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A direct imaging of amphiphilic catalysts assembled at the interface of emulsion droplets using fluorescence microscopy

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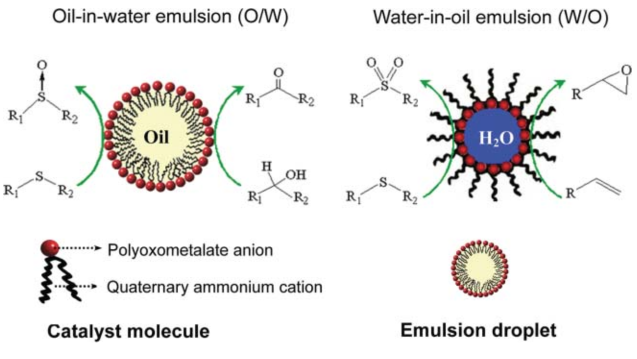
An amphiphilic fluorescent catalyst $Q_9[EuW_{10}O_{36}]$ (Q = $[(C_{18}H_{37})_2N^+(CH_3)_2]$), assembled in the interface of emulsion systems, was directly imaged by fluorescence microscopy; the catalyst shows high selectivity and activity in the oxidation of alcohols using H_2O_2 as oxidant and the catalyst can be easily separated and recycled by demulsifying.

One of the most important and interesting properties of surfactants in solution is that they form submicroscopic and supramolecular structures above a critical concentration.[1,2] When introducing surfactants into two or more immiscible liquids, the mixed systems can form emulsions under suitable conditions.[1,2] The emulsions have been widely used as media in food, cosmetics, pharmaceutical industries, nanoparticle synthesis, oil recovery, polymerization and biology, *etc.*[1–3]

Recently, catalysis in emulsion systems has attracted much attention because the emulsion catalysis could play an important role in the reactions in liquid multiphase systems, *e.g.*, organic reactions in water solvent. Our previous work reported the oxidation of sulfur-containing molecules to sulfones in diesel and the selective oxidation of alcohols to ketones, using H_2O_2 as oxidant in the emulsions (Scheme 1). Surfactant-type catalysts based on quaternary ammonium polyoxometalates (POMs), acting as surfactants, can be assembled in emulsion droplets, showing remarkably high selectivity and activity in the oxidation of organic molecules.[4] Emulsion catalysis could be a promising strategy to improve the mass-diffusion limitation in liquid multiphase systems, particularly for organic synthesis in water using homogeneous complex catalysts or enzymes.

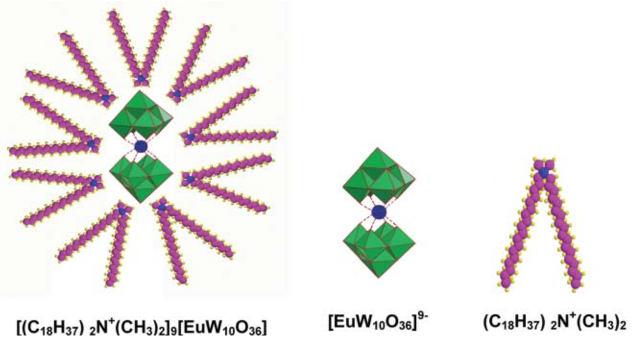


Scheme 1

However, it is still not well characterized where the surfactant catalyst is distributed in an emulsion system. It is a quite important subject to observe directly the distribution state and structure of the surfactant-type catalyst in reaction systems. A number of different experimental methods have been employed to characterize emulsion systems, such as small-angle neutron scattering (SANS),[2,5] small-angle X-ray scattering (SAXS),[2,6] light scattering,[2,7] fluorescence techniques,[2,8] nuclear magnetic resonance (NMR),[2] and TEM *etc.*[2] Although these methods have already provided useful information on many emulsion systems, a direct image of the catalyst distribution in an emulsion system has not been reported.

