Microemulsions for CO_2 Reduction

Deutsche Ausgabe: DOI: 10.1002/ange.201608695
Internationale Ausgabe: DOI: 10.1002/anie.201608695

Water-in-Supercritical CO_2 Microemulsion Stabilized by a Metal Complex

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Abstract: *Herein we propose for the first time the utilization of a metal complex for forming water-in-supercritical CO_2 ($scCO_2$) microemulsions. The water solubility in the metal-complex-stabilized microemulsion is significantly improved compared with the conventional water-in-$scCO_2$ microemulsions stabilized by hydrocarbons. Such a microemulsion provides a promising route for the in situ CO_2 reduction catalyzed by a metal complex at the water/$scCO_2$ interface.*

Carbon dioxide (CO_2) is the second most abundant solvent on earth after water.[1] Supercritical CO_2 ($scCO_2$) is generally regarded as a green solvent because it is readily available, inexpensive, nontoxic, nonflammable, has adjustable properties, and excellent mass transfer characteristics, and can be easily recaptured and recycled after use.[2] However, $scCO_2$ is a good solvent for many low polar substances and often a poor solvent for polar substances, because it has no dipole moment, very low dielectric constant, and low polarizability per volume, which restrict its applications in various fields. To form water-in-$scCO_2$ microemulsions with the assistance of emulsifiers allows the solubilization of different kinds of compounds within the dispersed phase and continuous phase, which can largely expand the utility of CO_2 in chemical reactions,[3] material synthesis,[4] and extraction.[5] The design of amphiphilic (CO_2-philic and hydrophilic) emulsifiers is crucial for the formation of water-in-$scCO_2$ microemulsions. Johnston and co-workers first reported the water-in-$scCO_2$ microemulsions in 1996, by utilizing a nontoxic ammonium carboxylate perfluoropolyether surfactant.[6] Since then, many microemulsifiers have been developed for the formation of water-in-$scCO_2$ microemulsions, including polymeric surfactants,[7] fully or partially fluorinated hydrocarbons,[8] and surfactants with specially designed molecular structures (e.g. double or trichain anionic surfactants).[9]

CO_2 has been regarded as an important carbon source for chemical synthesis, which is an ecologically and economically valuable solution to solve the problems of global warming and energy shortage.[10] To convert the thermodynamically stable and comparatively unreactive CO_2 molecules into energy rich and useful chemicals is quite a challenge. Among the diverse research in this area, the light driven CO_2 reduction catalyzed by photocatalyst (e.g. semiconductor,[11,12] graphitic carbon nitride,[13] transition-metal complex,[14] metal–organic framework[15]) under ambient conditions has great potential.[11] Generally, the photocatalytic reactions for CO_2 conversion are carried out in bulk solvent (e.g. acetonitrile or dimethyl formamide) and gaseous CO_2 at atmosphere is employed.

Herein we demonstrate for the first time that a metal complex favors the formation of water-in-$scCO_2$ microemulsions. In comparison with the conventional hydrocarbon emulsifiers, the water solubility in the metal-complex-stabilized microemulsion is greatly improved. More interestingly, such a microemulsion provides a novel route for the in situ CO_2 reduction photocatalyzed by a metal complex at the water/$scCO_2$ interface. This approach offers many advantages. First, the strategy is very efficient because the metal complex increases the interfacial area between both phases and promotes mass transfer. Second, the photocatalytic activity is tunable by adjusting the water content. Third, the product is easily separated since CO_2 can be removed by depressurization and no solvent is involved.

$Fe(tmhd)_3$ (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionato) was utilized as the stabilizer for microemulsion formation, which is highly soluble in $scCO_2$.[16] The phase behavior of the $H_2O/Fe(tmhd)_3/CO_2$ system was observed at different pressures and temperatures. The cloud-point pressure (P_c) is denoted as the minimum pressure at which the $H_2O/Fe(tmhd)_3/CO_2$ system keeps in one phase region. Figure 1 shows the dependence of P_c on the molar ratio of water to metal complex (W_0). It is well established that a small amount of water can be solubilized in continuous CO_2.[17] For example, the water solubility in pure CO_2 is 0.00361 $g\,L^{-1}$ at 10 MPa and 305.2 K,[18] which is 1 over 511 with respect to the

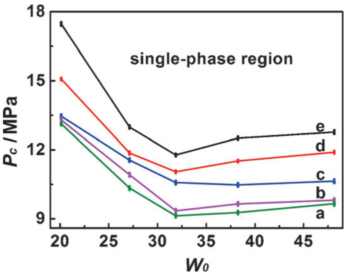

Figure 1. Dependence of the P_c of the $H_2O/Fe(tmhd)_3/CO_2$ system on W_0 at 305.2 K (a), 308.2 K (b), 313.2 K (c), 318.2 K (d), and 325.2 K (e). The concentration of $Fe(tmhd)_3$ is 2.273 $g\,L^{-1}$.

