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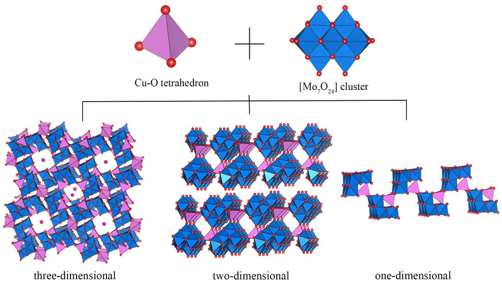
CMF-1~3 were firstly obtained by $[Mo_7O_{24}]^{6-}$ and Cu tetrahedra, and all showed excellent performance for the degradation of methylene blue.



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Various dimensional frameworks, CMF-1~3, were synthesized by using catalytically active $[Mo_7O_{24}]^{6-}$ clusters and Cu tetrahedra. After the thorough studies, the relationships between synthesis conditions and products were obtained and showed in composition diagrams. Besides, CMF-1~3 all showed excellent catalytic activities in the degradation of methylene blue.

Polyoxometalates (POMs) are a class of metal oxide clusters with tunable compositions, structures and potential applications in various fields[1, 2], especially in catalysis[3]. POM clusters usually act as homogeneous catalysts in reaction systems and favor high activity and selectivity, as they are soluble in many polar solvents, but the solubility of POM clusters may cause difficulties in the separation and recycling of the catalysts. In order to develop some easily recoverable and recyclable POM catalysts for practical applications, two strategies, namely "immobilization" and "solidification"[4], were taken to reach this goal. The first method is immobilizing isolated clusters on various types of porous supports by adsorption, ion exchange[5], and so on. According to the literature, POM clusters were generally loaded in the channel of mesoporous silicate and metal-organic frameworks (MOFs), or on the surface of polymer by amine groups[6]. Yamanaka's group designed acid catalysts composing POM molecules and organografted mesoporous silica SBA-15[7], which showed extremely high catalytic activity for ester hydrolysis in water. Su's group constructed hybrid material polyoxometalate metal-organic frameworks (POMMOFs)[8] by simple one-step hydrothermal reaction, where Keggin polyanions were alternatively arrayed as non-coordinating guests in the MOF matrix. Although these materials promotes the development of POMs as heterogeneous catalysts, these supports cannot provide enough stability to anchor POM species, which may lead to the leaching of POM clusters during recycling. The second strategy is solidifying POM clusters by synthesizing insoluble POM-based catalysts. Numerous examples were achieved with organic ligands[9-11], or inorganic ions[12] modified POM clusters. While these kinds of ligand-coating POM materials suffered from leaching of active sites due to the dissolving and degradation of POM complexes. Based on the previous works, people started connecting POM clusters tightly to construct porous pure-inorganic high-dimensional frameworks, which could not only overcome leaching of active species but also allow detailed studies about catalyst sites[13, 14]. In 2002, Huang's group reported the first three-dimensional framework $[Gd(H_2O)_3]_3[GaMo_{12}O_{42}]\cdot 3H_2O$[15], containing Silverton-type anions linked by Gd(III) cations but without permanent porosity. Recently Hill's group prepared Sn(II)-containing polyoxometalates[16], where all the clusters were connected through Na-O bond formed a 3-dimensional porous structure. However, the Na-O bonds are ionic bonds, which are not stable enough in real applications. In our previous work, we obtained a series of 3D frameworks based on transition metal ions and vanadoborate clusters, named as SUT-6~7. Among them, SUT-6[17] was an efficient heterogeneous precatalyst for the oxidation of alkylbenzenes while SUT-7[18] contained mesopores in its single network.

Although POM-based porous frameworks are realized as good heterogeneous catalysts as shown above, the studies on designed synthesis and assembling of POMs, especially molybdenum-based systems, into high-dimensional materials are still rare[19, 20]. Here, we used classical POM clusters $[Mo_7O_{24}]$ as building blocks to construct pure-inorganic high-dimensional frameworks, by hydrothermal methods with $Cu(NO_3)_2$, $(NH_4)_2Mo_7O_{24}\cdot 4H_2O$, acetic acid in H_2O at 180°C for 7 days. Under this synthesis condition, we synthesized a new 3D framework CMF-1. CMF-1 is a framework constructed by $[Mo_7O_{24}]$ clusters and four-coordinated Cu ions. Based on the origin of oxygen atoms, the connection of Cu and POM can be divided into two types, named as Mode-I, and II. As shown in Figure 1, in Mode-I, four oxygen atoms are from two

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$[Mo_7O_{24}]$ clusters, while in Mode-II, they are contributed by four different clusters.

