Monitoring the preparation of (Co)Mo/Al₂O₃ extrudates using spatially resolved spectroscopic techniques

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1. Introduction

Supported catalysts are of critical importance for our present day society, as they play a role in industrial processes such as oil refining, chemicals manufacturing and environmental applications [1]. The structure of these systems is complex. The active phase consists of **nm-scale** metal clusters, or metal sulfide and metal oxide phases deposited into the 10-100 nm pores of **mm-scale** support bodies. For optimum activity of the final catalyst, control on all these different length scales is required. In contrast to this complexity straightforward techniques are being used in the industrial preparation of supported catalysts. Pore volume impregnation, in which the active phase is applied to **pre-shaped** porous support bodies by addition of a metal-salt solution, is generally the method of choice [2]. The interaction between the different components in the impregnation solution and the support surface can have a large impact on the nature and distribution of metal oxide complexes in the final catalyst. An irreversible reaction of metal oxide complexes with the support or a strong (electrostatic) adsorption can bring about an eggshell distribution of the metal oxide phase after impregnation. A weak interaction on the other hand can lead to a redistribution of the metal oxide complexes during drying [3]. Although several studies dedicated to the physicochemical processes during the preparation of supported catalyst bodies have revealed the importance of these phenomena, characterization was always carried out after completion of the preparation process. Recently, spatially resolved spectroscopic techniques were developed that allow to monitor the nature and distribution of metal oxide precursors inside supported catalyst bodies, during their preparation [4-6]. Cobalt-promoted MoS₂ catalyst extrudates are still the main catalysts for the **hydrotreatment** of fuel streams [7]. Industrial impregnation solutions often

contain complexing agents, such as phosphate or organic compounds besides Mo-complexes and Co-complexes. In this paper it will be shown how a multi-technique approach can be applied to monitor the nature and macro-distribution of all components in the impregnation solution, throughout the preparation procedure of these materials. Due to the high Raman cross-section of Mo-O vibrations, Raman microscopy is ideally suited to study the speciation of Mo-complexes inside catalyst bodies [6]. The d-d transitions of Co^{2+} -complexes that can be observed by UV-Vis micro spectroscopy yield detailed information on the nature and distribution of the Co-precursor in the extrudates [4, 8, 9]. The experimental procedure used for the spatially resolved Raman and UV-Vis spectroscopy measurements are depicted in Figure 1. Analysis is carried out on bisected extrudates after impregnation, drying and calcination. Section 2 and 3 deal with the application of these techniques on $(\text{Co})\text{Mo}/\text{Al}_2\text{O}_3$ pellets.

Fig. 1. Lay out of a spatially resolved Raman and UV-Vis spectroscopy experiment on bisected pellets (left) and a non-invasive MRI experiment (right).

The application of Magnetic Resonance Imaging (MRI) in these studies provides the additional advantage that characterization can be carried out in a non-invasive manner. This is also illustrated in Figure 1. After **impregnation**, the **extrudate** is simply placed into the **RF-coil** of the spectrometer. A multinuclear MRI technique allows for the detection of the ¹H, ¹³C, ³¹P and ¹⁹⁵Pt NMR-signal [5]. The transport of phosphate and organic complexing agents can be monitored in a direct way, by determining the distribution of P and ¹³C nuclei inside extrudates after impregnation.

2. Raman spectroscopy

2.1. Introduction

The application of Raman micro-spectroscopy to study the preparation of Mo/Al₂O₃ pellets is evaluated in this section. The influence of the addition of citrate to (NH₄)₆Mo₇O₂₄ (AHM) impregnation solutions is investigated. Raman spectra are recorded on bisected pellets at different points in time after impregnation to monitor the transport of Mo-complexes during the ageing process. A similar analysis is carried out to evaluate the dispersion and distribution of the MoO_x phase in the pellets after calcination.

