

# 1 Response to Comment on Oil-Dispersed $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Nanoparticles as a 2 Catalyst for Improving Heavy Oil Oxidation

3 Seyedsaeed Mehrabi-Kalajahi, Mikhail A. Varfolomeev,\* Chengdong Yuan,\* Nikolay O. Rodionov,  
4 Almaz L. Zinnatullin, Farit G. Vagizov, and Yuri N. Osin



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5 **ABSTRACT:** The main goal of our previous work was to study the effect of coating the hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) particles with oleic acid  
6 on their catalytic properties for improving heavy oil oxidation (<https://doi.org/10.1021/acs.energyfuels.1c00657>). We concluded  
7 that “Compared with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA more efficiently catalyzed the combustion of heavy oil due to its good dispersion in  
8 heavy oil.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was found to be transformed into smaller size magnetite (Fe<sub>3</sub>O<sub>4</sub>), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> during  
9 heavy oil combustion process. These enhanced performances in the heavy oil combustion by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA could be favorable for  
10 improving the efficiency of the in situ combustion (ISC) technique in oilfields”. This conclusion was obtained on the basis of a joint  
11 analysis of the data of several experimental methods and techniques, such as porous medium thermo-effect cell (PMTEC) and  
12 thermogravimetry–infrared spectroscopy (TG–FTIR) experiments, scanning electron microscopy (SEM), energy-dispersive X-ray  
13 spectroscopy (EDX), X-ray diffraction (XRD), and Mössbauer spectroscopy. Recently, Pranaba K. Nayak claimed that the choice of  
14 Mössbauer spectroscopy was excellent but the inability to extract a great deal of information from the carefully obtained Mössbauer  
15 spectra makes the study and its subsequent discussion of not much use. In this response, we reiterate that the phase identification in  
16 our previous paper by Mössbauer spectroscopy was carried out correctly and the phase components were determined with good  
17 statistical accuracy.

## 18 ■ INTRODUCTION

19 In the comment,<sup>1</sup> Pranaba K. Nayak claim that “While the  
20 reported work was carried out certainly with meticulous  
21 planning, the analysis and presentation of the <sup>57</sup>Fe Mössbauer  
22 spectroscopic data... Unfortunately, they have not provided  
23 relative abundance of individual iron-bearing phases... They  
24 have not clearly mentioned the fitting scheme for spectra... and  
25 not provided the obtained hyperfine parameters (preferably in  
26 a tabular form)... It should also include additional mandatory  
27 information, such as line width... In summary, it can be  
28 understood that, although the choice of techniques was  
29 excellent... but the inability to extract a great deal of  
30 information from the carefully obtained Mössbauer spectra  
31 makes the study and its subsequent discussion of not much  
32 use”.

33 We disagree with the last comment because it is based on a  
34 subjective assessment of the presentation of the Mössbauer  
35 results and their reliability and significance for the conclusions  
36 of this study. The Mössbauer measurements were carried out  
37 carefully, with the interpretation of the spectra carried out on  
38 the basis of a least squares fit; the details of the experiment and  
39 mathematical processing are given in refs 43 and 44 of the  
40 original article.<sup>2</sup> Excessive filling of the article with additional  
41 Mössbauer parameters (for example, the width of the lines) for  
42 relatively well-resolved sextets would complicate the percep-  
43 tion of the article and lead to a departure from the usual  
44 practice inherent for many articles published in the journal  
45 *Energy & Fuels*, where the results of Mössbauer measurements

are used (see, e.g., refs 3–8). Therefore, in the original article,<sup>2</sup>  
46 the fitting results were given only for the main Mössbauer 47  
48 parameters, namely, isomer shift (IS), quadrupole splitting  
49 (QS), hyperfine field (HF), (see page 94 in ref 9), which are  
50 recognized indicators for the fingerprint technique to identify a  
51 specific phase.

