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Heterogeneous Catalysis

Chemical Probing within Catalyst Bodies by Diagonal Offset Raman Spectroscopy**

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Metal oxides dispersed on porous support materials are widely used as heterogeneous catalysts in oil-refining, environmental applications, and the manufacturing of bulk and fine chemicals. These millimeter-sized catalysts owe their activity to the formation of highly dispersed metal/metal oxide species possessing particular oxidation and coordination states.[1] Their efficiency depends on the kind of species formed, micro-distribution, and stability of the active phases. It is therefore of importance to understand the physical and chemical processes involved in the preparation of active catalysts.

Recently, space- and time-resolved techniques have been developed and carried out on several catalyst systems to study the interactions between the active species and the support surface in catalyst bodies. These techniques include Raman,[2] UV/Vis,[3] and IR[4] micro-spectroscopy, magnetic resonance imaging (MRI),[5] X-ray microscopy, and X-ray imaging.[6] However, these techniques have their limitations. To date the interiors of catalyst bodies can only be imaged invasively by Raman, UV/Vis, and IR spectroscopy by bisecting the sample for measurement. MRI is an indirect technique as it uses the ^{1}H NMR signal intensity of water to derive the micro-distributions of the catalytic phase. Complementary X-ray absorption tomography methods provide only contrast images and cannot distinguish chemical phases. The diffraction-based methods are non-destructive and provide bulk chemical information and as such allow for in situ studies. However, in the current form we cannot observe non-crystalline materials and require access to synchrotron radiation.

So far, in situ Raman spectroscopy has been used to monitor reactions on the surface of catalyst bodies or to study processes in reactors.[7] Recently, spatially offset Raman spectroscopy (SORS) for bulk measurements has been developed for a variety of applications, specifically measuring Raman spectra beneath the surface of turbid media.[8] SORS is based on the introduction of a spatial offset between the laser illumination and collection areas on the surface of a sample. Metal oxide containing catalyst bodies are porous and could also be likened to turbid media and therefore qualify as species to be studied by SORS. SORS would provide an accessible and invariably non-destructive approach to identify and quantify chemical species in situ in a time-resolved manner.

Our interest has been the development of the SORS technique for the study of catalyst bodies, specifically their preparation and operation. Herein, we report a method, a variant of SORS, which we have termed diagonal offset Raman spectroscopy (DORS), which allows for spatiotemporal in situ studies of catalyst bodies. DORS entails moving the sample diagonally across a laser probe and a collection head thereby increasing the distance between the point of illumination and the point of collection as shown in Figure 1. The laser probe and collector are fixed in position at a 90° angle. We found that the optimum angle for measurement of a cylindrical bulk object, such as a catalyst body, is a radial line at 45° with respect to the laser and/or collector. The extrudate can be rotated through 360° during collection to sample all parts of the object.

We show here the DORS method for studying the preparation of Mo-based catalysts. This catalyst system has previously been investigated by our group by Raman micro-spectroscopy.[2] When combined with Co/Ni these catalysts are used in hydrotreating processes for removal of sulfur, nitrogen, and metals from fuel streams.[9] The first step in the manufacture of Mo/γ-Al_2O_3 catalysts involves incipient wetness impregnation of the catalyst bodies with a solution containing a Mo precursor. The Mo complexes obtained after impregnation have been studied extensively.[10] However,

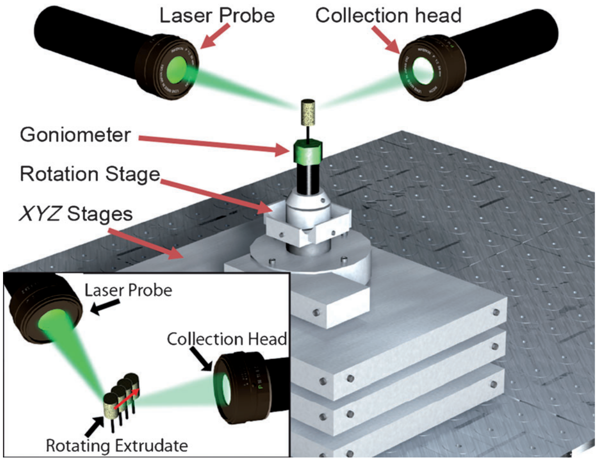

Figure 1. The DORS setup. The catalyst body is moved in *x* and *y* directions to increase the distance between the point of laser illumination and the point of collection.

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these studies, including those performed by our group, were limited to powders or to bisected catalyst bodies. In situ monitoring of the exterior and interior of the Mo-based catalyst bodies during equilibration has not been performed until now.