Herein we present a direct image of an amphiphilic catalyst in emulsion droplets using a surfactant-type fluorescent catalyst $Q_9[EuW_{10}O_{36}]$ that can be synthesized by using a combination of hydrophilic polyoxotungstoeuropate anions and lipophilic surfactant (Q = quaternary ammonium cation with long alkyl chains).† This amphiphilic catalyst has a characteristic fluorescence emission at 615 nm, which offers a possibility for the direct imaging of the surfactant-type catalyst assembled at the interface of the emulsion droplets using fluorescence microscopy.

Polyoxometalates (POMs) containing lanthanide elements such as Sm^{3+}, Eu^{3+}, $Tb^{3+}$and Dy^{3+} are of special interest as they can produce strong fluorescence,[9] and are usually used as fluorescent materials. We have synthesized the surfactant-type europium-substituted heteropolyoxotungstate (Eu-POM), $Q_9[EuW_{10}O_{36}]$ (Q = dimethyl dioctadecylammonium) and the structure of the amphiphilic catalyst is shown in Scheme 2. The luminescent properties of $Na_9[EuW_{10}O_{36}]$ have been investigated systematically.[9a,b] The photoexcitation of the O → M LMCT (O → W



Scheme 2

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ligand-to-metal charge transfer) band of $[EuW_{10}O_{36}]^{9-}$ displays the characteristic peaks of Eu^{3+} at $^5D_0 \rightarrow {}^7F_j$ (j = 0, 1, 2, 3, 4) in the red light region, 615 nm.[9] Here, the surfactant-type fluorescent $[(C_{18}H_{37})_2N^+(CH_3)_2]_9[EuW_{10}O_{36}]$ catalyst can be expected to serve as an emulsifying agent to stabilize the emulsion droplets instead of only a simple surfactant. Fluorescence microscopy observation was first performed with an aqueous phase with surfactant-type fluorescent catalyst. The results are shown in Fig. 1(A). It can be seen that the bright red spots appear in the whole region, indicating that the whole system shows the fluorescence of the amphiphilic catalyst because some catalyst is dissolved in water. When the amphiphilic fluorescent catalyst was introduced into a water–oil (dodecane) biphasic system, as shown in Fig. 1(B), bright circular-shaped fluorescent domains were clearly observed, indicating that the amphiphilic fluorescent catalyst is distributed at the water/oil interface of the dispersed emulsion droplets. This is a direct image of the O/W (dodecane-in-H_2O) emulsion systems formed using the fluorescent catalyst as the surfactant. The lipophilic quaternary ammonium cation of the surfactant catalyst may orient to the oil side, and the hydrophilic heteropolyanions to the aqueous side (Fig. 1(B)). The emulsion catalysis is different from most homogeneous catalysis. In the emulsion catalytic system, the amphiphilic catalyst is assembled at the interface of emulsion droplets, not in the continuous phase or inside the emulsion droplet. In other reaction media, the catalyst is usually dissolved in one phase and the reactions are normally carried out in a homogeneous or pseudohomogeneous phase.[2]

To test the catalytic property of the catalyst assembled in the emulsion system, the selective oxidation of 2-octanol with hydrogen peroxide as oxidant, as a model reaction, was investigated both with a biphasic catalytic system and emulsion catalytic system. The results are shown in Fig. 2. The homogenous catalyst $Na_9[EuW_{10}O_{36}]$ (without $(C_{18}H_{37})$ $_2N^+(CH_3)_2$) was monitored in aqueous–oil biphasic reaction systems, showing very slow reaction rate and giving only about 4% of conversion of 2-octanol in a reaction time of 8 h (Fig. 2(B)), By contrast, for 2-octanol and hydrogen peroxide mixed with amphiphilic catalyst ($[(C_{18}H_{37})_2N^+(CH_3)_2]_9[EuW_{10}O_{36}]$) with stirring, in which the metastable O/W emulsion (oil-in-H_2O) was formed, the amphiphilic catalytic system gave high activity and selectivity for the oxidation of the alcohol, giving 100% of conversion of 2-octanol and 100% selectivity under the same reaction conditions (Fig. 2(A)). The results suggested that the emulsion reaction system provides a high interfacial area and the reaction rates can be greatly increased. The emulsion catalysts served as both a catalyst to activate the substrate molecules and an emulsifying agent to stabilize the emulsion droplets. Moreover, the amphiphilic catalyst $Q_9[EuW_{10}O_{36}]$ can be easily separated and recycled from the reaction system by demulsifying by centrifugation. By contrast, the homogenous catalyst $Na_9[EuW_{10}O_{36}]$ cannot be recovered and separated.

