catalysts

Article

Synthesis and Regeneration of Nickel-Based Catalysts for Hydrodeoxygenation of Beech Wood Fast Pyrolysis Bio-Oil

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The supplementary material brings complementary information in order to support the discussion of the results presented in the manuscript.

Reactor details

Batch reactor details: 200 mL batch reactor with maximum temperature operation of 400 °C and maximum pressure of 360 bar. The reactor was built at Institute of Catalysis Research and Technology (IKFT) with of Inconel alloy 625 and equipped with a gas injector stirrer (torque 80 N·cm, Premex reactor AG). The heating system was controlled by a Labview Program.

Coke calculation

The amount of solid (coke) over the spent catalyst was calculated following the equation below:

$$m_{solid} = \frac{\%C_{spentcat} \times m_{catalyst}}{100 - \%C_{spentcat}} \quad \text{Equation (S1)}$$

Where the m_{solid} is the mass of coke (g) in the spent catalyst; $\%C_{spentcat}$ is the concentration of carbon deposited over the spent catalyst obtained by elemental analysis and $m_{catalyst}$ is the amount of catalyst (g) loaded to the reactor.

Results

Table S1. Elemental analysis and physicochemical properties of upgraded aqueous phases from different catalysts.

Properties	**Ni/SiO$_2$**	**Ni/ZrO$_2$**	**NiCu/SiO$_2$**	**NiCu/ZrO$_2$**
Upgraded Aqueous Phase (Wet Basis)				
C (wt.%)	11.6 ±0.14	11.5±0.01	15.8 ±0.14	13.6±0.01
H (wt.%)	11.45 ±0.07	11.45 ±0.07	11.3±0.01	11.3±0.01
O (wt.%)	73.9 ±0.14	74.35 ±0.35	70.15 ±0.07	72.5±0.01
N (wt.%)	2.9±0.01	2.6 ±0.42	2.65 ±0.07	2.5±0.01
Physicochemical Properties				
H_2O (wt.%)	74.35 ±0.21	74.5 ±0.028	67.15 ±0.21	72.35 ±1.20
pH	3.1±0.01	2.65 ±0.07	3.05 ±0.07	2.9±0.01
Density (g/cm^3)	1.028±0.07	1.026±0.01	1.034±0.01	1.031±0.01

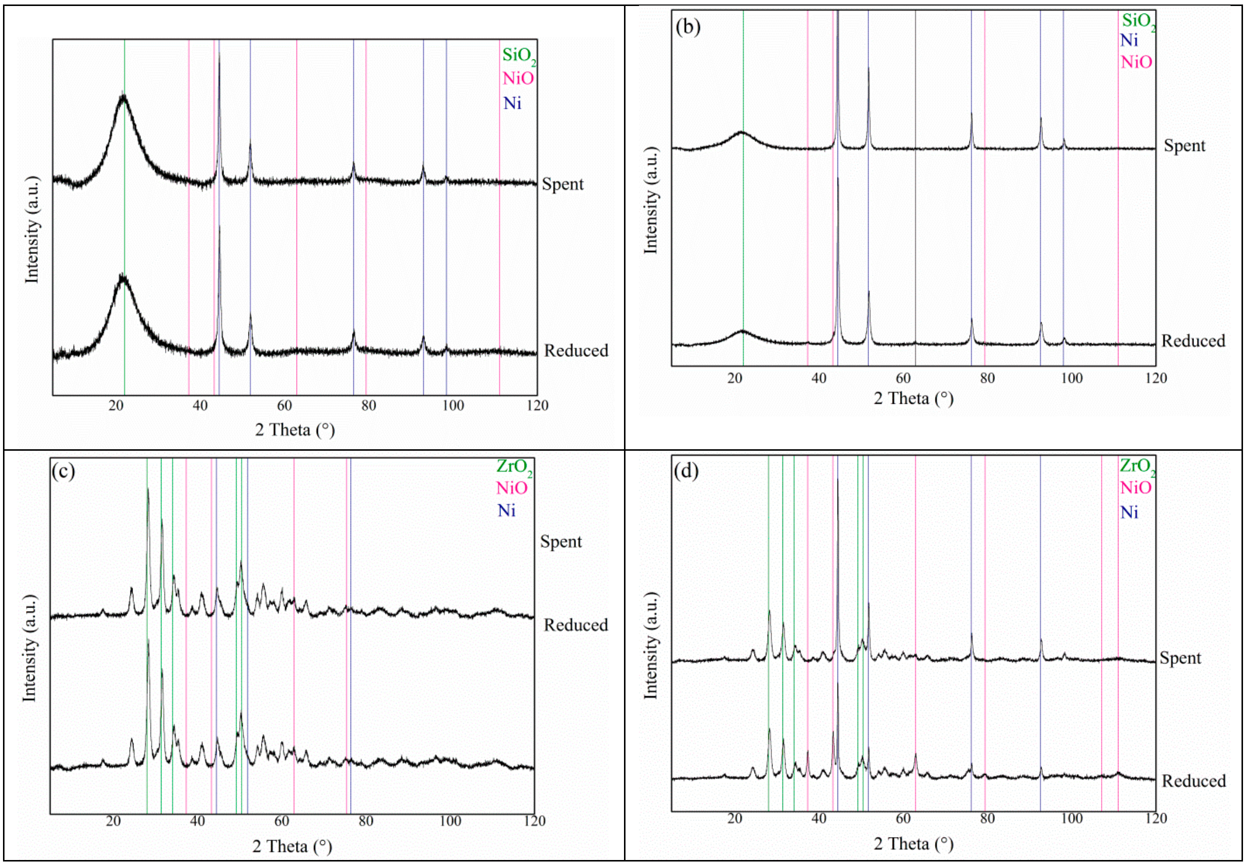

Figure S1. Fresh and spent catalysts. a)Ni/SiO_2; b) NiCu/SiO_2; c)Ni/ZrO_2; d) NiCu/ZrO_2.

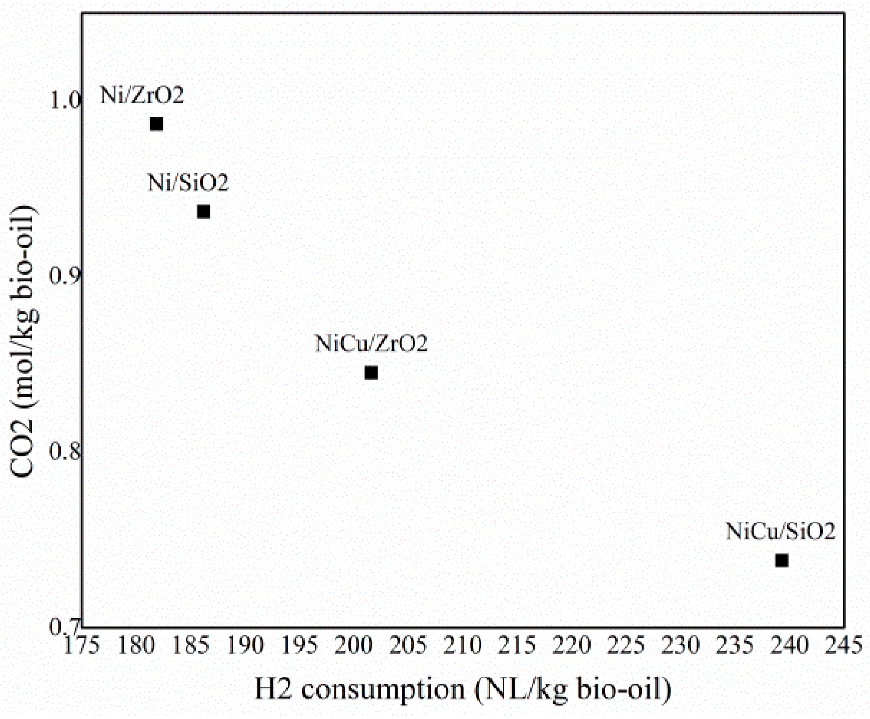

Figure S2. Correlation between the H_2 consumption and CO_2 produced by different catalysts.