CMF-1 is the first three-dimensional framework with $[Mo_7O_{24}]$ clusters. Its asymmetric unit contains one $[Mo_7O_{24}]$ cluster and three Cu ions, and the incorporation of Cu ions is clearly indicates by its black colour since copper-free products obtained by others are normally colorless or yellow-green. Among those three Cu ions, Cu2 ions are in Mode-I and form crown-like clusters $Cu_4[Mo_7O_{24}]_4$ as shown in Fig.1(c). Half-occupied Cu3 ions are in Mode-II and connect the crown-like building units into a three-dimensional structure. Cu1 ions are linearly coordinated by two ammonia molecules outside of the framework and block the windows of crown-like clusters. Based on the bond valence summation (Table S5), Cu1 is monovalent while Cu2 and Cu3 ions in the frameworks have mixed oxidation states, which is consistent with the XPS results with the ratio of Cu^+/Cu^{2+} about 1.0:1.7. In our copper-molybdenum system, these two coordination modes provide distorted tetrahedral coordination environment of copper ions because of the steric hindrance of clusters and they show potential application to stabilize monovalent copper ions which prefer to form a tetrahedral coordination. We believe that the formation of tetrahedrally coordinated Cu may be associated with the pH value and the addition of acetic acid. As acetic acid has weaker reducibility and coordination ability than amines, copper ions may form some metastable complexes with H_2O, NH_4^+ and CH_3COO^- in weak acidic solutions. When reacting at 180°C, these complexes dehydrated and linked with $[Mo_7O_{24}]$ clusters into high-dimensional framework. The topological structure of CMF-1 is analogous to that of the SOD zeolite, if we treat $[Mo_7O_{24}]$ clusters and Cu3 ions as nodes (Fig. S2).

During the exploratory work for the stable synthesis conditions of CMF-1, two new phases, CMF-2 and CMF-3 (Fig.2), were obtained. CMF-2 is a 2D framework constructed by $[Mo_7O_{24}]$ and Cu alternatively through Mode-II connections, and CMF-3 is a 1D structure with the Mode-I connections. The successful synthesis of CMF-1~3 indicates that Cu and $[Mo_7O_{24}]$ can form frameworks with various dimensions under different conditions. Here, we designed orthogonal experiments with several variables, such as temperature, the pH value, the amount of acetic acid and water, the amount and types of Cu and Mo. Through many experiments, we found four key factors: temperature, the amount of acetic acid, water, and molybdate, which will be discussed later. As for other factors, they do not have big influence on the results. For example, for the source of Mo, CMF-1 could be also synthesized with $H_3[PMo_{12}O_{24}]$, which means $[PMo_{12}O_{24}]$ clusters decomposed and formed $[Mo_7O_{24}]$ clusters at these reaction conditions. Besides that, these Cu-based products could only be obtained with acetic acid at pH 5~7. So we kept these values as constants in the systematic syntheses design. After orthogonal experiments and systematic syntheses, the stable region of each phase was determined and shown in the composition diagram[21] with the ratio of Mo/H_2O/acetic-acid at different temperatures.

The composition diagrams for Mo/acetic acid/water under different temperatures are shown in Fig. 3. Before discussing details, some comments should be noted here. Firstly, we set 0.5ml acetic acid, 2ml water, and 0.3mmol Mo as the criterion and plot the composition diagrams by their corresponding percentage. Besides that, the synthesis condition of CMF-1 and the reported $[CuMo_3O_{10}]\cdot H_2O$[22] are very similar in our studies, but they don't coexist in the same reactor and can both be synthesized as pure phases, so we sign them in the same position in composition diagram.

The effects of the four important synthesis factors are shown in Fig. 3. The predominant phase observed under the optical microscope is the 3D framework CMF-1 synthesized at both 180°C and 220°C with 0.3~0.6mmol molybdate and 0.5ml acetic acid. With increasing the amount of molybdate, the impurity Cu-free layered phase, signed as Phase B21[23], was obtained, which can be explained as decreasing the ratio of Cu/Mo_7. As mentioned previously, Cu ions act as linkers in CMF-1~3 and the ratio of Cu/Mo_7 in CMF-1 is 3:2. When adding more molybdate into the autoclave, the relative concentration of Cu ions decreased and Cu-free phase B21

