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Polyoxometalate-based purely inorganic porous frameworks with selective adsorption and oxidative catalysis functionalities†

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Purely inorganic porous frameworks using catalytically active $[MnV_{13}O_{38}]^{7-}$ clusters as nodes and rare earth ions as linkers have been successfully prepared. The POM-based porous framework is a kind of multifunctional material, which exhibits selective adsorption behavior and remarkable catalytic activity for the heterogeneous oxidation of sulfides.

In the past decade, metal–organic frameworks (MOFs), a new class of crystalline porous materials, have developed at an unusually fast pace and became one of the most prolific areas of research in chemistry and materials.[1] Through the combination of diverse metal-based building units and numerous organic linkers, MOFs possess rich structures and adjustable pore size, which are quite different from traditional porous zeolites.[2] Compared with zeolite materials, MOFs also have one major disadvantage, which is their weak stability. Therefore, it is exigent but challenging to obtain new types of porous materials that combine the sophistication and versatility of MOFs with the thermal stability of zeolites. Polyoxometalates (POMs), as a large subclass of metal oxide clusters, cover an enormous range in size and structure and thereby provide access to a huge library of readily available and controllable building units,[3] which can be covalently connected by various inorganic linkers or metal–organic bridges to form porous frameworks.[4] Since POM-based framework containing organic compositions usually possess low stability, linking diverse POM units to inorganic linkers to construct purely inorganic porous frameworks provides a promising way to achieve new types of porous materials possessing both versatility and stability.

Besides versatility and stability, multifunctionality is another demand for the new types of porous materials. POMs can act as excellent acid, redox, and bifunctional catalysts in a variety of synthetically useful selective transformations of organic substances, due to their strong Brönsted acidity and fast reversible multielectron redox transformation activity under mild conditions.[5] The excellent catalytic performance of POMs qualifies them as prime candidates for the designed construction of multifunctional materials combining porosity and catalytic activity.[6] As heterogeneous catalysts,[7] POM-based porous materials may possess several advantages, such as easier catalyst separation from the reaction mixtures and reducing contamination of products with traces of transition metal. On the other hand, compared to traditional POMs heterogeneous catalysts, obtained by the immobilization of POMs in high-surface-area supports, POM-based crystalline porous materials have the following advantages: the crystalline structure allows detailed knowledge about the pore structure and the nature of catalytic active sites; POMs are bound tightly in the porous framework as building units, which prohibits conglomeration and helps overcome catalyst leaching and deactivation.

Although POM-based inorganic porous materials possess these excellent features as mentioned above, to the best of our knowledge, studies on their designed synthesis and properties are quite scarce,[8] and no examples possessing catalytic activity have been reported to date. To achieve POM-based inorganic porous materials with catalytic performance, we choose the reaction system of the $[MnV_{13}O_{38}]^{7-}$ anion and rare earth ions (Ln^{3+}) based on the following considerations. Firstly, $[MnV_{13}O_{38}]^{7-}$ is a kind of redox catalytic active POM anion, and its catalytic performance has been extensively studied for the oxidation reaction.[9] Secondly, rare earth ions possess diverse coordination and bonding modes,[10] which make them more flexible in the connection with POMs and facilitate the formation of porous frameworks with a novel topology structure and large pore size. From this reaction system, we successfully obtained three new purely inorganic porous frameworks: $H[La(H_2O)_4]_2[MnV_{13}O_{38}]\cdot9NMP\cdot17H_2O$ (NMP = *N*-methyl-2-pyrrolidone) (**1**), $H[Ce(H_2O)_4]_2[MnV_{13}O_{38}]\cdot9NMP\cdot17H_2O$ (**2**), and $H[La(H_2O)_4]_2[MnV_{13}O_{38}]\cdot8NMP\cdot9H_2O$ (**3**).

The purely inorganic porous frameworks of **1–3** are all constructed by the covalent connection of heteropolyvanadate $[MnV_{13}O_{38}]^{7-}$ and trivalent lanthanide ions. Compounds **1** and **2** are isostructural. Therefore, compound **1** is described as an example below. In **1**, each $[MnV_{13}O_{38}]^{7-}$ anion links to four equivalent La^{3+} cations in two distinct ways: one way is $[MnV_{13}O_{38}]^{7-}$ is capped by the

