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.

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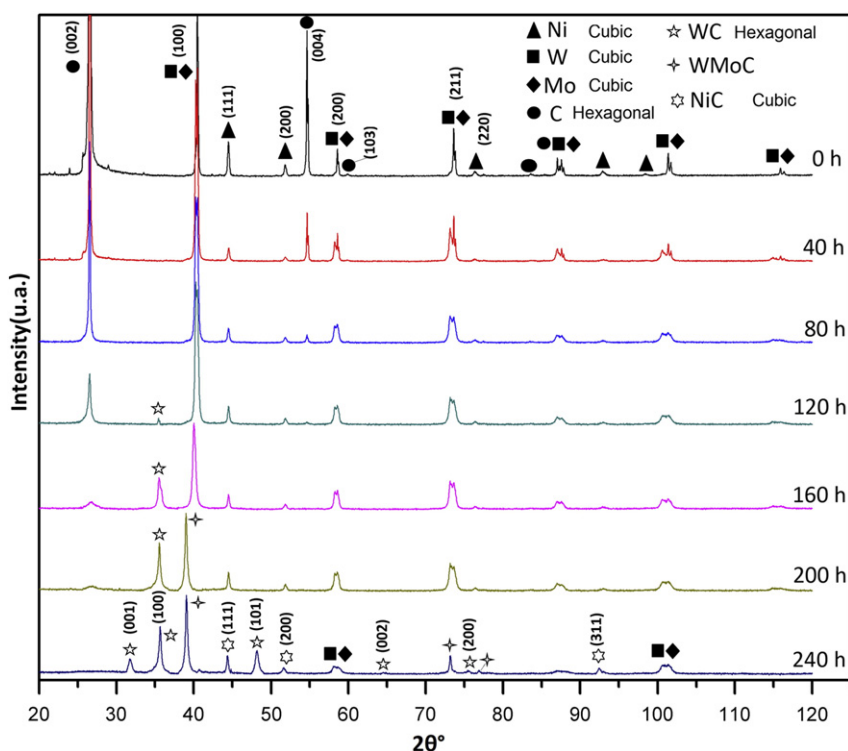
Fig. 1. XRD pattern of NiWMoC after different milling.

a particle size of $25 \pm 3 \, \mu m$. The graphite (99 + % purity) showed a mean particle size of $50 \pm 2 \, \mu m$.

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 ($1/2 \times 1/2$ in. and $3/8 \times 3/8$ in.) were used. In every stage of milling, the ball to powder weight ratio was 10:1.
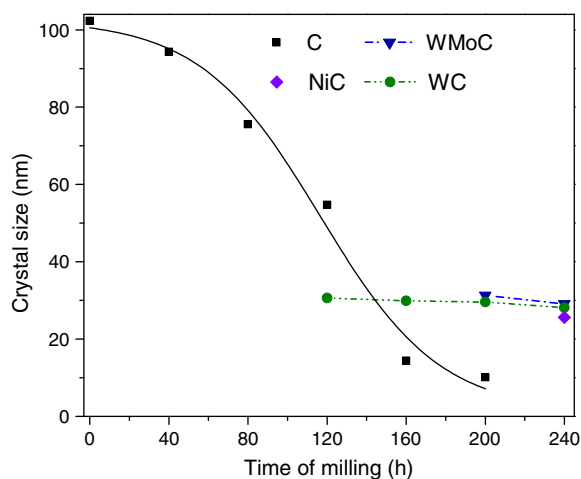

Fig. 2. Crystal size vs. milling time of nano-NiWMoC catalyst.

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 ($\lambda = 1.5406$ Å) radiation over a 2θ range from 20 to 110° at a speed of $4 \, min^{-1}$. The crystallite size (ι) 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:

