



Journal of Nanoscience and Nanotechnology Vol. 16, 8387–8395, 2016 www.aspbs.com/jnn

Gemini Surfactants and Polyoxometalates Hybrid Assemblies: Spacer Controlled Oxidative Desulfurization Activity

Zhuo Ma^{1,†}, Beibei Jin^{2,†}, and Yunfeng Qiu^{2,*}

¹ School of Life Science and Technology, Harbin Institute of Technology, 92 West Dazhi Street, Harbin, Heilongjiang, 150001, P. R. China ² State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China

Highly efficient, deep desulfurization of model oil containing benzothiophene, dibenzothiophene, or 4,6-dimethyldibenzothiophene has been achieved under mild conditions through the use of gemini surfactant-encapsulated $H_3AsMo_{12}O_{40}$ complexes (SEPGn: n = 2, 4, 6, 8, 10) as catalysts and H_2O_2 as an oxidant. The unique structure of gemini surfactant provides a delicate chemical environment to facilitate the formation of active peroxo-polyoxometalates species and the penetration of apolar sulfides. The rationally designed amphiphilic structures exhibit enhanced catalytic efficiency in the oxidation of sulfides compared to conventional surfactant-encapsulated POMs utilizing single positively charged surfactants with one or two tails because of the optimal interfacial pathway for both sulfides and H_2O_2 . Dibenzothiophene can be completely oxidized to its corresponding sulfone in 25 min under mild conditions. SEPG2 catalyst could be recycled ten times without obvious loss of activity due to its enhanced stability. Therefore, present work paves a new way to design the amphiphilic polyoxometalates via the introduction of unique surfactants through the molecular design concept.

Keywords: Polyoxometalates, Gemini Surfactants, Electrostatic Hybrid, Mesostructure, Desulfurization.

1. INTRODUCTION

Rational design of inorganic-organic hybrid supramolecular assemblies plays a vital role in obtaining novel multifunctional materials.^{1–4} Besides their intrinsic functions, supramolecular assemblies are highly desired as they exhibit cooperativity of individual building blocks.^{5–9} Recently, the ionic self-assembly (ISA) strategy, based on electrostatic interactions between two oppositely charged units, has been developed to be an effective way to construct supramolecular structures.¹⁰ As expected, the combination of inorganic components and organic compounds may integrate advantages of both elements and improve the performance of the hybrid complexes.^{11, 12}

Polyoxometalates (POMs), one of the most important inorganic structures building blocks, not only possess rich structural versatility, such as Keggin, Wells-Dawson, Linqvist types, and so on,^{13–18} but they also can be applied in a variety of oxidation reactions due to their reversible

redox activity.^{15, 19–25} However, crystalline POMs possess high lattice energy and are difficult to dissolve into most common organic solvent, resulting in a hindrance in their catalytic functionality.²⁶ Recent studies found that POMs could catalyze the oxidation of benzothiophene (BT) and its derivatives to their corresponding sulfones.^{27–37} These derivatives are the most refractory sulfur-containing molecules present in fossil diesel and are extremely difficult to remove by conventional hydrodesulfurization (HDS).³⁸ Catalytic oxidation of sulfur compounds by POMs is regarded as an attractive, complementary strategy for HDS, and resulting sulfones could be easily extracted by polar organic solvents or ionic liquids due to an enhancement in polarity.^{39–45}

To enhance the catalytic performance of POMs in the oxidation of sulfides, a variety of advanced catalytic POMs systems, such as microemulsion,^{46,47} reverse micelle,⁴⁸ ionic liquid three phase system,^{49–51} catalytic oxidation-extractive desulfurization,^{30,41,52} heterogeneous encapsulated complexes by cationic dendrimers,⁵³ and immobilized substrates⁵⁴ were developed. Although the

^{*}Author to whom correspondence should be addressed.

[†]These two authors contributed equally to this work.

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recovery problem could be well solved in heterogeneous systems, some of them need sophisticated preparation procedures as mass transfer issues arise. So far, surfactantencapsulated POMs (SEPs) proved to show satisfactory catalytic activity in emulsion systems.^{39, 55, 56} However, two critical aspects should be emphasized:

(1) the encapsulation of POMs by double or multiple alkyl chain surfactants will form an extremely dense hydrophobic layer and may consequently hinder the access of hydrophilic oxidizing agents (e.g., H_2O_2) to form active peroxo-POMs species inside the aggregates, resulting in a reduction of catalytic efficiency;⁵⁷

(2) single alkyl chain surfactant-mediated encapsulation may form a low density of hydrophobic alkyl chains around the active peroxo-POMs, which is harmful to capture apolar reagents.⁵⁸

Therefore, how to rationally design the SEPs with optimal alkyl chains density to balance the competition between the formation of active peroxo-POMs and the capture of apolar sulfides is the key aspect to address this issue.⁵⁶