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La^{3+} ion through its four terminal oxygen atoms coordinating to one La^{3+} ion, the other is $[MnV_{13}O_{38}]^{7-}$ supporting the La^{3+} ion through its one terminal oxygen atom coordinating to one La^{3+} ion. The arrangement of the four La^{3+} ions around the $[MnV_{13}O_{38}]^{7-}$ cluster can be regarded as an approximate square-planar mode. On the other hand, each La^{3+} cation connects with two equivalent $[MnV_{13}O_{38}]^{7-}$ anions (Fig. S2, ESI†). Each La^{3+} ion adopts the tricapped trigonal prism geometry, which is coordinated by five terminal oxygen atoms from two $[MnV_{13}O_{38}]^{7-}$ anions and four water molecules. Based on the above-mentioned connection modes, each $[MnV_{13}O_{38}]^{7-}$ anion is joined to four other $[MnV_{13}O_{38}]^{7-}$ anions through four La^{3+} linkers to form a 4-connected uninodal net with $4^2 \cdot 8^4$-lvt topology (Fig. S3, ESI†). The structure of **1** is wide open, and contains a multi-directional channel system. As shown in Fig. 1, these channels intersect with each other and run along six different directions: 21.47 × 10.65 Å along the [010] and [100] directions (Fig. S4, ESI†), and 20.04 × 10.65 Å along the [11−1], [1−11], [111] and [−111] directions (Fig. 1a and b). To our knowledge, this kind of six-directional intersecting channel system is scarce in POM-based porous frameworks, which is an important feature of **1** and **2** desired for a heterogenous catalyst. In compound **3**, the connection mode between the $[MnV_{13}O_{38}]^{7-}$ anion and the La^{3+} cation is the same as that in compound **1**. However, different from **1**, both the four La^{3+} ions connected with the same $[MnV_{13}O_{38}]^{7-}$ anion and the two $[MnV_{13}O_{38}]^{7-}$ anions linked to the same La^{3+} ion are nonequivalent in **3**, which has two types, respectively. The two types of $[MnV_{13}O_{38}]^{7-}$ anions possess the same structure and the two types of La^{3+} cations possess the same coordination geometry except for slight differences in bond lengths and angles (Table S3, ESI†). These differences result in **3** having a unique 3D structure different from **1**. Topologically, the 3D structure of **3** can be rationalized as a 2-nodal $4^2 \cdot 8^4$-ssb net (Fig. S5, ESI†). To our knowledge, this topological type is very rare. Also, different from **1**, the framework of **3** only contains three-directional intersecting channels: 21.54 × 13.76 Å along the [100] and [010] directions (Fig. 1c and d), and along the [001] direction with window dimensions of 22.69 × 6.38 Å (Fig. S6, ESI†). It is noteworthy that the frameworks of **1** and **3** have the same composition but different structure as described above, which belong to conformational isomers as categorized by Moulton and Zaworotko.[11] As suggested by their structures, the coordination flexibility of rare earth ions plays an important role in the formation of the isomers.

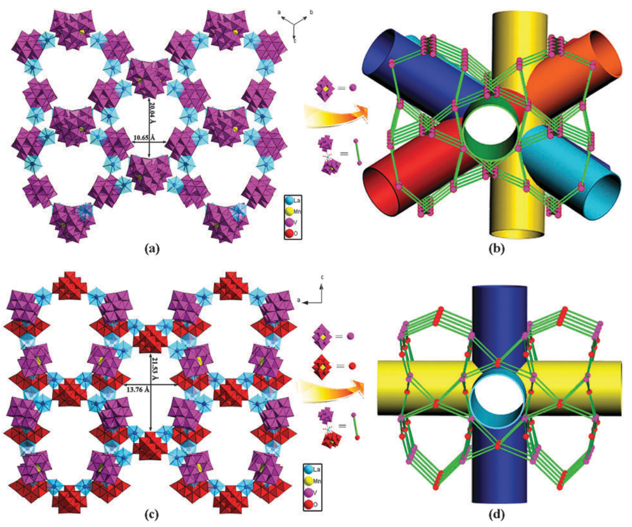


Fig. 1 (a) Polyhedral representation of the 3D framework with channels in compound **1**; (b) the topological representation of **1**, highlighting the six directional channels in the 3D framework; (c) the 3D polyhedral representation of compound **3**; (d) the topological representation of **3**. The three directional channels are shown interweaved.

The accessible void volumes of the 3D intersecting channels in **1–3** are 68.9%, 68.9% and 68.1% of the unit cell volumes estimated by PLATON/SOLV, respectively.[12] These values are comparable to the highest ones found in POM-based porous materials.[4c] Calculations based on the crystallographic results indicate that the surface area of **1–3** is 1538, 1527 and 1508.5 $m^2\ g^{-1}$,[13] respectively. These theoretical results show that the three purely inorganic frameworks are very open and encourage a detailed experimental investigation of their sorption capability and heterogeneous catalysis performances.

To study the adsorption properties, the water, methanol and ethanol adsorption isotherms for compound **2** were measured at 298 K. As shown in Fig. 2, the amount of water uptake increases with a P/P_0 increase and reaches 262 $cm^3\ g^{-1}$ at $P/P_0 = 0.75$. The saturated sorption amount of water is equivalent to the adsorption of about 34 H_2O molecules per formula unit. As for methanol, the sorption amount reaches 172 $cm^3\ g^{-1}$ at $P/P_0 = 0.85$, which is equivalent to the adsorption of about 22 CH_3OH molecules per formula unit. These results indicate that water and methanol molecules could enter freely into the channels. In contrast, the amount of ethanol sorption (2.4 $cm^3\ g^{-1}$ at $P/P_0 = 0.9$) was close to the surface adsorption and was negligible, which means that ethanol was not allowed to enter into the channels. Therefore, compound **2** could adsorb water (molecular area: 10.5 Å^2) and methanol (17.9 Å^2) molecules, but exclude larger ethanol (23.0 Å^2) molecules. Recently, bioethanol, as a sustainable energy source, has attracted much attention.[14] The purification of bioethanol, that is eliminating both methanol and water from bioethanol, is a critical problem for its widespread use.[15] The above adsorption studies show that compound **2** will be a promising material for separating both methanol and water from bioethanol.

