A new route to polyoxometalates via mechanochemistry†

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Mechanochemistry offers a new route to polyoxometalates (POMs) under mild conditions. The molybdenum isoPOM heptamolybdate and the molybdenum heteroPOMs of the Strandberg- and Keggin-type could be achieved from grinding together molybdenum oxide, potassium or ammonium carbonate and phosphate. The reactions were controlled by the stoichiometric ratio of the starting materials and the liquid used, with reaction times between 30 min and 3 h. In situ investigations of the syntheses reveal the formation of intermediates during the reactions. Their identification helps explaining the mechanism of formation of the intermediates as well as the final POMs.

Introduction

Polyoxometalates (POMs) are a material class of early transition metal oxygen cluster anions, with MoVVI, WVI, and VV as the most described metals. The counter ions on the other hand range from hydrogen atoms over small inorganic cations to complex molecules. If the cluster includes heteroanions such as PO$_4$$^3^-$ or SO$_4$$^2^-$ they are called heteroPOMs, otherwise isoPOMs. The first reported POM was the nowadays-called Keggin-type [PM$_{12}$O$_{40}$]$^{3^-}$, which was also, in its form of phosphothungstic acid, the first one where the structure could be determined from powder X-ray diffraction data in 1933. In the last decades POMs were intensively investigated, showing a huge range of structural varieties and properties. The structures can not only differ in size of cluster, ranging from 6 to over 300 metal oxide building blocks, but also by the incorporation of organic molecules and the usage of POMs as building units for metal–organic frameworks. The resulting varying properties make them useful for a wide range of applications, e.g. in catalysis, energy storage and medicine or as ion-exchangers sensors, and electrochromic devices.

POMs are usually synthesized in aqueous solutions, containing the respective metal oxoanions. For the condensation reactions the pH of the solution plays a crucial role and has to be adjusted by the usage of acids. The syntheses are done at different conditions, ranging from ambient temperature over reflux to hydrothermal conditions. The use of alternative methods is scarce. Yan and co-workers used microwaves to synthesize POMs out of sodium molybdate. In a solid-state synthesis, the Keggin-type POM as K$_3$PM$_{12}$O$_{40}$ (M = Mo, W) could be synthesized via heating a mixture of MO$_3$, K$_2$CO$_3$ and K$_2$HPO$_4$ at 500 °C for 30 h.

In the last decade mechanochemistry has gained a lot of interest as a synthetic method. The term is used for chemical reactions induced by mechanical energy and performed in hand mortars as well as ball, planetary and vibration mills. Mechanochemical reactions are increasingly used thanks to their easy handling, short reaction times, high conversion rates, a small production of waste, based on a high atom economy and the small amount of solvents used. Moreover, by using little quantities of liquids (liquid assisted grinding, LAG) the reaction outcome can be influenced regarding the yield, reaction times and the nature of the product. Mechanochemistry offers the possibility to create new compounds, not or only difficult achievable from solution. Thanks to the solid-state nature of the process, it is possible to follow in situ the reaction and several setups where developed, using X-ray diffraction, spectroscopy or temperature devices.

Although POMs are used in mechanochemical synthesis, e.g. to exchange the cation or to encapsulate the POM inside of a metal–organic framework (MOF), there is, to the best of our knowledge, no description of a direct mechanochemical synthesis. Such an alternative route could make the use of strong acids obsolete as well as decrease reaction times and the energy consumption. Beside that, a different synthetic route could lead to new and unknown structures. Moreover, the relatively higher stability of solid products may be an advantage against a possible reorganization of POMs in solution. Therefore, the goal of this work was to produce POMs mechanochemically from the scratch and to investigate the reaction process by using in situ methods.
Results and discussion

