Chinese Journal of Catalysis 35 (2014) 798–806

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journal homepage: www.elsevier.com/locate/chnjc

Minireview (Special Issue on Carbon in Catalysis)

Carbon nanohybrids used as catalysts and emulsifiers for reactions in biphasic aqueous/organic systems

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ARTICLE INFO

Article history:
Received April 17 2014
Accepted April 27 2014
Published 20 June 2014

Keywords:
Carbon nanomaterials
Nanohybrids
Emulsions
Biphasic aqueous/organic mixtures
Catalysis at water/oil interface
Biomass conversion
Fischer-Tropsch synthesis

ABSTRACT

This mini-review summarizes some novel aspects of reactions conducted in aqueous/organic emulsions stabilized by carbon nanohybrids functionalized with catalytic species. Carbon nanohybrids represent a family of solid catalysts that not only can stabilize water-oil emulsions in the same fashion as Pickering emulsions, but also catalyze reactions at the liquid/liquid interface. Several examples are discussed in this mini-review. They include (a) aldol condensation-hydrodeoxygenation tandem reactions catalyzed by basic (MgO) and metal (Pd) catalysts, respectively; (b) Fischer-Tropsch synthesis catalyzed by carbon-nanotube-supported Ru; and (c) emulsion polymerization of styrene for the production of conductive polymer composites. Conducting these reactions in emulsion generates important advantages, such as increased liquid/liquid interfacial area that consequently means faster mass transfer rates of molecules between the two phases, effective separation of products from the reaction mixture by differences in the water-oil solubility, and significant changes in product selectivity that can be adjusted by modifying the emulsion characteristics.

1. Introduction

Reactions in biphasic aqueous/organic mixtures are potentially interesting for industrial processes, in which the use of two liquid phases is unavoidable due to the feedstock composition or when it provides an operational advantage. For example, in the upgrading of bio-fuels derived from biomass pyrolysis, phase separation and biphasic mixtures are unavoidable due to the high water concentration of the feedstock (30%–40%) and the organic and less polar characteristics of the desirable product (deoxygenated fuels) [1]. In other cases, biphasic systems have been purposely created to facilitate the separation of products from unreacted reactants and catalysts, which can be recycled for maximum product yield [2].

Using emulsions in systems like these are attractive when valuable products can be separated into the other phase, preventing undesired secondary reactions. Partitioning of by-products on the basis of their relative solubility can result in substantial simplifications in the separation stages, obviating the need for steps such as distillation that might damage heat-sensitive compounds [3]. Moreover, emulsions greatly increase the liquid/liquid interfacial area, thus enhancing the rate of interfacial mass transfer. Molecular emulsifiers, such as detergents, polymers are typically employed to stabilize emulsions. Their role is to lower the interfacial tension between two phases, or create a film around the droplets making them repel each other, or increasing the viscosity of the continuous medium, maintain the droplets suspended. A major drawback of using molecular emulsifiers is their difficult separation from the reaction mixture, which requires expensive purification

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This work was supported by the US Department of Energy/EPSCOR (DE SC00044136.85).
DOI: 10.1016/S1872-2067(14)60119-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 6, June 2014

methods, such as membrane filtration [4]. This disadvantage can be overcome by replacing the molecular surfactants with amphiphilic catalyst particles that can be readily recovered and reused after each reaction cycle [5]. This novel methodology combines the advantages of phase transfer and heterogeneous catalysis [6,7]: (a) increased interfacial area, (b) enhanced mass transfer of molecules between the two phases, (c) simplified reaction/separation process by using a recoverable solid catalyst instead of surfactant, and (d) effective separation of products from the reaction mixture by differences in the water-oil solubility (avoiding heating that leads to product decomposition).

Such process improvements could have a major impact in the field of biomass conversion to fuels [8–12] (upgrading of pyrolysis oil and sugars), production of specialty chemicals [13] pharmaceuticals, deep desulfurization of fuel oil [14,15], and Fischer-Tropsch synthesis (FTS) [16,17].

Furthermore, when these particles have a compartmentalized surface that displays different wettabilities (i.e., Janus particles), the stabilization of the emulsions becomes more effective [18–25]. Contrary to homogeneous particles that have uniform wettability and a fixed contact angle, the Janus particles are a more complex system with asymmetric wettability that can exhibit a tailored hydrophilic/hydrophobic balance, and therefore modify the location of the three-phase contact angle. The tunable surface properties of Janus nanoparticles have attracted attention for applications as diverse as sensing, electronics, photonics, and drug delivery [26–31].

