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Surfactant-Encapsulated Polyoxometalates as Immobilized Supramolecular Catalysts for Highly Efficient and Selective Oxidation Reactions

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Abstract: A type of interesting immobilized supramolecular catalysts based on surfactant-encapsulated polyoxometalates has been developed for oxidation reactions. Through a sol-gel process with tetraethyl orthosilicate, hydroxyl-terminated surfactant-encapsulated polyoxometalate complexes have been covalently and uniformly bound to a silica matrix with unchanged complex structure. The formed hybrid catalysts possess a defined hydrophobic nano-environment surrounding the inorganic clusters, which is conducive to compatibility between the polyoxo-

Introduction

Polyoxometalates (POMs) are a class of well-defined early transition metal oxygen clusters, which exhibit distinctive structures and various functionalities.^[1] Due to their rich redox chemistry, POMs are commonly used as effective catalysts for selective oxidations of alkenes, alcohols, and sulfides to the corresponding epoxides, ketones, sulfoxides, and sulfones. These reactions are significant for both fundamental research and practical applications. For example, the oxidation of cyclohexene leads to the value-added epoxycyclohexane, which possesses high reactivity and is commonly used to prepare some well-known insecticides and unsaturated resins.^[2] As the main oxidation product of cyclohexanol, cyclohexanone is commonly used as the general solvent and raw material in the preparation of nylon-6 and nylon-

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Keywords: heterogeneous catalysis • polyoxometalates • selective oxidation • supported catalysts • supramolecular catalysis tively in the selective oxidation of several different kinds of organic compounds, such as alkenes, alcohols, and sulfides, and the main products were the corresponding epoxides, ketones, sulfoxides, and sulfones. More significantly, the catalyst could be easily recovered by simple filtration, and the catalytic activity was well retained for at least five cycles. Finally, the present strategy has proved to be a general route for the fabrication of supramolecular hybrid catalysts containing common polyoxometalates suitable for various purposes.

6,6.^[3] In addition, the oxidation of sulfides to the corresponding sulfoxides or sulfones is also an important type of organic reaction insofar as organic sulfur oxides are useful intermediates or active components in organic synthesis and biological applications.^[4] Furthermore, the oxidation of sulfides is also relevant to the petroleum industry.^[5] In a typical oxidative desulfurization process, sulfides are oxidized to the corresponding sulfones, which can be easily removed from fuel oil by extraction due to their high polarities.

Recently, a number of catalytic oxidation systems based on hydrogen peroxide and POMs have been applied for the above reactions. On the one hand, aqueous H₂O₂ is an ideal oxidant for liquid-phase reactions.^[6] On the other hand, POMs have advantages as redox catalysts.^[7] For example, they possess defined structures and fairly high thermal stabilities, which make them stable under general reaction conditions, and they facilitate fast and reversible multi-electron redox transformations under mild conditions, as a result of which they show high efficiency in terms of oxidant utilization and substrate conversion. Nevertheless, oxidation systems based on hydrogen peroxide and POMs still have some intrinsic limitations. Because of their high lattice energies, POMs are insoluble in common organic solvents and mass transfer between POM catalysts and organic substrates is

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always poor due to low compatibility. Several methods have been reported as efforts to overcome these shortcomings.^[8-16] Typically, through modification with cationic surfactants, the resulting surfactant-encapsulated POM (SEP) complexes can be well-dispersed in organic solvents,^[8] thereby effectively becoming homogeneous catalysts, which can improve the catalytic oxidation efficiency remarkably.^[9] However, this method makes recovery and reuse of the catalyst much more difficult. As an alternative, SEP catalysts prepared with dendritic cationic surfactants have been reported to be applicable to oxidation reactions,^[10] and these effectively avoided the aggregation of common SEPs in organic solvents and could be easily recovered by precipitation from organic solvents of low polarity.^[11] Moreover, through simple organic modification of the dendritic catalyst, chiral catalytic oxidation could also be realized.^[12] Cationic polyelectrolytes are also candidates for immobilizing POMs, whereby the obtained hybrid catalyst is insoluble in the reaction solvent, thus greatly simplifying the recovery process.^[13] Microemulsion formation is another effective approach, leading to considerable activity enhancement and

easier recovery of the POM catalysts.^[14] However, it has some disadvantages, such as complicated steps in the separation of products and recovery of the reaction system, as well as a solvent dependence.^[15] A reaction-controlled phase-transfer catalyst based on a special POM for the epoxidation of olefins has been reported,^[16] but this does not seem to be a general route suitable for various common POMs with strong catalytic properties. Therefore, exploring a general method for the fabrication of economically viable and environmentally friendly catalysts based on common POMs for highly efficient oxidation is of importance in POM chemistry, catalysis, and organic chemistry.

covalently anchored within a silica gel matrix.^[17,18] The immobilized supramolecular hybrid catalysts present specific features for the catalytic oxidation of organics. Thus, they possess a defined hydrophobic nano-environment to capture the organic substrate, which maximizes the catalytic efficiency. They are not solvent-dependent and are amenable to different POMs and so can meet different requirements. Through tuning the reaction conditions, they can be used for the selective oxidation of sulfides to sulfoxides, which is important for precursors or raw materials in drug preparations. They are stable under the specified reaction conditions and can be recovered by simple filtration and reused directly without obvious activity losses. Finally, the hybrid catalysts not only display high efficiency in the general oxidation of sulfides, but also are applicable for the selective oxidation of alkenes and alcohols to the corresponding value-added epoxides and ketones, which exhibit attractive potentials in fine chemical and biological synthesis as well as in the petroleum industry.

Through sol-gel condensation with tetraethyl orthosilicate

(TEOS), SEPs with hydroxyl groups at the periphery can be



Scheme 1. Schematic representation of the procedure for the fabrication of SHC-1 and the oxidation mechanism of sulfide, alcohol, and olefin substrates under the catalysis of SHC-1.

