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Nanoparticle cages as microreactors for producing acrolein from glycerol in the liquid phase<sup>†</sup>

Jiaojiao Zhang,‡<sup>ab</sup> Jie Zhao,‡<sup>c</sup> Xiaojing Cui,<sup>bd</sup> Xianglin Hou,<sup>ab</sup> Lijuan Su,<sup>ab</sup> Hongliang Wang<sup>e</sup> and Tiansheng Deng<sup>®</sup>\*<sup>ab</sup>

Liquid phase dehydration of glycerol to acrolein commonly suffers from a low acrolein yield because of severe side reactions of chemically active acrolein with itself or glycerol in the reaction system. Rapid separation of acrolein from the reaction system is one of the effective strategies to increase the yield of acrolein. Herein, a renewable water-in-oil Pickering emulsion with silica nanoparticle cages as microreactors was designed for liquid phase glycerol dehydration to acrolein. The influences of the oil phase types on the droplet size of the Pickering emulsion and the yield of acrolein were investigated in a microreactor. The smaller Pickering emulsion droplet showed a superior ability to intensify the separation of chemically unstable acrolein molecules from the nanoparticle cages and thus improved the yield of acrolein. A droplet size of about 11 µm was obtained with peony seed oil as the oil phase, in which 84.6% of acrolein yield was achieved.

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## 1. Introduction

With the development of green chemistry and the consumption of fossil energy, biomass has been widely used as a renewable alternative and a sustainable resource for the production of biofuels, materials and chemicals.<sup>1</sup> Glycerol, as the main byproduct in a biodiesel production process, accounts for 10 wt% of biodiesel.<sup>2</sup> With the increase of annual biodiesel production, the price of glycerol decreased continuously due to the increase of glycerol production. Therefore, the development and utilization of glycerol can not only solve the problem of glycerol surplus, but also increase the market competitiveness of biodiesel.<sup>3</sup> The conversion of glycerol to high-value-added fine chemicals, such as acrolein, glyceric acid, lactic acid, hydroxyacetone and so on, has been a great concern.<sup>4–9</sup> Among the



The liquid phase glycerol dehydration to acrolein is mainly conducted in sub- or supercritical water systems under the reaction conditions of 250-400 °C and 25-35 MPa and with ZnSO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, and WO<sub>3</sub>/TiO<sub>2</sub> as catalysts, affording an acrolein yield of 40-70%.<sup>12-14</sup> The extremely high temperatures and pressures make the industrial production difficult. Though mild reaction conditions were studied, the obtained acrolein yield was low.<sup>15,16</sup> It is highly desirable to design efficient liquid phase systems for obtaining a high acrolein yield under mild conditions. Because acrolein molecules are highly chemically active and can easily form humus with themselves or glycerol molecules under reaction conditions, their rapid separation from the liquid phase system is crucial to suppress the side reactions. However, the high viscosity of glycerol inevitably slows down the diffusion of acrolein drastically out of the reaction system, which aggravates the occurrence of side reactions and thus is detrimental to the acrolein yield. Therefore, the key to increase the acrolein yield is to separate the generated acrolein as soon as possible.

To enhance the separation efficiency of the produced acrolein, there is a need to (1) shorten the separation path of acrolein and (2) increase the separation area of acrolein, such as by forming an emulsion. However, forming emulsion

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<sup>&</sup>lt;sup>a</sup> Shanxi Engineering Research Center of Biorefinery, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001, China. E-mail: dts117@sxicc.ac.cn

<sup>&</sup>lt;sup>b</sup> Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

<sup>&</sup>lt;sup>c</sup> Institute of Coal Chemistry,

Chinese Academy of Sciences, Taiyuan 030001, China

<sup>&</sup>lt;sup>d</sup> State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001, China

<sup>&</sup>lt;sup>e</sup> Center of Biomass Engineering/College of Agronomy and Biotechnology, China Agricultural University, Beijing, 100193, China

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<sup>‡</sup> These authors contributed equally to this work.

