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Aqueous biphasic catalytic hydroformylation of higher olefins: Promotion effect of cationic gemini and trimeric surfactants

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Abstract

Six cationic gemini and trimeric surfactants: *N*,*N*′-didodecyl-*N*,*N*′-dimethyl piperazinium iodide (**2**), the monooxlate of *N*,*N*′-didodecylpiperazine (**3**), the hydrochloride of *N*,*N*′-didodecylpiperazine (**4**), the 1,3,5-trimethyl-1,3,5-tridodecylhexahydro-1,3,5-trazinium iodide (**5**), the monooxlate of 1,3,5-tridodecylhexahydro-1,3,5-triazine (**6**) and the hydrochloride of 1,3,5-tridodecylhexahydro-1,3,5-triazine (**7**) were prepared using the regular methods. These cationic surfactants and a double-chained surfactant, didodecyldimethylammonium bromide (**1**), were successfully applied as catalysis promotion agents in aqueous biphasic hydroformylation of higher olefins. The aqueous catalysts used in present study were RhCl(CO)(TPPTS)$_2$–TPPTS [TPPTS: P(m-C$_6$H$_4$SO$_3$Na)$_3$]. The experimental results showed that while all these cationic surfactants could accelerate the hydroformylation reaction, surfactants **1**, **2**, **6**, **7** exhibited more significant promotion effects. The influences of the surfactant anions on the reaction were also discussed. Of the three gemini surfactants **2**, **3**, and **4**, which were derived from *N*,*N*′-didodecylpiperazine, surfactant **2** with iodide as anion exhibited substantially higher promotion effect than surfactants **3** with monooxalate and **4** with chloride as anion, respectively. On the other hand, among the three trimeric surfactants **5**, **6**, **7**, which were derived from 1,3,5-tridodecylhexahydro-1,3,5-triazine, surfactants **6** with monooxalate and **7** with hydrochloride as anion displayed better acceleration effect than surfactant **5** with iodide as anion. Compared with the double-chained and single headed surfactant **1**, surfactant **2** containing two alkyl chains and cationic heads and surfactant **6** with three alkyl chains and cationic heads were superior additives to accelerate the hydroformylation reactions. When they were used as catalysis promotion additives, less water-soluble phosphine (TPPTS) was required to immobilize the rhodium catalyst in aqueous phase, and the hydroformylation reaction proceeded more regioselectively toward the valuable linear aldehyde under lower syngas pressure.

Keywords: Cationic surfactant; Gemini surfactant; Hydroformylation; Biphasic system; Higher olefin

1. Introduction

A number of advantages of the aqueous/organic biphasic catalysis system, such as environment benignity and facile catalyst recovery, promote researchers to extend the system to the hydroformylation of higher olefins. However, the reaction rate is notoriously low due to the extremely low solubility of the long chain olefins in water. Consequently, the mass transfer across the oil/aqueous phase boundary is greatly impaired. So far, extensive efforts including the addition of co-solvent [1], co-ligand [2], amphiphilic phosphine [3–5], modified cyclodextrin [6–10], and surfactant [11–17] into the reaction solution, as well as using supported aqueous phase catalyst [18], have been studied to improve the mass transfer rate. Of the above-mentioned various methods, the addition of surfactant is attractive because surfactants are easy to synthesize or commercially available.

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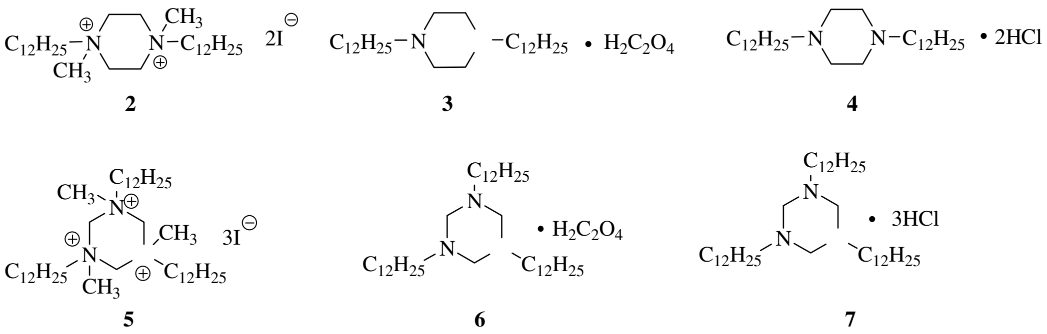

Scheme 1. Structures of cationic surfactants.