Considering the catalytic oxidation mechanism of apolar sulfides by amphiphilic POMs mesostructures, gemini surfactants were used to to encapsulate POMs through electrostatic interactions to fabricate the amphiphilic catalysts.^{59,60} In comparison with conventional surfactants STAB or DODA, which include one positive charge and one tail or two tails respectively, gemini surfactants have special structures of two positive charges, two alkyl chains, and one modulated spacer. Taking the stoichiometry of POMs and surfactants into account, the number of positive charges and the alkyl chains determine the density of alkyl chains around POMs in the as-synthesized hybrid structures. As aforementioned, the suitable density of alkyl chains will play an important role in providing an optimal pathway for the entrance of H₂O₂ and reagents. Additionally, it was found that the spacer length up to six carbon atoms might be curved greatly during the assembly process, and the long spacer might also block the active surface of POMs.^{60,61} Therefore, it is speculated that the catalytic efficiency of gemini surfactants and POMs complexes might be affected through the modulation of spacer length. Another feature of present catalytic system is that the strong electrostatic interactions between gemini surfactants with two positive charges and POMs with negative charges will increase the stability of catalyst, and hence make the catalyst recyclable and durable.⁶² It is noteworthy that the resulted sulfones will dynamically be released from the assemblies due to an increased polarity at the end of the reaction.^{54, 58} From this assumption, we may hypothesized that gemini surfactants would be the ideal building blocks to construct well-defined polyoxometalate-based mesostructures and thus provide suitable alkyl chains density around the catalytic centers.⁶³

In this paper, we report amphiphilic $H_3AsMo_{12}O_{40}$ (AsMo₁₂) catalyst-encapsulated by gemini surfactant that

demonstrates high catalytic efficiency for the oxidation of sulfides in the presence of hydrogen peroxide. The catalysts were prepared by ISA method. The SEPs catalysts were characterized by spectra and microscope analysis in detail. The kinetic catalytic activities of the catalysts were systematically evaluated in the deep desulfurization of model oil. We found that 100% sulfur removal could be achieved in 25 min under mild condition for DBT conversion to DBTO₂. Present work will provide a rational strategy to integrate the advantages of supramolecular chemistry and POM chemistry for the design of functional materials for ultra-deep desulfurization of diesel fuels.

2. EXPERIMENTAL SECTION

2.1. Materials

All reagents and solvents were commercially available and were used as such. $H_3AsMo_{12}O_{40}$ was synthesized according to previous reference.⁶⁴ The structure was characterized by FTIR and UV-vis spectra. Gemini surfactants were synthesized according to literature.⁶⁵

2.2. Synthesis of G2

1-bromooctadecane (1.834 g, 5.5 mmol, 1 equiv) was dissolved into 50 mL ethanol in a 100 mL round flask. N,N,N,N-tetramethylethylenediamine (0.745 ml, 5 mmol, 0.9 equiv) was slowly added into the above solution. The mixture was refluxed for over 48 h at 80 °C in oil bath. The solvents were dried under rotorvap at the end of reaction. 1.33 g white powders were obtained after a triply-repeated crystallization in CHCl₃/ethyl acetate mixing solvent was performed (isolated yield: 55%).

2.3. Synthesis of G4, G6, G8, and G10

N,*N*-dimethyloctadecylamine (1.64 g, 5.5 mmol, 1 equiv) and 1,4-dibromobutane (1.08 g, 5 mmol, 0.9 equiv) were dissolved into 50 mL ethanol in a 100 mL round flask. The mixture was refluxed for over 48 h at 80 °C in an oil bath. The solvents were dried under rotorvap at the end of reaction. The crude powder was washed twice using ethyl acetate. 1.66 g of this white powder was obtained after a triply-repeated crystallization in CHCl₃/Ethyl acetate mixing solvent was performed (isolated yield: 61%). G6, G8, and G10 were synthesized in the similar way. The structures of all gemini surfactants were characterized by FTIR and ¹H and ¹³C NMR.

2.4. Preparation of SEPs

G2 (135 mg, 0.096 mmol, 2 equiv) was dissolved into 5 mL ethanol under stirring. 10 mL $H_3AsMo_{12}O_{40}$ (90 mg, 0.048 mmol, 1 equiv) ethanol solution was slowly added into G2 ethanol solution, and light yellow color precipitates was formed immediately. The muddy mixture was filtered after reaction for 12 h and subsequently washed with ethanol three times. This yellow product, SEPG2, was

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138 mg (62%). The others-SEPG4, SEPG6, SEPG8, and SEPG10-were synthesized in a similar way. SEPSTAB and SEPDODA were also prepared in a similar way, except that the ratio of surfactant to POM was 3 to 1. The compositions of all SEPs were confirmed by UV-vis, FTIR, TG, EDS, and XPS.