52 However, we agree that it would be useful to provide more  
53 information in graphical and tabular form about the results of  
54 our Mössbauer measurements, as claimed by the author of this  
55 comment, at least in this response. In our response, we focused  
56 on addressing these comments.

## 57 ■ RESULTS AND DISCUSSION

58 We greatly appreciate the opportunity to respond to the  
59 comments concerning our article.<sup>1,2</sup> However, let us first clarify  
60 some inaccurate claims that were listed in the comment.

61 **Claim.** “They have fitted a sextet to the obtained spectrum  
62 (in Figure 3) and provided the hyperfine parameters  
63 concluding that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is the only constituent, which cannot  
64 be assured without information on the line width value.”  
65 “Similarly, a line width value needs to be reported for the

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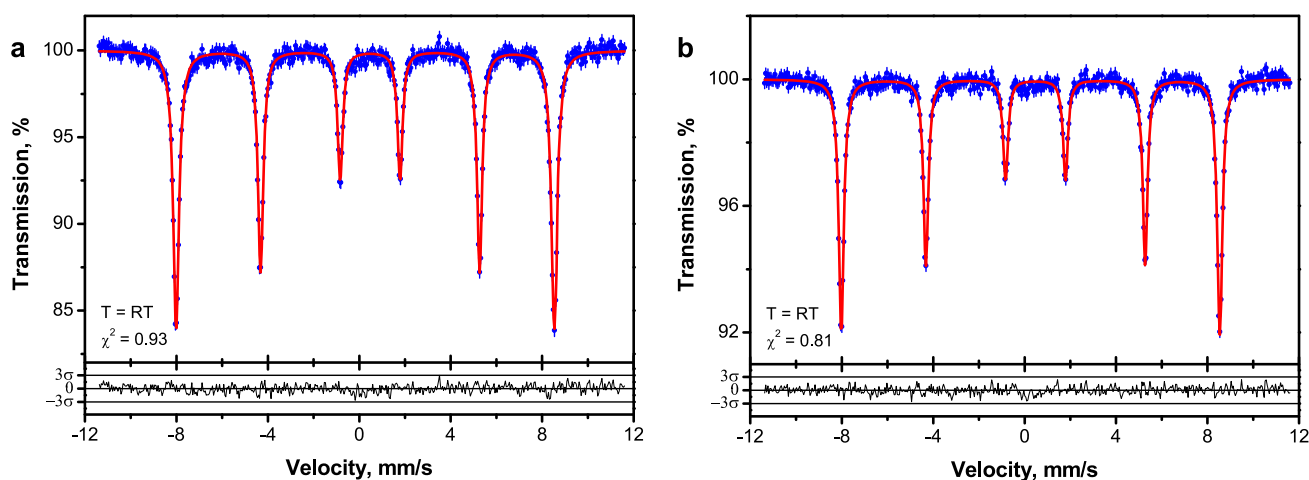


Figure 1. Mössbauer spectra of (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sample and (b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA sample.

Table 1. Hyperfine Parameters and Phase Identification of Mössbauer Spectra Components for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA Samples

	isomer shift (mm/s)	quadrupole splitting (mm/s)	hyperfine field (kOe)	line width (mm/s)	spectral area (%)	phase identification and reference
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> sample	0.37(1)	-0.21(1)	512(1)	0.30(1)	100	hematite <sup>10</sup>
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> @OA sample	0.37(1)	-0.22(1)	513(1)	0.27(1)	100	hematite <sup>10</sup>

