DOI: 10.1002/cplu.201400009



Polyoxometalate-Based Metal–Organic Frameworks as Catalysts for the Selective Oxidation of Alcohols in Micellar Systems

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A series of nanosized metal–organic frameworks (MOFs) encapsulating different polyoxometalates (POMs) including $H_3PW_4O_{12}$, $H_5PMo_{12}O_{40}$, $H_5PVMo_{10}O_{40}$, $H_5PV_2Mo_{10}O_{40}$, and $H_5PV_3Mo_{10}O_{40}$ was synthesized and used in the selective oxidation of alcohols. The catalyst with a uniform size and morphology offered easy accessibility between substrates and catalyst. At the same time, the MOF ensured that the POM was encap-

Introduction

Selective oxidation of primary and secondary alcohols into the corresponding aldehydes or ketones is undoubtedly one of the most important and challenging transformations in organic chemistry.^[1] Many catalysts have been developed to accomplish the reaction including (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO),^[2] metal oxides,^[3] hypervalent iodine,^[4] and so on. Another common and efficient route uses polyoxometalates (POMs) together with hydrogen peroxide (H₂O₂) as terminal oxidant, which has commonly been considered a "green oxidant" because of its high content of active oxygen species and coproduction of only water. Research published since the 1980s has established the high potential of POMs for activation of H₂O₂, thanks to the nanoarrays of d⁰ transition-metal ions such as W^{VI} , Mo^{VI}, and V^V exposed on their surfaces.^[5]

No matter which POM is used, however, separation and recovery are usually key problems to be solved owing to the solubility of POMs. Much effort has been devoted to the field of immobilizing POMs, with organic hybrids of POMs as an attractive possibility for various oxidation reactions. Examples include surfactant–POM combinations,^[6] coordination polymers,^[7] polymer–POM conjugates,^[8] and so on. However, the difficulty in controlling the separation, the aggregation of POMs in the preparation of the catalyst, and the limited variation in chemical formulation and functionality often limit their applications.

Lately, the use of transition metals, organic ligands, and POMs to assemble POM-based metal–organic frameworks has emerged as one of the approaches to solve the problems.^[9] A

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	Supporting information for this article is available on the WWW under
	http://dx.doi.org/10.1002/cplu.201400009.

sulated, which could dramatically prevent the assembly of the catalyst. Furthermore, the catalyst showed clear chemoselectivity, which was related to the size or accessibility of the substrates for surface pores. With cetyltrimethyl ammonium bromide aqueous solution as solvent, both improved reaction efficiency and simple recycling of the catalytic system were achieved to afford a green oxidation process.

stable host HKUST-1,^[10] as a well-known MOF, was reported to be able to encapsulate various Keggin-type POMs. Wee and co-authors reported on a microporous cubic material with strictly repetitive 5 nm-wide mesopores and the stability was enhanced by Keggin-type phosphotungstate (HPW) systematically occluded in the cavities constituting the walls between the mesopores.^[11] Although the approach successfully solved the problem of POM aggregation in catalytic processes and offers great potential for chemical and structural diversity, investigation of the catalytic properties of these kinds of materials is rather limited.^[12]

The use of water as a medium for promoting organic reactions is very important and has received much attention in recent years from the point of view of green and economical chemistry. To perform oxidation reactions in water, the solubility problem of substrates or catalysts must be overcome, because of the limited mutual solubility between water and organic agents. Micelles, which are dynamic clusters of surfactant molecules that possess both hydrophilic and hydrophobic structures, may associate in aqueous media to circumvent the problem. Micelles can concentrate the reactants within their small volumes; stabilize substrates, intermediates or products; and orient substrates. Thus, they can alter the reaction rate, mechanism, and regio- and stereochemistry.^[13]

In this study, selective oxidations were performed in micellar systems with MOF-encapsulated POMs as catalyst. A serious of nanosized metal–organic frameworks were synthesized encapsulating different POMs including $H_3PW_4O_{12}$, $H_5PMo_{12}O_{40}$, $H_5PVMo_{10}O_{40}$, $H_5PV_2Mo_{10}O_{40}$, and $H_5PV_3Mo_{10}O_{40}$ (noted as MOF-HPW, MOF-HPMo, MOF-HPMoV, MOF-HPMoV2, and MOF-HPMoV3, respectively), which all offered organized multiple porosity and high surface area. Their catalytic performance for the selective oxidation of various alcohols was tested and compared in a micellar system. Both improved reaction efficiency and simple recycling of the catalytic system were achieved in

cetyltrimethyl ammonium bromide (CTAB) micellar solutions. Thus a green oxidation process was achieved.