2.2. Experimental

Cylindrical γ -Al₂O₃ pellets (PV 1.1 ml/g, SA 200 m²/g) of 3 mm diameter and height were impregnated to incipient wetness with 1 M Mo (ex AHM) and 1 M Mo (ex AHM), 1 M citric acid solutions, yielding a MoO₃ loading of 14 wt% in the calcined catalyst. NH₄NO₃ was added to the impregnation solution in a 1 M concentration, to serve as an internal standard in measurements on pellets after impregnation. After ageing for 24 h, the pellets were dried at 120°C and calcined at 500°C in static air for 2 h. Raman spectra were recorded on bisected pellets at several points in time after impregnation and after drying and calcination. Measurements were performed using a Kaiser RXN spectrometer equipped with a 785 nm diode laser in combination with a Hololab 5000 Raman microscope. A 10x objective was used for beam focusing and collection of scattered radiation, resulting in a spot size on the sample of approximately 50 μ m.

2.3. Results and discussion

After impregnation, the solution is instantly adsorbed due to the capillary forces created by the pore-system of the support. Components in the impregnation solution, that have a weak interaction with the Al₂O₃ surface, such as NO₃⁻, travel with the flow of the solution and a homogeneous distribution of these anions is established almost instantaneously. The NO₃⁻ peak in the Raman spectra can therefore be used as an internal standard. The distribution of the Mo-complexes in the bisected pellets can be obtained from the intensity ratio of the MoO₂ and NO₃⁻ peaks in Raman spectra recorded at different positions inside the pellets. Mo₄(citrate)₂O₁₁⁴⁻ complexes are present in the Mo-citric acid impregnation solution and are found to remain stable inside the Al₂O₃ pores after impregnation. In Fig. 2, Raman spectra recorded at different positions

inside the pellets, 30 min and 3 h after impregnation with the Mo-citrate solution are presented. The $\text{Mo}_4(\text{citrate})_2\text{O}_{11}^{4-}$ distribution plots obtained from these spectra are presented in the same figure. It can be seen that in contrast to NO_3^- , an inhomogeneous distribution of Mo-complexes exists 30 min after impregnation. It takes up to 3 h before equilibration is complete and $\text{Mo}_4(\text{citrate})_2\text{O}_{11}^{4-}$ is present in equal concentration throughout the pellets. As a result of the acidity of the impregnation solution ($\text{pH} \sim 1$), protonation of the surface hydroxyls will take place and the net charge of the surface is positive [10]. Probably, a strong Coulomb interaction between the highly negatively charged Mo-complexes and the surface therefore exists and transport of these anions is a slow process [11].

Fig. 2: Plots showing the distribution of $\text{Mo}_4(\text{citrate})_2\text{O}_{11}^{4-}$ inside Al_2O_3 pellets 30 and 180 min after impregnation with a Mo-citrate solution. The corresponding spectra recorded near the core of the pellet (a), near the outside of the pellet (b) and on the exterior surface (c) are presented on the right for the same samples.

Impregnation with the AHM-solution (without citric acid) at its natural pH of 5 leads to the formation of $\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}^{3-}$ at the external surface of the pellets [12]. Intense peaks at 947, 899, 567 and 351 cm^{-1} indicate the presence of a $\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}^{3-}$ precipitate, as shown in Fig. 3 [13]. The formation of this compound is the result of a reaction between Mo-oxo-anions and Al^{3+} , created by dissolution of the support at low pH, as shown in Eq. 1. Inside the pellets, isolated MoO_4^{2-} and $\text{Mo}_7\text{O}_{24}^{6-}$ anions are present as far less intense bands are observed at 896 and 940 cm^{-1} respectively. Although $\text{Mo}_7\text{O}_{24}^{6-}$ is the only complex present in the AHM impregnation solution, the protonation of basic hydroxyls leads to an increase of the pH of the solution inside the pores. As a result, MoO_4^{2-} is formed as the reaction in Eq. 2 proceeds to the right.

The precipitation of $\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}^{3-}$ during impregnation has severe consequences for the nature of the Mo-phase obtained after calcination. The formation of crystalline MoO_3 (990, 815, 662, 373, 333, 284 and 237 cm^{-1}) was observed in calcined pellets at positions where $\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}^{3-}$ deposits are formed during impregnation (Fig. 3). Apparently, a considerable amount of Mo is contained in this precipitate, resulting in a high Mo-concentration at the external surface of the pellets. Locally, the available Al_2O_3 surface area is then not sufficient to accommodate the MoO_x in an amorphous overlayer and crystalline MoO_3 is formed at these positions.

