

New Heterogeneous Polyoxometalate Based Mesoporous Catalysts for Hydrogen Peroxide Mediated Oxidation Reactions

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Abstract: Inorganic–organic hybrid mesoporous materials were prepared by cocrystallization of a “sandwich” type polyoxometalate, $[\text{ZnWZn}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$, and branched tripodal organic polyammonium salts, tris[2-(trimethylammonium)ethyl]-1,3,5-benzenetricarboxylate or 1,3,5-tris[4-(*N,N,N*-trimethylammonium-ethylcarboxyl)phenyl]benzene trications. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed formation of three-dimensional perforated coral-shaped amorphous materials with the organic cations surrounding polyoxometalate anions. N_2 sorption analysis showed that the hybrid materials have a BET surface area of $\sim 30\text{--}50\text{ m}^2\text{ g}^{-1}$ and an average pore diameter of 36 Å leading to the classification of these materials as mesoporous materials with moderate surface areas. These hybrid materials behaved as very effective and selective heterogeneous catalysts for the epoxidation of allylic alcohols and oxidation of secondary alcohols to ketones with hydrogen peroxide as oxidant. The activity and selectivity of the heterogeneous catalysts based on the hybrid materials was similar to those of homogeneous catalysts based on the same $[\text{ZnWZn}_2(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ polyoxometalate.

Introduction

The diversity of research fields connected to the chemistry of polyoxometalates is significant and includes their application in many areas, including structural chemistry, analytical chemistry, surface chemistry, medicine, electrochemistry, and photochemistry.¹ However, perhaps one of the most extensively studied applications of polyoxometalates has been in the area of catalysis, where their use as both Brønsted acid catalysts and oxidation catalysts has been going on since the late 1970s.² A basic premise behind the use of polyoxometalates in oxidation chemistry is the fact that polyoxometalates are oxidatively stable. This, a priori, leads to the conclusion that for practical purposes polyoxometalates would have distinct advantages over widely investigated organometallic compounds that are vulnerable to decomposition due to oxidation of the ligand bound to the metal center. Since polyoxometalate synthesis is normally carried out in water by mixing the stoichiometrically required amounts of monomeric metal salts and adjusting the pH to a specific acidic value, many structure types are accessible by variation of the reaction stoichiometry, replacement of one or more addenda atoms with other transition or main group metals, and pH control. Thus, many structural variants of such transition-metal-substituting polyoxometalates are known but among the more significant for catalysis is the transition-metal-substituting “sandwich” type polyoxometalates, $\{[(\text{WZnTM}_2(\text{H}_2\text{O})_2)]_n(\text{ZnW}_9\text{O}_{34})_m\}^{q-}$, (TM = transition metal) Figure 1. These and other transition-metal-substituting polyoxometalates have been used for oxidative transformations with iodosobenzene,³ *N*-oxides,⁴ periodate,⁵ ozone,⁶ nitrous oxide,⁷ sulfoxides,⁸ and molecular oxygen⁹ as oxygen donors.

Oxidation reactions with hydrogen peroxide such as the epoxidation of alkenes¹⁰ and also oxidation of alcohols¹¹ as “green” methods for organic synthesis have over the past decade gained significant impetus and have been very recently reviewed. Soluble metal oxides, especially tungsten-, molybdenum-, and rhenium-based catalysts play an important role among the many metal-based catalysts that have been investigated and reported.

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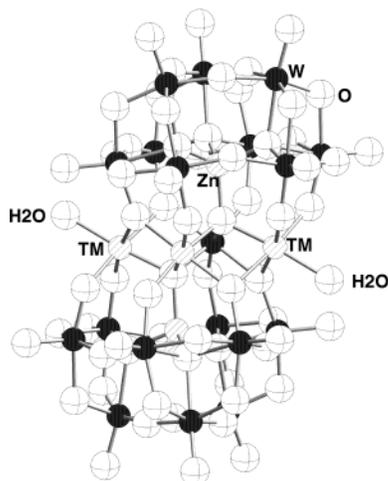


Figure 1. Ball and stick model of the $[(WZnTM_2(H_2O)_2)_2][(ZnW_9O_{34})_2]^{9-}$ polyoxometalate.