Results and Discussion

The concept of the catalysts

The catalysts were easily prepared from a synthesis mixture containing the molar composition of 18Cu/10BTC/POM/CTAB/ $170 \text{ EtOH}/2000 \text{ H}_2\text{O}$ (BTC = 1,3,5-benzenetricarboxylate). Thermogravimetric analysis (TGA) was applied to the catalysts as shown in Figure S1 in the Supporting Information. From the TGA data, weight contents of POMs were established to be 0.506, 0.429, and 0.330 for MOF-HPW, MOF-HPMo, and MOF-HPMoV2, respectively, which matched well with their corresponding theoretical values of 0.485, 0.374, and 0.362, respectively.

Chui et al. revealed that the polymer framework of HKUST-1 is composed of dimeric cupric tetracarboxylate units. Twelve carboxylate oxygen atoms from the two BTC ligands bind to four coordination sites for each of the three Cu²⁺ ions of the formula unit. For most POM-bearing MOFs, the POM is added to the hydrothermal synthesis and found in the cavities afterwards. In the case of the HKUST-1, however, strong interaction between Cu^{II} and Keggin-type ions is discovered, which leads to spontaneous self-assembly of microporous MOF-POM.^[14]

The Keggin ion acts as a templating species during synthesis and stabilizes the microporous structure by means of the synergism between the metal and Keggin ions.^[15] A Cu^{2+}/POM interaction directs Cu²⁺ ions to preferentially reside close to the positions needed to build the MOF framework. In such a scenario, the role of the organic linker is simply to connect the already structured Cu²⁺/POM units through complexation. Namely, the MOF assembly results in strictly systematic encapsulation of POM molecules. In addition, the nanosize and high surface area of Cu-MOF

(a) MOF-HPW (b) HKUST-1 (c) HPW 2000 1500 1000 500 Wavenumbers / cm

Transmission / %

Figure 1. IR spectra of a) MOF-HPW, b) HKUST-1, and c) H₃PW₄O₁₂ raw material.

hibited, which clearly differs from that of bare HKUST-1 (curve b). Also, when comparing the IR spectrum of the MOF with its relative POM (curve a with c), curves a and b show detectable changes around 1500 cm⁻¹ that are characteristic of C–H, C–C, and C=O vibrations, which suggests the formation of the framework, and which are absent from the spectrum of the POM alone. IR spectra of MOF-PMo, MOF-HPMoV1, MOF-HPMoV2, and MOF-HPMoV3 are shown in the Supporting Information.

To further confirm the structure of the MOF-POMs, X-ray diffraction (XRD) studies were also performed. Figure 2 shows the



Figure 2. I) XRD patterns of a) HKUST-1, b) MOF-HPW, and c) MOF-HPMo; II) XRD patterns in the low-angle region of d) MOF-HPMo and e) MOF-HPW.

make it an excellent choice for POM anchoring. MOFs and zeolites are very similar in terms of their porous structures, but quite different in the situation of immobilizing POMs. Therefore it would be expected that firstly, the MOF could be used as a catalyst for reactions and the accessibility between substrates and the catalyst could be maintained; and secondly, different from a normal support in which the active site is anchored on its surface, the MOFs ensured that the POM was encapsulated, which could dramatically prevent the assembly of the catalyst.

Figure 1 shows the IR spectra of MOF-HPW, HKUST-1, and H₃PW₄O₁₂ raw material. It can be seen that some characteristic peaks belonging to W–O vibrations around 1000 cm⁻¹ are exXRD pattern of MOF-HPW and MOF-HPMo, and the results for MOF-HPMoV, MOF-HPMoV2, MOF-HPMoV3, and POM raw materials are listed in the Supporting Information. From Figure 2, a high degree of mesoscopic ordering is confirmed by the sharp reflections appearing at low angles.

