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The detrimental effect of exposure to air on supported MoS_2

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Abstract

Although it is hardly ever explicitly discussed, slab-like supported MoS_2 catalysts are not stable upon exposure to air. Transmission electron microscopy studies show that for supported MoS_2, prepared using atmospheric pressure gas-phase sulphidation, particle size decreases upon exposure to ambient air for 24 h, whereas after 1 month of air exposure the number of slabs remaining has decreased significantly. For 40 bar liquid-phase sulphided supported MoS_2, a significant decrease in particle size is observed already after 5 min exposure to ambient air.

Keywords: Molybdenum sulphide catalysts; Stability upon exposure to air; TEM

1. Introduction

Practically all characterisation of (spent) sulphidic catalysts is performed ex situ. This means not only that the catalyst under study is prepared or used in one experimental set-up and the characterisation is performed in another, but also that the catalysts are transported from the one set-up to the other through ambient air, even though many authors try to minimise the time catalysts are exposed to air. This minimisation of exposure to air is often performed by blanketing the catalysts with an inert gas or with a (usually fast-evaporating) liquid. For Raney-Ni catalysts we have shown that this type of blanketing as published in literature leads to different characterisation results from real quasi in situ characterisation (where the catalysts are completely shielded from ambient air between activation and characterisation) [1].

It is often assumed that at least samples of Mo- and W-based hydrotreating catalysts, which have been sulphided and tested under industrial conditions, are not very sensitive to exposure to air, i.e. that their structure and composition do not change to any great extent upon contact with air and moisture from the ambient atmosphere. There may be some truth in this, although it has not been clearly established how much, but it is certainly not warranted to extend the assumption to samples which have been sulphided/tested under (much) milder conditions, and to take keeping the sample under a paraffin (e.g., heptane, decane) as the only precaution (see, e.g., [2–4]). However, already in 1998 the presence of non-slab sulphidic or oxysulphidic entities was reported using ‘quasi in situ’ TEM characterisation, where the catalysts are prepared in a different set-up from the characterisation equipment but exposure to ambient air is prevented by using a glovebox to prepare the TEM specimens, and a special protective-atmosphere TEM transfer holder is used to transport the samples from the glovebox to the microscope without exposure to air [5]. These entities had not been observed previously because the protective-atmosphere TEM transfer holder was not available earlier. Preventing exposure to air between catalyst preparation and TEM characterisation revealed the presence of previously undetected phases, because these phases change to TEM invisible monolayers of MoO_x or WO_x on the support material upon exposure to air. We have published a dedicated study regarding these entities, although their exact structure and composition still remain to be determined [6].

The current study shows that even fully sulphided MoS_2 slabs are sensitive to exposure to ambient air. We have used a first step of quasi in situ HRTEM characterisation to determine quantitatively the slab length and degree of stacking distribution for a fully sulphided MoS_2 catalyst. Subsequently, exactly the same areas of the catalyst were re-examined using HRTEM after exposure to air for 24 h and once again after 1 month.

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2. Experimental

2.1. Sulphidic catalyst preparation

Catalyst precursors were prepared by pore-volume impregnation of Mo (7% for catalyst A, 9% for catalyst B) from ammonia-heptamolybdate aqueous solution on gamma-alumina extrudates (SA = 300 m^2/g; PV = 0.72 ml/g) followed by drying and calcination at 450 °C. The catalysts were sulphided in fixed-bed downflow microreactors, which could be closed off at both ends. Catalyst A was sulphided in an H_2/H_2S 9:1 gas mixture, flow rate 63 ml/min, at atmospheric pressure. The temperature was increased from room temperature to 350 °C at 10 °C/min, followed by a 1 h isothermal period at the final temperature. The H_2/H_2S gasflow was maintained during cooling. Catalyst B was sulphided in liquid-phase 5.2% *t*-nonyl-pentasulphide $(C_9H_{19})_2S_5$ in *n*-hexadecane, WHSV 1.75 l/kg/h, at 40 bar H_2 pressure, and H_2 gas rate 250 Nl/kg (feed). The temperature was increased with 20 °C/h from room temperature to 340 °C, with a holding period of 5 h at 280 °C and one of 24 h at 340 °C. After cooling down, the sulphiding feed was replaced with *n*-heptane, and the catalyst was rinsed for a few hours.