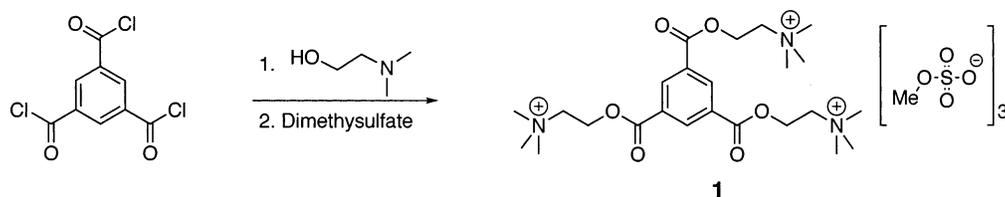
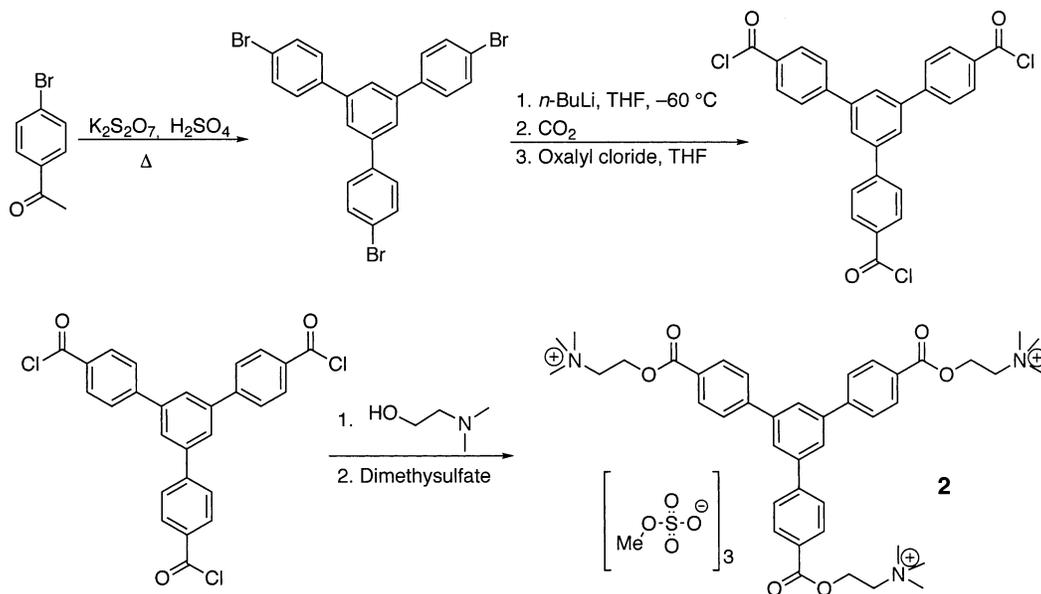
In this context, it was also found that the transition-metal-substituting polyoxometalates were stable and effective catalysts for oxidation with hydrogen peroxide.¹² For example, the manganese analogue of this polyoxometalate was originally successfully used for the epoxidation of more nucleophilic alkenes¹³ and then for oxidation of additional functional units.¹⁴ Just recently, the $[(WZnZn_2(H_2O)_2)_2][(ZnW_9O_{34})_2]^{12-}$ compound has been investigated as an exceptionally active catalyst for the chemo- and diastereoselective oxidation of allylic alcohols with hydrogen peroxide.¹⁵

Along with the development of concepts, synthetic techniques, and mechanistic understanding of the use of polyoxometalates as efficient oxidation catalysts, future practical application of polyoxometalate oxidation catalysis will also require methods for catalyst “engineering” to aid in catalyst recovery and recycle. In general one can discern between two broad approaches. The first basic approach is to immobilize a catalyst with proven catalytic properties onto a solid support leading to a catalytic system that may be filtered and reused. Such approaches include concepts such as simple use of catalysts as insoluble bulk material,¹⁶ which in some cases dissolves under reaction conditions,¹⁷ impregnation of a catalyst onto a solid and usually inert matrix,¹⁸ and attachment through covalent or ionic bonds of a catalyst to a support.¹⁹ The second basic approach is to use biphasic liquid–liquid systems, such that at separation

temperatures, which are usually ambient, the catalyst and product phases may be separated by phase separation; the catalyst phase is reused and the product is worked up in the usual manner. Numerous biphasic media have been discussed in the literature that include using catalysts in aqueous, fluorous, ionic liquid, super critical fluid, and other liquid phases. Since heteropoly acids can form complexes with or be dissolved in diethyl ether, an interesting twist especially useful for oxidation with the acidic $H_5PV_2Mo_{10}O_{40}$ was use the inexpensive poly(ethylene glycol) as solvent for aerobic oxidation of alcohols, dienes, and sulfides and Wacker type oxidations.²⁰ Beyond the simple use of poly(ethylene glycol) as solvent, the attachment of both hydrophilic poly(ethylene glycol) and hydrophobic poly(propylene glycol) to silica by the sol–gel synthesis leads to solid particles that upon dispersion in organic solvents lead to liquidlike phases termed solvent-anchored supported liquid-phase catalysis.²¹ The balance of hydrophilicity–hydrophobicity of the surface is important for tweaking the catalytic activity. Finally, it has been shown that a $Na_{12}[(WZnZn_2(H_2O)_2)_2][(ZnW_9O_{34})_2]$ assembled in situ in water is a very effective catalyst for oxidation of alcohols with hydrogen peroxide in aqueous biphasic media.²²

Polyoxometalate based hybrid compounds²³ have been constructed either by formation of covalent bonds between organic and inorganic moieties or by creation of electrostatic interactions²⁴ between the inorganic and organic components. Polyoxometalates are also important as building units of supramolecular complexes since they can exhibit diverse self-assembly properties for such supramolecular materials, thus controlling the formation of n -dimensional organic–inorganic hybrid networks in self-organization processes. Previously such an approach was used to prepare well-defined polyoxometalate-containing films.²⁵ To realize the potential self-assembly proper-

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Scheme 1. Synthetic Pathway for the Preparation of the Benzene-1,3,5-tricarboxylic Acid Tris(2-trimethylammonium ethyl) Ester Cation, **1****Scheme 2.** Synthetic Pathway for the Synthesis of Benzene-1,3,5-[tri(phenyl-4-carboxylic acid)] Tris(2-trimethylammonium ethyl) Ester, **2**

ties it is important to correctly design an organic component for the hybrid material synthesis.