2.5. Characterization Methods

The FT-IR spectra of the prepared catalysts were collected on a Perkin-Elmer 1710 Fourier transform spectrometer by KBr pellet method at room temperature. The XRD patterns were obtained on a Shimadzu 6000 powder diffraction system (40 kV, 100 mA), using CuK α radiation ($\lambda =$ 0.1541 nm) in a scanning range of 2-80° at a scanning rate of 1°/min. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained on Bruker AV-400 instrument, using CDCl₃ as the solvent and TMS as reference. TGA were performed on a Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE) with a heating rate of 10 °C \cdot min⁻¹ in N₂ atmosphere. SEM observations were performed on an FEI Quanta 200 scanning electron microscope. The acceleration voltage was set to 20 kV. The sample was stuck on the observation platform and sprayed with gold vapor under high vacuum for about 180 s. The characterization of lamellar structures of the catalysts was performed using a field emission TEM (TecnaiG2F30, FEI, US). The EDS was coupled with TEM and measured at 300 kV. 1 mg of sample was sonicated in 1 mL ethanol for 10 min. The ethanol slurry was then dropped onto a Cu grid covered with a thin film of carbon. The chemical composition was determined by XPS (Model K-Alpha, Thermo fisher Scienticfic Company, US) using a monochromated Al $K\alpha$ source and a pass energy of 50 eV at a base pressure of 1×10^{-8} mbar.

2.6. Catalytic Oxidation of Sulfides

The catalytic oxidation of DBT was carried out in a twonecked round-bottom flask (100 mL) connected with a reflux condenser and a thermometer. In a typical reaction, DBT (1527 ppm, 271 µmol) and catalyst (10 mg, 3.13 μ mol) were added to 50 mL hexane in the roundbottom flask under stirring. Afterward, the reaction was initiated by adding H_2O_2 solution (0.6 mL, 5940 μ mol) with 800 rpm/min stirring. The typical reaction temperature is 60 °C. To determine the initial and residual concentration of the selected sulfur compound in the organic phase, approximately 0.5 mL aliquots of liquid samples were withdrawn from the reactor at fixed time intervals and after filtration by 0.2 μ m PTFE membrane, the organic phase was analyzed by gas chromatography. GC was performed on Tianmei GC7900 equipped with a flame ionization detector (FID), using 30 m μ 0.25 mm SE-54 column. The main parameters were as following:

(a) BT, injector temperature, 250 °C; column oven temperature 150 °C; detector temperature, 250 °C; temperature program, 150–190 °C at 5 °C/min, 190 °C for 2 min,

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230–250 °C at 5 °C/min, 250 °C for 25 min, BT retention time is 4.3 min.

(b) DBT, injector temperature, 250 °C; column chamber temperature 210 °C; detector temperature, 250 °C; temperature program, 210–230 °C at 5 °C/min, 230 °C for 5 min, 230–250 °C at 5 °C/min, 250 °C for 25 min, DBT retention time is 6.46 min.

(c) 4,6-DMDBT, injector temperature, 250 °C; column chamber temperature 220 °C; detector temperature, 250 °C; temperature program, 220–230 °C at 5 °C/min, 230 °C for 3 min, 230–250 °C at 5 °C/min, 250 °C for 25 min, 4,6-DMDBT retention time is 8.6 min. Residual sulfide at each reaction time was calculated by a standard curve method.

Additionally, reaction conditions including temperature, time, and the amount of catalyst and H_2O_2 , were optimized. In order to test the catalytic recyclability of SEPG2, after the reaction, the catalyst was separated by filtration, washed with ethanol for three times, and dried in a vacuum desiccator at 60 °C overnight, and the recovered catalyst was then reused in the next run.

3. RESULTS AND DISCUSSION

3.1. Structure and Composition Analysis

As depicted in Scheme 1, gemini surfactants include two quaternary ammonium groups connected by a spacer with variable length. Each head group is attached to a hydrophobic tail. In the structures of gemini molecules, the hydrophobic tail contains 18 carbon atoms and the spacer length is composed of 2, 4, 6, 8, or 10 methylenes, respectively. In our preliminary study, $H_3AsMo_{12}O_{40}$ with ca. 1 nm size, one of the most common Keggin POMs like previous extensively studied 12-tungstophosphoric acid, was used to construct amphiphilic assemblies through ISA method due to its better oxidative properties.⁶⁶



Scheme 1. Illustration of the ISA procedure for the fabrication of gemini/POMs electrostatic complexes. The basic formular of gemini surfactants, the set of dicationic quaternary ammonium coumpounds (with an abbreviation of $C_sH_{2s}-\alpha$, $\omega-(C_{18}H_{37}-N^+(CH_3)_2Br^-)_2$ which are denoted as $C_{18}-C_s-C_{18}$ in present paper, where s refers to the number of carbon atoms in the chains of the spacer.) The length of spacer beyond 6 carbon atoms results in the block of POMs surfaces, and thus affair the formation of peroxo-POMs and hinder the penetration of apolar sulfides to the catalytic centers.

