ORIGINAL ARTICLE

In situ preparation of well-dispersed CuO nanocatalysts in heavy oil for catalytic aquathermolysis

Ming Chen[1] · Chen Li[1] · Guo-Rui Li[1] · Yan-Ling Chen[1] · Cheng-Gang Zhou[1]

Abstract

We developed an in situ synthesis strategy for preparing well-dispersed CuO nanoparticles as aquathermolysis catalyst for viscosity reduction in Shengli heavy oil (China). A $Cu(OH)_2$-contained microemulsion was employed as a carrier to disperse the precursor $Cu(OH)_2$ to the heavy oil phase. Under aquathermolysis condition (240 °C, 2.5 MPa of N_2), the $Cu(OH)_2$ precursors would first be converted in situ to well-crystallized and size-homogeneous CuO nanoparticles naturally, catalyzed by which the viscosity of Shengli heavy oil could be reduced as much as 94.6%; simultaneously, 22.4% of asphaltenes were converted to light components. The agglomeration of the in situ prepared monoclinic CuO nanoparticles could be negligible throughout the catalytic reaction. Based on the characterization results of ^{1}H NMR, elemental analysis and GC–MS of oil samples before and after catalytic aquathermolysis, the mechanism for viscosity reduction of heavy oil in the catalytic system was investigated.

Keywords $Cu(OH)_2$-contained microemulsion · In situ preparation · CuO nanocatalyst · Catalytic viscosity reduction · Heavy oil

1 Introduction

The rapidly increasing energy demand compels the urgent development of methods for high-efficiently utilization of unconventional energy reserves such as heavy oil (Muraza and Galadima 2015). However, the high viscosity and poor liquidity of heavy oil present a very challenging hurdle. Reducing the viscosity of heavy oil to improve its liquidity for feasible exploitation of heavy oil becomes the most critical issue (Guo et al. 2016; Kapadia et al. 2015). Catalytic aquathermolysis combines the catalytic function with steam at high temperature and pressure, where steam serves as the hydrogen radical donor to promote the decomposition of S-containing compounds and macromolecules, providing an enhanced catalytic efficiency (Clark and Hyne 1984). Due to its low cost and high efficiency, catalytic recovery of heavy oil has been recognized as a promising technology for exploitation which has attracted numerous efforts (Bano et al. 2015; Hou et al. 2017; Li et al. 2016; Ren et al. 2015). Transition metal (TM) species, including Fe (Galukhin et al. 2015; Mohammad and Mamora 2008; Qin and Xiao 2013), Cu (Chao et al. 2012; Li et al. 2013), Ni (Wang et al. 2014; Yusuf et al. 2016), Mo (Chen et al. 2009) and Co (Cao et al. 2016; Wu et al. 2016a, b), are effective catalytic centers when coordinated with certain oil-soluble or water-soluble ligands which enable satisfactory viscosity reduction efficiency from 62 to 90%. Recently, nanosized metal and metal oxides based on these TMs, which possess large specific surface area and high catalytic efficiency, have become a focal interest as aquathermolysis catalysts. Several nanocatalysts, involving Fe/FeO (Yang et al. 2014), Fe_2O_3 (Ovalles et al. 2015), Fe_3O_4 (Abdullah 2014), NiO (Noorlaily et al. 2013), Cu/CuO (Shokrlu and Babadagli 2014), ZrO_2 (Wang et al. 2012) and MoO_3 (Shuwa et al. 2015), are capable of achieving acceptable viscosity reduction. It has been recognized that Cu-based oxide behaves better than other TMs in the same catalytic conditions (Shokrlu and Babadagli 2014).