Owing to their fast reversible multielectron transformation activity, POMs have been extensively investigated as catalysts in a variety of oxidation reactions, including epoxidation

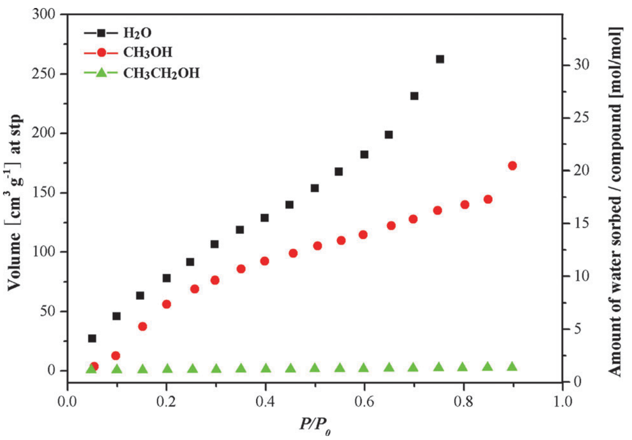
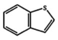
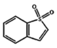
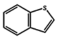
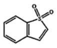
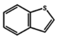
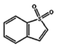
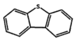
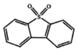
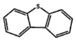
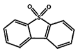
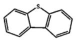
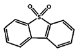
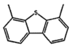
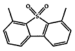
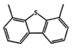
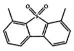
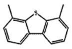
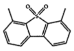


Fig. 2 Sorption isotherm of water, methanol and ethanol at 298 K for compound **2**.

Table 1 Oxidation of sulfide to sulfone with TBHP catalyzed by various catalysts[a]

Entry	Substrate	Product	Catalyst	*t*, h	Removal[b] %
1			**2**	4	98.8
2			$[MnV_{13}O_{38}]$	4	38.6
3			None	4	8.2
4			**2**	3	99.5
5			$[MnV_{13}O_{38}]$	3	79.5
6			None	3	48.1
7			**2**	6	99.1
8			$[MnV_{13}O_{38}]$	6	63.0
9			None	6	15.2

[a] Conditions: a mixture of catalyst (0.075 mmol), sulfide (0.4 mmol), and TBHP (2.0 mmol, 5 equiv.) in CH_2Cl_2 (2 mL) was stirred at 50 °C. [b] Based on HPLC analysis.

and desulfurization.[16] Thus, the oxidations of thiophene sulfides were chosen as test reactions to assess the catalytic activity of these POM-based inorganic frameworks. Oxidations of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in the presence of **2** were performed in CH_2Cl_2 medium at 50 °C using *tert*-butyl hydroperoxide (TBHP) as the oxidant respectively (Scheme S1, ESI†). The results of the catalytic runs along with blank experiments and experiments performed in the presence of solid $[NH_4]_7[MnV_{13}O_{38}]\cdot 18H_2O$ are presented in Table 1. The experimental data demonstrate that **2** shows fairly good catalytic activity for the oxidations of the three sulfur-containing substrates (Fig. S9 and S10, ESI†). The maximum substrate conversions were 98.8% achieved after 4 h for BT, 99.5% after 3 h for DBT and 99.1% after 6 h for 4,6-DMDBT. Moreover, the three substrates were finally oxidized into the corresponding sulfones with 100% selectivity as verified by FTIR (Fig. S11, ESI†) and GC-MS (Fig. S12, ESI†) measurements. As shown in Table 1, the catalytic activity of **2** is far superior to its solid precursors (compare entries 1–2, 4–5 and 7–8 respectively), which suggests that not only the surface but also the interior POM active sites of solid **2** take part in the catalytic reactions. Solid **2** can be almost completely recovered from the reaction vessel after a catalytic test run by simple centrifugal separation (Fig. S13, ESI†). X-ray powder diffraction data of the recovered catalyst gave no signs of decomposition (Fig. S17, ESI†). The recovered catalyst was reused in successive runs with only slightly decreased substrate conversion (Fig. S14, ESI†).

In conclusion, the new purely inorganic porous frameworks **1–3** based on catalytic active $[MnV_{13}O_{38}]^{7-}$ SBUs and rare earth linkers have been successfully synthesized. The porous framework of **2** exhibits remarkable selective adsorption behavior: adsorbing water and methanol, but excluding ethanol molecules. Moreover, the oxidation of sulfides catalyzed by **2** as a heterogeneous catalyst was investigated and it showed high activity. To our knowledge, **2** represents the first example of POM-based purely inorganic porous material possessing catalytic performance. This work demonstrates that it is a feasible way to construct crystalline porous materials with catalytic performance employing catalytic active POMs as SBUs.

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