The prepared hybrids were denoted as SEPG2, SEPG4, SEPG6, SEPG8, and SEPG10, respectively. The unique feature of gemini surfactants lies in the variation of spacer, which will greatly affects their physicochemical properties.^{67,68} In present work, gemini surfactants have two positive charges, and POMs have three negative charges, thus theoretically the basic formulas might be $(Gemini)_2 \cdot Br \cdot (AsMo_{12}O_{40})$. Therefore, the average of alkyl chains around single POMs in the desired structures will be four, which is between the numbers of (Stearyltrimethylaminium)₃AsMo₁₂O₄₀ (three alkyl chains) and (Dimethyldioctadecylammonium)₃AsMo₁₂O₄₀ (six alkyl chains). The adjusted density of alkyl chains might provide an optimal pathway for the entrance of H_2O_2 and reagents, and hence balance the competition between them. Additionally, inspired by previous reports, increasing the spacer length up to six carbon atoms, which might be curved greatly due to the flexibility of carbon chains, will lead to the over-coverage of the active surface of POMs, and thus decrease the activity in the oxidation reaction.

As shown in Figure 1(a), the fourier transform infrared spectroscopy (FTIR) of SEPG2, SEPG4, SEPG6, SEPG8, and SEPG10 clearly illustrate the characteristic vibrational absorption peaks of the AsMo₁₂ moiety and the gemini surfactants. The FTIR spectrum of G2 shows the asymmetric and symmetric vibrations of CH₂ at 2919 and 1851 cm⁻¹ and a scissoring band at 1491 cm⁻¹. Four different Mo–O bands were also observed at 964 cm⁻¹ (ν_{as} Mo–O_b–Mo), and 778 cm⁻¹(ν_{as} Mo–O_c–Mo). In contrast, the FTIR spectrum of SEPG2 shows bands at 2923 and 2852 cm⁻¹ for CH₂, and at 944 cm⁻¹ (ν_{as} As–O), 896 cm⁻¹ (ν_{as} Mo–O_c–Mo), and 795 cm⁻¹ (ν_{as} Mo–O_b–Mo), and 795 cm⁻¹ (ν_{as} Mo–O_b–Mo), and 795 cm⁻¹ (ν_{as} Mo–O_c–Mo) for As–O and different Mo–O bands. The obvious



Figure 1. (a) FTIR spectra of gemini surfactant with two carbon atom spacer (G2), AsMo₁₂, and SEPG2. Measured by KBr pellet method. (b) TGA of SEPG2 in nitrogen atmosphere with a scanning rate of 10 °C min⁻¹. (c) EDS coupled with TEM of SEPG2. (d) XPS of SEPG2.

shift of vibrational bands confirmed the presence of electrostatic interactions between positive G2 and negative $AsMo_{12}$. The FTIR results thus indicate that not only is the electrostatic interactions between gemini surfactants and $AsMo_{12}$ existent, but also that $AsMo_{12}$ maintain the intact keggin structure in all SEPs.

Thermogravimetric analysis (TGA) of SEPG2 in Figure 1(b) was carried out in nitrogen atmosphere at a scanning rate of 10 °C/min between 30 °C and 700 °C. In the case of SEPG2, a weight loss of 41% between 260 and 700 °C observed; this is consistent with a stepwise decomposition of cationic gemini molecules which is calculated to be 41.5%. The TGA data of the other SEPs could be explained in a similar way. Further, energy dispersive X-ray spectroscopy analyses (EDS) in Figure 1(c), coupled with 300 KV transmission electron microscopy (TEM), confirm the presence of As, W and C elements, and their quantitative ratios also indicate the intact structure of POMs and the chemical formulas of the amphiphilic units. Elemental analysis in Table I also confirmed the basically quantitative ratios of organic parts and inorganic parts in terms of the CHNO contents. Presumably, the combination of two gemini surfactants and one POMs require one negative Br ion to balance the charge ratio. As shown in Figure 1(c), we could barely observe the Br element in SEPG2, whereas the contents of Br element in other hybrids were difficult to observe due to the very low contents, which is almost close to the detection limit of EDS. Therefore, more sensitive X-ray photoelectron spectroscopy XPS measurement of SEPG2 and SEPG10 were further carried out to confirm the existence of Br element (Fig. 1(d)). Br signals were both measured at 67.63 eV. Thus, above analyzed results indicate that SEPG2 catalyst is composed of $(C_{42}H_{90}N_2)_2 \cdot Br \cdot$ (AsMo₁₂O₄₀) (denoted as SEPG2), and other amphiphilic units have corresponding compositions of $(C_{44}H_{94}N_2)_2$. $Br \cdot (AsMo_{12}O_{40})$ (denoted as SEPG4), $(C_{46}H_{98}N_2)_2 \cdot Br \cdot$ (AsMo₁₂O₄₀) (denoted as SEPG6), $(C_{48}H_{102}N_2)_2 \cdot Br \cdot$

Table I.CHNO elemental analysis of SEPG2, SEPG4, SEPG6, SEPG8,SEPG10, SEPSTAB, and SEPDODA.