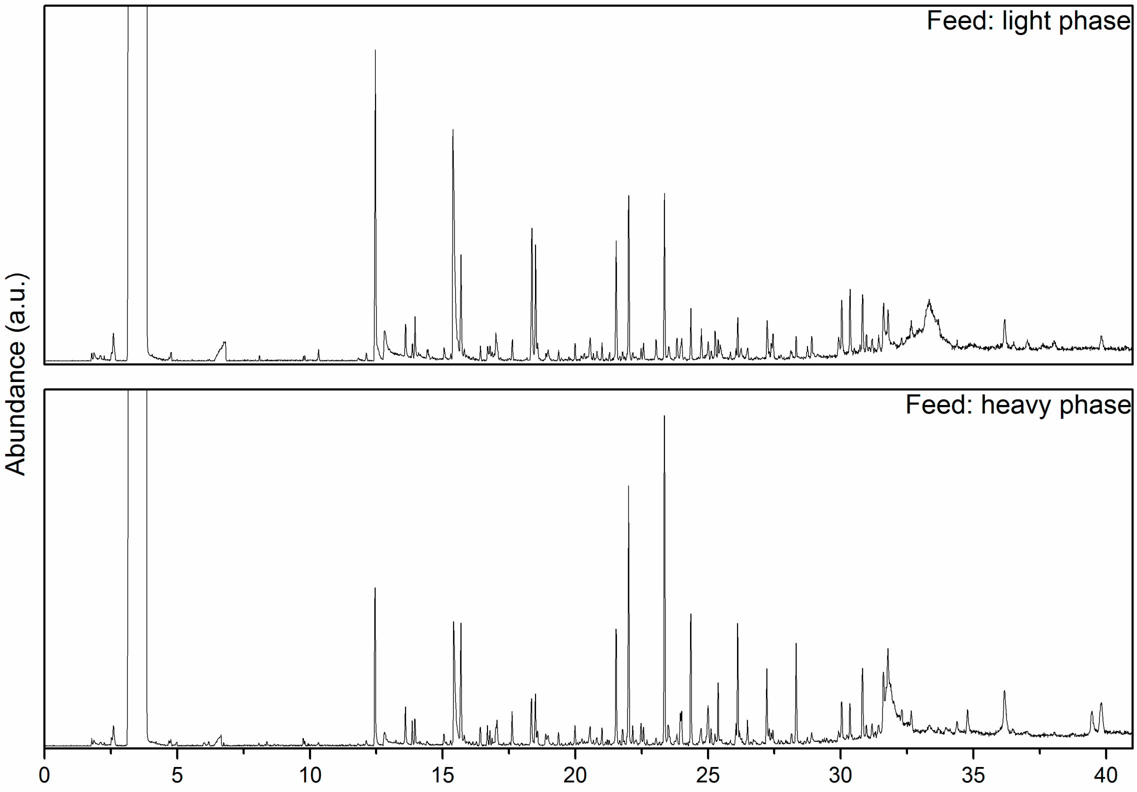

Fig S3. GC-MS Feedstock (light phase and heavy phase).

Table S2. Retention time of the main compounds identified in the feed (light and heavy phase).

Retention Time (min)	Compound
12.46	1-hydroxy-2-propanone
13.6	2-cyclopenten-1-one
13.85	2-methyl-2-cyclopenten-1-one
15.36	Acetic acid
15.7	Furfural
16.42	1-(2-furanyl)-ethanone
16.7	3-methyl-2-cyclopenten-1-one
17.7	Propylene glycol
18.34	1,2-ethanediol
18.46	1,2-ethanediol, monoacetate
19.97	3-methyl-cyclopentanone
21.53	2-hydroxy-3-methyl-2-cyclopenten-1-one
22.0	2-methoxy-phenol
23.36	2-methoxy-4-methyl-phenol
23.954	2-methyl-phenol
24.0	Phenol
24.35	4-ethyl-2-methoxy-phenol
25.0	4-methyl-phenol
25.116	3-methyl-phenol
25.36	2-methoxy-4-propyl-phenol
26.114	Eugenol
27.23	2-methoxy-4-(1-propenyl)-phenol
28.314	2-methoxy-4-(1-propenyl)-phenol
30.04	5-(hydroxymethyl)-2-furancarboxaldehyde
30.82	Vanillin
31.62	1-(3-hydroxy-4-methoxyphenyl)-ethanone

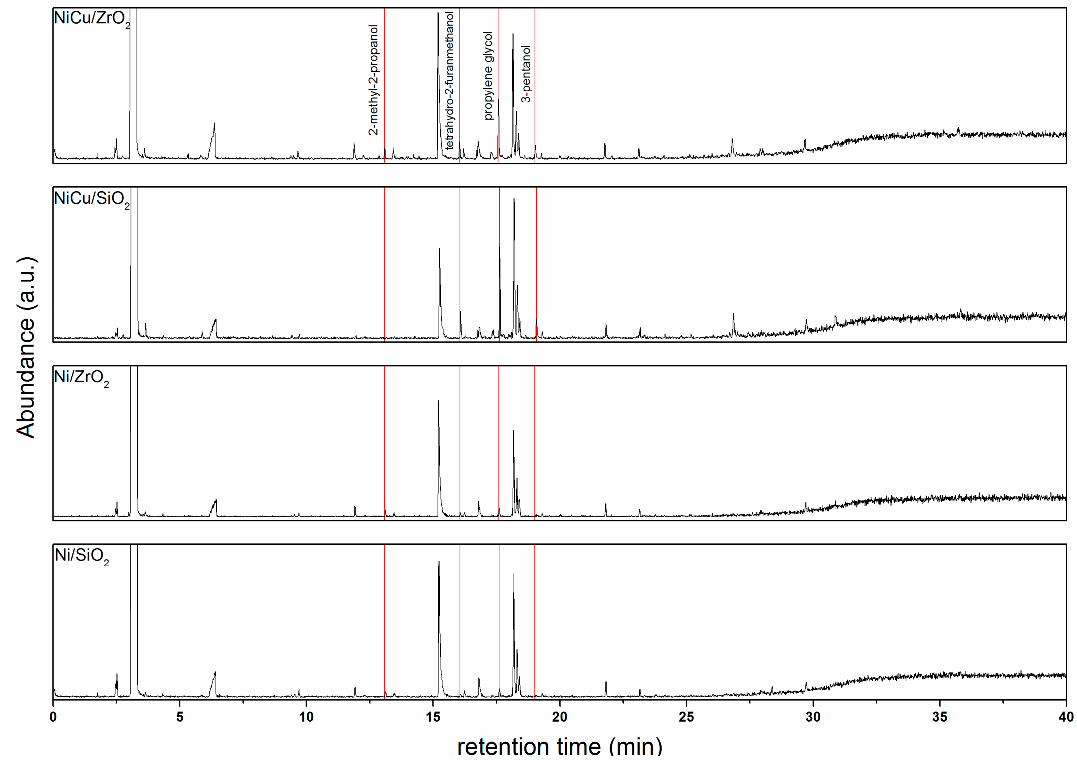

Fig S4. GC-MS aqueous phase after hydrodeoxygenation with different catalysts.

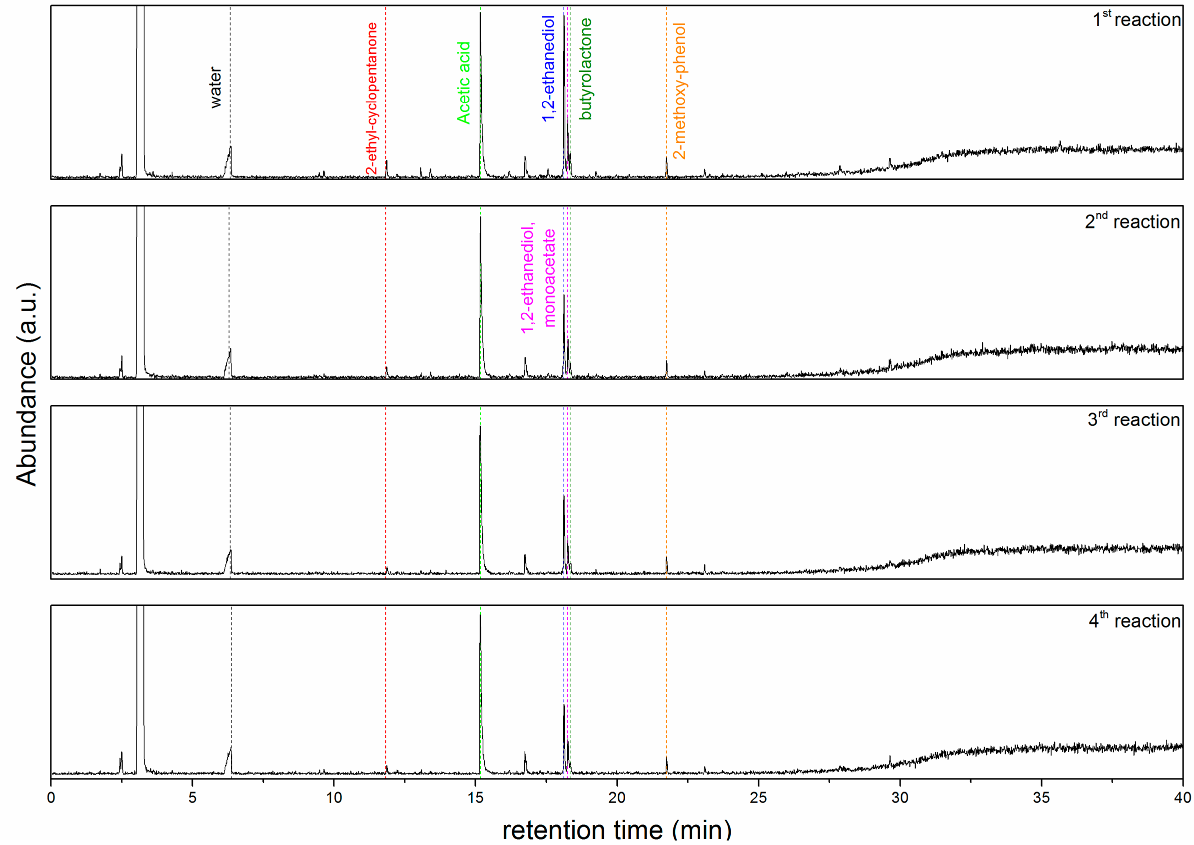

Fig S5. GC-MS aqueous phase over the consecutive reactions.