TEM and SEM images of MOF-HPW and MOF-HPMo (Figure 3; images of MOF-HPMoV are shown in the Supporting Information) indicate that the catalyst was a framework structure with uniform size and morphology. Viewed from the bright field, highly ordered mesostructures with long-range ordering could be observed, which testified that Keggin ions were contained in the microporous wall structures, next to the less dense mesopores in the structure. Parallel lines with a dis-

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Figure 3. a) TEM image of MOF-HPW; b) SEM image of MOF-HPW; c) TEM image of MOF-HPMo; d) SEM image of MOF-HPMo; e) TEM image of MOF-HPMoV2; f) SEM image MOF-HPMoV2.

tance of 3.6 nm could be observed in Figure 3c, similar to those previously reported in reference [11], which means that the catalyst we prepared follows an analogous structure. For MOF-HPMo and MOF-HPMoV, the size of the framework changed greatly, but the mesostructures were still clearly visible, which also confirmed that the Keggin ion acted as the templating species during the synthesis of MOF.

Exploration of the reaction conditions

First, MOF-HPW was taken as a model catalyst to show the important effect of micellar media upon the reactions. Oxidations of benzyl alcohol were studied in different systems and the comparative results are demonstrated in Figure 4. Three common surfactants were chosen to generate micellar systems

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including cationic surfactant cetyltrimethyl ammonium bromide (CTAB), anionic surfactant sodium dodecyl sulfate (SDS), and neutral surfactant TritonX-100 (TX-10). For all the surfactants, experiments were performed at their tenfold critical micellar concentration (10 cmc) in the presence of MOF-HPW. In addition, for comparison with micellar systems, acetonitrile, which is usually used in POMcatalyzed oxidations, was chosen as an organic solvent. As can be seen in Figure 4, the CTAB micellar system gave the best result, followed by acetonitrile, TX-10, and SDS, respectively. The yield of benzaldehyde was able to reach 98% after 3 h in CTAB aqueous solution, which was even faster than that in an organic solvent (acetonitrile solution). So using water as the reaction media was a good choice in view of the reaction efficiency as well as green and economical chemistry. The fact that the reaction could be facilitated by use of a cationic surfactant also testified to the nature of micellar reactions. The reactant benzyl alcohol accumulated not in the surrounding water phase, but in the micelle through interactions with the micelle surface or through insertion into the micelle itself, as was the catalyst. Since the oxidant H₂O₂ was in the aqueous phase,^[16] the oxida-



Figure 4. Oxidation of benzyl alcohol with MOF-HPW in different systems: a) CTAB micellar solution; b) CH_3CN ; c) TX-10 micellar solution; and d) SDS micellar solution.

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tion process took place at the surface of the micelles. As a result of the attraction of the POM anion to the cationic surfactant, the reaction rate was accelerated greatly in CTAB micellar solution.

To further optimize the reaction conditions, preliminary experiments were performed with benzyl alcohol as the substrate and H_2O_2 as the oxidant in CTAB micellar solution. The comparable results are summarized in Table 1. It was found

tions. ¹⁴ Entry	Catalyst	Catalyst amount [mg]	30% H ₂ O ₂ [mmol]	<i>т</i> [°С]	<i>t</i> [h]	Conv. [%]	Yield [%]		
1		- 5-		00	12	traco	traco		
		-	0	00	12	trace	trace		
2	HKUSI-I	50	0	80	12	trace	trace		
3	MOF-HPW	50	4	80	3	98	98		
4	MOF-HPW ^[b]	50	4	80	3	43	43		
5	MOF-HPW	100	4	80	2	96	96		
6	MOF-HPW	25	4	80	5	95	94		
7	MOF-HPW	50	2	80	3	83	82		
8	MOF-HPW	50	1	80	5	79	78		
9	MOF-HPW	50	4	25	12	trace	trace		
10	MOF-HPW	50	4	40	6	88	87		
11	MOF-HPW	50	4	60	4	92	91		
12	$H_3PW_4O_{12}\\$	50	4	80	3	99	99		
[a] Reaction conditions: benzyl alcohol (2 mmol), CTAB micellar solution (10 mL). [b] Reaction conditions: benzyl alcohol (2 mmol), H_2O (10 mL).									

that almost no product was obtained in aqueous solution without any catalyst (entry 1) or with HKUST-1 without POMs (entry 2). Also, if no surfactant was added, the reaction turned out to be less efficient in two phases (entry 4). For both MOF-HPW and MOF-HPMo, a catalytic amount of catalyst was enough for the reaction to proceed and reaction termination was observed on its removal. A further increase of catalyst amount would be meaningless. The reaction was initiated at about 40 °C and high temperature was clearly beneficial for the reaction. But at the same time, a high temperature accelerates the decomposition of H_2O_2 so more H_2O_2 was required to complete the reaction. The reaction conditions were finally optimized to be 80 °C with 4 mmol H_2O_2 .