#### Paper

needs addition of some surfactants, which are chemically active additives so that they have an adverse effect on the production of acrolein from glycerol. Pickering emulsion that does not need surfactants is an excellent emulsion stabilized by solid nanoparticles.<sup>17,18</sup> The nanoparticles in a Pickering emulsion can form nanoparticle cages as microreactors, not only sharply shorten the single reactor scale, but the large contact area of the water and oil phases will be realized to accelerate obviously the mass transfer between the two phases.<sup>19</sup>

In our previous work, a water/oil Pickering emulsion with a smallest droplet size of 30  $\mu$ m was developed for producing acrolein from glycerol in the liquid phase.<sup>20</sup> Compared with the conventional aqueous reaction system, the mass transfer intensification of Pickering emulsions promoted the acrolein yield from a low value of 20% to a moderate value of 48%. Noticeably, this yield was obtained with a 100% conversion of glycerol, indicating the presence of acrolein side reactions. Hence, it is still troublesome to suppress largely the side reactions of acrolein to obtain a high acrolein yield.

The generated acrolein diffused from the microreactor into the oil phase of the Pickering emulsion is shown in Scheme 1. The acrolein generated by the reaction inside the droplet entered the oil phase through the oil-water interface, and then entered the gas phase through the oil-air interface, and was condensed and collected by a condenser. In this process, the entry of acrolein from the water phase into the oil phase was the key to improving the reaction effect. There was no real diffusion equilibrium state in the actual reaction process, but research on the diffusion behavior of products in the droplet should be carried out in a steady state. In a very short time, the diffusion of acrolein through the oil-water interface and the oil-gas interface can be considered to be in a steady state. Therefore, according to Fick law, the diffusion flux of acrolein diffusing into the oil phase in the droplet is:

$$J_{\rm A} = -D_{\rm AW} \frac{{\rm d}C_{\rm A}}{{\rm d}r} \tag{1}$$

the diffusion flux of acrolein can be obtained by directly integrating the above formula:

$$J_{\rm A} = \frac{D_{\rm AW}}{r} (C_{\rm AI} - C_{\rm AO}) \tag{2}$$

where  $J_A$  means the diffusion flux of acrolein. The direction of  $J_A$  is opposite to the concentration gradient, so a minus sign is



Scheme 1 Schematic diagram of the generation and transfer path of acrolein in the Pickering emulsion.

added on the right of the formula (1). The higher the value of  $J_A$ , the faster the diffusion rate. DAW represents the diffusion coefficients of acrolein in the water phase, whose value is constant at a specific temperature and pressure.  $C_{AI}$  and  $C_{AO}$ mean the concentration of acrolein inside and outside of the droplet, respectively. The difference between  $C_{AI}$  and  $C_{AO}$  is mainly determined by the amount of acrolein produced upon the dehydration of glycerol in the droplet. The amount of produced acrolein is the same at the same time interval under fixed reaction conditions (such as temperature, pressure, catalyst, etc.). r is the radius of the droplet. A smaller r caused a bigger  $J_A$ , which means the produced acrolein can diffuse rapidly outside the droplet. Thus, a reduction of the droplet radius can improve the diffusion efficiency of acrolein, which effectively inhibited the side reactions and improved the yield of acrolein. Hence, the fabrication of emulsion systems with droplets of small size would favor a high acrolein yield.

However, it remains a great challenge to prepare small-sized emulsion systems. A common method to produce small-sized Pickering emulsions is to add organic surfactants as coemulsifiers to stabilize the emulsions.<sup>21-23</sup> However, the introduction of typical organic surfactants in a Pickering emulsion is troublesome for the separation and recycling of the emulsifiers. Moreover, auxiliary surfactants have a deleterious effect on the active substances, especially for the enzyme catalysts. To overcome this problem, an efficient strategy was developed by T. Ngai and co-workers, in which the Pickering emulsion was pretreated with tetraethyl orthosilicate to prepare a submicronsized emulsion by alkali treatment.24 However, the presence of base is detrimental to the acid-catalyzed reaction systems. More importantly, a common problem with small-sized Pickering emulsions is their poor thermal stability, which are commonly unstable at temperatures above 100 °C.<sup>19,25,26</sup> Thus, the design of a small-sized and thermally stable Pickering emulsion suitable for acid-catalyzed reactions remains a great challenge.

