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Mendeleev Commun., 2012, **22**, 152–153

Mendeleev
Communications

Transition metal-substituted polyoxometalates supported on MCM-41 as catalysts in the oxidation of cyclohexane and cyclooctane with H_2O_2

Jirarot Jatupisarnpong and Wimonrat Trakarnpruk*

Department of Chemistry, Faculty of Science and Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand. E-mail: Wimonrat.T@chula.ac.th

DOI: 10.1016/j.mencom.2012.05.014

The Keggin type polyoxometalates $(Bu_4N)_4HPW_{11}CoO_{39}$, $(Bu_4N)_4PW_{11}FeO_{39}$, $(Bu_4N)_4HPW_{11}CuO_{39}$ and $(Bu_4N)_4PW_{11}VO_{40}$ have been synthesized and supported on MCM-41 to be used as catalysts for the solvent-free oxidation of cyclohexane and cyclooctane with H_2O_2.

Keggin type polyoxometalates (POMs) are efficient catalysts for the oxidation of organic substrates.[1,2] Transition metal monosubstituted heteropoly anions have been used for the catalytic oxidation of alkenes with oxygen.[3] The catalytic homogeneous oxidation of cyclohexane and cyclooctane was performed in an acetonitrile solvent with H_2O_2: in the presence of the tetrabutylammonium salts of Keggin-type polyoxotungstates, $[XW_{11}O_{39}]^{n-}$ and $[XW_{11}MO_{39}]^{(n-m)-}$ (X = P, Si, B and M^{III} = Fe, Mn) afforded substantial amounts of alkyl hydroperoxides.[4] The tetrabutylammonium salts of $[Fe_4(H_2O)_2(PW_9O_{34})_2]^{6-}$, which are soluble in acetonitrile, showed higher cyclohexane conversion than $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (M^{II} = Co, Mn) but the main product was cyclohexyl hydroperoxide. The Fe and Co catalysts yielded 96 and 85% conversion of cyclooctane, respectively.[5] For the solvent-free reactions, surfactant-type polyoxoperoxometalates were prepared and shown to be effective for the epoxidation and oxidative cleavage of olefins to carboxylic acids with H_2O_2,[6] the synthesis of adipic acid[7] and the oxidation of hexanol and octanol.[8] The long-chain lipophilic cation in these catalysts acts as a phase transfer agent.

The POMs supported on porous solids have high surface areas and the numbers of accessible active catalytic sites. They combine the advantages of molecular complexes and reusable solids, as well as new activities and selectivities.[9,10] The selective oxidation of cyclohexane yields cyclohexanol and cyclohexanone, important intermediates in the production of adipic acid and caprolactam and in the manufacture of nylon-6 and nylon-66 polymers.

MCM-41 was prepared according to a published procedure[11] with $SiO_2:CTABr:NH_4OH:H_2O = 1.0:0.12:8:114$. The tetrabutylammonium salts of transition metal-substituted POMs: $(Bu_4N)_4HPW_{11}CoO_{39}$, $(Bu_4N)_4PW_{11}FeO_{39}$, $(Bu_4N)_4HPW_{11}CuO_{39}$ and $(Bu_4N)_4PW_{11}VO_{40}$ ($PW_{11}M$; M = Co^{II}, Fe^{III}, Cu^{II} or V^{V}) were synthesized and characterized as described elsewhere.[4,12,13] $PW_{11}M$ was incorporated into MCM-41 by incipient wetness impregnation (in MeCN) with 16 wt% loading[14] [this is a maximum loading at which the leaching of $PW_{11}M$ from the support was not observed when stirring $PW_{11}M$/MCM-41 in hot cyclohexane and H_2O_2 for 8 h, we also attempted to load $PW_{11}M$ higher than 16 wt% but found that leaching (>2 wt%) occurred]. The $PW_{11}M$/MCM-41 catalysts were studied by BET, XRD, FT-IR and ICP.[†]

The IR spectra of $PW_{11}M$/MCM-41 revealed the principal bands (W=O and W–O–W at 962–965 and 886–890 cm^{-1}, respectively) of $PW_{11}M$, confirmed the retention of the $PW_{11}M$ structure after immobilization. However, the band at 1082–1085 cm^{-1} attributed to ν_{as}(P–O) vibration was obscured by an intense and broad band of MCM-41. In the XRD diffraction patterns of $PW_{11}M$/MCM-41 samples (Figure 1), the absence of peaks due to crystalline $PW_{11}M$ phases indicates that $PW_{11}M$ is highly dispersed. The N_2 adsorption–desorption on $PW_{11}M$/MCM-41 exhibited a reversible type IV isotherm typical of mesoporous materials. The loadings of $PW_{11}M$ caused a decrease in the surface area (S_{BET}), pore volume and pore diameter of the catalysts (Table 1).