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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201608695.

amount of solubilized water in $Fe(tmhd)_3/CO_2$ system at the same pressure and temperature. Therefore, the amount of water solubilized in continuous CO_2 phase of $H_2O/Fe(tmhd)_3/CO_2$ system can be neglected. It indicates that a large amount of water is solubilized inside the reverse micelles formed by $Fe(tmhd)_3$, confirming the formation of water-in-$scCO_2$ microemulsion. The microemulsion with a W_0 value of 48 was achieved at 9.60 MPa and 305.2 K, meaning that 48 water molecules can be microemulsified by one $Fe(tmhd)_3$ molecule. For the reported water-in-$scCO_2$ microemulsions stabilized by conventional hydrocarbons (even fluorinated surfactant), the W_0 values are usually lower than 40,[6–9] except one report by Liu and Erkey.[8b] They prepared a water-in-$scCO_2$ microemulsion with a W_0 value up to 42 by utilizing a fluorinated surfactant $ROOCCH_2CH(SO_3Na)COOR$ ($R = F(CF_2)_6CH_2CH_2$) at 299 K, for which pressure as high as 37 MPa was required.[8b]

Herein, by using $Fe(tmhd)_3$, a microemulsion with a larger amount of water ($W_0 = 48$) can be formed, while the microemulsifying pressure is greatly lowered (9.60 MPa). Owing to the high water solubility, non-fluorinated and metal-containing character, $Fe(tmhd)_3$ is attractive for forming water-in-$scCO_2$ microemulsions, which may find special applications in chemical reactions and material synthesis. A detailed comparison on the water solubilities in the $scCO_2$-continuous microemulsions stabilized by the metal complex used in this work and hydrocarbons reported in literature is shown in Table S1 of the Supporting Information.

As shown in Figure 1, the P_c value first decreases with increasing W_0 and then slightly increases after passing through a minimum value. For the conventional CO_2-continuous microemulsions stabilized by surfactants,[19] the P_c monotonously increases with the increasing water content because a higher density of CO_2 is needed to form the microemulsions for solubilizing the internal phase.[20] The possible mechanism for this abnormal phenomenon will be discussed in following. Figure 1 also shows that at a fixed W_0 the P_c value increases with increasing temperature, which can be attributed to the decreased density of CO_2 at higher temperatures.[21]

The microstructures of the water-in-$scCO_2$ microemulsions stabilized by $Fe(tmhd)_3$ were investigated by synchrotron radiation small-angle X-ray scattering (SAXS) technique.[22,23] After subtracting the scattering from the high-pressure cell (Figure S1), the SAXS curves of the water-in-$scCO_2$ microemulsions stabilized by $Fe(tmhd)_3$ with different W_0 values at 15.00 MPa and 305.2 K were obtained (Figure 2). The relative intensity (I) of SAXS curves shifts to low scattering wavevector (q) with increasing W_0 values of microemulsions, indicating that the reverse micelles are enlarged gradually.[24] From the distance distribution function $P(r)$ curves, the diameter of the reverse micelles were determined to be 11.2, 13.1, 14.3, 14.6, and 15.2 nm for the microemulsions with W_0 values of 22, 25, 28, 33, and 45, respectively. Clearly, the size of reverse micelles increases with increasing W_0 value, which is similar to the results of water-in-$scCO_2$ microemulsions stabilized by hydrocarbon surfactants. It can be attributed to the micelle expansion caused by the solubilization of more amount of water inside the reverse micelles.