✉ Yan-Ling Chen
ylchen@cug.edu.cn

✉ Cheng-Gang Zhou
cgzhou@cug.edu.cn

[1] Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, People's Republic of China

In fact, heterogeneous Cu-based oxides have already been demonstrated to be efficient catalysts for desulfurization (Nair and Tatarchuk 2010; Wu et al. 2016a, b) and photocatalysis (Jiang et al. 2017; Nezamzadeh-Ejhieh and Amiri 2013). However, when serving as catalyst of aquathermolysis of heavy oil, the catalytic efficiency of Cu/CuO nanoparticles is highly correlated with the particle size and dosage (Greff and Babadagli 2011; Shokrlu and Babadagli 2014). In fact, one can easily envision that, under the high temperature during aquathermolysis, the nanoparticles would be easily agglomerated to larger ones which will decrease the catalytic activity considerably. On the other aspect, the dispersion of nanoparticles to the high-viscous oil phase is technically difficult, which should be another governing factor that determines the final viscosity reduction efficiency. Consequently, transporting the heterogeneous nanocatalysts to the heavy oil phase and preventing them from being aggregated emerge as crucial issues. Hashemi et al. (2013, 2014) suggested that the excellent lipophilicity of a microemulsion makes it a suitable carrier to transfer catalyst to the oil phase. Ni-metal nanocatalysts were in situ prepared for heavy oil hydrocracking, which converts 70% of resins and 50% of asphaltenes to aromatics and saturates at 370 °C under 11 MPa of H_2. Furthermore, the preparation of microemulsion catalyst is easy to implement under moderate conditions. Inspired by these results, we prepared a $Cu(OH)_2$-contained microemulsion as a carrier to disperse the $Cu(OH)_2$ precursors to the heavy oil phase. Under our catalytic aquathermolysis conditions (240 °C, 2.5 MPa of N_2), the precursors would be in situ naturally transformed to CuO nanoparticles. Catalyzed by the monoclinic CuO nanocatalysts, the viscosity of Shengli heavy oil could be reduced as much as 94.6%, during which 22.4% of asphaltenes were converted to light components. Our results expand application of microemulsions in aquathermolysis and propose a highly efficient and deployable approach to develop Cu or other TM oxide-based nanocatalysts for reducing the viscosity of heavy oil via catalytic aquathermolysis. This strategy may provide an alternative for steam injection stimulation of heavy oil.

2 Experimental section

2.1 Hydroxide microemulsion precursor preparation

All analytic grade chemicals purchased from Sinopharm Chemical Reagent were used without further purification. $Cu(OH)_2$-contained microemulsion was prepared by a reverse microemulsion method. Firstly, 2.00 g SP-80, 2.00 g TW-60, 2.00 mL isoamylol and 10.00 mL diesel were mixed and thoroughly dispersed ultrasonically for 20 min to obtain an oil phase. Secondly, 2.00 mL of NaOH (1.50 mol/L aq)

and 2.00 mL of $Cu(NO_3)_2$ (0.75 mol/L aq) were added into two equivalent oil phases under vigorous stirring, to form an alkali microemulsion and metal salt microemulsion, respectively. Subsequently, the NaOH microemulsion was mixed with the $Cu(NO_3)_2$ microemulsion in a water bath at 40 °C for 2 h to form $Cu(OH)_2$. The $Cu(OH)_2$-contained microemulsion precursor (labeled as CuME) was prepared for catalytic aquathermolysis. Upon mixing the two microemulsions, the droplets collide and coalesce, allowing the mixing of the precursor to produce nanoparticles (Santra et al. 2001). The Formation of $Cu(OH)_2$ nanoparticles was visually realized by the appearance of a blue color of the microemulsion mixture, which could be directly applied in aquathermolysis of heavy oil. For comparison, we also conduct a blank experiment to prepare the CuO nanoparticles under the same conditions (240 °C, 2.5 MPa N_2, 24 h) without the presence of heavy oil.