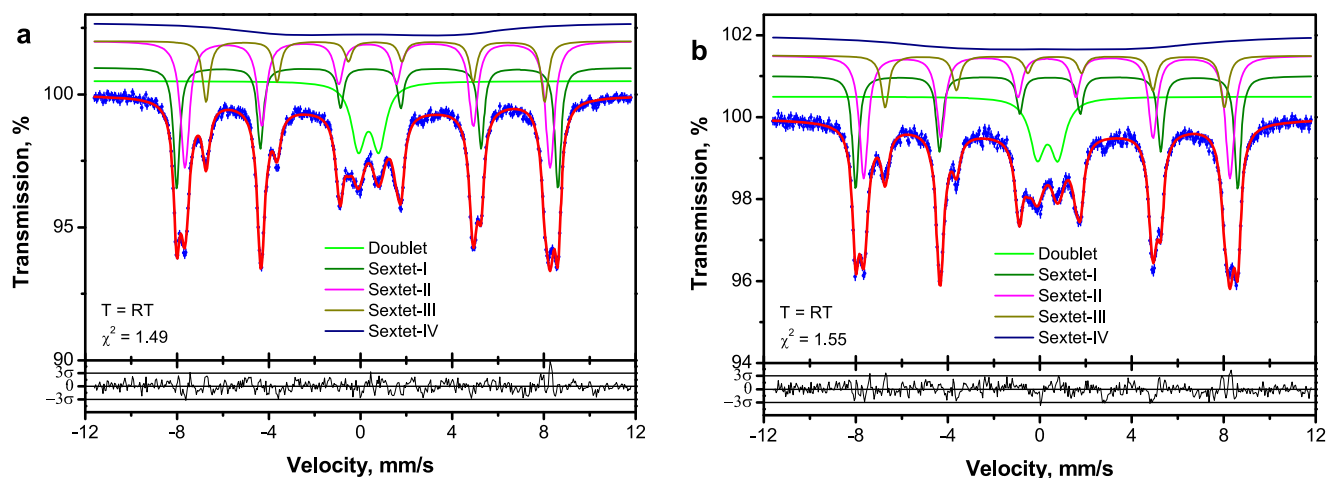


Figure 2. Mössbauer spectra of (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + oil sample and (b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA + oil sample treated at 400 °C.

66 spectrum shown in Figure 6, to authenticate the absence of any  
67 other iron-bearing phases in the sample.”

68 **Response.** The Mössbauer spectra referred to in this  
69 comment are shown in Figure 1. For the studied samples ( $\alpha$ -  
70 Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA samples), the best fit was obtained by  
71 fitting one sextet to the experimental data. The solid red line  
72 shows the result of the best fit. The lower part of the figure  
73 shows the residuals between the experimental data and the  
74 model curve in units of statistical error. The  $\chi^2$  values are  
75 displayed in the lower left corner of the figure. The hyperfine  
76 parameters obtained are presented in Table 1. As seen from  
77 Figure 1 and Table 1, the Mössbauer spectra are a well-  
78 resolved sextet with relatively narrow lines, and the hyperfine  
79 parameters of the sextet are in good agreement with the  
80 parameters of hematite published in the literature.<sup>10</sup> Using the  
81 spectrum given in the original article,<sup>2</sup> even without fitting, it is  
82 easy to estimate that the line widths are small in comparison to

the splitting between hyperfine lines, and these values are on 83  
the order of one-third of the velocity scale of 1 mm/s and even 84  
less but no more. As a result of the fitting, we found that the 85  
widths of the outer lines for samples 1 ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and 2 ( $\alpha$ - 86  
Fe<sub>2</sub>O<sub>3</sub>@OA) are 0.30 and 0.27 mm/s, respectively. The line 87  
width of sample 1 is slightly wider as a result of the thickness 88  
effect. Considering the acceptable values of  $\chi^2$  (0.93 and 0.81 < 89  
1) and stochastic distribution of residuals within  $\pm 3\sigma$  (Figure 90  
1), the obtained hyperfine parameters have good agreement 91  
with the literature as well as the results of X-ray diffraction 92  
analysis.<sup>2</sup> The doubts expressed by the author of this comment 93  
seem very strange to us on our conclusion that the observed 94  
sextet corresponds to hematite. 95