Mechanochemical synthesis

Most syntheses from solution are starting from molybdate, MoO$_4^{2-}$. To follow these routes in a solid-state synthesis would be difficult, since, depending on the desired POM, specific conditions regarding the solvent, pH, temperature and pressure are needed. Instead we wanted to use MoO$_3$ and add O$_2$ by using compounds who have good leaving group, e.g. carbonates with CO$_3^{2-}$. Our reactions are done in a vibration ball mill, where the reaction mixture is weighted together with steel balls into a steel jar, which is closed and mounted into a vibrating holder. Any gas formation during reaction would therefore be observed as a pressure release at the end of the reaction itself. The details of all lab syntheses can be found in the ESI.† The first idea was to create simple POMs with only one atom species. The isoPOM heptamolybdate [Mo$_7$O$_{24}$]$_{6}^{4-}$ is a well known member of the POM family. Other than most POMs it can be directly synthesized from solutions of MoO$_3$ in ammonium hydroxide by evaporation.41 This simple approach and high tendency to self-assembly made it an ideal candidate to prove if our approach could work. The isoPOM heptamolybdate could be produced within the compounds (NH$_4$)$_5$/K$_6$Mo$_7$O$_{24}$·4H$_2$O (1a, 1b). They are formed already by neat grinding of MoO$_3$ and NH$_4$HCO$_3$, but, as visible in the reaction equation in Fig. 1, for the full formation the addition of a small amount of water (30 μL to 500 mg) is needed. The respective Rietveld refinements can be found in the ESI.† Within 30 min a pure and highly crystalline compound could be produced.

In the next step we wanted to introduce heteroatoms in the POM structure. The Strandberg-type POM, [P$_2$Mo$_6$O$_{24}$]$_{4}^{4-}$, has a comparably high ratio of heteroatoms which is why we choose it as a first candidate. It could be realized within (NH$_4$)$_5$HP$_2$Mo$_5$O$_{23}$·3H$_2$O (2) and (NH$_4$)$_5$P$_2$Mo$_5$O$_{23}$·5.5H$_2$O (3), by grinding MoO$_3$, NH$_4$HCO$_3$ and NH$_4$H$_2$PO$_4$ in a ratio of 5 : 3 : 2 and 5 : 4 : 2, respectively (Fig. 1). The addition of water (100 μL and 50 μL, respectively) was necessary for the formation of a pure and highly crystalline product. The reaction times varied from 30 to 60 min. For 2 a structure from literature was used for the Rietveld refinement while the structure of the new compound 3 could be solved from PXRD data (see ESI†).

With the proof that even heteroPOMs can be synthesized, the Keggin-type POM, as probably the best known representatives of the POM material class, was an attractive candidate to be synthesized by our method. Its synthesis requires strong acidic conditions, which can not be applied in an mechanochemical synthesis. Nevertheless, the Keggin-type POM containing compounds (NH$_4$)$_5$/K$_7$P$_2$Mo$_5$O$_{23}$ (4a, 4b) could both be synthesized by grinding MoO$_3$, the respective bicarbonate and dihydrogen phosphate together (Fig. 1). It was necessary to add a mixture of water and ethanol to the reaction. With no solvent or ethanol alone almost no reaction could be observed, while with water as the only liquid the formation of a side product, with very broad peaks which could not be identified, was promoted. With 3 h the synthesis took much longer than the other ones presented in this paper. To prove the correct phase, we did Rietveld refinements (Fig. S3†). In both syntheses, a small amount of MoO$_3$ can still be detected, 3 wt% and 2 wt%, respectively. Milling a longer time or with heavier balls did not help to fully complete the reaction, since it promoted the formation of the unidentified side product as well.

Our results show that the formation of POMs via mechanochemistry can be a valid alternative. The isoPOM heptamolybdate could be synthesized within 30 min by ball milling with a small amount of water. The products were highly crystalline powders. The Rietveld refinements prove the purity of the compounds and no further cleaning step was needed. For the heteroPOMs a small variation of the amounts of the starting materials is enough to get full control over the formed product. By using the respective stoichiometric ratio always the exact POM is formed. Using liquid assisted grinding the Strandberg-type POM was produced as a highly crystalline and pure product within maximum 60 min. The Rietveld refinements do not show any additional reflections. For the Keggin-type POM the synthesis was more complicated. The balance had to be found between a high conversion rate and the production of a second phase. By choosing the correct parameter it was possible to synthesize the Keggin-type POM within 3 h with high purity.