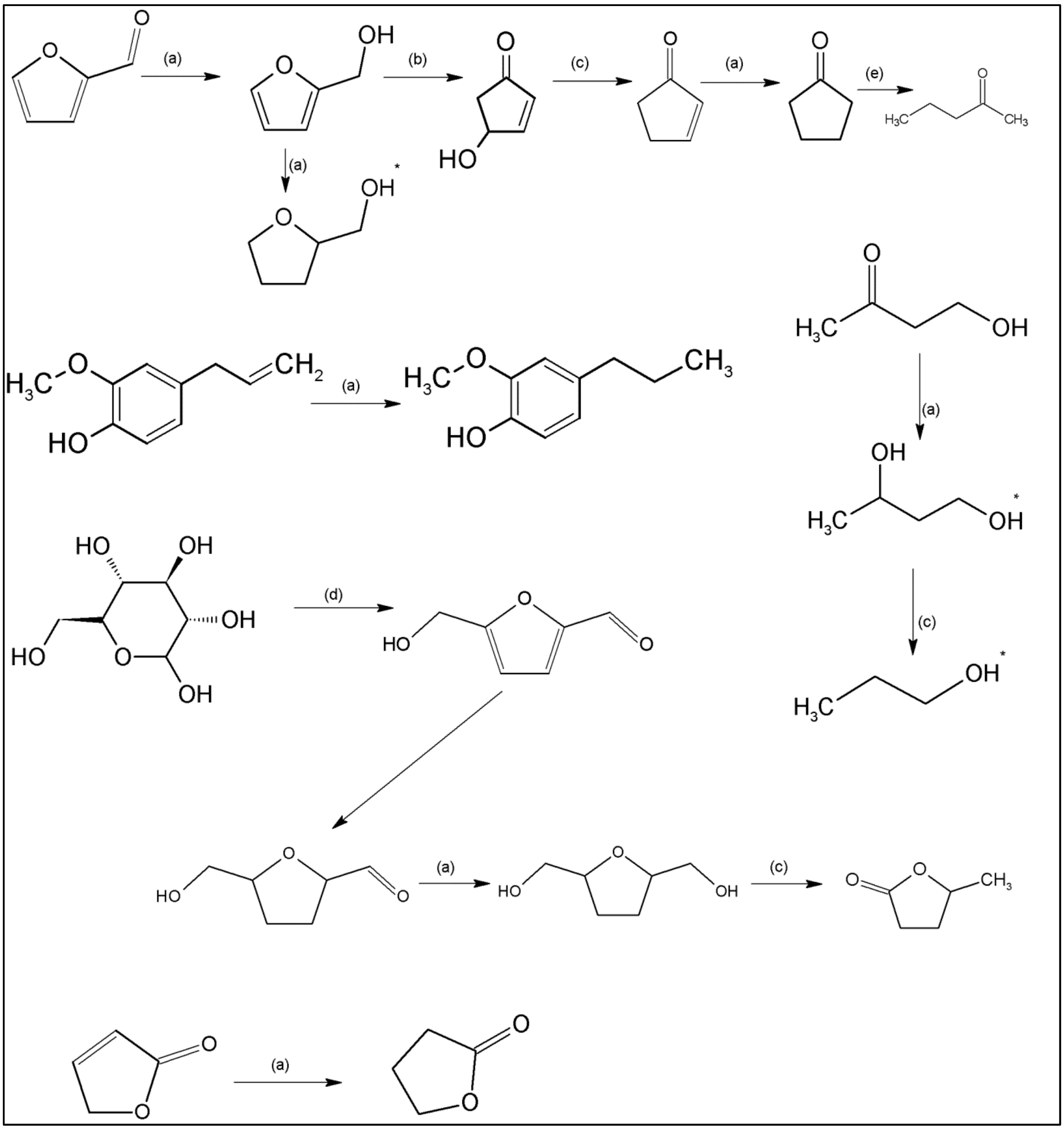

Fig S6. Reaction pathways identified after HDO reactions.(a)-hydrogenation; (b)-rearrangement; (c)-direct deoxygenation; (d)-dehydration; (e)-ring opening; * Products obtained with NiCu/SiO2 and NiCu/ZrO2 catalysts.