It is generally accepted that IS, QS, and HF are the main 96  
parameters for phase analysis in Mössbauer spectroscopy. The 97  
line width cannot be such a good fingerprint indicator, because 98  
the line width for the same phase depends upon many factors,<sup>9</sup> 99

**Table 2. Hyperfine Parameters and Phase Identification of Mössbauer Spectra Components for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + Oil and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA + Oil Samples Treated at 400 °C**

	component	isomer shift (mm/s)	quadrupole splitting (mm/s)	hyperfine field (kOe)	line width (mm/s)	spectral area (%)	phase identification and reference
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> + oil sample treated at 400 °C	doublet	0.35(1)	0.93(1)		0.73(1)	13(1)	$\gamma$ -FeOOH <sup>10</sup>
	sextet I	0.37(1)	-0.15(1)	515(1)	0.32(1)	22(1)	hematite <sup>10</sup>
	sextet II	0.31(1)	0.00(1)	493(1)	0.47(1)	33(1)	magnetite (A) <sup>10</sup>
	sextet III	0.64(1)	0.01(1)	457(1)	0.38(1)	13(1)	magnetite (B) <sup>10</sup>
	sextet IV	0.43(1)	-0.2(1)	257(20) <sup>a</sup>	1.00 <sup>b</sup>	18(1)	c
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> @OA + oil sample treated at 400 °C	doublet	0.34(1)	0.93(1)		0.77(1)	12(1)	$\gamma$ -FeOOH <sup>10</sup>
	sextet I	0.37(1)	-0.15(1)	515(1)	0.33(1)	21(1)	hematite <sup>10</sup>
	sextet II	0.31(1)	0.00(1)	493(1)	0.46(1)	31(1)	magnetite (A) <sup>10</sup>
	sextet III	0.65(1)	0.00(1)	457(1)	0.40(1)	12(1)	magnetite (B) <sup>10</sup>
	sextet IV	0.43(1)	-0.1(1)	271(20) <sup>a</sup>	1.00 <sup>b</sup>	24(1)	c

<sup>a</sup>Average value of the parameter over distribution. <sup>b</sup>The parameter was fixed during the fitting. <sup>c</sup>Small magnetic particles (presumably a magnetite-like and/or maybe a small pieces of various iron carbides) with a very inhomogeneous local environment of Fe ions in them or on their surface.

such as instrumental broadening,<sup>11</sup> the effect of the sample thickness,<sup>12</sup> diffuse broadening,<sup>13</sup> the effect of the particle size,<sup>14</sup> the uniformity of the local environment of the Mössbauer atom (defects, impurities, crystallinity, and others),<sup>15</sup> various relaxation effects associated with fluctuations of electric and magnetic fields on the nucleus,<sup>16</sup> etc. This is probably why the *Mössbauer Mineral Handbook*,<sup>17</sup> published by the Mössbauer Effect Data Center, contains only data on the temperature, isomer shift, quadrupole splitting, and hyperfine magnetic field. In most of the articles published in the journal *Energy & Fuels* (for example, in refs 3–8), the analysis of Mössbauer data is carried out only on the basis of these main parameters, without using information on the line widths for well-resolved doublets or sextets. In our case, we followed this common practice, which is inherent for *Energy & Fuels*.

For the reasons listed above, we disagree with these claims of this comment. The spectra of samples 1 and 2 correspond specifically to hematite, and the  $\chi^2$  fitting shows the absence of other iron-containing phases with a very good statistical accuracy.

**Claim.** Commenting on the results of the room-temperature (RT) Mössbauer measurements of the residues yielded from the isothermal (400 °C) oxidation experiments of heavy oil +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and heavy oil +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA, the author of this comment asserts that “While the information that they have obtained by XRD (Figure 20) and SEM–field emission scanning electron microscopy (FESEM) (Figure 22) are very straightforward and indicate the simultaneous presence of well-crystallized iron-bearing phases, the analysis and interpretation of Mössbauer spectroscopic data are incorrect, inadequate, and wanting. They have mentioned that “The chi-square fitting in Mössbauer spectra (Figure 21) reveals four components...””.