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

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.
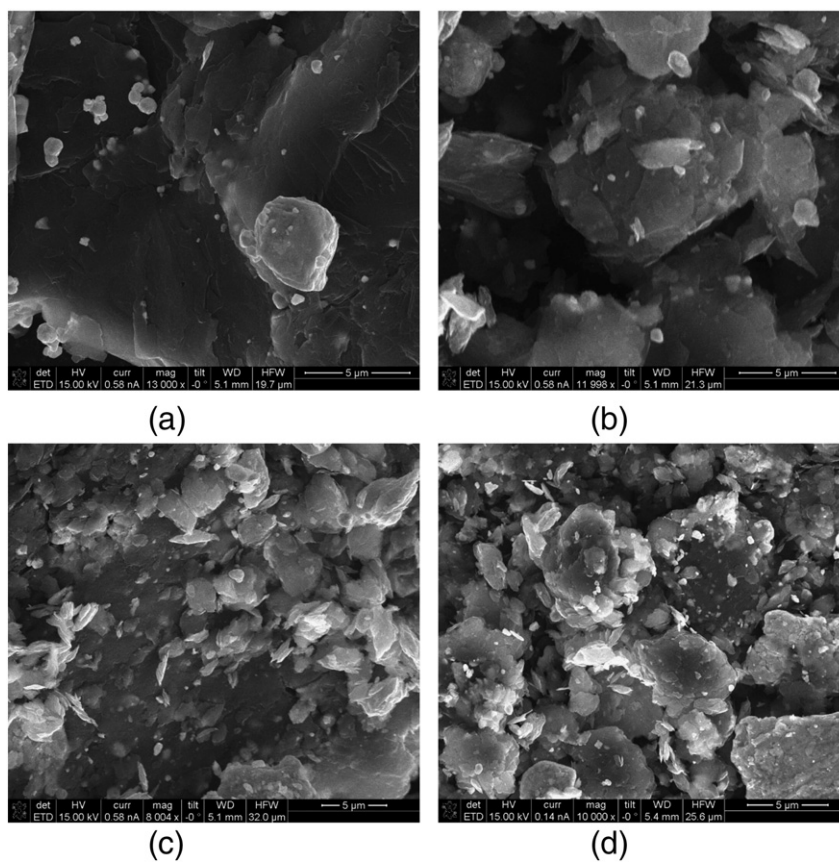
Fig. 3. SEM micrographs of nano–NiWMoC catalyst at a) 80 h, b) 160 h, c) 200 h and d) 240 h of milling.
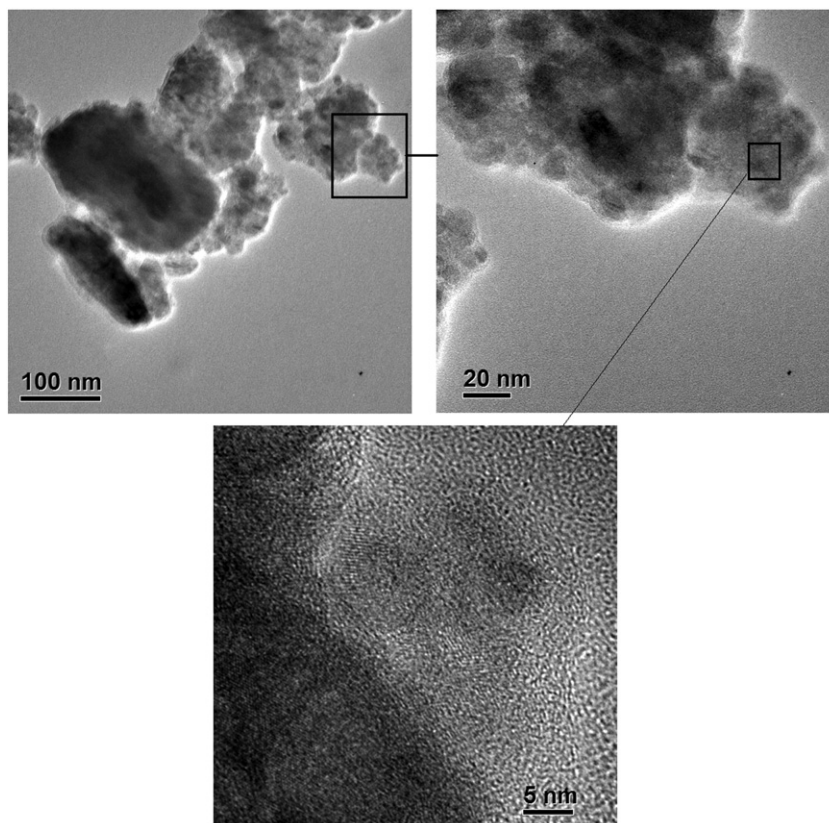

Fig. 4. TEM micrographs of nano-NiWMoC catalyst after 240 h of milling.

Table 1
AA (at.%) results of NiWMoC after different milling.