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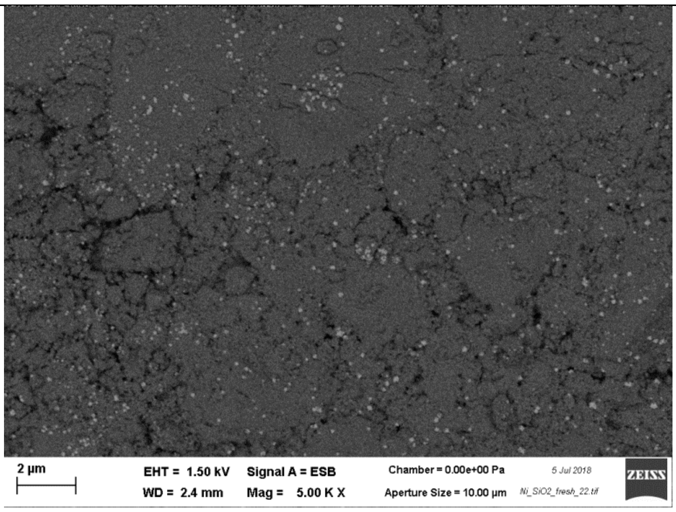
<td colspan="2">
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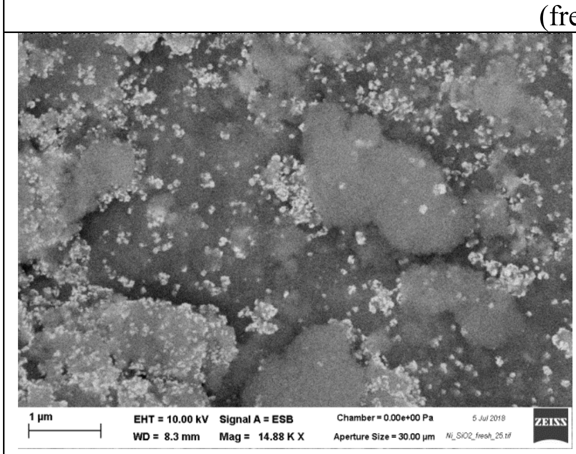
<td>
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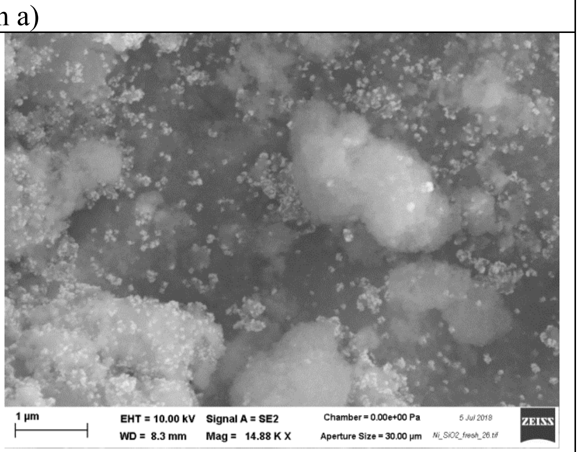
<td>
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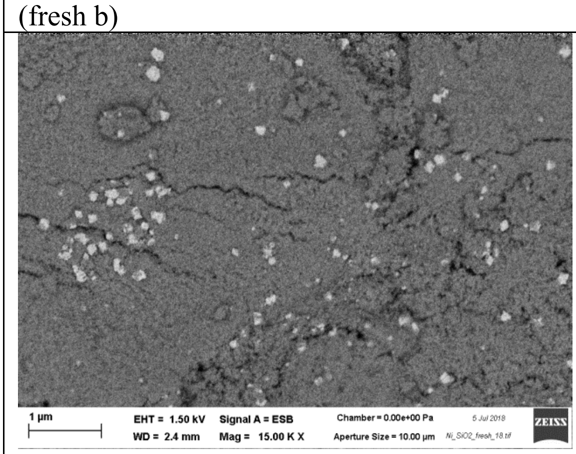
<td>
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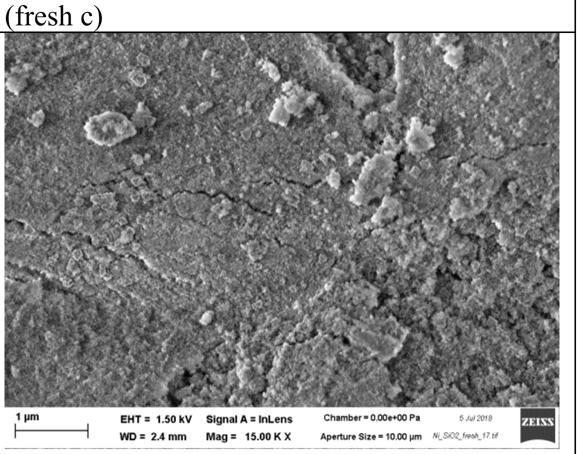
<td>
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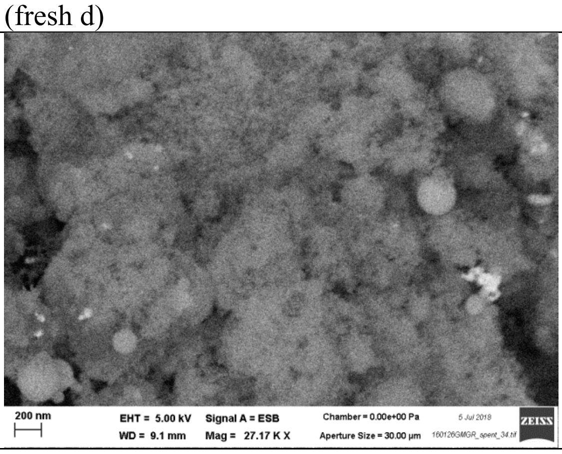
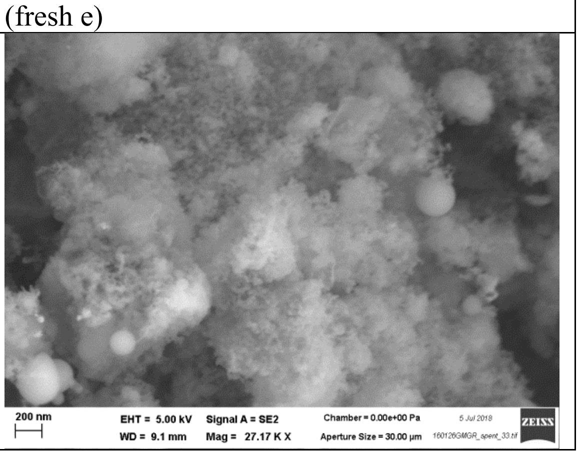
<td> </td>
<td> </td>
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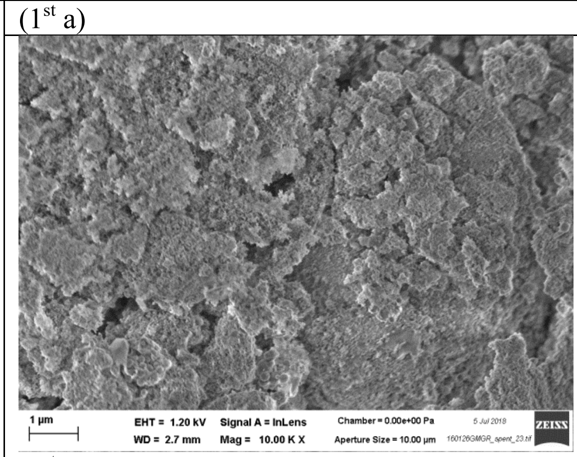
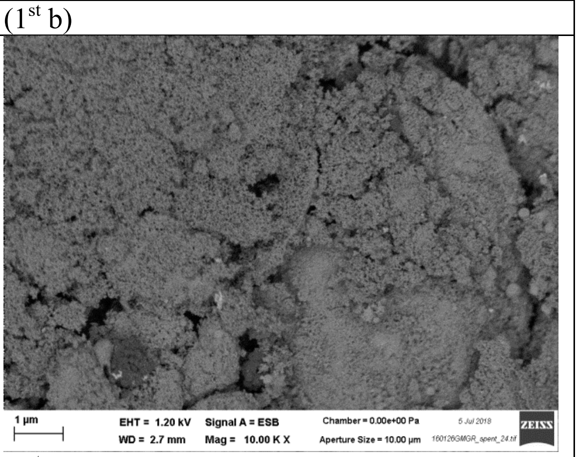
<tr><td>

(1st c)</td><td>

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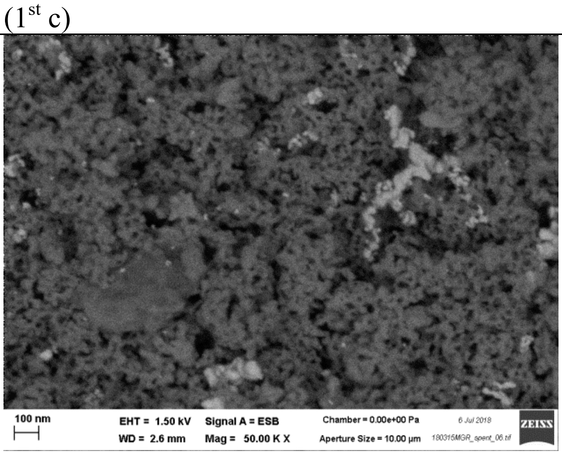
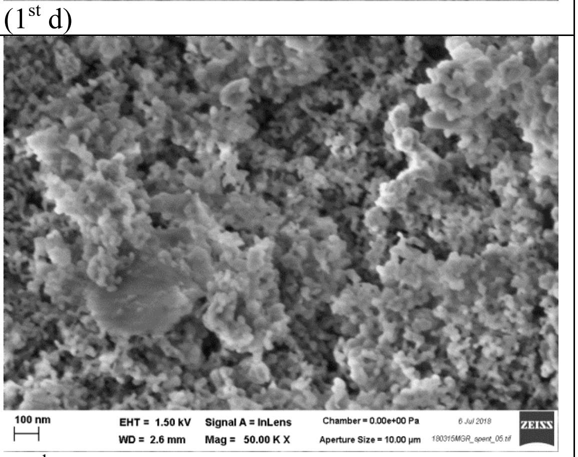
<tr><td rowspan="3">2nd reaction - spent</td><td>

(2nd a)</td><td>

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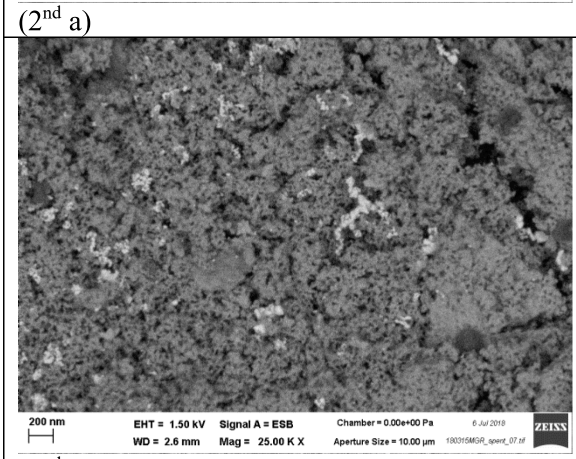
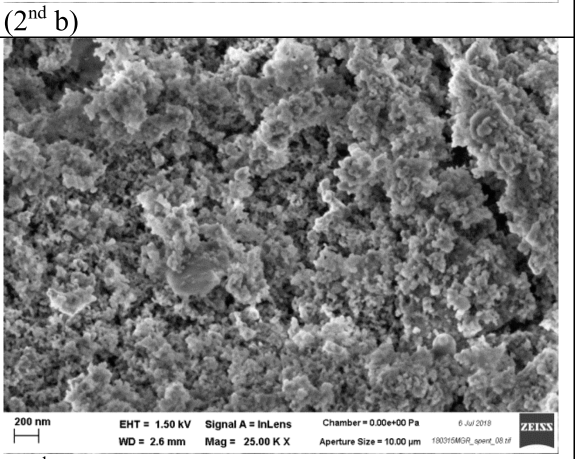
<tr><td>