With the optimized reaction conditions, the catalytic performance of MOFs with different kinds of POMs was tested and compared. As shown in Figure 5, similar results could be obtained with MOF-HPW and MOF-HPMo as catalysts. However, when the MOFs of vanadium-containing POMs were used as catalyst, notable improvement was observed in the oxidation efficiency of benzyl alcohol. Also, with an increase of the vanadium content in the POMs, the conversion of benzyl alcohol showed a rising trend. However, further oxidation reactions generated benzoic acid in a proportion that could not be neglected. The results showed excellent catalytic oxidizability of these vanadium-containing POMs, but at the same time, selectivity of the oxidation tended to be less controllable. The mechanism of the reaction occurs in two steps including the oxidation of organic substrate catalyzed by POMs and the regeneration of reduced POMs by H₂O₂ with the formation of



Figure 5. Oxidation of benzyl alcohol by MOFs with different POMs (selectivity was for benzaldehyde). Reaction conditions: benzyl alcohol (2 mmol), CTAB micellar solution (10 mL), catalyst (50 mg), H_2O_2 (4 mmol), 80 °C, 2 h.

water. A combined influence of framework Mo and V was supposed to be responsible for the activity difference between single POM-functionalized MOFs and vanadium-containing ones.^[17]

The distribution of products was further defined with MOF-HPW and MOF-HPMoV3 as catalyst. As shown in Figure 6, benzaldehyde was almost the only product in the MOF-HPW-cata-



Figure 6. Distribution of products with MOF-HPW and MOF-HPMoV3 as catalyst: a) conversion of benzyl alcohol with MOF-HPMoV3 as catalyst; b) yield of benzaldehyde with MOF-HPMoV3 as catalyst; c) yield of benzoic acid with MOF-HPMoV3 as catalyst; d) conversion of benzyl alcohol with MOF-HPW as catalyst; e) yield of benzaldehyde with MOF-HPW as catalyst. Reaction conditions: benzyl alcohol (2 mmol), CTAB micellar solution (10 mL), catalyst (50 mg), H_2O_2 (4 mmol), 80 °C.

lyzed system. Whereas for MOF-HPMoV3, the yield of benzaldehyde decreased after a maximum at 1 h. At the same time, benzoic acid was generated gradually and showed an increasing yield in the following reaction period. The total conversion of benzyl alcohol followed a similar trend to that of MOF-HPW. Overall, excellent selectivity could be obtained through controlling the reaction time for MOF-HPW and MOF-HPMo, whereas for vanadium-containing POMs, improvement in oxidation efficiency could be obtained but the selectivity of the oxidation tended to be less controllable.

All these facts indicated that it was still Keggin anions that served as the active species for oxidation reactions. The encapsulation process did not change the reaction mechanism and an activity decrease was not obvious either. The good catalytic

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performance of this system probably resulted from two aspects. First, the nanosized metal–organic framework containing the active sites provided a large surface area for the ready accessibility of substrate molecules. Second, a pseudo-homogeneous process was obtained owing to the assistance of an emulsion system, which also greatly increased the chances for the contact between substrate and catalyst.

Catalytic performance of MOF-HPW

To examine the utility and generality of this methodology for oxidation of alcohols, we applied the present system to a variety of substrates with MOF-HPW as the model catalyst. As shown in Table 2, the substrate scope could be extended to benzylic, allylic, heterocyclic, alicyclic, and aliphatic alcohols. In



all of the cases tested, ketones or aldehydes were the only detected products. Clearly, all primary benzylic alcohols were converted into their corresponding aldehydes in high yields. Secondary alcohols such as benzhydrol and 2-phenylethanol also gave moderate yields of 59 and 66%, respectively. Benzyl alcohol showed the highest yield among the substrates tested, and the introduction of another group (electron-withdrawing or electron-donating group) decreased the results more or less. When the volume of substituted groups did not differ much, substrates with electron-withdrawing groups performed better than the those with electron-donating groups. Furthermore, oxidations of some aliphatic alcohols were also tested as listed in Table 3. With double the amount of the catalyst, the activities exhibited by secondary alcohols were also not so bad in the system. Good to excellent conversions were observed



for allyl alcohol and cinnamyl alcohol. More importantly, it was found that the oxidative efficiency was not affected by the existence of a double bond and the double bond remained stable during the oxidation process. Isooctyl alcohol performed somewhat better than 1-C₈H₁₇OH, but unfortunately both results were unsatisfactory even after lengthening the reaction time.