Noticeably, the huge impact of the viscosity of the oil phase on the aqueous droplet size, and further the mass transfer of product(s), was not reported in the studies of water-in-oil Pickering emulsions. In this work, a novel strategy for the fabrication of a small-sized Pickering emulsion system was developed by tuning the viscosity of oil phases. Besides, cycle of the Pickering emulsion was carried out. The average droplet size of the Pickering emulsion decreased from 80 to 10  $\mu$ m upon varying the types of oil phases. Accordingly, the yield of acrolein increased largely from 61.8% to 84.6%, a value much higher than those reported in the liquid phase acrolein production from glycerol under similar reaction conditions.

### 2. Experimental details

#### 2.1. Modification of hydrophilic silica nanoparticles

The commercially available hydrophobic silica, named SN–C, was used directly as an emulsifier without any treatment. Emulsifiers with different surface properties were prepared by silylation of hydrophilic SNs (silica nanoparticles). (MeO)<sub>3</sub> Si(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>, (MeO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>, (MeO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub> and

 $(MeO)_3Si(CH_2)_{15}CH_3$  were applied as silvlation reagents. 1.0 g of hydrophilic SNs were dried at 125 °C for 4 h. The dried SNs were dispersed into 15 mL of toluene. Then 1.0 mmol of the given silvlation reagent (1.5 mmol of  $(MeO)_3Si(CH_2)_2CH_3$ ) was added into the mixture and heated under reflux at 110 °C for 4 h under an N<sub>2</sub> atmosphere. The modified hydrophilic silica nanoparticles were collected by centrifugation. Then, the obtained sample was dried at 80 °C under vacuum for 6 h after being washed with toluene five times. The resulting samples were designated as SN-C<sub>3-1.5</sub>, SN-C<sub>8-1.0</sub>, SN-C<sub>12-1.0</sub> and SN-C<sub>16-1.0</sub>, respectively.

#### 2.2. Preparation of the Pickering emulsion and the reaction

A detailed description of the reaction test runs in this study is provided elsewhere.<sup>20</sup> In brief, in a typical test run, 0.05 mol of KHSO4 as a catalyst was dissolved in 10 mL of 30 wt% glycerol aqueous solution (designated as solution 1) at 80 °C. Then, 20 mL of oil and 3.5 wt% (relative to the volume of the water phase) of the emulsifier (SN–C, SN– $C_{3-1.5}$ , SN– $C_{8-1.0}$ ,  $SN\text{-}C_{12\text{-}1.0}$  or  $SN\text{-}C_{16\text{-}1.0})$  were added to the solution 1. The resulting mixture was strongly stirred at 6500 rpm for 5 min to prepare the Pickering emulsion. Then, the obtained Pickering emulsion was heated promptly to 180 °C for 1 h to evaluate the production of acrolein from glycerol at 1 atm. Notably, the reaction took place in a distillation unit, where acrolein produced in the liquid phase was directly separated from the system by distillation and collected; a schematic diagram of the acrolein formed and diffused in the Pickering emulsion is shown in Fig. 1(A). After the reaction, the conversion of glycerol was almost complete, which was determined by HPLC (high performance liquid chromatography), while the yield of the



Fig. 1 (A) A schematic diagram of acrolein formed in Pickering emulsion and its diffusion path and (B) shows the optical microscopy images (a–d) of decane, hexadecane, ethyl oleate and peony seed oil, respectively. The scale bar is 100  $\mu$ m. The kinematic viscosity of oils is tested at 40 °C.

acrolein product was determined by GC (gas chromatography). For the cycle of the Pickering emulsion, 10 mL of 30 wt% glycerol aqueous were added and re-emulsified for each cycle. The reaction time for each cycle run was 0.5 h, except for 1 h in the last cycle run.