In situ investigations

In our experiments we used MoO$_3$ instead of MoO$_4^{2-}$, which is mostly used in solution based syntheses. Also we worked under much milder conditions. In no synthesis strong acids were added to the mixture. To enable the full potential of the mechanochemical synthesis of POMs a better understanding of the mechanisms is needed. For this reason, we investigated in situ the formation of the three POMs which we synthesized.

Both syntheses for the heptamolybdate in 1a and 1b were followed in situ and very similar pathways could be observed,
Among the reagents we could observe diffraction peaks of MoO$_3$ from the very beginning, while no peak of the respective bicarbonates are visible at any time during the milling. In both cases an intermediate phase is formed immediately. During the synthesis the rections of this phase vanish, while the ones of the product evolve. In the case of 1b, the peaks of MoO$_3$ get very weak in the first minutes but can still be detected until the end. The lab synthesis instead produced a pure compound. We used the setup of the Materials Science beamline at the SLS, Paul Scherrer Institute in Switzerland. Due to the machinery of the in situ setup, where the powder is measured in a special probing area, there is the possibility of caking powder in this area, when additional liquid is used. This is possibly the reason for this observed slight difference. For both reactions we were able to identify the intermediates, which are novel molybdenum carbonates, namely and respectively (NH$_4$)$_2$MoO$_3$CO$_3$ (5a) and K$_2$MoO$_3$•CO$_3$•0.5H$_2$O (5b). Both structures were solved from PXRD data. A detailed description, including crystallographic details and the Rietveld refinements can be found in the ESI.

For 1b we were able to isolate the intermediate by reacting MoO$_3$ with K$_2$CO$_3$ (1 : 1, LAG H$_2$O). In the potassium molybdenum carbonate 5b, molybdenum is coordinated by three oxygen atoms and bidentate by a carbonate ligand, resulting in a 1D chain structure (Fig. 2b, right). A comparison with an in situ powder pattern after 2 min clearly confirms this as the found intermediate.

For 1a the ammonium molybdenum carbonate 5a could only be synthesized within a mixture with 5a as the main compound with 66 wt% (see ESI†). The motif is similar to 5b (Fig. 2a, right), except that no water of crystallization is present. The comparison between a calculated powder pattern of 5a and the powder pattern after 80 s of the in situ investigation of 1a is proving that it is the quickly formed intermediate. In both cases the formation of the heptamolybdate happened via the formation of a molybdenum carbonate. The carbonate coordinates to the molybdenum, activating the MoO$_3$ and then CO$_2$ is evolved.

For the Strandberg-type POM we followed in situ the formation of 2. To prevent caking we halved the amount of water used. However, at the end the powder was wet and caked in the probing area of the in situ jar. Nevertheless, the reaction is proceeding and our gained data can still shed light on the reaction pathway. The 2D plot of the time-resolved powder patterns is shown in Fig. 3. As observed for the heptamolybdates, MoO$_3$ can be detected from the start. The additional reflections can not be assigned to the other starting materials.

**Fig. 2** 2D-plot of the in situ investigation of the respective synthesis using PXRD (left), and comparison of the observed intermediate compound with a novel synthesized structure (right) for (a) (NH$_4$)$_6$Mo$_7$O$_{24}$•4H$_2$O 1a and (b) K$_6$Mo$_7$O$_{24}$•4H$_2$O 1b. The molybdenum network for the intermediate is shown on the right for 5a and 5b, respectively.

**Fig. 3** 2D-plot of the in situ investigation for the synthesis of (NH$_4$)$_5$HP$_2$Mo$_5$O$_{23}$•3H$_2$O 2 using PXRD (left, * = position of the peaks of (NH$_4$)$_2$HPO$_4$(NH$_4$)HP), and comparison of the observed intermediate compound with the pattern of the novel synthesized structure (NH$_4$)$_5$HP$_2$Mo$_5$O$_{23}$•yH$_2$O 6 and of the calculated pattern of this compound using $x = 0.5$, $y = 2.5$ (right). The pattern from the lab synthesis does also contain peaks for NH$_4$H$_2$PO$_4$ and (NH$_4$)$_2$HPO$_4$. 