Complexes	%	С	Н	Ν	0
$(C_{42}H_{90}N_2)_2 \cdot Br \cdot (AsMo_{12}O_{40}),$	Expected	31.63	5.63	1.75	20.03
denoted as SEPG2	Found	31.49	5.82	1.91	19.95
$(C_{44}H_{94}N_2)_2 \cdot Br \cdot (AsMo_{12}O_{40}),$	Expected	32.53	5.83	1.72	19.7
denoted as SEPG4	Found	32.28	5.66	1.69	19.97
$(C_{46}H_{98}N_2)_2 \cdot Br \cdot (AsMo_{12}O_{40}),$	Expected	33.44	5.98	1.70	19.37
denoted as SEPG6	Found	33.15	5.95	1.85	19.07
$(C_{48}H_{102}N_2)_2 \cdot Br \cdot (AsMo_{12}O_{40}),$	Expected	34.31	6.12	1.67	19.04
denoted as SEPG8	Found	34.12	6.09	1.77	19.21
$(C_{50}H_{106}N_2)_2 \cdot Br \cdot (AsMo_{12}O_{40}),$	Expected	35.15	6.25	1.64	18.73
denoted as SEPG10	Found	35.07	6.15	1.63	18.92
$(C_{21}H_{46}N)_3 \cdot (AsMo_{12}O_{40}),$	Expected	26.97	4.92	1.5	22.78
denoted as SEPSTAB	Found	26.95	4.93	1.51	21.99
$(C_{38}H_{80}N)_3 \cdot (AsMo_{12}O_{40}),$	Expected	38.87	6.82	1.19	18.19
denoted as SEPDODA	Found	38.65	6.72	1.20	18.33

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 $(AsMo_{12}O_{40})$ (denoted as SEPG8), $(C_{50}H_{106}N_2)_2\cdot Br\cdot (AsMo_{12}O_{40})$ (denoted as SEPG10).

In present supramolecular system, the main assembly driving force is the electrostatic interaction between two positive charged gemini surfactants and three negative charged AsMo₁₂ which is much stronger than conventional single positive charged surfactants such as STAB, DODA, etc. All hybrids were prepared from ethanol. The resulted precipitates were found to be insoluble in many common solvents such as choloroform, ethanol, acetonitrile, or DMF, which would have helped to facilitate the recovery of the complex at the end of the reaction. Figure 2 shows that SEPG2 has sheet-like morphology with sizes in the range of 3–20 μ m, whereas SEPG4, SEPG6, SEPG8, and SEPG10 form 1–25 μ m bulk structures consisting of irregular aggregates with sizes of around 100 nm.

The TEM images illustrates that SEPG2 has sheet-like structures, and SEPG10 is composed of irregular aggregates of about 100 nm in diameter. HRTEM images in Figures 3(a)–(e) show that all hybrids exhibit lamellar structures. The well-ordered lamellar patterns exhibit layer spacing of about 3.10, 3.14, 3.36, 3.34, and 3.01 nm for SEPG2, SEPG4, SEPG6, SEPG8 and SEPG10, respectively.

To further study the lamellar morphology, small-angle powder XRD diffraction measurements on all hybrids were carried out. As shown in Figure 4(a), the layer spacings of SEPG2 are 3.09 and 1.58 nm, according to the Bragg equation, and the other SEPs exhibit similar layer spacings. It should be noted that SEPG2 exhibit a more intense, sharp first-order peak compared to the other hybrids with longer spacer length. In contrast, small-angle XRD pattern of all the other SEPs confirmed a layered structure with layer spacing of about 3.12, 3.32, 3.32, and 2.99 nm for SEPG4, SEPG6, SEPG8 and SEPG10, respectively, which agree with the analyses from HRTEM measurements. The lateral packing of the alkyl chains are in the range of 0.35



Figure 2. Scanning electron microscope (SEM) images of (a) SEPG2, (b) SEPG4, (c) SEPG6, (d) SEPG8, and (e) SEPG10. Inset in (a) is the contact angle of densely pressed film of SEPG2. The average contact angle is around 140° after averaging three measurement in different regions. In other four cases, similar contact angles are obtained. Scale bar in all images are 5 μ m.

b 3.14 nm 3.36 nm d 3.36 nm 3.36 nm 3.36 nm 5.34 nm 3.34 nm

Figure 3. High resolution transmission electron microscope (HRTEM) images of (a) SEPG2, (b) SEPG4, (c) SEPG6, (d) SEPG8, and (e) SEPG10. Respective layer spacing of lamellar structure is indicated by arrows. Scale bar in all images are 20 nm.

to 0.42 nm, calculated from the wide-angle powder XRD results of all hybrids in Figure 4(b). This reveals their close arrangement in the supramolecular structures. To confirm the encapsulation of surfactants, static angles of film samples were performed. Average angles for all samples are above 140° in Figure 2(a), indicating the hydrophobicity of the SEP surface.

