Highly stabilized foam by adding amphiphilic Janus particles for drilling geothermal wells

Lili Yang^{abc, &, *}, Tengda Wang^{ab, &}, Xiao Yang^{ab}, Guancheng Jiang^{ab, *}, Paul F. Luckham^c, Jianping Xu^{ab}, Xinliang Li^{ab}, Xiaoxiao Ni^{ab}

^a *State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum (Beijing), Beijing 102249, China*

^b *MOE Key Laboratory of Petroleum Engineering, China University of Petroleum, (Beijing), Changping District, Beijing 102249, China*

^c *Department of Chemical Engineering, Imperial College London, Prince Consort Road, London SW7 2AZ, UK*

Abstract

Fabricating Janus particles that consist of two distinct functional regions is an intriguing research topic. In this study, Janus particles with both hydrophilic and hydrophobic regions are fabricated and innovatively applied in foam drilling fluids as anti-high temperature and anti-calcium foam stabilizers. First, silica particles (approximately 500 nm) are partially covered by wax colloidosomes using the Pickering emulsion method. Then, amino-containing hydrophilic modifiers and a series of hydrophobic modifiers with different carbon lengths are successively utilized to adjust the hydrophilic-lipophilic balance (HLB) of the particles. The results show

* Corresponding author.

Tel.: +86 10 89732239; fax: +86 10 8973 2196; *E-mail address*: yangll@cup.edu.cn (L. Yang)

Tel.: +86 10 89732196; fax: +86 10 8973 2196; *E-mail address*: m15600263100_1@163.com (G. Jiang)

& These authors contributed equally to this work

that the (3-aminopropyl) triethoxysilane-SiO₂-dodecyltrimethoxysilane (NH₂-SiO₂-12C) Janus particles possess the best foam stability. Due to their suitable contact angle of 80°, high positive zeta potential and good surface activity, these foams display the characteristics of low surface tensions, high dilational elasticities, nonspherical shapes, large sizes and thick films, which together result in the extension of the drainage half-life from 448 s to 778 s in comparison with the foam of pure foaming agent solutions. Moreover, compared with a foam with no stabilizer or those stabilized by a soluble foam stabilizer and homogeneous hydrophobic-modified silica particles, NH₂-SiO₂-12C-stabilized foam can extend the drainage half-life to 668 s after hot rolling for 16 h at 280 °C and resist CaCl₂ concentration of 0.8 wt%. Benefiting from their excellent thermal stability and salt tolerance, these Janus particles are expected to be promising candidates for use as foam stabilizers in high-temperature and high-calcium conditions, including drilling, enhanced oil recovery, “waterless” fracturing and, especially, in geothermal wells.

Keywords: Janus particles, foam drilling fluid, foam stabilizer, high temperature, high salinity

1 Introduction

Aqueous foams have been widely applied in the food¹, cosmetics² and ceramics industries³⁻⁴. Additionally, foam fluids have been widely adopted in various petroleum engineering processes, such as air-foam drilling⁵, foam diversion acidizing⁶, foam

fracturing⁷ and foam enhanced oil recovery (EOR)⁸. Geothermal energy is a clean and renewable resource and has received increasing attention worldwide. Geothermal wells possess numerous cracks that water-based drilling fluid can easily penetrate and induce serious leakage. To solve these problems, foam fluids have become a key for the drilling geothermal wells⁹. A low density foam fluid was able to effectively reduce fluid loss because of the Jamin effect, which endows foam fluids with strong blocking abilities when they flow through pore throats¹⁰. In addition, foam fluids usually have high apparent viscosities, providing guaranteed cuttings transport¹¹. It has also been reported that foaming agents have excellent lubricity functionality¹² and can improve the efficiency, safety and economy of the drilling process. However, foams are intrinsically unstable both thermodynamically and kinetically, especially under high temperatures and high pressures. Thus, foam stabilizers are typically added to increase foam stability. To date, many foam stabilizers have been developed, such as hydroxyethyl cellulose (HEC), carboxymethyl cellulose (CMC), polyacrylamide and triethanolamine. The temperatures in the geothermal wells exceed 200 °C, and an abundance of highly charged cations exist in geothermal fluids. These soluble chemicals completely degrade at high temperatures, and highly charged cations disrupt their viscosities and surface activities¹³. Therefore, the development of high temperature- and high cationic ion-resistant foam stabilizers is desperately needed to solve these problems.

Using solid particles to stabilize foams appears to be a promising alternative solution. Solid particles can be adsorbed at the air/liquid interface, playing a

significant role in stabilizing foams or bubbles¹⁴⁻¹⁷. Owing to their high adsorption energies, the adsorption of solid particles at the air/liquid interface is irreversible. Simultaneously, the dilational elasticity of liquid films increases sharply¹⁸. These particles form a protective layer as a result, slowing down the collapse, coalescence and disproportionation of foams¹⁹⁻²⁰. To date, liquid foams have been successfully stabilized by organic particles²¹⁻²², inorganic particles²³⁻²⁵ and natural particles²⁶. Santini et al.²⁷ found that the wettability of a particle surface changed from hydrophilic to hydrophobic after cetyltrimethylammonium bromide (CTAB) adsorption, and a higher concentration of CTAB produced particles with greater hydrophobicities. Binks et al.²⁸ fabricated a stable foam by mixing silica nanoparticles and surfactants at a specific ratio. Sun et al.¹⁷ obtained a stable foam by adding partially hydrophobically-modified SiO₂ nanoparticles into a sodium dodecyl sulfate solution. Faure et al.²⁹ modified the surface of commercially available hydrophilic alumina particles by grafting with short fluorinated phosphonic acid and found the foaming suspension containing 100 g·L⁻¹ of the fluorinated particles could generate stable foam with drainage half-life time more than 10 h. Those studies infer solid particles can adsorb onto the air/water interface after partially-hydrophobic modification. However, the effectiveness of their adsorption is far from satisfactory.

Unlike particles with uniform surface wettabilities, Janus particles contain a definite distinction between their two surface regions that exhibit opposing wettabilities. By combining the Pickering effect and amphiphilic properties, Janus particles display high adsorption stabilities and high surface activities. Fujii et al.³⁰

fabricated gold-silica (Au-SiO₂)-based Janus particles by a vacuum evaporation and the polymer grafting method. They found that bubbles stabilized by PS-grafted Janus particles were the most stable compared to bare Au-SiO₂ Janus particles, PPFBE-grafted Au-SiO₂ Janus particles and bare SiO₂ particles. Therefore, silica particles can stabilize foams after appropriate surface modification. Because of their excellent thermal stabilities and high surface activities, Janus particles are promising candidates for use as foam stabilizers under high-temperature and high-salinity conditions.

In this study, wax colloidosomes were successfully prepared by the Pickering emulsion method. After hydrophilic modification with an amino-containing silane agent and separate hydrophobic modification with several silane coupling agents with different carbon chain lengths, a series of Janus particles that differed in their hydrophilic lipophilic balance (HLB) were fabricated. Interestingly, the as-prepared Janus particles displayed excellent foam stabilizing effects compared with those of a commonly used molecular stabilizer and homogeneous hydrophobic-modified silica particles. Furthermore, the treated foam possesses high-temperature resistance and high-calcium tolerance, and it is expected to be applicable as a foam drilling fluid for geothermal exploration.

2 Experimental

2.1 Materials

Fused silica particles (500 nm in diameter) were supplied by Alfa Aesar (Shanghai, China). The paraffin wax, with a melting point between 58 and 60 °C, used

in these experiments was obtained from the Sinopharm Chemical Reagent Company (Shanghai, China). Didodecyldimethylammonium bromide (DDAB), methyltriethoxysilane (1C), triethoxypropylsilane (3C), triethoxyoctylsilane (8C), dodecyltrimethoxysilane (12C), n-octadecanetrichlorosilane (18C), (3-aminopropyl)triethoxysilane (APTES), hexane and N,N-dimethyldodecylamine N-oxide (OB-2) were purchased from Energy Chemical (Shanghai, China). The anionic foaming agent AD300 was provided by Aoda Petrochemical Co., Ltd. (Shandong, China). Homogeneous hydrophobic-modified silica particles (SG) were supplied by Xuancheng Jingrui Nano Material Co., Ltd. (Anhui, China). The OTS used in these experiments was freshly purified by distillation under vacuum, and all other chemicals were directly used without further purification.