2.2. Transmission electron microscopy

TEM was performed using a Philips CM30T microscope equipped with an LaB_6 filament as the electron source, operated at 300 kV. To avoid exposure to air, samples were unloaded from the sulphidation reactor in a nitrogen glovebox. They were packed air-tight and transported to an argon glovebox near the microscopes, where they were mounted on Quantifoil micro-grid carbon film covered metal TEM grids. A few drops of a suspension of ground catalyst in dry *n*-hexane were put on the TEM grid and left to dry inside the glovebox. Grids were transferred to the TEM using a specially developed protective-atmosphere transfer TEM holder [7].

Catalyst A was mounted on a Au mixed mesh finder grid. After examining several areas of the grid in the TEM, the grid was exposed to ambient air for 24 h. Then the grid was reinserted in the TEM and exactly the same areas of catalyst were re-examined. The grid was then exposed to ambient air for a month, and again the same areas were re-examined using TEM. In order to study possible electron-beam induced effects, for each step also several areas of the catalyst were examined that had not been exposed to the electron beam previously.

For catalyst B, two experiments were performed starting from the same oxidic catalyst precursor and using the same sulphidation procedure. For each of these batches a small amount of catalyst was mounted on a copper TEM grid. One batch was sulphided and transferred to the TEM completely without exposure to air, i.e. quasi in situ. Another batch was sulphided, unloaded from the sulphidation reactor in a glovebox and exposed to ambient air for 5 min before being returned to the glovebox.

Quantification of the slab length and degree of stacking of the slabs was performed by examining about 400 individual slabs per sample. The length of each slab was measured by hand on calibrated prints of TEM negatives. The degree of stacking was determined by counting the number of layers in each individual supported particle of MoS_2. For each parameter an average value was determined for each sample. As the number of slabs per volume sample was much less for the 24 h air exposed catalyst A, only about 300 slabs were evaluated for this sample. For catalyst A exposed to air for 1 month, the number of slabs visible had decreased to such an extent that they could not be evaluated quantitatively.

3. Results and discussion

3.1. Atmospheric pressure sulphided catalyst

Catalyst A was evaluated completely without exposure to air, after 24 h exposure to air and after 1 month of exposure to air. For this sample, exactly the same areas of the catalyst were relocated on the TEM finder grid and re-examined. To make sure any electron-beam induced effects are excluded, also areas

