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Review

Nanomaterials and Technology Applications for Hydraulic Fracturing of Unconventional Oil and Gas Reservoirs: A State-of-the-Art Review of Recent Advances and Perspectives

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ABSTRACT: The application of hydraulic fracturing stimulation technology to improve the productivity of unconventional oil and gas reservoirs is a well-established practice. With the increasing exploration and development of unconventional oil and gas resources, the associated geological conditions and physical properties are gradually becoming more and more complex. Therefore, it is necessary to develop technologies that can improve the development benefits to meet these challenges. In recent years, improving the effect of hydraulic fracturing stimulation in unconventional oil and gas reservoirs through the use of nanomaterials and technologies has attracted increasing attention. In this paper, we review the current status and research progress of the application of nanomaterials and technologies in various aspects of hydraulic fracturing in unconventional oil and gas reservoirs, expound the mechanism and advantages of these nanomaterials and technologies in detail, and provide future research directions. The reviewed literature indicates that nanomaterials and technologies show exciting potential applications in the hydraulic fracturing of unconventional reservoirs; for example, the sand-carrying and rheological properties of fracturing fluids can be significantly enhanced through the addition of nanomaterials. The use of nanomaterials to modify proppants can improve their compressive strength, thus meeting the needs of different reservoir conditions. The fracturing flowback fluid treatment efficiency and purification effect can be improved through the use of nanophotocatalysis and nanomembrane technologies, while degradable fracturing completion tools developed based on nanomaterials can effectively improve the efficiency of fracturing operations. Nanorobots and magnetic nanoparticles can be used to more efficiently monitor hydraulic fracturing and to accurately map the hydraulic fracture morphology. However, due to the complex preparation process and high cost of nanomaterials, more work is needed to fully investigate the application mechanisms of nanomaterials and technologies, as well as to evaluate the economic feasibility of these exciting technologies. The main research objective of this review is to comprehensively summarize the application and research progress of nanomaterials and technologies in various aspects of hydraulic fracturing in unconventional oil and gas reservoirs, analyze the existing problems and challenges, and propose some targeted forward-looking recommendations, which may be helpful for future research and applications.

1. INTRODUCTION

Unconventional oil and gas refers to oil and gas resources that cannot be obtained using traditional development technologies, which can be economically exploited only through the use of novel technologies which improve reservoir permeability or fluid viscosity.[1,2] In recent years, with the increasing global demand for oil and gas resources, unconventional oil and gas resources represented, for example, by shale gas, tight sandstone gas, and coal-bed methane have gradually become a research hotspot in the oil and gas industry.[3,4] Unconventional oil and gas reservoirs typically have the following key characteristics: large-scale continuous distribution of oil and gas, indistinct trap boundaries, no natural industrial stable production, insignificant Darcy seepage, porosity lower than 10%, pore throat diameter less than 1 μm, and permeability less than 1 md.[5−7] Due to the poor physical properties of unconventional oil and gas reservoirs (e.g., low porosity and low permeability), it is usually necessary to use hydraulic fracturing technology to reconstruct the reservoir during commercial development in order to obtain high-yield industrial oil and gas flow.

As a widely used oil and gas stimulation technology, hydraulic fracturing has undergone more than 70 years of development since it was first successfully tested in North America in the 1940s.[8] In the process of hydraulic fracturing,

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the proppant is usually carried by the fracturing fluid into the formation and used to support the hydraulic fractures after fracturing, thereby forming artificial fractures with a certain conductivity in the formation, providing high conductivity channels for oil and gas seepage.[9] Fracturing fluid and proppant are the most critical materials in hydraulic fracturing technology, and their performance directly affects the effect of reservoir fracturing and the success rate of fracturing operations.[10] However, with the acceleration of the exploration and development of unconventional oil and gas resources, deep and even ultradeep reservoirs have gradually developed, and the reservoir conditions have become more complicated. The associated formation environment, with high temperature, high pressure, or even ultrahigh pressure, leads to higher requirements for the performance of the fracturing fluid, proppant, and downhole fracturing tools.[11]

In order to cope with the increasingly complex unconventional oil and gas production environment and to meet the needs for the rapid development of hydraulic fracturing technology, researchers have begun to make revolutionary innovations in unconventional oil and gas hydraulic fracturing technology by introducing nanomaterials and technologies to meet the needs of fracturing operations under different reservoir conditions. Nanotechnology is a science and technology that considers single atoms and molecules in the construction of substances.[12] Nanotechnology, including nanomaterial design, manufacturing, and nanomeasurement, has been widely used in electronic, biological, medical, aviation, military, and other fields.[13] Nanomaterials are a new type of functional materials, which have smaller size (usually 1−100 nm) and larger specific surface area than conventional granular materials (Figure 1), thus possessing higher reaction activity. Therefore, it is usually only necessary to add a small amount of nanomaterials in order to enhance the properties of matrix materials.[14]

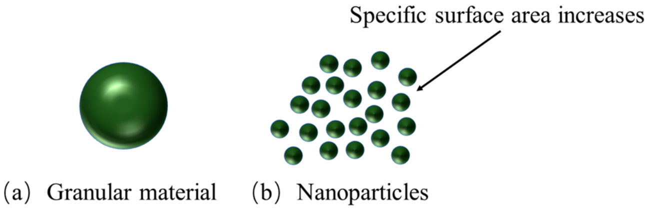


Figure 1. Specific surface area of nanoparticles. Reprinted with permission from ref 14. Copyright 2018 Science Technology and Engineering.

Nanomaterials, which exhibit unique optical, electrical, thermal, and magnetic properties due to their scale effects, have become a research hotspot in both academia and industry and have gradually entered the research field involving traditional and new fossil energy. In Table 1, the exciting applications of nanomaterials and technologies in different aspects of hydraulic fracturing in unconventional oil and gas reservoirs are presented.

In recent years, researchers have increasingly applied nanomaterials and technologies to the hydraulic fracturing of unconventional oil and gas reservoirs and have made some gratifying progress. The specific surface functionalization and surface activity of nanomaterials can be used to improve the performance of the fracturing fluid system, making them suitable for use in complex formation conditions, such as high temperature and high pressure.[15] Huang et al.[16] have systematically studied the effect of adding ZnO nanoparticles on the rheological properties of an amide amine surfactant. At low shear rate (less than 0.01 s^{-1}), the viscosity of the fracturing fluid system containing nanoparticles was significantly higher than that of the sample without nanoparticles, presenting better sand suspension ability. At 121 °C and 100 s^{-1}, the viscosity of the fracturing fluid containing nanoparticles was 5 times that of the sample without nanoparticles at a certain time. Meanwhile, Huang et al.[17] have also added 35 nm ZnO nanoparticles to VES and found that the nanoparticles and VES micelles form a quasi-cross-linked structure through van der Waals and electrostatic forces, which can improve the viscosity of the VES and reduce filtration. Fakoya et al.[18] have added different proportions of SiO_2 particles with particle size of 20 nm to a surfactant system, polymer system, and polymer−surfactant mixed system, studied the effect of adding nanoparticles on the rheology of different systems, and found that the surfactant base liquid with added nanoparticles is more suitable for the exploitation of unconventional oil and gas, effectively reducing the economic cost and reducing damage to the reservoir. Gurluk et al.[19] considered the problem that the surfactant base solution cannot be applied when the temperature is above 200 °F. By adding nanoparticles, the viscoelasticity of the surfactant base solution was improved, and the applicable temperature range of the surfactant base solution was increased to more than 200 °F, demonstrating that nanomaterials can significantly improve the temperature resistance and other properties of the surfactant base solution. Xiao et al.[20] have added new nanocomposite fibers to VES fracturing fluid in order to address the problems of coal-bed methane adsorption and difficulty in gel breaking of fracturing fluid. They found that the network structure of nanofibers can inhibit pulverized coal accumulation, reduce filtration loss, and reduce reservoir damage.

When the surface of a conventional proppant is coated with nanomaterials, it may show high compressive strength and good suspension capacity, such that it can be carried and laid further in the formation by the fracturing fluid, effectively supporting hydraulic fractures and providing a high number of channels for oil and gas flow. Huang et al.[21,22] have proposed the concept that nanoparticles can be used to control the migration of proppant debris and remove the blockages near the well, and developed a nanomaterial-coated proppant. The proppant takes advantage of the high surface activity of nanometal oxides (MgO, ZnO, Al_2O_3, TiO_2, ZrO_2) to coat and modify the surface of proppant matrix particles, thus detaining or trapping particles in the formation using van der Waals and electrostatic attraction forces, in order to control the migration of formation particles and stabilize the proppant accumulation layer. At the same time, nanoproppants can also be developed to improve the effect of hydraulic fracturing. Bose et al.[23] took the lead in putting forward the concept of a nanoproppant. The particle size of a nanoproppant is 100 nm to 1 μm, and the technical principle involves injecting these nanoproppants into the formation before pumping conventional fracturing proppant, such that they can fill in the natural microfractures on both wings of the fracture, thus supporting the microfractures and increasing the conductivity of the fracture network.

Fracturing flowback fluid has complex composition, high salt content, and many kinds of organic pollutants. Direct discharge will cause serious pollution to the environment. With more and

Table 1. Summary of the Nanomaterials and Technology Applications in Hydraulic Fracturing of Unconventional Oil and Gas Reservoirs

application field	mechanisms	advantages	refs
fracturing fluids	the spatial network structure of the fracturing fluid system is enhanced by adding nanoparticles to polymer solutions or cross-linked gel-fracturing fluids	1. improve the rheology of polymer-based fracturing fluid and its stability under high temperature and high pressure 2. reduce the amount of polymer 3. reduce the damage to the fractures conductivity	41−45
	additives such as nano drag reducer and drainage aid prepared based on nanomaterials can form a more stable solution system structure and reduce surface tension	1. high viscosity and excellent sand suspension performance 2. better temperature resistance, salt resistance, shear resistance, and drag reduction performance 3. reduce water lock damage and help to flow back after hydraulic fracturing	67−70
	nanoparticles combine with VES micelles to form a tight spatial network structure through chemisorption and surface charge interactions	1. improve temperature and shear resistance and reduce fracturing fluids filtration loss 2. enhance the sand-carrying performance of VES fracturing fluid	78,80,84−89
	nanoparticles can be adsorbed on the interface with the synergistic effect of surfactants and form a stable adsorption layer on the surface of the foam film, which plays a role in stabilizing the foam film	1. effectively inhibit the coalescence effect of bubbles and stabilize the foam 2. reduce the fracturing fluids filtration loss 3. improve sand-carrying performance	94,113−116
proppants	nanoscale proppants were prepared by nanoparticles for supporting micro/nanofractures in the reservoir	1. prevent the closure of microfractures and effectively increase the fractures area 2. improve the reservoir fractures network conductivity	23,125−127
	the surface of proppant matrix particles was coated with nanomaterials to improve its performance	1. improve proppant compressive strength and reduce the crushing of proppant 2. maintain the hydraulic fractures conductivity	129−133
fracturing flowback fluid treatment	nanophotocatalysts have the ability to oxidize and decompose pollutants under light and deeply purify fracturing flowback fluids	improve the treatment efficiency and treatment effect of fracturing flowback fluid, and it can be recycled	137−140,142
	utilize the nanofiltration characteristics to prepare separation membranes such as ultrafiltration and nanofiltration to separate pollutants in fracturing flowback fluids	effectively removal of dissolved solids and organic pollutants	144−146
degradable fracturing completion tools development	fracturing completion tools made of degradable nanocomposites can be dissolved in fracturing flowback fluids	simplify operation procedures, improve operation efficiency and fracturing effect	154−157
hydraulic fracturing monitoring and fractures mapping	nanorobots and nanosensors can enter the micro/nanopores of unconventional reservoirs with the injected fluid to monitor hydraulic fracturing in real time	real-time acquisition of hydraulic fracture morphology parameters and accurate evaluation of fracturing effect	163,165,166
	magnetic nanoparticles can be mixed with proppant and injected into the formation, and the location of the proppant can be detected by measuring the magnetic susceptibility to characterize the hydraulic fractures	precisely locate and track downhole proppant distribution and accurately map hydraulic fractures geometry	168,169

more attention paid to environmental protection all over the world and the gradual improvement of environmental protection policies and regulations, more and more attention has been paid to the treatment of fracturing flowback fluid. Due to the low efficiency of conventional treatment methods using fracturing flowback fluid and the incomplete purification of flowback fluid, preparation involving nanofiltration, ultrafiltration, and reverse osmosis separation membranes with nanotechnology or the advanced treatment of fracturing flowback fluid with nanophotocatalytic technology can significantly reduce the content of organic pollutants in the flowback fluid, thus achieving the goal of deep purification of fracturing flowback fluid.[24] Saien et al.[25] have evaluated the feasibility of using nano-TiO_2 to treat oilfield wastewater, found that nano-TiO_2 has the ability to degrade organic pollutants in wastewater, and proposed that the synergistic effect of photocatalytic and biodegradation methods can significantly reduce the chemical oxygen demand (COD) in the flowback liquid. Zangeneh et al.[26] prepared a new hydrophilic, antiscaling, self-cleaning nanopermeable membrane with visible photocatalytic effect based on reversed-phase method using B-TiO_2−SiO_2/$CoFe_2O_4$ nanoparticles modified poly(ether sulfone), which can be used to treat oilfield wastewater, including fracturing flowback fluid. Wang et al.[27] have used nanophotocatalytic treatment technology to treat fracturing flowback fluid. The treatment process involves initially removing the guanidine gum and other colloidal particles that failed to break the gel by coagulation, then improving the removal rate of COD by oxidation adsorption and, finally, conducting advanced treatment using nano-TiO_2 photocatalytic technology. The treated flowback fluid can fully meet sewage discharge standards and reinjection requirements, indicating that the treatment effect of nano-TiO_2 photocatalytic technology on fracturing flowback fluid is good.

Nanotechnology also shows unique advantages in the research and development of degradable fracturing completion tools and the characterization of reservoir hydraulic fractures. Baker Hughes has developed a degradable nanostructure material, DNC, which is mainly composed of matrix and reinforcing components. The matrix components are generally materials with low density, high strength, and low electrode potential (e.g., beryllium, magnesium, aluminum), which the reinforcing components are usually ceramics, oxides, nitrides, and so on. The density of DNC is 1.5−2.0 g/cm^3, its compressive strength is up to 830 MPa, its corrosion rate is up to 430 mg/(cm^2·h) in 3% KCl solution at 65 °C, and it can be decomposed within 82 h. Thus, it has the characteristics of low density, high strength, controllable degradation rate, and low cost.[28] Baker Hughes company has used this material to manufacture fracturing completion tools. At present, frac balls, smart gas lift valves, and other fracturing completion tools that can reduce and decompress fractures have been developed, which have been applied in the staged fracturing of unconventional oil and gas horizontal wells with good results. Saudi Aramco is exploring the use of magnetic nanoparticles to characterize hydraulic fracturing fractures. When sending electromagnetic pulses from injection wells to production wells, nanoparticles can reduce the propagation speed of electromagnetic waves. By measuring the propagation time difference of electromagnetic waves through the fluid before and after injecting magnetic nanoparticles, the shape of the fracturing fracture network around the wellbore can be drawn.[29] Agenet et al.[30] have prepared fluorescent nanoparticles for the intelligent tracing of fluids. Ryoo et al.[31] have prepared paramagnetic nanofluids through experiments and simulated the migration law of magnetic particles in porous media. While the above works are still in the stage of tackling key laboratory problems, they have shown the feasibility of industrialization. In addition, Saudi Aramco has developed a nanorobot that can map reservoir characteristics, and conducted field experiments on injection and recovery using a nanorobot with a size of 10 nm and no active detection ability in 2010, which verified that the nanorobot has a very high recovery rate, as well as good stability and fluidity.[32] When the nanorobot flows in the reservoir, it can record the pressure, temperature, porosity, permeability, fluid type, and other parameters of the oil and gas reservoir in real-time, following which the nanorobot can be recovered from the produced fluid. Through analysis of the obtained data, the reservoir fracture and geological fault characteristic map can be drawn, which not only can be used to realize detailed description of the reservoir, but can also be used for the monitoring and characterization of fracturing fractures. Additionally, its working efficiency is much higher than that of conventional microseismic monitoring, well logging, and other technical means, and the nanorobot can be recycled, which makes it have good economic value and broad application prospects.[33]

Although nanotechnology has greatly promoted innovation in hydraulic fracturing technology and technological progress, as well as improving the development benefits of unconventional oil and gas, nanotechnology and nanomaterials have not yet achieved large-scale commercialization in the development of global unconventional oil and gas resources. For widespread application, in-depth and systematic research on the application mechanisms and conditions pertaining to nanotechnology and nanomaterials is still required. This paper reviews the current application status of nanotechnology in the hydraulic fracturing of unconventional oil and gas reservoirs, focusing on the mechanisms and advantages of nanotechnology and nanomaterials, in terms of improving the performance of the fracturing fluid and proppant, fracturing flowback fluid treatment, degradable fracturing completion tool development, and hydraulic fracturing feature characterization, among other aspects. At the same time, combined with the actual needs for the development of hydraulic fracturing technology at present, the application prospects and technical challenges of nanotechnology in unconventional oil and gas hydraulic fracturing are discussed, and future development directions for nanotechnology in unconventional oil and gas reservoir hydraulic fracturing are proposed.