2.2 Fabrication of Janus Particles

2.2.1 Partial coverage of silica particles by wax colloidosomes

First, silica particles (1.0 g) were ultrasonically dispersed in 90 mL of deionized water. The particle suspension was then mixed with paraffin wax (10.0 g) and an aqueous solution of DDAB (10.0 mL) with concentrations varying from 0.5 to 1 mg·mL⁻¹. The mixture was heated to 70 °C with mechanical stirring at 1600 rpm for 30 min and then cooled to room temperature. As the temperature decreased, the paraffin wax solidified and turned into colloidosomes. The wax colloidosomes were washed with deionized (DI) water and ethanol to remove DDAB and free or weakly attached particles. Thereafter, the silica particles that were partially covered by the wax colloidosomes were dried under vacuum at 35 °C for 24 h.

2.2.2 Janus particles prepared by chemical modification

First, silica particles partially covered by wax colloidosomes (11.0 g) were chemically reacted with APTES (0.5 g) in a 2.0 wt% ethanol aqueous solution under mechanical stirring at 400 rpm for 48 h. Then, the colloidosomes were washed several times with DI water and ethanol to remove residual APTES. Subsequently, the colloidosomes were dispersed in dichloromethane to remove the wax, and (3-aminopropyl) triethoxysilane-SiO₂ (NH₂-SiO₂)-coated particles were collected by repeated centrifugation and dispersion. Finally, particles were reacted with 8.97×10^{-5} mol of 1C, 3C, 8C, 12C or 18C in an ethanol solution (50 mL) at 65 °C with stirring for 24 h. Finally, Janus particles (labelled NH₂-SiO₂-nC, where n represents 1, 3, 8, 12 or 18) were fabricated, collected by centrifugation, and dried under vacuum for 24 h.

2.3 Characterization of the wax colloidosomes and Janus particles

The surface morphology of the wax colloidosomes and the dissymmetrical characteristics of the Janus particles were observed by SEM. The images were acquired using an SU8010 (Hitachi, Japan) at an accelerating voltage of 10 kV. To visually observe the dissymmetrical characteristics of the NH₂-SiO₂ particles, the samples were modified by gold particles in advance.

The surface compositions of bare SiO₂, NH₂-SiO₂ and NH₂-SiO₂-nC particles were analyzed by XPS (K-Alpha, Thermo Fisher, USA). The samples were compressed into cylindrical pellets and detected by a monochromatic Al K Alpha X-ray gun emitting pass energies of 50 eV. TGA analysis was implemented on a PE Pyris 1 in the temperature range of 50 °C to 700 °C at a heating rate of 20 °C·min⁻¹ and under a constant 20 mL·min⁻¹ N₂ gas flow. Owing to the hydroscopic properties,

the above procedure was conducted after samples were dried at 100 °C for 10 min.

The wettability of the Janus surface was quantitatively evaluated by measuring the water wetting contact angle. To construct a flat surface, aqueous solutions of the bare SiO₂, NH₂-SiO₂ and NH₂-SiO₂-nC particles were sprayed onto a glass surface. Then, the contact angle of the dense surface was immediately measured 3 s after the water droplets (10 µL) had dropped and recorded by a camera.

The zeta potentials of aqueous dispersions of bare SiO₂, NH₂-SiO₂ and NH₂-SiO₂-nC particles were measured using a Malvern Zetasizer Nano series (Malvern, UK). The concentrations of all samples were 0.1 g·L⁻¹. Before measurement, all samples were dispersed by ultrasonication for 30 min. The average zeta potential was obtained by measuring each sample 3 times.

2.4 Influence of Janus particle surface composition on foam stabilization

The foam stability was tested by an improved Waring blender method. After bare SiO₂, NH₂-SiO₂ and NH₂-SiO₂-nC particles were added into a 10 mL aqueous solution of the foaming agent at a certain concentration, the mixture was stirred at 11,000 rpm for 1 min. Foaming ability and foam stability were evaluated based on the initial foam volume (V_0) and drainage half-life ($T_{0.5}$), which corresponds to the time required for drainage of the liquid to half its initial volume, i.e., 5 mL in this study. Surface tensions and dilational elasticities of the dispersions were recorded as a function of time by a tensiometer (Tracker-H, TECLIS, France) at an oscillation frequency of 0.1 Hz. The foams were observed with an optical microscope (Leica DM4 M, Leica Microsystems, Germany), which was equipped with an electron

multiplying CCD camera. Foam sizes and film thicknesses were analyzed by ImageJ software (National Institutes of Health, USA). The dispersion viscosity was measured on a HARRK WT Mac (Thermo Electron, Germany) with a cone-plate rotor. Inner surface of foam stabilized by $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles were observed by Cryo-SEM (S-4300, Hitachi, Japan).

2.5 Performance of the $\text{NH}_2\text{-SiO}_2\text{-12C}$ particles as foam stabilizers in a foam drilling fluid for geothermal wells

The foam stabilizing effect of the $\text{NH}_2\text{-SiO}_2\text{-12C}$ particles was compared with that of OB-2 and SG. Foam stabilizer (0.3 wt%) was added to a 10 mL foaming agent solution. After foaming by the Waring blender method, the foaming abilities and foam stabilities under high-temperature conditions and in the presence of CaCl_2 contaminants were measured as follows.

2.5.1 Thermal stability evaluation

The resistance of the three foam stabilizers to high temperatures was evaluated by hot rolling tests. A 350 mL foaming solution containing 0.4 wt% AD300 and 0.3 wt% foam stabilizer was hot rolled at 280 °C for 8 h, 16 h and 24 h. After cooling down, V_0 and $T_{0.5}$ were determined as described in the above measurements.

2.5.2 Salt tolerance evaluation

Ten milliliters of foaming solution containing 0.4 wt% AD300 and 0.3 wt% foam stabilizer was hot rolled at 280 °C for 16 h and then stirred at 11,000 rpm for 1 min. CaCl_2 , with a series of concentrations, was added to the mixture and stirred at 11,000 rpm at room temperature for 1 min. Then V_0 and $T_{0.5}$ were recorded as described in the above measurements.

3 Results and discussion

3.1 Fabrication and characterization of Janus particles

Janus particles were fabricated by the Pickering emulsion method (Figure 1(a)). Owing to their ability to lower the total free energy between water and oil, silica particles can adsorb to the water/wax interface. The Pickering emulsion method presents several outstanding advantages, including homogeneously selective chemical modification by fixing the silica particles, easy disposal of the free particles and a wide selection of modifying agents. Figure 1(b) shows the SEM images and size distribution of the wax colloidosomes. As discussed above, silica particles are indeed trapped and arranged orderly within the wax surface, which generates a protective monolayer. Furthermore, the sizes of the wax colloidosomes are distributed in an incredible narrow range because of the emulsification and anti-coalescence process. Based on the particles in Figure 1(c), we calculate the average penetration depth of the particles into the wax and the three-phase contact angle according to methods in the literature³¹. The three-phase contact angle of the wax colloidosomes is approximately 58.71°. The three-phase contact angle will determine the ratio of the hydrophilically- and lipophilically-modified areas on the silica particle surface and influence the subsequent hydrophilic- and lipophilic-modification process, which will directly affect the final HLB of the Janus particles. It should be noted that, for the sake of facilely fabricating the Janus particles, we introduce DDAB to attach to the silica particle surface, which can then be easily rinsed off from the particle surface and has no influence on the following modifications (Figure S1).