In this paper, therefore, we report on the synthesis of two tripodal polyammonium cations and their utilization as building blocks together with a “sandwich”-type polyoxometalate, $[(WZnZn_2(H_2O)_2)[(ZnW_9O_{34})_2]]^{12-}$, to yield a mesoporous material of moderate surface area. The hybrid material is an active and recyclable catalyst for the oxidation of allylic alcohols and alcohols with hydrogen peroxide. The $[(WZnZn_2(H_2O)_2)[(ZnW_9O_{34})_2]]^{12-}$ polyoxometalate was chosen because of (a) its known catalytic activity in liquid-phase hydrogen peroxide mediated oxidations, (b) its stability toward oxidative and hydrolytic decomposition, and (c) its ellipsoid egg shape, Figure 1, perceived to impair a closed-packed structure, thus favoring the formation of a porous material.

Results and Discussion

Synthesis and Characterization of the Organic-POM Hybrid Mesoporous Materials. The tripodal polyammonium cations, benzene-1,3,5-tricarboxylic acid tris(2-trimethylammonium ethyl) ester (**1**) and benzene-1,3,5-tris(phenyl-4-carboxylic acid) tris(2-trimethylammonium ethyl) ester (**2**) were synthesized according to synthetic Schemes 1 and 2, respectively.

The tripodal cation, **1**, was simply prepared by acylation of *N,N*-dimethylaminoethanol with 1,3,5-benzenetricarbonyl trichloride to yield the benzene-1,3,5-tricarboxylic acid tris(2-dimethylaminoethyl) ester, which was quaternized with dimethyl sulfate to yield the methyl sulfate salt of **1**.

The synthesis of tripodal cation **2** began by self-condensation of 4-bromoacetophenone to yield 1,3,5-tris(4-bromophenyl)benzene according to a literature procedure. Lithiation followed by carboxylation with carbon dioxide yielded 1,3,5-tris(4-carboxyphenyl)benzene. After preparation of the acyl chloride derivative, esterification with *N,N*-dimethylaminoethanol yielded the benzene-1,3,5-[tris(phenyl-4-carboxylic acid)] tris-(2-dimethylaminoethyl) ester, which was quaternized by methylation with an excess of dimethyl sulfate to yield the methyl sulfate salt of **2**.

Cocrystallization of 1 equiv of $Q_7Na_5[(WZnZn_2(H_2O)_2)[(ZnW_9O_{34})_2]]$ ($Q =$ tetrabutylammonium) dissolved in DMSO with 4 equiv of the methyl sulfate salts of **1** and **2**, also dissolved in DMSO, yielded white, amorphous solids almost immediately upon mixing the solutions, **1-POM** and **2-POM**, respectively. The materials were insoluble in a wide array of solvents: DMF, DMSO, NMP, THF, acetonitrile, acetone, chlorinated hydrocarbons, hydrocarbons, alcohols, and water.

The IR spectra of both materials, **1-POM** and **2-POM**, showed via the expected absorption maxima that both the polyoxometalate anion moiety $\{[(WZnZn_2(H_2O)_2)[(ZnW_9O_{34})_2]]^{12-}$ (934, 874 and 765 cm^{-1}) and the cations **1** ($\nu_{C-H(Ar)}$ 3027, $\nu_{C-H(Alk)}$ 2964, $\nu_{C=O}$ 1731, $\nu_{C=C}$ 1637 cm^{-1}) or **2** ($\nu_{C-H(Ar)}$ 3033, $\nu_{C-H(Alk)}$ 2961, $\nu_{C=O}$ 1713, $\nu_{C=C}$ 1636, 1606 cm^{-1}) were retained in the hybrid materials. Unfortunately, all attempts to slow rapid precipitation by dilution to obtain crystalline materials for X-ray

