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Synthesis of fluorinated nano-silica and its application in wettability alteration near-wellbore region in gas condensate reservoirs

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ABSTRACT

Fluorinated silica nanoparticles were prepared to alter rock wettability near-wellbore region in gas condensate reservoirs. Hence fluorinated silica nanoparticles with average diameter of about 80 nm were prepared and used to alter limestone core wettability from highly liquid-wet to intermediate gas-wet state. Water and *n*-decane contact angles for rock were measured before and after treatment. The contact angle measured 147° for water and 61° for *n*-decane on the core surface. The rock surface could not support the formation of any water or *n*-decane droplets before treatment. The functionalized fluorinated silica nanoparticles have been confirmed by the C—F bond along with Si—O—Si bond as analyzed by FT-IR. The elemental composition of treated limestone core surface was determined using energy dispersive X-ray spectroscopy analyses. The final evaluation of the fluorinated nanosilica treatment in terms of its effectiveness was measured by core flood experimental tests.

1. Introduction

In some gas reservoirs, known as retrograde gas condensate reservoirs, when the bottom hole pressure in a drilled well falls below the dew point, a liquid phase rich in heavier hydrocarbons is dropped out of gas. This liquid phase is commonly known as “condensate”. The condensate is trapped by the capillary forces or it is retained in the rock as a result of low liquid mobility. This condensate blockage around the well bore chocking can reduce the productivity of well by a factor of two or more.

The Arun field in Indonesia, one of the world’s retrograde gas condensate reservoir for example, showed that about 1.1% liquid drop out in the reservoir brings down the well productivity by about 50% as pressure falls below dew point pressure [1]. Wettability plays an important role in condensate accumulation around the well bore. The liquid low mobility because of heavy liquid-wetting of rocks around well bore is a major factor in liquid accumulation so it is regarded to be a key strategy for recovering of depleted productivity in gas condensate reservoir by altering the wettability of the rock from liquid-wetting to intermediate gas-wetting. Through wettability alteration, the liquid phase mobility for a gas–liquid system increases significantly showing capacity to improve gas well deliverability in a gas condensate reservoir.

Jadhunandan and Morrow [2] and Owolabi and Watson [3] have shown that altering the wettability to intermediate gas-wetting gives lower liquid saturation. Altering of rock wettability is achieved by adsorption of a surface tension reducing agent that causes repellency of the water and oil. Li and Firoozabadi [4] were the first who proposed the enhancement of gas well deliverability by wettability alteration of the near-wellbore region from strong liquid-wetting to preferential gas-wetting state. They used chemicals with fluoro functional group to alter wettability and showed that permanent gas-wetting state can be established in Berea sandstone and Kansas chalk through chemical treatment.

Tang and Firoozabadi [5], Mohanty and co-workers [6], Fahes and Firoozabadi [7], Kumar et al. [8] and Bang et al. [9] experimentally investigated the possible improvements in gas and condensate relative permeability by using flouro surfactants to alter the wettability of sandstone and limestone cores.

Dynamic fluidity in porous media can be changed by modifying the wettability of porous walls. Generally there are two factors affecting the wettability of solid surface: surface energy and surface roughness. Roughness on two or more length scales has been suggested to be responsible for superhydrophobicity observed on some plant leaves like the lotus leaf [10]. Therefore, superhydrophobic surfaces can be produced by creating rough structures by compounds with low surface free energy [11]. Various synthetic methodologies for obtaining such hydrophobic and oleophobic surfaces have been presented by electrochemical reaction and deposition [12], plasma etching [13], phase separation [14,15], sol–gel [16,17], solution-immersion [18], etc. Some of these methods suffer from certain limitations such as complicated process control, sever synthetic conditions and long preparation time, and hence it was necessary to find simple and effective techniques

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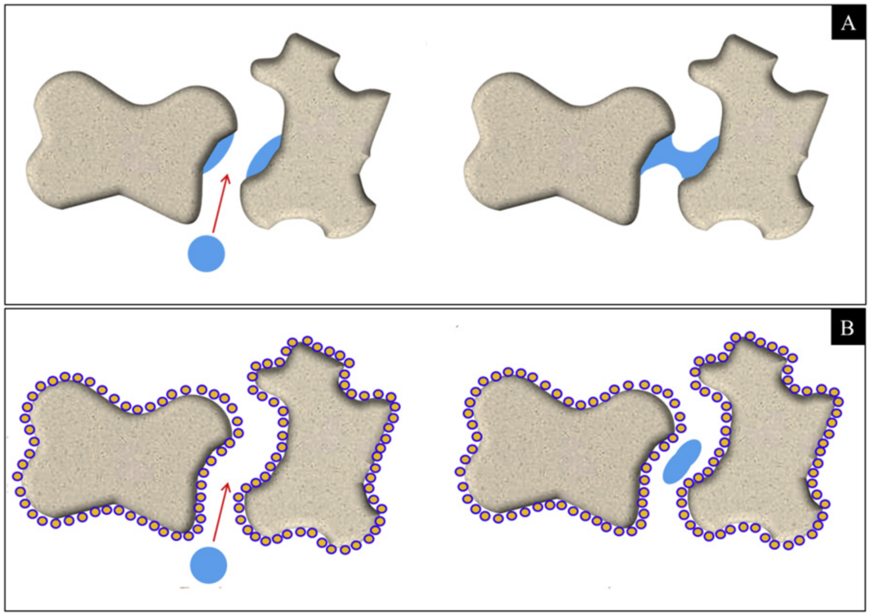