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intermediates. At the beginning only peaks of MoO$_3$ can be detected. No other starting materials could be observed. A reaction with the very similar compounds 2 and 3 prevented a pure synthesis. The details are described in the ESI.† In Fig. 3, on the right a comparison between an in situ pattern after 10 min and patterns from 6 (from the lab synthesis and calculated with $x = 0.5$, $y = 2.5$) is showing that 6 is the observed intermediate.

To investigate the formation of the Keggin-type POM we followed the synthesis of 4a in situ (Fig. 4, on the left). To lower the amount of caking we reduced the amount of liquid to 50 μL. Nevertheless, at the end of the powder was caked and after 4 h the synthesis did not proceed anymore but was also not completed. As seen before, also this reaction proceeds with the formation of intermediates. At the beginning only peaks of MoO$_3$ can be detected. No other starting materials could be observed. After 1.5 min 6 is formed as an intermediate, as in the synthesis of 2, followed by the formation of 2 after 3.5 min. Shortly after the reaction peaks of 6 are vanished. The peaks of 2 get less intense with time as well and are very weak after 4 h. The product 4a can be detected for the first time after 18 min. In the following hours it formed more and its crystallinity improves, as visible from the more intense and sharper diffraction peaks. After 4 h, no changes can be observed. The reaction is not complete, very likely because of the observed caking.

In all conducted syntheses we could observe intermediates, formed before the final product evolves. In the synthesis of heptamolybdate, molybdenum carbonates are formed immediately. These compounds where not described before, probably based on the reactivity of the carbonate ion and, for 5a, the short life time. During the synthesis of the Keggin-type POM the Strandberg-type POM is formed as an intermediate. The intermediates differ for the isoPOM and the heteroPOM reactions, but they have in common that they include a bigger amount of the basic anion, either carbonate or phosphate (Fig. 5). In all reactions a pressure release could be observed when the jar was opened, showing the evolution of CO$_2$. Therefore, the formation of molybdenum carbonates seems to be possible also in the heteroPOM reactions. Nevertheless, the respective compounds could not be observed during the ball milling. Based on the small amount of carbonate during the reactions, it might be possible that the formed amount is too small or the reaction is too fast. Grinding only MoO$_3$ and NH$_4$H$_2$PO$_4$, neat or as LAG with water, did not lead to a reaction. (NH$_4$)$_3$PMo$_{12}$O$_{40}$ instead reacts with MoO$_3$ even without the addition of ammonium carbonate, indicating that also the ammonium-ion and the acidity play an important role. Based on these results we can deduce that MoO$_3$ is activated by a nucleophilic attack. The activated species react with each other or with more starting material to form the final POM.

A comparison to the classical, solution based synthesis of POMs is difficult, since there mostly the more aggressive molybdate MoO$_4^{2-}$ is used. The formation process is supposed to happen via condensation and addition reactions. In the in situ investigations of our mechanochemical reactions we could not observe any MoO$_4^{2-}$ species or its condensation products, except for heptamolybdate, which is the final product of the synthesis of 1a and 1b. Additionally, NH$_4$MoO$_4$ was formed as a side product in the synthesis of 5a. Nevertheless, our results suggest that different mechanisms lead to the POM formation.
in the mechanochemical reaction than in the solution based methods.

With the possibility, to synthesize POMs via mechanochemistry, come several opportunities. The short reaction times lower the energy consumption of the process. The absence of strong acids, the low amount of liquids and the high atomic economy are a huge asset for less waste production and going towards green chemistry. As typical in mechanochemical reactions, the yield only depends on the possibility to remove the powder from the jar since the conversion is almost complete. Moreover, new compounds can also be stabilized in these conditions, as demonstrated by the synthesis of two new POMs containing the Strandberg-type POM and especially with the two new ammonium molybdenum carbonates. Host-guest compounds instead, where POMs are encapsulated into MOFs are already done mechanochemically. Now it might be possible, to create the POM on the side, while the MOF and the host-guest structure is formed. This might not only safe one production step, it also might allow the encapsulation of different POMs and create different structures. Also the new field of POMs as secondary building-units in MOFs is open for mechanochemical trials.