Milling time	Mo	Ni	W	C	Fe	Cr
40	25.00	9.98	14.93	49.81	0.18	0.10
80	24.81	9.94	14.93	49.73	0.37	0.22
120	24.84	9.92	14.82	49.73	0.43	0.22
160	24.78	9.91	14.56	49.82	0.68	0.25
200	24.79	9.96	14.29	49.82	0.82	0.31
240	24.81	9.98	14.22	49.81	0.85	0.32

Changes in the structures of the resins and asphalthenes in the heavy oil were analyzed before and after the reaction using a PerkinElmer 200 Spectrum Two FT-IR spectrometer.

3. Results and discussion

3.1. Structural and morphological properties of the catalysts

The X-ray results obtained at different stages of milling are shown in Fig. 1. Sharp peaks corresponding to C, Ni, W and Mo were observed before the milling of the mixed powders (0 h). With increasing milling time, the diffraction peaks of the powders decreased in their intensity and showed significant broadening as a result of the refinement of the crystal size and the increase in internal strain produced by mechanical impacts. Peaks associated with carbon disappeared completely in the sample milled for 240 h. At 120 h of milling, a very small reflection at 35.96° from the (100) plane is observed that corresponds to WC phase (PCPDWIN 65–4539). The sample milled for 240 h also showed the presence of the (001), (100), (101), (002) and (200) planes of the WC phase, which has a hexagonal Bravais lattice and is part of the P$\bar{6}$m2 space group. Peaks associated with carbon disappeared completely after 240 h of milling, whereas Ni peaks (44.50°–54.84°) were shifted at a very low angle, which may be due to the dissolution of carbon into the FCC structure of Ni [11]. The crystal size of the NiC was approximately 25.6 nm. The X-ray diffraction pattern of a (W–Mo)C intermetallic carbide phase was detected for the powder mechanically alloyed for 200 h. The formation of metallic carbide phases may be attributed to long milling time (from 160 to 240 h), which induced structural changes due to the transformation of the elemental powder mixtures and the diffusion process induced by the interaction of dislocations and grain boundaries that led to the refinement of the crystal size
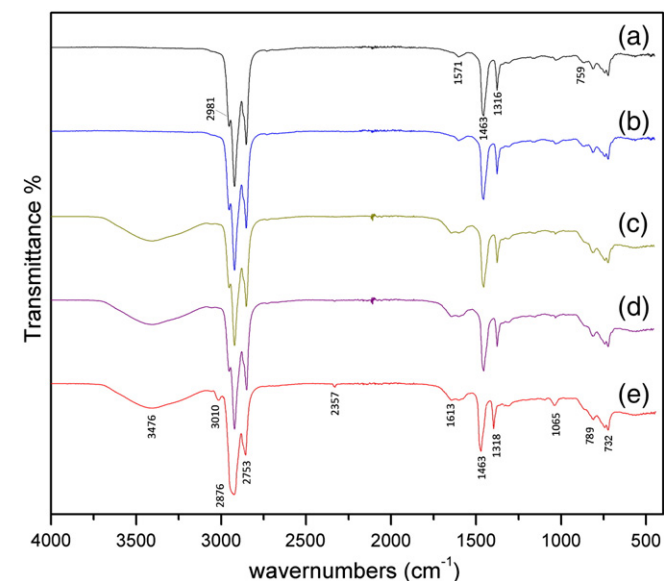

Fig. 5. IR spectra of nano–NiWMoC catalyst a) before reaction and at b) 0 h; c) 160 h; d) 200 h; e) 240 h of milling after aquathermolysis reaction.
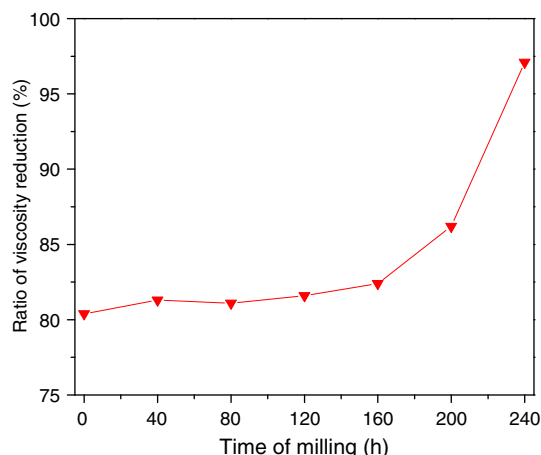

Fig. 6. Ratio of viscosity reduction of nano-NiWMoC catalyst synthesized at different milling times.