**Response.** The RT Mössbauer spectra of these samples obtained after the isothermal (400 °C) oxidation process are shown in Figure 2. In Figure 21 in the original article, the red solid line shows the resulting curve obtained from the  $\chi^2$  fitting. In Figure 2, the solid lines with different colors with offsets show the model sextets and the doublet, which compose the fitting curve. The residuals between the experimental data and the model curve are depicted in the bottom of the spectra. The  $\chi^2$  values of fit are shown on the bottom left corner of the panels. The best fit hyperfine parameters are presented in Table 2. In addition to the hyperfine parameters, Table 2 also presents the values of the line widths, relative areas of the

spectral components, and information about the supposed phase identification.

Analysis of these Mössbauer data allows us to conclude that the isothermal oxidation of heavy oil +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and heavy oil +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA samples at 400 °C leads to the appearance of four components in the spectra. The relative areas of these components are shown in Table 2.

Most of the spectral area is composed by the contribution from the Fe sites of magnetite (A and B sites). The contributions from hematite and a broadened sextet (sextet IV), which is probably from small particles with a very inhomogeneous local environment and noticeable defectiveness, are somewhat less. The broadened sextet was processed assuming the distribution of hyperfine parameters using the SpectRelax software.<sup>18</sup> The reconstruction of the distribution function for hyperfine magnetic fields revealed the broad Gaussian-like distribution with an average value of hyperfine fields close to 260 kOe. In addition to these components, a relatively wide paramagnetic doublet with the following hyperfine parameters is also observed: IS = ~0.34 mm/s and QS = 0.90 mm/s. Here, we have described the fitting scheme used to process the spectra of the heavy oil +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and heavy oil +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA samples after isothermal oxidation at 400 °C.

In our original article,<sup>2</sup> we stated that “The chi-square fitting in Mössbauer spectra (Figure 21) reveals four components... Besides  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, one paramagnetic phase with IS = 0.43 mm/s and QS = 0.93 mm/s was also observed, and these hyperfine parameters are the characteristics of ferric ions. Furthermore, there is a broadened sextet with the following parameters of averaged hyperfine: IS = 0.48 mm/s, QS = -0.1 mm/s, and H ~ 260 kOe. This component can be attributed to small magnetic particles”.

As you can see, the main conclusions on the interpretation of the results of Mössbauer measurements stated in the original article and given above in this response coincide.

Considering the acceptable values of  $\chi^2$ , the acceptable distribution of residuals within  $\pm 3\sigma$ , and the consistency of the hyperfine parameters of the identified components with the literature, we disagree with the claim that “... the analysis and interpretation of Mössbauer spectroscopic data are incorrect, inadequate, and wanting”. We believe that this claim is not substantiated.

Maybe the text in the original paper contains some confusing phrases. They are quite easy to understand and do

