This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A novel POMos-based hybrid with penta-coordinated Mo in trigonal bipyramid: structure and an efficient precursor for hydrodesulfurization catalyst

Ji-Lei Liang, Yu-Kun Lu,* Jin-chong Zhao, Xue-Hui Li, Yuan Pan, Meng-Meng Wu, Yun-Qi Liu* and Chen-Guang Liu

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis, China National Petroleum Corporation (CNPC), China University of Petroleum (East China), Qingdao 266555, P. R. China

The first POMos-based hybrid with penta-coordinated Mo in trigonal bipyramid for Mo-O clusters;

An efficient precursor for hydrodesulfurization catalyst.
A novel POMos-based hybrid with penta-coordinated Mo in trigonal bipyramid: structure and an efficient precursor for hydridesulfurization catalysis†

Ji-Wei Liang, Yu-Kun Lu,* Jin-chong Zhao, Xue-Hui Li, Yuan Pan, Meng-Meng Wu, Yun-Qi Liu* and Chen-Guang Liu

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The first POMos-based hybrid with penta-coordinated Mo in trigonal bipyramidal geometry for Mo-O clusters has been hydrothermally synthesized and characterized by IR, TG, XPS, and X-ray diffraction analysis. Structure analysis indicated penta-coordinated together with tetra-coordinated Mo existed in the POMos-based hybrid. The hybrid was successfully used as an efficient precursor for hydridesulfurization (HDS) catalysis for the first time.

Organic-inorganic hybrids have been attracting extensive interest in solid state materials chemistry owing to their unique structural diversities and interesting properties, which make them attractive for applications in catalysis, materials science and electrochemistry. In these fields, polyanionoxometalates (POMos), as one kind of significant Mo-O clusters with controllable shape and excellent property, are outstanding inorganic building blocks for the construction of POMos-based hybrids. As Zubieta indicated that POMos anions can be linked through secondary metal coordination groups forming POMos-based hybrids via self-assembly, a variety of novel POMos-based hybrids with {Mo_12O_42}^4−, {Mo_2O_33}^3−, {Mo_3O_35}^3−, {Mo_2O_24}^{4+}, {Mo_5O_26}^7−, {Mo_4O_19}^{10+} were synthesized. These works have greatly enriched the polyoxometalates (POMs) chemistry. Among various POMos-based hybrids, molybdenum is commonly tetra- or hex-coordinated, and no hybrid with penta-coordinated molybdenum in a trigonal bipyramidal manner is available since it is inherently coordinately unsaturated. As is well known that Ni-Mo-O clusters play an important role in the construction of HDS catalysts for the petroleum refining industry. Inspired by the self-assembly strategy of POMos-based hybrids in POMs chemistry, we selected rational organic ligand to link Ni-Mo-O clusters in impregnating solution and form a new POMos-based hybrid, which can not only enrich the POMs chemistry but also provide ideal precursor to develop more active HDS catalyst. On the basis of the above consideration, an interesting layered POMos-based hybrid, Ni_2[4,4’-bpy]Mo_2O_3(O_2C)_{14} (1) (4,4’-bpy=4,4’-bipyridine) was synthesized from the impregnating solution, in which penta-coordinated Mo1 in trigonal bipyramid and tetra-coordinated Mo2 in tetrahedron were found. To the best of our knowledge, this is the first example of penta-coordinated Mo in trigonal bipyramid geometry for Mo-O clusters. Moreover, Ni and Mo atoms are inserted in 1 with the Ni/Mo ratio of 0.5, an optimal ratio to prepare HDS catalyst. A preliminary study was carried out to explore the use of 1 as precursor for the HDS catalyst of dibenzothiophene (DBT), a representative sulfur compound in gas oil.

The first POMos-based hybrid with penta-coordinated Mo in trigonal bipyramidal geometry for Mo-O clusters has been hydrothermally synthesized and characterized by IR, TG, XPS, and X-ray diffraction analysis. Structure analysis indicated penta-coordinated together with tetra-coordinated Mo existed in the POMos-based hybrid. The hybrid was successfully used as an efficient precursor for hydridesulfurization (HDS) catalysis for the first time.