3.2. Desulfurization Evaluation

Previous studies have proven that the structures of surfactants play a vital role for catalytic oxidative desulfurization.^{56-58,69} Hence, we studied catalytic activities of gemini surfactants/AsMo12 catalytic systems for desulfurization of DBT with H2O2 as an oxidant. First of all, the effect of H₂O₂ concentration was checked. In a series of reactions, 1527 ppm DBT by weight and 10 mg dried SEPG2 powders were added to 50 ml model oil in the presence of 0.1-0.8 ml H₂O₂. The respective 100% sulfur removal time was 33, 26, 28, 25, and 30 min with 0.1, $0.2, 0.4, 0.6, and 0.8 \text{ ml H}_2O_2$. It is clear to see that 0.6 ml H_2O_2 gives rise to the shortest reaction time. Secondly, the reaction was also performed in the presence of different SEPG2 amounts, and it is found that more SEPG2 resulted in a shorter removal time. However, 10 mg SEPG2 was selected as our only model reaction due to its satisfactory removal time and the high cost of the catalyst. Finally, the



Figure 4. (a) Small-angle and (b) wide-angle X-ray powder diffraction (XRD) of SEPG2, SEPG4, SEPG6, SEPG8, and SEPG10.

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reaction temperature also plays an important role in catalytic activity. Higher temperatures, between 40 to 70 °C, will result in better catalytic activity. It is worth noting that higher reaction temperature is detrimental to the catalytic efficiency; a reaction temperature of 80 °C caused lower catalytic efficiency due to the fast decomposition of H_2O_2 . Taken all into consideration, as well as requiring the system to be practical with high efficiency and low cost, we selected the following optimal condition to run the catalytic oxidation reaction: 1527 ppm DBT and 10 mg dried SEPG2 powder added to 50 ml model oil in the presence of 0.6 mL H₂O₂ at 60 °C. Deep desulfurization with 100% conversion of DBT to DBTO₂ can be obtained in 25 min. The removal process of DBT was characterized by GC in Figure 5. The characteristic retention peak of DBT was completely diminished due to 100% conversion to DBTO₂.

To investigate the influence of spacer length on catalytic performance, gemini surfactants with 4 to 10 methylene spacer and $AsMo_{12}$ complexes were investigated to catalyze the oxidation of DBT. As shown in Figure 6, SEPG4, SEPG6, SEPG8, and SEPG10 show 100% sulfur removal in 35, 40, 70, 80, and 80 min under optimized conditions, respectively. Clearly, longer spacer lengths will gradually hinder the catalytic performance.

With the best catalytic conditions in hand, the performance of SEPG2 with H_2O_2 as an oxidant for the other two refractory sulfur substrates including BT and 4.6 DMDBT was evaluated. 95% conversion of 1527 ppm BT was finished in 70 min and the 100% conversion of 1527 ppm 4,6-DMDBT was achieved after 35 min.

To obtain the kinetic parameters for the catalytic oxidation of DBT, deep desulfurization experiments were performed with different spacer lengths of gemini surfactant-mediated encapsulated AsMo₁₂ catalyst complex. In the case of SEPG2, percentage sulfur removal and $\ln(C_t/C_0)$ are plotted versus reaction time in Figure 7,



Figure 5. GC of the conversion of DBT using SEPG2 catalytic system. The peak of DBTclearly vanishes after 25 min due to the complete oxidation of sulfides to sulfones.



Figure 6. Reaction time of different catalysts at 100% conversion of DBT. All catalytic reactions were performed under optimal conditions. H_2O_2 /sulfides/SEPGx=21.9/1/0.0115, H_2O_2 0.6 mL, 60 °C, model oil 50 mL (S content 1527 ppm).

where C_o and C_t are initial DBT concentration and DBT concentration at time *t*, respectively. The linear fit of the data shows that the catalytic reaction exhibits pseudo-fist-order kinetics for desulfurization of sulfides ($R^2 = 0.9699$). The rate constant k_{app} of the oxidation reaction was determined to be 0.19636 min⁻¹ on the basis of Eqs. (1) and



Figure 7. (a) Percentage sulfur removal of DBT and (b) $\ln(C_i/C_0)$ as a function of reaction time in the cases of SEPG2, SEPG4, SEPG6, SEPG8, and SEPG10, respectively. H₂O₂/sulfides/SEPGx = 21.9/1/0.0115, H₂O₂ 0.6 mL, 60 °C, model oil 50 mL (S content 1527 ppm).