2. APPLICATION OF NANOTECHNOLOGY IN HYDRAULIC FRACTURING OF UNCONVENTIONAL OIL AND GAS RESERVOIRS

Nanotechnology has been successfully introduced into the field of hydraulic fracturing technology, and has been substantially applied to improve several key aspects of hydraulic fracturing technology. This has, to a certain extent, promoted the development of hydraulic fracturing technology and is presently being intensively researched by many oil service companies and oil companies around the world. In this section, a comprehensive review of the latest research progress on nanotechnology in the hydraulic fracturing of unconventional oil and gas reservoirs is presented, and the mechanism of action and application conditions of nanotechnology in the hydraulic fracturing of unconventional oil and gas reservoirs are discussed.

2.1. Nanomaterial-Enhanced Fracturing Fluids.

The fracturing fluid is the working fluid in the hydraulic fracturing process, which plays the role of carrying the fracturing proppant into the formation and forming artificial fractures.[34] The fracturing fluid system is key to the success or failure of a fracturing operation. The fracturing fluid system needs to have the characteristics of high temperature resistance, good compatibility, little damage to the reservoir, and good gel-breaking performance. Considering the high surface activity and specific surface functionalization of nanomaterials, they can be applied to the fracturing fluid system. Adding nanomaterials to the fracturing fluid system can improve the comprehensive performance of the system through cross-linking between nanomaterials and polymers, synergistic effects with surfactants, and the formation of reversible cross-linking structures with micelles, which can effectively to solve the problems of large displacement and high pump pressure in the fracturing of unconventional oil and gas reservoirs, reduce the risk in the fracturing operation, and improve the success rate of fracturing operations.[35]

2.1.1. Polymer-Based Fracturing Fluids.

2.1.1.1. Role of Nanomaterials in Polymer-Based Fracturing Fluids.

Polymer-based fracturing fluids are mainly composed of a thickener, cross-linking agent, and gel breaker. This has always been an important direction of fracturing fluid research, due to their good performance, low production cost, and convenience of construction.[36] Guar gum polymer is the most commonly used polymer type in hydraulic fracturing. Guar gum is a high-molecular weight biopolymer, composed of a polysaccharide main chain and a galactose side chain.[37] However, the applicable temperature of guar gum generally does not exceed 82 °C. In order to further improve its temperature resistance, other forms of guar gum polymers and their derivatives have also been introduced in field applications, such as hydroxypropyl guar gum (HPG), carboxymethyl guar gum (CMG), and carboxymethyl hydroxypropyl guar gum (CMHPG).[38] However, due to the rising cost of guar beans and the instability of guar gum at high temperatures, researchers have developed synthetic polymers as substitutes, such as polyacrylamide polymers (PAM) and their derivatives, which have also been widely used in hydraulic fracturing.[39]

At present, polymer fracturing fluids have many shortcomings, such as high residue level after gel breaking, limited temperature resistance, and shear resistance. Some problems commonly occur with their application in different types of unconventional oil and gas reservoirs. Therefore, it is necessary to optimize the comprehensive performance and develop a polymer fracturing fluid system posing less damage to the reservoir and with better performance. The introduction of nanotechnology can solve this problem, to a certain extent. Adding nanoparticles to a polymer solution or cross-linked gel-fracturing fluid can enhance the spatial network structure of the fracturing fluid system, improving the rheology of the fracturing fluid and its stability under high temperature and high pressure, in order to effectively reduce the required amount of polymer, reduce the amount of gel-breaking residue, and reduce the damage to the conductivity of reservoir and hydraulic fractures.[36,40]

Fakoya et al.[41] have found that the apparent viscosity and viscoelasticity of solutions can be significantly improved with an increase in the concentration of nanoparticles by adding nano-SiO_2 (20 nm) to guar gum solution. This may be due to the physical adsorption of the guar gum molecular chain on the surface of SiO_2 nanoparticles, which causes the system to form a compact three-dimensional network structure, further enhancing the performance of the fracturing fluid. Liu et al.[42] have conducted an experimental study on the influence of different nanoparticles (e.g., nano-SiO_2, multiwall carbon nanotubes, graphene) on the performance of guar gel-fracturing fluid. The experimental results showed that nano-SiO_2 had the most significant enhancement effect on the performance of the fracturing fluid system, presenting the best shear stability, temperature stability, and viscoelasticity. This is because nano-SiO_2 particles play the role of core and skeleton in the fracturing fluid system, improving the comprehensive performance of the fracturing fluid. Alharbi et al.[43] have found that the addition of nanomaterials can reduce the viscosity loss of borate cross-linked guar jelly fracturing fluid under high pressure. At 55 MPa, the viscosity of conventional borate cross-linked guar jelly was reduced by about 97%, while the addition of different types of nanomaterials could increase the viscosity of the system by 6−9 times. This may be as the nanoparticles can interact with the free *cis*-hydroxyl groups released under high pressure, allowing the fracturing fluid system to maintain a certain degree of cross-linking and playing a role in stabilizing the fracturing fluid system.

Luan et al.[44] have synthesized a new copolymer (JNCH) using acrylamide, sodium styryl sulfonate, and acryloxyethyl trimethylammonium chloride as raw materials and compounded it with cross-linking agents and other additives to form a polymer fracturing fluid system. The system consists of 0.5% JNCH, 0.4% cross-linking agent, 0.3% antiswelling agent, 0.1% nanomaterials, 0.2% dispersant, and 0.3% filter aid. The experimental results demonstrated that the fracturing fluid system has good temperature resistance and shear resistance (the shear viscosity can reach 100 mPa·s at 170 °C and 170 s^{-1}), excellent drag reduction performance (the drag reduction rate of 0.05% JNCH is 75.17%), little damage to the reservoir, good gel-breaking performance, simple treatment of flowback fluid, good gel-breaking liquid permeability, and basic percolation recovery of 18.6%. After nanomaterials were added, the percolation recovery of the system was increased by 4.3−22.9%. The system possesses good antiswelling performance and can fully meet the needs of hydraulic fracturing operations in unconventional reservoirs such as shale oil. Ding et al.[45] have proposed a guar gum graft copolymer nanocomposite gel-fracturing fluid, mainly composed of guar gum graft copolymer thickener, nanomaterials (nano-SiO_2, cellulose nanofibers), and cross-linking agent. The nanocomposite gel-fracturing fluid is prepared by synthesizing guar gum graft copolymer, with guar gum or its derivant and acrylamide monomer as raw materials, then using the copolymer as thickener and adding a nanomaterial dispersion under the action of the cross-linking agent. By introducing hydrophilic flexible polymer branches into the guar gum semirigid macromolecular chain, mutual entanglement and adsorption with nanomaterials are enhanced, increasing the compatibility between the guar gum and nanomaterials and further enhancing the interaction between the nanomaterials and the polymer matrix. The prepared nanocomposite gel-fracturing fluid presented better temperature resistance, shear resistance, sand carrying capacity, and filtration reduction.

2.1.1.2. Nano-Cross-Linkers.

Cross-linking agents are commonly used additives in polymer fracturing fluids. A cross-linking agent can cross-link polymer macromolecules, such as guar gum or hydroxypropyl guar gum, in order to form new chemical bonds, with the resultant high-viscosity network structure providing excellent sand-carrying and fracturing ability to the fracturing fluid.[46] Due to the continuous increase in the price of guanidine gum used in the common boron cross-linking agent and the requirements of environmental protection with respect to the amount of cross-linking agent used, the application of boron cross-linking agent has become limited. Therefore, researchers have attempted to use nanomaterials to prepare nano-cross-linking agents with better performance. Compared with traditional cross-linking agents, nano-cross-linking agents have higher microsize and more surface action sites, thus effectively improving the cross-linking efficiency between polymer molecular chains and improving the rheology and stability of the fracturing fluid while reducing the required amounts of polymer and cross-linking agent.[47] Lafitte et al.[47] first proposed the use of a boric acid surface-modified nanolatex to prepare a guar gum cross-linking agent, and a boric acid-modified nanofunctional compound was developed as a cross-linking agent for guanidine gel-fracturing fluid. The particle size of nanoparticles in the boric acid-modified nanofunctional compound is 15 nm, much larger than the diameter of the boric acid radical particles. As it has multiple cross-linking sites, it presents high cross-linking efficiency and can be cross-linked with different guanidine gel molecules at lower concentration to form a gel with higher viscosity and strength. In addition, The optimal amount of boric acid required to form the gel is only 1/20 that required in ordinary boric acid cross-linked fracturing fluid, greatly improving the economy of fracturing operations.[48]

Traditional boron cross-linking agents need to be used at high pH, and will produce significant residues. The synthesis process of nano-cross-linking agents is complex and costly. In view of the above situation, Zhang et al.[49] have proposed a cross-linking agent based on nanocellulose. First, the surface of nanocellulose particles is modified by 3-aminopropyltriethoxysilane in order to obtain amino-modified nanoparticles (DB-1), and then organic boron (OBC) is modified on DB-1 to prepare boron-modified nanoparticles (NBC). It was found that, when the mass ratio of DB-1 and OBC decreases, the particle size of the boron-modified nanoparticles will gradually increase, resulting in poor dispersion and leading to a decrease in NBC cross-linking efficiency and an increase in cross-linking agent dosage. When the pH is 7, the nanocellulose cross-linking agent can cross-link 0.3 wt % hydroxypropyl guanidine gum, where the gel formed has good gel-breaking flowback, temperature resistance, shear resistance, and sand suspension properties. This preparation method not only simplifies the preparation process of nano-cross-linking agents but also gives the nano-cross-linking agent higher cross-linking efficiency, meeting the cross-linking demand under neutral conditions, reducing the amount of thickener needed, and reducing the fracturing cost, thus showing good application prospect.

Hurnaus et al.[50,51] have studied the effect of nanometal oxide particles on the guar gum cross-linking reaction, and found that the cross-linking reaction of titanium (zirconium) complex on HPG is not based on the exchange between the ligand of the complex and the *cis*-hydroxyl group on the HPG molecular chain but, instead, is due to the formation of a hydrogen bond between the hydroxyl group on the surface of TiO_2 (ZrO_2) generated by the in situ hydrolysis of titanium (zirconium) complex and the hydroxyl group on the HPG molecular chain. The specific surface area of a nano-cross-linking agent is the key factor affecting the cross-linking activity. A decrease in specific surface area will lead to weak cross-linking, or even no cross-linking reaction. Therefore, the cross-linking efficiency of nanoparticles is easily affected by some factors in the system (such as system pH and particle size of nanoparticles). It was also found that TiO_2 can effectively cross-link HPG when the system pH is 2−4 and the average particle size of nanoparticles is less than or equal to 10 nm. ZrO_2 nanoparticles with particle size of about 3 nm are the most effective for HPG cross-linking, while ZrO_2 with larger size (≥10 nm) can only facilitate weak cross-linking.

Zhang et al.[52,53] have prepared three kinds of nano-cross-linking agents using titanium tetrachloride, boric acid, and boron surface-modified alkoxy silicon compounds as modifiers, as well as amine-containing organosilane coupling agent KH550 and nano-SiO_2 as carriers. The main factors affecting the cross-linking time of the cross-linking agent (e.g., material ratio, temperature, reaction medium) were studied, and the structures of the different nano-cross-linking agents were characterized by Fourier transform infrared (FTIR) spectroscopy, laser particle size analysis, and X-ray diffraction (XRD). The experimental results showed that the three nano-cross-linking agents had a relatively tight network structure, and showed good cross-linking efficiency, temperature resistance, sand suspension, and gel-breaking performance. Xiong et al.[54] have prepared a titanium-modified nano-SiO_2 cross-linker. First, 60 mL of deionized water and ethanol, 3 g of γ-aminopropyltrimethoxysilane, 60 g of sodium silicate solution, and dilute hydrochloric acid to adjust the pH to 9 were mixed, and the temperature was increased to 60 °C. After reaction for 3 h, the solution was filtered and washed to obtain surface-modified nano-SiO_2, as shown in Figure 2a. Then, nano-SiO_2, xylene, and titanium tetrachloride were added into a three-mouth flask; the temperature was set at 100 °C for reaction for 5 h, and the titanium-modified nano-SiO_2 cross-linker was prepared through filtration, washing, and drying, as shown in Figure 2b. The particle size distribution range of the nano-cross-linker is 3−26 nm, mainly between 6 and 11 nm. After continuous shearing at 150 °C and 170 s^{-1} for 20 min, the viscosity of the nano-cross-linker cross-linked guanidine gel was determined as 62 mPa·s, indicating that the hydroxypropyl

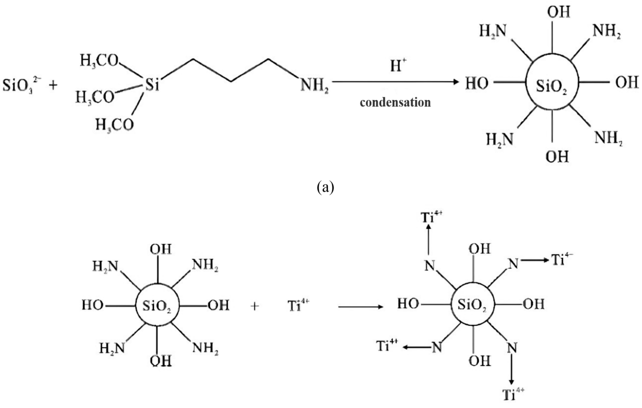


Figure 2. (a) Preparation of surface modified nano-SiO_2. (b) Preparation of titanium modified nano-SiO_2 cross-linker. Reprinted with permission from ref 54. Copyright 2021 Applied Chemical Industry.

guanidine gel cross-linked by the nano-cross-linker possessed good temperature and shear resistance.

Wu et al.[55] have developed a graphene oxide nano-cross-linking agent, where the silane coupling agent is modified onto the surface of graphene oxide through chemical reaction, following which a hydrophilic monomer is grafted to the surface, through surface initiation, in order to obtain a polymer molecular brush to prepare a graphene oxide nano-cross-linking agent. With the help of the reversibility of the noncovalent bond between the graphene surface-modified polymer and the polymer in the fracturing fluid, the cross-linker can achieve good shear dilution performance, reduce the friction between the fracturing fluid and the pipeline during transportation, reduce energy consumption, and form a stable cross-linking structure after reaching the reservoir fracture in order to stabilize the suspension proppant and graft the ionic polymer with ring structure. It also effectively improves the temperature and salt resistance stability of fracturing fluid. When the fracturing is completed and the working fluid flows back, under the action of shear, the cross-linking structure is damaged and the fluid viscosity is reduced. It can flow back quickly and effectively, thus reducing the pump pressure and water consumption.