In addition to enhancing the reaction activity, the preferential formation of the more valuable linear aldehyde is also beneficial and of great concern for the hydroformylation. The utilization of diphosphine with proper bite angle is an effective method [5,19] to obtain the higher L/B (mole ratio of linear to branched aldehyde). Furthermore, for the catalysis system containing monophosphine, the higher mole ratio of ligand to catalyst is usually applied to achieve a higher L/B value [20]. In the surfactant-containing system, an alternative means to improve the L/B value is the introduction of sterically hindered surfactant that could provide a beneficial micro-reaction environment for the formation of linear aldehyde. Our group reported that the gemini type surfactants could significantly increase L/B value [21–23]. In the present paper, we will describe the catalysis promotion effects of six gemini and trimeric surfactants. Their promotion effects were investigated in aqueous biphasic hydroformylation of higher olefin using RhCl(CO)$(TPPTS)_2$–TPPTS [TPPTS: P(m-$C_6H_4SO_3Na)_3$] as catalyst. The molecular structures of these surfactants are shown in Scheme 1. To our best knowledge, some of them so far have not been utilized in aqueous biphasic hydroformylation as reaction additives.

2. Experimental

2.1. Materials

Rhodium catalyst RhCl(CO)$(TPPTS)_2$ and water-soluble phosphine (TPPTS) were synthesized in our laboratory according to the report [24]. The dodecyl amine ($C_{12}H_{25}NH_2$), oxalic acid ($H_2C_2O_4$), formaldehyde (HCHO), methanol, 1,4-piperazine, 1-bromododecane, which were all AR reagents, 1-decene (sigma), and 1-dodecene (Fluka) were used without further purification. *N*,*N*′-Didodecylpiperazine was synthesized according to the method described elsewhere [25]. 1,3,5-Tridodecylhexahydro-1,3,5-triazine was synthesized according to the method [26]. Surfactants **1**, **2**, **5** [27] and surfactants **3**, **4**, **6**, **7** [26] were synthesized by following previously reported procedures. Distilled and deionized water was used in all these experiments. The syngas (H_2:CO = 1:1) was obtained by directly mixing hydrogen (99.99%) and carbon monooxide (99%).

2.2. Hydroformylation

The hydroformylation reactions were carried out in a 60 mL stainless autoclave with magnetic stirrer. A typical reaction procedure was conducted as following: after the introduction of rhodium catalyst, TPPTS, surfactant, water, and substrate (olefin), the autoclave was evacuated and purged with syngas three times. When the temperature reached the desired value, syngas was introduced. After a given reaction time, the stirring was stopped and the autoclave was quickly cooled to ambient temperature with cold water.

An HP 1890 series II gas chromatography (Hewlett Packard, Palo Alto, CA) equipped with a flame ionization detector was used. The separation was done on a SE-30 (30 m × 0.32 mm, d_f 0.25 μm) fused silica capillary column.

3. Results and discussion

Several preliminary experiments were conducted to investigate the different acceleration effects of the various surfactants. 1-Decene as a model substrate, was hydroformylated at 3.0 MPa (Syngas) and 100 °C using RhCl(CO)$(TPPTS)_2$ as the catalyst precursor. The variations of TOF (turnover frequency defined as the mole of olefin converted by per mole Rh per hour) against the surfactant concentrations were plotted (Fig. 1). A general and apparent trend that TOF values went up with the increase in the surfactant concentrations was observed. However, when surfactants **1**, **2**, **6** and 7 were used as catalysis promotion additives, the augments of TOF values were more significant than those when surfactants **3**, **4** and **5** were used. The hydroformylation reaction rate showed a significant enhancement even when the concentration of surfactant was only 1.0 mmol/L. For example, when the reaction was performed in the presence of surfactant **2**, the TOF value could reach 966.9 h^{-1}. In contrast, the TOF values in the systems containing surfactants **3**, **4** or **5** were still low (around 300 h^{-1}) even when the surfactant concentrations were increased to 8.0 mmol/L.

The surfactants **2**–**7** can be classified into two groups according to the structural characteristics. One group including surfactants **2**, **3**, **4**, was prepared from *N*,*N*′-did-