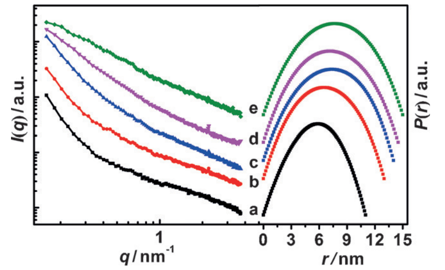


Figure 2. SAXS curves and the corresponding distance distribution curves of the water-in-$scCO_2$ microemulsions stabilized by $Fe(tmhd)_3$ with W_0 values of 22 (a), 25 (b), 28 (c), 33 (d), and 45 (e) at 15.00 MPa and 305.2 K.

The micropolarity of the nanosized water domain in water-in-$scCO_2$ microemulsions stabilized by $Fe(tmhd)_3$ was investigated by UV/Vis method using methylene blue (MB) as a probe.[25] MB is hydrophilic and can be well solubilized in water. No absorption was observed for the UV/Vis spectrum of MB in the $Fe(tmhd)_3/CO_2$ system (curve a in Figure 3), which can be ascribed to the absence of a water domain and confirms that $Fe(tmhd)_3$ exists in the form of single molecules. For the water-in-$scCO_2$ microemulsions with W_0 values of 22, 32 and 38, the maximum absorption wavelengths (λ_{max}) of MB center at 658.0 nm, 659.5 nm and 662.5 nm, respectively (Figure 3 curves b–d), confirming the existence of water domain in which MB molecules reside. Clearly, the λ_{max} of MB in microemulsion is red-shifted with the increasing W_0 value. Because the λ_{max} of MB is red-shifted with increasing polarity of microenvironment (Figure S2), such a red shift of λ_{max} of MB with increasing W_0 indicates the increased micropolarity of the nanosized water domain in microemulsion. This behavior is similar to those of the water-in-$scCO_2$ microemulsions stabilized by conventional hydrocarbons.[9a,20,22] The λ_{max} values of MB in the microemulsions are lower than that in bulk water (664.0 nm, Figure 3 curve e), suggesting that the micropolarities of the water domains in microemulsions are lower than that of bulk water.

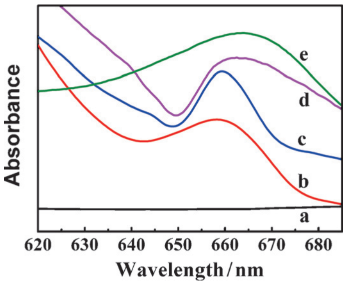


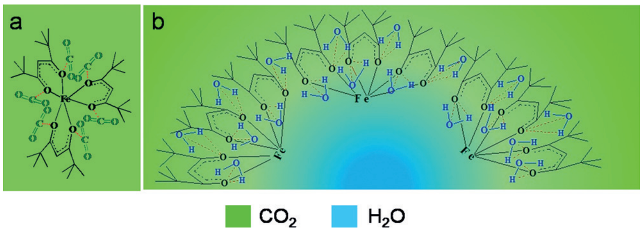
Figure 3. UV/Vis spectra of the $Fe(tmhd)_3/CO_2/MB$ system (a), $H_2O/Fe(tmhd)_3/CO_2/MB$ microemulsions with W_0 of 22 (b), 32 (c) and 38 (d) at 15.00 MPa, and the H_2O/MB system (e). The temperature is 305.2 K.

The above results show that $Fe(tmhd)_3$ is superior to hydrocarbons in producing water-in-$scCO_2$ microemulsions due to high water capacity at low pressure. The formation mechanism for the $Fe(tmhd)_3$-stabilized water-in-$scCO_2$

microemulsion was investigated by FT-IR spectra, which provides information on intermolecular interactions.[26] In the water-free $Fe(tmhd)_3/CO_2$ binary system, there is a strong absorption at 1728 cm^{-1} (Figure S3). It corresponds to the Lewis acid–Lewis base (LA–LB) interaction between CO_2 (as the LA) and the carbonyl group of $Fe(tmhd)_3$ (as the LB group), which has been widely utilized for the design of CO_2-philic materials.[27] Interestingly, this absorption disappears for the water-in-$scCO_2$ microemulsion, implying the breakage of the LA–LB interaction between CO_2 and $Fe(tmhd)_3$. Meanwhile, the absorption around 3500–3700 cm^{-1} moves to lower wavenumber. It indicates the formation of hydrogen bonding interactions between water and the carbonyl oxygen atom of $Fe(tmhd)_3$,[28] which may be the driving force for the reverse micelle formation.[29]