2.1.1.3. Nanogel Breakers. In order to completely break and flow back the polymer fracturing fluid in the hydraulic fracture after reservoir fracturing, it is often necessary to add a certain amount of breaker (oxidant or enzyme) to the fracturing fluid, in order to degrade the polymer and reduce the viscosity of the fracturing fluid. However, the direct addition of a gel breaker will destroy the fracturing fluid system prematurely, affecting the fracture-making performance of the fracturing fluid and having an adverse impact on the fracturing operation. In order to provide the polymer fracturing fluid with not only good sand carrying property, but also to completely break the gel and return to the formation after the proppant is laid, researchers have proposed that the gel breaker be encapsulated in a special polymer which delays the release of the gel breaker.[56,57] At present, resin encapsulants are often used to encapsulate gel breakers, but some of these may not be completely broken or remain unbroken in the process of gel breaking, resulting in incomplete gel breaking and limited flowback of the fracturing fluid. In view of the above situation, some researchers have attempted to improve the gel breaker by introducing nanomaterials to control the gel-breaker release, in orders to improve the gel-breaking efficiency, promote the backflow of fracturing fluid, and reduce damage to the formation.[58] Sun et al.[59] have proposed a method for preparing a gel breaker using a modified carbon nanotube immobilized composite enzyme. The specific process is as follows: first, the carbon nanotubes are oxidized with concentrated nitric acid and concentrated sulfuric acid to obtain the modified carbon nanotubes as the immobilized enzyme carrier. Then, the enzyme complex consisting of mannanase, cellulase, and protease is immobilized on the carbon nanotubes to obtain the modified carbon nanotube immobilized complex enzyme. Finally, a viscous liquid is prepared using a chitosan and Arabic gum solution, which is coated on the surface of the modified carbon nanotube immobilized complex enzyme. After being dried, the gel breaker can be prepared. The prepared gel breaker has a protective film on the surface, which can prevent the early loss of viscosity when added to the fracturing fluid. The viscosity retention rate of the fracturing fluid before gel breaking reached 100%, and the lasting gel-breaking capacity was higher than 98 h. In addition, the fracturing fluid can meet the flowback requirements without treatment, reduce damage to the formation, and significantly improve oil and gas production.

Li et al.[60] have prepared core−shell fracturing fluid gel-breaker microspheres containing ammonium persulfate using the inverse microemulsion method. The microspheres are composed of a hydrophilic core and hydrophobic shell, where the core is coated with an oxidized gel breaker. It is used to delay or control water absorption and expansion of the microsphere through the hydrophobic effect of the shell and binding of the cross-linking agent in the core, thus realizing slow release of the gel breaker. Indoor experimental results showed that the microsphere extends the viscosity half-life of the solution from a few minutes when ammonium persulfate is directly added to 1 h. At the same time, the pH decline rate tends to slow down and the decline range gradually decreases, indicating that the coating of the microsphere inhibits the rate of hydrogen ion production by oxidative degradation of polyacrylamide in the solution, such that the microspheres can slow down the action of ammonium persulfate through delaying swelling, thus reducing the free radical oxidative degradation rate of polyacrylamide in aqueous solution. Pu et al.[61] have proposed a nanoencapsulated breaker with controllable delivery and release, which is made of a hydrophobic polymer wall material, gel breaker, dichloromethane (DCM), a nonsolvent oil or external water phase, and surface modified material. The size of the nanocapsule breaker is small, with particle size between 50−500 nm. After the oil and gas enter the reservoir, the nanocapsule can be carried into the micro nanoscale fractures by the fracturing fluid, followed by accurately releasing the breaker and delay the gel-breaking time of the thickener in the fracturing fluid, in order to realize the controllable release and efficient gel breaking of the breaker. In this way, the proppant placement effect is improved, the conductivity of micro−nanoscale fractures is increased, and the fracturing effect is enhanced.

Meng et al.[62] have designed a mannanase gel breaker with delayed release. A nanoparticle system originally used for drug delivery, namely, polyethylenimine (PEI)-dextran sulfate (DS) polyelectrolyte composite nanoparticles (PECNPs), was tentatively introduced. PECNPs possess a microcapsule structure formed through layer-by-layer self-assembly involving a cationic coating agent (PEI) and anionic coating agent (DS) through electrostatic alternative adsorption at low concentration. Charged mannanase molecules are added in the preparation process, which are combined into the microcapsule through electrostatic and spatial interactions. The excess charge on the outer surface of polyelectrolyte nanoparticles also contributes to the stability of the colloid. Through the experimental study of the gel breaker, it was found that the nanoparticles can delay the gel-breaking time by about 60 min at 30 and 50 °C. When the temperature reaches 70 °C, the gel-breaking time can only be delayed by 30 min, indicating that the temperature affects the slow-release performance of nanoparticles to a certain extent. At the same time, it was also found that the pH application range of the nanoparticles was between 6 and 8.5, and the particle size and potential of the nanoparticles decreases with an increase in pH. The gel breaker is evenly mixed with the fracturing fluid, and the mannanase will not be released immediately after being injected into the formation. After a certain time, the coating agent on the surface will be broken, due to the change of formation temperature and pressure, such that the mannanase will be released to react with the fracturing fluid, thus promoting the fracturing fluid to begin gel breaking. The introduction of the new nanoparticle system helps to improve the temperature tolerance and pH tolerance of the mannanase gel breaker, which has great application potential in improving the production of unconventional tight oil and gas.

2.1.2. Water-Based Fracturing Fluids. Water-based fracturing fluids are some of the most widely used fracturing fluid systems in the hydraulic fracturing of unconventional oil and gas reservoirs worldwide. At present, the most widely used water-based fracturing fluids are slickwater fracturing fluids.[63] A slickwater fracturing fluid system is mainly composed of clean water, and many additives need to be added during actual on-site fracturing operations, including bactericides, clay stabilizers, gel breakers, scale inhibitors, drag reducers, fluid loss reducers, and so on, in order to improve the temperature stability and salt resistance of the fracturing fluid, reduce filtration, improve the conductivity of hydraulic fractures, ensure complete gel breaking, and reduce damage to the formation.[64] The most important additive in slickwater fracturing fluid is the drag reducing agent, which is used to reduce the friction of water and turn it into slickwater. Compared with clean water, it can reduce the resistance by 40−50%, thus realizing large displacement pumping.[65,66] Commonly used drag reducers are mainly composed of polyacrylamide polymers. However, due to the defects in the molecular structure of polyacrylamide polymers, they are prone to curl fracture and loss of drag reduction function in high-temperature and high-salinity environments. Due to their small size, high surface activity, and large specific surface area, nanomaterials possess the basic conditions to alter the traditional slickwater fracturing fluid. Therefore, nanomaterials may be combined with traditional high-molecular weight polymers to develop slickwater fracturing fluid with better performance, thus making up for the deficiencies of conventional slickwater fracturing fluids and improving the fracturing effect in unconventional oil and gas reservoirs.

In the late stage of tight gas reservoir development, water lock damage gradually appears, flowback after fracturing is difficult, and the effective permeability of the reservoir is low. Liu[67] have developed a slickwater fracturing fluid with nano/microemulsion drainage aid. The fracturing fluid system is mainly composed of the nano/microemulsion drainage aid, drag reducer, and clay stabilizer. Among them, the nano/microemulsion drainage aid molecule is nanoscale, the interior of the micelle is an organic solvent, and the exterior is a nonionic surfactant. Adding the nano/microemulsion drainage aid to the slickwater fracturing fluid not only effectively inhibits the expansion of formation clay and reduces damage to the formation but also reduces the surface tension—more than 40% lower than that of conventional slickwater, thus reducing the water lock damage to the reservoir. As such, it is conducive for flowback in tight gas wells after fracturing. A field test of the slickwater fracturing fluid showed that the average flowback rate of the test well after fracturing was 52.41%, more than 2 times higher than that of a conventional slickwater hydraulic fracturing well, and the fracturing effect was effectively improved. Zhou et al.[68] have proposed a preparation method for a nano drag reducer and a slickwater fracturing fluid system. The nano drag reducer is prepared by modifying the surface of a molybdenum disulfide nanosheet with acrylamide, then polymerizing the comonomer and functional group-modified molybdenum disulfide nanosheet. The viscosity of the slickwater fracturing fluid prepared with the prepared nano drag reducer reached 70 mPa·s, much higher than that of the conventional slickwater fracturing fluid, and it presented excellent sand suspension performance. At the same time, the developed slickwater fracturing fluid also had the advantages of temperature resistance, salt resistance, and shear resistance, and showed good applicability in large-scale model volume fracturing reconstruction of unconventional reservoirs, such as shale.

Xing et al.[69] have synthesized a novel nanocomposite drag reducer (PASD-SiO_2) with acrylamide, sodium 4-phenylethylenesulfonate, dimethyl hexadecyl ammonium bromide, and surface-modified nanosilica as raw materials and experimentally evaluated the performance of the prepared nanocomposite drag reducer. The experimental results showed that the addition of the nanosilica particles enhanced the network structure of the solution system, improved the structural stability, improved the thermal stability of the solution system at high temperature, and led to higher apparent viscosity. At the same time, a drag reduction performance test also showed that, compared with a conventional drag reducer, the drag reduction efficiency of the prepared nanocomposite drag reducer was improved by 9.7%, and the new slickwater fracturing fluid prepared by the nanocomposite drag reducer had good temperature, salt, and shear resistance.

Wang et al.[70] have made use of nanoemulsion CND and a high-viscosity drag-reducing agent (HVFR) FR-900 to prepare a new type of multifunctional slickwater fracturing fluid. The main component of the nanoemulsion CND is an anionic nanosurfactant, while the main component of FR-900 is a polyacrylamide copolymer. The performance of the slickwater fracturing fluid system was evaluated through laboratory experiments. The experimental results indicated that adding a certain proportion of nanoemulsion CND improved the viscosity of the slickwater fracturing fluid (Figure 3) and improved both the single-particle and dynamic sand-carrying performance of the fracturing fluid. At the same time, the addition of nanoemulsion CND did not affect the drag reduction performance of the FR-900 (Figure 4). The prepared hydrostatic fracturing fluid has the advantages of reducing interfacial tension, fast gel breaking, less residue, and good sand-carrying properties. The prepared slickwater fracturing

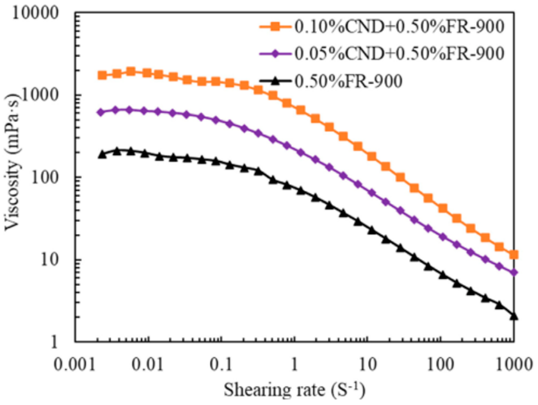


Figure 3. Viscosity of FR-900 mixed with CND under continuous shear. Reprinted with permission from ref 70. Copyright 2022 Elsevier.

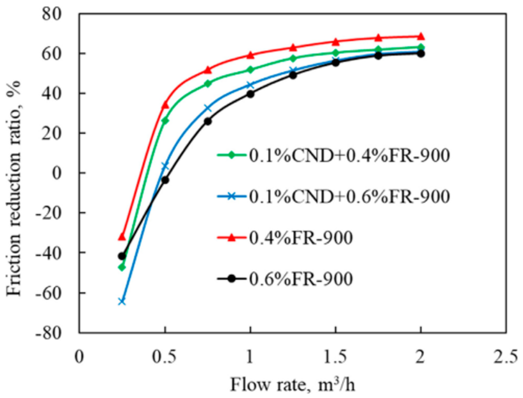


Figure 4. FR-900 and CND friction reduction test results. Reprinted with permission from ref 70. Copyright 2022 Elsevier.

fluid was applied in a field test, and the daily production of tight oil in the trial production stage was 26.5 tons/day, while the daily production under conventional slickwater fracturing was only 5−6 tons/day, and the stimulation effect was obvious.

Li et al.[71] have developed an alcohol-soluble slickwater fracturing fluid system composed of polyacrylamide polymers, nanoparticles, surfactants, and organic alcohols. By adding the nanoparticles, surfactants, and polyacrylamide polymers to the organic alcohols under a stirring rate of 2000−3000 rpm, then adjusting the stirring rate to 1000−2000 rpm and stirring for 15−60 min, the alcohol-soluble slickwater fracturing fluid system was prepared. The physical accumulation of nanoparticles in the organic alcohol solvent provides structural viscosity, which has a strong suspension effect on polymer particles, and the formed suspension system has good stability. At the same time, the introduction of low polarity organic alcohol reduces the binding effect with the polymer, hindering the binding effect of water and low molecular weight organic alcohol on polymer, as there is a competitive mechanism between water and the low molecular weight organic alcohol that have been combined with polymer, thus, the swelling of the polymer is effectively inhibited. The developed slickwater fracturing fluid has the advantages of a high polymer content, strong water solubility, simple preparation, little damage to the formation, and low cost. It can be widely used in the development of low permeability and ultralow permeability reservoirs.

2.1.3. Viscoelastic Surfactant-Based Fracturing Fluids. Since the introduction of surfactant-based fracturing fluid by Schlumberger at the end of the last century, it has received extensive attention both at home and abroad. In recent years, researchers have successively developed surfactant-based fracturing fluids with better performance, carried out large-scale field applications, and achieved good fracturing effects and economic benefits.[72] A viscoelastic surfactant (VES) can form worm-like micelles in aqueous solution. These micelles wind around each other to form a reversible three-dimensional network structure, such that the prepared fracturing fluid system has the characteristics of strong viscoelasticity, no residue after gel breaking, fast flowback speed, low likelihood of forming filter cakes, and little damage to the reservoir.[73,74] Huang et al.[75] reported, for the first time, a systematic study considering the incorporation of nanoparticles into VES. Nanoparticles (35 nm) with unique surface morphology and surface activity were added to VES, which combined with VES micelles through chemical adsorption and surface charge interaction to form a spatial network structure, thus maintaining the viscosity of VES at high temperatures and producing a viscous pseudofilter cake to control fluid loss and improve the effects of proppant transportation and placement. When the VES micelles were disrupted with an internal breaker, the viscosity of the fluid dropped dramatically and the pseudofilter cake broke into brine and nanoparticles. As these particles are small enough, they can flow back, together with the production fluid, through the micro nanopore throat of the reservoir, thus not harming the reservoir.

Due to the instability of VES fracturing fluid under high temperature, high pressure, and high shear rate, some researchers have aimed to significantly improve the temperature and shear resistance of VES fracturing fluids, reduce the fluid loss of VES fracturing fluids, and further enhance the sand-carrying performance of VES fracturing fluids by combining nanomaterials with VES fracturing fluids to take advantage the unique physical and chemical properties of nanomaterials.[75−77] Hanafy et al.[78] have investigated the effects of the shape, size, and surface properties of nanoparticles on the micellization and cross-linking process of anionic VES fracturing fluid. It was found that the addition of spherical or rod-shaped silica nanoparticles to 4 wt % in an anionic VES system can increase the apparent viscosity by 50% at 280 °F. The presence of octahedral and rod-shaped iron oxide nanoparticles had no significant effect on the VES fluid. When spherical and octahedral nanoparticles were added to 4 wt % VES system at 350 °F, the apparent viscosity was increased by 9 times. This indicates that the addition of nanoparticles with specific shape to VES helps to enhance the entanglement between micelles, forming a closer network structure and further improving the viscosity and thermal stability of the VES fracturing fluid. Xiao et al.[79] have prepared a nanocomposite fiber-based anionic VES fracturing fluid by adding functional nanocomposite fibers to anionic VES fracturing fluid in order to address the problems of fracture development in coal seams and the large adsorption capacity of surfactants. They conducted an indoor experimental evaluation of the performance of the surfactant fracturing fluid. Based on the experimental results, it was determined that the optimal length range of the nanocomposite fibers was 6−12 mm and the optimum mass fraction was 0.4−0.7%. Adding 0.3% nanocomposite fibers reduced the fluid loss rate of fracturing fluid by 40%, while adding 0.4 and 0.6% nanocomposite fibers under the condition of shear rate of 5000 s^{-1} reduced the friction by about 16 and 25%, respectively. This demonstrates that the addition of nanocomposite fibers can significantly improve the comprehensive performance of anionic VES fracturing fluid systems, and their application in coal seam fracturing can effectively alleviate the accumulation of pulverized coal, prevent proppant backflow, reduce fluid loss, and reduce damage to fracture conductivity.