2.2 Catalytic aquathermolysis

The laboratory catalytic aquathermolysis experiments were carried out for 100 g oil samples with an oil:water ratio of 8:2 and 3 mL CuME in a 500 mL FYX-0.5 high-pressure reactor for 24 h at 180–260 °C under an atmosphere of 2.5 MPa N_2. After reaction, the mixture was dumped into a 150-mL beaker. The viscosity of the oil samples before and after reaction was measured with a BROOKFIELD DV-II+ programmable viscometer at 50 °C. The dehydration of the oil samples was conducted on an ultrasonic crude rapid dehydration instrument (BT-350, Hubei Broad Electronics Co. Ltd., China). The water contents of the dehydrated samples were determined with a Karl Fischer (Coulomb) SF101 tester (Precision Instrument Co. Ltd., Taizhou, Jiangsu, China) following the GB/T1146-2009 standard of People's Republic of China. The measured water contents of the samples, either before or after the catalytic aquathermolysis, are all below 0.002 wt% (Ren et al. 2015). The viscosity reduction efficiency was calculated by the formula $(\eta^0 - \eta)/\eta^0 \times 100\%$, where η^0 and η represented the viscosity of extra-heavy oil before and after aquathermolysis, respectively. As displayed in Table 1, an optimal viscosity reduction rate as well as acceptable energy consumption could be achieved at 240 °C. For comparison, aquathermolysis of heavy oil only with $NaNO_3$ or CuO was implemented under the same conditions. Similarly, all oil samples were dehydrated prior to measurement. The four components (saturated hydrocarbons (SH), aromatic hydrocarbons (AH), resins and asphaltenes) before and after reaction were separated from the oil samples by an Al_2O_3 chromatography column according to the industrial standard of China Petroleum SY/T 5119-1995. The catalyst was recovered from the heavy oil by dilution with toluene for further characterization.

Table 1 The viscosity reduction efficiency of CuME at different temperatures (180–260 °C)

Temperature, °C	Viscosity, mPa s	Viscosity reduction efficiency, %
–	24,150 ± 100	–
180	7088 ± 140	71.08 ± 0.02
200	5090 ± 100	79.20 ± 0.02
220	3020 ± 80	87.67 ± 0.01
240	1300 ± 40	94.70 ± 0.01
260	1076 ± 30	95.61 ± 0.01

2.3 Characterization

The hydrodynamic diameter of the microemulsion was investigated using dynamic light scattering (DLS, Nano ZS90, Malvern, UK). The solids isolated from CuME and recovered catalyst were characterized with an X-ray diffractometer (XRD, D8-FOCUS, Bruker, Germany). The collected catalyst after aquathermolysis and the comparative CuO nanoparticles were characterized by transmission electron microscopy (TEM, Philips CM12, Holland). The C, H, N and S contents and structural information of resins and asphaltenes were measured with an elemental analysis instrument (EA, VARIO EL-2, Germany) and proton nuclear magnetic resonance spectroscopy (using tetramethylsilane (TMS) as internal reference and CDCl$_3$ as solvent, ^{1}H NMR, BRUKER Ascend400, Germany), respectively. Light components and gas were analyzed on a gas chromatograph–mass spectrometry (GC–MS, Agilent GC7890A-MSD5975C, USA, Column: Agilent 122-5562HP-5MS 5% Phenyl Methyl Silox 30 m × 250 μm × 0.25 μm).

3 Results and discussion

Based on DLS results displayed in Fig. 1, the size of the microemulsion droplets was uniform and mainly concentrated in the range 105–122 nm. The morphological features of the separated catalysts after aquathermolysis were next examined with TEM. Figure 2b shows that the particles were mostly round shaped with the diameters ranging from 5 to 10 nm. No particle agglomeration was observed, suggesting that the microemulsion could achieve a good dispersion of the particles in the catalytic reaction system. XRD profiles of the particles separated from CuME and the aquathermolysis reaction indicated well-crystallized Cu(OH)$_2$ and monoclinic CuO without impurity, respectively, as displayed in Fig. 3. According to this evidence, we can rationally conclude that the Cu(OH)$_2$ precursors, dispersed by the microemulsion, have been converted in situ to CuO during aquathermolysis. In fact, since the conversion from Cu(OH)$_2$ to CuO could
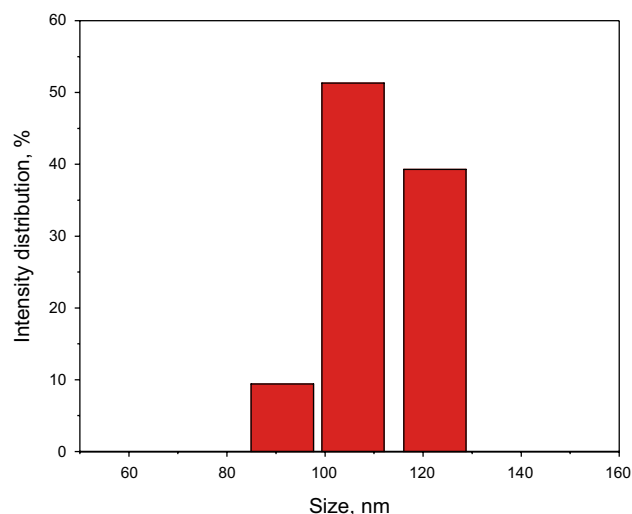
Fig. 1 DLS result of the Cu(OH)$_2$-containing microemulsion droplets