The main products of the catalyzed oxidation of cycloalkanes with H_2O_2 were cycloalkanol, cycloalkanone and cycloalkyl hydroperoxide[15] (Scheme 1)[‡] with trace amounts of acids. Table 1 summarizes the results of the oxidation of cyclohexane and cyclooctane.

Blank reactions without catalysts or H_2O_2 and in the presence of MCM-41 were performed and no oxidation products were detected. The activity of the catalysts depended on the transition

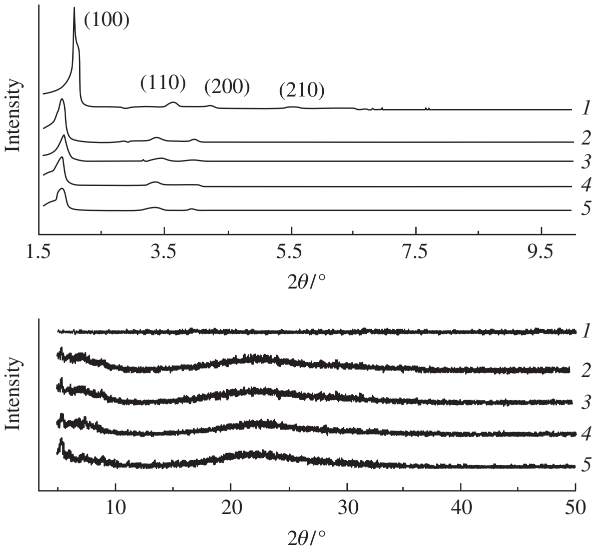

Figure 1 XRD patterns of (*1*) MCM-41 and (*2*)–(*5*) $PW_{11}M$/MCM-41 [M = (*2*) Co^{II}, (*3*) Fe^{III}, (*4*) Cu^{II} and (*5*) V^{V}].

[†] Specific surface areas were measured using the BET method on a BELSORP-mini. XRD measurements were performed on a Rigaku DMAX 2002/Ultima Plus powder X-ray diffractometer. The IR spectra were obtained on a Nicolet FT-IR Impact 410 spectrophotometer with a pressed KBr pellet. The amount of $PW_{11}M$ was analyzed by inductive coupled plasma emission (ICP, Perkin Elmer model PLASMA-1000).

[‡] A substrate (92 mmol), 5 wt% catalyst and aqueous H_2O_2 (30%) were added to a 60 ml Parr reactor. The reactor was heated to 80 °C and stirred for 8 h. The catalyst was separated, and the products were extracted with diethyl ether and dried. They were analyzed by GC [Varian CP-3800 GC chromatograph; CP-Sil (30 m×0.25 mm) column].

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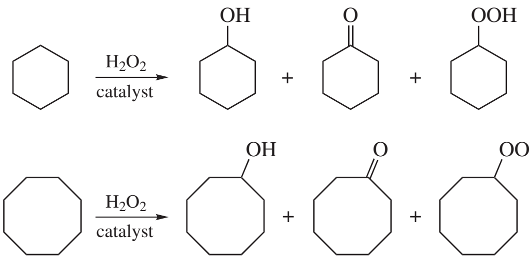

Scheme 1

Table 1 Oxidation of cyclohexane and cyclooctane (catalyst, 0.4 g; substrate, 92 mmol; H_2O_2/substrate molar ratio, 4:1; reaction time, 8 h; temperature, 80 °C).

Substrate	Catalyst	S_{BET}/ $m^2 g^{-1}$	Pore volume/ $cm^3 g^{-1}$	Pore diameter/ nm	Conversion (%)[a]	Selectivity (%)[b]		
						-one	-ol	-OOH
Cyclohexane	MCM	980	0.82	2.97	0	—	—	—
	$PW_{11}Co$/MCM	760	0.41	2.75	15	73	27	0
	$PW_{11}Co$/MCM[c]	760	0.41	2.75	17	72	28	0
	$PW_{11}Fe$/MCM	790	0.42	2.68	13	35	55	10
	$PW_{11}V$/MCM	754	0.38	2.66	19	76	24	0
	$PW_{11}Cu$/MCM	765	0.40	2.72	18	70	30	0
Cyclooctane	$PW_{11}Co$/MCM				19	74	26	0
	$PW_{11}Fe$/MCM				16	33	53	14
	$PW_{11}V$/MCM				21	74	26	0
	$PW_{11}Cu$/MCM				20	72	28	0
Cyclohexane	$PW_{11}Co$[d]				5	40	60	0
	$PW_{11}Fe$[e]				16	13	8	81
	$PW_{11}Cu$[d]				11	36	64	0