Zhang et al.[80] have developed a low-concentration VES fracturing fluid (NAVES) using SiO_2 nanoparticles. The NAVES system is mainly composed of 0.01% SiO_2 and 1% EDAA. As surfactant micelles are attached to the surface of negatively charged SiO_2 nanoparticles and form a dynamic network structure through electrostatic interaction, the viscosity of the fracturing fluid system can still be maintained above 33 mPa·s under 70 °C for 2 h, while the viscosity of 1% EDAA is 24 mPa·s under the same conditions. The NAVES system can be completely broken within 100 min; there is no residue after gel breaking, and its viscosity can be reduced to less than 5 mPa·s. A sand-carrying performance test showed that, at 25 °C, the settling rate of quartz sand in the NAVES system is 0.0021 cm/s, lower than that in traditional VES fracturing fluid. Therefore, the NAVES system can be applied to the fracturing of unconventional tight oil and gas reservoirs, due to its good viscoelasticity, high temperature and shear resistance, sand-carrying performance, and low cost. Hu et al.[81] have prepared a temperature-resistant VES fracturing fluid system (4% sulfonate Gemini surfactant (DS18-3-18) + 3% organic alcohol NA + 0.02% cellulose nanofibers (CNFs)) by adding organic alcohol NA and CNF to DS18-3-18 as the main agent and evaluated the performance of the temperature-resistant VES fracturing fluid system through indoor experiments. The experimental results showed that the addition of organic alcohol NA and CNFs in the fracturing fluid system increases the micelle size in the solution, makes the microstructure arrangement more compact and complex, significantly improves the temperature resistance of the fracturing fluid, and allows the viscosity of the fracturing fluid to be maintained above 20 mPa·s at 100 °C and 170 s^{-1}, indicating that the addition of nanomaterials can significantly improve the performance of the fracturing fluid. The new temperature-resistant VES fracturing fluid system has the advantages of strong viscoelasticity, simple preparation process, good temperature resistance and shear resistance, and good sand-carrying performance, which can fully meet the needs of on-site fracturing operations.

The worm-like micelles in VES fracturing fluid are long, self-assembled linear aggregates composed of surfactants or other amphiphilic molecules, which can be intertwined to form a network structure. At a certain concentration, they show good viscoelasticity and rheology.[82,83] Many researchers have systematically studied the mechanisms by which nanoparticles improve the rheological properties of worm-like micelles. Dai et al.[84] have investigated the effect of SiO_2 nanoparticles with size of 7−40 nm on the rheological behavior of a worm-like micelle system (WMS) composed of CTAB and Nasal mixing system, and found that the nanoparticles significantly enhanced the structure of the worm-like micelles. Luo et al.[85] have found that adding barium titanate ($BaTiO_3$) nanoparticles to the worm-like micelle solution can significantly improve the viscoelasticity and viscosity of the worm-like micelles, as well as enhancing the structure of the worm-like micelles. Nettesheim et al.[86] have studied the effect of nanosilica on the viscoelasticity of worm-like micelles formed with the mixed system of CTAB and sodium nitrate ($NaNO_3$). They experimentally found that when SiO_2 nanoparticles (with a diameter of 30 nm) with a charge similar to that of the cationic worm-like micelle solution were included, the viscoelasticity and viscosity of the worm-like micelle solution increased significantly. Zhao et al.[87] have investigated the effect of SiO_2 nanoparticles on the enhanced worm-like micelle system (NEWMS). NEWMS was prepared by mixing CTAB solution and nasal solution. When SiO_2 nanoparticles were added to the mixed solution, it was found that the viscosity of NEWMS reached a maximum. Compared with the traditional worm-like micelles without SiO_2 nanoparticles, NEWMS had higher viscosity and better viscoelasticity. At the same time, the added SiO_2 nanoparticles were attracted by the hydrophilic head-groups of the surfactants and formed a double-layer circular structure through electrostatic interaction; moreover, in the presence of sodium salicylate (nasal), the aggregation of surfactant molecules on the nanoparticles increased, resulting in the formation of a new micelle−nanoparticle junction (Figure 5). Although researchers have put forward many views through research, more experimental research needed to elucidate the mechanisms by which nanoparticles reinforce worm-like micelle systems (e.g., NEWMS). It is also necessary to evaluate the effects of nanoparticle additives on the rheology, thermal stability, and shear resistance of VES fracturing fluid, in order to develop VES fracturing fluids with better performance, based on NEWMS mechanisms, to adapt to different reservoir conditions.

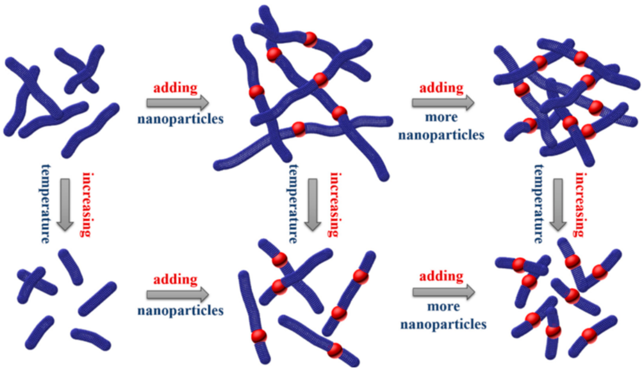


Figure 5. Nanoparticle-enhanced worm-like micellar structure due to formation of micelle−nanoparticle junctions. Reprinted with permission from ref 87. Copyright 2017 MDPI.

Bello et al.[88] have prepared a VES fracturing fluid based on cetyltrimethylammonium bromide (CTAB) and graphene oxide nanoparticles, and studied the rheological properties of the fracturing fluid system through laboratory experiments. It was found that the interaction between nanoparticles and surfactant micelles essentially comprised physical cross-linking between micelles. When the surfactant concentration in the fracturing fluid system is 1−3 wt %, a cylindrical micelle network structure will be formed. At the same time, the addition of graphene oxide nanoparticles not only can improve the viscoelasticity of the fracturing fluid system, but also promotes the extension and cross-linking of micelles. Yang et al.[89] have proposed a PINVES fracturing fluid prepared from sodium oleate (NaOA), potassium chloride (KCl), surface-modified cellulose nanofibers (SMCNF), and deionized water. The rheological behavior of PINVES fracturing fluid and the interaction mechanism between SMCNF and worm-like micelles (WLMS) were studied. The experimental results showed that SMCNF and worm-like micelles (WLMS) are cross-linked by hydrogen bonds. When the concentration of SMCNF is high, the relaxation time of PINVES is longer and its elasticity is higher, while the sulfonic acid and hydrophobic groups on the surface of SMCNF tend to destroy the WLMS network. At this time, SMCNF plays a major role in controlling the rheological behavior of the PINVES fracturing fluid and, due to the addition of SMCNF, PINVES fracturing fluid presents better temperature resistance and sand-carrying properties than conventional VES fracturing fluid.

2.1.4. Foam-Based Fracturing Fluids. Foam is an aggregate of bubbles with multiple interfaces separated by a thin film of liquid. The liquid film is the base fluid of the foam, which can be mainly classified into water-based, acid-based, alcohol-based, or liquid CO_2-based, among which water-based foam is the most widely used; however, this can cause damage to water-sensitive formations, while the gas phase is mainly carbon dioxide and nitrogen.[90,91] Foam fracturing fluids have the characteristics of strong sand-carrying ability, little damage to reservoirs, less filtration loss, and easy flowback, which make them more suitable for the stimulation of low and ultralow permeability in water-sensitive and heterogeneous oil and gas reservoirs. However, as foam fluids are typically a thermodynamically unstable system, their stability will be significantly reduced under the conditions of high temperature, high pressure, high salt, and/or high pH, and their spontaneous decay will greatly reduce the fracturing stimulation effect.[91−93] Therefore, it is usually necessary to add thickeners, such as hydroxypropyl guar gum or polyacrylamide, to the foam fracturing fluid during fracturing operations, in order to enhance the viscosity of the foam base fluid, strengthening the stability and sand-carrying properties of the foam.[94] Traditional foam thickeners have problems such as high residue content, incomplete gel breaking, and great damage to formation permeability, which restrict their fracturing stimulation effect in reservoirs, to a certain extent.[94,95]

In view of this, researchers have tried to add nanomaterials to foam fracturing fluid systems, in order to improve the comprehensive performance of the foam fracturing fluid.[96,97] The main mechanism for improving the foam stability by nanoparticles involves the adsorption and aggregation of nanoparticles at the gas−liquid interface; that is, nanoparticles can be adsorbed onto the surface of the foam film, having a synergistic effect with the surfactants to form a stable adsorption layer. As the interfacial desorption energy of nanoparticles is much larger than that of the surfactant molecules, the nanoparticles can be stably adsorbed on the interface and play a role in stabilizing the foam film, thereby effectively inhibiting the coalescence effect of the bubbles and achieving the effect of stabilizing the foam.[98−101] As shown in Figure 6, the forms of adsorption and aggregation of nanoparticles at the interface are mainly monolayer, thick multilayer, and particle aggregate networks.[102−104] Compared with surfactants, the adsorption of nanoparticles at the gas−liquid interface is irreversible, which can allow for more effective stabilization of the foam and further increases in the elasticity of the foam surface. Moreover, nanoparticles can also hinder the flow of the liquid phase in the foam film and retard thinning of the foam film, thus preventing coarsening and coalescence of the foam.[105,106]

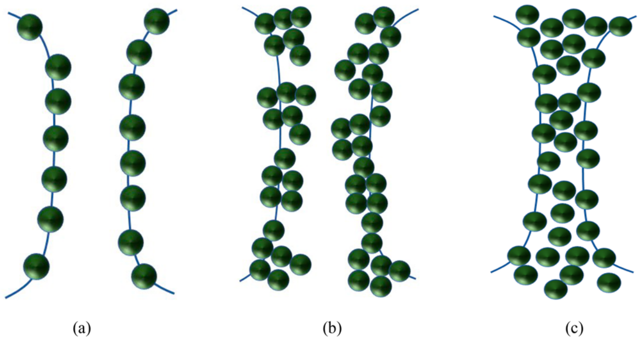


Figure 6. Images showing that the adsorption form of particles on the interface is (a) monolayer, (b) thick multilayers, and (c) aggregated particles adsorbed at the interface and bulk. Reprinted with permission from ref 104. Copyright 2014 Elsevier.

Lv et al.[94] have prepared a carbon dioxide foam fracturing fluid by adding SiO_2 nanoparticles, and systematically studied the performance of the resultant foam fracturing fluid. Due to the adsorption of SiO_2 nanoparticles at the gas−liquid interface, the interfacial roughness was increased, such that the viscoelastic modulus of the gas−liquid interface was enhanced under high temperature and high pressure, and the resistance to foam film and the ability to restore deformation are enhanced. The experimental results showed that when the foam fraction was 50−93%, 0.5% SiO_2 nanoparticles can increase the effective viscosity of the foam fracturing fluid by 2.2−4.8 times while, at the same time, enhancing the gas−liquid two-phase fluid-loss control ability of the carbon dioxide foam fracturing fluid system and also weakening the sensitivity of the gas−liquid two-phase filtration coefficient to the permeability, thereby reducing the permeability damage to the reservoir. Li et al.[107] have proposed a stable carbon dioxide water-based foam fracturing fluid. The water-based foam fracturing fluid uses carbon dioxide and the fracturing fluid for the gas−liquid phase. After the foaming treatment, the carbon dioxide water-based foam fracturing fluid is formed, with foam quality of 52−75 wt %. The carbon dioxide water-based foam fracturing fluid is mainly composed of nanoparticle−composite hydrophobically modified polymer or surfactant− and polymer−composite nanoparticles. The preparation method is simple, and the fluid has good stability and foam viscoelasticity, showing potential for its application in fracturing production and the upgrading of shale reservoirs, in order to improve the fracturing effect and oil and gas recovery.

Li et al.[108] have developed a carbon dioxide foam fracturing fluid with high sand-carrying properties. The main components of the foam fracturing fluid system are 0.3−0.5% thickener, 0.25−0.4% polyelectrolyte nanocomposite, 0.1−0.5% cross-linking agent, 0.03−0.05% foaming agent, 10−30% brine, and residual liquid carbon dioxide. Experimental evaluation results showed that the carbon dioxide foam fracturing fluid containing nanomaterials has the characteristics of easy degradation and gel breaking, low residue content, and low comprehensive damage rate of the core, furthermore, due to the addition of polyelectrolyte nanocomposite materials, the life and stability of the foam are significantly improved, thereby greatly reducing the liquid filtration rate, improving the fracture capacity of the fracturing fluid, and improving the sand slurry and sand-carrying performance of the fracturing fluid. Thus, the fracturing stimulation effect is greatly improved. Ishii et al.[109] have studied the stability of a foam fracturing fluid containing CNFs under high temperature and high pressure. The stabilities of foam systems containing CNF and CMC sodium salt (NaCMC) were compared experimentally, where the results showed that the half-life of the CNF foam was longer than that of NaCMC foam, especially when the CNF concentration was above 0.1 wt %. Thus, CNF have better performance as foam stabilizer than NaCMC, which may be due to the formation of a reticular structure in the CNF-containing foam system covering the gas−liquid interface, thereby improving the foam stability.

Nanoparticles can be adsorbed at the gas−liquid interface, and as such, an important factor is the wettability of the particles.[105] Binks et al.[110] have found that hydrophilic SiO_2 nanoparticles and cationic surfactant CTAB can synergistically stabilize foam. The foam stabilization mechanism is that a part of the free CTAB exists in the base liquid, in the form of a foaming agent, while another part of the CTAB is adsorbed on the negatively charged hydrophilic SiO_2 nanoparticles due to

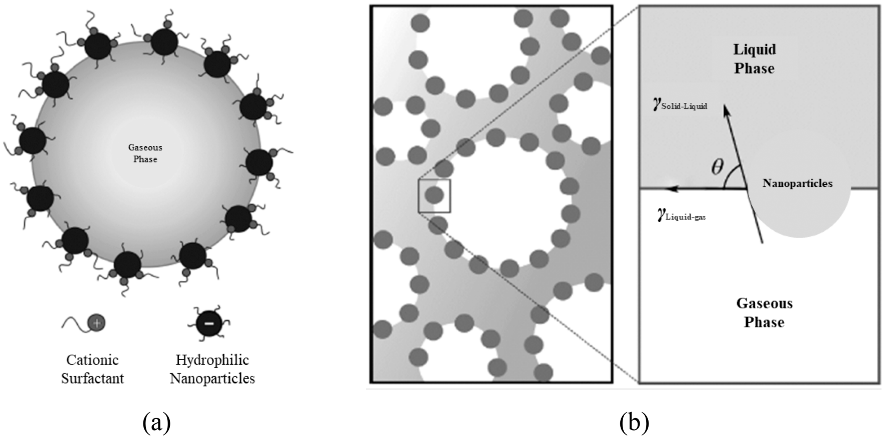


Figure 7. (a) Schematic diagram of the foam stabilization mechanism of hydrophilic nanoparticles and surfactants. (b) Schematic diagram of the foam stabilization mechanism of partially hydrophobic nanoparticles and surfactants. Reprinted with permission from refs 105 and 111. Copyright 2006 Wiley and 2017 Chemical Industry and Engineering Progress.

the electrostatic force and van der Waals force. The exposed hydrophobic tails of CTAB make the adsorbed SiO_2 nanoparticles hydrophobic, and the wettability-modified SiO_2 nanoparticles are adsorbed at the air/water interface after foaming, thereby stabilizing the foam (Figure 7a). As shown in Figure 7b, some hydrophobic nanoparticles can be adsorbed on the gas−liquid surface to form a monolayer film, which can effectively stabilize the foam system.[111] Sun et al.[112] have found that the synergistic effect of hydrophobic SiO_2 nanoparticles and anionic surfactant sodium dodecyl sulfate (SDS) could stabilize the generated foam. The foam stabilization mechanism is caused by an electrostatic interaction, which leads negatively charged anionic surfactant molecules to be adsorbed on the surface of the positively charged hydrophobic nanoparticles. Then, these surfactant-adsorbed nanoparticles are adsorbed on the gas−liquid interface, forming a spatial barrier layer that not only increases the elasticity of the bubble surface, but also further prevents the flow of the liquid phase, thus stabilizing the foam.

Yekeen et al.[113] have conducted a systematic experimental study on the effect of adding different types of nanoparticles to a sodium dodecyl sulfonate foam system. The results showed that the positively charged nanoparticles significantly improved the stability of the sodium dodecyl sulfonate foam system, where TiO_2 and Al_2O_3 nanoparticles effectively increased the life of the sodium dodecyl sulfonate foam system, among which TiO_2 nanoparticles increased the life from 540 to 1260 s, while Al_2O_3 nanoparticles increased it from 540 to 1440 s. This indicates that the use of electrostatic adsorption between nanoparticles and surfactants can significantly improve the stability of sodium dodecyl sulfonate foam systems. In addition, Yekeen et al.[114] have investigated the conditions for the optimal performance of stabilized CO_2 foams considering the synergistic effect of nanoparticles and surfactants. Foam stability experiments were conducted by screening the best-performing nanoparticles and surfactant types, in order to compare the performance of CO_2 foams under subcritical and supercritical conditions. It was found that increasing nanoparticle concentration improved the stability of subcritical CO_2 foams while, for supercritical CO_2 foams, 0.5 wt % SiO_2 was the ideal concentration to achieve maximum stability. Although the surfactant (SDS) produced finer foam in the initial moments, its foam collapsed faster and showed a polyhedral shape and thinner lamellae with respect to time (Figure 8a). In contrast, the SiO_2−SDS solutions generated relatively stable foams with uniform or finer shape and denser lamellae (Figure 8b). In addition, for conventional foam fracturing fluids, oil can easily disperse on the thin-liquid film of foam, destroying the foam lamellae and accelerating the decay and coarsening of the foam. However, for the nanoparticle-surfactant CO_2 foam system, the oil will emulsify to form tiny droplets, which are included into the foam thin-liquid film, as well as the plateau borders, thus slowing the decay process and improving the stability and durability of the foam.