To fabricate amphiphilic Janus particles, APTES is first grafted onto the silica particles ($\text{NH}_2\text{-SiO}_2$). Actually, $\text{NH}_2\text{-SiO}_2$ already has amphiphilic Janus characteristics due to the different compositions and specific wettabilities between the raw portion and the amino-modified portion. To demonstrate the two distinct regions of the Janus surface, gold nanoparticles are utilized and mixed with the $\text{NH}_2\text{-SiO}_2$ particles, which is a common method to detect amino groups³². As shown in Figure 1(d), gold nanoparticles adsorbed onto specific regions of the particles due to the surface coating with amino groups. Apart from these regions, no gold particles can be seen inside the red circle. At the same time, the surface area within the red circle was found to be nearly equal to that of the previously protected area. Thus, amino groups were selectively decorated onto one region of the silica surface, which was well prepared for hydrophobic modification in the other regions.

For hydrophobic modification at the unreacted surface, $\text{NH}_2\text{-SiO}_2$ particles were directly modified by 1C, 3C, 8C, 12C and 18C molecules. Owing to the low concentration of -OH and steric hindrance of the amino-modified semi-sphere, hydrophobic substituent groups are prevented from modifying the APTES coated surfaces and can thus preferentially modify the previously protected areas.

3.2 Characterization of the Janus particles

3.2.1 XPS and TGA Characterization

The surface compositions of bare SiO_2 , $\text{NH}_2\text{-SiO}_2$ and $\text{NH}_2\text{-SiO}_2\text{-nC}$ (n=1, 3, 8, 12, and 18) particles were first examined by XPS (Figure S2). Compared with bare SiO_2 , nitrogen and carbon elements appear on the $\text{NH}_2\text{-SiO}_2$ surface. These results indicate that APTES was successfully coated onto the SiO_2 surface. After the

NH₂-SiO₂ particles were subsequently grafted with nC (n=1, 3, 8, 12 and 18), the percentage of carbon on the surface increases, while those of nitrogen, oxygen and silicon vary to different degrees. Considering that XPS is a semiquantitative analytical method and that the asymmetry of the Janus particles might induce uncertainty in the scanning area, we further adopt a TGA method to determine the composition of the Janus particles (Figure 1(e)). By analyzing the differences in the weight losses determined for bare silica, NH₂-SiO₂ and NH₂-SiO₂-nC (n=1, 3, 8, 12, 18) particles, the organic component on the NH₂-SiO₂ particles is approximately 0.78%, and the respective hydrophobic component on the NH₂-SiO₂-nC (n=1, 3, 8, 12, and 18) particles is approximately 1.93%, 2.61%, 3.26%, 8.76% and 16.10%, respectively. Therefore, APTES and nC (n=1, 3, 8, 12, and 18) have been coated onto the surface of the silica particles. In addition, as the alkylation tail length increases, the hydrophobic composition on the NH₂-SiO₂-nC particles increases.

3.2.2 Contact angle measurements

Static water contact angle measurements of particles sprayed onto a glass surface were conducted to investigate the wettabilities of SiO₂, NH₂-SiO₂ and NH₂-SiO₂-nC particles. Figure 2(a₁) shows that the contact angle of pure SiO₂ particles is 13.95° in our study, owing to the hydrophilic silanol groups on their surface. After partial modification by APTES, the flat-surface contact angle of the NH₂-SiO₂ increases to 39° (Figure 2(a₂)). Although the contact angle increases, the formed surface is still relatively hydrophilic. After hydrophobic modification of the other portion of the

spheres by 1C, 3C, 8C, 12C and 18C, the respective average flat-surface contact angles increase to 62.11° , 62.64° , 78.37° , 81.78° and 126.19° (Figure 2(a₂-a₇)), indicating an increase in the hydrophobic wettability and the successful coating of the hydrophobic group onto the NH₂-SiO₂ spheres.

3.2.3 Water/oil interface adsorption experiment

To verify the amphiphilic properties of the NH₂-SiO₂-nC Janus particles, we added them to a mixture of water and hexane and directly observed the position where they suspended and the morphology of the meniscus. As Figure 2(b₁, b₄) and Figure S3 show, NH₂-SiO₂-nC (n=1, 3, 8, 12 and 18) Janus particles strongly adsorb to the water/hexane interface. Moreover, we found that NH₂-SiO₂-8C and NH₂-SiO₂-12C readily promote the generation of an emulsion, inferring a reduction of the interfacial tension, the amphiphilic properties of these Janus particles and the strong adsorption of the Janus particles onto the water/hexane interface. By comparison, bare silica particles disperse only in the water phase (Figure 2(b₂)) due to being fully covered by silanol groups, which cause the silica particles to be hydrophilic. In contrast, particles homogeneously modified by 12C disperse only in the hexane phase (Figure 2(b₃)), as surface modification by only 12C rendered hydrophobic particles. Therefore, all the data discussed above provide valid evidence that amphiphilic Janus particles were fabricated successfully.

3.2.4 Zeta potential

Owing to the electric barrier between the negative surface of the SiO₂ particles and the negative air/water interface, adjusting the surface charges of the particles

would promote easier adsorption onto the air/water interface³³⁻³⁴. Moreover, the surface charge also affects the coalescence stability and distribution uniformity of the particles³⁵. The zeta potentials of bare SiO₂, NH₂-SiO₂ and NH₂-SiO₂-nC particles were measured and are shown in Figure 2(c). The SiO₂ particles are negatively charged with a potential of -36.4 mV owing to -OH groups covering the entire surface. Therefore, the SiO₂ particles disperse well in water and tend to adsorb less onto the air/water interface (Figure 2(b₂)). After reacting with APTES, the average Zeta potential of the NH₂-SiO₂ particles decreases to -10.1 mV. Specifically, the NH₂-SiO₂ particles are cationic on their APTES-modified side due to hydration of the amino group, while they are anionic on their other side. During hydrophobic modification, many of the -OH groups previously embedded within the wax are replaced by the carbon chains, and these areas become neutral. Consequently, the respective zeta potential of the NH₂-SiO₂-nC (n=1, 3, 8, 12, and 18) Janus particles convert to +6.89, +10.2, +11.8, +16.7, and +10.5 mV, respectively. The zeta potential change from negative to positive not only indicates that the modifications are successful but also reflects a conversion of the surface electronic properties. According to the value of the zeta potential, the NH₂-SiO₂-12C Janus particles possess the best coalescence stability and distribution homogeneity among all the NH₂-SiO₂-nC (n=1, 3, 8, 12, and 18) Janus particles.

3.3 Influence of the Janus particle surface composition on foam stabilization

Through the above characterization of the Janus particles, we firmly believe that the NH₂-SiO₂-nC (n=1, 3, 8, 12 and 18) Janus particles were fabricated as expected.

Next, we examined the influence of the surface composition on the foaming abilities and stabilization properties of the Janus particles. A commercially available anionic surfactant, AD300, was selected as the foaming agent, and the critical micelle concentration (CMC) was measured using the pendant drop method. As shown in Figure S4, the surface tension decreases rapidly with increasing foaming agent concentration and eventually reaches an equilibrium platform. It can be seen that the CMC is approximately 0.35 wt%, after which the surface tension remains 37.3 mN/m and no longer decreases. For the sake of a consistent foaming process, we selected 0.4 wt% as the foaming agent concentration for all following experiments. It can be seen from Table 1 that all the foams with added $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8$, and 12) particles have the same V_0 of 110 mL, while $\text{NH}_2\text{-SiO}_2\text{-18C}$ slightly decreases the foam volume. These results suggest similar foaming abilities despite different foam stabilizers being added, which might be related to the Marangoni effect where the concentration of the adsorbed surfactant molecules during foaming is the dominant factor for determining the foaming volume. This explanation can be verified by the fact that a foam stabilized by heterogeneously modified $\text{NH}_2\text{-SiO}_2$ particles also has a V_0 of 110 mL. The slight influences of the other particles on the foam volume might be due to their overly hydrophilic (bare silica and homogeneously modified $\text{NH}_2\text{-SiO}_2\text{-NH}_2$ particles) or overly hydrophobic (SG particles) properties, while the OB-2 molecular stabilizer acts as a foam booster that increases V_0 to 140 mL.