#### 2.3. Characterization of the emulsifier

The contact angle (water–solid–air) of the SiO<sub>2</sub> nanoparticles was measured on a Drop Shape Analyzer DSA-100. Transmission electron microscopy (TEM) imaging of SiO<sub>2</sub> nanoparticle samples was performed on a JEM-2100 microscope operated at 200 kV. Thermogravimetric (TG) analysis of the SiO<sub>2</sub> nanoparticles was implemented on a SETSYS EVOLUTION TGA 16/18 (France) under a nitrogen atmosphere with the temperature increasing from 25 °C to 800 °C at a rate of 20 °C min<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Characterization of the emulsifier

The water contact angle of SN–C was as high as 148.2° (Fig. S1, ESI†). The strong hydrophobicity of the emulsifier benefits the formation of water-in-oil Pickering emulsion. The hydrophobic SiO<sub>2</sub> nanoparticles were spherical with an average diameter of 20 nm, as evidenced by TEM (Fig. S2, ESI†). TG (thermogravimetric) analysis illustrated that the nanoparticles have good stability upon heating at 500 °C (Fig. S3, ESI†).

#### 3.2. Effect of oil on the Pickering emulsion

Microscopy images of the Pickering emulsions formed in different oil phases are shown in Fig. 1(B) and Fig. S4, ESI.<sup>†</sup> High internal phase Pickering emulsions<sup>27</sup> were prepared from decane, hexadecane, ethyl oleate and peony seed oil. The former had a volume fraction of about 80% and the latter had a volume fraction of over 95%. As the viscosity of the oil phase increases, the droplet size of the Pickering emulsions gradually decreased, from 80 to under 11  $\mu$ m. The average droplet size  $\overline{D}$  was calculated by using the equation

 $\overline{D} = \sum_{i=1}^{n} x_i D_i$ , where  $x_i$  is the ratio of droplets with diameter  $D_i$  as

shown in Fig. S4 (ESI<sup>†</sup>). With the decreased emulsion droplet size, the relative Pickering emulsion interface area increased from 0.76 even to 5.45 m<sup>2</sup>. A much smaller droplet size below 11  $\mu$ m was achieved when the peony seed oil was used as the oil phase of the Pickering emulsion. Vegetable oils have a higher viscosity and their greater shear stress at the same stirring speed (during the preparation of the Pickering emulsion) than long-chain alkanes confers on them a higher ability to produce and stabilize the water-in-oil Pickering emulsion to produce smaller droplets.

#### 3.3. Catalytic reaction in the Pickering emulsion

The small droplet in the  $SiO_2$  nanoparticle cage of the Pickering emulsion acted as a microreactor. The micron scale size and large oil-water interface area of the microreactor greatly improved the substance transfer rate in water and oil. Therefore, this could be a

Table 1 Preparation of acrolein under different Pickering emulsions

Entry	Oil phase	Distribution coefficient	Kinematic viscosity (cSt)	Glycerol conv. (%)	Acrolein yield (%)
$1^a$	Decane	0.360	0.97	>99.0	51.8
$2^a$	Dodecane	0.295	1.45	>99.0	55.6
$3^a$	Tetradecane	0.271	2.10	>99.0	62.9
$4^a$	Hexadecane	0.255	2.93	>99.0	69.9
$5^{b}$	Ethyl oleate	0.794	4.89	>99.0	79.2
6 <sup><i>c</i></sup>	Peony seed oil	0.693	26.57	>99.0	84.6
7 <sup>c</sup>	Flaxseed oil	0.654	25.51	>99.0	80.9
8 <sup>c</sup>	Soybean oil	0.593	33.12	>99.0	79.7
9 <sup>c</sup>	Olive oil	0.562	39.02	>99.0	79.1
$10^d$	Peony seed oil			_	0
$11^d$	Flaxseed oil			_	0
$12^d$	Soybean oil			_	0
$13^d$	Olive oil			_	0
$14^e$	Peony seed oil			>99.0	56.0
$15^e$	Peony seed oil			>99.0	40.2
$16^e$	Peony seed oil			>99.0	74.1
17 <sup>f</sup>	Peony seed oil			>99.0	72.4
$18^{f}$	Peony seed oil			>99.0	61.3
$19^g$	Peony seed oil			>99.0	78.8
$20^g$	Peony seed oil			>99.0	75.1
$21^g$	Peony seed oil			>99.0	70.3
	•				