occur at very low temperature (60–120 °C) (Lu et al. 2004), while the microemulsion is unstable, the catalytic aquathermolysis performance should mainly originate from the CuO nanoparticles, which are the dominative driving force to hydrocrack the asphaltenes.

Table 2 shows the viscosity and content of the four components (saturated hydrocarbon (SH), aromatic hydrocarbon (AH), resins and asphaltenes, SARA) of oil samples before and after aquathermolysis. Without catalyst or with only NaNO$_3$, the viscosity of oil sample was only reduced by 23.6%, where the variations of the four components were very slight, which suggested that there was no visible catalytic stimulation. Consequently, the cracking extent of heavy oil in the three reactions (without catalyst, with NaNO$_3$, and with only microemulsion) is at a parallel level, leading to almost identical SARA distribution. The viscosity reduction should mainly result from pyrolysis, which suggests that the existence of NaNO$_3$ has no promotive influence on aquathermolysis of heavy oil. When adding the pure microemulsion (organic solvent and emulsifier) to the reactor, the viscosity could be decreased by 65.7%; however, the components almost remain intact, suggesting the viscosity reduction should be mainly ascribed to the emulsification effect. As the CuO nanoparticles, formed in situ from the CuME microemulsion, involve in the aquathermolysis, the viscosity of heavy oil was reduced by 79.5%; simultaneously, the asphaltenes were reduced, while the SH contents were increased, which demonstrated that CuO could bring about irreversible transformation of heavy components into light ones. When Cu(OH)$_2$-contained microemulsion participated in the catalytic aquathermolysis reaction, a viscosity reduction efficiency as high as 94.6% could be obtained. The viscosity reduction should be ascribed to the considerable decrease in asphaltenes which were reduced by 22.4%

Fig. 2 TEM result of CuME after reaction (**a** without heavy oil and **b** with heavy oil)
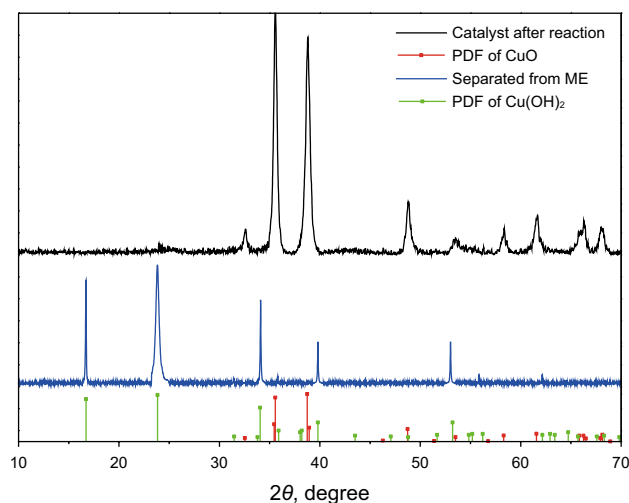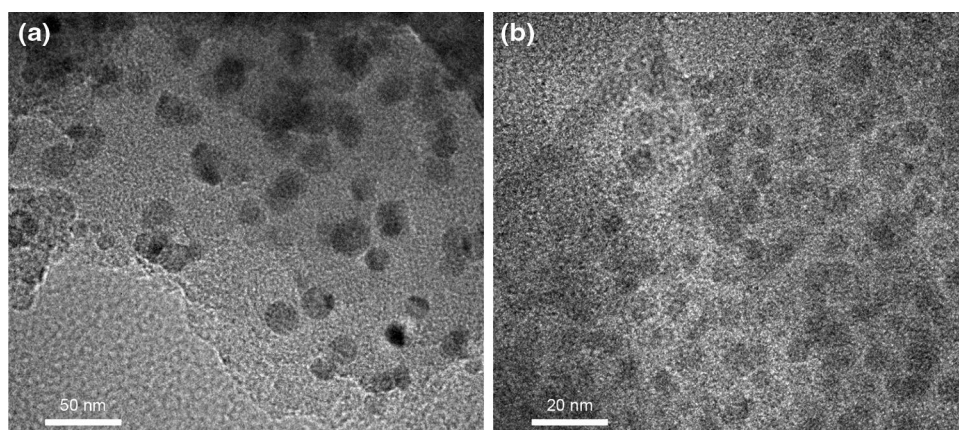

