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Short Communication

Temperature-induced hydrophobicity transition of MXene membrane for directly preparing W/O emulsions

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ABSTRACT

Although hydrophilic membranes are desired for reducing resistance to water permeation, hydrophilic surfaces are not used in the water-in-oil (W/O) membrane emulsification process because water spreads on the hydrophilic surface without forming droplets. Here, we report that a hydrophilic ceramic membrane can form a hydrophobic interface in diesel at a higher temperature; interestingly, the experiments show that the contact angle increases when the temperature rises. The hydrophilic membrane surface evolves into a hydrophobic interface, particularly near the boiling point of water, resulting in a water contact angle of 147.5° ± 1.2°. This work established a method for preparing W/O monodispersed emulsions by direct emulsification of hydrophilic ceramic membranes at a temperature close to the boiling point of water. Additionally, it made high flux of membrane emulsification of monodispersed W/O emulsions possible, which satisfied the industrial requirements of fluidized catalytic cracking in the petrochemical industry.
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Membrane emulsification (ME) has emerged as a viable option for producing stable monodispersed emulsions due to its low energy consumption, low surfactant content, adjustable emulsion particle size, and narrow distribution [1–3]. The ceramic membrane has afforded clear advances in the ME field with its high permeability and strong anti-pollution ability [4–6]. Generally, ceramic membranes present a strong hydrophilic surface, which has been widely investigated and applied in preparing oil-in-water (O/W) emulsions [7–9]. The membrane surface needs to be modified to retard the spread of water droplets on the surface of the membrane to prepare monodispersed water-in-oil (W/O) emulsions [2]. According to the previous reports, surface modification of membranes is primarily accomplished using a silane coupling agent and immersing them in oil [10,11]. However, the hydrophobic modification process of the membrane material is complicated, and the flux of the membrane is significantly lower when compared to the original membrane. The Leidenfrost effect has been proven to be a promising application, as it provides a perfect hydrophobic state with little contact with the surface [12–14].

Here, we report an interesting phenomenon. We found that as the temperature increases, the water contact angle on hydrophilic MXene-based ceramic membranes increases. The water droplets on the oil–water–solid interface can produce a Leidenfrost-like effect on the membrane surface [15,16], resulting in a positive hydrophobic effect when the temperature rises [12–14]. A hybrid hydrophobic state has been established on a hot liquid–solid surface, as opposed to classical Leidenfrost droplets. In a high-temperature environment, a thin layer of water vapor film will be produced on the surface [13,14,17], reducing the contact area between the droplet and membrane surface, thereby resulting in a higher wetting angle. As a result, the hydrophobicity transition achieved at high temperatures also suggests a route to using an untreated hydrophilic membrane to directly prepare W/O emulsions.

We designed a liquid–liquid–solid system composed of diesel and an MXene-based ceramic membrane, then a deionized water droplet of 5 μl was dropped on the surface of the MXene-based ceramic membrane at different heating temperatures, as shown in Fig. S1 (in Supplementary Material). The wetting angle of the MXene-based ceramic membrane correspondingly increases when the simulated system temperature rises, as shown in Fig. 1(a). It is interesting to note that under simulated conditions of 90 and 100 °C (as shown in Fig. S2), the hydrophobicity of the MXene-based ceramic membrane in diesel remains stable, which is mostly reflected in the constant value of contact angles, 128° ± 1.2° and 148° ± 1.2°, respectively. As shown in Fig. 1, the droplets exhibit hydrophilicity at a low-temperature surface, but as the surface temperature increases, the wetting state of the droplets first