Reaction conditions: 0.05 mol KHSO<sub>4</sub>, 10 mL of 30 wt% glycerol aqueous, 20 mL of oil phase, 3.5 wt% SN–C, 180  $^{\circ}$ C, 1 h. <sup>*a*</sup> Oil phase is long-chain alkanes. <sup>*b*</sup> Oil phase is ethyl oleate. <sup>*c*</sup> Oil phase is vegetable oils. <sup>*d*</sup> Control experiments of vegetable oils. <sup>*e*</sup> 0.05 mol of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and NaHSO<sub>4</sub>, respectively. <sup>*f*</sup> 0.04 and 0.03 mol of KHSO<sub>4</sub>. <sup>*g*</sup> First, second and third recycling of the Pickering emulsions formed in peony seed oil. For each recycle, the Pickering emulsion was re-emulsified after adding 10 mL of 30 wt% glycerol aqueous. The reaction time was 0.5 h for each cycle run, except for 1 h in the last cycle run. The kinematic viscosity of oil phases was measured at 40  $^{\circ}$ C.

great advantage for the preparation of acrolein from glycerol in the Pickering emulsion microreactor.

Then, in order to test the effect of the reaction, acrolein from glycerol dehydration was obtained in the Pickering emulsion microreactor with different oil phases (Fig. S5, ESI<sup>+</sup>). As shown in Table 1 (entries 1-9), the yields of acrolein in the Pickering emulsions with low viscosity long-chain alkanes as the oil phase ranged from 52% to 70%, while they were all higher than 75% when the high viscosity ethyl oleate and renewable vegetable oils were used as the oil phases. This result proved that the high viscosity oil phase was beneficial to increase the yield of acrolein, which may be related to the formation of small Pickering droplets. However, with the increase of oil phase viscosity under the same preparation conditions, the droplet size cannot be reduced indefinitely. High viscosity vegetable oils had the smallest droplet sizes, about 10 µm (Fig. S5, ESI<sup>†</sup>). Particularly, the highest acrolein yield of 84.6% was obtained when peony seed oil was used as the oil phase, which was higher than the most reported value (less than 80%, Table S1, ESI<sup>†</sup>). It was also possible that vegetable oil was hydrolyzed to glycerol, and thus the acrolein yield increased. To rule out this possibility, control experiments were carried out under the same reaction conditions but without glycerol. No formation of acrolein was observed (Table 1, entries 10-13). Thus, acrolein in the Pickering emulsions with vegetable oils as the oil phase was formed from glycerol, and not from the vegetable oils.

The Pickering emulsions formed from the vegetable oils had a better effect of improving the yield of acrolein than the

long-chain alkanes, which could be due to the smaller-sized droplets. However, for the ethyl oleate as the oil phase of the emulsion, the droplet size was similar to that of the long-chain alkanes, and the yield of acrolein in the Pickering emulsion formed by ethyl oleate was higher than that of the long-chain alkanes. Therefore, there may be other factors promoting the yield of acrolein in the Pickering emulsion. Hence, the solubility of acrolein in different oils was considered as an important factor affecting the yield of acrolein and was investigated. As shown in Table 1, the distribution coefficient of acrolein was the highest in ethyl oleate, the second in vegetable oil, and the poorest in long chain alkanes. In particular, though the size of the droplet formed with ethyl oleate showed no obvious difference to tetradecane and hexadecane (50 µm vs. 56 and 52 µm), the great difference in acrolein solubility (0.794 vs. 0.271 and 0.255) makes the generated acrolein transfer from the water phase to the oil phase quickly, thus obtaining a better yield of acrolein. As a result, the acrolein solubility in the oil phase showed a secondary significance in improving the mass transfer of acrolein in the Pickering emulsion.