The possibilities of other metal complexes stabilizing water-in-$scCO_2$ microemulsions were investigated, that is, iron(III) acetylacetonate ($Fe(acac)_3$), $Zn(tmhd)_2$, and ferrocene (see their molecular structures in Figure S4). $Fe(acac)_3$ and $Zn(tmhd)_2$ can microemulsify $scCO_2$ and water well. The maximum W_0 values of the microemulsions stabilized by $Fe(acac)_3$ and $Zn(tmhd)_2$ at approximately 9.35 MPa and 305.2 K can reach 39 and 24, respectively (Table S1), which are comparable to or lower than that of $Fe(tmhd)_3$ at the same pressure and temperature ($W_0 = 41$). It can be attributed to the more carbonyl groups in molecules of $Fe(tmhd)_3$ and less carbonyl groups of $Zn(tmhd)_2$. Ferrocene, which can be well solubilized in $scCO_2$[16] but cannot form hydrogen bond with water, failed to microemulsify $scCO_2$ with a small amount of water ($W_0 = 6$) at 10 MPa and 305.2 K. These results further confirm that the hydrogen-bonding interactions between the metal complex and water play a key role to promote the formation of water-in-$scCO_2$ microemulsion.

Based on the above results, a mechanism for the formation of water-in-$scCO_2$ microemulsion stabilized by metal complex is proposed. In absence of water, $Fe(tmhd)_3$ exists in $scCO_2$ as monomers and interacts with CO_2 molecules through LA–LB interaction (Scheme 1 a). With the addition of a small amount of water, the CO_2 molecules that interact with $Fe(tmhd)_3$ are replaced by water molecules due to the stronger hydrogen-bonding interactions between water and $Fe(tmhd)_3$, as evidenced by FT-IR spectra. There are multiple hydrogen-bonding sites on the ligand and water may act as "glue" to bond the $Fe(tmhd)_3$ chains together, driving the aggregation of $Fe(tmhd)_3$ molecules into reverse micelles.[29] The CO_2-philic groups (tri-methyl chains) point outside of the reverse micelles, and the CO_2-phobic sites (metal ions) are inside of the reverse micelles (Scheme 1 b). Therefore, the small amount of water promotes the reverse micelle formation, resulting in the decrease of P_c with increasing water content at the beginning stage shown in Figure 1.[30] At higher water content, more and more water molecules are present in free form and a water nanodomain is created to produce water-in-$scCO_2$ microemulsion. At this stage, the P_c increases with the increasing water content because a higher density of CO_2 is needed for solubilizing the internal phase (Figure 1).[20]



Scheme 1. The formation of water-in-$scCO_2$ microemulsion stabilized by $Fe(tmhd)_3$. a) $Fe(tmhd)_3$ monomer solubilized in $scCO_2$; b) $Fe(tmhd)_3$ monomers assemble into a reverse micelle on the addition of water.

The water-in-$scCO_2$ microemulsion stabilized by a metal complex provides a promising route for chemical reaction and nanomaterials synthesis. Herein we propose the in situ photocatalytic reduction of CO_2 to give formic acid in the microemulsion by utilizing $Fe(tmhd)_3$ as both a stabilizer for the microemulsion and a catalyst for CO_2 conversion (Figure 4 A). With triethanolamine (TEOA) as the sacrificial electron donor,[15] a Xe lamp simulating natural sunlight was turned on to start the photoreaction for 12 h. The product was analyzed by high-performance liquid chromatography and ^1H NMR spectra (Figure S5 and S6). The number of molecules of substrate transformed in unit mole of active site of catalyst is denoted as turnover number (TON).

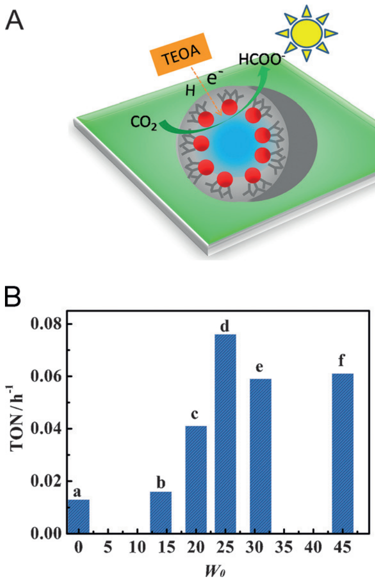


Figure 4. A) Photocatalytic CO_2 reduction in the water-in-$scCO_2$ microemulsion. B) Amount of formic acid produced in the $Fe(tmhd)_3/CO_2$ system (a), $H_2O/Fe(tmhd)_3/CO_2$ system (b), and water-in-$scCO_2$ microemulsions with different W_0 values (c–f). The pressure is 13.50 MPa.