Herein we propose a new strategy of using supramolecular hybrid catalysts (SHCs) based on SEP complexes for highly efficient and selective oxidation reactions. The catalysts efficiently facilitate the oxidation of alcohols, alkenes, and sulfides with H_2O_2 as the oxidant and can be conveniently recovered and reused (Scheme 1). Through electrostatic interactions, the counter ions of the POMs can be replaced by quaternary ammonium cations, such as di(11-hydroxyundecyl)dimethylammonium (DOHDA), and a series of SEP supramolecular complexes can be easily obtained.^[17] The structure of SEPs is similar to that of a reverse micelle catalyst system, which could improve the compatibility between the organic substrate and the POM catalytic centre.

Results and Discussion

Composition and structure of SHC-1: To clarify the generality of the designed construction approach for POMs, we take the most common one, $[PW_{12}O_{40}]^{3-}$ (POM-1), as an example. The ammonium surfactant di(11-hydroxyundecyl)dimethylammonium bromide (DOHDA·Br) was synthesized according to a previously reported procedure.^[17] The cationic ammonium DOHDA and the anionic POM-1 could be combined through electrostatic interactions, and the resulting complex (SEP-1) precipitated in water.^[17] Thus, the formed SEP-1 possesses a hydrophilic inorganic POM-1 core and a hydrophobic organic shell composed of alkyl chains with hydroxyl groups at their termini, which is similar to a reverse micelle, as shown in Scheme 1. The following detailed characterization supports the description of the structure of SEP-1.

Characteristic vibrations attributable to DOHDA at 2926 (v_{as} CH₂), 2853 (v_{s} CH₂), and 1467 cm⁻¹ (δ CH₂), and to POM-1 at 1077 (v_{as} P–O_a), 982 (v_{as} W=O_d), 897 (v_{as} W–O_b–W), and 812 cm⁻¹ (v_{as} W–O_c–W) appear in the IR spectrum of SEP-1, which confirm the success of the encapsulation step (Figure 1a). Furthermore, elemental analysis (EA) results revealed that all three negative charges of POM-1 had been neutralized with DOHDA cations, hence the structural formula proposed for SEP-1 is (DOHDA)₃PW₁₂O₄₀ (Table 1). Besides EA, TGA measurements also verified the

Table 1. Summary of EA results for SEP-1 and fresh and recovered SHC-1 catalysts.

Element mass content	Si %	P %	W %	С%	W/P	W/C	Si/W
SEP-1 (found)	_	0.79	54.65	21.55	69.52	2.54	_
$(DOHDA)_{3}PW_{12}O_{40}$ (calculated)	-	0.77	54.73	21.42	71.07	2.56	_
SHC-1 (freshly prepared)	24.02	0.22	14.63	5.67	67.82	2.58	1.64
SHC-1 (reused 5 times)	24.75	0.22	14.97	5.77	67.37	2.59	1.65

formation of the proposed structure. Assuming that the organic component decomposed completely and that the only inorganic residual species at 900 °C were P_2O_5 and WO_3 , the total residue found of 70.83% (Figure 1b) was in perfect agreement with the calculated value of 70.67% based on the postulated structural formula. These data imply that the



Figure 1. a) IR spectra of SEP-1 and SHC-1 in KBr pellets and b) TGA curve of SEP-1.

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chemical structure of SEP-1 is indeed as we expected, that is, one POM-1 polyanion bearing three negative charges with three DOHDA cations electrostatically bound on its surface (Scheme 1).

The six hydroxyl groups at the periphery of each SEP-1 endow the complex with good solubility in the mixed solvent of ethanol and water and facilitate the subsequent condensation with the sol-gel precursor TEOS.^[17,18] After the condensation reaction with TEOS, SEP-1 units are uniformly grafted within a silica matrix through their terminal hydroxyl groups, yielding the supramolecular hybrid catalyst (SHC-1) based on SEP-1 complexes. The characteristic vibration bands attributable to DOHDA at 2926 (v_{as} CH₂)

and 2853 cm^{-1} ($v_s \text{ CH}_2$), and to POM-1 at 982 ($v_{as} \text{ W=O}_d$) and 812 cm^{-1} ($v_a \text{ W=O}_c\text{-W}$) are clearly observed in the IR spectrum of SHC-1 (Figure 1a), which confirm the successful incorporation of SEP-1 into the silica gel matrix. Besides these vibrations, two new signals can

be seen in the IR spectrum of SHC-1. A band centred at 1068 cm⁻¹ (ν Si–O–Si), characteristic of siliceous material, is clearly observed, suggesting the successful hydrolysis and condensation of TEOS and the formation of a silica network. A vibration band at 1143 cm⁻¹ (v Si–O–C) confirms the expected condensation between TEOS and the hydroxyl groups at the periphery of the SEP-1 units and the formation of Si-O-C bonds, indicative of chemical anchoring of SEP-1 in the silica matrix. ³¹P NMR spectra of SEP-1 and SHC-1 are presented in Figure 2a. The chemical shifts of the P atoms present in SEP-1 and SHC-1 match that of the P in pure POM-1 ($\delta \approx -15.5$ ppm),^[19] which suggests that the structure of POM-1 is essentially retained during the encapsulation and sol-gel condensation process. XPS analysis also confirmed the structural integrity of POM-1 in SHC-1. As shown in Figure 2b, the 2p level binding energy (BE) of the P atoms present in SHC-1 is 134.07 eV, which is consistent with that in SEP-1 (134.12 eV). Furthermore, by comparison of the salient elemental compositions (Table 1), it can be seen that the W/P and W/C mass ratios in SEP-1 and SHC-1 are almost identical, suggesting that the C in the hybrid catalyst originated entirely from the SEP-1, and that the hydrolysis of TEOS was complete under the specified experimental conditions. Moreover, the loading of SEP-1 in SHC-1 was estimated to be about 27 wt%, based on the W content from the elemental composition measurement, and this value is consistent with the anticipated value (30 wt%) calculated from the overall proportions of SEP-1 and TEOS.

Figure 3 displays the nitrogen-sorption isotherm and the corresponding pore size distribution curve of SHC-1. The Brunauer–Emmett–Teller (BET) surface area of SHC-1 was estimated to be $365.9 \text{ m}^2 \text{g}^{-1}$ with a total pore volume of $1.05 \text{ cm}^3 \text{g}^{-1}$. Because a silica matrix prepared by the present procedure would normally exist in an amorphous state, SHC-1 exhibits a wide pore size distribution, as shown in



Figure 2. a) ³¹P NMR ($[D_6]$ DMSO) spectra and b) XPS spectra of P (2p level) of SEP-1 (bottom), freshly prepared SHC-1 (middle), and recovered SHC-1 (top).