Fig. 3. Raman spectra recorded near the center (a), near the outside (b) and on the external surface (c), of Al_2O_3 pellets after impregnation with an AHM-solution and after calcination of this material. A 2-D plot of the intensity at 816 cm^{-1} shows the distribution of MoO_3 in the calcined pellets.

2.4. Conclusions

Ligand promoted dissolution of the Al_2O_3 support leads to the precipitation of $\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}^{3-}$ at the external surface of the pellets during the ageing process and the formation of bulk MoO_3 after calcination. The addition of citric acid to the impregnation solutions prevents this reaction ensuring that merely amorphous Mo-oxide phases are formed after calcination.

3. UV-Vis spectroscopy

3.1. Introduction

After impregnation of Al_2O_3 pellets with CoMo solutions, the transport of its different components is monitored using spatially resolved UV-Vis spectroscopy. More specifically, the influence of the addition of citric and

phosphoric acid on the stability of a $\text{H}_2\text{PMo}_{11}\text{CoO}_{40}^{5-}$ heteropolyanion inside the Al_2O_3 pore system is investigated.

3.2. Experimental

Cylindrical $\gamma\text{-Al}_2\text{O}_3$ pellets (PV 1.1 ml/g, SA 200 m^2/g) of 3 mm diameter and height were impregnated to incipient wetness with different 0.5 M Co, 1 M Mo solutions. Catalysts prepared from these solutions would contain 14 wt% MoO_3 and 4 wt% CoO after calcination. Phosphoric acid and citric acid were added to the solutions to study the influence of these complexing agents on the speciation of Co- and Mo-complexes inside the pellets after impregnation. Solution (CoMoP(0.1)) contained phosphate at a concentration of 0.1 M. Another solution (CoMoP(0.3)CA(0.2)) contained 0.3 M phosphate and 0.2 M citric acid.

Fig. 4. Schematic presentation and photo of the UV-Vis micro-spectroscopy set-up used for the spatially resolved UV-Vis measurements on catalyst pellets.

Raman and UV-Vis spectra were recorded on the bisected pellets at several points in time after impregnation. UV-Vis spectra were obtained using a house-built set-up, which is schematically depicted in Fig. 4. The use of optical fibers with different diameter allows one to record a UV-Vis spectrum from a small spot of 50–100 μm on the sample. Manipulation of the sample can be carried out with great precision with the aid of an automated X-Y-Z-table. The sample is placed in an environmental cell under water-saturated air to prevent dehydration of the wet pellets during measurements.

3.3. Results and discussion

From an extensive spectroscopic study on the speciation of complexes in CoMoP-solutions, it was found that 90% of all Mo present in the CoMoP(0.1) solution is contained in a $\text{H}_2\text{PMo}_{11}\text{CoO}_{40}^{7-}$ heteropolyanion [8]. This specific complex is stable in acidic CoMo-solutions at P:Mo ratios between 0.05 and 0.2. $\text{H}_2\text{PMo}_{11}\text{CoO}_{40}^{7-}$ in solution shows distinct bands in Raman (971 cm^{-1}) and UV-Vis spectroscopy (17800 cm^{-1} and 22000 cm^{-1}) and is therefore an ideal candidate to evaluate the use of the spatially resolved Raman and UV-Vis techniques in catalyst preparation. Furthermore, heteropolyanions containing both Co and Mo are considered as interesting precursors for the CoMoS active phase [14, 15]. UV-Vis spectra recorded on pellets after impregnation with the CoMoP(0.1) solution are presented in figure 5. 15 min after impregnation, Mo-complexes are present only near the outside of the pellets. The O-Mo⁶⁺ charge transfer band in the UV-Vis region is only observed in spectra recorded at these positions. This slow transport of Mo-complexes is in line with the observations in the previous paragraph (Fig. 2). At the same time, Co²⁺ is present throughout the pellets as the d-d transition band is observed for all positions. After 180 min, a homogeneous distribution of Mo-complexes is obtained. However, the position of the d-d transition band at 19300 cm^{-1} shows that $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is present throughout the support. Clearly, a disintegration of the heteropolyanion has taken place inside the Al₂O₃ pore system. This is most likely caused by a reaction of phosphate with the Al₂O₃ surface, resulting in a withdrawal of phosphate from the solution inside the pores. Adsorption of phosphate is reported to proceed on basic hydroxyl groups (Al₃OH), as presented in Eq. 3. and/or on coordinatively unsaturated Al³⁺-sites on the Al₂O₃ surface at low pH [16]. A disintegration of the heteropolyanion and the formation of $\text{H}_x\text{Mo}_7\text{O}_{24}^{(6-x)-}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is the result.