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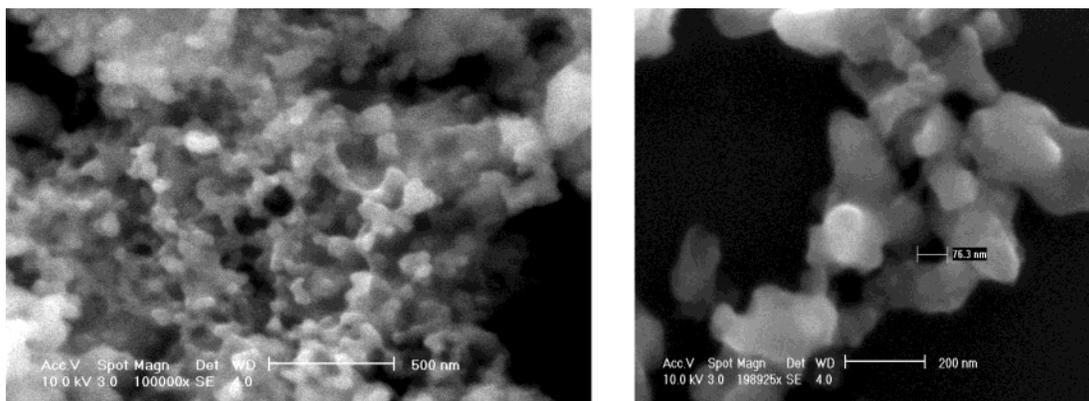


Figure 2. Typical SEM images of hybrid materials **1-POM** (left) and **2-POM** (right).

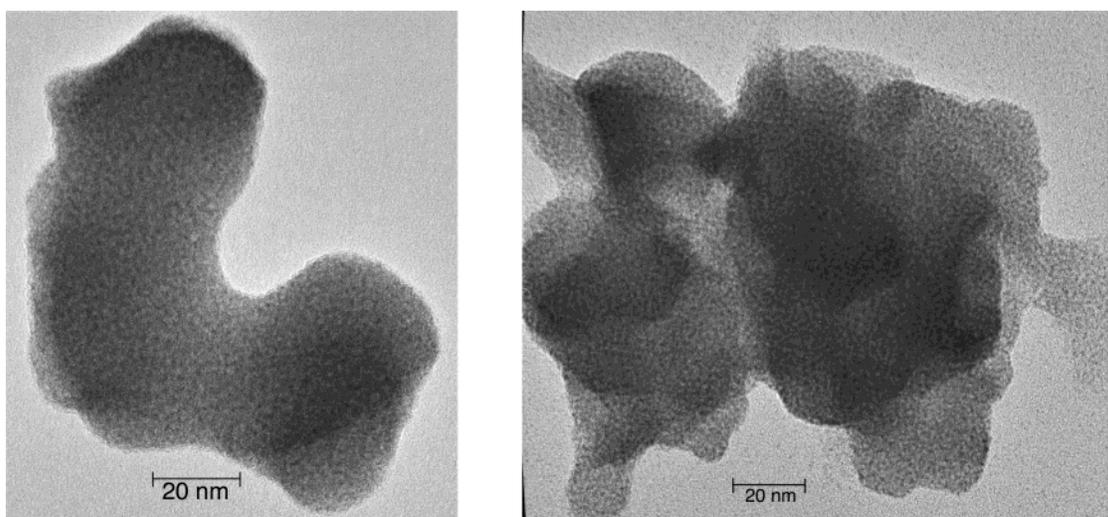


Figure 3. TEM images of materials **1-POM** (left) and **2-POM** (right).

diffraction analysis were unsuccessful, but investigation by means of electron microscopy was possible and used to determine the morphology of complexes **1-POM** and **2-POM**. The scanning electron micrographs, Figure 2, of **1-POM** and **2-POM** revealed the formation of three-dimensional perforated coral-shaped amorphous materials. The channels and cavities observed in Figure 2 have various inner diameters and are arranged in irregular way.

Unfortunately, the dielectric properties of the materials did not permit more highly magnified images to be obtained. Figure 3 shows a typical transmission electron microscope (TEM) image in which the specimen appears to be granular with small highly contrasting dots situated within a more poorly contrasting substance. The diameter average found for the black dots is ca. 1.8 nm, which is approximately the cross-section diameter of the $\{[(WZnZn_2(H_2O)_2)[(ZnW_9O_{34})_2]]^{12-}$ polyanion (dimensions of ~ 1.0 to ~ 1.5 nm for the X-ray crystal structure of $\{[WZnZn_2(H_2O)_2][ZnW_9O_{34}]_2\}^{12-}$).²⁶ We believe that the poorly contrasting substances are the organic polycations surrounding polyoxometalate anions.

N_2 sorption analyses were carried on both the **1-POM** and **2-POM** materials. The isotherms of **1-POM** and **2-POM** are best described as type IV isotherms, noting especially the steep slope at high relative partial pressures, with a hysteresis loop

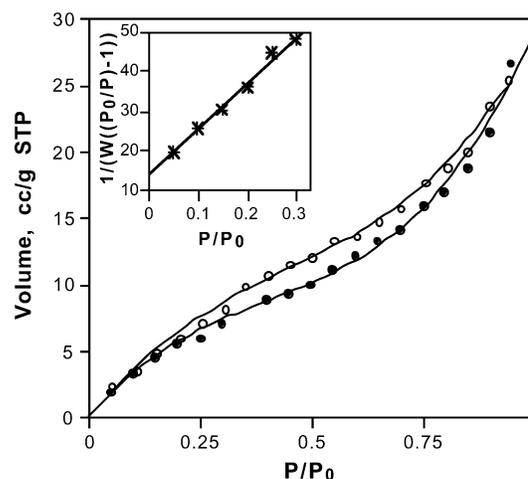
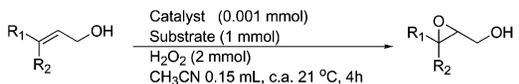