To evaluate the foam stabilizing effect of the $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18) Janus particles, the drainage half-life ($T_{0.5}$) was recorded. According to Table 1, the

NH₂-SiO₂ particles are able to extend T_{0.5} from 448 s to 564 s, while the NH₂-SiO₂-NH₂ and bare silica particles have no positive stabilizing foam effect compared with that of the pure AD300 solution. This provides valid evidence that particles with heterogeneous wettability are advantageous to foam stability, which results from the increased amount of adsorption onto the surface of the foam, and better ability to decrease interfacial tension and thus provide a stronger barrier against Ostwald ripening, drainage and coalescence¹⁹⁻²⁰.

When the NH₂-SiO₂ particles are further modified by nC (n=1, 3, 8, 12, and 18), the stabilizing foam ability is continually improved. Interestingly, we find that the foam stability increases with increasing length of the carbon chain up to twelve units and then decreases when the length of the carbon chain reaches eighteen units. It can be seen that the foam stabilization effects of NH₂-SiO₂-8C, NH₂-SiO₂-12C and NH₂-SiO₂-18C are better than those of NH₂-SiO₂-1C and NH₂-SiO₂-3C. Notably, the most stable foam, with a T_{0.5} of 778 s, was that stabilized by NH₂-SiO₂-12C at a concentration of 0.3 wt%, while NH₂-SiO₂-8C at 0.6 wt% and NH₂-SiO₂-18C at 0.9 wt% displayed the best foam stabilizing abilities for their compositions, corresponding to drainage half-lives of 731 s and 740 s, respectively. Therefore, the best stabilizing foam ability of the NH₂-SiO₂-nC (n=1, 3, 8, 12, 18) Janus particles varies depending on the surface alkyl chain length. The NH₂-SiO₂-12C Janus particles proved to be the best stabilizer, based on the least concentration needed to achieve the best foam stability performance.

Foam stability is related to Ostwald ripening, drainage and coalescence, which

are influenced by the surface tension, surface elasticity, viscosity, zeta potential, size, size distribution and film thickness. To study the above phenomena, dispersions composed of 0.4 wt% AD300 (with no stabilizers) and mixed dispersions stabilized with 0.3 wt% of $\text{NH}_2\text{-SiO}_2$ or $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$, and 18) particles were prepared for all following experiments. Surface tension (γ) of dispersions was measured first. It can be seen from Figure 3(a) that all the surface tensions decrease gradually and slowly over time and turned to a platform finally, and the surface tension values follow the sequence of $\text{NH}_2\text{-SiO}_2\text{-1C} > \text{NH}_2\text{-SiO}_2\text{-8C} > \text{NH}_2\text{-SiO}_2\text{-18C} > \text{NH}_2\text{-SiO}_2 \approx \text{NH}_2\text{-SiO}_2\text{-3C} > \text{AD300} > \text{NH}_2\text{-SiO}_2\text{-12C}$. In particular, only the dispersion with the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles presents a surface tension of $29.42 \text{ mN}\cdot\text{m}^{-1}$, which is lower than the AD300 solution value of $30.56 \text{ mN}\cdot\text{m}^{-1}$, in the platform region. This indicates that the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles possess excellent interfacial activity and synergistic effects with AD300 and hence produce a dense adsorption layer, while the other particles affect the adsorption of AD300 and produce higher surface tension values. Although the increase in surface tension produces no negative impact on the foaminess, it might not be beneficial for decreasing foam drainage or improving foam stability, according to the Laplace equation. However, all the $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$, and 18) Janus particles display a better foam stabilizing effect compared with the pure AD300 solution, thereby the underlying mechanism should be further analyzed.

Dilational elasticity (E) determines the mechanical strength of a foam film (Figure 3(b)). It can be seen that the dilational elasticity displays a similar trend as

that of the foam stability: it increases as alkyl chain length increases up to twelve units and then decreases when the chain length reaches eighteen. These results suggest that foam stabilized by the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles produces a strong film, which is of great importance to foam stabilization. According to the Gibbs stability criterion $E > \gamma/2$ ¹⁸, where E is the dilational elasticity (mN/m) and γ is the surface tension (mN/m), a foam with a high dilational elasticity and low surface tension should completely prevent Ostwald ripening from occurring in the foam, neglecting the relaxation process and thus display good stability. Combined with the results of the surface tension measurements, the mixed dispersion of AD300 and the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles is the only foam whose dilational elasticity is greater than half of its surface tension at any given time. Therefore, the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles possess the best foam stability from an elasticity fluid mechanics perspective. As far as the other $\text{NH}_2\text{-SiO}_2\text{-nC}$ Janus particles, especially the $\text{NH}_2\text{-SiO}_2\text{-1C}$ and $\text{NH}_2\text{-SiO}_2\text{-18C}$ particles, E is lower than $\gamma/2$; therefore, they have less ability to stabilize foam.

The viscosity of the base fluid is one of the most important factors in foam stability. Many cellulose-based derivatives and polyacrylamides have been used to stabilize foams due to their viscosification effects. To determine whether foam stabilization of the Janus particles also derives from their viscosification, we measured the viscosities of the base fluids used in our study. However, the viscosities of all mixed dispersions is very low and similar to that of the blank, as the shear rates range from 10 s^{-1} to 100 s^{-1} (Figure 3(c)). Therefore, the foam stabilities in our study

have no relationship with the viscosity.

The morphologies of the foams were observed with an optical microscope (Figure 4). As the carbon chain increases, the foams become substantially less spherical, and the changes in those stabilized by $\text{NH}_2\text{-SiO}_2\text{-8C}$ and $\text{NH}_2\text{-SiO}_2\text{-12C}$ particles are especially obvious. Foam deformation from spherical to non-spherical usually indicates that many particles have been adsorbed onto the air/water interface. Similarly, non-spherical bubbles and oil droplets have been studied by other researchers^{14,30,36}. Under mutual extrusion, foam deforms from spherical to non-spherical and uneven shearing forces elongate the bubbles, and the Janus particles adsorbing to the interface prevent the foam from returning to a spherical shape¹⁴. It is believed that coalescence of the bubbles is inevitable, but the particles adsorbing onto the air/water interface have formed a protective layer to prevent coalescence.

By thoroughly analyzing the bubble sizes and film thickness (Table S1 and Figure S5), it can be seen that the surface alkyl chain length of the $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18) Janus particles has a great impact on the foam size and film thickness. A large size can decrease the Laplace pressure, but it can easily rupture when the foam is too large; therefore, the influence of foam size is uncertain. A positive relationship was found between the foam size and alkyl chain length when the alkyl chain length was lower than twelve units long, and there was a decrease when the alkyl chain length was greater than twelve units long in our study, which is in accordance with the foam stabilities. It can be concluded that the Laplace pressure predominates the influence of size on foam stability. Thick films would prevent foam fracture in the

case of drainage and therefore influence foam stability. For the relationship between film thickness and alkyl chain length, there seems to be no strong trend. However, it can be seen that foam stabilized by the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles possesses the thickest films. Therefore, the foams stabilized with Janus particles tend to be more stable as the alkyl chain length approaches twelve units.