[a] Based on the gas chromatographic peak areas. [b] Expressed as a percentage of the total products; -ol = cycloalkanol; -one = cycloalkanone; -OOH = cycloalkyl hydroperoxide. [c] H_2O_2/acetic acid molar ratio, 1:1. [d] Cyclohexane, 18.5 mmol; catalyst, 0.04 mmol; H_2O_2/cyclohexane molar ratio, 2:1; MeCN, 10 ml; 80 °C, 12 h; [e] Same as *d* but at 60 °C.[4]

metal introduced. The activity increased in the order V > Cu > > Co > Fe. Compared between the supported and the unsupported catalysts, $PW_{11}M$/MCM showed higher selectivity for cyclohexanone, except for $PW_{11}Fe$/MCM, revealing the ability of solid matrices, MCM-41 to control surface reactions modifying the adsorption–desorption equilibria of reagents, reaction intermediates and products. The polar surface of the siliceous support is expected to favor the accumulation of produced alcohols at the interfaces and, consequently, oxidation to ketones. These results are in agreement with published data.[10] No cycloalkyl hydroperoxide was detected (except for the case of $PW_{11}Fe$/MCM), this is similar to the result over $(Bu_4N)_7H_3[Co_4(H_2O)_2(PW_9O_{34})_2]$.[16] The addition of acetic acid led to a further increase in the cyclohexane conversion in the presence of $PW_{11}Co$/MCM from 15 to 17%. This can be attributed to the stabilization of H_2O_2 as peroxy acetic acid species. $PW_{11}Fe$/MCM showed 10 and 14% selectivity for cycloalkyl hydroperoxide in cyclohexane and cyclooctane, respectively. The hydroperoxide was presumably formed by Fe^{III}-initiated generation of $HO^{\bullet}$.[16] However, the cycloalkyl hydroperoxide formation is much less than that with the unsupported catalyst. We performed oxidation in the absence of a solvent. Cyclooctane can also be oxidized by these catalysts with higher conversions. The most active catalyst $PW_{11}V$/MCM gave a higher conversion (21%) of cyclooctane than that reported (16%).[10] The solid catalysts could be filtered off and reused, the activities dropped ~1–2% after the third run without change in product selectivity. This is due to some leaching (13–14% $PW_{11}M$ remained, analyzed by ICP) or surface coverage of the catalysts after triple use. However, the structure of the MCM-41 support was not collapsed, as shown in Figure 2. Diffraction peaks from MCM-41 are still observed, except with reduction in peak intensities. Figure 3 shows the N_2 adsorption–desorption isotherm of $PW_{11}V$/MCM, which still reveals mesoporous structure.

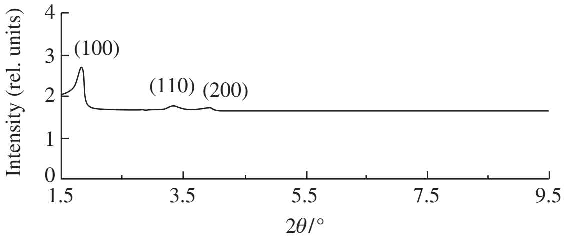

Figure 2 XRD pattern of $PW_{11}V$/MCM after use.

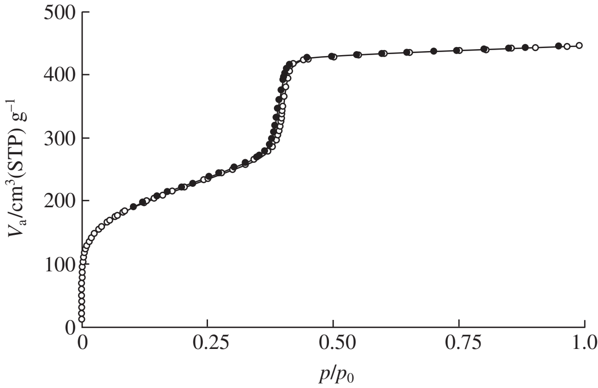

Figure 3 Nitrogen adsorption–desorption isotherm of $PW_{11}V$/MCM after use.

The oxidation on these $PW_{11}M$/MCM catalysts occurs *via* a radical pathway since no products were detected upon the addition of a radical scavenger (2,6-di-*tert*-butyl-4-methylphenol).[17]

This work was supported by a research grant ‘The 90th Anniversary of Chulalongkorn University Fund’.

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Received: 27th September 2011; Com. 11/3804