

Chapter 4

Discussion

4.0 Discussion

In principal, four different families of materials have been produced in a controlled manner by precipitation as a function of pH, counter-ions, temperature and concentration. However the analytical methods used need to be evaluated critically. TEM shows the presence of fine and large particles in every sample. Integral methods such as Raman spectroscopy and XRD are more sensitive to bigger particles or bulk structure whereas TEM will analyse the smaller ones or just focus on the edges at a very thin layer on the surface.

Powder X-ray diffraction could identify most of the phases obtained by referring to the references available from PDF and ICSD database. The most complicated analysis is to identify and to determine the trends in the supramolecular phase structure pattern where there is no clear indication of the trend of the pattern. The supramolecular phase was produced using ammonium and potassium as counter-ions. This means that supramolecular phase can only be obtained by spontaneous precipitation at low temperature using large cation. Supramolecular phase using ammonium as counter-ion can only be obtained at 30 °C at any concentration of molybdenum and acid. But at 50 °C, no real trend was observed because the supramolecular $\text{Mo}_{36}\text{O}_{112}^{4-}$ and hexagonal Molybdenum Oxide phase yielded randomly independent of molybdenum and acid concentration. In addition, at this temperature spontaneous precipitation did not occur in the samples which yielded hexagonal phase and for this reason it needed to be further heated.

This is the reason for the formation of hexagonal phase. Spontaneous precipitation did not occur at 50 °C. This could be due to the reaction mechanism which is changing at this temperature. 50 °C is the most important border line as the temperature dependent investigations show. Even by calculating the ratio of acid and molybdenum concentration, no significant trend was observed. At 70 °C, hexagonal phase is observed in all cases. Thus, temperature is the only parameter which affects the phases when ammonium is used as counter-ion. By comparing the pattern of supramolecular with previous literature especially by Muller and Zhang [47, 49], the pattern was found to be similar in terms of the presence of the intense peak at lower angle. This indicates structure with big unit cell and many small peaks which are badly resolved at higher angle. There is always the appearance of intense peak at approximately 7 °. After the refinement process, the average d-spacing is 12.7. There are no obvious trends observed in the value of d-spacing to be correlated with the synthesis process. . One of the samples also shows that this characteristic peak is shifted to the right with lower d-spacing and the reason is unknown even after correlation with the parameter used in the synthesis. By comparing all supramolecular phase patterns especially from ammonium sample in terms of d-spacing, they are quite different to each other which could be due to different concentration of proton and ammonium in the sample.

Supramolecular phase from potassium counter-ion precipitated spontaneously at low temperature and high molybdenum concentration. Acid concentration does not influence the phase obtained. Potassium as counter-ion yielded 3 types of phases, supramolecular phase, hexagonal and trimolybdates. Supramolecular phase was obtained at low temperature and high molybdenum concentrations.

Hexagonal molybdenum oxide was produced at high temperature but low molybdenum concentration while trimolybdate was produced only at highest temperature, 70 °C depend on molybdenum concentration [54].

Hexagonal molybdenum oxide can be obtained from 3 counter-ions, ammonium, potassium and sodium. The hexagonal-molybdenum oxide from ammonium counter-ion is identified from Powder Diffraction File (PDF-39-35) of Ammonia Molybdenum Oxide $(\text{NH}_3)_3 \text{MoO}_3$. Hexagonal phase from ammonium counter-ion is yielded depending on temperature. It can only be obtained by raising the temperature at low molybdenum concentration regardless of the acid concentration. The peaks match well except the presence of small shoulder on the left, in most of the peaks. This indicated the presence of another phase of hexagonal structure with different lattice parameter. There are another 2 references which matched well with the observed pattern. One of it claimed that the structure is cubic by indexing the pattern [61]. The unit cell parameters of all references are different from each other. Thus, indicating that hexagonal phase is a family. Precipitation using potassium as counter ion yielded potassium molybdenum oxide hydrate $(\text{KM}_3\text{O}_{15}.\text{OH}.2\text{H}_2\text{O})$.

Actually, hexagonal phase obtained in the sample is a major phase. More than one phase is present in the sample but the minor phase is unknown. Thus, the hexagonal phase does not contain pure hexagonal molybdenum oxide.