#### 3.4. Mass transfer of acrolein in the Pickering emulsion

In order to understand the factors affecting the yield of acrolein in the Pickering emulsion, the transfer effects of acrolein molecules in the Pickering emulsion formed by hexadecane, ethyl oleate and peony seed oil were studied, respectively. As shown in Fig. 2, the acrolein concentration in the oil phase of the Pickering emulsion increased with the prolonged reaction time. At the same reaction time, the acrolein concentration in the oil phase followed the order of  $C_{\text{peony seed oil}} > C_{\text{ethyl oleate}} > C_{\text{hexadecane}}$ . The droplet size of the Pickering emulsion formed in peony seed oil, 11 µm, was much smaller than those formed in ethyl oleate and hexadecane, 50 and 52 µm. Thus, the droplet size was the main reason for enhancing the transfer of acrolein. This result was consistent with above demonstration that small-sized emulsion droplets can promote the transfer of acrolein from water to oil phases (formula (2)). But for ethyl oleate and hexadecane, the small difference in the emulsion size resulted in a large difference



Fig. 2 Acrolein concentration as a function of reaction time in the Pickering emulsions with peony seed oil and hexadecane as the oil phase. Reaction conditions: 0.05 mol KHSO<sub>4</sub>, 10 mL of 30 wt% glycerol aqueous, 20 mL of oil phase, 3.5 wt% SN-C, 180 °C.

in the yield of acrolein, which was mainly caused by the ability to dissolve acrolein of the oil phase. In a word, the Pickering emulsion system with smaller-sized droplets and the oil with a high ability to dissolve acrolein can enhance the transfer rate of acrolein out of the aqueous phase to improve the acrolein yield.

#### 3.5. Effect of the catalyst

The production of acrolein by dehydration of glycerol catalyzed by Brønsted acid has been widely accepted. The catalytic effects of several mineral acids were studied and the results are shown in Table 1 (entries 6 and 14–16). Although strong acids can promote glycerol conversion into acrolein, due to the oxidation of  $H_2SO_4$  at a high concentration, the water in the solution in the reaction process increases the acid concentration of the reaction system with evaporation in the reaction process, increasing the possibility of humus formation. For  $H_3PO_4$  as a catalyst, the weaker acid may cause a lower yield of acrolein. In order to obtain more efficient catalytic effects, the acid salts of polybasic mineral acids of strongly acidic nature were used in the preparation of acrolein from glycerol. Compared with NaHSO<sub>4</sub>, KHSO<sub>4</sub> had a better catalytic effect, possibly due to the influence of metal ions on acids.

In addition to the type of acid, the amount of catalyst also had a significant influence on the catalytic effect. With the increase of  $KHSO_4$  concentration (Table 1 entries 6, 17 and 18), the yield of acrolein increased gradually. However, due to the limitation of  $KHSO_4$  solubility, the amount of catalyst cannot be increased indefinitely. The yield of acrolein was the highest when 0.05 mol  $KHSO_4$  was used as the catalyst.