(2nd c)</td><td>

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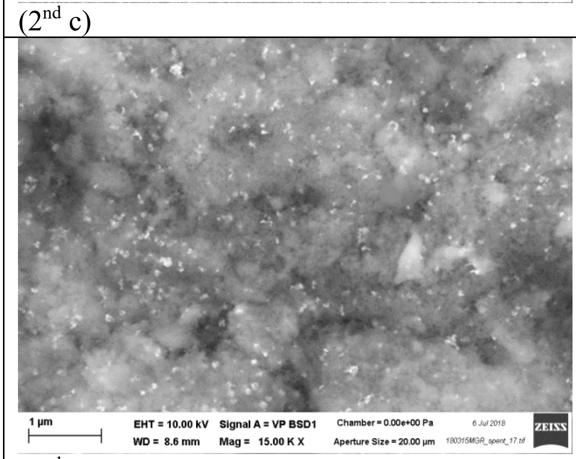
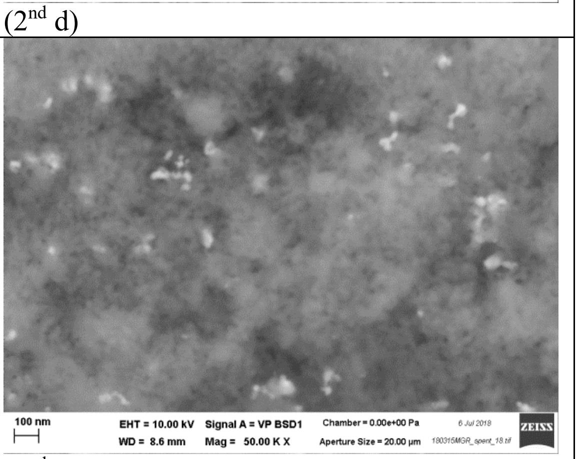
<tr><td>

(2nd e)</td><td>

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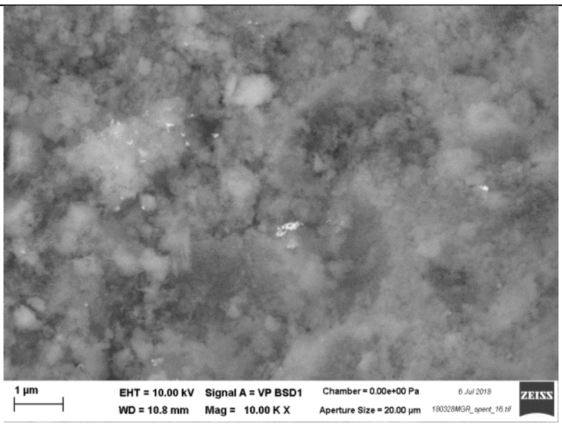
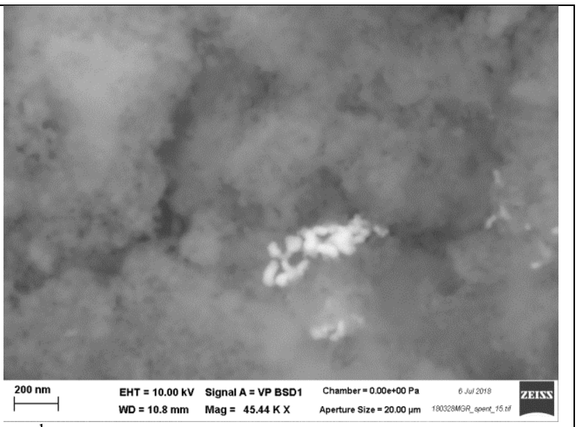
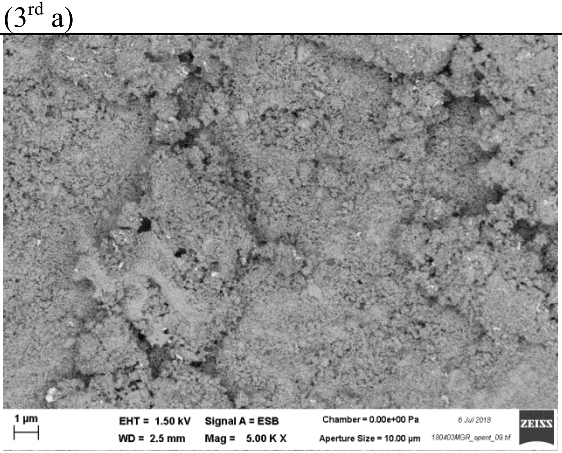
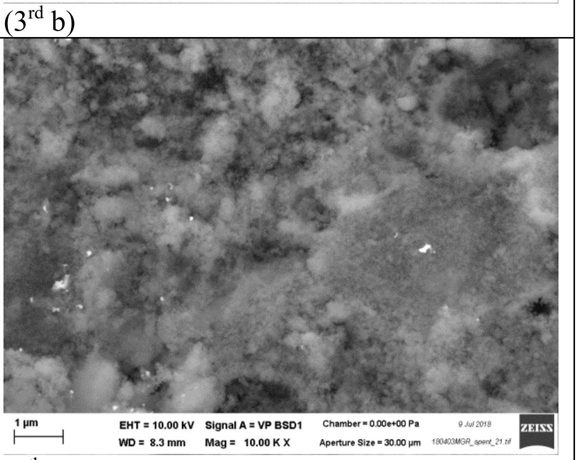
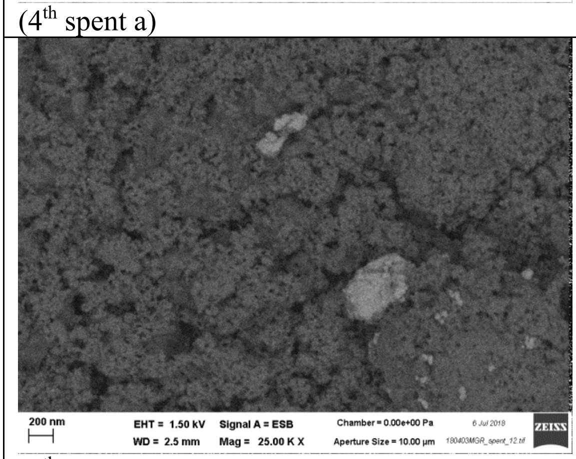
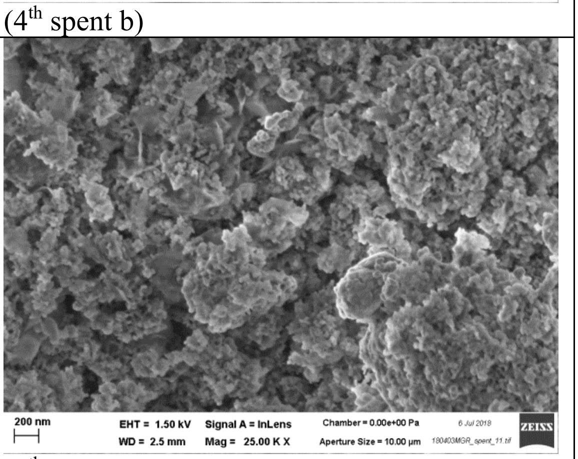
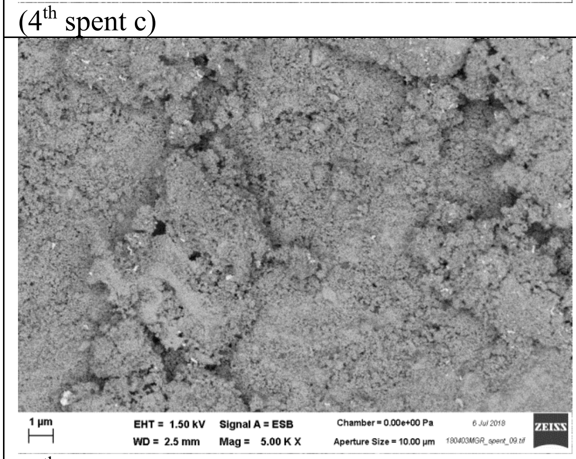
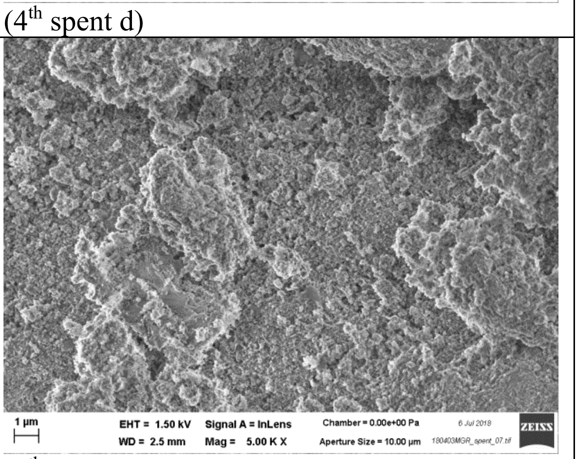
3rd reaction - spent	 (3rd a)	 (3rd b)
4threaction - spent	 (4th spent a)	 (4th spent b)
	 (4th spent c)	 (4th spent d)
	 (4th spent e)	 (4th spent f)