There has been considerable interest in obtaining hexagonal MoO_3 phase structure with empty channels. Hexagonal phase with empty tunnel are believed to be catalytically active. The cations are however essential to stabilise the structure of hexagonal MoO_3 . Few researchers claimed that they succeed in obtaining hexagonal MoO_3 with empty tunnel [54, 58, 60]. Guo *et al.* [54] have prepared hexagonal MoO_3 by ion-exchange reaction and they claimed that they have succeeded in producing the first hexagonal MoO_3 structure with empty tunnel where no researchers have succeeded before. Caiger [55] observed hexagonal MoO_3 which are partially dehydrated and deammoniated ammonium decamolybdate. Sotani [56] determined hexagonal MoO_3 from two different cations, ammonium and sodium and assumed that both cations have stabilised the structure of the compound and influence the transformation temperature. Feist [57] claimed that he has developed a novel method for the synthesis of hexagonal molybdenum oxide in which the large one-dimensional channels are empty and variety of monovalent cations, such as H^+ , Li^+ and Na^+ , can be readily inserted.

There are few reasons why lithium does not form any hexagonal phase at high temperature but orthorhombic. Lithium is too small to be inserted into the channel, so there is no possibility to form any hexagonal structure but formed orthorhombic. Lithium is a small cation polarising water and creates a sphere of hydration shell which sticks to it (hydrodynamic radius). So the cation becomes bigger with the water shell and it does not fit into the hexagonal channel. Thus, it fails to direct the $[\text{Mo}_2\text{O}_{10}]^{2-}$ into the hexagonal channel and leads to linear arrangement ending with orthorhombic MoO_3 . However bigger cation such as potassium are loosely bound to water and form smaller water cluster, hence it fits into the channel and form this hexagonal and enter the channel easily [59].

The XRD pattern of samples obtained from lithium cation shows mixture of narrow and broad peaks which corresponds to orthorhombic MoO_3 may due to disordered in the unit cell. After comparing with the hkl value obtained from the reference, it reveals that the structure is disordered along b-direction. The layered structure along b-direction are tilted to each other resulting in a defect along one direction.

Raman spectroscopy seems to be a good method to analyse these materials because low crystallinity and even glassy substances are accessible.

By comparing with literature, several researchers used Raman to investigate polyoxomolybdates in aqueous solutions and there is proof that Raman spectrum of both polymolybdates which exist in solution and solid state are identical [37]. Moreover the herein described materials show bands at different position and therefore are easy to distinguish.

Consequently, the band position is used to assign the material to a certain family of materials. Relative band intensities however vary a lot and do not show a clear trend. Therefore the intensities are used to describe the various members of the families and their defect or real structures.

One very important control variables which described above is the counter-ion. Precipitation is clearly influenced by the size and their related properties such as activity and ionic strength. Looking at the series $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{NH}_4^+$ the smallest ion Li^+ is not sufficient to cause a spontaneous precipitation. It is noteworthy that only in this case orthorhombic MoO_3 was obtained. Neither the next ion in this series lead to a spontaneous precipitation.

Heating however yields hexagonal MoO_3 (reported by Garin, J L, Blanc, J M) the same structure as reported by Krebs and labelled as Mo_3O_{16} . Potassium is the first ion that can cause spontaneous precipitation leading to a supramolecular phase. By heating, trimolybdate [51] or the hexagonal MoO_3 is yielded whereas ammonia will only yielded supramolecular or hexagonal MoO_3 .

Two different mechanisms can be discussed in this respect. First a template effect might play a role. Second ionic strength and activity will lead to different solubility products and therefore the above described structures - assuming that they have different solubilities - will be obtained.

Based on Lehn's definition of supramolecular chemistry being chemistry beyond the molecule intermolecular forces such as van der Waals forces, London dispersion forces and hydrogen bonding become important. It is likely that the comparatively soft NH_4^+ could serve as an endo-template. Fragments of the Octamolybdate will group around the ammonia. Subsequently these nanoclusters in solution will interlink. As soon as the particle size is big enough and a certain amount of species is formed, the solubility product is exceeded and precipitation of the hexagonal MoO_3 sets in. A retrosynthetic approach corroborates to this idea. Taking the ammonia inside the channel as a centre, only a few Mo-O-Mo bridges need to be broken to yield these nanocluster building blocks.

A comparable mechanism should be possible with K^+ , taking into account that the molecule has got reasonably big hydration sphere. However K^+ seems to be the border line for this mechanism because under some experimental conditions (high Mo concentration, 70 °C and spontaneous precipitation) the layered Trimolybdate structure is obtained. Applying the above described conditions no spontaneous precipitation could be achieved with Na^+ as counter ion.

Thus only hexagonal MoO_3 is obtained. With Li^+ the situation changes completely because only orthorhombic MoO_3 is obtained. The smaller the ion (referring to Lithium) the more difficult it becomes to build up a stable spherical wrapping consequently layered structures are obtained from smaller ions and channel structures from bigger ones.