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(2). As shown in Table II, the TOF of the oxidation reaction was 5.775×10^{-2} s⁻¹ for SEPG2. Oxidation of DBT to DBTO₂ could be completed in about 25 min. In brief conclusion, the catalytic reaction obeys pseudo-first-order kinetics with 100% selectivity for DBTO₂, which was further confirmed by FTIR and NMR.^{70,71} Additionally, the kinetic parameters for the oxidation reaction of DBT by other SEPs were investigated in a similar way. All cases obey the pseudo-first-order kinetics for the desulfurization of DBT to DBTO2. As summarized in Table II, the rate constant k_{app} was 0.1409, 0.14072, 0.05711, and 0.05507 min⁻¹, and the TOF was 4.198×10^{-2} , $3.646 \times$ 10^{-2} , 2.12×10^{-2} , and 1.886×10^{-2} s⁻¹ for SEPG4, SEPG6, SEPG8, and SEPG10, respectively. As shown in Table II, the constant $k_{\rm app}$ and TOF of SEPG2 in the oxidation of BT and 4,6-DMDBT are 0.03703 and 0.14651 min⁻¹, and 2.832×10^{-2} and 3.58×10^{-2} s⁻¹, respectively. The higher reactivity of the DBT compared to BT can be explained by the electron densities on sulfur atoms, which is 5.758 for DBT and 5.739 for BT, respectively.⁷² Although the electron density of 4,6-DMDBT is the highest (5.760), its reactivity is lower than that of DBT, this is due to the steric effect from the alkyl groups at the 4 and 6 positions. Comparing the catalytic efficiency of the oxidation of DBT by all SEPs, SEPG2 exhibited the highest rate constants k_{app} and TOF than those of SEPs with longer spacer length.

$$-\frac{dC_t}{d_t} = kC_t \quad \text{Copyright: Ame(1)an} \\ \ln\left(\frac{C_t}{C_0}\right) = -kt \quad (2)$$

To enhance the potential application, scaled-up experiments in which the volume of model oil was increased twenty times to 1000 ml gave about 99% sulfide conversion in 65 min. It should be noted that although sulfone gradually precipitated during reaction, the catalytic activity was not affected visibly. At the end of the reaction, the SEPG2 could be filtered and washed by ethanol for three times. The recycled SEPG2 could be reused at least ten

Table II. K_{app} and TOF of different SEP catalytic systems in the oxidation of BT, DBT, and 4,6-DMDBT.

Catalyst	Sulfides	S content (ppm) ^[a]	$k_{ m app} \ ({ m min}^{-1})^{[b]}$	$\begin{array}{c} \text{TOF} \\ (\text{s}^{-1})^{[c]} \end{array}$
SEPG2	DBT	1527	0.19636	$5.775 imes 10^{-2}$
SEPG4	DBT	1527	0.1409	$4.198 imes 10^{-2}$
SEPG6	DBT	1527	0.14072	$3.646 imes 10^{-2}$
SEPG8	DBT	1527	0.05711	2.12×10^{-2}
SEPG10	DBT	1527	0.05507	1.886×10^{-2}
SEPSTAB	DBT	1527	0.06242	1.585×10^{-2}
SEPDODA	DBT	1527	0.0393	1.447×10^{-2}
SEPG2	BT	1527	0.03703	2.832×10^{-2}
SEPG2	4,6-DMDBT	1527	0.14651	$3.58 imes 10^{-2}$

Notes: [a] By weight; [b] Apparent rate constant; [c] Turn-over frequency

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times without obvious loss of catalytic activity, and about 95.7% DBT conversion could be obtained in 25 min in ten trials.

3.3. Comparison Study with Conventional Catalysts

To further highlight the important effect of gemini surfactants on oxidation efficiency, we prepared two control catalyst complexes using STAB and DODA as encapsulating agents, which are two types of commonly used surfactants. Using SEPSTAB and SEPDODA catalytic systems, 100% DBT conversion was completed in 80 and 110 min, respectively. As shown in Table II, single and double tailed surfactants both exhibited lower catalytic efficiency than those of SEPG2, SEPG4 and SEPG6. Comparing the rate constant k_{app} and TOF of all catalysts, the catalytic activity of SEPSTAB and SEPDODA was comparable to those of SEPG8 and SEPG10. The low catalytic efficiency of SEPG8 and SEPG10 might be due to the gauche conformation of long spacers where partial covering of the POM surfaces occurred, thus resulting in the inability of H_2O_2 or sulfides to access the POMs.⁶¹ As a result, the unique structures of gemini surfactant plays a significant role in the deep desulfurization efficiency of the catalyst. Comparing current state-of-the-art amphiphilic POM based catalysts in two phase catalytic systems, the SEPG2 catalytic system presented herein is one of the most efficient desulfurization systems present in literature.^{39, 46, 57}

¹ It has been generally accepted that amphiphilic SEPbased catalytic systems allow for the catalysis of this oxidation reactions. The catalysts accumulate at the interface to stabilize the droplet, possibly acting as emulsifying agents.⁷³ There are two key aspects to determine the catalytic efficiency of SEPs, which include

(1) oxidation by H_2O_2 coming from droplet to form an active peroxo species of POMs, and

(2) mass transfer of apolar reagents coming from a continuous phase. Therefore, the interfacial region composed of SEPs is of great importance for the desulfurization process.