Figure 3b, and it is difficult to determine its exact pore size. However, it is clear that the size of the pores is sufficient to allow entry of the organic substrate and hence its contact with the SEP catalytic centres. To evaluate the hydrophobicity of the hybrid catalyst incorporating hydrophobic SEP units, comparative static water contact angle measurements were carried out on SHC-1 and pure silica gel prepared in the same way. Because of the porous structure, a water droplet was quickly adsorbed by pure silica gel and so the contact angle was considered to be effectively 0°. In contrast, the water contact angle on SHC-1 was measured as 54° (Figure 3a, inset), suggesting that the hydrophobicity of SHC-1 was greatly increased due to the incorporation of SEP-1. The hydrophobic region in SHC-1 is considered to be an important factor for promoting the catalytic activity, as evidenced by the following results.

Catalytic activity of SHC-1: The oxidation of dibenzothiophene (DBT), which is considered to be the main sulfide pollutant in fuel oil, was firstly selected as a model reaction to evaluate the catalytic activity of SHC-1. $30 \% H_2O_2$ was selected as the oxidant and the solvent was acetonitrile. The reaction was performed under rather mild conditions ($40 \degree C$ and stirring at 300 rpm), and the amounts of H_2O_2 and SHC-1 were optimized to be as low as possible while still retaining acceptable conversion, reaction rate, and efficiency of H_2O_2 usage. Through monitoring the reaction by HPLC (Figure 4), we observed that at the beginning (0 min) there was only one component in the reaction system, the reten-



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Figure 3. a) Nitrogen-sorption isotherms and (inset) static water contact angle, and b) micro- and (inset) *meso*-pore size distributions of SHC-1.



Figure 4. HPLC diagrams for the oxidation of DBT in acetonitrile under the catalysis of SHC-1.

tion time (t_R) of which was about 1.87 min. This component could be assigned as the substrate DBT. With increasing reaction time, a new signal attributable to the product (t_R = 1.54 min) emerged and gradually increased, with a concomitant decrease in the DBT peak, consistent with oxidation of the sulfide. The substrate DBT was consumed completely and the amount of product reached its maximum value in quite a short time (42 min), indicating that the reaction was complete and that SHC-1 was very active despite being deployed at a very low level (0.25 mol%) with respect to the DBT.

The composition of the product was examined by IR, ¹H NMR, and mass spectrometry (MS). As shown in Figure 5a, compared with the substrate DBT, two characteristic vibrations appeared at 1288 (v_{as} SO₂) and 1166 cm⁻¹ (v_{s} SO₂)

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Figure 5. a) IR and b) 1 H NMR spectra of substrate DBT (bottom) and product DBTSF (top), in KBr pellets and in [D₆]DMSO, respectively.

strictly obeys pseudo-first-order kinetics, consistent with results reported for homogeneous catalytic systems.[5b,20] Table 2 lists the main kinetic parameters of the oxidation of DBT under the catalysis of SHC-1 and other typical catalysts based on POM-1. The rate constant k of the oxidative reaction catalyzed by SHC-1 was determined as 0.111 min⁻¹ on the basis of Equation (1). This value is close to that measured for the homogeneous phase-transfer system (0.16 min^{-1}) , which indicates a similarly high efficiency of SHC-1 in the catalytic oxidation of DBT. It is known that immobilization normally causes sharp decreases in catalytic activity. However, it is significant for catalyst recovery and reuse, which is demanded in practical applications. The present designed catalyst exhibits advantages in terms of both high catalytic activity and ease of recovery. The turnover frequency (TOF) is another key parameter to evaluate the relative catalytic activity of a catalyst, which is determined as the number of moles of substrate converted (N_s) per mol of catalyst $(N_{\rm C})$ in unit time, as described by Equation (2). The activity of SHC-1 (TOF=9.52) was found to be relatively high by comparison with the TOFs obtained for different catalytic systems. It should be mentioned that in most previously reported research in this area, catalytic oxidations of organic sulfides have usually been performed in the presence of a large excess of the oxidant H_2O_2 to accelerate the reaction. In contrast, only a stoichiometric amount of H_2O_2 has been used in our case. From comparison of the efficiencies of H₂O₂ usage, which is defined as the molar ratio of the reacted amount to the added amount of H₂O₂, it can

Table 2. Comparison of catalytic activities of POM-1-based catalysts for the oxidation of DBT.

in the IR spectrum, suggesting that the product was a sulfone compound. Based on the corroborating evidence provided by the ¹H NMR (Figure 5b) and mass spectra (Figure S18 in the Supporting Information) of the product, we concluded that the substrate DBT had been completely oxidized, with the gener-

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Reaction system	$T [^{\circ}C]^{[a]}$	t [min] ^[b]	$k [\min^{-1}]^{[c]}$	TOF [min ⁻¹]	C [%] ^[d]	E [%] ^[e]
SEP/SiO ₂ (heterogeneous)	40	42	0.111	9.52	100	80
bare $H_3PW_{12}O_{40}^{[20]}$ (homogeneous)	50	60	0.078	1.72	100	1.2
phase transfer ^[9] (homogeneous)	50	25	0.160	0.07	100	30
microemulsion ^[14] (heterogeneous)	60	90	0.013	5.32	100	66.7

[a] T=reaction temperature. [b] t=reaction time. [c] k=reaction rate constant. [d] C=conversion. [e] E=efficiency of H₂O₂ usage.

ation of dibenzothiophene sulfone (DBTSF) as the sole product.

