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An insight into the intensification of aqueous/organic phase reaction by the addition of magnetic polymer nanoparticles

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HIGHLIGHTS

- L–L heterogeneous reaction was accelerated by magnetic polymer nanoparticles.
- The overall volumetric mass transfer coefficient of substrate was evaluated.
- The generation of Pickering emulsion allowed a high specific surface area.
- The function of MA, PTC and MPN were compared in parallel.

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ABSTRACT

The intensification mechanism of aqueous/organic phase reaction by the addition of magnetic polymer nanoparticles was investigated. To understand how nanoparticles intensify the liquid–liquid (L–L) reaction, three reaction enhancement strategies of mechanical agitation (MA), the addition of magnetic polymer nanoparticles (MPN) or phase transfer catalyst (PTC) were compared in Montanari oxidation system. A mass transfer mathematical model was established to describe the oxidation reaction process owing to its inherently fast characteristic of the oxidation of selected substrate (benzyl alcohol). Moreover, the influence of the nanoparticles concentration on the biphasic reaction was explored. The results indicate that the emulsification of nanoparticles is the main reason to intensify the L–L reaction, and the mass transfer specific surface area (a_{ow}) is a crucial factor to accelerate the reaction rate. In addition, the emulsion type also plays a significant role to influence the overall mass transfer coefficient (K) of substrate.

1. Introduction

Numerous industrially important heterogeneous systems involve two immiscible liquids. For these systems, with or without chemical reaction, interfacial area is an important variable in deciding the efficiency of the operation [1]. For instance, the rates of alkaline hydrolysis of a variety of formate esters, reduction of certain substituted nitroaromatics with aqueous Na_2S_x, nitration of aromatic substances such as benzene, toluene, etc. and higher olefins, etc., in mechanically agitated liquid–liquid contactors, are found to be dependent on interfacial area, and the overall rate of the reaction per unit volume of dispersion can be substantially increased by increasing the interfacial area [2]. However, owing to the incompatibility in such reaction system, the insufficient interaction of reactants in the two phases results improvable reaction rate. It is well known that, for an inherent fast reaction, the overall reaction rate is normally dominated by the contact specific area between the two phases. Herein, both in industry and in laboratory, intensifying drop-dispersion in continuous phase is an efficient way to increase the overall reaction rate and shorten the reaction time.

Traditionally, stirring, optimization of the structure of agitator or reactor, ex-field assistance (such as ultrasonic) [3,4] were applied to enhance a heterogeneous reaction rate by strongly mixing the liquids. Another choice is the addition of phase transfer catalyst (PTC) [5] or emulsifier [6] to form non-thermodynamically stable emulsion, which can significantly enhance the overall reaction rate and reduce the operation time. Apart from the above techniques, for decades, it was widely reported that nanoparticles could be adsorbed on the drop surface forming a stable particle layer and playing a similar role as surfactant does in an oil–water

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Nomenclature

a_{ow}	specific surface area [$m^2\ m^{-3}$]
c	concentration [mol L^{-1}]
c^*	equilibrium concentration at oil–water interface [mol L^{-1}]
C	surface coverage
d	impeller diameter [m]
d_p	diameter of particles [m]
d_i	diameter of droplets [m]
d_{32}	Sauter mean diameter [m]
D	diffusion coefficient [$m^2\ s^{-1}$]
E	enhancement factor
H	partition coefficient
Ha	Hatta number
k	mass transfer coefficient [m s^{-1}]
k_r	intrinsic reaction rate constant [L $mol^{-1}\ s^{-1}$]
K	overall mass transfer coefficient [m s^{-1}]
Ka_{ow}	overall volumetric mass transfer coefficient [s^{-1}]
L	vessel diameter [m]
m_p	mass of particles [kg]
M	solvent molecular weight [g mol^{-1}]
n_i	number of drops with the d_i droplet size
N	stirring speed [r s^{-1}]
N'	overall volumetric mass transfer rate [mol $L^{-1}\ s^{-1}$]
r	radius of droplets [m]
Re	impeller Reynolds number ($Nd^2\rho_c/\mu_c$)
Re_d	Reynolds number in dispersed phase
Sc	Schmidt number ($\mu_c/\rho_c D_c$)
Sh	Sherwood number
T	temperature [K]
V	volume [m^3]
V_b	molar volume of solute at normal boiling point [$m^3\ mol^{-1}$]
We	Weber number ($N^2d^3\rho_c/\sigma_{ow}$)
x	solvent association parameter, water, x = 2.6; non-polar solvent, x = 1