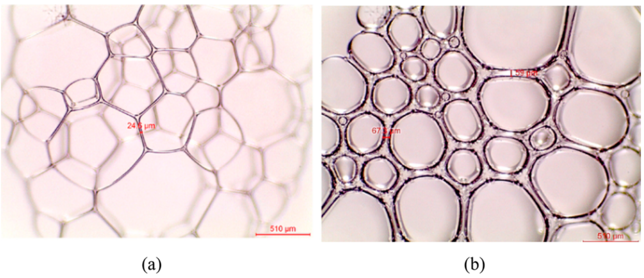


Figure 8. Morphology of (a) SDS stabilized foam and (b) SiO_2−SDS stabilized foam. The foam in (a) was generated with 0.5 wt % SDS, and the foam in (b) was generated with 0.5 wt % SDS and 1.0 wt % SiO_2. Reprinted with permission from ref 114. Copyright 2021 Elsevier.

Verma et al.[115] first proposed the use of iron oxide nanoparticles to improve the thermal stability of foam fracturing fluids. A more stable foam system can be produced by adding iron oxide nanoparticles with a concentration of 0.5 wt % to the mixture of surfactant (SDB and CAPB). The addition of iron oxide nanoparticles plays a role in stabilizing the foam, and the thermal stability of the foam system containing iron oxide nanoparticles was increased by 52% at 80 °C. From Figure 9a,b, it can be seen that the foam with nanoparticles will form rougher surfaces around their bubbles, compared with those without nanoparticles. Nanoparticle foam surfaces with more roughness and stronger films can prevent the proppant from sliding over the rough surface of the ferric oxide bubbles easily, thereby prolonging the proppant suspension time. Figure 9c,d shows the sphericity of 20/40 mesh sand proppant particles and their suspension in a

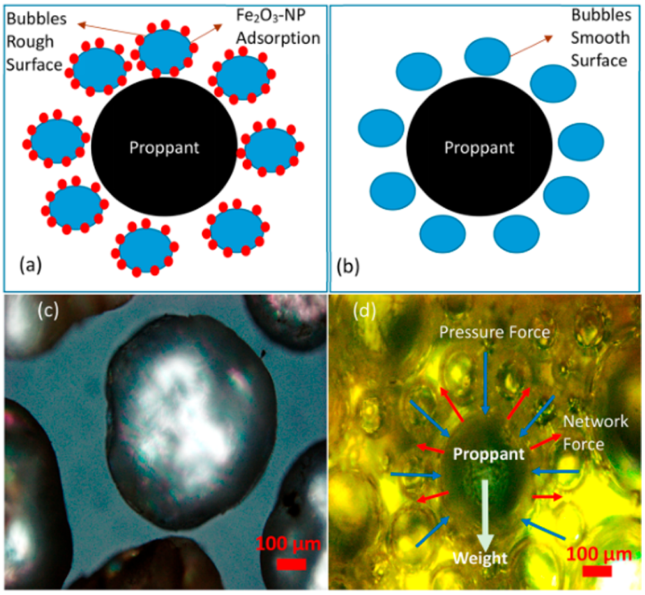


Figure 9. (a) Schematic illustration of nanoparticle-stabilized foam bubbles for providing effective uplifting force on the proppant. (b) Foam bubbles without nanoparticles being susceptible to deformed by the proppant settling, providing the weak uplifting force on the proppant. (c) Microscopic image of 20/40 mesh proppant. (d) Microscopic image of proppant deposited in nanoparticle-incorporated foam bubbles, forces exerted on the film and bubbles surrounding the proppant. Reprinted from ref 115. Copyright 2019 American Chemical Society.

nanoparticle foam system. It can be seen that the proppant settling is affected by different forces. Due to the formation of a high-density, stable foam system, the settling velocity of the proppant can be reduced to a certain extent. Moreover, the addition of ferric oxide nanoparticles helps to maintain the apparent viscosity of the foam system, enhance the proppant transport ability, and evenly distributes proppant in the reservoir, thereby enhancing the fracture conductivity.

In addition, nanoparticles and nonionic surfactants can also play a role in synergistic foam stabilization. However, unlike ionic surfactants, nonionic surfactants do not ionize in water but, instead, mainly through the hydrogen bond formed between the ether oxygen group on the surfactant molecules and the hydroxyl group on the nanoparticles.[106] Li et al.[116] have studied the interaction mechanism between different concentrations of nonionic surfactants $C_{12}E_{23}$ and nano-SiO_2, and found that when the surfactant concentration was low, a loose single adsorption layer was formed on the surface of nanoparticles. With an increase in surfactant concentration, under the action of van der Waals force and hydrogen bonds, the surfactant molecules formed a denser single adsorption layer on the surface of the nanoparticles, at which time the hydrophobic end of the surfactant is exposed in the liquid phase, thus increasing the hydrophobicity of nanoparticles. If the surfactant concentration continues to increase, the surfactant molecules will form a bimolecular adsorption layer on the surface of the nanoparticles, which will restore the hydrophilicity of the nanoparticles, at which point the synergistic effect between the nanoparticles and surfactant will disappear. A schematic diagram of the interaction mechanism is presented in Figure 10.

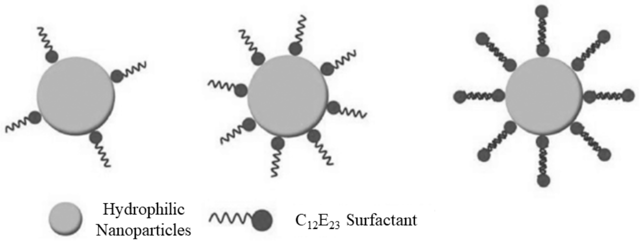


Figure 10. Schematic diagram of the interaction mechanism between nanoparticles and different concentrations of nonionic surfactants. Reprinted with permission from ref 106. Copyright 2020 Modern Chemical Industry.

Nanoparticles can also improve the performance of VES foam fracturing fluid systems. The mechanism by which viscosity is enhanced and foam is stabilized involves the nanoparticles being adsorbed by viscoelastic surfactant molecules, thus stabilizing the foam at the gas−liquid interface. Meanwhile, at the same time, the worm-like micelles formed by the viscoelastic surfactant are interconnected by the nanoparticles, forming a tight spatial network structure which further improves the viscosity of the foam fracturing fluid.[92] Yang et al.[92] have found, through experimental research, that the half-life of a VES foam fracturing fluid containing nano-SiO_2 was close to 80 min at 90 °C, and the thermal stability of the fracturing fluid system was greatly improved. Moreover, compared with a VES foam fracturing fluid without nano-SiO_2, the viscoelasticity and suspended sand properties were significantly improved, and the gel-breaking time was greatly shortened, allowing for the novel fluid to fully meet the requirements of fracturing operations. Zhu et al.[117] have analyzed the microscopic properties of nano-SiO_2-stabilized VES foams at different temperatures using cryo-SEM, optical microscopy, and other technical means. They found that, at 30 °C, the VES-stabilized foam system containing mass fraction 3% EAPB + 1% SiO_2 had the lowest liquid discharge and the largest bubble number. Meanwhile, the addition of nano-SiO_2 could further connect the slender worm-like micelles and help to form a strong particle−micelle network. This, in turn, slowed down the diffusion rate of gas in foam and delayed the coarsening of bubbles, thus enhancing the stability of the foam. Moreover, Zhu et al.[118] have also studied the proppant settling behavior in a VES foam fracturing fluid system with nanoparticles, and found that the proppant could be well-suspended within 90 min at low temperatures, but high temperatures greatly changed the settling behavior of proppant. In addition, with the addition of nanoparticles, they could adsorb on the bubble liquid film, making the foam surface rough, providing resistance to and hindering settling of the proppant, thus significantly improving the suspended sand ability of the nanoparticle−VES foam fracturing fluid system.

2.2. Nanomaterial-Enhanced Proppant Performance.

Proppants are mainly used to support artificial fractures after pump shutdown and fracturing fluid filtration in order to form a high diversion channel to the wellbore in the formation.[119,120] As tight reservoirs, such as shale, have micro/nanopore structure and some natural microfractures are distributed, microfractures will also be generated when the reservoir forms a complex fracture network through fracturing reconstruction. However, the particle size of conventional fracturing proppants is not small enough to be carried into induced and naturally existing microfractures by the fracturing fluid. Therefore, these microfractures will be closed after fracturing construction, reducing the conductivity of the reservoir fracture network and inhibiting extension of the fracture network.[15,121,122] Barati and Bose[123] have proposed that a nanoproppant can be injected into the formation to maintain the opening of microfractures, thus improving fracture conductivity. Meanwhile, Bose et al.[23] have also evaluated the potential of fly ash for preparing nanoproppants and found that nano fly ash particles can fill the microfractures in unconventional tight reservoirs and promote the expansion of complex fracture network. As shown in Figure 11, the formation can maintain the opening of microfractures and expand these microfracture networks after injecting a nanoproppant, while a larger proppant can be used to maintain the opening of main fractures. The high surface/volume ratio and other characteristics of nanoparticles fully meet the needs for the development of nanoproppants. Compared with conventional proppants, nanoproppants show unique and excellent features and can be transported to deeper fractures or microfractures, effectively improving the conductivity of the reservoir fracture network, promoting the flow of oil and gas and improving the productivity of hydraulic fracturing wells.[124]

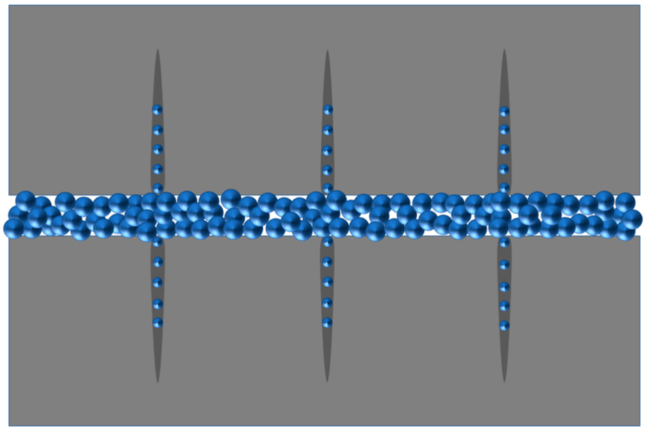
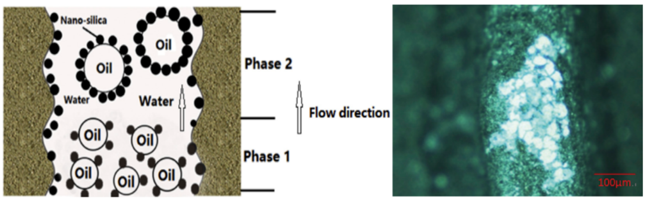


Figure 11. Schematic diagram of the distribution of proppant and nanoproppant in fractures and microfractures. Reprinted with permission from ref 23. Copyright 2015 Elsevier.

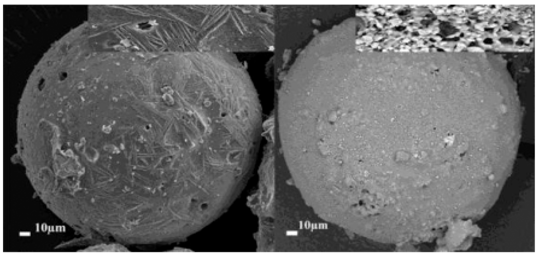
Liu et al.[125] have proposed a Pickering emulsion for hydraulic fracturing of shale reservoirs. The Pickering emulsion was prepared and stabilized using nanosilica. During the fracturing process, the emulsion structure is broken, releasing the nanoscale silica, which are adsorbed on the surface of cracks or assembled in the fracture. Nanosilica is uniformly distributed on the shale surface in low-concentration Pickering emulsion, which plays a role in stabilizing shale and preventing clay hydration. In a high-concentration Pickering emulsion, nanosilica can aggregate in fractures, preventing fracture closure. As shown in Figure 12a, a schematic diagram of the adsorption mechanism of nanoparticles in Pickering emulsions, when the Pickering emulsion contacts the shale surface, some solid nanoparticles will be released. From the first to the second stage, the oil droplets will gradually accumulate and the nanoparticles will be adsorbed onto the surface of the fractures. At the same time, a reverse water flooding experiment was carried out. When the Pickering emulsion was completely driven out from the fracture, microscopic observation of the residual solid nanoparticles in the channel was carried out. As shown in Figure 12b, it was found that a large number of solid nanoparticles still existed; even if the size of these particles is small, after a certain scale of local accumulation, they can still provide a very considerable support capability. As Pickering emulsion itself contains nanoparticles as a proppant, it can not only replace the traditional proppant pumping process, simplify the fracturing operation procedure, and improve the efficiency of fracturing operations, but also maximize the effective fracture area, increase the volume of reservoir reconstruction, and enhance the effect of fracturing.



(a) (b)

Figure 12. (a) Adsorption mechanism of solid nanoparticles. (b) Microscopic image of nanoparticle residue after reverse water flooding. Reprinted with permission from ref 125. Copyright 2018 Elsevier.

Danso et al.[126] have combined previous field and laboratory research and concluded that, after hydraulic fracturing of reservoirs with conventionally sized proppant (<149 μm), most hydraulic fractures were not effectively propped. Micro- and nanoproppant can be designed to have structure matching the distribution of microfractures in a reservoir. After entering the microfractures, they consolidate into clusters or columnar clusters, effectively supporting natural and induced microfractures, forming high-conductivity channels, and increasing oil and gas production. Danso et al.[126] have discussed the optimal size of micro- and nanoproppant to effectively support induced fractures, and suggested that the optimal size of micro- and nanoproppant should be between 1/3 and 1/7 of the minimum size of natural fractures in the reservoir. The material sources for the preparation of micro- and nanoproppant were analyzed and studied, and industrial wastes such as granite waste powder, waste foundry sand, and blast furnace slag were proposed as potential raw materials for the preparation of micro- and nanoproppant. Wang et al.[127] have developed a micro- and nanoproppant for supercritical CO_2 fracturing. The micro- and nanoproppant was prepared from fly ash, one of the wastes of thermal power generation. It has small particle size and its suspension performance in low-viscosity fracturing fluid is better. When supercritical CO_2 fracturing technology is used to reconstruct shale reservoirs, the micro- and nanoproppant is carried into the reservoir by supercritical CO_2 fracturing fluid and is laid into natural microfractures and fissures, which can prevent the closure of microfractures and plays a role in maintaining the conductivity of fracture network and promoting the expansion of fracture network. Fan et al.[128] have used low-grade bauxite and micron-scale SiO_2 as main raw materials, water glass, nano-SiO_2, and manganese oxide as auxiliary materials and combined plasma dynamic sintering and later high-temperature sintering to prepare an ultralow density proppant. They discussed the effects of different manganese oxide doping amounts and sintering time on phase composition, bulk density, apparent density, and crushing rate (69 MPa). The experimental results showed that the apparent density of the prepared ultralow density proppant was 1.639 g/cm^3, the crushing rate was 8.91% at 69 MPa, the optimal doping amount of manganese oxide was determined to be 7.5 wt %, and the optimal sintering temperature and sintering time were 950 °C and 2 h, respectively. It can be seen, from Figure 13a,b, that after doping with manganese oxide, the rod-shaped particles in the proppant gradually became thinner and shorter, forming a “wooden club” shape. These “wooden club”-shaped particles form a network structure, and the glass phase gradually decreases, which is conducive to improving the compressive strength of the proppant. At the same time, based on the classical Perkins−Kern−Nordgren fracturing model, the settling and migration laws of the ultralight proppant in fractures were simulated, and it was found that the ultralight proppant migrated a longer distance in the horizontal direction than conventional proppant. The internal distribution was also relatively more uniform, which can fully meet the needs of clean water fracturing in medium and deep oil wells.