Fig. 3 XRD spectrum for catalyst after reaction and particles separated from CuME

through the aquathermolysis reaction, leading to a corresponding increment of saturates by 23.2% as well as a slight increase in aromatics.

The two heavy components, from the original heavy oil and the post-reacted sample catalyzed by the $Cu(OH)_2$ microemulsion, were next measured by ^1H NMR spectra to reveal the physicochemical variation information of resins and asphaltenes (Table 3). In addition, the elemental analysis of the two heavy components (Table 4) showed that the S and N heteroatoms in resins and asphaltenes were also reduced by a certain extent after aquathermolysis. For asphaltenes, the content of H_A (6.0–9.0) increased significantly upon catalytic aquathermolysis, indicating that the amount of un-substituted aromatics has been increased; such an increment was also observed for resins. This may originate from the partial elimination of heteroatoms (S, N) in the aromatic rings, which would lead to a ring-opening process. Simultaneously, the content of H_β (1.0–2.0) and H_γ (0.5–1.0) in resins and asphaltenes decreased, suggesting the

Table 2 Four components and viscosity of oil samples before and after reaction

	Viscosity, mPa s	SH, %	AH, %	Resins, %	Asphaltenes, %
Before reaction	$24,150 \pm 100$	16.45 ± 0.03	42.78 ± 0.04	21.01 ± 0.05	19.76 ± 0.05
After reaction without catalyst	$18,450 \pm 100$	16.81 ± 0.04	42.85 ± 0.03	21.04 ± 0.05	19.30 ± 0.03
After reaction with $NaNO_3$(aq)	$18,437 \pm 100$	16.84 ± 0.03	42.82 ± 0.02	21.02 ± 0.03	19.32 ± 0.04
After reaction with microemulsion	8283 ± 70	16.80 ± 0.05	42.79 ± 0.05	21.07 ± 0.04	19.14 ± 0.04
After reaction with CuO	4950 ± 70	18.86 ± 0.04	42.96 ± 0.03	21.15 ± 0.02	17.03 ± 0.03
After reaction with CuME	1300 ± 40	20.27 ± 0.05	43.14 ± 0.03	21.25 ± 0.05	15.34 ± 0.04

Table 3 ^1H NMR of resins and asphaltenes: (a) before reaction and (b) after reaction with CuME

Group composition, %	H_A (6.0–9.0)	H_α (2.0–4.0)	H_β (1.0–2.0)	H_γ (0.5–1.0)
Resins (a)	4.34	18.23	62.88	14.55
Resins (b)	11.61	19.08	55.17	14.14
Asphaltenes (a)	6.98	23.76	55.14	14.12
Asphaltenes (b)	13.93	22.62	49.79	13.66

Table 4 Element analysis of resins and asphaltenes: (a) before reaction and (b) after reaction with CuME