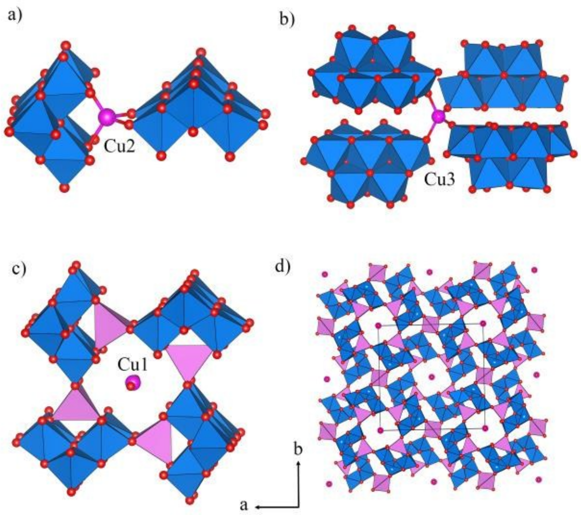

Fig. 1 Two coordination modes in these series of frameworks, a) mode-I, b) mode-II, respectively; c) crown-like clusters $Cu_4[Mo_7O_{24}]$ in CMF-1; d) full structure of CMF-1 viewing along the [001] direction.

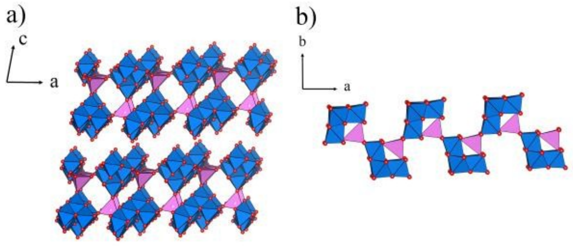

Fig. 2 a) Layered structure of CMF-2 viewing along the *b*-axis; b) a chain in CMF-3 along the *a*-axis.

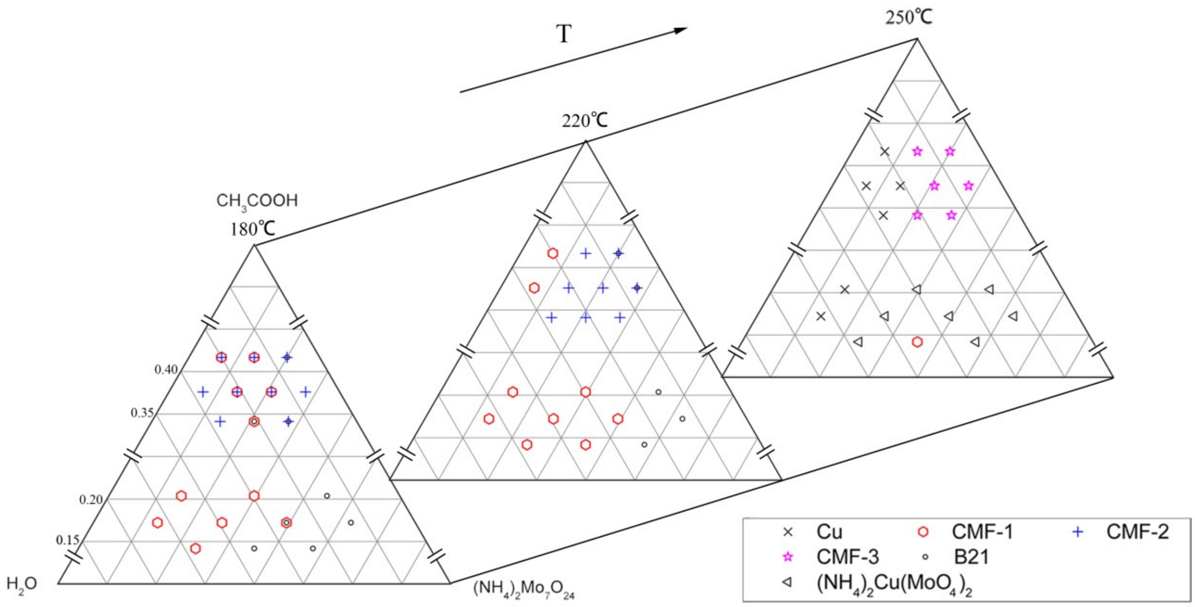

Fig. 3 Composition diagrams for $(NH_4)_2Mo_7O_{24}\cdot4H_2O$/ H_2O/ acetic acid under different temperatures.