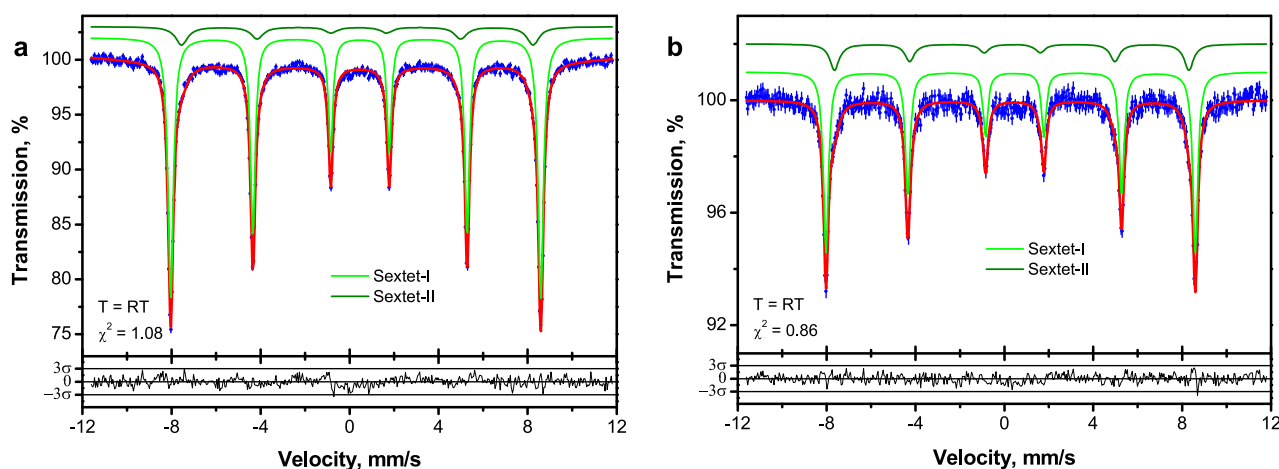


Figure 3. Mössbauer spectra of (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + oil sample and (b)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA + oil sample treated at 500 °C.

Table 3. Hyperfine Parameters and Phase Identification of Mössbauer Spectra Components for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + Oil and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA + Oil Samples Treated at 500 °C

	component	isomer shift (mm/s)	quadrupole splitting (mm/s)	hyperfine field (kOe)	line width (mm/s)	spectral area (%)	phase identification and reference
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> + oil sample treated at 500 °C	sextet I	0.37(1)	−0.19(1)	515(1)	0.29(1)	87(1)	hematite <sup>10</sup>
	sextet II	0.38(1)	−0.07(1)	489(1)	0.67(1)	13(1)	maghemite <sup>10</sup>
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> @OA + oil sample treated at 500 °C	sextet I	0.37(1)	−0.18(1)	515(1)	0.28(1)	79(1)	hematite <sup>10</sup>
	sextet II	0.34(1)	−0.03(1)	494(1)	0.51(1)	21(1)	maghemite <sup>10</sup>

not change the reliability of our conclusions, if we take into account the fact that the text in the original article states that all X-ray and Mössbauer measurements were carried out at room temperature on samples obtained after the isothermal oxidation process. However, we noticed one mistake. For example, in the text, the isomer shift for the doublet is indicated equal to 0.43 mm/s. In fact, the value of the isomer shift for the doublet was 0.34 mm/s. We greatly appreciate the opportunity to correct this mistake and present in more details the graphical and tabular results of the Mössbauer measurements of the samples obtained after isothermal oxidation at 500 °C.

Figure 3 shows the Mössbauer spectra of the residues yielded from the isothermal (500 °C) oxidation experiments of heavy oil +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and heavy oil +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA samples. The best fit hyperfine parameters of the identified components are shown in Table 3. Analysis of the Mössbauer data shows that, after oxidation at 500 °C, two iron-containing phases are observed: hematite and maghemite. The hyperfine parameters of the spectral components are in good agreement with the literature.

## CONCLUSION

The results of Mössbauer measurements were used in our work for a comparative phase analysis of the starting compounds ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA) and the products of heavy oil +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and heavy oil +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@OA samples after the isothermal oxidation process at 400 and 500 °C. Following the practice of many works published in *Energy & Fuels*, the results of phase identification in our article are given with either an indication of the detected phase (hematite, magnetite, and maghemite) or the main hyperfine parameters (IS, QS, and HF) of the identified component. All of these data are given in the text of the original article. The quality of the experimental spectra and the result of mathematical processing (the  $\chi^2$

values and the residual plots) of the spectra allow us to assert that the phase analysis was carried out correctly and the phase components were determined with good statistical accuracy. The requirement of the author of this comment that “the reporting of line width mandatory for all practical purposes” for spectra with well-resolved and narrow lines ( $\Gamma = 0.27$  and  $0.30$  mm/s in Figures 3 and 6<sup>2</sup>) must be indicated as superfluous. Nevertheless, in this response, we have provided additional information about the results of Mössbauer measurements in graphical and tabular form, as recommended by the author of the comment. Besides the main parameters (IS, QS, and HF), the tables also include the values of line widths, spectral line areas, and phase identification. In addition to the model components, the figures also show the values of  $\chi^2$ .