A proof-of-principle study of DORS has been carried out on a catalyst body showing two different micro-distributions of Mo complexes. A cylindrical γ-Al_2O_3 extrudate was impregnated with a solution containing 1.3 M [Mo] ammonium heptamolybdate (AHM) and 0.65 M phosphoric acid. The extrudate was measured after 30 min of equilibration and subsequent drying at room temperature overnight. To the solution 0.75 M NH_4NO_3 were added to provide an internal standard as nitrate (Raman band at 1049 cm^{-1}) is homogeneously distributed.

2D backscatter Raman maps of the bisected extrudate were obtained by a Raman scanning method developed in house. The maps in Figure 2a show an exterior ring containing $HP_2Mo_5O_{23}^{5-}$[2,11] (Mo-P) with bands located at 370, 395, 885, and 936 cm^{-1}. The backscatter Raman spectra recorded at the core of the extrudate display bands at 936 and 950 cm^{-1}, although the intensity of the latter band is highest. The two bands signify a mixture of Mo-P and $(NH_4)_3[Al(OH)_6Mo_6O_{18}]$, an Anderson-type heteropolyanion[12] with bands at 375, 570, 900, and 950 cm^{-1}, referred to as Al-Mo.

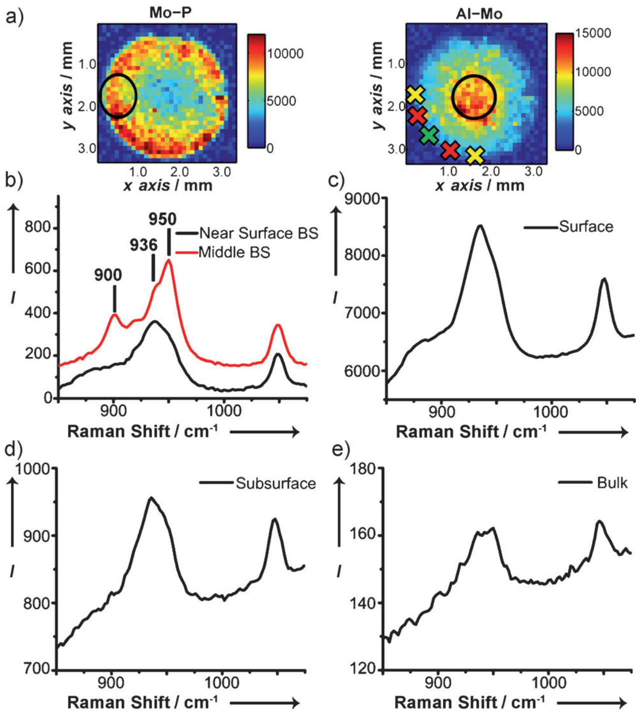

Figure 2. a) 2D backscatter (BS) Raman maps of the intensities of Raman bands of Mo-P (936 cm^{-1}) or Al-Mo (950 cm^{-1}). b) BS Raman spectra near the surface and in the middle of a bisected extrudate (as marked by the black circles). c–e) Raman spectra obtained from the surface, subsurface, and bulk by DORS. The extrudate was impregnated with 1.3 M [Mo] AHM, 0.65 M H_3PO_4, and 0.75 M NH_4NO_3. The green (surface), red (subsurface), and yellow (bulk) crosses on the 2D Raman maps depict the positions of the points of illumination and/or collection for DORS. The spectrum from the bulk represents an average of 20 measurements to improve the signal-to-noise ratio.

A DORS measurement before bisection was conducted rotating the extrudate by 360° with 4.5° steps and three *xy* positions. The positions of the points of illumination and point of collection on the extrudate are schematically shown by the crosses in the 2D maps in Figure 2a. The overall intensity of the Raman bands decrease significantly as the distance between the points of illumination and collection increases because of absorption and scattering of photons. This makes measurement times of 10 s necessary. The surface of the extrudate is measured when the point of illumination and collection overlap (green cross). The corresponding DORS Raman spectrum (Figure 2c) is similar to that obtained in the backscatter mode near the surface (Figure 2b) showing that mainly Mo-P is present. The subsurface is measured when the distance between the point of illumination and collection is increased as depicted by the red crosses. The shoulder at 950 cm^{-1} in the Raman spectrum increases relative to the band at 936 cm^{-1}, corresponding to the increasing concentration of Al-Mo towards the core of the extrudate. The third position is depicted by the yellow crosses. The intensity of the Raman bands of Al-Mo has increased relative to that of Mo-P, showing that for this *xy* position the bulk (surface + interior) is measured. The spatial resolution is close to the spot size for a surface DORS measurement. It increases to the millimeter range when the bulk is measured because of the (multiple) scattering of photons through the sample.[13] The results show that we are able to discriminate between surface and bulk contributions to the Raman spectrum by DORS in an industrially relevant catalyst extrudate.

