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Short Communication

Electrostatic immobilization of substrate and polyoxotungstate catalyst at the surface of micelles for enhanced reaction efficiency in water

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ABSTRACT

Polyoxometalate (POM)-based micellar catalysts were prepared by assembling the Keggin tri-anion $[PW_{12}O_{40}]^{3-}$ and (L)-*N*-acetylmethioninate salts of Gemini surfactants in water. Contrary to conventional catalytic systems, we propose a new approach in which the POM catalyst and the substrate to be oxidized ((L)-*N*-acetylmethioninate) are both localized at the surface of micelles by electrostatic interaction before the reaction. The high local concentration of reactants due to their confinement at the surface of micelles enhances the reaction kinetics. Catalyst recovery experiments showed that, after two cycles of reactions, the activity of the catalysts was not changed.

1. Introduction

The design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances is an approach that is applicable to all aspects of chemistry [1,2]. One of the current trends in catalysis is focused on the use of transition metal complexes with low catalyst loading in water and their reuse. However, there are some drawbacks associated with these catalysts such as the leaching of the metal, the low solubility of organic substrates and the decrease of the catalyst activity and selectivity in water [3]. Therefore, one of the most crucial issues for chemists is the search for sustainable, economic and efficient catalytic systems for chemical transformations. Among possible approaches, micellar catalysis [4–6] has been investigated extensively for several decades. Micelles can induce acceleration or improve the selectivity of a given reaction in aqueous media, due to a high local concentration of reactants in their structure. Their hydrophilic surface and hydrophobic core allow the solubilization and confinement of substrates and catalysts in the restricted volume. Among micelle-based catalysts, polyoxometalate (POM)-containing micelles are still under-represented [7–10]. POMs are distinctive inorganic transition metal–oxygen clusters that are the source of fascinating architectures [11,12] with an almost unmatched range of physical and chemical properties, and are able to form dynamic structures ranging in size from nano- to micrometer scale [13]. To the best of our knowledge, the main strategy reported, so far, for the preparation of POM-containing aggregates [14] involves the solubilization of surfactant-encapsulated POM (SEP) hybrids [15,16] in organic solvents or in water. However, this approach could be limited in its efficiency by the poor solubility of SEP in water, due to the strong interaction between POM and the surfactant. In order to keep the solubility of POM-surfactant hybrids in water, the amount of POM has to be adjusted to that of the surfactant. Confining reactants at the surface of micelle before the reaction provides a convenient and efficient strategy for enhancing the reaction kinetics compared to the conventional procedure in which substrate molecules are added into the mixture containing micelle catalysts. In this case, reactants are more sensitive to the ambient environment of the medium (solvent, oxidant).

Herein, we propose another approach in which substrate molecules ((L)-*N*-acetylmethioninate) [17] and the POM catalyst ($[PW_{12}O_{40}]^{3-}$) are both immobilized at the surface of micelles obtained from (L)-*N*-acetylmethioninate salts of Gemini surfactants with various alkyl chain lengths in water, in order to tune and probe the enhancement of the reaction efficiency. Furthermore, the structure of Gemini is known to lower the critical micellar concentration (cmc) compared to the corresponding monomeric surfactants [18]. The effect of micelles on

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[2] The project leads were Reiko Oda and Sylvain Nlate, who wrote the paper and also were in charge of the topic and scientific part of the project.

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the POM properties will be investigated in detail with respect to non-micellar POM catalysts.

2. Experimental

2.1. Preparation of POM-based micellar catalysts in which POM and substrate molecules are localized at their surfaces

2.1.1. General procedure for the synthesis of Gemini (L)-N-acetylmethioninate *3a–d*

Gemini bromide [Gemini(Br)$_2$] [19] (1 equiv.) and silver (L)-*N*-acetylmethioninate [Ag(L-acmet)] **2** (2.2 equiv.) were dissolved in water or a mixture of water and methanol. The mixture was stirred for 1 to 12 h at room temperature or 40 °C, depending of the length of the alkyl chain of surfactant. The solvent was removed under vacuum and the residue was extracted with methanol, filtered off and evaporated under vacuum. [Gemini(L-acmet)$_2$] **3a–d** were obtained as white solids in 80 to 97% yields.

2.1.2. Critical micelle concentration (cmc) of *3a–c* and *3a* in the presence of POM anion

The cmc of **3a–c** was measured at 25 °C as follows: A solution of **3a–c** (e.g. 20 mM) was prepared in pure water and successively added to a known volume of ultrapure water. In the presence of POM, a mixture of **3a** (10 mM) with POM (0.05 mM) was prepared in water and successively added into ultrapure water. The conductivity κ was plotted as a function of surfactant concentration C, and the cmc was obtained from the concentration, which corresponds to the intersection of the conductivity κ extrapolated from the experimental values below ($S1 = \kappa C < cmc$) and beyond the cmc ($S2 = \kappa C > cmc$).