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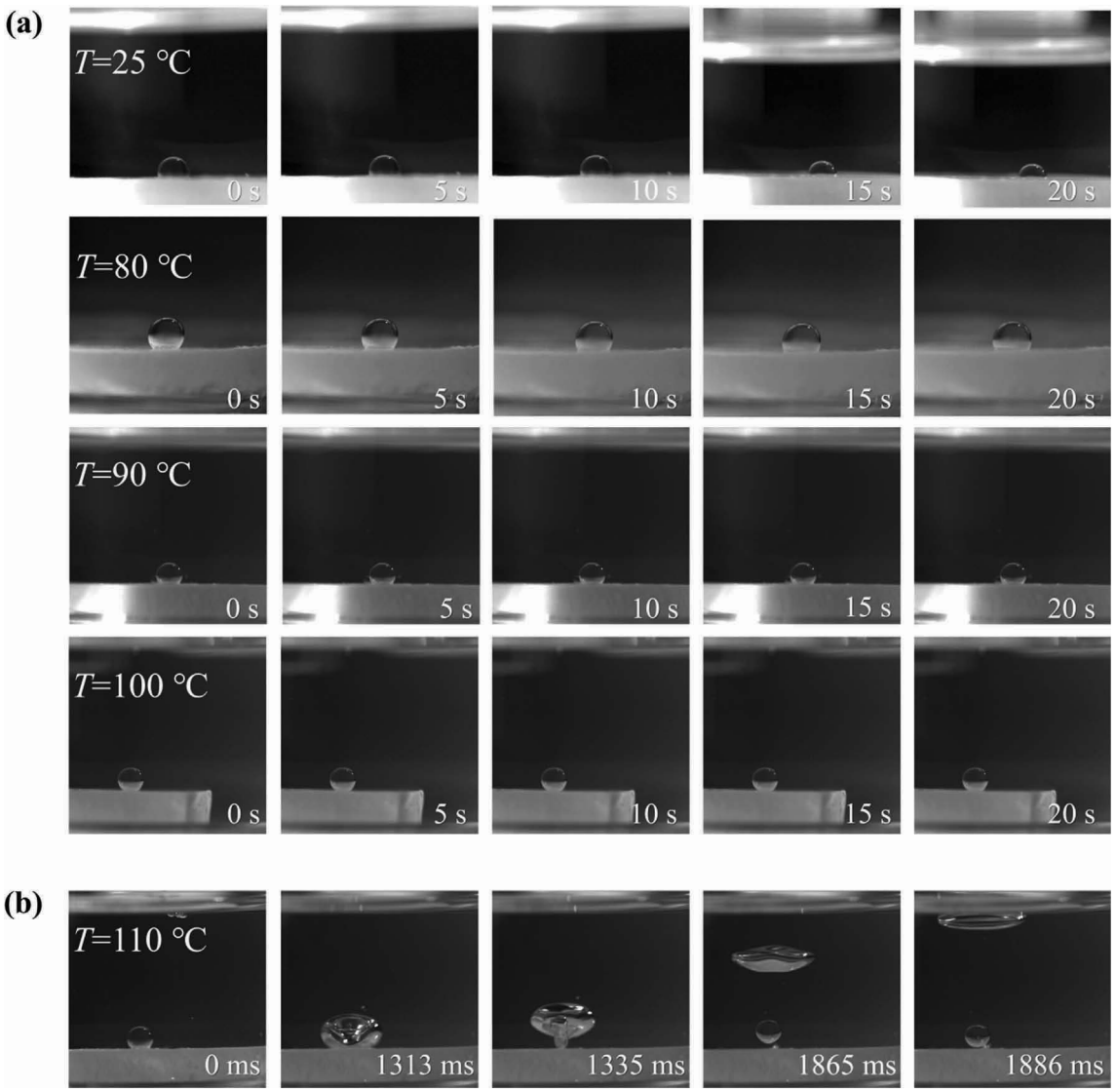

Fig. 1. (a) A sequence of images of water contact angle of the oil–MXene-based interface at temperatures below the water boiling point. (b) A series of representative snapshots taken from the side shows the diffusion and boiling processes of the droplet in the oil–MXene-based interface above the water boiling point.

changes to a transitional non-wetting state. When the temperature of the oil–MXene-based interface is higher than the boiling point of water, the water droplets change to a film boiling state. This phenomenon may be attributed to the membrane exhibiting hybrid hydrophobic in the high-temperature liquid–solid system due to the formation of vapor film beneath the drop [18,19]. Additionally, when the temperature is high enough (>110 °C, as shown in Fig. 1 (b)), a complete vapor layer will be produced, which is manifested as the complete separation of the liquid droplets from the solid membrane surface. The water droplets on the oil–water–solid interface in the experiment are similar to the classic Leidenfrost phenomenon. The difference is that the transition observed at a superheated temperature is significantly lower than the classic Leidenfrost phenomenon.

A feasible mechanism according to the above tests is shown in Fig. 2. At low temperatures, the gravity of the water drop is greater than the buoyancy, and the water drop settles on the surface of the membrane. Due to the hydrophilic nature of MXene-based ceramic membrane, water droplets in the system will spread after passing through the membrane, resulting in coalescence between adjacent water droplets. At high temperatures, the partial vaporization of water droplets creates a water vapor layer and the non-wetting state also prevents coalescence between water droplets. The contact angle of a single water droplet in an MXene-based ceramic membrane is mainly affected by three interfacial tensions: water–oil interfacial tension, water–solid interfacial tension, and oil–water interfacial tension. According to Young's equation, the contact angle θ of water droplets on the membrane surface can be expressed as:

$$\cos\theta = \frac{\delta_{so} - \delta_{sw}}{\delta_{wo}}$$

where δ_{so} represents the solid–oil interfacial tension, δ_{sw} represents the solid–water interfacial tension, and δ_{wo} represents the water–oil interfacial tension.