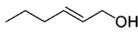
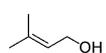
Figure 4. Adsorption isotherm and BET plot (insert) for **1-POM**. (● - N_2 adsorption; ○ - N_2 desorption).

of type H₃, Figure 4.²⁷ The isotherms and adsorption–desorption curves are typical for mesoporous materials. BET surface areas of 51 and 27 m² g⁻¹ were calculated for **1-POM** and **2-POM**, respectively. Pore size distribution curves calculated by Barret-Joyner-Halenda (BJH) method indicated an average pore size of 36 ± 6 Å for both hybrid materials. The N_2 sorption

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(27) The isotherms were measured three times on each sample and showed no significant changes, indicating the materials are stable.

Table 1. Epoxidation of Primary Allylic Alcohols with H₂O₂ Catalyzed by **1-POM** and **2-POM**


Substrate	Catalyst	Conversion, mol %	Selectivity, mol %
	1-POM	100	87
	2-POM	100	99
	1-POM	100	99
	2-POM	100	99
	1-POM	99	98
	2-POM	99	97

experiments thus lead to the classification of **1-POM** and **2-POM** as mesoporous solids with moderate surface areas.²⁸

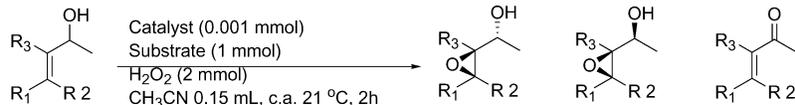
Catalytic Oxidation with Hydrogen Peroxide. A principle application of the mesoporous hybrid materials, **1-POM** and **2-POM**, was as new heterogeneous catalysts for oxidation reaction with hydrogen peroxide. Therefore, we performed several experiments to test the catalytic activity of **1-POM** and **2-POM**. Epoxidation of allylic alcohols was conducted at catalyst/allylic alcohol substrate/hydrogen peroxide (30% aqueous) molar ratios of 1:500:1000 in acetonitrile. The results in Table 1 for the oxidation of primary allylic alcohols show that both **1-POM** and **2-POM** effectively catalyze the epoxidation of the primary allylic alcohols in excellent conversion and chemoselectivity.

To probe the diastereo- and chemoselectivity of epoxidation reactions catalyzed by **1-POM** and **2-POM**, the epoxidation of chiral allylic alcohols was further studied, Table 2. The results reveal that these chiral allylic alcohols were oxidized with these heterogeneous catalysts with reactivities and diastereoselectivities comparable to reactions carried out with the {[WZnZn₂(H₂O)₂][(ZnW₉O₃₄)₂]}¹²⁻ polyoxometalate dissolved

in 1,2-dichloroethane.¹⁵ Chemoselectivity toward oxidation was somewhat lower than in the biphasic liquid/liquid system possibly because the formation of the proposed template intermediate¹⁵ that leads to epoxidation versus alcohol oxidation is hindered in a heterogeneous catalyst. The results indicate that for these heterogeneous catalysts, similar to the homogeneous catalytic system,¹⁵ metal alkoxide bonding of the allylic alcohol to peroxy-metal catalytic center of the polyoxometalate provides assistance in oxygen transfer in a stereoselective way depending on the allylic strain. Thus, for *Z*-3-penten-2-ol and 4-methyl-3-penten-2-ol with 1,3 allylic strain there is a high *threo:erythro* diastereoselectivity, whereas as for *E*-3-penten-2-ol with no allylic strain there is low diastereoselectivity. Diastereoselectivity is not effected by the porous nature of **1-POM** and **2-POM**; no shape selective features of the materials are observed.

Finally, the hydrogen peroxide mediated oxidation catalyzed by **1-POM** and **2-POM** of aliphatic secondary alcohols has been tested as well (catalyst/alcohol substrate/hydrogen peroxide, 30% aqueous molar ratios of 1:250:500 in acetonitrile at 60 °C). The results, presented in Table 3, show high conversion, especially with **2-POM** based on the more extended tripod cation and full selectivity to the ketone product. Notably, also there appear to be no shape constraints on catalytic activity, since it was observed that the linear 2-pentanol and cyclic cyclooctanol reacted at the same rates; the kinetic profiles were essentially identical.

