SUPPORTING INFORMATION

Optimization and intensification of hydrosilylation reaction using microreactor system

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GC vs. *in situ* IR monitoring of the reaction progress

Initially the selectivity and conversion to be reported in this article were calculated from gas chromatography (GC) measurements. However *in situ* IR method has many advantages. Monitoring of the reaction using in-situ IR is relatively simple, and as one can see on the example in Figure S1, the peak corresponding to vibrations of Si-H band disappears with the progress of the reaction and on the basis of data obtained from IR spectroscopy, it easy to determine the conversion of substrate.

Comparing the results of GC and *in situ* IR analysis for all performed reactions we have got to the conclusions that in situ IR is more accurate and faster analytical technique that can be successfully used in the determination of the hydrosilylation reaction progress. The obtained results, of the conversion of Si-H bond in reactions between HMTS and 1-octene, from GC and *in situ* IR were very similar (Figure S2 and Table S1). However for the reactions of HMTS with 3-allyloxy-1,2-propanediol (Figure S3 and Table S2) and allyl glycidyl ether (Figure S4 and Table S3) data obtained from GC was higher than results calculated from IR spectra. Such observation was anticipated by us, as the difference in the observed results from both analytical techniques may come from higher values of the convention of substrates from samples submitted for the GC analysis as a result of longer time the reaction mixture had before being analyzed.

![Graph](image-url)

*Figure S1.* The disappearance of Si-H band with the progress of the reaction (temperature 80°C, concentration of catalyst: 1x10⁻⁴ mol Pt/mol Si-H monitored by *in situ* IR.
Thus, in our opinion, *in-situ* IR is a more precise method of controlling the progress of the reaction due to: (i) no additional analyzes being required to determine the Si-H bond conversion and because (ii) one can obtain the results in real time. In result, we have focused on presenting the results collected from *in situ* IR as we believe this is better reaction monitoring method.
**Figure S2.** Conversion of Si-H bond (at 913 cm$^{-1}$) – comparison data obtained from GC and IR for reaction between HMTS and 1-octene performed at 65°C and with concentration of catalyst $1 \times 10^{-6}$ mol Pt/mol Si-H (■ – data from GC; ○ - data from *in situ* IR).
Table S1. Comparison of data obtained from GC and *in situ* IR (conversion of Si-H bond, in percent) for the reaction between HMTS and 1-octene in batch.

<table>
<thead>
<tr>
<th>T, conc. of the catalyst [°C; mol Pt/mol Si-H]</th>
<th>conversion of Si-H bond [%]</th>
<th>1 min</th>
<th>10 min</th>
<th>20 min</th>
<th>30 min</th>
<th>40 min</th>
<th>50 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GC</td>
<td>IR</td>
<td>GC</td>
<td>IR</td>
<td>GC</td>
<td>IR</td>
<td>GC</td>
</tr>
<tr>
<td>80°C, 1x10⁻⁴</td>
<td></td>
<td>98.1</td>
<td>77.7</td>
<td>98.7</td>
<td>92.6</td>
<td>99.5</td>
<td>96.0</td>
<td>100</td>
</tr>
<tr>
<td>80°C, 1x10⁻⁵</td>
<td></td>
<td>92.8</td>
<td>66.3</td>
<td>96.6</td>
<td>94.3</td>
<td>96.8</td>
<td>96.3</td>
<td>97.1</td>
</tr>
<tr>
<td>80°C, 1x10⁻⁶</td>
<td></td>
<td>41.4</td>
<td>12.5</td>
<td>85.6</td>
<td>73.1</td>
<td>93.5</td>
<td>87.3</td>
<td>96.3</td>
</tr>
<tr>
<td>65°C, 1x10⁻⁴</td>
<td></td>
<td>93.7</td>
<td>69.3</td>
<td>95.9</td>
<td>93.6</td>
<td>97.4</td>
<td>95.7</td>
<td>98.1</td>
</tr>
<tr>
<td>65°C, 1x10⁻⁵</td>
<td></td>
<td>96.6</td>
<td>31.0</td>
<td>96.3</td>
<td>93.4</td>
<td>96.9</td>
<td>95.0</td>
<td>97.5</td>
</tr>
<tr>
<td>65°C, 1x10⁻⁶</td>
<td></td>
<td>34.9</td>
<td>14.8</td>
<td>82.1</td>
<td>74.9</td>
<td>93.6</td>
<td>89.8</td>
<td>95.8</td>
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</table>
Figure S3. Conversion of Si-H bond (at 913 cm$^{-1}$) – comparison data obtained from GC and IR for reaction between HMTS and 3-allyloxy-1,2-propanediol performed at 80°C and with concentration of catalyst 1x10$^{-6}$ mol Pt/mol Si-H (■ – data from GC; ● - data from in situ IR).
Table S2. Comparison of data obtained from GC and *in situ* IR (conversion of Si-H bond, in percent) for the reaction between HMTS and 3-allyloxy-1,2-propanediol in batch.