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \tag{1}$$

$$\text{TOF} = \frac{N_{\text{S}}}{N_{\text{C}} \times t} \tag{2}$$

Furthermore, on the basis of the amounts of substrate and product in the reaction mixture sampled at certain specified times, plots of conversion and $\ln (C_t/C_0)$ versus reaction time *t* could be constructed, as depicted in Figure 6, where C_0 and C_t represent the initial DBT concentration and the concentration at time *t*, respectively. A linear relationship (Figure 6b) expressed by Equation (1) indicates that the reaction be concluded that besides its high reaction rate and activity, SHC-1 also exhibits a high efficiency of H_2O_2 usage, which is economical and much more suitable for practical industrial applications.

Catalytic oxidation reaction process: To clarify the catalytically active components present in SHC-1, we have monitored the catalytic activity of pure silica gel and the support (SHC-1 without POM-1) in the oxidation of DBT under the same reaction conditions. The results showed that no oxidation of DBT occurred in 5 h. Therefore, we surmise that the excellent catalytic activity of SHC-1 in the oxidation of DBT must stem from the high redox catalytic activity of POM-1 and the supramolecular synergy during the reaction process. In the presence of H_2O_2 , POMs are readily oxidized to active peroxide species.^[21] Simultaneously, substrates of low polarity such as DBT, dissolved in a polar solvent (ace-

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Figure 6. a) Diagram of reaction conversion and b) plot of $\ln(C_t/C_0)$ versus the reaction time for the oxidation of DBT in acetonitrile under the catalysis of SHC-1.

tonitrile), tend to adsorb at the more hydrophobic region composed of the alkyl chains of surfactants surrounding the POMs due to hydrophobic interactions. DBT molecules are oxidized to DBTSF once they reach the active sites of the peroxide POMs, whereupon the POMs return to their original state. In the meantime, the product DBTSF, which is of much higher polarity than DBT, is easily released from the hydrophobic region of SHC-1 and moves to the bulk polar acetonitrile, which allows the reaction to proceed efficiently. Thus, SHC-1 is suitably predisposed for easy capture of the substrate and release of the product in acetonitrile, which seems to play a role similar to that of the operation of an enzyme in a biological system, and this feature maximizes the catalytic activity. It is known that the chemical shift of a proton is sensitive to its local environment and ¹H NMR measurement has proved to be an effective technique for detecting the location of guest molecules in micelle systems and the interactions between them.^[22] Therefore, the ¹H NMR spectra of DBT in the presence of pure silica gel, SEP-1, and SHC-1 were obtained to examine the adsorption and location of DBT in different matrices, and the data are shown in Figure 7a. In each case, the concentration of DBT was identical and the mol ratio between DBT and the hybrid catalyst was controlled at 400:1, precisely the same conditions as employed in the catalytic reactions. From the comparison, it can clearly be seen that the ¹H NMR signals of the DBT protons became lower in intensity and broader in the presence of SHC-1 compared to those of pure DBT

Figure 7. ¹H NMR ($[D_6]$ DMSO) spectra of a) DBT and b) DBTSF in pure state (first from bottom), in the presence of pure silica gel (second), SEP-1 (third), and SHC-1 (top).

in solution. These changes in the ¹H NMR signals of DBT can be attributed to a restriction of molecular mobility, which suggests a strong interaction between the DBT molecules and SHC-1.^[22] Furthermore, by comparing the ¹H NMR spectra of DBT in the presence of SHC-1 and SEP-1, it can be ascertained that the adsorption and enrichment of DBT most probably occurs in the interior of SEP-1 in the hybrid catalyst.^[22] In addition, compared with the spectrum of the free substrate in solution, the ¹H NMR signals of DBT are shifted to lower field in the presence of SHC-1 due to the electron-withdrawing effect of POM-1. Therefore, based on the above experimental results, we propose that the DBT molecules tend to accumulate in the hydrophobic region of SEP-1 in SHC-1, close to the surface of the POM-1 catalytic centres under the reaction conditions, which is propitious to the catalytic oxidation process. We have also examined the location of the product DBTSF under the reaction conditions by applying the same procedure. In this case, we did not observe any broadening or shifting of the ¹H NMR signals, as shown in Figure 7b. Therefore, in contrast to the substrate DBT, the product DBTSF prefers to move to the bulk acetonitrile under the reaction conditions due to its relatively high polarity, which may also promote the efficiency of the catalytic oxidation.

Recovery and reuse of SHC-1: In addition to their high catalytic activity and efficiency, the present catalysts proved to be stable under the applied reaction conditions and could be easily recovered by simple filtration and then reused without

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any further treatment. We have compared the structure of the recovered catalyst with that of the freshly prepared one on the basis of EA and IR measurements. The W/C and W/ Si elemental mass ratios in the recovered SHC-1 catalyst were almost the same as those in the freshly prepared one, as is evident from Table 1, indicating that the SEP-1 complexes were firmly bonded within the silica matrix and that no POMs had dissociated from the silica matrix into the reaction solution. The almost identical IR spectrum of the recovered catalyst also supports the stability of the hybrid catalyst (Figure S7 in the Supporting Information). ³¹P NMR measurements and XPS analysis were also used to check the structural integrity of the POM-1 after the catalytic oxidation cycle. As shown in Figure 2a, the ³¹P chemical shift of the recovered SHC-1 was exactly the same as that of the freshly prepared catalyst. Because the ³¹P NMR signal is sensitive to the chemical environment of the phosphorus atom, the unchanged chemical shift implies that the POM-1 returns to its initial state after a catalytic oxidation cycle and that its structure is quite stable under the applied reaction conditions,^[19] which is similar to previously reported results.^[14] The 2p level of the P atoms present in the recovered SHC-1 remained consistent with that of the freshly prepared SHC-1, as assessed by XPS analysis (Figure 2b), further confirming the structural integrity of SHC-1 during the reaction process. The recovered SHC-1 could be reused directly without any special treatments, making it very economical and

thus suitable for practical industrial applications. More importantly, the catalytic activity and efficiency of the recovered SHC-1 were found to be as high as that of the freshly prepared catalyst, and no sign of a decrease in the catalytic activity was found over five cycles.