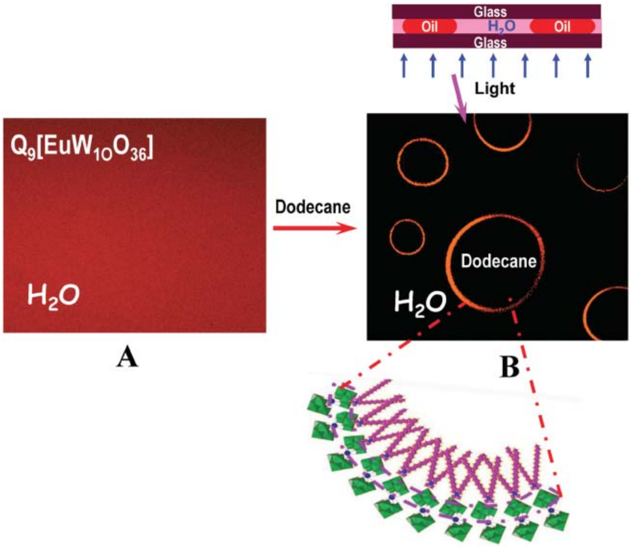

Fig. 1 Fluorescence microscope images of the emulsion systems. (A) 15 ml of H_2O and 0.001 g of the amphiphilic $[(C_{18}H_{37})_2N^+(CH_3)_2]_9$-$[EuW_{10}O_{36}]$ catalyst. (B) 2 ml of dodecane (oil), 15 ml of H_2O and 0.001 g of the amphiphilic $[(C_{18}H_{37})$ $_2N^+(CH_3)_2]_9[EuW_{10}O_{36}]$ catalyst.

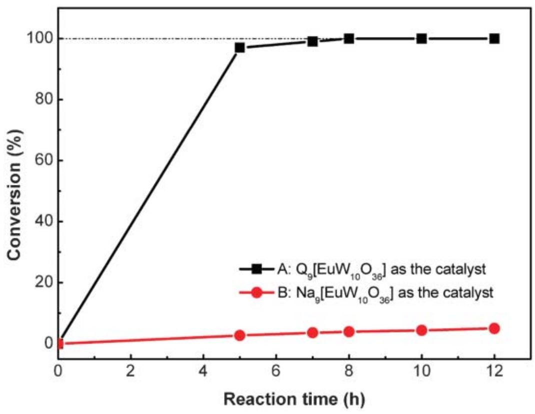

Fig. 2 Selective oxidation of 2-octanol to 2-octanone in different reaction systems. (A) $[(C_{18}H_{37})_2N^+(CH_3)_2]_9[EuW_{10}O_{36}]$ as catalyst in the emulsion system, (B) $Na_9[EuW_{10}O_{36}]$ as catalyst in the biphasic reaction system. *Reaction conditions*: 0.05 mol of 2-octanol, 0.08 mol of H_2O_2 (30 wt%) and 0.015 mmol of the catalyst, 80 °C.

The emulsion system can also be applied to the oxidation of other alcohols.‡ The results are summarized in Table 1. The catalyst gave a conversion of 100% for 2-pentanol, with pentanone selectivity of 100%, and also 100% conversion for cyclopentanol. Cyclohexanol and 1-phenylpropanol can be completely oxidized to the corresponding cyclohexanone and propiophenone with a selectivity of 100% under the same reaction condition. The amphiphilic catalyst shows remarkable activity and selectivity in the oxidation of alcohols to ketones in the emulsion catalytic system, and the TON (turnover number) is about 5000, while the

Table 1 Selective oxidation of alcohols in O/W emulsion systems using the fluorescent molecule $[(C_{18}H_{37})_2N(CH_3)_2]_9[EuW_{10}O_{36}]$ as catalyst