3.4. Possible Mechanism Analysis

The highly efficient deep desulfurization of SEPG2 could be explained as follow. First of all, $AsMo_{12}$ clusters encapsulated by gemini surfactants, resulting in the formation of amphiphilic supramolecular structure, plays an important role in stabilizing the emulsion system. The catalysts stay at the interface which provides oxidation reaction sites. The accumulation of SEPs at the interface was observed by SEM (data not shown). Secondly, the unique structures of gemini surfactants have significant effects on the ordered lamellar structure of catalysts and thus affect the catalytic performance.⁷⁴ It has been generally known that the long alkyl chains on the surface of POMs serve as the entrance of H₂O₂ and apolar reagents. For the formation of active peroxo-POMs species in the presence of hydrophilic



For the production of peroxo-POMs: From easy to difficult

Scheme 2. The average ratio of the number of alkyl chains to POMs is 3/1, 4/1, and 6/1, for the corresponding basic building unit of a) SEP-STAB, b) SEPG2, and c) SEPDODA, respectively. The loose packing alkyl chains in SEPSTAB (a) will impede the entrance of sulfides due to the weak hydrophobic interactions. The interaction of hydrophilic H_2O_2 with POMs to form active peroxo-POMs species was hindered due to the confined space and too strong hydrophobic alkyl chains fence in the case of SEPDODA (c). The suitable packing density of alkyl chains in the case of SEPG2 (b) will provide the optimal pathway for the penetration of H_2O_2 as well as the entering of sulfides.

 H_2O_2 ,⁷⁵ the alkyl chain density should be as low as possible. However, the high density of alkyl chains that assemble into ordered structures is beneficial; it also absorbs the apolar sulfides as stronger hydrophobic-hydrophobic interactions are present. This conflict was balanced by introducing the unique structure of gemini surfactant with a two carbon atom spacer. In the case of SEPG2, as seen in Scheme 2, there are four alkyl chains around one POM, which is between that of SEPSTAB (three alkyl chains) and SEPDODA (six alkyl chains). Thus, the alkyl chains fences of SEPG2 provide suitable entrance for both H_2O_2 and apolar sulfides. That is, based on present results, the unique structures of gemini surfactants balanced the individual requirements of H2O2 and sulfides, thus providing an ideal catalytic sites for the oxidation of sulfides. When the spacer length was above two carbon atoms, the catalytic efficiency decreased gradually with respect to the increasing spacer length. It may be attributed to the fact that long spacer on the surface block catalytic clusters that are pertinent to H₂O₂ interaction. This assumption was clearly illustrated in the cases of SEPG8 and SEPG10, in which the catalytic capabilities were decreased significantly, values close to those seen in SEPSTAB and SEPDODA complexes. Finally, gemini surfactants with two positive charges make the electrostatic interactions with negative POMs much stronger than the interactions between conventional single positive head surfactants and POMs.^{76,77} This increase in binding affinity enhances the stability of SEPs and possibility of the catalytic performance.

4. CONCLUSION

In summary, gemini surfactants and $AsMo_{12}$ have been used to prepare ordered amphiphilic SEPs by ISA to provide enhanced catalytic activity capabilities in the

deep desulfurization of model oil. A suitable alkyl chain density, which can be tailored through the variability of gemini surfactant architectures, offers an ideal path for the penetration of H_2O_2 and corresponding activation of peroxo-POMs species. Also, this suitable alkyl chains density allows for the trapping of apolar sulfides by hydrophobic-hydrophobic interactions. This functional lamellar structure contained highly efficient catalytic sites for the oxidation of sulfides by active POM species. Compared to conventional STAB and DODA systems, present SEPs have better dual functionality for both hydrophobic substrates and hydrophilic oxidants. In the case of SEPG2 catalytic system, 100% sulfur removal could be achieved in 25 min under mild condition for DBT conversion to DBTO₂, also exhibiting good efficient catalytic performance for the conversion of BT and 4,6-DMDBT reagents. In addition, the scaled-up experiment in which the volume of model oil was increased from 50 to 1000 mL proceeded smoothly and gave 99% sulfur removal in 65 min. The strong electrostatic interactions between gemini surfactants and POMs endows the prepared assemblies good stability which make it durable and recyclable. Taken together, present study provides an efficient way to remove the refractory S-containing molecules present in diesel under mild conditions.

As a proof of concept study, present catalytic efficiencies could be further improved in terms of enhancing the utilization of H_2O_{23} decreasing the reaction temperature, the recycle of sulfones product by means of optimizing the reaction conditions or the selection of POMs with better redox properties than present AsMo₁₂. Related investigations are under study. However, the 100 % sulfur removal performance under mild conditions in present catalytic system still makes it possible to be complementary of HDS and will provide solutions to the changing sulfur limitations imposed by the governments.

Acknowledgments: Financial supports from Natural Science Foundations of China (Nos. 21103035) and Open Project of State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (No. ES201514).

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Received: 25 April 2015. Accepted: 22 May 2015.

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