(a) (b)

Figure 13. (a) SEM image of MnO undoped ultralow density proppants. (b) SEM image of MnO doped (7.5 wt %) ultralow density proppants. Reprinted with permission from ref 128. Copyright 2020 The Chinese Journal of Process Engineering.

In addition to vigorously developing nanoproppants, in recent years, the use of nanomaterials to modify the surface of proppants has gradually become a hotspot in the field of hydraulic fracturing proppants. Researchers have used different types of nanomaterials to coat the surface of the proppant matrix particles in order to enhance the comprehensive properties of the proppant. Haque et al.[129] have combined multiwalled carbon nanotube (MWNT) fibers phenolic resins to coat North American white sand to prepare a nanocomposite resin-coated proppant. It was found, through laboratory experiments, that the nanocomposite resin coating can significantly improve the compressive strength and conductivity of the proppant. Compared with the same mesh proppant without coating, the long-term conductivity of the prepared 30/50 mesh- and 40/70 mesh-coated proppant was increased by 244 and 100%, respectively. Under the stress condition of 12,000 psi, the broken particles of the film-coated proppant were less, and the crushing rate was far less than that of the noncoated proppant. Xu et al.[130] have invented a multifunctional coated proppant. The proppant is mainly prepared by coating the surface of the matrix particles with a nanoparticle-reinforced composite material coating. The formed proppant coating has better affinity with the aggregate, allowing for stronger adhesion between the aggregate and the coating, and the surface of the proppant after coating is complete and has high sphericity. This kind of fracturing proppant modified by nanoparticles and a composite material coating possesses the characteristics of low density, high compressive strength, and strong suspension capability, which can meet the needs of unconventional oil and gas reservoir hydraulic fracturing operations.

Li et al.[131] have proposed a long-term antiscaling coating proppant. This proppant is composed of an inner core, a corrosion- and scale-inhibition layer, and a protective layer sleeved from the inside to the outside, wherein the inner core is a modified proppant and the corrosion- and scale-inhibition layer is composed of polyaspartic acid and phosphine compound corrosion and scale inhibitors, vinyl polymer dispersant, and bonding agent, and the protective layer is composed of soluble nanomaterials. The antiscaling coated proppant is carried by the fracturing fluid to the front of the artificial fractures in the initial stage of hydraulic fracturing sand addition. When the protective layer is dissolved, the corrosion- and scale-inhibition components attached to the proppant core are slowly released under the action of the dissolution rate control agent, such that the coated proppant has the characteristics of good scale inhibition effect, long action time, not being limited by seasonality, not easy to disperse, simple operation, and so on. Tabatabaei et al.[132] have developed a nanomaterial coating-modified proppant. The matrix particle of the coating proppant is a resin-coating proppant. During preparation, 1 wt % SDS and 0.5 mg/mL graphite nanoplatelets (GNPs) were first added to 300 mL of deionized water, which were then dispersed using an ultrasonic bath for 1 h to prepare a mixture. Then the proppant matrix particles were added to the mixture, sonicated in an ultrasonic bath for 1 h, followed by stirring for 2 h, and then washed with 500 mL of deionized water three times to remove excess GNPs and SDS. Finally, drying in a fume hood was carried out to obtain the nanomaterial-coated proppant. The conductivity and compressive strength of the proppant treated with GNP were significantly improved, and the surface wettability was altered, making it highly hydrophobic. Its application in oil well hydraulic fracturing is conducive to fracturing fluid flowback and may significantly improve oil recovery.

Ishtiaq et al.[133] have used glass beads as the proppant matrix and applied a mixed solution prepared using urethane resin, acetone, reduced graphene oxide (rGO)/carbon nanotubes

Figure 14. (a) Glass bead urethane-coated proppant containing 0.1% CNTs. (b) Glass bead urethane coated containing 0.5% CNTs. (c) Glass bead urethane-coated proppant containing 1% CNTs. Reprinted with permission from ref 133. Copyright 2022 Springer.

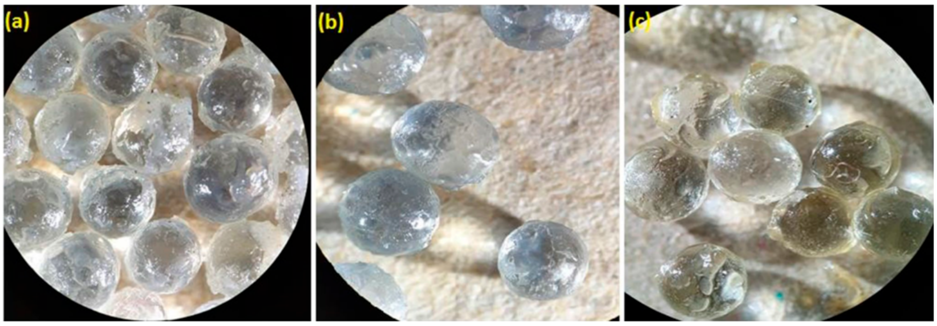


Figure 15. (a) Glass bead urethane-coated proppant containing 0.1% rGO. (b) Glass bead urethane-coated proppant containing 0.5% rGO. (c) Glass bead urethane-coated proppant containing 1% rGO. Reprinted with permission from ref 133. Copyright 2022 Springer.

Table 2. Compressive Strength of CNT-Coated Glass Bead Proppant with Different Concentrations[a]

concentration of CNTs (%) in urethane resin	max load applied (kN)	compressive strength (MPa)	increase in compressive strength (%)	fines generated (g)	fines generated (%)
uncoated	9.183	2923.125		0.3301	6.15
0.1	12.847	4089.387	39.90	0.2553	4.76
0.5	16.868	5369.251	83.68	0.1954	3.64
1.0	13.536	4308.56	47.40	0.0736	1.37

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Table 3. Compressive Strength of rGO-Coated Glass Bead Proppant with Different Concentrations[a]

concentration of rGO (%)	max load applied (kN)	compressive strength (MPa)	increase in compressive strength (%)	fines generated (g)	fines generated (%)
uncoated	9.183	2923.125		0.3301	6.15
0.1	12.957	4124.395	41.10	0.1863	3.47
0.5	11.832	3766.278	28.84	0.4255	4.95
1.0	11.285	3592.182	22.89	0.2963	5.52

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(CNTs), and so on to the surface of the proppant matrix particles by dripping. The nanomaterial (CNTs/rGO) composite urethane-coated proppant was prepared after drying and curing (Figures 14 and 15).

Ishtiaq et al.[133] have studied the compressive strength of urethane CNT-coated glass bead proppants with different concentrations. It can be seen from Table 2 that the 0.5% CNT-coated glass bead proppant showed the highest compressive strength, due to the role of CNTs as reinforcing fibers in the resin system. However, with the increase of CNT concentration, when the CNT concentration exceeds 0.5%, the compressive strength of the proppant begins to decrease. This is due to the agglomeration of CNTs on the surface of the proppant coating, resulting in an uneven surface coating on the proppant matrix. When the proppant is under pressure, the thinner part of the surface coating will break first, reducing the compressive strength of the proppant. At the same time, as the surface of the proppant contains a urethane coating, the fine particles produced by crushing of the proppant can be contained within the proppant, effectively reducing the generation of fine particles.

Ishtiaq et al.[133] have also studied the compressive strength of a glass bead proppant with reduced graphene oxide (rGO) urethane coating at different concentrations. It can be seen from Table 3 that the compressive strength of the rGO urethane-coated glass bead proppant starts to decrease after the rGO concentration exceeds 0.1%. This is because, as the loading concentration of rGO in the urethane resin increases, the hydrogen bond attraction between rGO layers increases, resulting in agglomeration of rGO, uneven coating formed on the surface of the proppant, and the thinner part of surface coating becoming prone to crushing, which reduces the compressive strength of the proppant. When the concentration of rGO is 0.1%, the number of fine particles generated in the urethane coating is minimized. When the concentration of rGO in urethane resin is higher, a higher percentage of fine particles is produced. This may be due to the high degree of rGO aggregation and the formation of highly uneven coating on the surface of proppant, which makes it impossible to evenly distribute the applied load, resulting in higher crushing of the proppant particles.

2.3. Fracturing Flowback Fluid Treatment Using Nanotechnology. In the process of hydraulic fracturing of unconventional oil and gas reservoirs, a large amount of fracturing flowback fluid will be produced, which contains organic pollutants, bacteria, chemicals, and so on, such that it cannot be reused and is difficult to deal with, while its direct discharge will pollute the environment.[134] The commonly used treatment methods for flowback fluid include biodegradation, physical separation, chemical reaction, and so on, but these treatment methods generally have problems associated with low efficiency and high cost. Therefore, many researchers have begun to study the possibility of treating fracturing flowback fluid using nanomaterials.[135] The applications of nanomaterials in fracturing flowback fluid treatment mainly include photocatalytic technology and membrane separation technology. Among them, photocatalytic technology is based on the photocatalytic characteristics of some nanoparticles, that is, using the pollutant oxidation and decomposition ability of nanophotocatalysts under light in order to purify fracturing flowback fluid.[136] Grzechulska et al.[137] have prepared various titanates through mixed calcination of KOH [$BA(OH)_2$ or $Ca(OH)_2$] and titanium dioxide slurry with microcrystalline structure, which were used as photocatalysts to treat oily wastewater. Bessa et al.[138] have used gas chromatography (GC) to evaluate the photocatalytic degradation efficiency of TiO_2 (anatase) on pollutants in water produced from an oil field in the Rio de Janeiro Campos Basin, Brazil, and analyzed and studied the reasons for the significant reduction in wastewater toxicity. Two types of photocatalysts (Aldrich and Degussa P25) were used, in which Aldrich TiO_2 particles were more corrosion-resistant and had better treatment effect on the produced water, thus proving that TiO_2-induced semiconductor photocatalytic technology is a promising method for oil and gas wastewater treatment.

Zielińska-Jurek et al.[139] have prepared a series of Pt–N/TiO_2 photocatalysts using a sol–gel method. The catalysts were characterized by XRD, scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), and X-ray photoelectron spectroscopy (XPS). The experimental results showed that the best results were obtained when the sample with molar ratio of Ti/N equal 1:4, the particle size of platinum nanoparticles was about 3 nm, and the prepared photocatalyst sample had an anatase structure. Under vis and UV/vis light irradiation, the photocatalytic activity was evaluated by measuring the decomposition rate of phenol in aqueous solution. Compared with N-TiO_2 and Pt-TiO_2 samples, the photocatalytic activity of Pt-N/TiO_2 samples was significantly improved, due to the synergistic effect of nitrogen and platinum. In addition, Zielińska-Jurek et al.[140] have also combined a TiO_2 photocatalyst with magnetic oxide nanoparticles to enhance the separation and recyclability of the nano-TiO_2 photocatalyst. Fe_3O_4/TiO_2 and $Fe_3O_4@SiO_2/TiO_2$ nanocomposites were prepared through a heteroagglomeration method. The photocatalytic activity of the prepared nanocomposites was evaluated, and the decomposition rates of pollutants in shale reservoir flowback fluid were compared. At the same time, the removal rate of COD was measured to determine the $Fe_3O_4@SiO_2/TiO_2$ photocatalytic degradation effect, and it was found that the COD can be reduced by 40% after 180 min of UV–vis light irradiation, the $Fe_3O_4@SiO_2/TiO_2$ nanocomposites can be reused after recycling, and the decomposition efficiency was not significantly reduced.

Zhao et al.[141] have proposed a combined process of flocculation and preoxidation (Fenton oxidation)-catalyzed ozonation with zeolite-supported nano-TiO_2 adsorption on montmorillonite for treating fracturing flowback fluid. In Figure 16a, a TEM image of zeolite is shown. The zeolite is in the shape of a hollow tube, which is beneficial as it provides a large specific surface area for the supported catalyst. As shown in Figure 16b,c, in the nano-TiO_2/zeolite catalyst, the nano-TiO_2 particles (with particle size of about 10–20 nm) are evenly dispersed on the surface of the zeolite, without obvious agglomeration. It can be observed from the images that the blank zeolite is not covered by nano-TiO_2, as shown in the yellow box in Figure 16b. As shown in Figure 16d, the lattice spacing of nano-TiO_2 was mostly 0.35 nm, which conforms to the (101) crystal plane of TiO_2, indicating that the nano-TiO_2 is highly crystalline. From the above analysis, it can be seen that zeolite is conducive to the uniform dispersion of nano-TiO_2 particles, which can improve its catalytic performance in wastewater treatment.

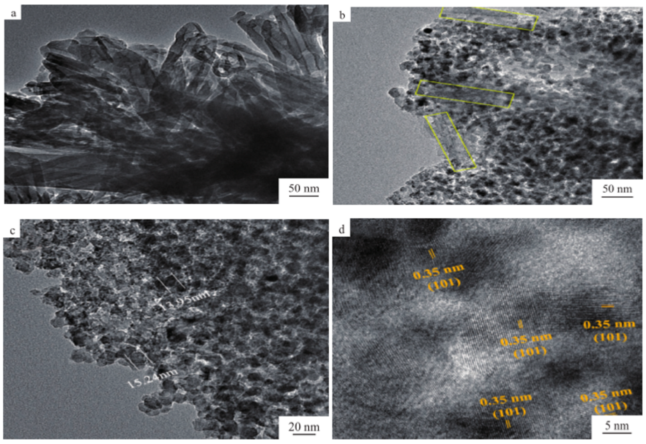

Figure 16. (a) TEM image of zeolite. (b–d) TEM images of nano-TiO_2/zeolite. Reprinted with permission from ref 141. Copyright 2019 Environmental Protection of Chemical Industry.

As shown in Figure 17a, protosodium-based montmorillonite has a clear sheet structure. As shown in Figure 17b,c, the nano-zerovalent iron (particle size 20–50 nm) reduced by $NaBH_4$ is spherical or ellipsoidal. As shown in Figure 17c, nano-zerovalent iron presents a slight aggregation phenomenon, which is due to the small particle size and large specific surface area of the nanomaterials, which lead to its instability and strong magnetic and van der Waals forces between nanoiron particles that easily aggregate with each other.

Zhao et al.[141] have also experimentally studied the removal effect of various influencing factors on COD. According to the experimental results, the optimal experimental conditions for COD removal were determined, where the adsorption time was 4 h, the dosages of catalyst and montmorillonite-loaded nano-zerovalent iron adsorbent were 1.0 and 5.0 g/L, respectively, and the ozone introduction time was 5 min. Under the optimal experimental conditions, the COD was reduced from 4032.60 to 37.03 mg/L, and all indices of the treated effluent met the first-level standard in the wastewater discharge standard GB8978-1996. The treated flowback fluid was used to prepare fracturing fluid. The viscosity measured at the temperature of 80 °C was 4.4 mPa·s, which not only was higher than the fracturing fluid prepared from untreated flowback fluid but also presented a certain improvement in temperature resistance. Additionally, the fluid can also be recycled.

Lei et al.[142] have adopted the photocatalytic advanced treatment technology to use nano-ZnO, modified nano-ZnO, and coconut-shell-activated carbon-supported nano-ZnO as photocatalysts in order to carry out advanced treatment of fracturing flowback fluid under ultraviolet light catalysis. It was found that the coconut-shell-activated carbon loaded with nano-ZnO had the best removal effect on the COD in the flowback fluid, and the experimental results showed that the best conditions for the treatment of flowback fluid by coconut-shell-activated carbon loaded with nano-ZnO are as follows: dosage of nano-ZnO loaded on coconut-shell-activated carbon, 2 g/L; UV irradiation time, 4 h; and pH, 4. The flowback fluid treated with coconut-shell-activated carbon-loaded nano-ZnO met the wastewater discharge standard GB8978-1996. At the same time, the reusability of the coconut-shell-activated

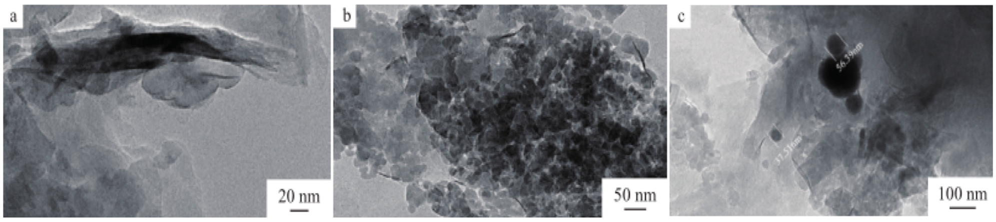

Figure 17. (a) TEM image of montmorillonite. (b,c) TEM images of nano-zerovalent iron/montmorillonite. Reprinted with permission from ref 141. Copyright 2019 Environmental Protection of Chemical Industry.