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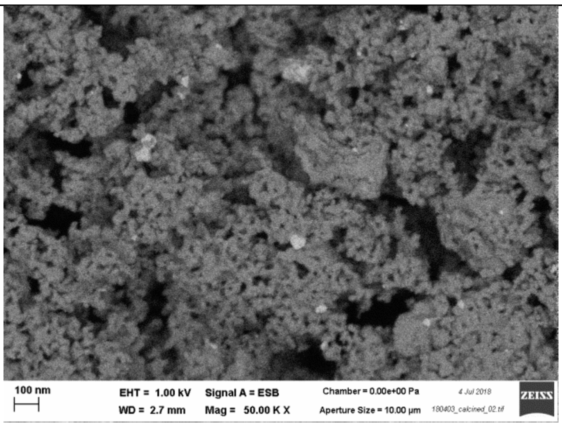
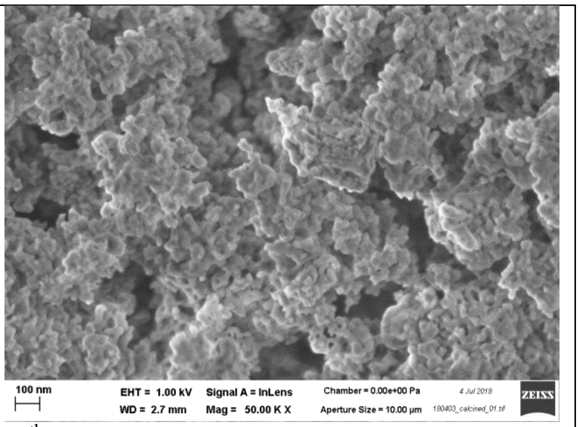
<td> (4th calcined a)</td>
<td> (4th calcined b)</td>
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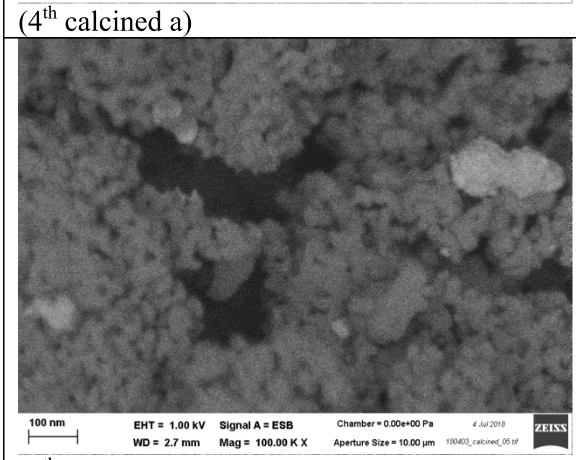
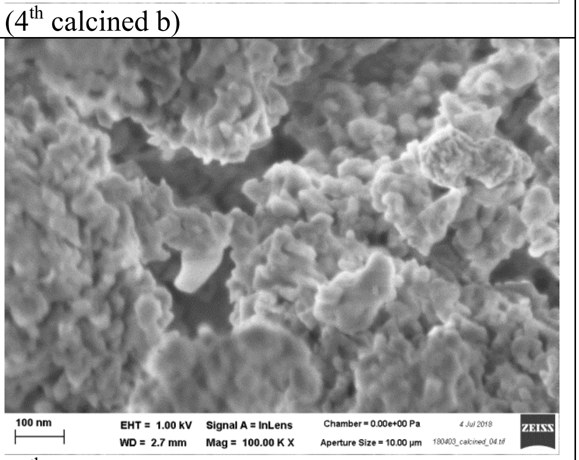
<td> (4th calcined c)</td>
<td> (4th calcined d)</td>
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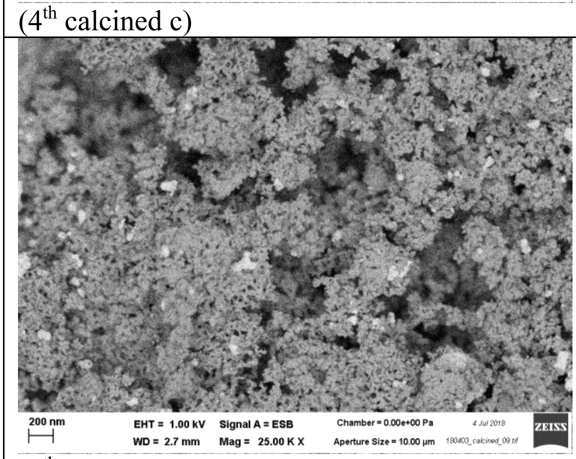
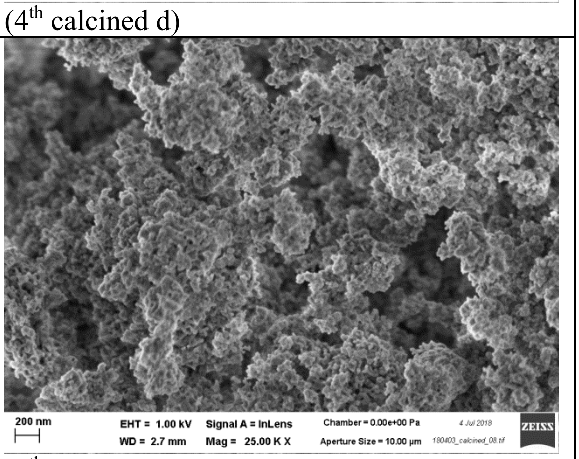
<td> (4th calcined e)</td>
<td> (4th calcined f)</td>
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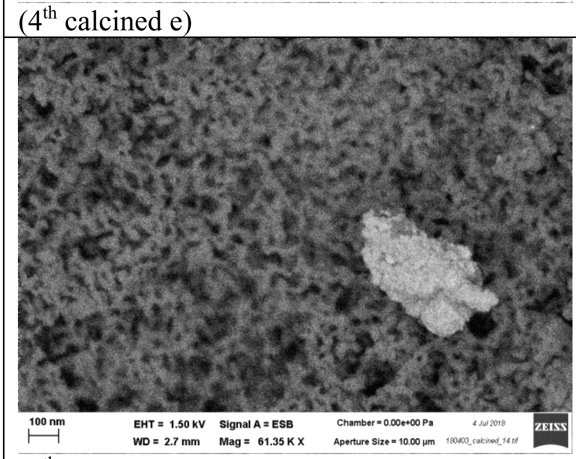
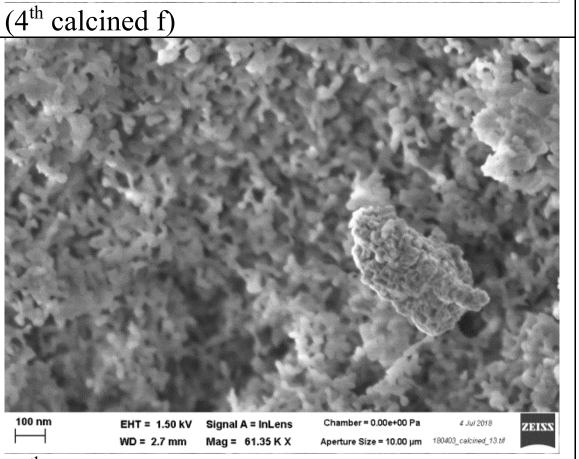
<td> (4th calcined g)</td>
<td> (4th calcined h)</td>
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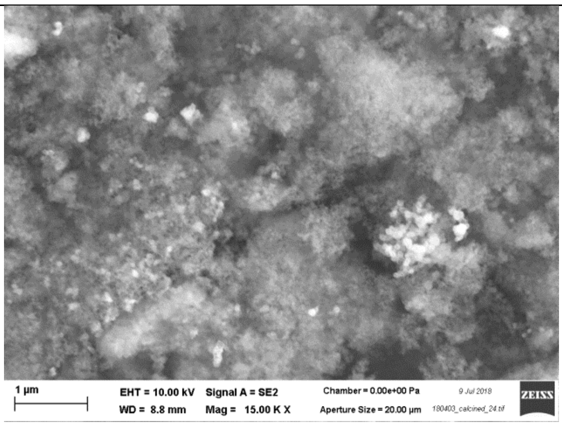
<td>