In the water-free $Fe(tmhd)_3/CO_2$ system or the $H_2O/Fe(tmhd)_3/CO_2$ heterogeneous system with W_0 of 14 at 13.50 MPa, only a small amount of formic acid was produced (a and b in Figure 4 B). Interestingly, there is a remarkable improvement for the TON once the water-in-$scCO_2$ microemulsion is formed (c–f in Figure 4 B). The TON increases with the increasing W_0 value of the water-in-$scCO_2$ microemulsion and reaches a maximum 0.076 h^{-1} at $W_0 = 25$, which is almost five-times higher than that obtained from Fe(tmhd)$_3$/CO$_2$ system (TON = 0.013 h^{-1}). It can be attributed to the large number of interfaces provided by the microemulsion, which promote the contact between the components and enhances mass transfer, thus improving the reaction efficiency.[31] After passing through the maximum, the TON drops with increasing water content. The bell-shaped curve of TON with W_0 value is similar to that of the biocatalysis proceeding in water-in-oil microemulsion and the drop of the TON at higher W_0 value may be mainly caused by the more hydration of Fe(tmhd)$_3$.[32] In addition, since the light scattering is more significant for larger micelles, it is expected that the efficiency of the photocatalytic reaction would drop at higher W_0 value because less light can reach the metal complex. The TON for formic acid produced in the water-in-scCO$_2$ microemulsion is higher than or comparable to those photocatalyzed by MIL-101(Fe) or functionalized NH$_2$-MIL-101(Fe) using acetonitrile as solvent (0.016 h^{-1} and 0.050 h^{-1}, respectively).[33]

To confirm the reaction efficiency in the water-in-scCO$_2$ microemulsion, some comparison experiments were carried out. First, a normal water-in-octane microemulsion ($W_0 = 25$) stabilized by Fe(tmhd)$_3$ was prepared and applied for the photocatalytic reduction of CO$_2$, where CO$_2$ was bubbled into the reaction system. The TON to give formic acid is 0.0037 h^{-1}, which is rather smaller than that of the water-in-scCO$_2$ microemulsion with the same W_0 values (0.076 h^{-1}). It indicates that the high-density CO$_2$ is favorable for promoting the photoreaction. Second, the photocatalytic reduction of CO$_2$ was carried out in the commonly used organic solvent (acetonitrile) using Fe(tmhd)$_3$ as photocatalyst. No formic acid was detected, implying the interfaces are requisite to the photocatalytic reduction. Based on the above results, it can be concluded that the existence of an interface and the high-density CO$_2$ co-contribute to the high reaction efficiency of the photocatalytic reduction of CO$_2$ in the water-in-scCO$_2$ microemulsion.

In conclusion, metal complexes have been found to be efficient in microemulsifying scCO$_2$ and water to produce water-in-scCO$_2$ microemulsions. The microemulsion stabilized by the metal complex has a great water capacity than the conventional water-in-scCO$_2$ microemulsions stabilized by hydrocarbons. The hydrogen-bonding interactions between the metal complex and water are believed to be the driving force for the formation of the water-in-scCO$_2$ microemulsions. The microemulsion has been applied for the in situ photocatalytic CO$_2$ reduction to give formic acid with high efficiency. The water-in-scCO$_2$ microemulsions stabilized by a metal complex open up promising routes for CO$_2$ transformation into valuable chemicals, controlling chemical reactions, and synthesizing functional materials (e.g. metal–organic frameworks).

Acknowledgements

We thank the National Natural Science Foundation of China (21525316, 21133009, U1232203, 21021003), Chinese Academy of Sciences (QYZDY-SSW-SLH013).

Keywords: CO$_2$ reduction · iron complexes · microemulsions · photocatalysis · supercritical CO$_2$

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 13533–13537
Angew. Chem. **2016**, *128*, 13731–13735

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Received: September 6, 2016