started appearing and finally dominated the product. The stable regions of 2D CMF-2 appear at 1.5ml acetic acid regions at 180°C and 220°C, because large amounts of acetic acid can reduce copper ions to monovalent. When increasing the amount of molybdate at 180°C, CMF-2 is obtained together with CMF-1, and then with Cu-free phase B21, indicating the similar trend as that in the synthesis of CMF-1. We can also get the pure CMF-2 in the 220°C composition diagram, which might be due to the increase of reducibility caused by the higher temperature. However, the results at 250°C composition space are quite different as the reducibility of system is so strong that Cu ions can be reduced to Cu metal. As shown in Figure 3, when adding 0.3mmol Mo, we only obtained brick-red amorphous powder with metallic luster at the water-rich end which were determined as elementary copper by SEM and EDS (Fig. S14). At this temperature, $[Mo_7O_{24}]$ clusters play an important role in stabilizing Cu^+ ion and preventing it from further reduction. Thus, with more molybdate in the reactors, the one-dimensional phase CMF-3, was synthesized with 1.5ml acetic acid and a known zero-dimensional phase, $(NH_4)_2Cu(MoO_4)_2$[24], was obtained when adding 0.5ml acetic acid. Based on the above analysis of these diagrams, some regularities were obtained: the products are mainly determined by the reducibility of system and the ratio of building blocks. Among them, the former depends on temperature and the amount of acetic acid, while the latter lies on the concentration of molybdate as that of copper is kept as a constant. As for the amount of water, it is difficult to study its effects due to the presence of excess water, while some water effects can be obtained based on the composition diagrams. Firstly, with more water in the reaction system, the purity of products increases but yield decreases. Secondly, high-dimensional products can be obtained with large amount of water, i.e. CMF-1 could only be synthesized with 4ml~8ml water, while CMF-3 was synthesized with 2ml~6ml water.

Due to the fast reversible multi-electron transformation activity[25], POMs could be used as a kind of green and cheap catalyst for the removal of organic pollutants from water. Methylene blue (MB), as a representative of the dye pollution in water, was selected for investigating the catalytic activities of CMF-1~3 in this work. When adding 0.0412g CMF-1 to a fresh MB dye aqueous solution (C_0= 3mg/100ml, 50ml), the solution became colorless in several minutes at weak alkaline conditions (7~8) without light irradiation, suggesting the degradation of the dye (Fig. 4). We explored the catalytic efficiency by re-using the catalysts for five successive cycles. After each experiment, the catalysts were centrifuged and heated at 160°C for 2h and then re-used in the next experiment. Comparing with other materials[26, 27] which need at least 2h to decompose 90% of MB under light irradiation, CMF-1~3 show much better efficiency even without light irradiation. The ICP-AES result of the content of Mo ions in methylene blue shows that about 13% of Mo ions were dissolved in the methylene blue solutions during catalytic progress.

In conclusion, the systematic investigation of the $(NH_4)_2Mo_7O_{24}\cdot4H_2O/H_2O$/acetic acid system at different temperatures resulted in syntheses of three compounds ranging from one-dimensional to three-dimensional. By a series of experiments, we found the key reaction variables and obtained the stable regions of each compounds in composition diagrams. This work demonstrates that the $[Mo_7O_{24}]$ clusters can be used to construct pure-inorganic frameworks, which show wonderful activities in degradation of dyes. The regularities obtained here can be used to design new frameworks in similar POM systems.

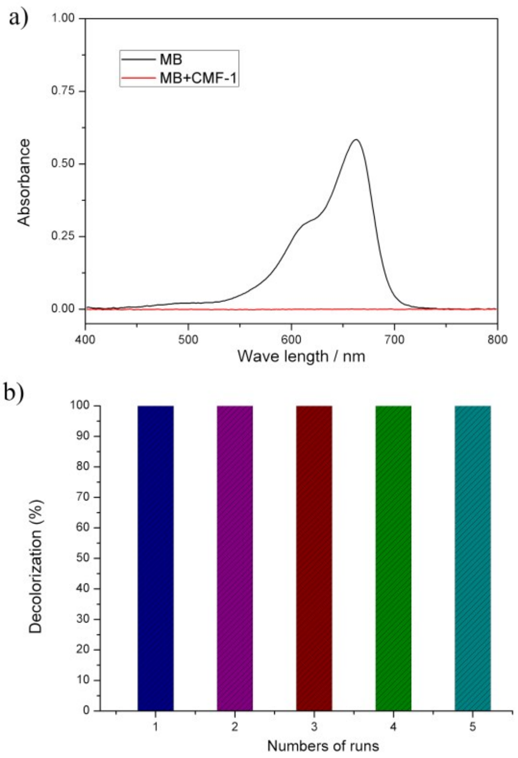

Fig. 4 Degradation of Methylene blue. a) UV-vis results of the solution before and after adding the CMF-1 catalyst; b) recycling experiments on the degradation of MB with CMF-1 as catalyst.

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