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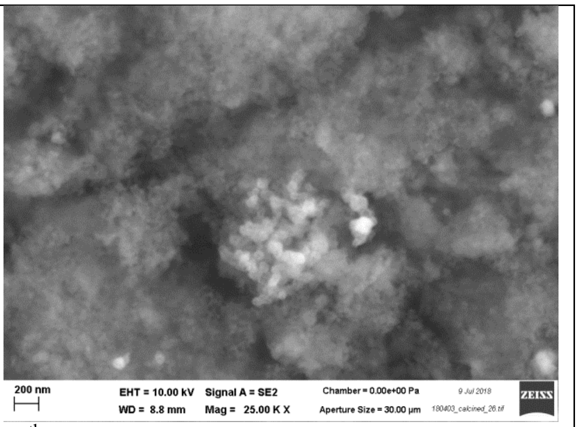
<td>

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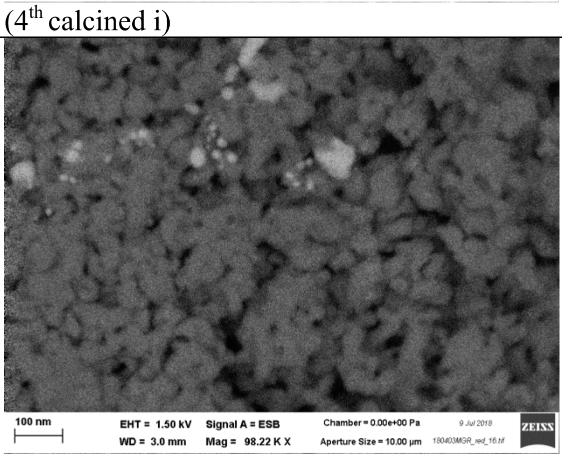
<td>

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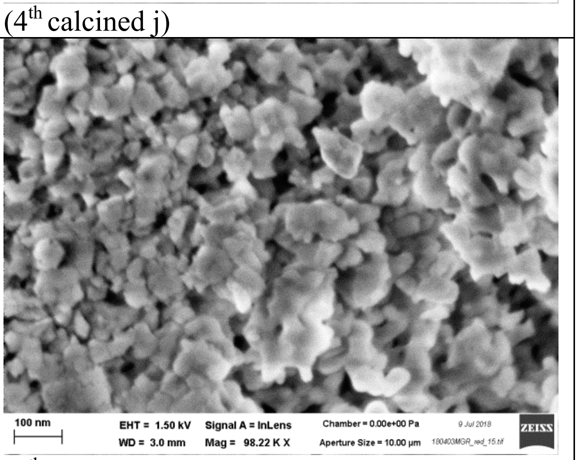
<td>

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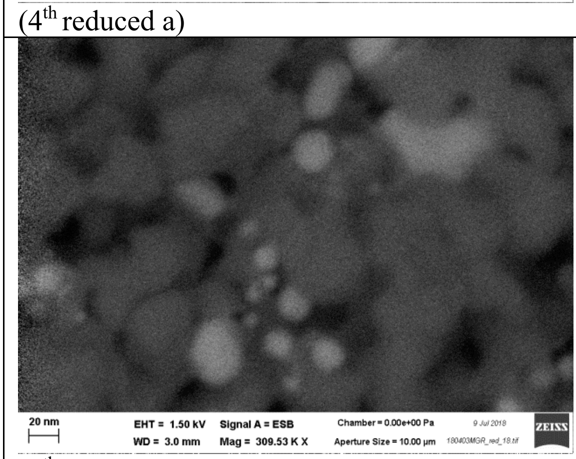
<td>

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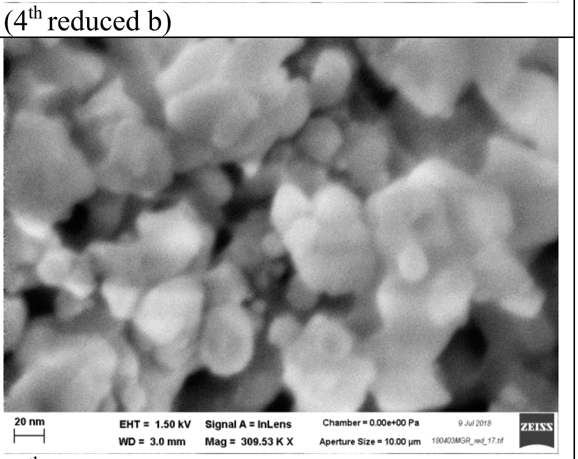
<td>

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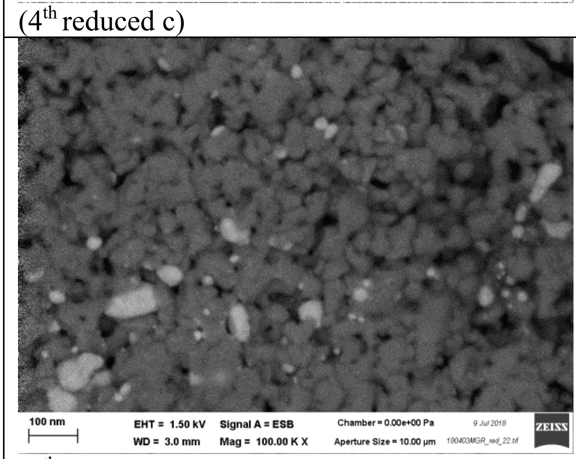
<td>

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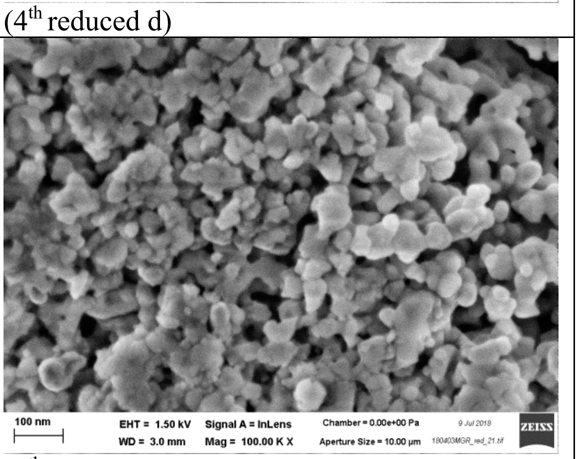
<td>