#### 3.6. Effect of the emulsifier

It was noticed that the silica emulsifier was located at the interface of the water and oil phases. Its surface properties may affect the properties of the Pickering emulsion, and consequently influence the yield of acrolein. Silica with the surface modified by different silvlation reagents were applied as emulsifiers, and the effect of the emulsifier surface on the acrolein yield was investigated in the Pickering emulsions with tetradecane and peony seed oil as the oil phase, respectively. The hydrophilic silica was chosen as the precursor for surface silvlation, and the silvlated SN samples were designated as SN-C<sub>3-1.5</sub>, SN-C<sub>8-1.0</sub>, SN-C<sub>12-1.0</sub> and SN-C<sub>16-1.0</sub>. As shown in Fig. S1 (ESI<sup>†</sup>), the nanoparticles of the silvlated SN samples were spherical with an average diameter of 20 nm. TG analysis indicated that the silylated SN samples showed good stability upon heating at 450 °C (Fig. S3, ESI<sup>†</sup>). As shown in Fig. 3A, the yield of acrolein was gradually enhanced with the increase of the water contact angle of the emulsifiers. This enhancement resulted from the improved stability of the Pickering emulsion. With SN-C<sub>3-1.5</sub> as the emulsifier, the Pickering emulsion with either tetradecane or peony seed oil as the oil phase showed poor stability (Fig. 3B) so that the acrolein yield was relatively low (Fig. 3A). When the surface of the emulsifier became more hydrophobic, the Pickering emulsions were more stable, which facilitated the formation of smaller droplets and thus enhanced the acrolein yield. The Pickering emulsion with peony seed oil



**Fig. 3** (A) Effect of the silica emulsifiers in Pickering emulsions on the yield of acrolein. (B) Microscopy images of the Pickering emulsion with different silica emulsifiers. Reaction conditions: 3.5 wt% emulsifier, 180 °C for 1 h. P-1 to P-4: peony seed oil as the oil phase, the emulsifiers were SN-C<sub>3-1.5</sub>, SN-C<sub>8-1.0</sub>, SN-C<sub>12-1.0</sub> and SN-C<sub>16-1.0</sub>, respectively. T-1 to T-4: tetradecane as the oil phase, the emulsifiers were SN-C<sub>3-1.5</sub>, SN-C<sub>8-1.0</sub>, SN-C<sub>12-1.0</sub> and SN-C<sub>12-1.0</sub> and SN-C<sub>12-1.0</sub> and SN-C<sub>16-1.0</sub>, respectively. The scale bar is 100  $\mu$ m. Error bar represents the standard deviation of three measurements.

as the oil phase had a smaller droplet size compared with that with tetradecane as the oil phase, leading to a higher yield of acrolein. Thus, for the Pickering emulsions, a hydrophobic silica emulsifier was beneficial to the acrolein yield.

#### 3.7. Recycling of the Pickering emulsion

The separation and recovery of catalysts were the main problems faced by liquid phase catalytic systems. Pickering emulsions also faced the problem of recycling the emulsifiers. What's more, for producing acrolein from glycerol, the glycerol transformed gradually into humus with the prolonged reaction time, making it difficult to recover the emulsion system. Besides, the acid catalyst was dissolved in glycerol aqueous, making the catalyst separation and recycling more difficult. To tackle the emulsifier separation and catalyst recycling problems, an additional glycerol solution was added, and the whole system was reemulsified before each recycling run. For each cycle, the reaction time was set to 0.5 h to reduce the formation of humus as much as possible. The first, second and third recycling results are listed in Table 1, entries 19–21. With the increasing recycling number, the yield of acrolein gradually decreased. This decrease may result from the deposition of the formed humus on the surface of the silica emulsifier which reduced the stability of the Pickering emulsion.

# 4. Conclusions

In summary, a small droplet of water-in-oil Pickering emulsion prepared by a high viscosity oil phase can efficiently promote the production of acrolein from glycerol due to the mass transfer intensification effect. Moreover, the high solubility of the oil phase for acrolein promoted the transfer of acrolein from the aqueous phase to the oil phase. This combined mass transfer intensification effect was the most obvious on the Pickering emulsion with peony seed oil as the oil phase, leading to the highest acrolein yield of 84.6%. Furthermore, the effects of the surface properties of the silica emulsifier on the transfer of acrolein at the water-oil interface and consequently on the acrolein yield were investigated. When the surface of the silica emulsifier became hydrophobic via silvlation treatment, both the transfer rate and yield of acrolein were enhanced. The recycling of the Pickering emulsion was investigated, and the acrolein yield changed from 84.6% to 70.3% after three recycling runs, indicating that the Pickering emulsion in this work is a sustainable and green system for efficient acrolein production from glycerol dehydration.

# Conflicts of interest

There are no conflicts to declare.

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