Single-crystal X-ray diffraction analysis reveals that 1 consists of two-dimensional Ni-O-Mo bimetallic oxide networks connected by coordination of 4,4’-bpy with Mo and Ni to generate a three-dimensional framework. As shown in Fig. 1, two Ni and two Mo sites exist in the asymmetric unit of 1, and they are connected by oxygen bridges. In fact, two crystallographic Ni sites both have half occupation of sites. Hence, the ratio of Ni/Mo is 0.5. The hybrid is structurally related to the POMos-based hybrids with dimolybdate {Mo_2O_2}_4^8−, but there are some differences. In the available POMos-based hybrids with {Mo_2O_3}_4^8−, both of the molybdenum sites are tetra-coordinated in tetrahedron_10^h or hex-coordinated in octahedron_10^h. However, it is noteworthy that the geometry of the Mo1 site in 1 is trigonal.
bipyramid, \{O(MoO_3)N\}, with three o xo groups in the equatorial position and two axial positions occupied by a N atom of 4,4'-bpy and a O of o xo group (Fig. S1, ESI†). The three equatorial bonds make almost perfect trigonal angles with the actual values of 116.2 (154), 118.0 (152), and 120.5 (156)° (Table S2, ESI†), and the sum of three angles is 354.7°. Mo1 atom is displaced by 0.23 Å toward the O from the equatorial plane of the three oxygen atoms (Fig. S2, ESI†). The axial N-Mo-O is slightly bent (177.9 (145)°), with a short Mo-O bond distance of 1.953 (27) Å, and long Mo-N bond distance of 2.314 (37) Å, presumably because of stress imposed by the bridging system.15 By contrast, the geometry of the Mo2 site is \{MoO_4\} tetrahedron. To the best of our knowledge, two compounds with penta-coordinated molybdenum were reported by Anderson,14 however, they were organometallic compounds, and this is the first example of POMos-based hybrid with penta-coordinated molybdenum-oxo cluster in trigonal bipyramid geometry. Besides, The principal axis of the two trigonal bipyramids reported by Anderson is more bent (167.0°, 169.4°) than that of 1 (177.9°), indicating the trigonal bipyramid of 1 is more perfect (Fig. S3, ESI†). The bond valence sum calculations for the Mo atoms (Table S3, ESI†) was calculated by using parameters given by Brown,15 and the results give the average value 5.96 and 5.93 for Mo1 and Mo2, respectively, indicating that the hybrid contains MoVI centers. The XPS gives two peaks at 231.7 eV and 234.8 eV ascribed to MoVI 3d5/2 and MoVI 3d3/2, respectively (Fig. S4, ESI†).16 All these results further confirm the structure analysis above.

The hex-coordinated Ni in 1 is in a slightly elongated octahedral adduct, \{Ni(NiO_2)N\}, of which the axial positions are occupied by two nitrogen donors from two 4,4'-bpy (Ni-N = 2.137(39) Å, N-Ni-N = 180°). The equatorial plane is defined by two oxygen donors from two \{MoO_4\} with Ni–O bond distance of 2.084(33) Å and two oxygen donors from two \{O(MoO_3)N\} with Ni–O bond distance of 2.087(36) Å. The Ni atom is exactly located in the center of the equatorial plane.

As shown in Fig. 2, each \{Ni(NiO_2)N\} octahedron can be viewed as an effective junction via four o xo groups to link two Mo1 and two Mo2 atoms into a novel two-dimensional layered network. Notably two \{MoO_4\} tetrahedra, two \{Ni(NiO_2)N\} octahedrons and two \{O(MoO_3)N\} trigonal bipyramids, are linked alternatively in a pattern of corner sharing to form a unique 6-member \{Mo_{2}N_{2}O_{2}\} ring. Then, the rings are connected to each other via corner sharing into a two-dimensional layered network. Finally, the bimetallic layers are connected by 4,4'-bpy, generating a three-dimensional layered structure with the adjacent bimetallic layer distance of 7 Å as shown in Fig. 3. Interestingly, two different coordination modes of 4,4'-bpy are found in Fig. 3. On one hand, some 4,4'-bpy are planar with two N atoms coordinated to Ni sites, forming square channels (11.43×11.40 Å). On the other hand, two pyridine rings of other 4,4'-bpy are twisted with two N atoms coordinated to Ni and Mo, respectively. The square channels are subdivided into three narrow windows due to this coordination mode. For such framework, a 4,4'-bpy coordinating to two different kinds of metal centers is really rare.

The IR spectrum of 1 (Fig. S6, ESI†) exhibits two bands at 933 and 889 cm\(^{-1}\) which can be attributed to the Mo=O stretching vibrations, while those from 648 to 860 cm\(^{-1}\) are associated to the Mo–O–Mo bending vibrations.65 Besides, the bands at 1612, 1538, 1485, 1406 and 1213 cm\(^{-1}\) can be regarded as the vibrations of 4,4'-bpy ligands.18

![Fig. 2 Two-dimensional layered structure consisting of 6-member \{Mo_{2}N_{2}O_{2}\} rings viewed along the ac plane in polyhedral representation.](image)

![Fig. 3 3-dimensional layered structure of 1 linked by 4,4'-bpy with two different coordination modes of 4,4'-bpy viewed along the ac plane.](image)

![Fig. 4 The sulfided, synthesized and simulated XRD patterns of 1.](image)

The thermal stability of 1 was investigated and the TG curve (Fig. S7, ESI†) shows that it is thermal stable under 360 °C and then it begins to decompose, and the total weight loss is 40.53%, corresponding to the release of the 4,4'-bpy ligands, which is in accordance with the calculated value of 39.25% (–1.5 4,4'-bpy),

...
and the residue should be NiO and MoO₃.