$\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}^{(6-x)-}$ and $\text{Mo}_4(\text{citrate})_2\text{O}_{11}^{4-}$ complexes are present in the CoMoP(0.3)CA(0.2) impregnation solution, while all Co is contained in $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ [8]. After impregnation with this solution, a slow transport of Mo-complexes is again observed as the O-Mo⁶⁺ charge transfer band is absent in spectra recorded near the center of the pellet, 15 min after impregnation. After 240 min, a homogeneous distribution of Mo-complexes is obtained and the appearance of a band at 17600 cm^{-1} indicates that $\text{H}_2\text{PMo}_{11}\text{CoO}_{40}^{5-}$ heteropolyanions are actually formed at all positions in the pellets. This was confirmed by Raman spectroscopy, where a peak at 971 cm^{-1} was observed in spectra recorded at all positions in the sample. In the impregnation solution, the

phosphate concentration is too high to allow for the formation of $\text{H}_2\text{PMo}_{11}\text{CoO}_{40}^{5-}$ and $\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}^{(6-x)-}$ is formed instead. However, the reaction of phosphate with the support leads to a decrease of the phosphate concentration inside the pores. Apparently, after withdrawal of phosphate from the solution, its resulting concentration in the pore system is just right for the formation of the heteropolyanion. The reaction of phosphate with the Al_2O_3 surface results in an increase in pH of the solution inside the Al_2O_3 pores, as can be seen in Eq. 3. Therefore, the addition of citric acid to the solution is probably required to make sure the pH is sufficiently low for the formation of $\text{H}_2\text{PMo}_{11}\text{CoO}_{40}^{5-}$.

3.4. Conclusions

Impregnation of Al_2O_3 pellets with a solution containing $\text{H}_2\text{PMo}_{11}\text{CoO}_{40}^{5-}$ heteropolyanions leads to the disintegration of this complex due to a reaction of phosphate with the Al_2O_3 support. As a result of their stronger interaction with the surface transport of Mo^{6+} -complexes proceeds much slower than that of Co^{2+} -complexes when acidic CoMo impregnation solutions are used. $\text{H}_2\text{PMo}_{11}\text{CoO}_{40}^{5-}$ can be stabilized inside the pellets by the addition of additional phosphoric and citric acid.

Fig. 5. UV-Vis spectra recorded at different positions inside the Al_2O_3 support bodies, 15 min and 180 min after impregnation with CoMoP(0.1) solution, and, 15 min and 240 min after impregnation with the CoMoP(0.3)CA(0.2) solution. The distance from the core of the pellets is indicated on the right.

4. Magnetic Resonance Imaging

4.1. Introduction

The results in the previous section showed the large influence of complexing agents on the speciation of metal oxide complexes in CoMo/Al₂O₃ pellets. Unfortunately, Raman and UV-Vis spectroscopy do not allow for the direct detection of these compounds in the catalyst bodies. In this section, it is shown how MRI can be used to monitor the transport of phosphate in Al₂O₃ extrudates. Furthermore a general perspective is given on the applicability of MRI techniques in catalyst preparation studies.

4.2. Experimental

A dry Al₂O₃ extrudate (PV 0.43 ml/g, SA 180 m²/g) was immersed into an aqueous solution of H₃PO₄. Two-dimensional imaging was performed on this extrudate using 2-pulse spin-echo sequence in the plane transverse to the sample axis without slice selection. In this way, the distribution of ¹H and ³¹P nuclei in the extrudate can be determined. Subsequently, an Al₂O₃ extrudate, saturated with water was placed in a cylindrical NMR sample tube (4.2 mm i.d.) containing a 0.76 M H₃PO₄ solution and the same measurements were performed every 4 min. Cylindrical γ -Al₂O₃ extrudates, 3.2 mm in diameter and 12 mm long, were used in these experiment. All imaging experiments were performed on a Bruker Avance DRX 300 MHz spectrometer equipped with imaging accessories.