Based on the results in Table 2, 4-methylbenzyl alcohol and 4-methoxybenzyl alcohol, which were thought to perform similar to or even better than benzyl alcohol, gave lower yields instead. The MOF catalyst seemed to be chemoselective. So, to probe the chemselectivity, substrates with increasing dimensions were tested. The volume and dimension of the substrates were calculated by using Gaussian 03 at the B3LYP/6-31G++ (d,p) level.^[18] As illustrated in Figure 7, the conversion of benzyl alcohol with a dimension of 89.35 cm³mol⁻¹ reached



Figure 7. Chemoselectivity of MOF-HPW toward substrates with different dimensions (units in Å).

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98% after 3 h. In contrast, the conversion of 4-methylbenzyl alcohol and 4-methoxybenzyl alcohol with dimensions of 101.27 and 107.57 cm³ mol⁻¹, respectively, decreased to 95 and 92% under similar conditions. 4-tert-Butylbenzyl alcohol, a larger alcohol with molecular dimension of 142.72 cm³ mol⁻¹ gave a conversion of about 63% after 12 h. Although the 4-tertbutyl group activated the benzene ring the most (better than the methyl and methoxy group), the conversion of 4-tert-butylbenzyl alcohol was the lowest. The catalytic activity and selectivity of the MOF seemed to depend on the size of the substrates and their accessibility to surface pores. It is thereby reasonable that the reactants with smaller sizes such as benzyl alcohol could diffuse swiftly through the pores. In contrast, the substrates with larger sizes were not readily diffused through the pores, but they may adsorb onto the surface pores containing Keggin complexes, and the polyanions catalyzed the reaction at the surface of the pores. In many systems, the aliphatic alcohols with longer carbon chains performed better than the shorter ones.^[2,7] The same trend was observed in this system when comparing the reaction efficiency of $nC_8H_{17}OH$ and nC12H25OH. However, nC12H25OH also showed a higher conversion than $nC_{16}H_{31}OH$, which was assumed to be due to this chemoselectivity.

Overall, the MOF-HPW catalyst demonstrated great catalytic activity. For a series of alcohols including benzylic, allylic, heterocyclic, and alicyclic alcohols as substrates, good to excellent yields were obtained with ketones or aldehydes as the only detected products. Furthermore, the catalyst showed clear chemoselectivity, which was related to the size of the substrates or their accessibility to surface pores.

The advantage of the catalytic system lies in not only the high catalytic activity in aqueous solvent with H_2O_2 as oxidant, but also the easy recovery of both catalyst and solvent. Since both the catalyst and solvent were immiscible with diethyl ether, the catalytic system could be recovered after extraction, to the maximum amount. After completion of the oxidation reaction, the mixture was allowed to cool to room temperature and was extracted with diethyl ether. The aqueous layer, containing the catalyst, was able to be separated and reused with the addition of substrate without any treatment. The organic layer, containing the products, was analyzed after drying with anhydrous sodium sulfate. When benzyl alcohol was used as a model substrate, the procedure was successfully repeated five times without any great loss of catalytic activity (Figure 8).

Conclusion

In conclusion, we have synthesized a series of POM-based metal-organic frameworks in this study. The catalysts were easily prepared and exhibited an ordered size and morphology. The nanosized MOF-POMs, which offered organized multiple porosity and high surface area, were proven to be an efficient catalyst for various alcohol oxidations in CTAB micellar solution. With MOF-HPW as model catalyst, a wide set of aliphatic, allylic, heterocyclic, and benzylic alcohols were oxidized into their corresponding carbonyl compounds with good to excellent yields. The reaction conditions, generality of the method-



Figure 8. The recycling study. Each column represents the conversion of benzyl alcohol; the lines represent the selectivity of benzaldehyde.

ology, selectivity, and reusability of MOF-HPW were further studied in detail. The catalytic activity and selectivity of the catalyst seem to depend on the size of the substrates and their accessibility to surface pores. The reactants with smaller sizes such as benzyl alcohol could diffuse swiftly through the pores thus a higher efficiency was obtained. Also, good recyclability was exhibited in the CTAB micellar system. After completion of the oxidation reaction, the mixture was allowed to cool to room temperature and was extracted with diethyl ether. The catalyst remained in the aqueous layer for use in the next run. With benzyl alcohol as substrate, the procedure was successfully repeated five times without any great loss of catalytic activity.