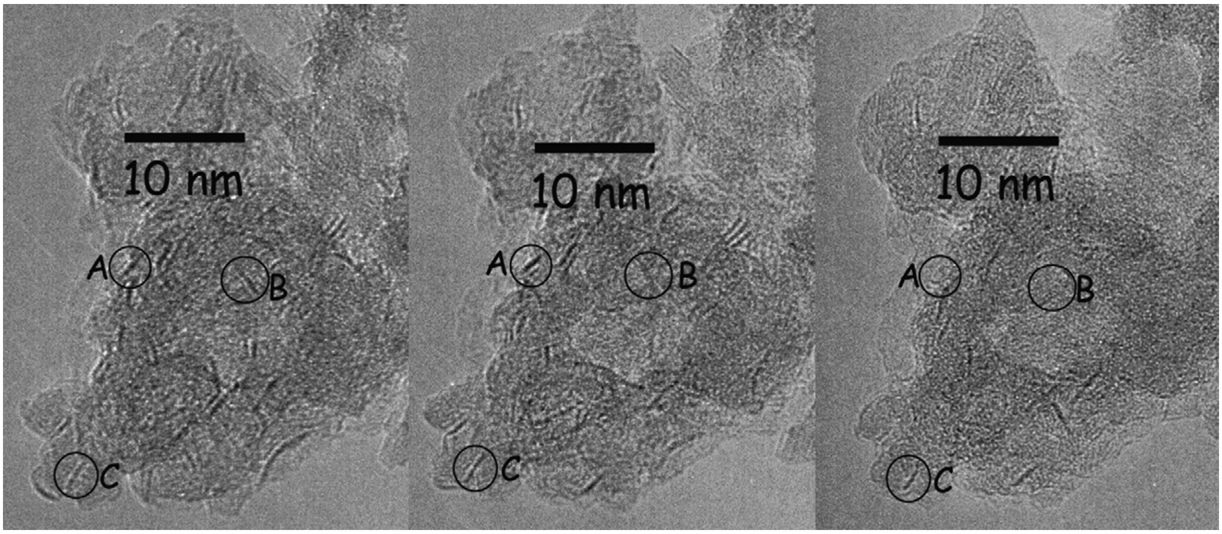

Fig. 1. TEM of the same area of catalyst A. Left: completely quasi in situ; centre: after 24 h of air exposure; right: after 1 month of air exposure.

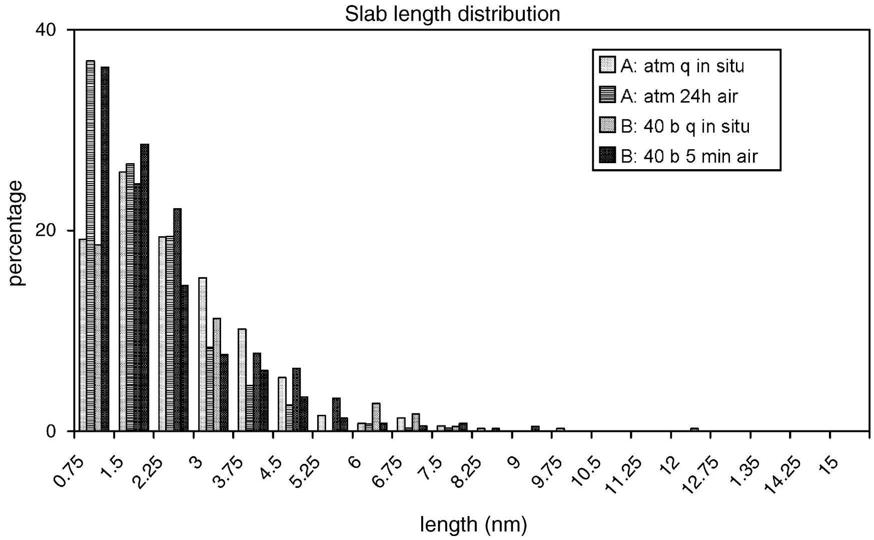

Fig. 2. The slab length distribution for the samples that were evaluated quantitatively.

of the catalyst not yet exposed to the electron beam have been investigated after each subsequent step. No differences were observed between electron-beam exposed and unexposed areas of the catalyst. Already after 24 h exposure to air, the MoS_2 particle size has decreased significantly. The average slab length has decreased from 2.4 to 1.8 nm, whereas the degree of stacking is stable at 1.2 layers. After 1 month of exposure to air, the number of visible slabs has decreased significantly: they have been at least partially oxidised by oxygen from the ambient air. Fig. 1 shows a TEM image of the same representative area of each step of the procedure. Already after 24 h of air exposure the slabs are less clearly visible and quite a few of them are not visible at all anymore. After 1 month of air exposure these effects are much more pronounced. The area labelled ‘A’ contains a slab that has decreased in size after 24 h of exposure to air and disappeared completely after 1 month of air exposure. The area labelled ‘B’ contains a slab that has already become invisible after 24 h of exposure to air, and is thus not visible either after 1 month of air exposure. The area labelled ‘C’ contains a slab that has not decreased in size significantly after 24 h of exposure to air, but has decreased in size after 1 month of air exposure. The slabs decrease in size gradually upon exposure in air. For easy comparison of the quantitative data these are given in Figs. 2 and 3 and summarised in Table 1.