In conclusion, the differences in the hydrophobic surface composition and content of the $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18) Janus particles influences the surface wettability and zeta potential, which govern and stabilize the surface tensions, dilational elasticities, morphologies, foam sizes and film thicknesses. These factors eventually determine the foam stability. Surface wettability, affecting HLB, is the predominant factor in adsorption efficiency. Suitable wettability results in high adsorption at the air/water interface. An HLB below or exceeding this balance will produce a negative effect. The $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles can decrease the interface tension, inferring a high adsorption and synergistic effect with AD300. Furthermore, surface electronic properties opposite to those of the foaming agent benefit the adsorption efficiency of the Janus particles by decreasing the electrical barrier. The $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18) particles have been converted into positive particles, benefiting their adsorption onto the negative air/water interface. In addition, the high adsorption of the particles sterically impedes the drainage process. For a given amount of Janus particles, a homogeneous distribution will cover more of the air/water interface than if the particles aggregate. The high zeta potential of the Janus particles guarantees an excellent foam coalescence stability due to steric

hindrance and electrostatic repulsion. By comparison, all parameters of the foam stabilized by the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles contribute to the foam stability. The contact angle of the $\text{NH}_2\text{-SiO}_2\text{-12C}$ particles is 81.78° , which is comparable to the best contact angle (approximately 80°) for absorption onto a surface¹⁵. In addition, $\text{NH}_2\text{-SiO}_2\text{-12C}$ has the highest zeta potential, therefore easily absorbing onto the air/water interface. All of these advantages contribute to the stability of the foam against Ostwald ripening, drainage and coalescence by steric and electrostatic interactions, owing to producing a foam with high dilational elasticity, a low interface tension, large foam size and good film thickness. With respect to the other prepared particles, they have unsuitable wettabilities and low zeta potentials and thus their foam stabilizing performance does not compare with that of the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles.

3.4 Foam stability performance of $\text{NH}_2\text{-SiO}_2\text{-nC}$ compared with OB-2, SG

Table 2 shows that the molecular foam stabilizer OB-2 can increase the initial volume, while the foam stabilized by the homogeneously hydrophobic foam stabilizer SG has a similar initial volume as that of the foam stabilized by the Janus particles. OB-2 improves the foaming ability by comparison, but it has the lowest foam stability. In fact, OB-2 only increases $T_{0.5}$ from 448 to 488 s, which is far lower than the half-lives of the $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$, and 18) Janus particles. SG merely increases the drainage half-life to 515 s, although they have been previously applied for stabilizing foam. Compared with the OB-2 molecules and SG particles, all the $\text{NH}_2\text{-SiO}_2\text{-nC}$ Janus particles in our study exhibit outstanding advantages, which may

be attributed to their amphiphilic properties and steric effects of the $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$, and 18) Janus particles.

OB-2 is a weakly cationic surfactant, and it decreases the air/water surface tension to approximately $25.1 \text{ mN}\cdot\text{m}^{-1}$ in platform region (Figure 3(a)), which explains its high foaming ability. However, OB-2 stabilized foam has the lowest dilational elasticity of the samples (Figure 3(b)), thus leading to a low foam stability. By comparison, the SG particles slightly increase the air/water interface tension, but have no influence on the foaminess, similar to the effects of the $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$, and 18) Janus particles. In addition, the adsorption energy of the particles, which reflects the energy required for a particle to desorb from the air/water interface into the bulk water phase, is several orders of magnitude higher than that of the OB-2 molecule¹⁴. Therefore, the SG particles can stabilize the foam, although the stabilizing performance is not as good as that of the $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$, and 18) particles.

The foams stabilized by the SG particles and OB-2 molecules were also investigated by optical microscopy (Figure 4 and Figure S5). It can be seen that bubbles formed only by a foaming agent and those stabilized by OB-2 exhibit a spherical morphology and smaller size than that of the other foams. Non-spherical bubbles were observed in SG stabilized foams similar to those stabilized by the $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$, and 18) Janus particles, suggesting that foams stabilized by particles have a non-spherical characteristic.

The $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$, and 18) Janus particles show potential as foam

stabilizer alternatives. By adjusting their composition and the content and size of the modified area, the wettability can be optimally tuned for adsorption onto the air/water interface and synergy with the foaming agent, thus improving foam stability. Based on previous theories³⁸⁻⁴¹, we propose a structure for the foams stabilized by the $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$, and 18) Janus particles. As shown in Figure 4(a), the $\text{NH}_2\text{-SiO}_2\text{-nC}$ Janus particles cooperated with the foaming agent to form three layers between the gas phase and the plateau boundary, which means that the foam film is composed of two layers and a third layer stabilizes this structure. The innermost layers have been observed in Figure 4(j) that $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles cooperate with foaming agent and form a dense layer on air-water interface.

3.5 Performance of the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles as foam stabilizers in foam drilling fluid

According to statistics, global geothermal resources are equivalent to 4.948×10^{15} t of standard coal, which could meet the needs of humans for hundreds of thousands of years at current consumption rates⁴². Limited by currently developed techniques, higher temperature geothermal resources (>200 °C) indicate higher transformation efficiencies. Thus, inevitably encountering extremely high temperatures is the most troublesome challenge when drilling geothermal wells. During circulating in the annulus, foam drilling fluids are most likely contaminated by inorganic salts, such as CaCl_2 and NaCl . These inorganic salts, especially their highly charged cations, can deteriorate drilling fluids and influence the stability of the drilling foam through decomposition of the foaming agent and foam stabilizer. Thus, thermal stability and salt tolerance must be considered.

3.5.1 Thermal stability evaluation

In our study, the temperature resistance of a foam was evaluated by measuring V_0 and $T_{0.5}$ after mixed dispersions of AD300 with OB-2, SG and $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particle stabilizers were hot rolled at 280 °C for 8 h, 16 h and 24 h. As the hot rolling time increased from 0 to 24 h, the foaming ability of all mixed dispersions decreased but by a different degree (Figure 5(a)). When the mixed dispersion contained $\text{NH}_2\text{-SiO}_2\text{-12C}$ or SG particles, V_0 decreased from 110 mL to 70 mL after hot rolling at 280 °C for 24 h. By comparison, V_0 of the dispersion with OB-2 decreased from 140 mL to 47 mL after hot rolling for 8 h and increased to 65 mL after hot rolling for 24 h. The foaming ability was affected by the surface tension (data not given) such that an increase in the surface tension due to the thermal decomposition of OB-2 and the adsorption of AD300 onto the particles would decrease the foam volume. It has been reported that V_0 must exceed 50 mL and $T_{0.5}$ should simultaneously be greater than 360 s to meet drilling engineering needs⁴³. Therefore, all dispersions except that of AD300 with OB-2 are suitable for use in drilling geothermal wells. With respect to foam stability (Figure 5(b)), the mixed dispersion with the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles possesses the best stability. After hot rolling for 24 h at 280 °C, the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles still extended $T_{0.5}$ to 668 s, while the SG particles and OB-2 molecules gradually became ineffective and began to have a deleterious impact on the foam stability compared with the blank dispersion. Thus, the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles have excellent resistance to high temperatures of 280 °C and are the best foam stabilizers compared with SG and OB-2.

3.5.2 Salt tolerance evaluation

Considering that the $T_{0.5}$ of the OB-2 and SG dispersions decreased below 360 s after hot rolling at 280 °C for 16 h and was predicted to be worse when the dispersion was contaminated by CaCl_2 , we only evaluated the CaCl_2 tolerance of a mixture of AD300 and $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles compared with an AD300 dispersion (Figure 5(c)). As the concentration of CaCl_2 increased, the V_0 of the AD300 dispersion and that stabilized by the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles both decreased continuously. In addition, $T_{0.5}$ first increased and then decreased. However, a blank dispersion could only resist 0.3 wt% CaCl_2 , while the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles increased the CaCl_2 resistance of the foam up to 0.8 wt%. Thus, the $\text{NH}_2\text{-SiO}_2\text{-12C}$ particles displayed excellent CaCl_2 tolerance, which may be attributed to their surface activity. Because of their excellent thermal stability and CaCl_2 tolerance, Janus particles can be utilized as foam stabilizers in high-temperature geothermal well drilling.

