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Short Communication

Use of unsupported, mechanically alloyed NiWMoC nanocatalyst to reduce the viscosity of aquathermolysis reaction of heavy oil

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ABSTRACT

Ni, W, Mo and C catalysts were mixed and mechanically processed at room temperature for different grinding times: 0, 40, 80, 120, 160, 200 and 240 h. The phases at every stage of milling were studied by X-ray diffraction (XRD). The powders were used in the catalytic aquathermolysis reaction of heavy oil. X-RD showed by increasing the milling time from 0 to 240 h, nanostructured carbide phases were synthesized with a crystallite size ranging from 125.6 to 10.1 nm, which was confirmed by high resolution transmission electron microscopy (HRTEM). The performance of the nano-catalysts in the heavy oil before and after the reaction was analyzed by Fourier transform infrared spectroscopy (FT-IR). As the milling time increased, the ratio of the viscosity reduction of the heavy oil increased from 80.4% to 97.1% by using the catalyst milled for 240 h.

1. Introduction

With the shortage of light crude resources and the increasing demand for energy resources, heavy oil and bitumen are important hydrocarbon resources that play increasingly important roles in the global economy and that have attracted worldwide interest [1]. However, the high viscosity and solidification of these resources cause difficulties in their exploitation. Consequently, reducing their viscosity to enhance oil recovery is an important focus of study [2,3]. In addition, the current petroleum industry demands the development of new nanostructured catalysts for reducing the viscosity of heavy and extra-heavy oils (cracking) during aquathermolysis [3]. J. B. et al. [4] began studying in this field in the 1980s; the researchers explored the details of the chemical reactions between steam, heavy oil and minerals and described all of these reactions collectively as aquathermolysis [3–5]. They discovered that injected steam can not only reduce the viscosity of heavy oil but also react with some components of heavy oil, thereby leading to changes in the properties and compositions of heavy oils [4]. Some authors have reported various unsupported metallic catalysts [6]. Chen et al. [3] used two types of catalysts (Ni and Mo) and discovered nine types of mechanisms that occur during the aquathermolysis reaction: pyrolysis; depolymerization; hydrogenation; isomerization; ring opening; oxygenation, alcoholization, and esterification; and reconstruction. It was also discovered that the Ni catalysts caused greater changes in the resin, saturated hydrocarbon and oxygen-containing groups. Le et al. [7] synthesized an unsupported catalyst by hydrotreating via a reflux method, demonstrating catalysts with a high surface area and dense active phase. Bocarando et al. [8] studied the effect of nickel concentration on hydrodesulphurization (HDS) using a Ni–Mo–W sulfide catalyst. The results suggest that the variation in the nickel concentration leads to an increase in the specific surface area. Most of these synthesis methods used to prepare catalysts are expensive and produce low catalyst volumes. Mechanical alloying(MA) is an alternative, simple and useful technique for synthesizing different phases at room temperature from elemental powders and can also be used to synthesize novel alloys that cannot be created using any other process [9]. In view of these previous investigations and considering that MA has not been used widely for catalytic applications, the objective of this study was to study the performance of unsupported nanostructured NiWMoC in the catalytic aquathermolysis of a heavy oil as well as to determine the relationship between the phases obtained during MA and the viscosity reduction of the heavy oil.

2. Experimental procedure

2.1. Materials

Elemental powders from Sigma Aldrich were mixed to yield a WMoC-42 wt.% WC-33 wt.%–NiC composition. The nickel powder (99.8 + % purity) featured particles measuring approximately (11 ± 3 μm) with an irregular morphology. The tungsten powder (99.9 + %purity) particles showed an irregular shape with a mean size of approximately 5 ± 2 μm. The molybdenum powder (99.8 + % purity) showed