In order to confirm the purity of 1, the XRD measurement has been performed, as shown in Fig. 4. The result shows that the experimental XRD pattern of 1 is in good agreement with the simulated pattern based on the result from single-crystal X-ray diffraction via Mercury 1.4.2 software, indicating that the bulk hybrid is pure. Then the hybrid was sulfided as the catalyst. The XRD pattern of the sulfided hybrid exhibits weak peaks of MoS₂ at 14.1°, 33.1°, 39.8° and 59.2°, indicating poorly crystallized structure of the MoS₂ which is the active phase for the HDS catalyst of DBT. It is noted that Ni was incorporated at the edge of MoS₂ and no sulfide of Ni was found.

![Fig. 5 HRTEM image of the sulfided hybrid.](image)

The sulfided hybrid was observed by high-resolution transmission electron microscopy (HRTEM) and the image is presented in Fig. 6. The black fringes correspond to the MoS₂ slabs. These bent fringes presents a spacing of 0.62 nm which is the characteristic of (002) basal planes of MoS₂ crystallite. The fringes appear relatively stacked and disordered, and the number of the stacking layer is around 5-10. Since the hybrid is multi-layered, highly stacking MoS₂ crystallites are formed after sulfidation, which is favored for the preparation of HDS catalyst. The high stacking layer number may mean higher hydrogenation ability of the catalyst.

<table>
<thead>
<tr>
<th>DBT conversion (%)</th>
<th>Product selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h 2 h 3 h 4 h</td>
<td>k₂₎ offenses</td>
</tr>
<tr>
<td>22.5 63.2 81.6 92.8</td>
<td>4.4 30.3 58.2 1.9</td>
</tr>
</tbody>
</table>

Determining at about 50% of total DBT conversion, obtained by dividing DDS into HYD, DDS= BP, HYD=CHB.

The catalytic results of DBT HDS are shown in Table 1. The DBT conversion can reach 92.8% at 4 h, indicating higher catalytic activity of the catalyst compared to the reported results by Klimova and co-workers. This can also be observed from the value of overall pseudo-first order rate constant k₂₅ offenses shown in Table 2. There are two pathways in DBT HDS: one is the direct desulfurization (DDS) route to yield biphenyl (BP), and the other is through the hydrogenation (HYD) route to produce cyclo-hexylbenzene (CHB) with tetra-hydridobenzothiophene and hexa-hydridobenzothiophene as intermediates. Table 1 also shows the reaction product distributions obtained at 50% of DBT conversion to distinguish the individual contributions of the HYD and DDS routes to the overall HDS performance of the sulfided hybrid. The catalyst showed larger amounts of CHB in comparison with BP and much higher hydrogenation ability, indicating that the catalyst is more favorable for the HYD pathway.

In summary, the first example of POM-based hybrid with penta-coordinated molybdenum in trigonal bipyramidal geometry for Mo-O clusters was hydrothermally synthesized and structurally characterized. More interestingly, penta-coordinated molybdenum together with tetra-coordinated molybdenum exists in the hybrid. Investigation of the catalytic activity property indicated that the hybrid can serve as an efficient HDS catalyst precursor. This work not only enriches the POMs chemistry but also expands the application of POMs in HDS field successfully for the first time. As a continuance of the work, we will investigate the catalytic property of POMs in HDS field in detail.

This work was supported by the National Basic Research Program of China (No. 2010CB226905), the Natural Science Foundation of China (No. 21176258, U1162203, 21301190), the Fundamental Research Funds for the Central Universities, (No. 13CX06039A, 13X02007A), Shandong Provincial Natural Science Foundation, China (No. ZR2011BQ004), and China Postdoctoral Science Foundation (2012MS21384) are gratefully acknowledged.

### Notes and references

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis, China National Petroleum Corporation (CNPC), China University of Petroleum (East China), Qingdao 266555, P. R. China. E-mail: lyq@upc.edu.cn, liuyq@upc.edu.cn

*Electronic Supplementary Information (ESI) available: [Experimental details, Table 1](https://doi.org/10.1039/b000000x)**


12. Ni4(4,4’-bpy)MoO4(4,4’-bpy)3O4 (I). A mixture of (NH4)2MoO4 (0.374 g, 0.3 mmol), Ni(NO3)2 (0.145 g, 0.05 mmol), and 4,4’-bpy (0.165 g, 1.06 mmol) and H2O (30 mL, 1667 mmol) was stirred and the pH value was adjusted to 5.8. The resulting suspension was sealed in a 50 mL Teflon lined reactor and kept at 140 °C for 3 days. After cooling the autoclave to room temperature, green block crystals were obtained (yield: 38% based on Mo). Elemental analysis for C3H2MoNi4O14 calc (%): C, 30.16; H, 2.01; N, 7.04; Ni, 9.83; Mo, 32.15. found: C, 29.66; H, 1.72; N, 7.07; Ni, 9.72; Mo, 32.11. IR (KBr, cm⁻¹): 3440 (w), 1637 (m), 1609 (m), 1554 (w), 1532 (w), 1516 (w), 1488 (s), 1410 (s), 1356 (w), 1335 (w), 1322 (w), 1218 (s), 1079 (s), 1049 (s), 944 (m), 869 (w), 800 (w), 943 (w), 863 (w), and 779 (w).