4. Conclusion

Janus particles with heterogeneous wettabilities were innovatively adopted for use in foam drilling fluids as foam stabilizers. Using the Pickering emulsion method, a series of Janus particles, $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18), were fabricated by selectively modifying SiO_2 particles with APTES on one hemisphere and then coupling silane agents with different carbon chain lengths onto the other hemisphere. The composition, wettability and zeta potential can thus be adjusted. By comparison, the $\text{NH}_2\text{-SiO}_2\text{-nC}$ particles have much better foam stabilities than those of OB-2

molecules, hydrophobic SG particles, bare silica particles and $\text{NH}_2\text{-SiO}_2$ particles. In particular, the $\text{NH}_2\text{-SiO}_2\text{-12C}$ particle-stabilized foam displays the largest size, thickest film, highest elasticity and longest drainage half-life. Therefore, the $\text{NH}_2\text{-SiO}_2\text{-12C}$ particles were identified as the most suitable candidate for use as foam stabilizers. Their excellent stabilizing property was attributed to their appropriate contact angle (approximately 80°) and high positive zeta potential. When used in a foam drilling fluid dispersion, the $\text{NH}_2\text{-SiO}_2\text{-12C}$ particles remained effective at the high temperature of 280°C and 0.8 wt% CaCl_2 contamination. Thus, the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles are expected to be useful as foam stabilizers in high-temperature and high-salinity conditions, such as geothermal well drilling, enhanced oil recovery and “waterless” fracturing.

5. Acknowledgments

This work was supported by the National Science Foundation of China (grant No. 51604290 and 51874329); and startup foundation of China University of Petroleum (Beijing) (grant No. ZX20150392).

Associated content

Supporting information: This file contains the water contact angle of bare SiO_2 , DDAB-covered SiO_2 and DDAB-covered SiO_2 after rising by ethanol, XPS curves of bare SiO_2 , $\text{NH}_2\text{-SiO}_2$, $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18) particles, photographs of $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18) Janus particles dispersed in a mixture of water and hexane, the surface tension of foaming agent solution at various concentrations from 0 to 0.8 wt% and optical microscopy photographs of foam for size and film

thickness statistics.

6. References

- (1) Kapetas, L.; Bonnieu, S. V.; Danelis, S.; Rossen, W. R.; Farajzadeh, R.; Eftekhari, A. A.; Shafian, S. R. M.; Bahrim, R. Z. K. Effect of Temperature on Foam Flow in Porous Media. *J. Ind. Eng. Chem.* **2016**, *36*, 229-237.
- (2) Arzhavitina, A.; Steckel, H. Foams for Pharmaceutical and Cosmetic Application. *Int. J. Pharm.* **2010**, *394*, 1-17.
- (3) Nor, M. A. A. M.; Hong, L. C.; Ahmad, Z. A.; Akil, H. M. Preparation and Characterization of Ceramic Foam Produced Via Polymeric Foam Replication Method. *J. Mater. Process. Technol.* **2008**, *207*, 235-239.
- (4) Comas, H.; Laporte, V.; Borcard, F.; Miéville, P.; Krauss, J. F.; Caporini, M. A.; Gonzenbach, U. T.; Juillerat-Jeanneret, L.; Gerber-Lemaire, S. Surface Functionalization of Alumina Ceramic Foams with Organic Ligands. *ACS Appl. Mater. Interfaces* **2012**, *4*, 573-576.
- (5) Ma, W.; Zhou, Y.; Su, X.; Guo, J.; Wang, Y. Performance Evaluation and Application of Circulative Micro-Foam Drilling Fluid. *Sino-Global Energy* **2010**, *15*, 57-59.
- (6) Zhang, Y.; Huang, Z.; Chen, Y.; Jiao, T.; Zhang, Y. Performance of Nitrogen Foam Diversion Acidizing of D27 Well in Offshore Suizhong 36-1 Oilfield. *Offshore Oil* **2009**, *29*, 42-47.
- (7) Zhaomin; Zhang; Songyan; Qichao; Jinqiao. Current Situation and Prospect of Research and Application of Clean Foam Fracturing Fluid. *Special Oil & Gas Reservoirs* **2014**, *21*, 1-6.
- (8) Farzaneh, S. A.; Sohrabi, M. A Review of the Status of Foam Application in Enhanced Oil Recovery. In *EAGE Annual Conference & Exhibition incorporating SPE Europe*, Society of Petroleum Engineers: London, UK, 2013; pp 1-15.
- (9) Zhang, Z.; Njee, J.; Han, M.; Shan, Z.; Zhang, M.; Sun, F. Successful Implementation of Ht Geothermal Drilling Technology in Kenya. In *IADC/SPE Asia Pacific Drilling Technology Conference and Exhibition*, Society of Petroleum Engineers: Tianjin, China, 2012; pp 1-7.
- (10) Brookey, T. "Micro-Bubbles": New Aphron Drill-in Fluid Technique Reduces Formation Damage in Horizontal Wells. In *SPE Formation Damage Control Conference*, Society of Petroleum Engineers: Lafayette, Louisiana, 1998; pp 1-12.
- (11) Martins, A. L.; Lourenco, A. M. F.; de Sa, C. H. M. Foam Property Requirements for Proper Hole Cleaning While Drilling Horizontal Wells in Underbalanced Conditions. *SPE Drill. Complet* **2001**, *16*, 195-200.
- (12) Li, J.; Zhang, C.; Cheng, P.; Chen, X.; Wang, W.; Luo, J. Afm Studies on Liquid Superlubricity between Silica Surfaces Achieved with Surfactant Micelles. *Langmuir the Acs Journal of Surfaces & Colloids* **2016**, *32*, 5593-5599.
- (13) Jia, Z. F.; Zao-Yuan, L. I.; Zhong, J. X. Inorganic Salts and Their Concentrations: Effects on the Viscosity of Hydrophobically Associating Polymer Solution. *Drilling Fluid & Completion Fluid* **2007**, *24*, 55-57.