[10]. Fig. 2 shows a crystal size graph of the elemental powders (before milling) and the phases formed during the milling process. In the first stage (0 h), the crystal size was approximately 126 nm and reaches 10.1 nm after 240 h of milling. SEM micrographs of samples submitted to different milling times are shown in Fig. 3. The average particle size after 80 h of milling (Fig. 3(a)) was approximately 20 μm, which decreased to less than 5 μm after 240 h of milling; agglomerations of smaller particles were also observed (Fig. 3(d)). TEM micrographs of the nano-NiWMoC catalyst after 240 h of milling are shown in Fig. 4. The crystallite size of the nano-NiWMoC catalyst is in agreement with that calculated by the Scherrer equation and the XRD spectrum.

3.2. Elemental composition

The chemical compositions of the powders milled for 40, 80, 120, 160, 200 and 240 h are shown in Table 1. AA revealed the presence of both chromium and iron in the samples in addition to carbon, molybdenum, nickel and tungsten. The iron content increased as the milling time of MA increased due to the transformation of the elemental powders mixtures into metallic carbides, the small size of the powder particles, the large available surface area and the formation of new surfaces during milling. Iron carbide was probably formed during the process, but it was not detected by XRD, possibly because only a very small amount was formed. Nevertheless, this phase would not have affected the catalytic performance of the powders because it is known that iron is an efficient hydrotreating catalyst during aquathermolysis [3].

3.3. Catalytic performance

Fig. 5 shows the FT-IR spectrum of the heavy oil after different milling times of MA. The weak peak at 3476 cm^{-1} indicates a series of alcohol reactions which only appeared for the catalyst after 160 h of milling and can be attributed to structural changes of nano-NiWMoC catalyst during the reaction. The bands 2981 cm^{-1}, 2876 cm^{-1} and 2753 cm^{-1} peaks observed before reaction are the characteristic absorption peaks of methyl and methylene groups, and the peaks at 1463 cm^{-1} and 1318 cm^{-1} indicate that the oil samples contain a condensed aromatic ring [12]. The strong bands at 2876 cm^{-1} and 2753 cm^{-1} observed after the reaction are the absorption peaks of methylene groups indicating that the hydrogenation reaction occurred due to the breakage of C=O bonds in heavy oil molecules. The weak peak at 2357 cm^{-1} vibration gained intensity for the catalyst after 240 h of milling, which indicates an increasing of saturate content from heavy oil due to the hydrogenation reaction of unsaturated content from C–H bonds [13]. It can also be attributed to: 1) the mix of metals and nano-metallic

carbide phases synthesized during MA, mainly during the final stages; 2) the refinement of crystal size for the catalyst after 240 h of milling and during catalytic aquathermolysis. The sea water in the emulsion was heated to 200°C, so this can prevent the agglomeration of the particles improving their performance in the ratio of viscosity reduction. The absorption peaks at 1463 cm^{-1} and 1318 cm^{-1} can be attributed to the presence of condensed aromatic rings while the peak at 1613 cm^{-1} obtained after 160 h of milling suggests the reduction of the aromatic content of reacted samples, which could be attributed to the probable pyrolysis of C=O [12,14]. After the reaction, the 1065 cm^{-1} peak became appreciably strong, suggesting that decarboxylation, hydrodesulfurization and the aromatic ring of the reacted samples were reduced as the heavy oil was cracked during the aquathermolysis, promoting the transformation from a content of heavy species to one of light species, such as resins and asphaltene containing groups [12,15]. Moreover, Fig. 6 shows the dependence of the ratio of the viscosity reduction of the heavy oil on milling time. The ratios of viscosity reduction ranged from 80.4% to 97.1%. The similar activities of the materials milled from 0 to 120 h can be attributed to the mix effect of thermal cracking: as the particle size decreases, sea water acts as an ionic liquid and the formation of WC. The catalyst synthesized by 240 h of milling exhibited a high catalytic activity, which can be attributed to the formation of nanostructured WMoC, NiC and WC phases. However, nickel promotes the hydrotreating process, and the presence of NiC alloy probably prevented the catalysts from being poisoned leading to an increase in catalytic activity performance [15]. The changes in the viscosity indicate that the viscosity is strongly dependent on the MA milling time due to the increase in the number of defects in the crystalline phase, which can improve the number of active sites in the catalysts, the crystal size and the formation of metallic carbide phases, mainly over the longest milling period. MA is a low-cost technique that can produce catalysts powders with nanoscale particles in large quantities compared with other methods [2,6,8]. Further research is required to understand the exact mechanism in the catalyst heavy oil reaction; moreover, catalyst leaching and reusability for the removal of oil should be the subjects of future studies.