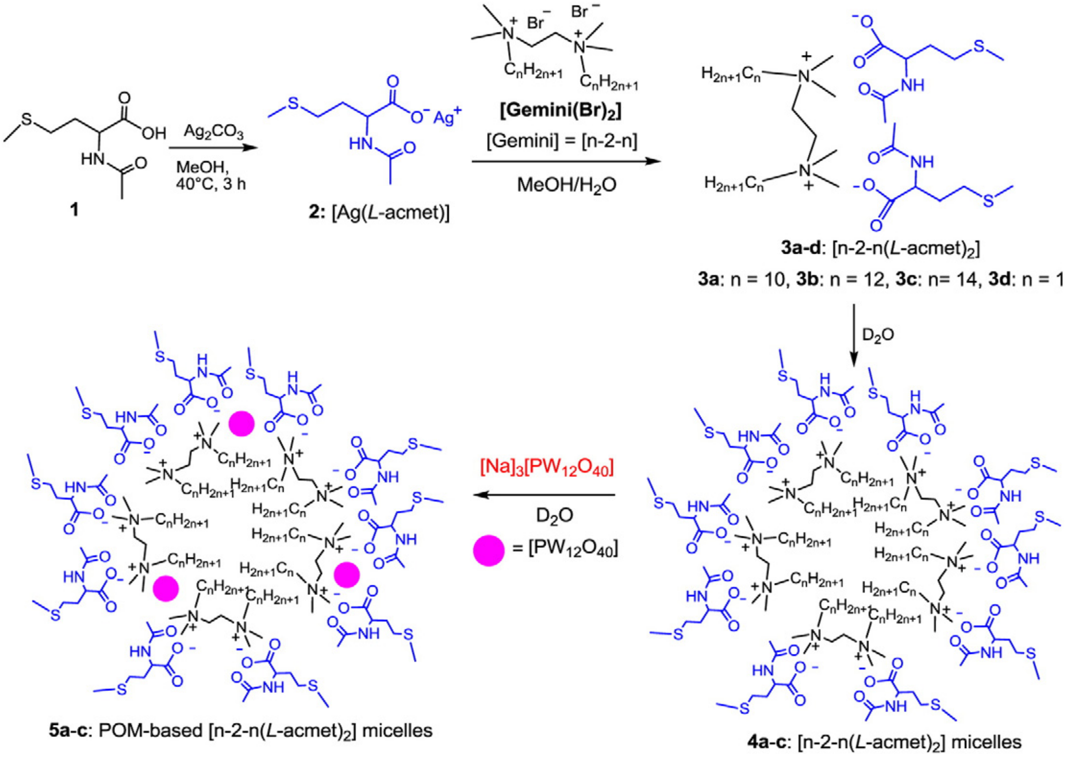
2.1.3. Catalytic oxidation of (L)-N-acetylmethioninate immobilized on micelles with POM, catalyst recovery and recycling

To a mixture of **3a**–**d** (10 mM) and Na$_3$[PW$_{12}$O$_{40}$] (0.1 mM) in 1 mL D$_2$O was added 22 mM of aqueous H$_2$O$_2$ (35%). The mixture was stirred at 25 °C and monitored by ^{1}H NMR. Upon reaction completion, an aqueous solution of HBr (20 mM) was added to the reaction mixture, followed by centrifugation of the latter. The water layer containing *N*-acetylmethionine-oxide **7** was separated from a precipitate of POM-based Gemini bromide. After lyophilization of the water layer, a white solid of **7** was obtained. To regenerate the catalytic system, the precipitate of POM-based Gemini bromide was dissolved in a mixture of water and methanol (0.2:0.8; v:v), and two equiv. of **2** was added to this solution. The precipitate of AgBr formed during the anion exchange was filtered off and the filtrate was evaporated under vacuum, yielding [POM-Gemini(L-acmet)$_2$] hybrid. The latter was analyzed by ^{1}H, ^{31}P NMR and IR spectroscopy before a new catalytic experiment, the solvent and H$_2$O$_2$ being adjusted to the amount of the catalyst.

3. Results and discussion

3.1. Preparation of POM-based Gemini (L)-N-acetylmethioninate micelles

In order to build catalytic micellar systems in which both substrate molecules and the catalyst are localized at their surface, we have selected the Keggin tri-anionic POM [PW$_{12}$O$_{40}$]$^{3-}$ for its catalytic efficiency [20], and (L)-*N*-acetylmethioninate as a model substrate for the presence of a sulfide group for catalytic oxidation tests, and its facility to be confined at the surface of cationic micelle by anion exchange. Gemini bromide [Gemini(Br)$_2$] or [n-2-n(Br)$_2$] of various alkyl chain length (n = 10, 12 and 14) were prepared by alkylation of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine with the corresponding alkyl bromide. [Gemini(Br)$_2$] reacts with **2** to give the corresponding [Gemini(L-acmet)$_2$] **3a–d** (Scheme 1). Compounds **3a–c** are highly soluble and form micelles **4a–c** in water, with (L)-*N*-acetylmethioninate as the counterion. Adding an aqueous solution of Na$_3$[PW$_{12}$O$_{40}$] to the micellar solution **4a–c** gives POM-containing micelles **5a–c**. The amount of POM was adjusted to keep the solubility of POM-based micelles in water. The structures of **3a–d** and the presence of POM in micelles



Scheme 1. Preparation of POM-containing micelles.