- (14) Fujii, S.; Yokoyama, Y.; Nakayama, S.; Ito, M.; Yusa, S.; Nakamura, Y. Gas Bubbles Stabilized by Janus Particles with Varying Hydrophilic-Hydrophobic Surface Characteristics. *Langmuir* **2018**, *34*, 933-942.
- (15) Horozov, T. S. Foams and Foam Films Stabilised by Solid Particles. *Current Opinion in Colloid & Interface Science* **2008**, *13*, 134-140.
- (16) Hunter, T. N.; Pugh, R. J.; Franks, G. V.; Jameson, G. J. The Role of Particles in Stabilising Foams and Emulsions. *Adv. Colloid Interface Sci.* **2008**, *137*, 57-81.
- (17) Sun, Q.; Li, Z. M.; Wang, J. Q.; Li, S. Y.; Li, B. F.; Jiang, L.; Wang, H. Y.; Lu, Q. C.; Zhang, C.; Liu, W. Aqueous Foam Stabilized by Partially Hydrophobic Nanoparticles in the Presence of Surfactant. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2015**, *471*, 54-64.
- (18) Stocco, A.; Drenckhan, W.; Rio, E.; Langevin, D.; Binks, B. P. Particle-Stabilised Foams: An Interfacial Study. *Soft Matter* **2009**, *5*, 2215-2222.
- (19) Du, Z. P.; Bilbao-Montoya, M. P.; Binks, B. P.; Dickinson, E.; Ettelaie, R.; Murray, B. S. Outstanding Stability of Particle-Stabilized Bubbles. *Langmuir* **2003**, *19*, 3106-3108.
- (20) Kam, S. I.; Rossen, W. R. Anomalous Capillary Pressure, Stress, and Stability of Solids-Coated Bubbles. *Journal of Colloid & Interface Science* **1999**, *213*, 329-339.
- (21) Nakayama, S.; Hamasaki, S.; Ueno, K.; Mochizuki, M.; Yusa, S.; Nakamura, Y.; Fujii, S. Foams Stabilized with Solid Particles Carrying Stimuli-Responsive Polymer Hairs. *Soft Matter* **2016**, *12*, 4794-4804.
- (22) Subramaniam, A. B.; Abkarian, M.; Stone, H. A. Controlled Assembly of Jammed Colloidal Shells on Fluid Droplets. *Nat. Mater.* **2005**, *4*, 553-556.
- (23) Dickinson, E.; Ettelaie, R.; Kostakis, T.; Murray, B. S. Factors Controlling the Formation and Stability of Air Bubbles Stabilized by Partially Hydrophobic Silica Nanoparticles. *Langmuir* **2004**, *20*, 8517-8525.
- (24) Gonzenbach, U. T.; Studart, A. R.; Tervoort, E.; Gauckler, L. J. Ultrastable Particle-Stabilized Foams. *Angew. Chem. Int. Ed.* **2010**, *45*, 3526-3530.
- (25) McCall, W. R.; Kim, K.; Heath, C.; La, P. G.; Sirbuly, D. J. Piezoelectric Nanoparticle-Polymer Composite Foams. *ACS Appl. Mater. Interfaces* **2014**, *6*, 19504.
- (26) Iqbal, S. H.; Webster, J. The Trapping of Aquatic Hyphomycete Spores by Air Bubbles. *Transactions of the British Mycological Society* **1973**, *60*, 37-48.
- (27) Santini, E.; Kragel, J.; Ravera, F.; Liggieri, L.; Miller, R. Study of the Monolayer Structure and Wettability Properties of Silica Nanoparticles and Ctab Using the Langmuir Trough Technique. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2011**, *382*, 186-191.
- (28) Binks, B. P.; Kirkland, M.; Rodrigues, J. A. Origin of Stabilisation of Aqueous Foams in Nanoparticle-Surfactant Mixtures. *Soft Matter* **2008**, *4*, 2373-2382.
- (29) Faure, S.; Volland, S.; Crouzet, Q.; Boutevin, G.; Loubat, C. Synthesis of New Fluorinated Foaming Particles. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2011**, *382*, 139-144.
- (30) Fujii, S.; Yokoyama, Y.; Miyazaki, Y.; Shiono, T.; Ito, M.; Yusa, S.; Nakamura, Y. Micrometer-Sized Gold-Silica Janus Particles as Particulate Emulsifiers. *Langmuir* **2013**, *29*, 5457-5465.

- (31) Jiang, S.; Granick, S. Controlling the Geometry (Janus Balance) of Amphiphilic Colloidal Particles. *Langmuir* **2008**, *24*, 2438-2445.
- (32) Perro, A.; Reculosa, S.; Bourgeat-Lami, E.; Duguet, E.; Ravaine, S. Synthesis of Hybrid Colloidal Particles: From Snowman-Like to Raspberry-Like Morphologies. *Colloids & Surfaces A Physicochemical & Engineering Aspects* **2006**, *284*, 78-83.
- (33) Abdel-Fattah, A. I.; El-Genk, M. S. Sorption of Hydrophobic, Negatively Charged Microspheres onto a Stagnant Air/Water Interface. *Journal of Colloid & Interface Science* **1998**, *202*, 417-429.
- (34) Williams, D. F.; Berg, J. C. The Aggregation of Colloidal Particles at the Air—Water Interface. *Journal of Colloid & Interface Science* **1992**, *152*, 218–229.
- (35) Jesionowski, T. Influence of Aminosilane Surface Modification and Dyes Adsorption on Zeta Potential of Spherical Silica Particles Formed in Emulsion System. *Colloids & Surfaces A Physicochemical & Engineering Aspects* **2003**, *222*, 87-94.
- (36) Kim, J. W.; Lee, D.; Shum, H. C.; Weitz, D. A. Colloid Surfactants for Emulsion Stabilization. *Adv. Mater.* **2008**, *20*, 3239-3243.
- (37) Saul, G. Generalizations of the Young-Laplace Equation for the Pressure of a Mechanically Stable Gas Bubble in a Soft Elastic Material. *J. Chem. Phys.* **2009**, *131*, 589.
- (38) Jauregi, P.; Varley, J. Colloidal Gas Aphrons: Potential Applications in Biotechnology. *Trends Biotechnol.* **1999**, *17*, 389-395.
- (39) SPINELLI; Luciana, S.; NETO; Genecy, R.; FREIRE; Layla, F. A.; MONTEIRO; Vitor; LOMBA; Rosana. Synthetic-Based Aphrons: Correlation between Properties and Filtrate Reduction Performance. *Colloids & Surfaces A Physicochemical & Engineering Aspects* **2010**, *353*, 57-63.
- (40) Lye, G. J.; Stuckey, D. C. Structure and Stability of Colloidal Liquid Aphrons. *Colloids & Surfaces A Physicochemical & Engineering Aspects* **1998**, *131*, 119-136.
- (41) Deng, T.; Dai, Y.; Wang, J. A New Kind of Dispersion : Colloidal Emulsion Aphrons. *Colloids & Surfaces A Physicochemical & Engineering Aspects* **2005**, *266*, 97-105.
- (42) Zhou, Z. Y.; Liu, S. L.; Liu, J. X. Study on the Characteristics and Development Strategies of Geothermal Resources in China. *Journal of Natural Resources* **2015**, *30*, 1210-1221.
- (43) Lai, X.; Lou, Y.; Yuanzhi, Q. U.; Shan, Z. Foam Drilling Fluid Technology for Ultra-High Temperature Geothermal Wells. *Drilling Fluid & Completion Fluid* **2009**, *26*, 37-38.

Captions

Figure 1. (a) Diagram for the fabrication of Janus particles by the Pickering emulsion method. (b) SEM images of the colloidosomes. The inset shows the size distribution of the wax colloidosomes as measured by DLS. (c) Magnification of the area of the red square in (b). (d) SEM images of the $\text{NH}_2\text{-SiO}_2$ particles coated with gold particles. The red circle outlines the areas that are not decorated by gold particles. (e) TGA of the SiO_2 , $\text{NH}_2\text{-SiO}_2$, and $\text{NH}_2\text{-SiO}_2\text{-nC}$ Janus particles.

Figure 2. (a1-a7) Water contact angles of bare SiO_2 particles, and $\text{NH}_2\text{-SiO}_2$, $\text{NH}_2\text{-SiO}_2\text{-1C}$, $\text{NH}_2\text{-SiO}_2\text{-3C}$, $\text{NH}_2\text{-SiO}_2\text{-8C}$, $\text{NH}_2\text{-SiO}_2\text{-12C}$, and $\text{NH}_2\text{-SiO}_2\text{-18C}$ Janus particles, respectively. (b1-b3) Photographs of the $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles, bare SiO_2 particles and homogeneous lipophilic silica particles modified by 12C and dispersed in a mixture of water (yellow) and hexane (colorless). (b4) Magnification of the area of the red rectangle in (b1). (b5) Magnification of the area of the blue rectangle in (b3). (c) Zeta potentials of aqueous dispersion of the SiO_2 , $\text{NH}_2\text{-SiO}_2$, $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18) particles at a concentration of $0.1 \text{ g}\cdot\text{L}^{-1}$.

Figure 3. (a) Surface tension, (b) dilational elasticity and (c) viscosity of a 0.4 wt% pure AD300 solution (blank) and mixed dispersions of 0.4 wt% AD300 with 0.3 wt% $\text{NH}_2\text{-SiO}_2$ particles, 0.3 wt% $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18) Janus particles, 0.3 wt% SG particles and 0.3 wt% OB-2 molecule.