Fig. 1. The state of liquid droplet through the pores: (A) containing liquid film and (B) after the adsorption of SiO_2 nanoparticles.

for rapid screening of large amounts of chemicals in altering wettability for delivering solvents to these chemicals at appropriate concentrations. There have been some reports on preparation of fluorinated silica nanoparticles in alcohol solutions, for example Wang et al. [19] and Brassard et al. [20] prepared fluorinated silica nanoparticles to generate surface superhydrophobicity for routine applications such as production of coating that can impart waterproof and anti-soiling properties to clothes, footwear, car windshields and urban monuments or anti-corrosion. Because discrete particle size of silica nanoparticles can diffuse deep into the layers of rock with low permeability, it seems that such particles can effectively remove the liquid film of pore surfaces and reduce the flow resistance significantly by preparing low drag surface for microchannels in rock. Fig. 1 shows the state of liquid droplet through the pores before and after adsorption of fluorinated silica nanoparticles on the pore surface.

The literature on nanoparticles used in reservoir application to change wettability of reservoir rock by their adsorption on porous walls is hardly reported, though Binshan et al. [21] have used one kind of polysilicon, with sizes ranging from 10 to 500 nm, in oil field to enhance water injection by changing the wettability of porous media. Also Onyekonwu and Ogolo [22] studied wettability and permeability changes caused by adsorption of nanometre structured polysilicon on the surface of porous media. Their studies showed that some kind of polysilicons dispersing in ethanol are very good agents for enhancing oil recovery and in this respect ethanol is very good for dispersing polysilicon in reservoirs, in order to change rock wettability. Both studies showed that wettability of reservoir rock is altered by adsorption of polysilicon nanoparticles on the rock surface.

It seems that in gas condensate reservoirs, the nanostructure of fluorinated nanoparticles on the pore surface allows for increased stability of gas pockets formation and reducing the contact area of a liquid droplet with the rock surface.

Recently, our group has reported the change of wettability of limestone rock in such a manner that showed remarkable characteristics of hydrophobic/oleophobic properties by using a sol–gel process [17]. By sol–gel process a fluorinated polymeric network was formed, as a smooth coated film, on the rock surface that behaved as water and oil repellent by mechanism of lowering the surface energy.

Here we report a simple method to create a superhydrophic surface using fluorinated silica nanoparticles by combination of two phenomena: surface roughening and adjustment of surface free energy.

In this study, we tried to find a new and effective method to remove liquid banking near-wellbore region in gas condensate reservoir by modifying the reservoir rock wettability with fluorinated nanoparticles. Four series of fluorinated nano-silica were prepared by changing the ratio of reactants and tried to find the best samples. The fluorinated silica nanoparticles were synthesized by co-hydrolysis of tetraethylorthosilicate (TEOS) and a fluorinated alkylsilane (FAS) in ethanol/NH_4OH solution by changing the ratio of FAS/TEOS. Fluorine is the most electronegative element which interacts with carbon atom to form strong carbon–fluorine bond resulting in a fluorinated chemical with low reactivity which also exhibits high degree of water and oil repellency [23]. In this method a flouroalkylsilane was used as an additional functional group which possessed water and oil repellency. Flouroalkylsilanes are classes of synthetically produced organic chemicals containing perfluoroalkyl residues (all hydrogen atoms replaced by fluorine). They have excellent thermal stability. Fourier transform infrared spectrophotometer (FT-IR), energy dispersive X-ray spectroscopy (EDX) and scanning electron microscope (SEM) images were used to characterize the nanoparticles.

The prepared nanoparticles in ethanol solution can be easily used in gas condensate reservoirs to change the liquid wettability of pore surfaces to gas wettability state by adsorption of fluorinated silica nanoparticles. We believe that this fluorinated nano-silica can improve the productivity of the reservoirs and mitigate condensate and water blocking in gas wells.

2. Experimental

2.1. Chemicals

Tetraethoxysilane (TEOS, 98%) and ethanol were purchased from Merck. Ammonium hydroxide (25% in water) was obtained from Arman Sina. Nonafluorohydroxyltriethoxy silane (FAS-9, 95%) was purchased from ABCR. We also used *n*-heptane, *n*-decane