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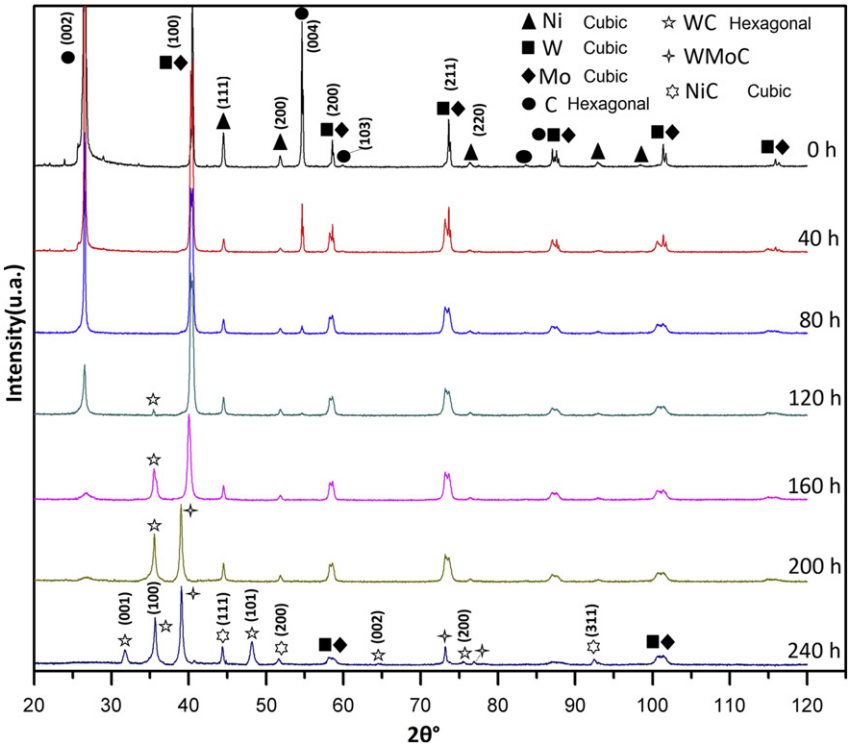

Fig. 1. XRD pattern of NiWMoC after different milling.

a particle size of 25 ± 3 μm. The graphite (99 + % purity) showed a mean particle size of 50 ± 2 μm.

2.2. Catalyst preparation

The raw materials were mixed in a low energy ball mill for 0, 40, 80, 120, 160, 200 and 240 at rotational speed of 500 rpm. The powders and milling balls were loaded and sealed in a stainless steel container inside of a glove box containing a high purity argon atmosphere. To avoid cross contamination, cylindrically shaped zirconia (ZrO_2) grinding media with a high density and two different sizes (1/2 × 1/2 in. and 3/8 × 3/8 in.) were used. In every stage of milling, the ball to powder weight ratio was 10:1.

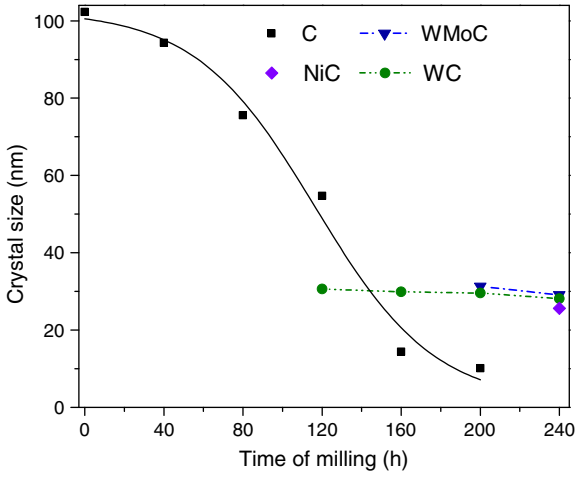

Fig. 2. Crystal size vs. milling time of nano-NiWMoC catalyst.

2.3. Analysis

2.3.1. Structural and morphological characterization

The structural phase analysis was carried out via a Bruker AXS D8 Focus diffractometer using CuK_α (λ = 1.5406 Å) radiation over a 2θ range from 20 to 110° at a speed of 4 min^{-1}. The crystallite size (¿) of the milled samples was calculated from XRD line broadening according to the Scherrer equation [10]. XRD patterns were analyzed using the database software from the international center for diffraction data: ICDD PDF-2(2003).

Scanning electronic microscopy (SEM) was carried out using a FEG Nova 200 from FEI Company at a voltage of 15 kV. High resolution transmission electron microscopy was carried out using an FEI Tecnai G-20 at 200 kV. HRTEM samples were prepared by ultrasonic dispersion in ethyl alcohol. The composition of the MA powders was analyzed by the atomic absorption (AA) method using a PerkinElmer 200 instrument.

2.3.2. Aquathermolysis reaction

To evaluate their catalytic performance, the samples were tested in the aquathermolysis reaction of the heavy oil UTSIL, which has a viscosity of 1.13 Pa s. The experiments were carried out by places 50 g of oil, 50 g of sea water and 1 g of catalyst into a reactor at a pressure of 3 MPa. The temperature of the reaction system was held at 200°C for 24 h. A greater amount of catalyst sample (1 g) was placed in the emulsion than that reported in the literature (0.3 g)[2]. These reaction parameters were optimized in preliminary tests. The viscosity of the resulting heavy oil was determined by a BROOKFIELD DV-II + PRO Viscometer before and after the reaction with samples submitted to different milling times. The ratio of the viscosity reduction was calculated according to the following equation:

$$\Delta\eta\% = ((\eta_0 - \eta)/\eta_0) \times 100 \quad (1)$$

where, $\Delta\eta\%$ is the ratio of viscosity reduction, η_0 is the viscosity of the oil before the reaction, and η is the viscosity of the oil after the reaction.