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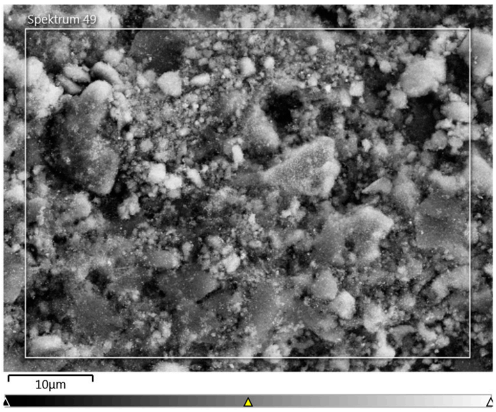
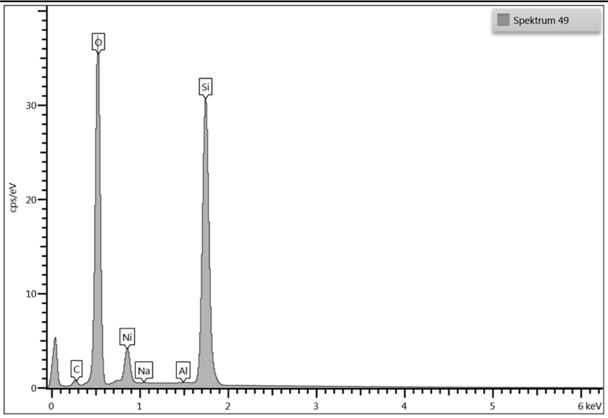
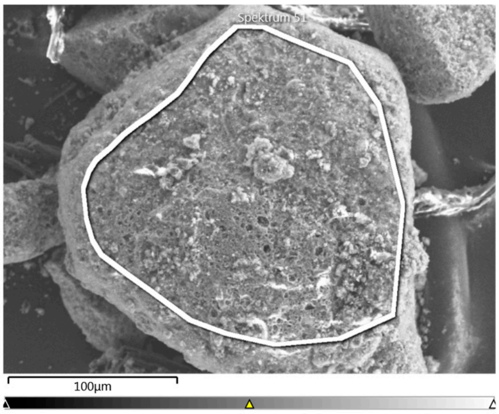
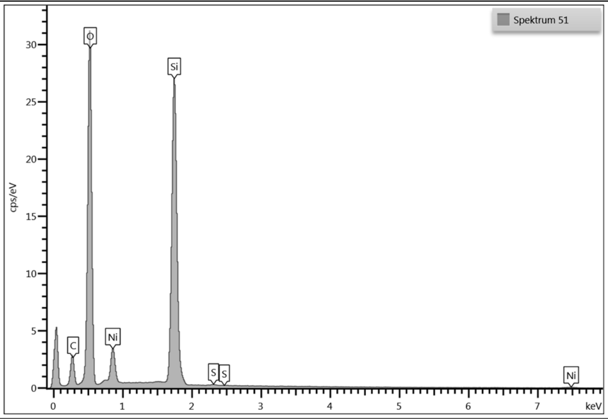
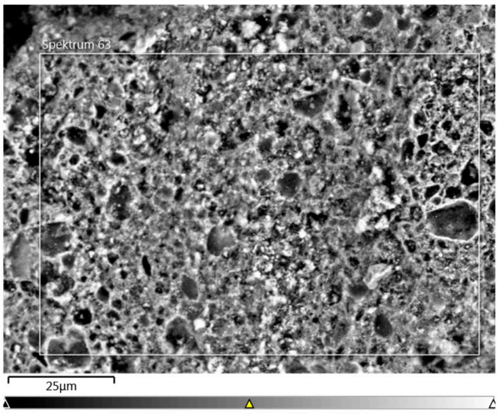
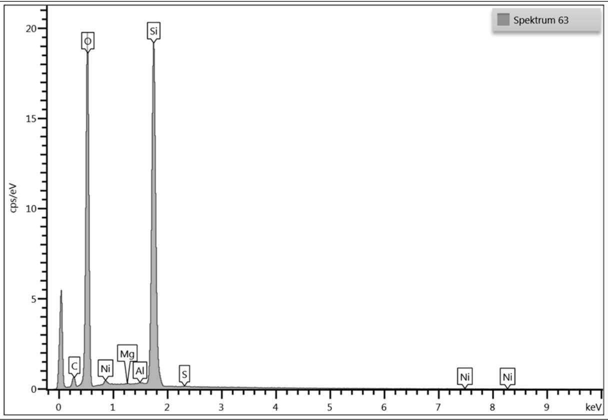
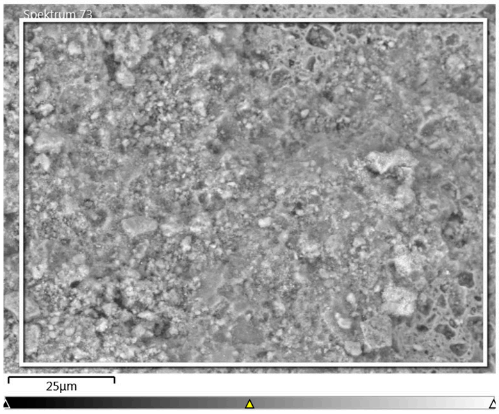
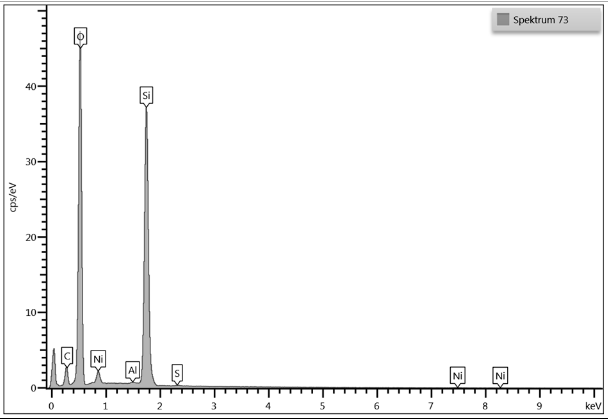
Fig S7. Compilation of the main pictures obtained by SEM-EDX. Brighter parts are attributed to nickel particles.

Fresh Ni/SiO_2 catalyst		
1st reaction - spent		
2nd reaction - spent		
3rd reaction - spent		

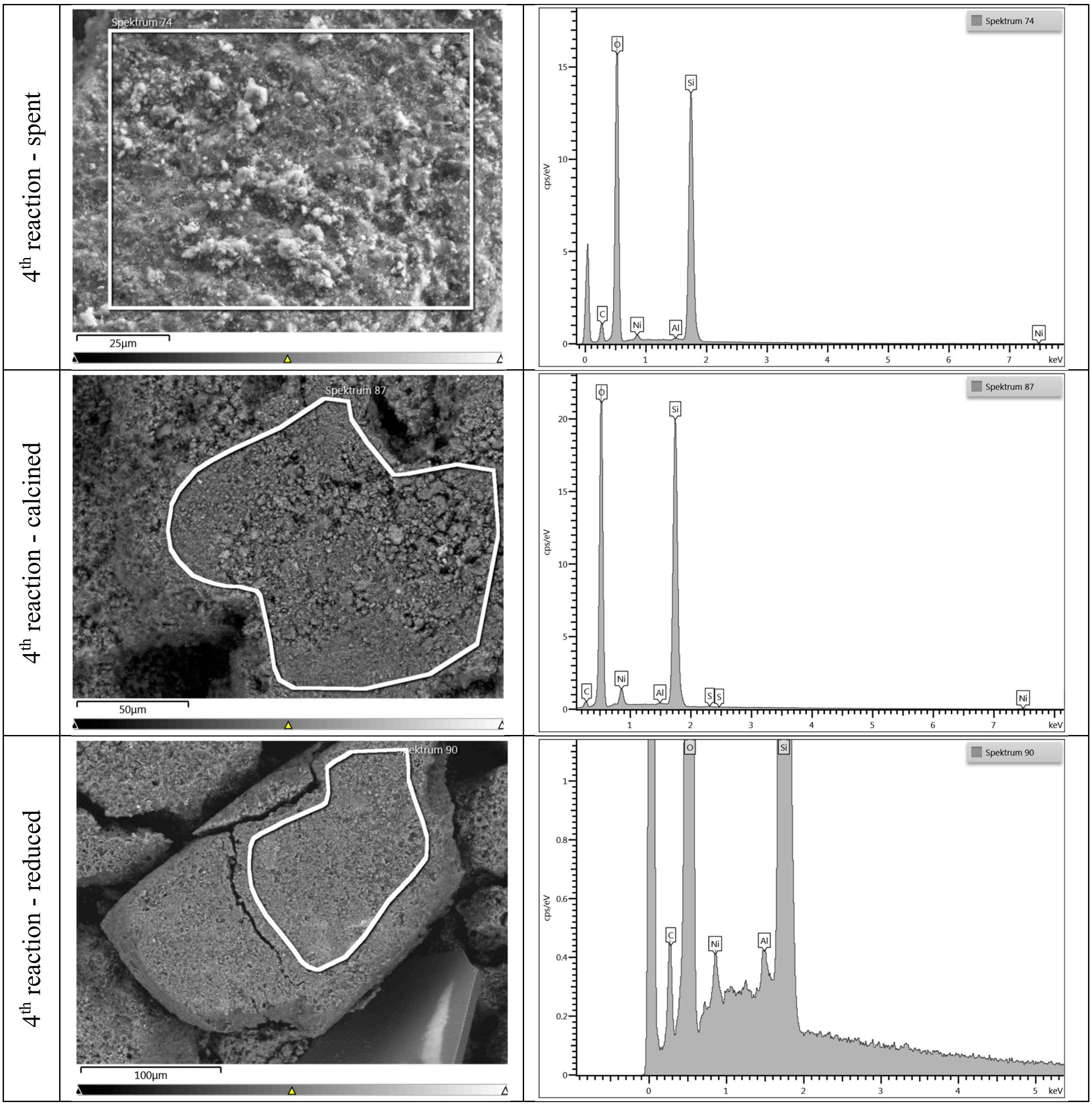


Fig S8. EDX of selected regions.

Table S3. Elemental composition obtained by EDX of selected regions.

Spectrum	C (wt.%)	Si (wt.%)	S (wt.%)	Ni (wt.%)
Fresh Ni/SiO$_2$	2.9	39.5	-	9.6
1st reaction (spent)	12.1	44.9	0.2	7.3
2nd reaction (spent)	6.8	42.2	0.1	1.1
3rd reaction (spent)	9.1	37.4	0.1	2.4
4th reaction (spent)	10.1	37.9	-	1.8
4th reaction (calcined)	3.5	41.8	0.1	6.4
4th reaction (reduced)	3.6	44.5	-	1.2