Solvent effects on the catalytic activity of SHC-1: To evaluate the influence of solvent polarity on the kinetics of the reaction, we have investigated the catalytic activity of SHC-1 in acetone, chloroform, hexane, and dodecane in addition to acetonitrile. The key kinetic parameters of the reactions in different solvents were obtained by monitoring the reactions by HPLC and are listed in Table 3. The DBT molecules were completely oxidized to DBTSF in all of the reaction solvents, and the conversion reached 100%, as indicated in Figures 8a and b. The reactions in all of the solvents conformed to pseudo-

Table 3. Summary of the catalytic activities of SHC-1 for the oxidation of DBT in various solvents.

Solvent	Т	t	k	TOF	С	Е
	[°C] ^[a]	[min] ^[b]	$[\min^{-1}]^{[c]}$	$[\min^{-1}]$	[%] ^[d]	[%] ^[e]
acetonitrile	40	42	0.111	9.52	100	80
acetone	40	58	0.078	6.90	100	80
chloroform	40	153	0.030	2.61	100	80
hexane	40	43	0.107	9.30	100	80
dodecane	40	38	0.118	10.5	100	80

[a] T=reaction temperature. [b] t=reaction time. [c] k=reaction rate constant. [d] C=conversion. [e] E=efficiency of H₂O₂ usage.

first-order kinetics, as indicated by the plots of $\ln(C_t/C_0)$ versus the reaction time *t* (Figures 8c and d), while the reaction rates changed with the solvents employed in a regular manner. For acetonitrile, acetone, and chloroform, the reaction rates decreased with decreasing polarity of the solvent (Figure 8c). This may be ascribed to variations in the distribution of DBT between the solvent and the hydrophobic nano-environment of the SHC-1, which affect the supramolecular synergy of adsorption, oxidation, and desorption during the reaction. Because of the low polarity of DBT molecules, the hydrophobic interaction favouring migration of the DBT from the solvent to the hydrophobic region becomes weaker with decreasing polarity of the solvent, resulting in a decrease of the reaction rate on going from acetonitrile to acetone and then to chloroform. The regular change



Figure 8. a, b) Reaction conversions of DBT and c, d) plots of $\ln(C_t/C_0)$ versus reaction time under the catalysis of SHC-1 in different solvents: acetonitrile (filled squares, **n**), acetone (stars), chloroform (filled triangles, **a**), hexane (empty circles, \bigcirc), and dodecane (empty triangles, \triangle).

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of the reaction kinetics in different solvents with various polarities further confirms the existence of supramolecular synergy of microenvironment and catalysis during the reaction process. Interestingly, for hexane and dodecane, the reaction rates rise again (Figure 8d), even though the polarities of these solvents are much lower. This characteristic can be readily attributed to the low solubility of the product DBTSF in hexane and dodecane, and the deposition of DBTSF in these nonpolar solvents accelerates the leaving of the product from the reaction site, promoting the reaction more effectively. As is well known, hexane and dodecane are commonly used to simulate fuel oil due to their similar compositions and polarities. The good performance of the present catalyst in these two solvents holds promise for its application in oxidative desulfurization.

Catalytic activity of SHC-1 in the selective oxidation of different sulfides: Three other sulfides, diphenylsulfide (DPS), methylphenylsulfide (MPS), and dimethylsulfide (DMS), were also employed as substrates to evaluate the catalytic activity of SHC-1. The reaction processes were monitored by HPLC, and plots of conversion and $\ln(C_t/C_0)$ versus the reaction time t are depicted in Figure 9. As with DBT, it can be seen that the reactions of all of the other substrates conform to pseudo-first-order kinetics (Figure 9b). From comparisons of the TOFs and the detailed kinetic parameters of the reactions summarized in Table 4, it can be seen that SHC-1 displays high catalytic activity for the oxidation of these sulfides, implying that it is applicable to different substrate species. The reaction rates and TOFs for the oxidations of the other three substrates to the corresponding sulfones are much higher than those for DBT, which may be attributed to the low aromaticity and favourable spatial aspects of these sulfides compared with DBT. IR and NMR analyses indicated that no other byproducts were generated in the reactions (Figures S19-S24 in the Supporting Information). The conversion and selectivity in favour of the oxidation of these sulfides to the corresponding sulfones reached 100% under the employed conditions.

Table 4. Summary of the catalytic activities of SHC-1 for the oxidation of different sulfide substrates to the corresponding sulfones and sulfoxides.

Substrate	Reaction conditions ^[a]	t [min] ^{b]}	Main product	TOF [min ⁻¹]	C [%] ^[c]	S [%] ^[d]
DBT	А	42	DBTSF	9.52	100	100
DPS	А	22	DPSF	18.18	100	100
MPS	А	24	MPSF	16.67	100	100
DMS	А	17	DMSF	23.52	100	100
DBT	В	120	DBTSO	7.25	87	66
DPS	В	90	DPSO	11.11	100	100
MPS	В	70	MPSO	14.29	100	100
DMS	В	70	DMSO	14.29	100	100

[a] Conditions: A: T=40 °C, solvent=acetonitrile, mol ratio of substrate, oxidant, and catalyst = 1:2.5:0.0025; B: T=40 °C, solvent=acetonitrile, mol ratio of substrate, oxidant, and catalyst = 1:1:0.001. [b] *t*=reaction time. [c] C=conversion. [d] S=selectivity.

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Figure 9. a) Reaction conversions and b) plots of $\ln(C_t/C_0)$ versus reaction time in acetonitrile under the catalysis of SHC-1 for different sulfides: DBT (filled squares, **•**), DPS (stars), MPS (filled triangles, **•**), and DMS (empty circles, \odot).

Because of the importance of sulfoxides in organic synthesis and biological applications,^[4,23] the selective oxidation of sulfides to sulfoxides was further investigated. Through reducing the amounts of H_2O_2 and SHC-1, we could control the oxidative reactions of sulfides to the stage of sulfoxides with high selectivity. As shown in Table 4, the selectivity in favour of dibenzolthiophene sulfoxide (DBTSO) reached 66%, and in the cases of DPS, MPS, and DMS, the selectivity in favour of the corresponding sulfoxide even reached 100%.

