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Highly efficient microreactors with simultaneous separation of catalysts and products in deep desulfurization

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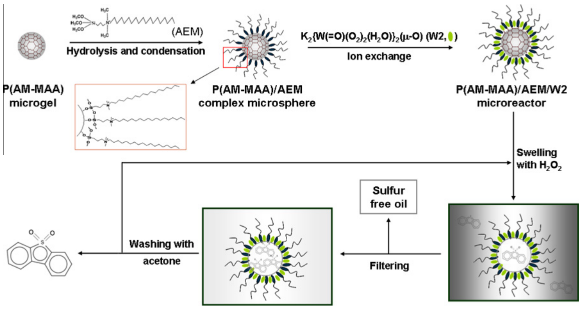
HIGHLIGHTS

- Catalysts and products were simultaneously separated from reactive system.
- Remarkable features for the microreactors have core/shell structure.
- The core store water-soluble substances and the shell is amphiphilic and catalytic.
- The microreactors could make integration of reactor and extractor into one system.

GRAPHICAL ABSTRACT

Procedure for preparation of P(AM-MAA)/AEM/W2 composite microspheres with hydrogel core and phase transfer catalysts shell.



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ABSTRACT

The complex microspheres using the poly(acrylamide-*co*-methacrylic acid) (P(AM-MAA)) microgels as core and the phase transfer catalysts (tungstate of the complexes of 3-(trimethoxysilyl)-propyldimethyl-octadecylammonium) as shell were prepared. The feasibility that the complex microspheres as reusable microreactors were used for the catalytic oxidation of Dibenzothiophene (DBT) was studied, and the effects of some factors on the conversion of DBT were investigated. The results indicated that the prepared complex microspheres make the reusability not only possible but also high catalytic efficiency in catalytic oxidation of DBT. The microgel core could store water-soluble oxidant (H_2O_2), and the phase transfer catalysts shell on the surface of microgel could realize the catalytic oxidation of DBT on the interface between oil phase and water phase. The hydrogel core as water phase and the shell as phase transfer catalysts complex combined in one microsphere make the simultaneous separation of catalysts and water phase possible. It is worth mentioning that enhancement of the mass transfer is extremely important for the microreactors with hydrogel core due to the extensive hydrogen bonding network obstructing water movement. The results indicated that introduction of PAM into the microgels, control of amounts of the phase transfer catalysts and cross-linking degree in microgel are resultful for enhancement of the mass transfer. The proposed protocol has a common suitability to construct microreactors used in oil/water catalytic systems.

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1. Introduction

To meet the new emission control standards, ultra-deep desulfurization has become very imperative for the petroleum refining industry [1]. Traditionally, hydrodesulfurization (HDS) is the major process in refineries to eliminate S from crude gas and from refined petroleum products such as gasoline or petrol, jet fuel, diesel fuel, and fuel oil [2–3]. However, some sulfur-bearing molecules such as benzothiophene and dibenzothiophene with alkyl substituent groups are exceedingly difficult to eliminate by means of conventional hydrodesulfurization [4–5]. At present, the possible tactics to improve deep desulfurization include adsorption desulfurization [6–8], extraction desulfurization [9–10], oxidation desulfurization (ODS) [11–13], and bioprocesses desulfurization [14–15]. Among these strategies, selective oxidation combined with extraction shows a promising prospect for high desulfurization efficiency. In this approach the heterocyclic sulfur-containing compounds are oxidized into the corresponding sulfone or sulfoxide with polarity, and then the polar sulfones are extracted by polar solvent. In the oxidation process, the amphiphilic catalysts in W/O emulsion system are usually used, and they exhibit very high catalytic activities for all sulfur-containing compounds in both model and actual diesel due to high interfacial surface area. [16–17]. Li et al. [16] employed a recoverable catalyst ($[(C_{18}H_{37})_2N^+(CH_3)_2]_3[PW_{12}O_{40}]$) assembled in an emulsion to selectively oxidize the 4,6-dimethyldibenzothiophene-like compounds to sulfone via using hydrogen peroxide as oxidant in diesel. After the sulfone being isolated from the diesel using an extractant, the S content in diesel can be reduced from 500 ppm to 0.1 ppm. From the point of view of separation, the recovery and reuse of the quaternary ammonium heteropolyoxotungstates is relatively difficult. The demulsification and catalyst recovery still faced challenges for industry in a large-scale unit [18]. Since Lo et al. first reported the combination of chemical oxidation and extraction with IL[Bmim]PF_6 in ultra-deep desulfurization [19]. This method has increasingly drawn attention. More recently, a variety of ILs having the ability to extract and oxidize S-compounds in diesel have been designed in order to decrease the harm of IL to the environment [20], increase desulfurization efficiency [21–23], and enhance the surface area and adsorption rate [24]. Combining catalytic oxidation with ILs extraction shows to be a promising approach to desulfurization for remarkable enhancement of S-compound conversion. It is worth mentioning that the costs and vague environmental impact of ILs lead to the restriction of their use in industry.