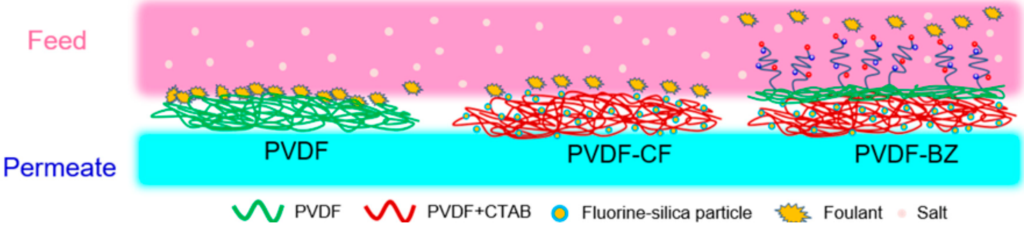

Figure 18. Schematic diagram of electrospun PVDF, base PVDF membrane with an omniphobic surface (PVDF-CF), bilayer PVDF (PVDF-BZ) membrane structure. Reprinted with permission from ref 148. Copyright 2020 MDPI.

carbon-loaded nano-ZnO was also studied, and it was used repeatedly four times under the best conditions determined in the experiment. The removal efficiency of COD did not differ much, indicating that the prepared coconut-shell-activated carbon-supported nano-ZnO catalyst was completely reusable and, thus, had good stability and economical applicability. Liu et al.[143] have successfully synthesized a MnO_2-modified $BiVO_4$ composite photocatalytic oxidant using a one-step hydrothermal method and used it for the treatment of shale gas flowback wastewater. The synergistic effect of photocatalysis and oxidation made great contributions to the removal of COD from wastewater. It was found that when the catalyst dosage was 0.6 g, the pH was 3, and the visible light irradiation time was 4 h, the prepared $BiVO_4/MnO_2$ presented the best photocatalytic oxidation activity, and the COD removal rate reached 65.5%, which was better than that of single $BiVO_4$ or MnO_2. Under these experimental conditions, the COD value can be reduced from 188 to 64.9 mg/L, which meets the first-level standard limit requirements in the wastewater discharge standard GB8978-1996.

In addition to utilizing the photocatalytic properties of nanomaterials to treat fracturing flowback fluids, fracturing flowback fluids can also be treated using separation membranes based on ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and so on. Riley et al.[144] have proposed a wastewater treatment system coupling bioactive filtration (BAF) and membrane separation technology (UF and NF). Their research results showed that when micro-organisms naturally exist in oil and gas production wastewater, an elastic biofilm can be formed to effectively remove the organic pollutants in oil and gas production wastewater, and the possible membrane pollution problem in the subsequent treatment of wastewater by membrane separation technology can be avoided. At the same time, the BAF-UF-NF system can be used to treat fracturing flowback fluids from different wells. The results showed that biological treatment is still an effective wastewater treatment technology, where UF and NF processes can greatly reduce the turbidity of flowback fluid and minimize the pollutant content as far as possible. Moreover, a large number of dissolved solid substances and more than 99% of organic matter were removed from the flowback fluid treated with the BAF-UF-NF system. This indicates that the BAF-UF-NF system provides an efficient and reliable fracturing flowback fluid treatment scheme.

Keshtkar et al.[145] have developed a polyamide−silica nanoparticle reverse osmosis membrane for reducing COD in fracturing flowback fluid. The prepared reverse osmosis membrane can fully meet the discharge standard for the treatment of fracturing flowback fluid. Through experimental research, it was found that, with an increase in poly(ether sulfone) polymer content in reverse osmosis membrane, the porosity and density of membrane decrease while the separation rate increases. Furthermore, when the nanoparticles content in the membrane increases to about 2%, the separation percentage also increases due to an improvement in membrane hydrophilicity.

Hu et al.[146] have reported a zwitterionic polymer brush composed of poly(sulfobetaine methacrylate) (PSBMA) grafted onto the surface of a commercial nanofiltration (NF) membrane by electron transfer−atom transfer radical polymerization (ARGET-ATRP), in order to enhance the antifouling performance of the membrane, especially against organic pollutants. It was experimentally determined that the prepared VNF1-PSBMA membrane showed extremely high performance, where its pure water flux was 86.3 LMH, the sodium sulfate removal rate was 95.67%, and the J/J_0 ratio upon fouling was 73.5% higher than that of the pristine VNF1 membrane at 50% recovery of shale gas wastewater (SGW). The VNF1-PSBMA membrane could effectively remove dissolved organics, especially protein-based organic matter in SGW. This indicates that the grafted zwitterion-modified membrane has great application potential in terms of improving membrane performance and controlling membrane fouling and is suitable for treating shale gas production wastewater with complex components.

In addition to using the above methods to treat fracturing flowback fluids, researchers have also attempted to combine nanotechnology and other technical means to treat fracturing flowback fluids more efficiently. Abass et al.[147] have developed a nano-Fe-mediated anaerobic-oxic membrane bioreactor

(FAMBR) system. Compared with the conventional AMBR system, the FAMBR system has a significantly better COD removal effect, due to the introduction of nano-Fe ions, and has a better degradation effect for specific pollutants, such as polycyclic aromatic hydrocarbons, in fracturing flowback fluid.

Chiao et al.[148] have developed an electrospun polyvinylidene fluoride bilayer (PVDF-BZ) membrane for enhancing fouling and wetting resistance. The PVDF-BZ membrane is mainly composed of PVDF-CTAB and PVDF nanofibers (Figure 18). The surface properties of the PVDF-CTAB nanofibers facing the permeate stream were modified to form an omniphobic surface, while the surface properties of the PVDF nanofibers facing the feed stream were modified to form a hydrophilic surface. The omniphobic surface contained silica nanoparticles, which were salinized to reduce their surface energy. The hydrophilic surface contained a zwitterionic polymer, poly(glycidyl methacrylate-sulfobetaine methacrylate), which was grafted onto the alkali-treated PVDF nanofibers through a "grafting to" modification in order to form a tight antifouling hydration layer. The membrane was challenged with aqueous NaCl solution containing SDS, amphoteric electrolytes, and crude oil. In the presence of SDS and crude oil, the membrane was relatively stable and presented salt rejection (>99.9%). When actual hydraulic fracturing produced water was treated with the membrane, a significant decrease in fouling rate was observed within 4 h. This demonstrates that it is very important to tune and optimize the membrane surface properties, in order to maximize the flux and salt rejection, thus improving the treatment efficiency of hydraulic fracturing produced water.

Membrane distillation (MD) is a technology based on thermal-driven evaporation. It is regarded as an ideal process for purifying fracturing produced water, due to its approximately 100% rejection rate of dissolved solids, no chemical reaction mechanism, and low energy consumption requirements. Said et al.[149] have investigated a novel MD technology involving nanophotonics-enhanced solar membrane distillation (NESMD). The technology integrates photothermally active nanoparticles to provide localized water heating. As shown in Figure 19, compared with the conventional direct contact membrane distillation (DCMD) technology, NESMD technology uses 100% renewable energy (in the form of sunlight) to drive the distillation process, but the hydrophobic membrane is coated with a hydrophilic, microporous, carbon black nanoparticle-infused membrane, which can scatter photons under sunlight and, thus, produce highly localized photothermal heat. Their experimental results showed that when using NESMD technology to treat wastewater, the interception rate of total dissolved organic carbon is between 72.5 and 96% and the interception rate of total dissolved solids is higher than 99%. This indicates that NESMD technology can be used to efficiently treat wastewater while reducing economic costs, alleviating water resource shortages, and minimizing the risk of environmental pollution, which can provide a new idea for the treatment of fracturing flowback fluids.

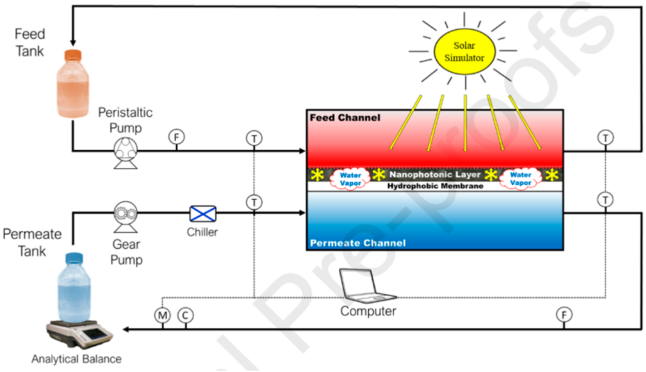

Figure 19. Schematic diagram of NESMD membrane distillation configuration. Reprinted with permission from ref 149. Copyright 2020 Elsevier.

2.4. Development of Degradable Fracturing Completion Tools Using Nanomaterials. Horizontal well staged hydraulic fracturing technology is a stimulation technology widely used in unconventional oil and gas reservoir reconstruction, in which the material used for fracturing completion tool development determines the success or failure of the technology.[150] In recent years, the vigorous development of nanotechnology and nanomaterials has injected new vitality into the research and development of hydraulic fracturing completion tools. Schlumberger, Baker Hughes, ConocoPhillips, Saudi Aramco, Chevron, and other oil service companies have successively formulated and implemented nanotechnology research and development plans in order to develop new degradable nanocomposites for the manufacture of downhole fracturing completion tools, in order to effectively improve fracturing operation efficiency and reduce fracturing costs.[151] Baker Hughes has introduced IN-Tallic degradable frac balls, which are made of a nanocontrollable electrolytic metal (CEM) material, which has high strength and possesses chemical properties that conventional materials do not have.[151−153] The frac balls made of this degradable nanomaterial have low specific gravity and high strength and can migrate underground along with the fluid. During the fracturing process, they can maintain their original shape and strength, and are insoluble in the fracturing fluid. In this way, they can ensure the smooth progress of fracturing operations, and will be completely degraded before or shortly after the well is put into operation in order to ensure that the oil and gas flow channel is unblocked and there is no tubing resistance; in this way, the whole fracturing process not only has reduced the pumping time, but the efficiency of the fracturing operation is also improved. Although the manufacturing cost of these decompressible frac balls is slightly higher, this cost is much lower than the production losses. IN-Tallic degradable frac balls have been widely used in multistage hydraulic fracturing operations of unconventional tight reservoirs in North America and elsewhere around the world (Figure 20). More than

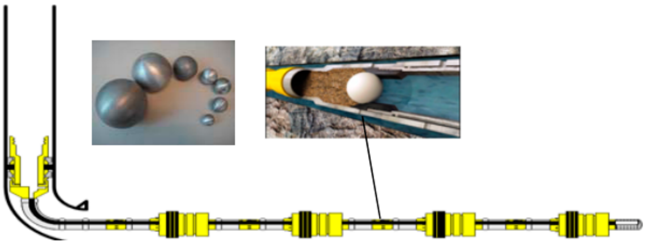

Figure 20. Schematic diagram of IN-Tallic degradable frac ball in multistage hydraulic fracturing of horizontal wells. Reprinted with permission from ref 151. Copyright 2015 China Petroleum Machinery.

100,000 multistage fracturing operations have been completed, and good stimulation results have been achieved.[153] In addition, Baker Hughes has developed the industry's first fully degradable, fully soluble SPECTRE fracturing bridge plug (Figure 21). Compared with other bridge plugs, the SPECTRE fracturing bridge plug is made of the same controllable electrolytic metal (CEM) material as IN-Tallic degradable frac balls, and all of its components are soluble materials, including slips and rubber.[154] The SPECTRE fracturing bridge plug is insoluble in slickwater and fracturing fluid, is only dissolved in fracturing flowback fluid, and can be produced directly without drilling and grinding after fracturing, with basically no bridge plug debris flowback and residue. The SPECTRE fully soluble fracturing bridge plug has been successfully applied in more than 80,000 multistage fracturing stimulation operations all over the world, achieving satisfactory fracturing stimulation effects.

Figure 21. Baker Hughes SPECTRE fully soluble fracturing bridge plug. Reprinted with permission from ref 154. Copyright 2019 Journal of Yangtze University(Natural Science Edition).

Xu et al.[155] have reported a smart gas lift valve made of degradable nanocomposites. The smart gas lift valve incorporates a time-controlled disintegrable plug made of a nanostructured composite material, which is used as a temporary dummy valve during well completion. This dummy valve is converted into a live valve for gas lift simulation, through in situ disintegration of the disintegrable plug in brine during the cleanup process. This new smart gas lift valve simplifies multiple slickline trips or well interventions, thus reducing production costs and risks, as well as improving the efficiency of off-shore well completion operations.

In addition, researchers have developed a variety of fracturing completion tools using different types of nanomaterials. Peng et al.[156] have proposed a preparation method for carbon fiber modified polyaryletherketone nanocomposites and used them to prepare frac balls. The preparation process for the carbon fiber modified polyaryletherketone nanocomposites is as follows: first, the polyaryletherketone is dried at 100−120 °C for 6−8 h. After the polyaryletherketone are dried, carbon fiber and a heat stabilizer are mixed and stirred evenly, uniformly dispersed in toluene using ultrasonic treatment, and finally heated to 80−100 °C and kept for 6 h to remove the toluene solvent. The preparation method of this nanocomposite is relatively simple, the quality of the prepared product is relatively stable, and the production efficiency is high. When using nanocomposites to prepare frac balls for oil well completion, the prepared frac balls have high compressive capability and good temperature resistance, presenting broad application prospects. Zhang et al.[157] have developed a degradable fracturing packer setting ball, which is prepared from a degradable nanocomposite, and which has the characteristics of high strength, lightweight, and easy flowback after fracturing operation. It can meet the needs of fracturing operations of oil and gas wells with a pumping pressure of 50 MPa and a depth of 3000 m. A field test demonstrated that the packer was intact after fracturing, and no fracturing setting balls were found, indicating that they had been completely dissolved. The successful development and application of the degradable packer setting balls can effectively simplify the fracturing operation process, improve the operation efficiency, reduce the fracturing cost, and provide reference for the subsequent development of a series of fracturing supporting tools, such as degradable bridge plugs, perforating guns, packers, fracturing casings, ball seats, anchoring tools, and so on. Jia et al.[158] have proposed a preparation method for degradable fracturing temporary plugging balls. The temporary plugging balls are mainly prepared from new degradable polyester materials composed of polycaprolactone, polyglycolic acid, polylactic acid, chain extender triglycidyl isocyanurate, nanosilica, and so on. By adjusting the ratio of each component in the raw material of the temporary plugging ball, the degradation temperature of the material can be adjusted to meet the degradation requirements associated with different bottom hole temperatures. Due to the addition of nanosilica in the preparation process of the degradable fracturing temporary plugging ball, the defects of the traditional temporary plugging ball can be overcome, such as low compressive strength, narrow temperature range, and unstable plugging. The prepared degradable fracturing temporary plugging balls have the advantages of simple preparation, wide source of raw materials, low cost, and so on, and their application for fracturing stimulation in high temperature and high pressure reservoirs can effectively play the role of temporary plugging and diverting.