Conclusion

Our results show that POMs can be formed mechanochemically from simple building blocks. Under mild conditions and in a fast and easy manner we could synthesize iso- and hetero-POMs with varying counter ions. In situ investigations revealed that the formation goes via metal oxygen clusters, incorporating the basic anions of the starting materials. This first mechanistic insight shows that the molybdenum oxide is activated by a nucleophilic attack before the final product is formed. This new route to polyoxometalates provides a big range of possibilities, from synthesizing POMs in short times, to finding new structures or to find new ways to encapsulate them into porous frameworks.

Author contributions

Manuel Wilke planed and conducted the research and wrote the manuscript. Nicola Casati participated in the data analysis and supported the writing.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 M. T. Pope and A. Müller, Angew. Chem., Int. Ed. Engl., 1991, 30, 34–48.
2 A. Misra, K. Kozma, C. Streb and M. Nyman, Angew. Chem., Int. Ed., 2020, 59, 596–612.
3 D.-L. Long, R. Tsunashima and L. Cronin, Angew. Chem., Int. Ed., 2010, 49, 1736–1758.
4 J. F. Keggin, Nature, 1933, 131, 908–909.
5 D. Wang, L. L. Liu, J. Jiang, L. J. Chen and J. W. Zhao, Nanoscale, 2020, 12, 5705–5718.
6 D.-Y. Du, J.-S. Qin, S.-L. Li, Z.-M. Su and Y.-Q. Lan, Chem. Soc. Rev., 2014, 43, 4615–4632.
7 A. Bijelic, M. Aureliano and A. Rompel, Angew. Chem., Int. Ed., 2019, 58, 2980–2999.
8 W. Xu, X. Pei, C. S. Diercks, H. Lyu, Z. Ji and O. M. Yaghi, J. Am. Chem. Soc., 2019, 141, 17522–17526.
9 J. T. Rhuile, C. L. Hill, D. A. Judd and R. F. Schinazi, Chem. Rev., 1998, 98, 327–358.
10 J. Zhao, K. Li, K. Wan, T. Sun, N. Zheng, F. Zhu, J. Ma, J. Jiao, T. Li, J. Ni, X. Shi, H. Wang, Q. Peng, J. Ai, W. Xu and S. Liu, Angew. Chem., Int. Ed., 2019, 58, 18032–18039.
11 S. Uchida, Chem. Sci., 2019, 10, 7670–7679.
12 H. Gu, C. Guo, S. Zhang, L. Bi, T. Li, T. Sun and S. Liu, ACS Nano, 2018, 12, 559–567.
13 X.-X. Jin, W.-D. Yu, Y.-M. Nie, M.-S. Liu and J. Yan, Dalton Trans., 2016, 45, 3268–3271.
14 Y.-M. Nie, S. Liang, W.-D. Yu, H. Yuan and J. Yan, Chem.–Asian J., 2018, 13, 1199–1205.
15 F. Goubin, L. Guénée, P. Deniard, H. J. Koo, M. H. Whangbo, Y. Montardi and S. Jobic, J. Solid State Chem., 2004, 177, 4528–4534.
16 P. Baláž, M. Achimovičová, M. Baláž, P. Billik, Z. Cherkezova-Zheleva, J. M. Criado, F. Delogu, E. Dutková, E. Gaffet, F. J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii and K. Wieczorek-Ciurowa, Chem. Soc. Rev., 2013, 42, 7571–7637.
17 K. Tanaka and F. Toda, Chem. Rev., 2000, 100, 1025–1074.
18 T. Friščič, Chem. Soc. Rev., 2012, 41, 3493–3510.
19 S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščič, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, T. Frič, Z. Cherkezova-Zheleva, J. M. Criado, F. Delogu, E. Dutková, E. Gaffet, F. J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii and K. Wieczorek-Ciurowa, Chem. Soc. Rev., 2013, 42, 7571–7637.
20 E. Boldyrev, Chem. Soc. Rev., 2013, 42, 7719–7738.
21 A. D. Katsenis, A. Puškarić, V. Štrukil, C. Mottillo, P. A. Julien, K. Užarević, M.-H. Pham, T.-O. Do, S. A. J. Kimber, P. Lazić, O. Magdysyuk, R. E. Dinebier, I. Halasz and T. Friščič, Nat. Commun., 2015, 6, 6662.
22 M. Wilke, L. Batzdorf, F. Fischer, K. Rademann and F. Emmerling, RSC Adv., 2016, 6, 36011–36019.
23 M. Wilke, A. G. Buzanich, U. Reinholz, K. Rademann and F. Emmerling, Dalton Trans., 2016, 45, 9460–9467.
24 C. Mottillo and T. Friščič, Molecules, 2017, 22, 144.
25. A. E. M. Beedle, M. Mora, C. T. Davis, A. P. Snijders, G. Stirnemann and S. Garcia-Manyes, *Nat. Commun.*, 2018, **9**, 3155.