The obtained results show that temperature and the proton to molybdenum ratio is another important control variable. 50 °C is the most important border line as the temperature dependent investigations show. Therefore at this temperature most likely the reaction mechanism has changed. High molybdenum concentrations and low temperature (30 °C) lead to a spontaneous precipitation of a supramolecular compound which is similar to the $\text{Mo}_{36}\text{O}_{112}$ reported by Krebs [54]. Low concentration and high temperature leads to the formation of hexagonal MoO_3 [38] the same structure as reported by Krebs and labelled as Mo_5O_{16} , orthorhombic MoO_3 or Trimolybdate depending on the counter ion.

According to Tytko [51] the $\text{Mo}_{36}\text{O}_{112}$ is the major compound in solution at low pH and precipitates as soon as the solubility product is reached. It is remarkable that the connectivity has changed compared to the starting material.

In the AHM precursor only corner sharing octahedra are observed. In the $\text{Mo}_{36}\text{O}_{112}$, edge sharing connectivity prevails and the pentagonal bipyramid as structural motif, which appears in catalytic active material like Mo_5O_{14} , is formed. Corner sharing also turns up in the hexagonal MoO_3 .

Krebs [25] points out that $\text{Mo}_{36}\text{O}_{112}$ is only stable in the mother liquor. Water is responsible for the hydrogen bonding which is probably the dominating coherent force in this molecule. As soon as water is removed the compound will decompose to some extent. This explains the variation in XRD. Nevertheless the close similarity of the XRD to the reference and the exact agreement of the Raman band positions corroborates to the idea that the main structural motives prevail.

Investigating the reaction in the solid phase against the differences due to counter ions are striking. Using ammonia as a counter ion, the final transformation is taking place at 50 °C, a higher temperature than in the potassium case.

The XRD pattern of the orthorhombic MoO_3 obtained from Li_2MoO_4 shows broad signals and a comparatively high background indicating low crystallinity. One reason for this is that the degree of polymerisation due to a condensation in water at the chosen conditions is too low to form big crystalline particles resulting in smaller particles or the solubility product is reached too early.

The broadening of the peak also could be due to disordered in the structure of orthorhombic because normally orthorhombic MoO_3 has a narrow and sharp peak in the diffraction pattern.

Transmission electron microscopy (TEM) has been performed in order to compare and to act as a supplement with the results obtained from XRD investigation. TEM deals with surface structure instead of XRD which reveal structure bulk. Several interesting images have been selected from few sets of samples. Edges with amorphous layer were observed in the outer most layer found in most of the samples. Most probably the amorphous layer is caused by the vacuum. The sample was investigated under vacuum which may vaporise O_2 or N_2 that might change the structure from crystalline to amorphous in the surface regions (outer most parts).

XRD indicated supramolecular structure where the majority of intense peaks appeared at lower angles and revealing the presence of a structure with a very big unit cell. As clearly seen from figures, the sample consists of well developed crystals with well crystalline structure in contrast to the XRD result. One possible reason for this difference is that XRD favours bulk structure and particle size which is bigger than 30 Å while TEM favours structure on the surface and is able to reveals the structure even with a very small particle less than 30 Å. TEM investigated the structure at the edge of the particle where the layer is thinner and could not reveal lattice in the inner part which is thicker. The bright spots in electron diffraction pattern indicate one single crystal with a big particle which reveals to be a pure crystal.

Distinct spots indicated that the crystal is definitely crystalline. The huge area of 100 nm revealed to be well crystalline in one single phase of crystal which is pure.

Comparison observed between XRD and HRTEM in terms of lattice spacing in the characteristic sample prepared by decreasing pH from ammonium cation. It is clearly seen from the plot (referring to supramolecular $\text{Mo}_{36}\text{O}_{112}^{4-}$ diffraction pattern), that the XRD pattern has a much more intense peak at lower angle and do not fit well with HRTEM investigation. In contrary, the peak with low intensity at higher angle agreed quite well. Perhaps, the structure in the sample from XRD investigation is not similar to the one obtained in HRTEM investigation. For this reason, both results do not agree well. One more possible reason is that HRTEM might not be suited for a very large d-spacing. Apart from that, TEM is a method which focus just on the surface but XRD reveals structure in the bulk. TEM does not see the overall structure dealing in very thin layer on the surface with 100 nm depth and XRD observed the averages of the structure in the samples. The most probable reason for the peaks at lower angle not matching well to the d-spacing obtained from HRTEM is because the unit cell is too close to the central spot. In addition, HRTEM is not suitable for quantitative analysis to compare with XRD because it reveals such a small area in a very thin layer on the selected surface.