2.5. Monitoring and Mapping Hydraulic Fractures Using Nanotechnology.

When using hydraulic fracturing technology to reconstruct unconventional oil and gas reservoirs, it is usually necessary to obtain the original parameters, such as reservoir physical properties, natural fracture distribution, fault characteristics, and fluid types, in order to formulate a reasonable fracturing operation scheme. During the hydraulic fracturing operation, it is also necessary to monitor the hydraulic fractures in real-time, obtain parameters such as fracture network shape, map the actual shape of the hydraulic fractures, and use these as a theoretical basis to optimize the fracturing design, in order to provide guidance for subsequent fracturing operations in unconventional oil and gas wells presenting similar geological conditions.[159] Microseismic monitoring is one of the most commonly used hydraulic fracturing monitoring techniques in the field, which is also the most effective and intuitive hydraulic fracture monitoring method.[160] Microseismic monitoring technology can characterize the height, length, spacing, location, and shape of hydraulic fracturing fractures, but it cannot accurately explain the geometry of connected fractures or obtain the reservoir proppant distribution and the permeability of fluid in the fracture network in an accurate and real-time manner; further, it cannot be used to accurately evaluate the actual shape of the reservoir fracture network and fracturing effect.[161] In recent years, the introduction of nanotechnology for monitoring and mapping hydraulic fracturing fractures has received extensive attention. Researchers have committed to using nanotechnology to monitor the hydraulic fracturing process in real-time and map the reservoir fracture network shape, thus helping to improve the understanding of the fracture distribution after hydraulic fracturing in unconventional oil and gas reservoirs, in order to improve the comprehensive development benefits of unconventional oil and gas. Nanosensors and nanorobots developed from advanced nanoparticles or nanomaterials can follow the injected fluid into the micro/nanopores of unconventional oil and gas reservoirs in order to monitor hydraulic fractures.[162] Nanoparticles with identification properties, such as electromagnetic and/or acoustic wave response, may be injected into the formation, following which an imaging technology can be used to map the reservoir, in order to identify the proppant, fluid, and the location of hydraulic fractures and natural fractures in the near-wellbore zone. The characterization accuracy of the reservoir with such methods is much higher than that with traditional technology.[29]

Stephenson et al.[163] have used nanotechnology to detect oil and gas reservoirs by grafting and modifying the surface of the sensor matrix material with nanoparticles to enhance the Raman spectrum intensity of the material surface. It was not until 2009 that nanoparticles that could be used to detect fracture parameters appeared, which spurred a substantial shift from wellbore measurements to formation measurements.[164] Saudi Aramco has proposed and developed a reservoir nanorobot based on the combination of a chemical molecular system and a mechanical system.[165,166] A field test in 2010 verified the stability and reliability of these nanorobots, through the injection of 250 barrels of diluted nanorobots into the Arab-D formation, which marked a milestone in nanorobot research.[167] The spatial resolution of the reservoir nanorobot detection technology is much higher than that of seismic, well-logging, and core 3D scanning analyses. This makes it possible to conduct targeted quantitative analysis of the whole reservoir and fluid, map natural fracture and fault characteristics of the reservoir, identify and determine high seepage channels, and accurately describe the spatial distribution of oil/gas/water and the location of the remaining oil and gas. At present, the developed reservoir nanorobots do not have multifunction detection and movement capabilities. It is expected that the next generation of reservoir nanorobots will be put into use within 5−10 years, and the comprehensive performance will be greatly improved. These are expected to have multiparameter identification and transmission functions and possibly even a certain oil displacement capacity.[13]

Aderibigbe et al.[168,169] have stated that nanoparticles have great application potential in reservoir characterization and monitoring. Core−shell superparamagnetic nanoparticles (60−70 nm) have been synthesized and used in a mixture with a contrast agent and a proppant, such that the position of the proppant could be detected by magnetic susceptibility measurement. At the same time, the spatial distribution of nanoparticles in porous media was studied using a numerical simulation method. The simulation results showed that the nanoparticles were mainly concentrated on the hydraulic fracture plane filled with proppant in tight formations. Compared with the surrounding porous media, the concentration of nanoparticles in hydraulic fractures was higher, allowing for more accurate location and tracking of the proppant in the reservoir, as well as improving the fracture detection ability. These results indicate that this technology may be used to more accurately characterize the geometry of hydraulic fractures, being of great significance for the optimal design of hydraulic fracturing in tight reservoirs.

Sun[160] has prepared superparamagnetic Fe_3O_4 nanoparticles with a particle size of about 20 nm and, on this basis, prepared a water-based nanoferrofluid with good stability using polyethylene glycol 4000 as the surface stabilizer. Experimental evaluation indicated that the density of the nanoferrofluid is slightly higher than that of water (1.011−1.080 g/mL), its viscosity is 2.84−8.20 mPa·s, and its magnetic susceptibility is 0.063−0.244. Based on static magnetic field theory and numerical simulation, the convection and diffusion processes of magnetic nanoparticles in fractures and formation media were studied. The simulation results showed that the magnetic susceptibility of the fracture area can be significantly improved by injecting nanoferrofluid, more than 100 times greater than that of the formation overall. The magnetic nanoparticles were mainly distributed in fractures and formation areas near the fracture surface. At the same time, due to the existence of nanoferrofluid in the fracture, the induced magnetic field can be obviously generated under the action of a geomagnetic field, and the induced magnetic field is affected by the injection time of the nanoferrofluid and fracture parameters. This research showed that it is theoretically feasible to inject nanoferrofluids into hydraulic fractures for hydraulic fracture monitoring, showing exciting application potential.

Morrow et al.[170] have stated that the magnetic properties of nanomagnetite (nMag), which produces a huge contrast between particles and the surrounding tissue, can be used to obtain information such as the reservoir characteristics of hydraulic fracturing oil and gas wells. Magnetite nanoparticles (nMag) with an average particle size of 15 nm were synthesized, and the required relative concentration and quantity of nMag for single-well detection were discussed. At the same time, the single-well cost for using nMag was also estimated, and the application prospect of nMag was considered. Although nMag can be used for imaging typical sandstone or limestone reservoirs, its dosage is too large and the cost will be too high. In this case, magnetic nanoparticles with magnetic susceptibility significantly higher than that of nMag should be selected. Therefore, Morrow et al.[171] have prepared a series of ternary manganese and zinc ferrite nanoparticles (Mn−Zn ferrite NPs) with a different Mn/Zn ratio for fracture detection of unconventional oil and gas reservoirs, such as shale. The size of the Mn−Zn ferrite NPs (7 ± 1 nm) was smaller than that of the nMag (11.82 nm) prepared under the same conditions, and the Mn−Zn ferrite compositions have a higher positive magnetic susceptibility. With an increase in the Mn/Zn ratio, the mass magnetic susceptibility increased sharply until the ratio exceeded 0.4, after which the mass magnetic susceptibility decreased slightly with an increase in manganese content. The mass magnetic susceptibility of the prepared Mn−Zn ferrite NPs was higher than that of nMag, but it is easily affected by temperature, with the magnetic susceptibility decreasing along with an increase in temperature. The mass magnetic stability of nMag was lower by about 6.5 times. This means that a large amount of superparamagnetic NP tracers, such as Mn−Zn ferrite NPs, need to be used for downhole imaging of shale reservoirs. However, due to the presence of a large amount of paramagnetic clays, such as illite, in shale reservoirs, a decrease in the magnetic susceptibility of paramagnetic clays can help to increase the signal-to-noise ratio of Mn−Zn ferrite nanoparticles under the temperature conditions of shale reservoirs. Therefore, the dosage of Mn−Zn ferrite NPs can be reduced, to a certain extent, the cost can be reduced, and the economic benefit can be improved.

Liu et al.[172] have studied the feasibility of using magnetic nanoparticles to monitor hydraulic fractures in deep oil and gas wells. The magnetic proppant was prepared using superparamagnetic nanoparticles. The magnetic proppant had the same compressive strength as the traditional proppant, is not easily affected by complex conditions such as high temperature and high pressure in the formation, and the effective magnetic susceptibility contrast of the rock−fluid−proppant system was greater than 0.4−0.5. After the magnetic proppant is injected into the formation, it can be activated by external excitation, enhancing the magnetic properties of the proppant when hydraulic fractures need to be detected. By measuring the magnetic field changes before and after the hydraulic fracture is filled with magnetic proppant, the magnetic anomaly responses can be used to determine the basic characteristics of hydraulic fractures. However, due to the small size of the fractures in deep reservoirs and the flow interference of some fluids, the magnetic anomaly signals generated by the hydraulic fractures containing magnetic proppant are very weak, and a high-sensitivity magnetometer is required to detect the changes in this weak magnetic field. Through systematic research, Liu et al.[172] has stated that magnetic proppants can be fully applied to the hydraulic fracturing of oil and gas wells in order to realize the real-time monitoring of hydraulic fractures and to more accurately evaluate the reservoir reconstruction effect after hydraulic fracturing.

Al-Shehri et al.[173,174] have developed FracBots (Fracture Robots) for monitoring and mapping hydraulic fractures in unconventional reservoirs, as well as measuring other wellbore parameters. These FracBots were injected during hydraulic fracturing operations, 3D proppant placement constellation maps were established through an autonomous localization algorithm, and a novel cross-layer communication framework based on magnetic induction (MI) FracBot networks was developed, which uses the unique properties of the MI domain to determine the locations of randomly deployed Fracbot nodes. The FracBots are positioned in hydraulic fractures during hydraulic fracturing, so that they can work efficiently in complex underground environments and realize the use of wireless underground sensor networks (WUSNs) for the mapping of hydraulic fractures.

The specific workflow of FracBots is to assuming that FracBots are statically and uniformly distributed in hydraulic fractures, the base station located in the wellbore releases energy through the fractures and transfers the energy to the MI-based FracBots distributed in the hydraulic fractures, and establishes communication with the FracBot sensors. The FracBots then collect and sense reservoir parameters, and use MI communication technology to transfer the energy to the nearby FracBot sensors, which transmit the data back to the base station at the wellbore through a continuous relay of multiple FracBots nodes. Finally, the base station collects information from the data transmitted by FracBots in the hydraulic fracture, and then forward the corresponding data through the ground gateway. This FracBot technology will undoubtedly significantly improve the efficiency of monitoring and mapping hydraulic fractures. Al-Shehri et al.[174] have been developing the second-generation FracBot, which is a miniaturized version of the current FracBot with optimized hardware and software solutions, that is expected to have smaller size and more powerful functions. At present, FracBot has not yet been tested in the actual field. In the future, the more mature FracBot technology can be applied to hydraulic fracturing operations in unconventional oil and gas reservoirs in order to improve the efficiency of hydraulic fracture monitoring and provide more accurate reservoir hydraulic fracture network mapping, providing strong support for the efficient development of unconventional oil and gas reservoirs.

3. FUTURE RESEARCH AND RECOMMENDATIONS

Nanomaterials and technologies have shown great application potential in the field of hydraulic fracturing of unconventional oil and gas reservoirs, and some exciting progress has been made, but many challenges still remain. In this section, the future applications and development directions of nanomaterials and technologies for hydraulic fracturing in unconventional oil and gas reservoirs are discussed, within the context of the current actual needs of unconventional oil and gas reservoir hydraulic fracturing operations. The main knowledge gaps identified from the review and recommendations for future research are presented in the following.

(1) At present, the interaction mechanisms between nanomaterials and various components of different types of fracturing fluids have not been fully studied. Therefore, it is necessary to combine various technical means to carry out in-depth and systematic research on the microscopic interaction mechanism between nanomaterials and different fracturing fluid components, so as to optimize the preparation process of fracturing fluid systems and further improve the comprehensive performance of fracturing fluids to meet the needs of hydraulic fracturing in unconventional oil and gas reservoirs.

(2) The applications and research of nanomaterials in supercritical carbon dioxide fracturing fluids are still relatively few. It is explored to introduce nanomaterials into supercritical carbon dioxide fracturing fluids to improve the sand-carrying performance of the fracturing fluid system, reduce the filtration loss of fracturing fluid, and improve the applicability of supercritical carbon dioxide fracturing fluids in hydraulic fracturing stimulation of unconventional oil and gas.

(3) Due to the high cost of nanomaterials and their complicated preparation processes, the large-scale production of nanomaterial-coated proppants cannot be realized at present, thus limiting the industrial application of nanomaterial-coated proppants. Therefore, on the basis of existing research, it is necessary to continue to develop low-cost functional nanomaterials on the basis of the existing research, as well as to optimize proppant surface treatment processes to develop a low-cost multifunctional proppant suitable for unconventional reservoir conditions.

(4) Future studies should explore raw materials with potential application value for use in preparing nanoproppants, such as bauxite waste rock, various silicon-containing waste residues, and other industrial wastes, or materials such as mineral sand and river sand that are widely distributed in nature, thus not only realizing the effective utilization of resources, but also reducing the cost of fracturing operations.

(5) The use of a single photocatalytic or membrane separation technology to treat fracturing flowback fluids will lead to problems, such as difficulty in recovering powder catalysts and the generation of pollution. In the future, combining photocatalytic technology and membrane separation technology to prepare photocatalytic separation membranes can be considered, while introducing nanomaterials to optimize the structure and performance, combined with deep oxidation technology to form a multilevel treatment system for fracturing flowback fluids. Thus, the separation and decomposition efficiency of pollutants can be improved, and the deep purification of fracturing flowback fluids can be realized.

(6) In order to better solve many problems present in the process of hydraulic fracturing completion operations in unconventional reservoirs (e.g., more debris after perforation, easily blocked holes, difficult drilling and grinding), a series of degradable fracturing tool systems (e.g., degradable ball seats, packers, perforating guns, fracturing casings) applicable to fracturing completion operations in unconventional reservoirs can be developed using nanomaterials to simplify the fracturing operation process while reducing the risk and improving the efficiency of fracturing operations.

(7) Although the use of nanorobots, magnetic nanoparticles, and FracBot technology for fracture monitoring and characterization is theoretically feasible, the comprehensive consideration of factors, such as development benefits, economic costs, and other factors for further evaluation of their feasibility is required. At the same time, in order to adapt to complex reservoir conditions (e.g., high temperature and high pressure), it is also necessary to optimize and improve their structure and function.

(8) As high-quality nanoparticles are relatively scarce and high cost, how to reduce the production cost of nanomaterials and achieving large-scale production are important challenges that must be faced in the future. It is suggested that research efforts to develop low-cost and high-quality nanoparticles be intensified, in an effort to lower the threshold to the large-scale commercial application of nanomaterials.

(9) The literature reviewed indicated that most of the exciting research is still in the laboratory stage, and large-scale field trials have not been carried out, indicating that more field trials should be conducted to validate the research findings, promote the conversion of research findings and the practical application of nanotechnology, and realize the efficient development of unconventional oil and gas.

4. CONCLUSIONS

A review of the application status and research progress of nanomaterials and technologies for hydraulic fracturing stimulation in unconventional reservoirs was conducted in this paper, and expounds in detail the application mechanisms of nanomaterials and technologies in enhancing the performance of fracturing fluids and proppants, the efficient treatment of fracturing flowback fluids, the development of degradable fracturing completion tools, and hydraulic fracture monitoring and mapping. The concluding remarks and future research directions are presented. The reviewed literature indicated that nanomaterials and technologies have broad application prospects in the field of unconventional oil and gas hydraulic fracturing, which can break the pattern of existing hydraulic fracturing technology systems, thereby bringing revolutionary breakthroughs to hydraulic fracturing technology. The following are the main findings of the review.

(1) The addition of nanomaterials to polymer-based fracturing fluids, water-based fracturing fluids, VES fracturing fluids, and foam-based fracturing fluids can effectively enhance their rheological properties, sand-carrying properties, thermal stability, and other properties through cross-linking between nanomaterials and polymers, the formation of reversible cross-linked structures with micelles and synergistic interactions with surfactants, which are conducive to the formation of higher quality hydraulic fracture networks during the hydraulic fracturing stimulation in unconventional reservoirs.

(2) The use of nanomaterials to modify the surface of the fracturing proppant (i.e., through coating) can significantly improve properties such as the compressive strength of the proppant, such that it can more effectively support hydraulic fractures, while nanoscale proppants prepared from industrial wastes such as fly ash can be placed into micro- and nanofractures in unconventional reservoirs to further improve the conductivity of the fractures network, increase the reservoir stimulation volume, and provide high-conductivity channels for oil and gas seepage.

(3) Compared with conventional fracturing flowback fluid treatment methods, nanophotocatalysis and membrane separation technologies can be used to more efficiently remove pollutants from fracturing flowback fluids, achieving the purpose of deep purification of fracturing flowback fluid. In addition, some emerging technologies (e.g., membrane distillation technology) are regarded as ideal processes for the treatment of fracturing flowback fluids, due to their approximate 100% rejection rate of dissolved solids, no chemical reaction mechanism, and low energy consumption, which can provide new ideas for the efficient treatment of fracturing flowback fluids.

(4) Degradable fracturing completion tools made of nanomaterials have more desirable properties (e.g., low density, high strength, good temperature resistance), and are generally insoluble in fracturing fluid, only being dissolved in fracturing flowback fluid. Additionally, they leave basically no residue after fracturing, which can simplify the fracturing operation process and greatly improve the efficiency of fracturing operations.

(5) Magnetic nanoparticles can be mixed with proppants and injected into a formation to monitor and characterize hydraulic fractures by detecting the distribution of magnetic nanoparticles in the formation and fractures. The emerging FracBot technology not only is posed to improve the monitoring efficiency of hydraulic fractures, but can also facilitate the mapping of more accurate hydraulic fractures morphology in reservoirs, due to its high integration and multifunctional features.

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