Group composition, wt%	C	H	S	N	Average N_H/N_C
Resins (a)	81.92 ± 0.02	10.07 ± 0.03	4.86 ± 0.01	1.17 ± 0.02	1.48 ± 0.01
Resins (b)	81.82 ± 0.03	9.98 ± 0.01	4.19 ± 0.03	1.04 ± 0.02	1.46 ± 0.01
Asphaltenes (a)	83.64 ± 0.02	8.25 ± 0.02	5.23 ± 0.03	1.11 ± 0.04	1.18 ± 0.01
Asphaltenes (b)	83.13 ± 0.01	8.33 ± 0.02	4.72 ± 0.02	1.02 ± 0.03	1.20 ± 0.01

Table 5 f_A (aromaticity), H_{AU}/C_A (aromaticity condensation) and BI (branching index) of resins and asphaltenes: (a) before reaction and (b) after reaction with CuME

	f_A	H_{AU}/C_A	BI
Resins (a)	0.29	0.67	0.12
Resins (b)	0.35	0.88	0.13
Asphaltenes (a)	0.45	0.50	0.12
Asphaltenes (b)	0.48	0.63	0.13

decomposition of long side-chains. However, we mentioned that H_α (2.0–4.0) in asphaltenes decreases upon aquathermolysis, while the value in resins behaves inversely. This phenomenon indicates that some of the fragmented aromatics from asphaltenes might be transferred to resins, which could also be reflected by the slightly decreased N_H/N_C of resins, and the slightly increased content of resins (Table 2). In contrast, after aquathermolysis, the N_H/N_C of asphaltenes increases, which indicates that hydrogenation might take place in the catalytic reaction system.

Based on the improved Brown–Ladner methods (Suzuki et al. 1982), the structural parameters (the aromaticity (f_A,
$$f_A = \frac{\frac{N_C}{N_H} - \frac{1}{2H_t}(H_\alpha + H_\beta + H_\gamma)}{\frac{N_C}{N_H}}, H_t = H_A + H_\alpha + H_\beta + H_\gamma),$$
the aromaticity condensation (H_{AU}/C_A, $\frac{H_{AU}}{C_A} = \frac{\frac{H_A}{H_t} + \frac{H_\alpha}{2H_t}}{\frac{N_C}{N_H} - \frac{1}{2H_t}(H_\alpha + H_\beta + H_\gamma)}$) and branching index (BI, $BI = \frac{2 \times H_\gamma}{3 \times (H_\alpha + H_\beta)}$)) were calculated and are shown in Table 5. Under the aquathermolysis of CuO nanocatalyst, the f_A and BI of the two heavy components increased due to the cleavage of side-chains and opening rings, leading to increments of saturates and aromatics (Table 2). Meanwhile, the enhanced H_{AU}/C_A of both asphaltenes and resins points to a lower degree of aromatic condensation, indicating that both the fragmentation of large aromatic pieces as well as hydrogenation has occurred.