Substrates	Time (h)	Conversion (%)	Selectivity (%)
2-Pentanol	5	100	100
2-Octanol	8	100	100
Cyclopentanol	5	100	100
Cyclohexanol	3	100	100
1-Phenylpropanol	5	100	100

[a] *Reaction conditions*: 0.05 mol of alcohol, 0.08 mol of H_2O_2 (30 wt%) and 0.01 mmol of $[(C_{18}H_{37})_2N(CH_3)_2]_9[EuW_{10}O_{36}]$ catalyst, 80 °C. The catalyst can be recycled.

TON is only about 200 in the biphasic reaction systems. The results indicate that the state of the amphiphilic catalyst, assembled at the interface of the emulsion droplets, not only maintains the stability of the emulsion droplets but also provides a higher interfacial surface area where the reaction takes place, resulting in a higher reaction encounter probability and a greater interphase mass transport relative to liquid–liquid biphase reaction systems.

In summary, an amphiphilic fluorescent catalyst $Q_9[EuW_{10}O_{36}]$ ($Q = [(C_{18}H_{37})_2N^+(CH_3)_2]$) was synthesized and a metastable emulsion was formed when the catalyst was added to biphasic systems and the emulsion droplets formed in the O/W emulsion systems were directly imaged by fluorescence microscopy. This provides direct evidence that the amphiphilic catalyst is assembled at the interface of the emulsion systems. The emulsion reaction medium functions as highly dispersed nanoreactors and behaves like a homogeneous catalyst. The catalyst shows high selectivity and activity in the oxidation of alcohols using H_2O_2 as oxidant. Moreover, the emulsion catalysts can be easily separated and recycled by demulsifying.

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Notes and references

† *Preparation of amphiphilic catalysts based on quaternary ammonium europium-substituted heteropolyoxotungstate $Q_9[EuW_{10}O_{36}]\cdot 32H_2O$.* The polyoxotungstoeuropate $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$ was prepared as described by Peacock and Weakley and Sugeta and Yamase.[9a,b] The preparation of amphiphilic $Q_9[EuW_{10}O_{36}]\cdot 32H_2O$ catalysts is as follows: 0.3 mmol of $Na_9[EuW_{10}O_{36}]\cdot 32H_2O$ was dissolved in 15 ml of water, then a quaternary ammonium salt (2.7 mmol, $Q = [(C_{18}H_{37})\ _2N^+(CH_3)_2]$) in 30 ml of alcohol (95%) was added dropwise into the above aqueous solution with stirring. A white precipitate was immediately formed. After continuously stirring for 6 h, the white precipitate was collected by filtration, washed with cold water and dried at 40 °C in vacuum for 24 h to produce the amphiphilic $Q_9[EuW_{10}O_{36}]\cdot 32H_2O$ catalyst. IR (KBr, cm^{-1}): ν = 2953, 2918, 2850, 1484, 1468, 1380, 945 ($W–O_d$), 870 ($W–O_b–W$), 842 ($W–O_c–W$), 814 ($W–O_c–W$), 721 ($W–O_c–W$). Anal. calc.: for $[(C_{18}H_{37})_2N^+(CH_3)_2]_9$-$[EuW_{10}O_{36}]\cdot 32H_2O$ ($C_{342}H_{792}N_9O_{68}W_{10}Eu$, 8110.33): C 50.65, H 9.84, N 1.55; found: C 51.21, H 9.71, N 1.62%.

‡ *Oxidation of alcohols in an O/W emulsion system.* The selective oxidation of alcohols in the O/W emulsion system was typically carried out as follows. A 100-ml Erlenmeyer flask was charged with 0.05 mol of alcohol, 0.08 mol of H_2O_2 (30 wt%) and 0.01 mmol of the $Q_9[EuW_{10}O_{36}]\cdot 32H_2O$ catalyst. This mixture was heated to 80 °C under vigorous stirring, and the turbid W/O emulsion was formed. After the reaction was complete, the water and oil layer was separated by centrifugation, and then analyzed by GC.

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