Catalytic activity of SHC-1 in the oxidation of different substrates: The epoxidation of alkenes and the oxidation of alcohols were also tested as model reactions to evaluate the catalytic activity of SHC-1, and the compositions and structures of the substrates and products were determined by ¹H NMR measurements. Figure 10a shows the ¹H NMR spectra of the substrate cyclohexene and its oxidation product. With the disappearance of the signals of the H_a protons with characteristic chemical shifts for double bonds at δ = 5.67 ppm and a shift of the H_b and H_c proton signals to higher field, the signals of the product developed, having typical chemical shifts of epoxides at δ =2.87, 1.57, and 1.26 ppm. This result indicated that the only product of the oxidation of cyclohexene was epoxycyclohexane, and that

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Figure 10. Monitoring of the oxidation reactions of a) cyclohexene and b) cyclohexanol by $^1{\rm H}$ NMR (CDCl_3) spectra.

the selectivity reached 100% under the catalysis of SHC-1. Similarly, the oxidation of cyclohexanol under the catalysis of SHC-1 was also monitored by ¹H NMR spectroscopy. As indicated in Figure 10b, the oxidation of cyclohexanol generated cyclohexanone as the only product based on the chemical shift analysis, and the conversion and selectivity of this transformation reached 100% in 5 h under the catalysis of SHC-1. The key kinetic parameters of the above reactions are listed in Table 5, from which it is apparent that the catalytic oxidations of cyclohexanol are associ-

fabrication of supramolecular hybrid catalysts containing common POMs suitable for various requirements.

Conclusions

In summary, we have designed and fabricated a novel immobilized supramolecular hybrid catalyst based on surfactantencapsulated polyoxometalate complexes for use in catalytic oxidation reactions. Supramolecular interactions are not only central to the construction process of the hybrid catalyst, but also play a crucial role in promoting the activity of the catalyst during the reactions. Defined hydrophobic nano-environments around the POM in the catalyst tend to capture the substrates of low polarity, such as sulfides, and release the strongly polar oxidized product, in this case sulfones. This property leads to enhanced catalytic activity, and the rates of the catalytic reactions in different solvents conformed well to pseudo-first-order kinetics. Besides displaying high reaction activity, the hybrid catalyst proved to be stable under the applied reaction conditions and moreover met the requirements of easy recovery and reuse. The catalyst combines a reverse-micelle-like supramolecular catalytic system with immobilization through the sol-gel technique and concurrently possesses the advantages of both homogeneous and heterogeneous catalysts. Furthermore, the catalyst shows high efficiency in the oxidation of sulfides in general. Through adjusting the reaction conditions, the selective oxidation of sulfides to sulfoxides can also be achieved. Finally, the catalyst has also been found to be effective in the selective oxidation of alkenes and alcohols to the corresponding epoxides and ketones. Because of the catalytic activity and selectivity of the hybrid catalyst for the oxidation of sulfides, alkenes, and alcohols, we believe that this kind of supramolecular hybrid catalyst may have potential application in diverse syntheses.

Table 5. Summary of catalytic activities of SHC-1 for the oxidation of different substrates.

Substrate	Reaction conditions	$T \left[{}^{\bullet} \mathbf{C} \right]^{[\mathbf{a}]}$	t [min] ^[b]	Main product	TOF [min ⁻¹]	C [%] ^[c]	S [%] ^[d]
cyclohexene	solvent = acetonitrile	25	120	epoxycyclohexane	7.17	86	100
cyclohexanol	S/O/C ^[e] 1:1:0.001	40	300	cyclohexanone	1.33	100	100

[a] T=reaction temperature. [b] t=reaction time. [c] C=conversion. [d] S=selectivity. [e] S/O/C=mol ratio of substrate, oxidant, and catalyst.

ated with relatively high TOF values, suggesting high catalytic activity and potential applications of SHC-1 for oxidations of alkenes and alcohols.

Finally, to verify that the present method for the fabrication of supramolecular hybrid catalysts is equally applicable to other common POMs, we have also evaluated the catalytic activities of hybrid catalysts composed of different POMs, such as $[EuP_5W_{30}O_{110}]^{12-}$ (POM-2), prepared according to the same strategy as SHC-1. The results showed that such catalysts performed equally as well as SHC-1, suggesting that the present strategy offers a general approach for the **Experimental Section**

Reagents and materials: Dimethylamine [(CH₃)₂NH], tetraethyl orthosilicate (TEOS), hydrogen peroxide (30% aqueous solution), and 12-phosphotungstic acid ($[PW_{12}O_{40}]^{3-}$, POM-1) were of analytical grade and were purchased from Beijing Chemical Reagents Company. 11-Bromoundecanol

 $[Br(CH_2)_{11}OH]$ was purchased from Sigma-Aldrich. Dibenzothiophene (DBT), diphenylsulfide (DPS), methylphenylsulfide (MPS), and dimethylsulfide (DMS) were purchased from Alfa Aesar. All chemicals were used directly without any further purification. $[EuP_5W_{30}O_{110}]^{12-}$ (POM-2) with K⁺ counter ions was synthesized according to a published procedure.^[24]

Synthesis of DOHDA: $(CH_3)_2NH$ (1.26 g, 28 mmol) and $Br(CH_2)_{11}OH$ (1 g, 4 mmol) were dissolved in ethanol (50 mL), such that the initial molar ratio of $(CH_3)_2NH$ to $Br(CH_2)_{11}OH$ was controlled at 7:1. The reaction mixture was refluxed with stirring for 24 h and then cooled to room temperature. The solvent and excess $(CH_3)_2NH$ were removed under reduced pressure to leave a white solid. The crude product was re-