26. J. L. Howard, Q. Cao and D. L. Browne, *Chem. Sci.*, 2018, **9**, 3080–3094.

27. D. Tan and F. García, *Chem. Soc. Rev.*, 2019, **48**, 2274–2292.

28. T. Friščić, I. Halasz, P. J. Beldon, A. M. Belenguer, F. Adams, S. A. J. Kimber, V. Honkimaki and R. E. Dinnebier, *Nat. Chem.*, 2013, **5**, 66–73.

29. X. H. Ma, W. B. Yuan, S. E. J. Bell and S. L. James, *Chem. Commun.*, 2014, **50**, 1585–1587.

30. L. Batzdorf, F. Fischer, M. Wilke, K. J. Wenzel and F. Emmerling, *Angew. Chem., Int. Ed.*, 2015, **54**, 1799–1802.

31. H. Kulla, M. Wilke, F. Fischer, M. Röllig, C. Maierhofer and F. Emmerling, *Chem. Commun.*, 2017, **53**, 1664–1667.

32. H. Kulla, S. Haferkamp, I. Akhmetova, M. Röllig, C. Maierhofer, K. Rademann and F. Emmerling, *Angew. Chem., Int. Ed.*, 2018, **57**, 5930–5933.

33. K. Užarević, N. Ferdelji, T. Mrla, P. A. Julien, B. Halasz, T. Friščić and I. Halasz, *Chem. Sci.*, 2018, **9**, 2525–2532.

34. P. F. M. de Oliveira, A. A. L. Michalchuk, A. G. Buzanich, R. Bienert, R. M. Torresi, P. H. C. Camargo and F. Emmerling, *Chem. Commun.*, 2020, **56**, 10329–10332.

35. S. Hu, C. Ma, F. Zhan, Y. Cao, P. Hu and Q. Zhen, *Chem. Pap.*, 2017, **71**, 1323–1329.

36. F. M. Santos, H. I. S. Nogueira, A. M. V. Cavaleiro, E. D. Gomes and M. S. Belsley, *Inorg. Chim. Acta*, 2017, **455**, 600–606.

37. R. Mao, F. Zhan, N. Bu, Y. Cao, P. Hu, G. Gong and Q. Zhen, *Mater. Lett.*, 2016, **173**, 111–114.

38. M. Wilke, M. Klimakov, K. Rademann and F. Emmerling, *CrystEngComm*, 2016, **18**, 1096–1100.

39. X. Zhao, Y. Duan, F. Yang, W. Wei, Y. Xu and C. Hu, *Inorg. Chem.*, 2017, **56**, 14506–14512.

40. X. Zhao, L. Gong, C. Wang, C. Wang, K. Yu and B. Zhou, *Chem.–Eur. J.*, 2020, **26**, 4613–4619.

41. H. T. Evans, B. M. Gatehouse and P. Leverett, *J. Chem. Soc., Dalton Trans.*, 1975, 505–514.

42. V. Ban, Y. Sadikin, M. Lange, N. Tumanov, Y. Filinchuk, R. Černý and N. Casati, *Anal. Chem.*, 2017, **89**, 13176–13181.

43. E. Petrus, M. Segado and C. Bo, *Chem. Sci.*, 2020, **11**, 8448–8456.

44. K. J. Ardila-Fierro and J. G. Hernández, *ChemSusChem*, 2021, **14**, 2145–2162.