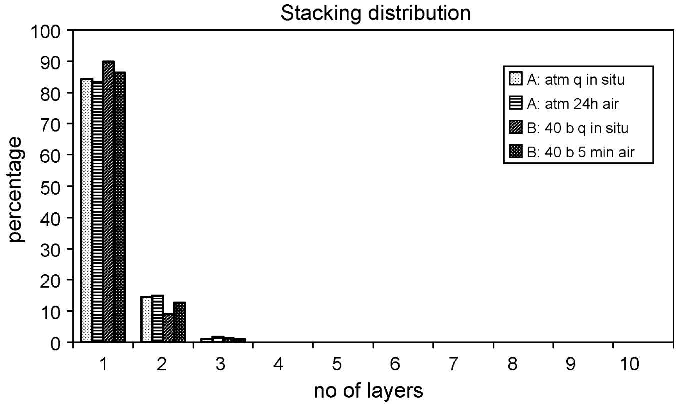

Fig. 3. The degree of stacking distribution for the samples that were evaluated quantitatively.

3.2. 40 bar sulphided catalyst

As there is the possibility that atmospheric pressure sulphidation leads to less well-sulphided catalysts that intrinsically have lower stability [8], an experiment with a 40 bar sulphided catalyst was performed as well. This catalyst was examined using TEM either after sulphidation and completely quasi in situ TEM specimen preparation, or after the complete extrudates had been exposed to ambient air for about 5 min Already for this brief exposure to air of the non-ground extrudates, a significant decrease in average slab length is observed: the average slab length is 2.5 nm for the quasi in situ prepared catalyst and 1.9 nm for the catalyst after 5 min of exposure to ambient air. Again, the degree of stacking does not change upon brief exposure to air, and at 1.1 layers is similar to that found for catalyst A. The quantitative evaluation of the slab length and the degree of stacking is given in Figs. 2 and 3, respectively, and summarised in Table 1.

Many commercial sulphidic catalysts are used in the form of extrudates. For TEM analysis, these are often embedded in resin and cut into slices of about 50 nm thickness [9]. This preparation method retains information on the distribution of

Table 1
Average slab length and degree of stacking

Sample	Average slab length (nm)	Average stacking (layers)
A: 1 bar q in situ	2.4	1.2
A: 1 bar 24 h	1.8	1.2
B: 40 bar q in situ	2.5	1.1
B: 40 bar 5 min	1.9	1.1

the active phase over the extrudates that is lost when grinding to a powder, although the thickness of the slices means that very small slabs are not visible any more [9]. Even though it is very likely that the catalysts are shielded from air properly once they are embedded in the resin, they are often exposed to air briefly during the embedding process. Our current results show that exposing fully sulphided extrudates to ambient air for only 5 min already has a pronounced effect on slab size, and should be excluded, e.g. by performing the embedding process in a protective atmosphere glove box using sulphided extrudates that have not been exposed to air.

Catalyst B contains some areas where MoS_2 has aggregated into larger particles, so-called ‘nests’ of slabs. They are presumably formed in catalysts with higher Mo loading where inhomogeneities in Mo distribution over the support material occur. Any locally higher concentrations of molybdenum salt or molybdenum oxide on the support material will lead to larger particles of MoS_2 upon sulphidation. These nests are close in structure to bulk MoS_2 and as they presumably have only a small contribution to catalytic processes they have not been included in the evaluation of the slab dispersion. Their stability in air has not been examined.

4. Conclusions

Supported MoS_2 catalysts are very sensitive to exposure to air. Already after 5 min of exposure to ambient air the average particle size decreases significantly, whereas after 1 month of exposure to air the number of slabs per volume of catalyst visible in TEM has decreased significantly. Any characterisation of these catalysts should always be performed (quasi) in situ, i.e. without exposure to air between catalyst preparation and characterisation.

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