The stability of the mesoporous materials under catalytic conditions was tested by catalyst recycle–recovery experiments using cyclooctanol as a model substrate. Both **1-POM** and **2-POM** showed nearly quantitative conversion and selectivity to cyclooctanone over five reaction cycles (1 mmol cyclooctanol, 2 mmol H₂O₂ (30% aqueous), 0.004 mmol catalyst, 0.5 mL acetonitrile, 60 °C, 5 h). The catalyst was recovered after each cycle by filtration. After the fifth catalytic cycle the IR spectra measured showed no significant structural changes for **1-POM** or **2-POM**. Also, repeat measurements of the adsorption isotherms showed the same isotherm with calculated surface

Table 2. Epoxidation of Chiral Allylic Alcohols with H₂O₂ Catalyzed by **1-POM** and **2-POM**


Substrate	Catalyst	Conversion, mol %	Selectivity	
			Chemo epoxide:ketone	Diastereo (<i>threo:erythro</i>)
	1-POM	95	56:44	81:19
	2-POM	99	67:33	84:16
	Homogeneous ¹⁵	95	95:05	88:12
	1-POM	91	82:18	57:23
	2-POM	90	89:11	59:41
	Homogeneous ¹⁵	90	95:05	57:43
	1-POM	96	85:15	92:08
	2-POM	96	87:13	93:07
	Homogeneous ¹⁵	99	95:05	95:05

Table 3. Oxidation of Secondary Alcohols with 30% H₂O₂ Catalyzed by **1-POM** and **2-POM**

substrate	catalyst	conversion, mol %
2-pentanol	POM-1	92
	POM-2	94
2-hexanol	POM-1	86
	POM-2	94
2-heptanol	POM-1	62
	POM-2	89
2-octanol	POM-1	40
	POM-2	90
cyclopentanol	POM-1	92
	POM-2	92
cyclohexanol	POM-1	94
	POM-2	99
cyclooctanol	POM-1	99
	POM-2	100

areas and pore sizes of similar values ($\pm 3\%$). Furthermore, filtered solutions of acetonitrile and hydrogen peroxide heated for 5 h at 60 °C in the presence **1-POM** or **2-POM** showed no catalytic activity or evidence of zinc or tungsten metals.

Conclusions

Mesoporous catalytic materials has been formed by preparing insoluble inorganic–organic hybrid compounds based on a tripodal organic triammonium cation and a catalytically active polyoxometalate species, $[\text{WZnZn}_2(\text{H}_2\text{O})_2][(\text{ZnW}_9\text{O}_{34})_2]^{12-}$. The mesoporosity of the material, average pore diameter 36 Å, allows oxidation of a number of organic substrates irrespective of the molecular shape. Based on similar molecular designs, a future goal will be certainly to obtain crystalline materials with well-defined pores so that shape-selective catalytic oxidation based on polyoxometalates may be envisioned.

Experimental Section

Benzene-1,3,5-tricarboxylic Acid Tris(2-dimethylaminoethyl) Ester. A solution of 1.0 g (3.8 mmol) of 1,3,5-benzenetricarbonyl trichloride in 6 mL of CH₂Cl₂ was added to a solution of 1 g (1.13 mL, 11.3 mmol) of *N,N*-dimethylethanolamine and 0.5 g of sodium hydroxide in 6 mL of water over 15 min with rapid stirring, which was then continued for 3 h. The organic layer was separated, diluted with 20 mL of CH₂Cl₂, washed with water, dried over anhydrous sodium sulfate, and concentrated under vacuum. The product is light oil (0.95 g, 59%) and was additionally dried under high vacuum for 3 h. The product was sufficiently pure enough to use without further purification. ¹H NMR (C₆D₆) δ 2.14 (18 H, s), 2.42 (6 H, t, *J* = 5 Hz), 4.34 (6 H, t, *J* = 5 Hz), 9.17 (3 H, s) ppm. ¹³C NMR (CDCl₃) δ 45.45, 57.39, 63.17, 130.93, 134.45, 164.65 ppm. IR (film casted from solution) ν 3087, 2971, 2947, 2863, 2822, 2771, 1731, 1607, 1457, 1396, 1367, 1325, 1239, 1154, 1109, 1062, 1041, 1016, 931, 852, 821, 781, 740, 721 cm⁻¹.

Benzene-1,3,5-tricarboxylic Acid Tris(2-trimethylammonium ethyl) Ester Cation, 1. To a solution of 0.5 g (1.2 mmol) of benzene-1,3,5-tricarboxylic acid tris(2-dimethylaminoethyl) ester in 5 mL of CHCl₃ was 0.37 mL (0.49 g, 3.9 mmol) of dimethyl sulfate. The mixture was refluxed for 1.5 h, cooled, and filtered. The hygroscopic solid formed was dried under high vacuum and stored in desiccator. ¹H NMR (DMSO-*d*₆) δ 3.19 (s, 27 H), 3.36 (s, 9 H), 3.84 (br t, *J* = 5 Hz, 6 H),

4.50 (brt, *J* = 5 Hz, 6 H), 8.54 (s, 3 H) ppm. IR (film casted from solution) ν 3038, 2962, 2874, 1723, 1614, 1578, 1475, 1359, 1233, 1173, 1085, 1010, 993, 956 cm⁻¹.