Generally, as the surface temperature increases, the surface tension of the liquid decreases, and the wettability is expected to improve [19]. However, in our experiment, the water droplets on the oil–water–solid interface heated to near water boiling temperature can sustain contact angles as high as 148° ± 1.2° (Fig. 1(a)), the reason for which is that as the temperature of the droplet rises, partial vaporization occurs on its surface, resulting in a thin vapor

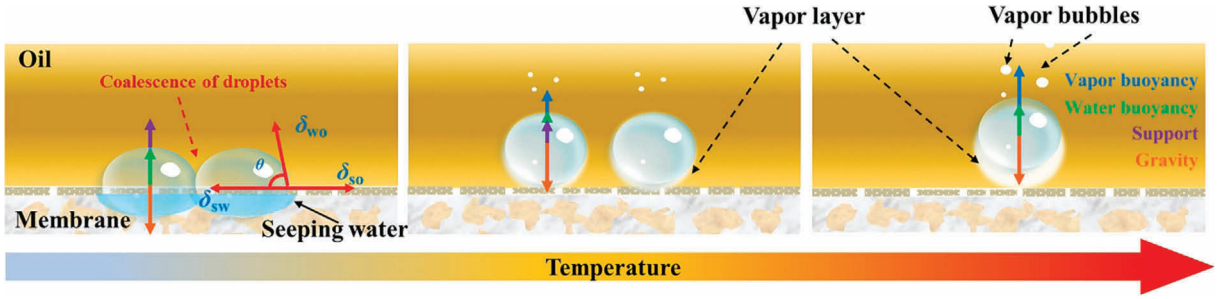

Fig. 2. Schematic of water droplet behavior on the oil–MXene-based interface when the temperature rises to a high temperature environment.

layer. The vapor layer will adhere to the surface of the droplet. When these spontaneous vapor layers are sufficient to overcome the capillary pressure and gravity of the droplets themselves [12], the contact between the droplet and membrane surface is reduced. It is most frequently manifested as a sudden increase in the contact angle. When the temperature reaches 100 °C, the thickness of the vapor layer on the surface of the water droplet reaches a critical value as the droplet vaporization rate gradually increases. The contact angle of the water droplet with the membrane surface reaches the maximum value of 147.5° ± 1.2° at this point. When the temperature reaches 110 °C, it exceeds the boiling point of water. At 1313 ms, the surface of the water droplet rapidly vaporizes, generating enough buoyancy that is greater than the gravity of the droplet [20]. It lifts the droplet for a short distance and then falls off at 1865 ms. At this point, the droplet begins to split into two parts: one is lifted out of the oil phase, while the other is deposited on the membrane surface to form a new vapor layer.

Our previous work has concluded that hydrophobic MXene-modified membranes are more conducive for preparing the monodisperse submicron W/D emulsions because 2D nanochannels can prevent the coalescence of emulsifiers [2]. The above experiments reveal that the temperature-induced oil–MXene-based interface exhibits hybrid hydrophobic phenomena. This liquid–liquid–solid system also exists in the membrane emulsification process. Based on that, we designed the high-temperature direct membrane emulsification to prepare the monodisperse W/O emulsions with hydrophilic MXene-based ceramic membranes. The schematic diagram of the experiments is shown in Fig. S2. Specifically, the W/O emulsions were prepared using a hydrophilic MXene-based ceramic membrane with a pore size of ~ 12.9 nm (a detailed description of the MXene-based ceramic membrane preparation method has been provided in Figs. S4–S6), diesel as the continuous phase, and deionized water as the dispersed phase. Tubular MXene-based ceramic membranes were placed in a stainless steel membrane module where the membrane emulsification took place. In the process of the ME experiment, the continuous phase (diesel phase) circulates inside the ME device through the peristaltic pump device. The use of a peristaltic pump can avoid the continuous agitation of the continuous phase in the pipeline, thus affecting the stability of the prepared emulsion. Simultaneously, the disperse phase (water phase) passed through the MXene-based membrane by a plunger pump. The leakage of liquid

