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Copper stearate as a catalyst for improving the oxidation performance of heavy oil in in-situ combustion process



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ABSTRACT

Copper stearate was applied as a catalyst for the oxidation of heavy oils. The catalytic effect was investigated by high-pressure differential scanning calorimetry (HP-DSC) and accelerating rate calorimetry (ARC). The results showed that copper stearate significantly improved the oxidation performance including decreasing activation energies, enhancing combustion efficiency of coke, and reducing induction time and ignition temperature. CuO nanoparticles were in-situ formed due to the decomposition of copper stearate. To understand the catalytic mechanism, the catalytic effect of copper stearate was compared with nickel stearate, iron stearate and CuO. Furthermore, the existed form and transition of copper stearate during the oxidation process of crude oil were investigated using thermogravimetric analyser coupled with FTIR-spectrometer (TG-FTIR), HP-DSC, X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The results indicated that copper stearate and in-situ formed CuO nanoparticles played their catalytic roles as a homogeneous and heterogenous catalyst in low and high-temperature ranges, respectively. It was believed that the high catalytic activity of CuO can be not only attributed to those well-known catalytic mechanisms, but also benefits from the well-distribution of both copper stearate and in-situ formed CuO nanoparticles.

1. Introduction

In-situ combustion (ISC) is an effective thermal recovery process for heavy oils and natural bitumen. In this process, air is injected into oil reservoirs, and a part of the oil-in-place is ignited by electrical methods, chemical methods, gas burner, or injecting thermal agents [1–3]. Once ignited, combustion is supported by continuous air injection, and combustion front starts to self-propagate forward under the sufficient air supply to displace downstream oil to production wells [1,3].

Compared to other enhanced oil recovery (EOR) methods for heavy oils (steam flooding [4], vapor extraction [5], and electrical heating [6]), ISC has its own unique advantages: 1) air has an endless supply and no geographical restriction [2]; 2) it should have a higher energy utilization ratio as no extra fuel must be purchased except that air needs to be compressed; 3) ISC potentially combines various oil recovery mechanisms of other EOR methods because of a complex set of physical, chemical and displacement processes occurred in reservoirs: oil viscosity reduction caused by heating and possible in-situ oil upgrading, oxidation and cracking of the oil, distillation, front displacement, miscible or near-miscible flooding of flue gas, steam and hot water flooding, etc [1]. Simultaneously, the heavy oil usually contains sulfide, such as hydrogen sulfide. The removal of sulfide increases the cost and difficulty of the refinery of heavy oil. In ISC processes, hydrogen sulfide can be combusted and generate sulfuric acid that will be further dissolved in formation water. The entire process can release some additional heat to the formation and at the same time achieve an in-situ removal of sulfide from the heavy oil without producing more carbon dioxide [7,8]. However, although ISC process can provide such potential benefits, its field application is much less implemented than steam injection. One of the main reasons that limits the wide application of ISC process is the unstable propagation of combustion front.

Using catalyst is considered as a feasible method to sustain a stable combustion front by enhancing coke deposition and heat release during the combustion process of fuel. As early as 1970s, it was reported that metals, metal oxides and metal chlorides can catalyze coke deposition process of pure hydrocarbons both in yield and structure [9,10]. With

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