M Mo AHM-solutions were used to study the speciation of Mo(VI)-complexes in a broad pH range. The reaction equations for the formation of H_{*x*}Mo₇O₂₄^{(6-*x*)-} and H_{*x*}Mo₈O₂₆^{(4-*x*)-} polyanions from MoO₄²⁻ under acidic conditions are given in Eqs. (1) and (2). The formation constants of the complexes as formulated in Eq. (3), have been determined by different authors with the aid of potentiometric titrations [6–8]. In some cases, the formation of polyanions consisting of 2 or 19 Mo-atoms was proposed, as well. The molecular formulas of the isopolyanions that were considered in the models proposed in the different publications are listed in Table 2 [7].



$$\beta_{\text{mp}} = \frac{[\text{H}_x\text{Mo}_m\text{O}_y]}{[\text{MoO}_4^{2-}]^m [\text{H}^+]^p} \quad (3)$$

Raman spectra recorded on 0.10 M Mo solutions in the pH range 2–8 are presented in Fig. 1. The theoretical speciation of Mo(VI)-complexes in these solutions was determined from the formation constants of isopolyanions reported by different authors [4,7,8,15]. The resulting concentration plots are

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