In view of structure micelle, a micelle-like microgel surface covalently bonded phase transfer catalysts could be used as micelle-like microreactor with simultaneous separation of catalysts and products in deep desulfurization. In this complex microsphere, the phase transfer catalysts are immobilized onto the surface of the core microgel, and the core can be used not only to store water-soluble reactants but also to extract polar products. As a result, the phase transfer catalysts immobilized onto the shell of the microreactors, the water phase trapped in the microreactor core, and the polar product extracted into the microreactor core can be simultaneously separated when the complex microspheres are separated from the medium. Based on the protocol mentioned above, these new kinds of reused microreactors with core–shell structure used in catalytic oxidation of DBT were reported by us [25–29]. The results verified the reusable feasibility of this kind of the microreactors used in deep desulfurization. Unfortunately, the catalytic efficiency is relatively lower due to unfavorable mass transfer resulting from the dense catalysts shell or the microsphere with large size. To eliminate this disadvantage, in the present work, the surface of poly(acrylamide-*co*-methacrylic acid) (P(AM-MAA)) microgels were immobilized by 3-(trimethoxysilyl)-propyldimethyl-octadecylammonium chloride (AEM) to form P(AM-MAA)/AEM microspheres, and then the catalytic species $\{W(=O)(O_2)_2(H_2O)\}_2(\text{-}\mu\text{—}O)^{2-}$ (W2) were introduced into the P(AM-MAA)/AEM microspheres by ionic exchange between $K_2\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{—}O)$ and AEM. Finally, the P(AM-MAA)/AEM/W2 microreactors with the P(AM-MAA) microgel core and the phase transfer catalysts shell formed by the complex between AEM and W2 were constructed. Compared with the similar microreactor reported by us in literature [28], PAM is especially introduced into the microgels for enhancement of mass transfer and the extraction. PMAA with –COOH groups form strong hydrogen bonds with water compared with PAM, which results in the significant decrease of water mobility in the microgels [30–32]. Therefore, introduction of PAM into PMAA microgels is expected to increase water mobility in the microspheres for enhancement of mass transfer. In addition, AM could be used to extract sulfones [33], and PAM introduced into the PMAA microspheres is anticipated to improve the microsphere ability in extraction of sulfones. Furthermore, compared with those of the complex microspheres in our previous work, the loaded amount of the phase transfer catalysts AEM/W2 on the surface is markedly reduced for decrease of mass transfer resistance. The results obviously indicated that the strategies mentioned above are resultful in enhancing reusability, catalytic efficiency and extracted effect. The protocol proposed here is beneficial for construction of the reusable catalytic material used in deep-desulfurization even for preparation microreactors used in liquid–liquid biphasic catalysis system.

2. Experimental section

2.1. Materials

3-(trimethoxysilyl)-propyldimethyl-octadecylammonium chloride (AEM, 42 vol% in methanol) was obtained from AEGIS ENVIRONMENTS. Acrylamide (AM), Methacrylic acids (MAA), Dibenzothiophene (DBT) were purchased from Alfa Aesar. *N*,*N*′-methylene bisacrylamide (BA), ammonium persulfate (APS), decalin, *N*,*N*,*N*′,*N*′-tetramethylene diamine (TMEDA), potassium tungstate (K_2WO_4), Span-80, Tween-80, cyclohexane, acetone, NaOH, and anhydrous alcohol were analytical-grade regents and used as received.

2.2. Synthesis of P(AM-MAA)/AEM/W2 complex microspheres

The process for the preparation of P(AM-MAA)/AEM/W2 complex microspheres is shown in Scheme 1, and the details are described as follows.

2.2.1. Synthesis of P(AM-MAA) microgels

P(AM-MAA) microgels were synthesized according to the previous report [25], and amounts of AM, MAA and BA were listed in Table 1.

2.2.2. Synthesis of P(AM-MAA)/AEM complex microspheres

P(AM-MAA)/AEM complex microspheres were fabricated by the impregnation approach referring to a previous literature [28]. A typical synthesis process is described below. P(AM-MAA) microgels (0.1 g) were immersed into 0.2 mL of alcohol solution containing AEM (0.16 g), and the residual alcohol was subsequently removed under vacuum condition. A petri dish containing the dried microspheres was suspended in a sealed container containing H_2O for 15 min, the resultant sample was then heated at 60 °C for 10 h, the P(AM-MAA)/AEM complex microspheres were finally obtained. The complex microspheres loaded different amount of AEM (the ratio of AEM to P(AM-MAA) microgels in