dissolved in water and the pH of the solution was adjusted to 9.0 using Na₂CO₃. The solution was extracted with CHCl₃ (3×50 mL), and the organic layers were combined, dried (MgSO₄), and concentrated. The resulting white pure product was dimethyl(11-hydroxydecyl)amine (0.78 g, 90%). ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=1.28 (m, 14H), 1.47 (m, 2H), 1.56 (m, 2H), 2.25 (s, 6H), 2.28 (t, 2H), 3.64 ppm (t, 2H). A portion of the resulting dimethyl(11-hydroxydecyl)amine (1.0 g, 4.64 mmol) and Br(CH₂)₁₁OH (1.44 g, 5.73 mmol) were dissolved in ethanol (50 mL) and the solution was heated at reflux with stirring for 48 h. After cooling to room temperature, the mixture was concentrated to 3-5 mL by removing excess solvent under reduced pressure. Cold diethyl ether (30 mL) was then added to the residue. The white precipitate formed was collected by filtration and washed several times with cold diethyl ether to give white pure DOHDA (1.84 g, 85%). ¹H NMR (500 MHz, $[D_6]$ DMSO, 25°C, TMS): $\delta = 1.24$ (m, 28H), 1.38 (m, 4H), 1.61 (m, 4H), 2.96 (s, 6H), 3.19 (m, 4H), 3.35 (m, 4H), 4.29 ppm (t, 2H). Preparation of SEPs: SEP-1 was prepared as follows. An aqueous solution of POM-1 (3 mol L⁻¹, 20 mL, 0.06 mol) was added to an aqueous solution of DOHDA (6 mol L⁻¹, 30 mL, 0.18 mol). After stirring for 30 min, the precipitate formed was collected by filtration and washed several times with deionized water. It was dried in vacuo for 5 h to give white pure SEP-1. The preparation of surfactant DOHDA encapsulated POM-2 (designated as SEP-2) was similar to that of SEP-1, except that the mol ratio of surfactant to POM-2 was adjusted to 12:1 for charge balance.

Preparation of SHCs: SHC-1 was prepared as follows. As a typical procedure, SEP-1 (0.1 g) was dissolved in a mixture of ethanol (1 mL) and water (0.33 mL). The solution was stirred vigorously, and then TEOS (0.9 g) was added. When the mixture was visibly homogeneous, the stirring was stopped and the resulting sol-gel was aged for two weeks. A transparent gel hybrid catalyst was obtained, which was ready for further structural measurement and subsequent catalytic oxidation of sulfide after drying in vacuo for 1 day. Supramolecular hybrid catalyst containing SEP-2 (SHC-2) was prepared according to the same procedure.

Characterization of SHCs: The compositions of the surfactant DOHDA, SEP-1, SEP-2, SHC-1, and SHC-2 were determined by ¹H NMR, FTIR, EA, inductively coupled plasma atomic emission spectroscopy (ICPAES), and thermal gravimetric analysis (TGA) measurements. ¹H NMR spectra were recorded on a Bruker Ultra-Shield TM 500 MHz spectrometer using tetramethylsilane (TMS) as a standard. FTIR spectra were collected on a Bruker IFS66 V FTIR spectrometer equipped with a deuterated triglycine sulfate detector (32 scans). The spectra were recorded with a resolution of 4 cm⁻¹. The organic element content was measured by EA, which was carried out on a Flash EA1112 from Thermo-Quest Italia Sp.A. The inorganic element content was determined by ICPAES. TGA was carried out on a Perkin–Elmer 7 series thermal analysis system. The hydrophobicity of SHC-1 was assessed by measurements of static water contact angle, which were performed at room temperature using a drop-shape analysis system (DSA 10MK2 KRUSS).

Reaction procedure for the catalytic oxidation of sulfides: The catalytic oxidation of sulfides to sulfones was typically performed as follows. Taking the oxidation of DBT as an example: DBT (0.1 g) and 30 % H_2O_2 (0.15 g) were dissolved in acetonitrile (100 mL) in a round-bottomed flask. SHC-1 (0.020 g) that had been triturated to about 100–200 µm in diameter was then added. The mol ratio of DBT, H_2O_2 , and polyoxometalate was 1:2.5:0.0025, which was calculated on the basis of the loading values of SEP-1 in the hybrid catalyst. The reaction mixture was stirred at 300 rpm at 40°C and the progress of the reaction was monitored by TLC and HPLC. When the reaction was complete (42 min in this case), the solid hybrid catalyst was filtered off, washed with acetonitrile, and recovered. The procedure for the catalytic oxidation of sulfide to sulfoxide was similar to that described above, but the mol ratio of DBT, H_2O_2 , and polyoxometalate was adjusted to 1:1:0.001.

The same methodology was followed in other solvents, for catalytic oxidations of different sulfides, or with SHC-2, except that the amounts of the oxidant $\rm H_2O_2$ and the catalyst were varied.

Reaction procedure for the catalytic oxidation of cyclohexene: Cyclohexene (0.1 g) and $30 \% \text{ H}_2\text{O}_2$ (0.14 g) were dissolved in acetonitrile (10 mL) in a round-bottomed flask. SHC-1 (0.016 g) that had been triturated to

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about 100–200 μ m in diameter was then added. The mol ratio of cyclohexene, H₂O₂, and polyoxometalate was kept at 1:1:0.001, which was calculated on the basis of the loading values of SEP-1 in the hybrid catalyst. The reaction mixture was stirred at 300 rpm at 25 °C and the progress of the reaction was monitored by TLC and ¹H NMR. When the reaction was complete (120 min in this case), the solid hybrid catalyst was filtered off, washed with acetonitrile, and recovered.

Reaction procedure for the catalytic oxidation of cyclohexanol: Cyclohexanol (0.1 g) and 30% H_2O_2 (0.11 g) were dissolved in acetonitrile (10 mL) in a round-bottomed flask. SHC-1 (0.013 g) that had been triturated to about 100–200 µm in diameter was then added. The initial mol ratio of cyclohexanol, H_2O_2 , and polyoxometalate was kept at 1:1:0.001 based on the loading value of SEP-1 in the hybrid catalyst. The reaction mixture was stirred at 300 rpm at 40°C and the progress of the reaction was monitored by TLC and ¹H NMR. When the reaction was complete (300 min in this case), the solid hybrid catalyst was filtered off, washed with acetonitrile, and recovered.

Characterization of catalytic activity: Aliquots (1 mL) of the reaction mixture were withdrawn and filtered at certain times. The filtrates were carefully collected and concentrated to dryness. The compositions and contents of the mixtures were determined by IR, NMR, MS, and HPLC. The HPLC analysis was performed on an Agilent 1100 system with a ZORBAX Eclipse XDB-C8 column ($d=5 \mu m$, l=150 mm). The eluent was acetonitrile/H₂O (90:10), and a diode-array multiple-wavelength detector was used.