1,3,5-Tris(4-carboxyphenyl)benzene.²⁹ 1,3,5-tri(4-bromophenyl)-benzene³⁰ (2 g, 3.7 mmol) was dissolved in 25 mL of anhydrous THF under Ar. The stirred solution was cooled to -60 °C and a 1.6 M solution of *n*-BuLi in hexanes (7 mL, 11.2 mmol) was added dropwise. A light-green precipitation of the aryllithium derivative was formed. Predried gaseous carbon dioxide was passed into the mixture at -60 °C to give a colorless precipitate of the lithium salt. The mixture was allowed to warm and was quenched with 50% aqueous acetic acid. The solid product was filtered and recrystallized from acetic acid to give 0.93 g (57%) of white microcrystals. ¹H NMR (DMSO-*d*₆) δ 8.05 (s, 12 H), 8.08 (s, 3 H) ppm. IR (film casted from solution) ν 3071, 2985, 1697, 1608, 1423, 1318, 1294, 1245 cm⁻¹.

Benzene-1,3,5-[tris(phenyl-4-carboxylic acid)] Tris(2-dimethylaminoethyl) Ester. Into a flask flushed with Ar, 0.5 g (1.1 mmol) of 1,3,5-tri(4-carboxyphenyl)benzene was placed and 20 mL of anhydrous THF was added. Oxalyl chloride (20 mL, 21 mmol) was slowly added dropwise with a syringe pump. The mixture was refluxed for 10 h and then the excess oxalyl chloride was distilled off. To the resulting solid 20 mL of anhydrous THF was added. The solution was cooled with an ice bath and pyridine (0.05 mL, 0.6 mmol) was added followed by dropwise addition of 0.34 mL (3.63 mmol) of *N,N*-dimethylaminoethanol. The solution was allowed to warm and stirred for 24 h and then quenched with an aqueous sodium hydrogen carbonate solution and extracted with chloroform (3 \times 50 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and evaporated to give 0.3 g (42%) of light oily solid. ¹H NMR (DMSO-*d*₆) δ 2.2 (s, 18 H), 2.6 (t, *J* = 6 Hz) 4.4 (t, *J* = 6 Hz), 8.07 (s, 12 H), 8.09 (s, 3 H) ppm. ¹³C NMR (DMSO-*d*₆) δ 165.48, 144.19, 140.63, 129.75, 129.04, 127.61, 125.75, 62.71, 57.27, 45.41 ppm. IR (film casted from solution) ν 2948, 2862, 2821, 2771, 1716, 1608, 1597, 1456, 1392, 1369, 1338, 1274, 1183, 1115, 1018, 850, 767, 701 cm⁻¹.

Benzene-1,3,5-[tris(phenyl-4-carboxylic acid)] Tris(2-trimethylammonium ethyl) Ester (2). To a solution of benzene-1,3,5-[tris(phenyl-4-carboxylic acid)] tris(2-dimethylaminoethyl)ester (0.4 g, 0.61 mmol) in anhydrous THF (20 mL) 0.17 mL (1.84 mmol) of dimethyl sulfate was added. In ~2 min the quaternary ammonium salt **2** started to precipitate. The mixture was stirred for additional 6 h and filtered; the solid was washed with anhydrous ether and dried under high vacuum to give 0.45 g (72%) of a white hygroscopic solid. ¹H NMR (DMSO-*d*₆) δ 3.21 (s, 27 H), 3.36 (s, 9 H), 3.84 (br t, *J* = 6 Hz, 6 H), 4.75 (brt, *J* = 6 Hz, 6 H), 8.12 (s, 15 H) ppm. ¹³C NMR (DMSO-*d*₆) δ 164.97, 144.49, 140.60, 129.96, 128.50, 127.71, 125.91, 63.96, 58.79, 52.94, 52.79 ppm. IR (film casted from solution) ν 3130, 3040, 3003, 2950, 1713, 1607, 1481, 1376, 1272, 1246, 1114, 1059, 1008, 953, 894, 847, 764, 747 cm⁻¹.

(*n*-Bu₄N)₇Na₅[(WZnZn₂(H₂O)₂][(ZnW₉O₃₄)₂]. Na₁₂[(WZnZn₂(H₂O)₂][(ZnW₉O₃₄)₂]²⁶ (1.52 g, 0.25 mmol) was dissolved in 10 mL of water and to this solution 0.84 g (3 mmol) of *n*-tetrabutylammonium chloride dissolved in 5 mL of water was added. The mixture was stirred vigorously and acidified by one drop of HCl (conc). Acidification initiated precipitation of quaternary ammonium salt of POM. White precipitate was filtered off, washed 3 times with water, and dried under high vacuum for 48 h. Elemental analysis C₁₁₂H₂₅₂N₇Na₅O₆₈W₁₉Zn₅ exptl (calcd): C 19.88 (20.02); H 3.63 (3.78); N 1.44 (1.46); Na 1.10 (1.71); Zn 4.95 (4.87); W 50.32 (51.98); O (16.19). IR (KBr) ν 2961, 2935, 2874, 1483, 952, 886, 774 cm⁻¹.