DORS was used to dynamically measure an incipient wetness impregnation of a cylindrical γ-Al_2O_3 extrudate with a solution containing 1.3 M [Mo] AHM. As an internal standard 0.75 M NH_4NO_3 were added. Before impregnation, the solution at pH 5 mainly contains heptamolybdate ($Mo_7O_{24}^{6-}$) with Raman bands located at 896 and 942 cm^{-1}.[2] The impregnation was carried out in situ on an extrudate in a glassware mounted in the DORS setup. Equilibration times of 5 to 75 min were investigated in 10 min intervals. Three *xy* positions of the sample were used to study surface, subsurface, and bulk identical to the positions depicted by the crosses in Figure 2. The sample was rotated to three positions within a 45° angle in 22.5° steps. The measurements for these three angles were averaged to obtain the Raman spectra displayed in Figure 3.

Upon impregnation, hydration of the alumina surface into aluminum hydroxide-like layers occurs.[14] The pH of the solution in the pores is below the point of zero charge (pzc) of the support (7.8)[15] resulting in protonated hydroxy groups (Al-OH_2^+) on its surface. During the first 15 min of equilibration, Mo is present as $Mo_7O_{24}^{6-}$ (with a vibration band at 940 cm^{-1}). Within 30 min equilibration, $Mo_7O_{24}^{6-}$ reacts with alumina under acidic conditions[2,12] to form $Al(OH)_6Mo_6O_{18}^{3-}$ with Raman bands at 570, 898, and 947 cm^{-1} [Reaction (1)]:

$$12\,Mo_7O_{24}^{6-} + 7\,Al_2O_3 + 27\,H_2O + 30\,H^+ \rightarrow 14\,Al(OH)_6Mo_6O_{18}^{3-} \quad (1)$$

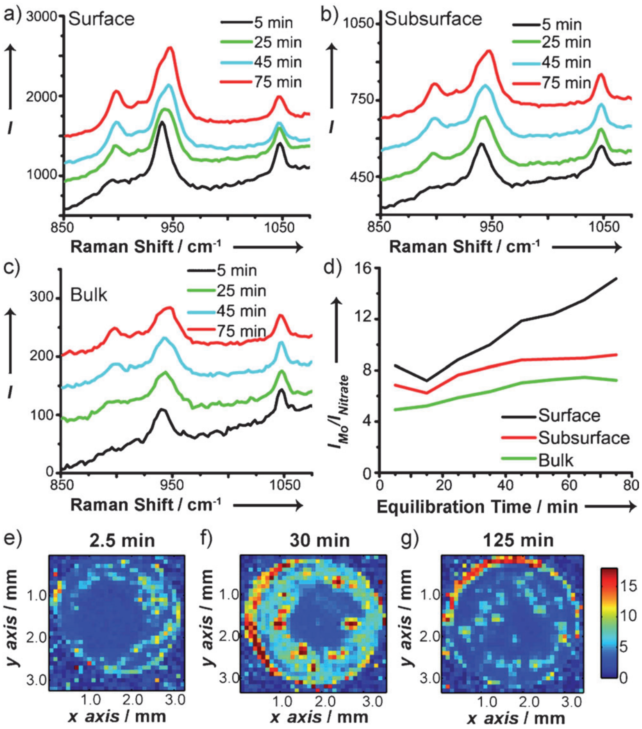

Figure 3. A dynamic DORS measurement of an extrudate impregnated with a solution containing 1.3 M [Mo] AHM and 0.75 M NH_4NO_3. Raman spectra were obtained from the surface, subsurface, and bulk after 5 to 75 min equilibration in 10 min intervals. The intensity of bands from 900–1000 cm^{-1} (I_{Mo}) to the intensity of the 1049 cm^{-1} band ($I_{nitrate}$) ratio is plotted against the impregnation time for surface, subsurface, and bulk. 2D maps of the I_{Mo} to $I_{nitrate}$ ratio obtained in the backscatter mode of a bisected extrudate after 2.5, 30, and 125 min of equilibration followed by overnight drying.

The Raman intensity of Al-Mo increases with equilibration time as more Al-Mo is formed, especially after 45 min equilibration. Heating of the extrudate by laser exposure (for 5 min every 10 min) does not lead to drying of the surface of the extrudate, but does speed up the formation of Al-Mo by 15 min.