Small particles are suited for HRTEM investigation instead of big particle because the big particle is too thick to be electron transparent. In general, HRTEM needs very thin layer at approximately maximum 100 nm. Different orientation and arrangement of lattice spacing reveals different type of particles which are agglomerated and overlapped. The d-spacings corresponds to d-spacings of corner-sharing MoO_6 . There are no significant trends or difference in the structure either the d-spacing or orientation of lattice fringes as the acid concentration is increased or decreased.

Figure 3.39 C indicates no crystallinity or amorphous structure in this characteristic particle. This sample (256) was synthesized at 30 °C, 0.7 M of molybdenum concentration and precipitated with 1.0 M of acid concentration. This characteristic sample was prepared to complete the set of temperature variables. Even though the electron diffraction pattern reveals an amorphous structure, but HRTEM images have indicated some small arrangement which are crystalline.

HRTEM images in Figure 3.39C which have been marked with two circles, indicates a small hint that there are still crystalline areas found in this amorphous surface structure. Perhaps this is due to the onset of crystal growth. The XRD investigation revealed a supramolecular structure in this particular sample (sample 256).

In contrast to sample 1 shown in Figure 3.36 A and 3.36B which also have supramolecular structure investigated by XRD indicated crystalline structure on the surface. Perhaps, the area selected in sample 256 is amorphous but not the inner part which could not be seen by TEM because it is too thick.

Figure 3.40 displays image of sample 227. It revealed a crystalline structure on the surface. This sample was prepared at higher temperature (50 °C) compared to sample 256 shown in figure 3.39. All other parameters were set to be fixed including the speed of acid addition. The electron micrograph indicates two types of particle size distribution, one with small particle and one with very big particles. The HRTEM image shown in Figure 3.39B was taken from the small particle while electron diffraction pattern shown in Figure 3.40B was taken from the big particle. Both revealed crystalline structure on the surface. The spots are bright to show that it is well crystalline.

This image indicates one orientation revealed that the crystal is from one well developed single crystal. Both small and big particles can be distinguished by the way it was oriented, whereby the small particles were oriented in a different way in contrast with the big particles which has one way of orientation. As a result, the big particle has a well-developed crystal compared to the small particle. Even the size of the particles is significantly different, 200 nm for the big crystal and 0.2 nm for the small one. The XRD investigation revealed a hexagonal structure which has sharp and narrow peaks indicated a well crystalline structure in the compound.

The XRD pattern may not reveal the particle size distribution because all peaks width are almost similar except the presence of shoulders on the left of every peak especially at higher angle. As explained in the XRD part, the presence of this extra shoulders revealed the presence of second hexagonal phase with different lattice parameter. The reason for this is, XRD observed the structure in the bulk which might not detect the small particle as TEM did. HRTEM observed two values of d-spacing, 3.4 Å and 3.8 Å which corresponds to MoO₆ octahedra edge sharing and corner sharing respectively.

Overall images revealed both well crystalline and amorphous areas found in the samples. There are no special trends in the distribution of crystalline and amorphous areas among the samples. Vast amounts of different lattice spacing were also found in the samples measured using HRTEM. This observation suggests the presence of several phases. There are trends observed while temperature of preparation is raised. As the temperature is raised, more developed crystals are found. The sample synthesized at 70 °C has a bigger well developed crystal than sample prepared at 30 °C.

SEM images which have been shown in Figure 3.42 indicates difference on morphology and the particle size of different samples with varying acid concentration. Both images shown significant difference in morphology and size. The shape of particles in sample 5 is more rectangular-like compared to sample 1. Sample 1 has predominantly small particles without any special shape instead of big particles with rectangular-like shape.

Seems like, acid concentrations give real difference on the shapes of the particles where high acid concentration will give a more rectangular-like shape. Even the particles sizes in sample 5 are smaller compared to sample 1. Probably high acid concentration will lead to the distribution of small particles. In conclusion, the higher the acid concentration the more rectangular-like shape and the smaller the size of particles produced. There are two types of particle size distribution in both samples, the big and small one are in good agreement with TEM result which also indicated two types of particle size.

SEM images shown in Figure 3.43 are 2 samples prepared at different temperature. Both samples have different particles shape, where sample 256 has rectangular-like shape while sample 232 has a hexagonal shape of particles. The sizes of the particles are also different whereby sample 232 which has hexagonal shape is bigger than sample 256. The higher the temperature applied, the bigger the sizes of the particles and the more hexagonal shape produced. This is in agreement with TEM result whereby it also showed higher temperature, produces bigger crystal and a more well-developed crystal. The XRD and Raman results were also in good agreement with this characteristic sample which resulted in hexagonal phase structure.