POM-1 and POM-2. (*n*-Bu₄N)₇Na₅[(WZnZn₂(H₂O)₂][(ZnW₉O₃₄)₂] (0.0485 mmol) was dissolved in 5 mL of DMSO and to this solution was added to solution of **1** or **2** (0.194 mmol in 5 mL of DMSO).

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Within ~1 min the mixture became milky and a white solid started to precipitate. The mixture was left for 24 h to complete the precipitation and then the solid was separated from the liquid by centrifugation. **POM-1** and **POM-2** were thoroughly washed with 10 mL of DMSO, ethanol (2×10 mL), and diethyl ether (2×10 mL) and dried under high vacuum for 10 h. **POM-1**: Elemental analysis $C_{96}H_{168}N_{12}O_{92}W_{19}Zn_5$ exptl (calcd): C 16.35 (17.00); H 2.79 (2.50); N 2.29 (2.48); W 49.76 (51.50); Zn 4.91 (4.82); O (21.70). IR (KBr) ν 3026, 2964, 1731, 1637, 1482, 1375, 1331, 1247, 1120, 1010, 938, 877, 765, 737 cm^{-1} . **POM-2**: Elemental analysis $C_{168}H_{216}N_{12}O_{92}W_{19}Zn_5$ exptl (calcd): C 25.31 (26.22); H 2.62 (2.83); N 2.23 (2.18); W 43.31 (45.39); Zn 4.04 (4.25); O (19.13). IR (KBr) ν 3033, 2961, 2874, 1713, 1636, 1607, 1478, 1380, 1275, 1187, 1115, 1017, 937, 875, 766, 699 cm^{-1} .

TEM Studies. A JEOL 100CX transmission electron microscope, with accelerating voltage of 100 kV, was used to obtain the morphology of the material. Specimens of materials were prepared by dispersing the particles in ethyl alcohol by ultrasonic treatment and dropping them onto a holey carbon film supported on a copper grid. The samples were unstable under electron beam radiation, fading during observation in 20–40 s.

SEM Studies. A Fei (Philips) XL 30 ESEM-FEG with accelerating voltage of 10 kV was used. Specimens of materials were prepared by dispersing the particles in ethyl alcohol by ultrasonic treatment and dropping them onto a silicon slides.

General Procedure for Catalytic Oxidation of Primary Allylic Alcohols by POM-1 and POM-2. In a typical reaction, the specific substrate (1 mmol) was dissolved in 0.15 mL of acetonitrile and **POM-1** or **POM-2** (0.001 mmol) was added. The reaction was initiated by addition of 30% H_2O_2 (0.2 mL, 2.0 mmol) to the solution at ~21 °C with magnetic stirring (~1000 rpm) under an ambient atmosphere. After 4 h, 1 mL of EtOAc was added to the reaction mixture. The resulted mixture was stirred for 15 min and the organic phase of the mixture was separated and dried over Na_2SO_4 . Conversions of the substrate were measured by GLC using a 5% phenylmethylsilicone column (30 m, 0.32 mm i.d., 0.25 μm coating). Products were identified by GC-MS analysis using the same column. There is a ca. $\pm 2\%$ error for the

values in Table 1. Hydrogen peroxide conversion was essentially quantitative.

General Procedure for the Catalytic Epoxidation of Chiral Allylic Alcohols by POM-1 and POM-2. In a typical reaction, the specific substrate **1** (1 mmol) and dimethyl isophthalate (0.4 mmol), as internal standard, were dissolved in 0.15 mL of acetonitrile. **POM-1** or **POM-2** (0.001 mmol) were added and the reaction was initiated by addition of 30% H_2O_2 (0.2 mL, 2.0 mmol) to the solution at ~21 °C with magnetic stirring (~1000 rpm) under an ambient atmosphere. After 2 h, 1 mL of CH_2Cl_2 was added to the reaction mixture. The resulted mixture was stirred for 15 min and the organic phase of the mixture was separated and dried over Na_2SO_4 , and the solvent was removed (20 °C, 50 mbar). The conversions, yields, and product ratios were determined by 1H NMR analysis directly on the crude mixture. There is a ca. $\pm 5\%$ error for the values in Table 2. Hydrogen peroxide conversion was essentially quantitative.

General Procedure for Catalytic Oxidation of Secondary Alcohols by POM-1 and POM-2. In a typical reaction, the specific substrate **1** (0.5 mmol) was dissolved in 0.15 mL of acetonitrile and **POM-1** or **POM-2** (0.002 mmol) was added. The reaction was initiated by addition of 30% H_2O_2 (0.1 mL, 1.0 mmol) to the solution at ~60 °C with magnetic stirring (~1000 rpm) under an ambient atmosphere. After 5 h vials were cooled by ice bath and then opened and 1 mL of EtOAc was added to the reaction mixture. The resulted mixture was stirred for 15 min and the organic phase of the mixture was separated and dried over Na_2SO_4 . Conversions of the substrate were measured by GLC using a 5% phenylmethylsilicone (30 m, 0.32 mm ID, 0.25 μm coating) column. There is a ca. $\pm 2\%$ error for the values in Table 3. Hydrogen peroxide conversion was essentially quantitative.

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