Other fundamental characterization data of all of the samples and details of the monitoring the catalytic reactions can be found in the Supporting Information.

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- a) Chem. Rev. 1998, 98. The entire issue is devoted to polyoxometalates; b) Polyoxometalate Chemistry: From Topology via Self-Assembly to Application (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, 2001.
- [2] a) Applied Homogeneous Catalysis with Organometallic Compounds (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, 1996, p. 411;
 b) K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, Science 2003, 300, 964–966.
- [3] a) U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. Da Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinace, E. L. Pires, *Appl. Catal.* A 2001, 201, 1–17; b) K. Sato, M. Aoki, J. Takaji, R. Noyori, J. Am. Chem. Soc. 1997, 119, 12386–12387; c) Y. Xu, P. Landon, D. Enache, A. F. Carley, M. W. Roberts, G. J. Hutchings, *Catal. Lett.* 2005, 101, 175–179.
- [4] a) P. Metzner, A. Thuillier, Sulfur Reagents in Organic Synthesis, Academic Press, London, 1994; b) J. Drabowicz, P. Kielbasinski, M. Mikolajczyk, in The Chemistry of Sulfones and Sulfoxides (Eds.: S. Patai, Z. Rappoport, C. Stirling), Wiley, New York, 1988; c) I. Fernández, N. Khiar, Chem. Rev. 2003, 103, 3651–3706; d) B. Sreedhar, P. Radhika, B. Neelima, N. Hebalkar, A. K. Mishra, Catal. Commun. 2008, 10, 39–44.
- [5] a) M. A. Cortes-Jácome, M. Morales, C. A. Chavez, L. F. Ramírez-Verduzco, E. Lopez-Salinas, J. A. Toledo-Antonio, *Chem. Mater.*

2007, *19*, 6605–6614; b) P. De Filippis, M. Scarsella, *Energy Fuels* **2003**, *17*, 1452–1455.

- [6] G. Strukul, Catalytic Oxidation with Hydrogen Peroxide as Oxidant, Kluwer, Dordrecht, 1992.
- [7] a) I. V. Kozhevnikov, Chem. Rev. 1998, 98, 171–198; b) N. Mizuno,
 M. Misono, Chem. Rev. 1998, 98, 199–218; c) G. Maayan, R. Popovitz-Biro, R. Neumann, J. Am. Chem. Soc. 2006, 128, 4968–4969;
 d) J. W. Han, C. L. Hill, J. Am. Chem. Soc. 2007, 129, 15094–15095.
- [8] D. G. Kurth, P. Lehmann, D. Volkmer, H. Cölfen, M. J. Koop, A. Müller, A. Du Chesne, *Chem. Eur. J.* 2000, *6*, 385–393.
- [9] D. Huang, Y. Wang, L. Yang, G. Luo, Ind. Eng. Chem. Res. 2006, 45, 1880–1885.
- [10] a) S. Nlate, L. Plault, D. Astruc, *Chem. Eur. J.* 2006, *12*, 903–914;
 b) S. Nlate, L. Plault, D. Astruc, *New J. Chem.* 2007, *31*, 1264–1274;
 c) L. Plault, A. Hauseler, S. Nlate, D. Astruc, J. Ruiz, S. Gatard, R. Neumann, *Angew. Chem.* 2004, *116*, 2984–2988; *Angew. Chem. Int. Ed.* 2004, *43*, 2924–2928.
- [11] H. Li, H. Sun, W. Qi, M. Xu, L. Wu, Angew. Chem. 2007, 119, 1322– 1325; Angew. Chem. Int. Ed. 2007, 46, 1300–1303.
- [12] C. Jahier, M. Cantuel, N. D. McClenaghan, T. Buffeteau, D. Cavagnat, F. Agbossou, M. Carraro, M. Bonchio, S. Nlate, *Chem. Eur. J.* 2009, 15, 8703–8708.
- [13] a) A. Haimov, H. Cohen, R. Neumann, J. Am. Chem. Soc. 2004, 126, 11762–11763; b) A. Haimov, R. Neumann, J. Am. Chem. Soc. 2006, 128, 15697–15700.

- [14] C. Li, Z. Jiang, J. Gao, Y. Yang, S. Wang, F. Tian, F. Sun, X. Sun, P. Ying, C. Han, *Chem. Eur. J.* **2004**, *10*, 2277–2280.
- [15] V. Nardello-Rataj, L. Caron, C. Borde, J. Aubry, J. Am. Chem. Soc. 2008, 130, 14914–14915.
- [16] Z. Xi, N. Zhou, Y. Sun, K. Li, Science 2001, 292, 1139-1141.
- [17] a) W. Qi, H. Li, L. Wu, Adv. Mater. 2007, 19, 1983–1987; b) W. Qi,
 H. Li, L. Wu, J. Phys. Chem. B 2008, 112, 8257–8263.
- [18] P. Judeinstein, J. Titman, M. Stamm, H. Schmidt, Chem. Mater. 1994, 6, 127–134.
- [19] a) H. Kim, Y. Shul, H. Han, *Appl. Catal. A* 2006, 299, 46–51; b) W. Kuang, A. Rives, M. Fournier, R. Hubaut, *Appl. Catal. A* 2003, 250, 221–229.
- [20] M. Te, C. Fairbridge, Z. Ring, Appl. Catal. A 2001, 219, 267-280.
- [21] L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Doremieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J. M. Bregeault, *Inorg. Chem.* 1994, 33, 871–878.
- [22] Y. Luan, A. Song, G. Xu, Soft Matter 2009, 5, 2587–2595; D. Smejkalova, A. Piccolo, Environ. Sci. Technol. 2008, 42, 8440–8445.
- [23] a) A. A. Lindén, L. Kruger, J. E. Backvall, J. Org. Chem. 2003, 68, 5890–5896; b) V. Cimpeanu, V. I. Parvulescu, P. Amoros, D. Beltran, J. M. Thompson, Chem. Eur. J. 2004, 10, 4640–4646.
- [24] I. Creaser, M. C. Heckel, R. J. Neitz, M. T. Pope, *Inorg. Chem.* 1993, 32, 1573–1578.

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