The intensity of Mo complex bands is divided by the intensity of the nitrate band to get a relative distribution of the Mo complexes in the extrudate. Figure 3 d shows that the $I_{Mo}/I_{nitrate}$ ratio is higher at the surface than in the bulk indicating that more Mo complex is present near the surface of the extrudate than in the interior. The ratio increases as Al-Mo is formed during equilibration, especially near the surface. The ν(Mo=O) vibration bands at 900 and 947 cm^{-1} are typical for Al-Mo, whereas that at 940 cm^{-1} is typical for $Mo_7O_{24}^{6-}$. The Raman band at 900 cm^{-1} appears later in the bulk indicating that formation of Al-Mo starts near or at the surface of the extrudate. The DORS results suggest a gradient of Al-Mo towards the core of the extrudate during equilibration.

2D Raman scans of bisected extrudates after 2.5, 30, and 125 min of equilibration and subsequent drying overnight have been carried out to confirm the DORS results as shown in Figure 3. Al-Mo is mostly present in the outer shell in the form of hotspots (areas of around 0.1 mm in diameter) and near or at the exterior surface of the extrudate. The center contains Al-Mo at a lower concentration without hotspots. The radius of this center decreases from 1 mm after 2.5 min to 0.5 mm after 125 min of equilibration. This shows a delayed transport of the Mo complexes to the center of the extrudate. The delay is due to the strong electrostatic interaction between the negatively charged Mo complex ions and the positively charged support.[2] The concentration of $Mo_7O_{24}^{6-}$ near the surface of the extrudate is therefore high, moving the equilibration of Reaction (1) to the right. The subsequent formation of hotspots of Al-Mo leads to the observed higher concentration of Al-Mo at the exterior surface of the catalyst body, confirming the results obtained by DORS.

The DORS results show that Al-Mo does not form during 2.5 min equilibration and is only present at low concentration after 30 min of equilibration. The Al-Mo observed in the dried bisected extrudates is therefore formed during the drying process, showing that drying alters the measured micro-distributions of Al-Mo. The non-invasive DORS method circumvents this problem. The formation of hotspots of Al-Mo under wet conditions does not occur until equilibration of 45 min and longer. More hotspots form and grow in size in the region with elevated $Mo_7O_{24}^{6-}$ concentrations during continued equilibration.

The formation of hotspots in Co-Mo/γ-Al_2O_3 catalysts has been reported earlier.[6b] However, the formation of enriched regions in the form of hotspots of Al-Mo in extrudates has not been reported previously by Bergwerff et al.,[2] even though an impregnation solution was used similar to that used here. The support used by Bergwerff et al. had a higher point of zero charge of 8.8–9.0 than that used in this work (7.8). The buffering effect of the support is therefore stronger in the former case, resulting in a higher solution pH in the pores and different species of Mo-complexes. $Mo_7O_{24}^{6-}$ is mainly present at solution pH of 5–6, whereas MoO_4^{2-} is predominant at pH 6 and higher.[16] Because of the buffering influence of the support with higher pzc, $Mo_7O_{24}^{6-}$ was mostly converted to MoO_4^{2-}. Without $Mo_7O_{24}^{6-}$ reaction (1) does not occur and hotspots of Al-Mo do not form. This shows that, in addition to the impregnation solution, the γ-Al_2O_3 support should be chosen according to the desired type of micro-distribution of the active phase.

We have successfully carried out DORS measurements to study the dynamics of incipient wetness impregnation of extrudates previously studied by invasive micro-spectroscopic methods. We are able to distinguish between processes occurring in the exterior and interior of extrudates. The advantage of DORS is that it is non-invasive and can be combined with existing bulk sampling techniques such as X-ray tomography to yield complementary information. The aim for future experiments is to study drying and calcination steps in the preparation of catalyst bodies and to monitor in situ reactions in an extrudate by DORS. These experiments will be carried out in combination with other bulk sampling techniques.

Experimental Section

Extended details of the experimental and DORS method can be found in the Supporting Information. Cylindrical γ-Al_2O_3 extrudates (3 mm in diameter and height) were impregnated with a solution containing 1.3 M [Mo] ammonium heptamolybdate and 0.75 M ammonium nitrate. To the impregnation solution 0.65 M phosphoric acid was added for the static DORS measurement. A tunable 300 mW 532 nm laser set at 35 mW with a spot size of around 100 µm was used for DORS measurements. The laser, optics, and collection software were provided by Cobalt Light Systems. A Kaiser Holograms data acquisition system was used to record the Raman spectra. The collection time was 10 s averaged over three acquisitions. 2D backscatter Raman scans were performed on bisected extrudates at 100 µm intervals using a 15 mW 532 nm Kaiser RamanRxn1. The collection time was 1 s averaged over three acquisitions.

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