Figure 4. (a) Illustrative picture of $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18) Janus particles distributed on a foam film. (b)-(i) Optical microscopy images of a foam of

pure AD300 and those stabilized by OB-2 molecules, SG particles, $\text{NH}_2\text{-SiO}_2\text{-1C}$ Janus particles, $\text{NH}_2\text{-SiO}_2\text{-3C}$ Janus particles, $\text{NH}_2\text{-SiO}_2\text{-8C}$ Janus particles, $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles and $\text{NH}_2\text{-SiO}_2\text{-18C}$ Janus particles, respectively. The scale bar is 200 μm . (j) Theoretical relationship between the film thickness and bubble size. The Scale bar is 50 μm and 2 μm in (j) and the inset, respectively.

Figure 5. (a) Foam volume and (b) drainage half-life of foams fabricated after adding a 0.4 wt% AD300 solution (blank), or a mixed dispersion of 0.4 wt% AD300 and 0.3 wt% $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles, 0.3 wt% OB-2 molecules and 0.3 wt% SG particles. Samples were hot rolled at 280 °C for 0, 8, 16 and 24 h. (c) CaCl_2 tolerance evaluation of foams fabricated after adding a mixed dispersion of 0.4 wt% AD300 and 0.3 wt% $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles compared with a blank after being hot rolled at 280 °C for 16 h.

Table 1. Foaming abilities and foam stabilities of a 0.4 wt% AD300 solution and mixed dispersions of 0.4 wt% AD300 stabilized with a series of particles and OB-2 molecules at different concentrations.

[QCE1][Ed22]

Figure 1. (a) Diagram for the fabrication of Janus particles by the Pickering emulsion method. (b) SEM images of the colloidosomes. The inset shows the size distribution of the wax colloidosomes as measured by DLS. (c) Magnification of the area of the red square in (b). (d) SEM images of the NH₂-SiO₂ particles coated with gold particles. The red circle outlines the areas that are not decorated by gold particles. (e) TGA of the SiO₂, NH₂-SiO₂, and NH₂-SiO₂-nC Janus particles.

[Ed23]

Figure 2. (a1-a7) Water contact angles of bare SiO₂ particles, and NH₂-SiO₂, NH₂-SiO₂-1C, NH₂-SiO₂-3C, NH₂-SiO₂-8C, NH₂-SiO₂-12C, and NH₂-SiO₂-18C Janus particles, respectively. (b1-b3) Photographs of the NH₂-SiO₂-12C Janus particles, bare SiO₂ particles and homogeneous lipophilic silica particles modified by 12C and dispersed in a mixture of water (yellow) and hexane (colorless). (b4) Magnification of the area of the red rectangle in (b1). (b5) Magnification of the area of the blue rectangle in (b3). (c) Zeta potentials of aqueous dispersion of the SiO₂, NH₂-SiO₂, NH₂-SiO₂-nC (n=1, 3, 8, 12 and 18) particles at a concentration of 0.1 g·L⁻¹.

Figure 3. (a) Surface tension, (b) dilational elasticity and (c) viscosity of a 0.4 wt% pure AD300 solution (blank) and mixed dispersions of 0.4 wt% AD300 with 0.3 wt% NH₂-SiO₂ particles, 0.3 wt% NH₂-SiO₂-nC (n=1, 3, 8, 12 and 18) Janus particles, 0.3 wt% SG particles and 0.3 wt% OB-2 molecule.

Figure 4. (a) Illustrative picture of $\text{NH}_2\text{-SiO}_2\text{-nC}$ ($n=1, 3, 8, 12$ and 18) Janus particles distributed on a foam film. (b)-(i) Optical microscopy images of a foam of pure AD300 and those stabilized by OB-2 molecules, SG particles, $\text{NH}_2\text{-SiO}_2\text{-1C}$ Janus particles, $\text{NH}_2\text{-SiO}_2\text{-3C}$ Janus particles, $\text{NH}_2\text{-SiO}_2\text{-8C}$ Janus particles, $\text{NH}_2\text{-SiO}_2\text{-12C}$ Janus particles and $\text{NH}_2\text{-SiO}_2\text{-18C}$ Janus particles, respectively. The scale bar is $200\ \mu\text{m}$. (j) Theoretical relationship between the film thickness and bubble size. The Scale bar is $50\ \mu\text{m}$ and $2\ \mu\text{m}$ in (j) and the inset, respectively.

Figure 5. (a) Foam volume and (b) drainage half-life of foams fabricated after adding a 0.4 wt% AD300 solution (blank), or a mixed dispersion of 0.4 wt% AD300 and 0.3 wt% NH₂-SiO₂-12C Janus particles, 0.3 wt% OB-2 molecules and 0.3 wt% SG particles. Samples were hot rolled at 280 °C for 0, 8, 16 and 24 h. (c) CaCl₂ tolerance evaluation of foams fabricated after adding a mixed dispersion of 0.4 wt% AD300 and 0.3 wt% NH₂-SiO₂-12C Janus particles compared with a blank after being hot rolled at 280 °C for 16 h.

Table 1. Foaming abilities and foam stabilities of a 0.4 wt% AD300 solution and mixed dispersions of 0.4 wt% AD300 stabilized with a series of particles and OB-2 molecules at different concentrations.

Particles		C [*] _{AD300} (wt%)	V ₀ (mL)	T _{0.5} (s)
Type	C _P ^{**} (wt%)			
Blank	0	0.4	110	448
Bare SiO ₂	0.15	0.4	100	407
	0.3	0.4	100	412
	0.6	0.4	90	391
	0.9	0.4	90	391
NH ₂ -SiO ₂	0.3	0.4	100	521
	0.6	0.4	90	564
	0.9	0.4	90	548
NH ₂ -SiO ₂ -NH ₂ ^{***}	0.15	0.4	110	445
	0.3	0.4	110	455
	0.6	0.4	110	443
NH ₂ -SiO ₂ -1C	0.15	0.4	110	501
	0.3	0.4	110	580
	0.6	0.4	110	553
NH ₂ -SiO ₂ -3C	0.15	0.4	110	631
	0.3	0.4	110	691
	0.6	0.4	110	616
NH ₂ -SiO ₂ -8C	0.3	0.4	110	688
	0.6	0.4	110	731
	0.9	0.4	110	663
NH ₂ -SiO ₂ -12C	0.15	0.4	110	717
	0.3	0.4	110	778
	0.6	0.4	110	714
NH ₂ -SiO ₂ -18C	0.3	0.4	100	679
	0.6	0.4	100	702
	0.9	0.4	100	740
	1.2	0.4	105	701
	1.5	0.4	100	707
	1.8	0.4	100	707
OB-2	0.3	0.4	140	488
SG	0.3	0.4	110	515

* Concentration of AD300 in the foam fluid

** Concentration of particles in the foam fluid

*** SiO₂ homogeneously modified by APTES

Highly stabilized foam by adding amphiphilic Janus particles for drilling geothermal wells

Lili Yang^{abc, &, *}, Tengda Wang^{ab, &}, Xiao Yang^{ab}, Guancheng Jiang^{ab, *},
Jianping Xu^{ab}, Xinliang Li^{ab}, Xiaoxiao Ni^{ab}

^a State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum (Beijing), Beijing 102249, China

^b MOE Key Laboratory of Petroleum Engineering, China University of Petroleum, (Beijing), Changping District, Beijing 102249, China

^c Department of Chemical Engineering, Imperial College London, Prince Consort Road, London SW7 2AZ, UK

Janus particles, having both hydrophilic and hydrophobic parts and showing excellent interface activity, are fabricated and innovatively applied in foam drilling fluid as anti-high temperature and -calcium foam stabilizer.

* Corresponding author.

Tel.: +86 10 89732239; fax: +86 10 8973 2196; E-mail address: yangll@cup.edu.cn (L. Yang)

Tel.: +86 10 89732196; fax: +86 10 8973 2196; E-mail address: m15600263100_1@163.com (G. Jiang)

& These authors contributed equally to this work