Experimental Section

Materials and methods

All the solvents and reagents were purchased from Sinopharm Chemical Reagent Co. Ltd and were used without further purification. IR spectra were recorded on a NICOLET NEXUS870 instrument. Products were identified by using a 6820 gas chromatograph (GC) with an Agilent Technologies HP-Innowax (30 m×0.32 mm× 0.5 µm). XRD data were collected with Cu_{Kα} radiation on Bruker C8 ADVANCE spectrometer. TEM images were recorded on a JEM-2100 instrument. TGA was performed on a TGA/SDTA851e instrument under a N₂ atmosphere from 50 to 700 °C, with a heating rate of 10 °Cmin⁻¹ and N₂ flowing rate of 30 mLmin⁻¹. Calculation of the volume was performed by using Gaussian 03 at the B3LYP/6-31G + +(d,p) level.

Catalyst preparation

Preparation of HKUST-1: HKUST-1 was prepared according to Reference [10b]. In a typical procedure, a slurry of $Cu(OH)_2$ (0.98 g, 0.01 mol) in water (18 mL) was added to a solution containing trimesic acid (TA, 1,3,5-benzenetricarboxylic acid; 2.1 g, 0.01 mol), dimethyl formamide (DMF, 10 mL), and ethyl alcohol (46.6 mL) under moderate stirring. The molar composition of the resulting mixture was $1 Cu/1 TA/12.9 DMF/80 EtOH/100 H_2O$. The crystallization was carried out at room temperature under moderate stirring. Afterwards, the product was recovered by filtration and washed with ethanol, and finally dried at 65 °C.

Preparation of MOF-POM: MOF-POM was prepared according to Reference [11] with some expansion. In a typical synthesis, copper(-II) nitrate trihydrate (1.45 g, 6 mmol) and POMs (0.33 mmol) were dissolved in distilled water (12 mL). Another solution containing BTC (98%, 0.70 g, 2.8 mmol) and CTAB (0.12 g, 0.33 mmol) dissolved in absolute ethanol (16 mL) was prepared and mixed with the solution mentioned above under vigorous stirring. The mixture was kept stirring for approximately 30 min at room temperature and then aged without stirring for a further 5 days. After filtration, the solid product was washed with water before it was dried in air at 60 °C for 24 h. To remove CTAB, Soxhlet extraction with ethanol was performed for 48 h at 105 °C. Finally, the product was dried in air at 60 °C.

Oxidation process of alcohols

General procedure: In a typical process, alcohol (2 mmol) and CTAB solution (10 mL, 10 cmc) were added to a 50 mL round-bottomed flask. The mixture was stirred at room temperature for 5 min and catalyst MOF-POM (50 mg) and H_2O_2 (4 mmol) were then added. The temperature of the mixture was raised to 60 °C to initiate the reaction. The progress of the reaction was monitored by GC with samples taken periodically. The samples were cooled to room temperature, extracted with Et₂O three times, and dried over anhydrous Na₂SO₄ before being analyzed by GC.

Acknowledgements

We thank the Scientific Innovation Program of Jiangsu Porvince (no: CXLX13_198) for support of this research.

Keywords: alcohols · metal–organic frameworks · micelles · oxidation · polyoxometalates

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Received: January 7, 2014 Published online on

FULL PAPERS

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Polyoxometalate-Based Metal-Organic Frameworks as Catalysts for the Selective Oxidation of Alcohols in Micellar Systems



It's what's inside that counts: A series of polyoxometalate (POM)-based metalorganic frameworks (MOFs) was prepared and used in the selective oxidation of alcohols. Experiments with these MOFs were carried out in cetyltrimethyl ammonium bromide micellar solutions. With various alcohols as substrates, better to excellent conversion and selectivity were presented (see figure). Thus a green and efficient process was obtained.