4. Conclusions

Nano-NiWMoC catalysts were produced by MA. Metallic carbide phases were observed after 240 h of milling. The viscosity of a heavy oil was reduced from a reduction ratio of 80.4% to 97.1%, and the best catalyst was produced after 240 h of milling. The results regarding the viscosity reduction are supported by the changes in the contents of resins and asphaltenes during the catalytic aquathermolysis reaction analyzed by FT-IR spectroscopy.

References

[1] Rohallah Hashemi, Nashaat N. Nassar, Pedro Pereira Almao, Enhanced Heavy Oil Recovery by in Situ Prepared Ultradispersed Multimetallic Nanoparticles: A Study of Hot Fluid Flooding for Athabasca Bitumen Recovery, Energy Fuel 27 (2013) 2194–2201.
[2] Yanling Chen, Yuanqing Wang, Lu. Jiangyi, Wu. Chuan, The viscosity reduction of nano-keggin-$K_3PMo_{12}O_{40}$ in catalytic aquathermolysis of heavy oil, Fuel 88 (2009) 1426–1434.
[3] Yuanqing Wang, Yanling Chen, Jing He, Pei Li, Chao Yang, Mechanism of Catalytic Aquathermolysis: Influences on Heavy Oil by Two Types of Efficient Catalytic Ions: Fe^{3+} and Mo^{6+}, Energy Fuel 24 (2010) 1502–1510.
[4] J.B. Hyne, J.W. Greidanus, Aquathermolysis of Heavy Oil, Proceedings of the 2nd International Conference on Heavy Crude and TarSands, Caracas, Venezuela, 1982, pp. 25–30.
[5] Ling Lan, Shaohui Ge, Kunhong Liu, Yuandong Hou, Xiaojun Bao, Synthesis of Ni_2P promoted trimetallic $NiWMo/\gamma-Al_2O_3$, J. Nat. Gas Chem. 20 (2011) 117–122.
[6] B.S. Zhang, Y.J. Yi, W. Zhang, C.H. Liang, D.S. Su, Electron microscopy investigation of the microstructure of unsupported Ni–Mo–W sulfide, Mater. Charact. 62 (2011) 684–690.
[7] Zhang Le, Long Xiangyun, Li Dadong, Gao Xiadong, Study on high-performance unsupported Ni–Mo–W hydrotreating catalyst, Catal. Commun. 12 (2011) 927–931.
[8] J. Bocarando, R. Huirache-Acuña, W. Bensch, Z.D. Huang, V. Petranovskii, S. Fuentes, G. Alonso-Nuñez, Unsupported Ni–Mo–W sulphide HDS catalysts with the varying nickel concentration, Appl. Catal. A Gen. 363 (2009) 45–51.
[9] C. Suryanarayana, Mechanical alloying and milling, Prog. Mater. Sci. 1 (2001) 184.
[10] L. Diaz Barriga Arceo, E. Orozco, E. Mendoza Leon, E. Palacios Gonzalez, F. Leyte Guerrero, V. Garibay Febles, Nanostructures obtained from a mechanically alloyed and heat treated molybdenum carbide, J. Alloys Compd. 434–435 (2007) 799–802.
[11] Hugh O. Pierson, Handbook of refractory carbides and nitrides, Noyes Publications, 1996. 1–2.
[12] Kun Chao, Yanling Chen, Jian Li, Xianmin Zhang, Bingyang Dong, Upgrading and visbreaking of super heavy oil by catalytic aquathermolysis with aromatic sulfonic copper, Fuel Process. Technol. 104 (2012) 174–180.
[13] W.U. Chuan, L.E.I. Guang-Lun, Y.A.O. Chuan-jin, S.U.N. Ke-ji, Gai Ping-yuan, C.A.O. Yan-bin, Mechanism for reducing the viscosity of extra-heavy oil by aquathermolysis with an amphiphilic catalyst, J. Fuel Chem. Technol. 38 (2010) 684–690.
[14] X.U. Hong-xing, P.U. Chun-sheng, Experimental study of heavy oil underground aquathermolysis using catalyst and ultrasonic, J. Fuel Chem. Technol. 39 (2011) 606–610.
[15] L.I. Wei, Z.H.U. Jian-hua, Q.I. Jian-hua, Application of nano-nickel catalyst in the viscosity reduction of Liaohe extra-heavy oil by aqua-thermolysis, J. Fuel Chem. Technol. 35 (2007) 176–180.