## AUTHOR INFORMATION

### Corresponding Authors

Mikhail A. Varfolomeev – Department of Petroleum Engineering and Department of Physical Chemistry, Kazan Federal University, Kazan 420008, Russia; [orcid.org/0000-0001-8578-6257](https://orcid.org/0000-0001-8578-6257); Email: [vma.ksu@gmail.com](mailto:vma.ksu@gmail.com), [mikhail.varfolomeev@kpfu.ru](mailto:mikhail.varfolomeev@kpfu.ru)

Chengdong Yuan – Department of Petroleum Engineering and Department of Physical Chemistry, Kazan Federal University, Kazan 420008, Russia; [orcid.org/0000-0002-7327-8092](https://orcid.org/0000-0002-7327-8092); Email: [megycd@163.com](mailto:megycd@163.com)

### Authors

Seyedsaeed Mehrabi-Kalajahi – Department of Petroleum Engineering and Department of Physical Chemistry, Kazan Federal University, Kazan 420008, Russia; [orcid.org/0000-0001-6959-6410](https://orcid.org/0000-0001-6959-6410)

Nikolay O. Rodionov – Department of Physical Chemistry, Kazan Federal University, Kazan 420008, Russia



256 **Almaz L. Zinnatullin** – Institute of Physics, Kazan Federal  
257 University, Kazan 420008, Russia  
258 **Farit G. Vagizov** – Institute of Physics, Kazan Federal  
259 University, Kazan 420008, Russia  
260 **Yuri N. Osin** – Interdisciplinary Center for Analytical  
261 Microscopy, Kazan Federal University, Kazan 420018,  
262 Russia