In this contribution, a special case of Janus particles is discussed. They are the so-called carbon nanohybrids, which are composed of carbon nanomaterials (hydrophobic) fused to oxide nanoparticles (hydrophilic), which are able to stabilize emulsions and, when properly functionalized, catalyze reactions at the water/oil interface (i.e., liquid/solid/liquid interfacial catalysis) [5,32]. The amphiphilic character of these nanohybrids makes them segregate naturally to the water/oil interface, thus becoming suitable for the stabilization of emulsions with small droplet sizes with remarkable stability. Two important advantages of these nanohybrids over conventional Janus particles are a higher surface area and a higher extent of penetration into the organic liquid phase, due to the presence of the lipophilic carbon nanotubes. In addition, by using carbon nanotubes (CNT) it is possible to reduce the external diffusion limitations by functionalizing the outer surface of the CNT with the catalytic species. Nanotubes are more accessible than conventional supports having meso and microporosities. Additionally, by changing the type of CNT used one can vary the metal dispersion, e.g. multi-wall carbon nanotubes (MWCNT) have a more defective surface than single-wall carbon nanotubes (SWCNT) [33].

2. Carbon nanohybrids as effective stabilizers of Pickering emulsions

According to the Bancroft's rule [34], the continuous phase of an emulsion is that with a higher affinity for the emulsifier. The relative affinity of a given emulsifier for the two phases can be described in terms of the hydrophilic-lipophilic balance (HLB) [35]. When the emulsifier is a surfactant, the HLB number can be used to determine its ability to stabilize water-in-oil (low HLB, more hydrophobic) or oil-in-water (high HLB, more hydrophilic). In Pickering emulsions, fine solid particles adsorbed at the water/oil interface sterically hinder the coalescence of droplets and effectively stabilize the emulsion [36]. As shown in Fig. 1, when the contact angle between the water and the particle at the water/oil interface is 90° the particle's tendency to stay at the interface is highest and the emulsion is most stable. Analogous to the case of surfactants, the phase with the highest affinity for the particle, i.e. the one that wets the particle more effectively will form the continuous phase. Therefore, a more hydrophilic particle will create a contact angle below 90° and will tend to stabilize oil-in-water emulsions, while contrarily, a more hydrophobic particle will stabilize water-in-oil emulsions. Completely hydrophilic (or hydrophobic) particles will show the tendency to be solely in one of the phases and therefore the emulsions that they form are less stable. These trends can be changed when the water/oil volume ratio during the preparation of the emulsion is varied. For example, by increasing the amount of the dispersed phase, one can obtain the inverse emulsion [19,24,32]. That is, for a more hydrophobic particle that tends to form a water-in-oil emulsion, the inverse emulsion can be obtained at high water/oil volume ratios.

2.1. SWCNTs carbon nanotubes/oxide nanoparticles

An efficient nanohybrid for catalytic applications is one that has high stability at the water/oil interface, but at the same time, stabilizes catalytically active nanoparticles at the desired side of the interface. That is, one can expect that particles located on the hydrophobic end of the nanohybrid will catalyze reactions occurring in the organic phase, while those placed on the hydrophilic side will catalyze reactions in the aqueous phase [5]. In this sense, carbon nanohybrids are particularly attractive because they exhibit tunable properties that can be adjusted during synthesis or with simple post-synthesis treatments. For example, as produced pristine SWCNT are highly hydrophobic, but can be amphiphilic if they are combined with oxide nanoparticles. When the SWCNT are produced catalytically by decomposition of carbon-containing molecules (e.g., CO, methane, ethanol) over supported metal catalysts, one can

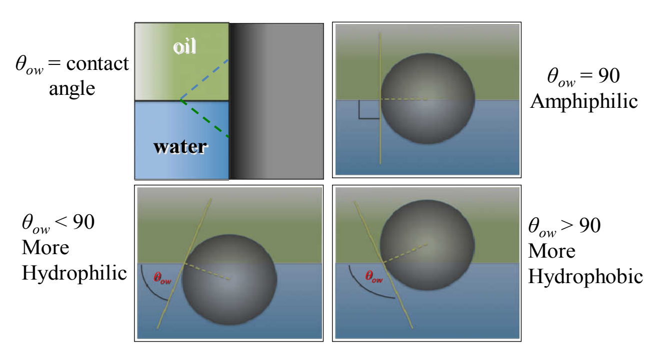

Fig. 1. Effect of the hydrophobic/hydrophilic balance on the contact angle of the water/oil interface and preferential position of the particle.