4.3. Results and discussion

The distribution of ¹H and ³¹P nuclei in the dry Al₂O₃ extrudate immersed in the H₃PO₄ solution is presented in Figure 1. From the equal intensity of the ¹H signal recorded throughout the sample, it can be concluded that the pores in the entire extrudate are instantly filled with the impregnation solution. However, as a result of the interaction of phosphate with the support surface, its transport is slow and the presence of ³¹P nuclei is only detected near the outside of the extrudate. The transport of the phosphate is further monitored in the experiment with the pre-soaked extrudate.

Figure 6: ^{31}P images showing the distribution of phosphate in a single Al_2O_3 extrudate 5 min (a), 60 min (b), 90 min (c), 120 min (d), 170 min (e), 200 min (f), 250 min (g), 325 min (h), 350 min (i), 375 min (j), 400 min (k), and 1100 min (l) after immersion into a 0.76 M H_3PO_4 solution.

Figure 6 shows a sequence of images detected on this extrudate using the ^{31}P NMR signal. A slow transport of phosphate is observed, as it takes approximately 1 day before the phosphate reaches the center of the extrudates. This points to a strong interaction between phosphate and the support. These measurements are in line with the observations in part 3, where a decrease in the phosphate concentration was observed through the disintegration and formation of $\text{H}_2\text{PMo}_{11}\text{CoO}_{40}$ in an indirect manner. A similar approach can be used to monitor the distribution of complexing agents such as citric acid and nitrilotriacetic acid using ^{13}C MRI, although enriched samples will probably have to be used, due to the low natural abundance of this nucleus.

Besides the detection of complexing agents, it is also possible to monitor the distribution of metal oxide complexes inside impregnated Al_2O_3 bodies in a non-invasive manner. When the metal oxide precursor salt contains diamagnetic ions with a large enough magnetogyric ratio, as is the case for V^{5+} , direct imaging of the metal-ion transport becomes feasible [5]. The distribution of paramagnetic cations such as Cu^{2+} and Co^{2+} can be envisaged using an indirect ^1H NMR technique [17]. The presence of these cations leads to a decrease in the T_1 and T_2 relaxation time of the solvent protons and a decrease in the ^1H NMR signal at these positions. The concentration of paramagnetic cations can thus be derived from the intensity in the ^1H NMR signal.

Diamagnetic cations that adsorb to the Al_2O_3 surface can have an effect on the T_1 relaxation time of solvent protons inside the Al_2O_3 pores. A decrease of the nuclear spin-lattice relaxation time is generally observed for a liquid filling the

pores of the Al₂O₃ support, as compared to a regular solution. Probably, this is partly due to liquid-surface interactions. It is observed that the adsorption of Pt⁴⁺ complexes to the Al₂O₃ surface increases the T₁ relaxation time of the water inside the pores [18]. Using a special pulse sequence, by which T₁ weighted images are recorded, it is possible to detect the distribution of these complexes inside the Al₂O₃ extrudates. The presence of Mo⁶⁺ complexes absorbed to the Al₂O₃ surface can be expected to have a similar effect, yielding possibilities for the investigation of CoMo/Al₂O₃ systems.

4.4. Conclusions

The transport of phosphate in Al₂O₃ extrudates can be monitored in a non-invasive manner using MRI and is found to be extremely slow when impregnation is carried out with an aqueous H₃PO₄ solution. Although many aspects of the technique are still unexplored, interesting possibilities exist for the direct and indirect detection of metal-complexes and complexing agents inside catalyst bodies.

5. Conclusions

The examples described in this paper clearly illustrate the potential of spatially resolved spectroscopic techniques for studying the preparation of supported catalysts. By using a combination of techniques, the nature and distribution of all components of the impregnation solution can be monitored. Through insight into the physico-chemical processes that take place, a better control of the preparation process can be obtained. Studies are ongoing to determine the influence of preparation on the catalytic activity of Co/Al₂O₃ Fischer-Tropsch and Mo/Al₂O₃ HDS catalysts.

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