Greek letters

ρ	density [kg m^{-3}]
σ	interfacial tension [N m^{-1}]
μ	dynamic viscosity [Pa s^{-1}]
ϕ	volume fraction of dispersed phase

Subscripts

c	continuous phase
d	dispersed phase
o	oil phase
w	water phase
p	particles
ow	oil–water interface

system to minimize the surface energy to form the so-called Pickering emulsion [7]. The strong attachment of the particles onto the oil/water interface hinders the droplets coalescence, thus forming a more stable emulsion [8]. The Pickering emulsion technology gives us a new avenue to increase the reaction rate of biphasic reactions through forming highly dispersed micro-reactors with a larger oil/water interface area [9]. Up to now, Pickering emulsions have been employed as an approach for various applications such as preparation of Janus materials, selectively permeable capsules, core–shell structure catalyst and hollow microspheres [10–12]. However, the application of Pickering emulsions to chemical reactions was rarely investigated. Very recently, Pera-Titus et al. made a minireview to describe the relevant biphasic reactions in Pickering emulsions [13]. Comparing with traditional emulsion, the solid particle emulsifiers could be irreversibly adsorbed on the liquid–liquid interfaces, and probably can be recycled [14,15].

So far, researches showed that several factors affect the formation and stability of Pickering emulsion. There was a discovery revealing that the particle concentration influenced the emulsion droplet size, because the interfacial area was related to the amount of nanoparticles [16]. The surface properties of nanoparticle also influence the properties of Pickering emulsion [17]. Stiller et al. investigated the influence of the wettability of different surface modified titanium dioxides on the type and stability of Pickering emulsion, and found that the long-term stability of water-in-oil emulsions increased with increasing apparent contact angle value against water [18]. Tarimala et al. found that hydrophobic and hydrophilic solid particles could assemble at the oil–water interface at the same time [19]. Yu et al. changed the surface properties of Ru/CNT-TiO_2 by modulating the amount of CNT component and found the increasing catalytic activity for the selective oxidation of benzyl alcohol to benzaldehyde in the emulsion system [20].

In recent years, the preparation and application of magnetic particles has attracted great attention because of their unique properties [21–23]. In our previous works, we demonstrated that magnetic polymer nanoparticles (MPN) supported TEMPO showed a high activity for the oxidation of alcohols in a dichloromethane–water based Montanari system [24–26]. A special chain length adjustable ionic liquid covalently nano-magnetic hydrophobic polymer supported TEMPO was prepared to form a micelle-like architecture and used in the above reaction. The most interestingly, from the aforesaid serial work, it was found that these nanoparticles tethered TEMPO catalysts demonstrated much higher activity than their soluble counterparts in the biphasic Montanari oxidation of alcohols. We also found that a L–L reaction can be accelerated even by unsupported polystyrene nanoparticles. This result directs us to analyze the universal mechanism of this phenomenon. Recently, we established a general strategy to enhance the alcohol oxidation reaction rate in Montanari system by introducing surface wettability tunable magnetic nanoparticles into the biphasic media [27]. Although it was assumed that the reaction enhancement phenomenon could be ascribed to a formation of Pickering emulsion and possible enrichment of reactants around the catalyst, the definite mechanism of the enhanced reaction is not quite clear.

In this work, we compared three reaction enhancement strategies to understand how nanoparticles intensify a biphasic Montanari oxidation reaction in view of mass transfer. Over the past 20 years, chemoselective oxidation of alcohols to carbonyl compounds is a kind of typically important reaction by using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as an efficient catalyst, NaClO as a oxidant and NaBr as a cocatalyst. It is a typical liquid–liquid (L–L) biphasic reaction in which the NaClO and NaBr exist in water phase and the substrate alcohol is dissolved in oil phase. For comparison, the Montanari oxidation reactions with or without the addition of magnetic polymer nanoparticles (MPN) or phase transfer catalyst (PTC) were depicted according to classic fluid and reaction equations. It should be noticed that the magnetic polymer nanoparticles (MPN) forming Pickering emulsion mechanism to intensify L–L reaction is universal and not limited to this report.