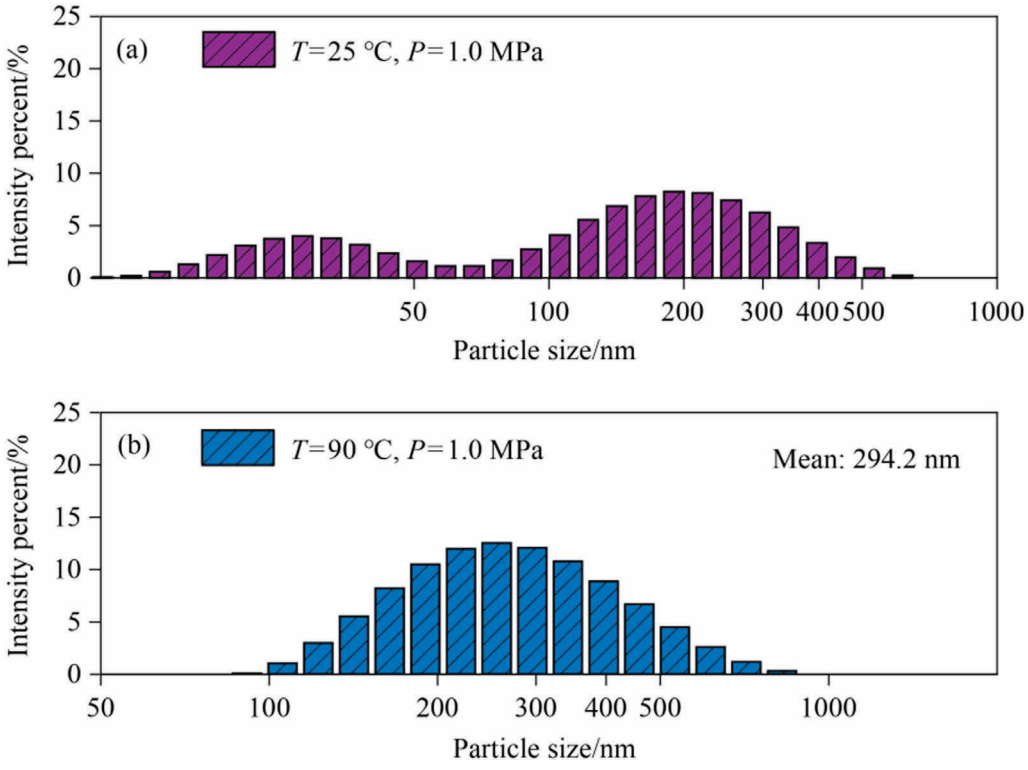

Fig. 3. Droplet size distributions for water-in-oil emulsions obtained by direct membrane emulsification using MXene-based ceramic membrane at (a) T = 25 °C, P = 1.0 MPa; (b) T = 90 °C, P = 1.0 MPa.

and gas should be avoided during the entire experiment. Compared with the emulsion prepared using conventional ME at room temperature (25 °C), the heating temperature of the emulsion prepared using the direct ME method was selected at 90 °C. If the water boiling point temperature is used for a long time to perform the ME process, the water phase will gradually evaporate, which is not conducive to the formation of monodisperse W/O emulsion.

Afterward, the emulsion prepared using a direct hydrophilic ceramic membrane was compared at high temperature (90 °C) and room temperature (25 °C) under the same operating pressure. The particle size and dispersion of the W/O emulsions produced at the above two temperatures were measured using a Malvern Zetasizer Nano Series (Nano ZS90, Malvern Instruments, UK). The emulsions prepared using ME at room temperature (25 °C) and high temperature (90 °C) show bimodal (Fig. 3(a)) and unimodal distributions (Fig. 3(b)), respectively. Correspondingly, the intensity percentage function curves (Fig. 3(b)) show an excellent unimodal distribution (polydispersity index = 0.252). This is mainly because the W/O emulsions are prone to coalescence on the surface of the hydrophilic MXene-based ceramic membrane during the conventional membrane emulsification process at room temperature, and it exhibit a bimodal distribution. When the temperature reached 90 °C, the unique hybrid hydrophobic phenomenon in the liquid–liquid–solid system effectively prevented droplets coalescence. Therefore, the particle size of the W/O emulsion exhibits a unimodal distribution. It is clearly illustrated in Fig. 3(b) that the emulsion obtained by the high-temperature (90 °C) ME process had a relatively narrow particle size distribution, with a mean particle size of 294.2 nm.

In summary, a hydrophobicity transition of hydrophilic ceramic membranes in high-temperature oil has been reported. When the temperature of the liquid–solid system reaches 90 °C and 100 °C, deionized water droplet shows a Leidenfrost-like effect at the liquid–solid interface, and the water contact angle on the membrane surface reaches 128° ± 1.2° and 148° ± 1.2°, respectively. This strategy was used to study the difference between the ME at room temperature (25 °C) and high temperature (90 °C). It was concluded that high-temperature ME was preferable for producing monodisperse emulsions. Additionally, the method proposed in this study has a promising advantage, wherein it satisfies the industrial requirements for fluidized catalytic cracking in the petrochemical industry in practice.

CRediT Authorship Contribution Statement

Yingxiang Ni: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Can Yuan:** Methodology, Resources, Data curation, Writing – original draft, Validation. **Shilong Li:** Methodology, Resources, Formal analysis. **Jian Lu:** Investigation, Validation, Formal analysis. **Lei Yan:** Methodology, Formal analysis, Investigation, Writing – review & editing. **Wei Gu:** Methodology, Formal analysis, Validation. **Weihong Xing:** Resources, Supervision, Project administration, Funding acquisition. **Wenheng Jing:** Conceptualization, Writing – review & editing, Resources, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cjche.2022.05.006.

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