To detect the structural variation in light components, GC–MS measurement of SH, AH and gas was also taken. The content of n-alkanes (Fig. 4a) and monoaromatic steranes (Fig. 4b) are enhanced sharply after catalytic aquathermolysis with the Cu(OH)$_2$ microemulsion. The retention time of the increased SH after aquathermolysis lies mainly in the range 30–70 min, C$_{16}$–C$_{23}$ linear alkanes increased
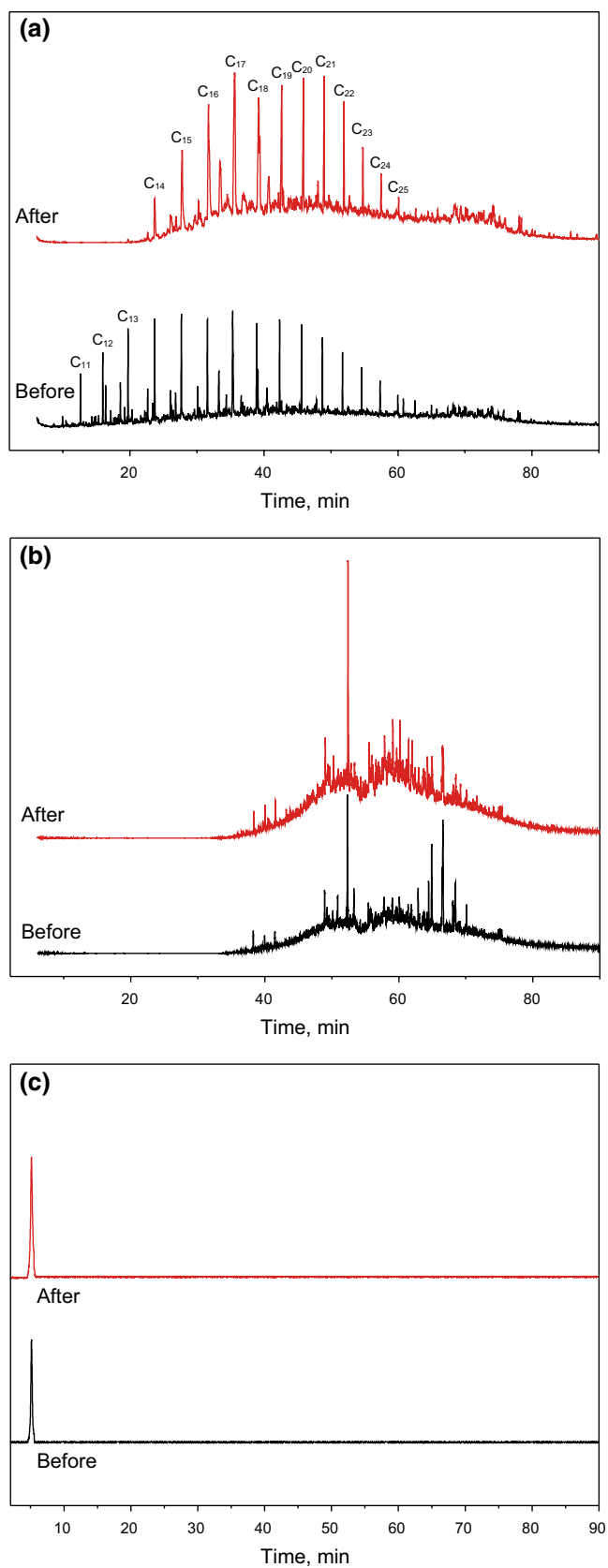
after catalytic aquathermolysis reaction, consistent with our speculation in the ^{1}H NMR and EA analysis. Meanwhile, monoaromatic steranes in AH increase, as shown in Fig. 4b, which could be ascribed to the aromatic debris split from the heavy components (resins and asphaltenes). The content of small molecules in the gas collected after reaction with CuME is more than that of without any catalyst, while the increment of small molecules resulted from the cleavage of heavy components and the breaking of long side-chain structures.

It is understandable that the microemulsion is composed of surfactants (SP-80 and TW-60) and solvents (isoamylol, diesel and a little water), which have rather excellent compatibility with heavy components. As a consequence, the CuO catalyst, transported by the microemulsion, can be homogeneously distributed in the heavy component. Catalyzed by the in situ synthesized CuO nanoparticles, long side-chains of the heavy components should be dissociated accompanied with aromatic ring opening and fragmentation, leading to considerably increased viscosity reduction.

4 Conclusion

In this work, we prepared Cu(OH)$_2$ microemulsion for reducing the viscosity of Shengli heavy oil. The microemulsion can transfer and disperse the Cu(OH)$_2$ precursors into the heavy oil phase; simultaneously, the Cu(OH)$_2$ can be converted in situ into size-homogeneous CuO nanoparticles without agglomeration under the catalytic aquathermolysis conditions, which achieved a satisfactory viscosity reduction efficiency of 94.6%. Under the aquathermolysis with CuO nanocatalyst, the heavy components (resins and asphaltenes) could be converted to light components (SH and AH) through the cleaving of C–S bonds, breaking of long side-chain structures, opening rings as well as hydrogenation of unsaturated aromatics in heavy components. The results suggest that the in situ prepared ultra-dispersed nano-CuO catalyst provides a highly efficient and deployable choice for developing Cu or other TM oxide-based nanocatalysts for reducing the viscosity of heavy oil via catalytic aquathermolysis.

Fig. 4 GC-MS spectra of M/Z
57 in SH (**a**), spectra of M/Z
253 in AH (**b**) and gas (**c**)
before and after reaction

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