263 Complete contact information is available at:  
264 <https://pubs.acs.org/10.1021/acs.energyfuels.1c03543>

## 265 Notes

266 The authors declare no competing financial interest.

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## 271 ■ REFERENCES

- 272 (1) Nayak, P. K. Comment on Oil-Dispersed  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Nanoparticles  
273 as a Catalyst for Improving Heavy Oil Oxidation. *Energy Fuels* **2021**,  
274 DOI: 10.1021/acs.energyfuels.1c03123.
- 275 (2) Mehrabi-Kalajahi, S.; Varfolomeev, M. A.; Yuan, C.; Rodionov,  
276 N. O.; Zinnatullin, A. L.; Vagizov, F. G.; Osin, Y. N. Oil-Dispersed  $\alpha$ -  
277 Fe<sub>2</sub>O<sub>3</sub> Nanoparticles as a Catalyst for Improving Heavy Oil  
278 Oxidation. *Energy Fuels* **2021**, *35*, 10498–10511.
- 279 (3) Yu, D.; Zhao, L.; Zhang, Z.; Wen, C.; Xu, M.; Yao, H. Iron  
280 Transformation and Ash Fusibility during Coal Combustion in Air  
281 and O<sub>2</sub>/CO<sub>2</sub> Medium. *Energy Fuels* **2012**, *26*, 3150–3155.
- 282 (4) Zhao, J.; Feng, Z.; Huggins, F. E.; Huffman, G. P. Character-  
283 ization of Impregnated Iron Catalysts on Coal. *Energy Fuels* **1996**, *10*,  
284 250–253.
- 285 (5) Hadebe, S. W.; Leckel, D. Iron Removal from High-Temperature  
286 Fischer–Tropsch-Derived Distillate through Thermal Treatment.  
287 *Energy Fuels* **2013**, *27*, 5161–5167.
- 288 (6) Yamashita, H.; Ohtsuka, Y.; Yoshida, S.; Tomita, A. Local  
289 Structures of Metals Dispersed on Coal. 1. Change of Local Structure  
290 of Iron Species on Brown Coal during Heat Treatment. *Energy Fuels*  
291 **1989**, *3*, 686–692.
- 292 (7) Huffman, G. P.; Ganguly, B.; Zhao, J.; Rao, K. R. P. M.; Shah,  
293 N.; Feng, Z.; Huggins, F. E.; Taghiei, M. M.; Lu, F. Structure and  
294 Dispersion of Iron-Based Catalysts for Direct Coal Liquefaction.  
295 *Energy Fuels* **1993**, *7*, 285–296.
- 296 (8) Cosultchi, A.; Ascencio-Gutiérrez, J. A.; Reguera, E.; Zeifert, B.;  
297 Yee-Madeira, H. On a Probable Catalytic Interaction between  
298 Magnetite (Fe<sub>3</sub>O<sub>4</sub>) and Petroleum. *Energy Fuels* **2006**, *20*, 1281–  
299 1286.
- 300 (9) Wertheim, G. K. *Mössbauer Effect: Principles and Applications*;  
301 Academic Press: New York, 1964; DOI: 10.1016/C2013-0-12103-4.
- 302 (10) Oh, S. J.; Cook, D. C.; Townsend, H. E. Characterization of  
303 Iron Oxides Commonly Formed as Corrosion Products on Steel.  
304 *Hyperfine Interact.* **1998**, *112*, 59–66.
- 305 (11) Maddock, A. G. *Mössbauer Spectroscopy: Principles and*  
306 *Applications of the Techniques*; Horwood: Chichester, U.K., 1997;  
307 Horwood Chemical Science Series.
- 308 (12) Margulies, S.; Ehrman, J. R. Transmission and Line Broadening  
309 of Resonance Radiation Incident on a Resonance Absorber. *Nucl.*  
310 *Instrum. Methods* **1961**, *12*, 131–137.
- 311 (13) Cherepanov, V. M.; Gabbasov, R. R.; Yurenaya, A. Y.; Nikitin, A.  
312 A.; Abakumov, M. A.; Polikarpov, M. A.; Chuev, M. A.; Panchenko, V.  
313 Y. Study of the Brownian Broadening in the Mössbauer Spectra of  
314 Magnetic Nanoparticles in Colloids with Different Viscosities.  
315 *Crystallogr. Rep.* **2020**, *65*, 398–403.
- 316 (14) Chuev, M. A. Multi-Level Relaxation Model for Describing the  
317 Mössbauer Spectra of Single-Domain Particles in the Presence of  
318 Quadrupolar Hyperfine Interaction. *J. Phys.: Condens. Matter* **2011**,  
319 *23*, 426003.

- (15) Wertheim, G. K. Mössbauer Effect: Applications to Magnetism. *J. Appl. Phys.* **1961**, *32*, S110–S117. 320 321
- (16) Cianchi, L.; Moretti, P.; Mancini, M.; Spina, G. Mossbauer  
322 Spectra in Paramagnetic Relaxing Systems. *Rep. Prog. Phys.* **1986**, *49*,  
323 1243–1291. 324
- (17) *Mössbauer Mineral Handbook*; Stevens, J. G., Khasanov, A. M.,  
325 Miller, J. W., Pollak, H., Li, Z., Eds.; Mössbauer Effect Data Center:  
326 Asheville, NC, 1998. 327
- (18) Matsnev, M. E.; Rusakov, V. S. SpectrRelax: An Application for  
328 Mössbauer Spectra Modeling and Fitting. *AIP Conf. Proc.* **2012**, *1489*,  
329 178–185. 330