<table>
<thead>
<tr>
<th>T, conc. of the catalyst [°C; mol Pt/mol Si-H]</th>
<th>1 min</th>
<th>10 min</th>
<th>20 min</th>
<th>30 min</th>
<th>40 min</th>
<th>50 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GC</td>
<td>IR</td>
<td>GC</td>
<td>IR</td>
<td>GC</td>
<td>IR</td>
<td>GC</td>
</tr>
<tr>
<td>80°C, 1x10^-4</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>80°C, 1x10^-5</td>
<td>95.3</td>
<td>0.1</td>
<td>60.2</td>
<td>76.0</td>
<td>100</td>
<td>87.9</td>
<td>100</td>
</tr>
<tr>
<td>80°C, 1x10^-6</td>
<td>3.4</td>
<td>0.0</td>
<td>5.3</td>
<td>4.5</td>
<td>11.4</td>
<td>4.7</td>
<td>11.5</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65°C, 1x10^-4</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>65°C, 1x10^-5</td>
<td>88.8</td>
<td>0.2</td>
<td>94.4</td>
<td>55.4</td>
<td>100</td>
<td>71.0</td>
<td>100</td>
</tr>
<tr>
<td>65°C, 1x10^-6</td>
<td>0</td>
<td>0</td>
<td>5.5</td>
<td>0.2</td>
<td>5.7</td>
<td>0.2</td>
<td>5.8</td>
</tr>
</tbody>
</table>
Figure S4. Conversion of Si-H bond (at 913 cm$^{-1}$) – comparison data obtained from GC and IR for reaction HMTS and allyl glycylid ether performed at 65°C and with concentration of catalyst 1x10$^{-5}$ mol Pt/mol Si-H (■ = data from GC; ○ = data from in situ IR).
Table S3. Comparison of data obtained from GC and *in situ* IR (conversion of Si-H bond, in percent) for the reaction between HMTS and allyl glycidyl ether in batch.

<table>
<thead>
<tr>
<th>T, conc. of the catalyst [°C; mol Pt/mol Si-H]</th>
<th>conversion of Si-H bond [%]</th>
<th>1 min</th>
<th>10 min</th>
<th>20 min</th>
<th>30 min</th>
<th>40 min</th>
<th>50 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GC</td>
<td>IR</td>
<td>GC</td>
<td>IR</td>
<td>GC</td>
<td>IR</td>
<td>GC</td>
<td>IR</td>
</tr>
<tr>
<td>80°C, 1x10^{-4}</td>
<td>90.2</td>
<td>0.6</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>80°C, 1x10^{-5}</td>
<td>7.5</td>
<td>0</td>
<td>15.7</td>
<td>9.8</td>
<td>19.8</td>
<td>13.2</td>
<td>21.1</td>
<td>15.5</td>
</tr>
<tr>
<td>80°C, 1x10^{-6}</td>
<td>~2</td>
<td>0</td>
<td>~2</td>
<td>1.1</td>
<td>~2</td>
<td>1.4</td>
<td>~2</td>
<td>1.7</td>
</tr>
<tr>
<td>65°C, 1x10^{-4}</td>
<td>90.4</td>
<td>0.9</td>
<td>92.1</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>65°C, 1x10^{-5}</td>
<td>10.4</td>
<td>0.2</td>
<td>11.5</td>
<td>8.2</td>
<td>12.5</td>
<td>11.3</td>
<td>17.3</td>
<td>14.2</td>
</tr>
<tr>
<td>65°C, 1x10^{-6}</td>
<td>~1</td>
<td>0</td>
<td>~1</td>
<td>0.9</td>
<td>~1</td>
<td>1.1</td>
<td>~1</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Table S4. Experimental conditions in microreactor system (1.4 volume) including flow rates of HMTS and olefins in different residence time.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.510:0.890</td>
<td>0.440:0.960</td>
<td>0.430:0.970</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>0.044:0.096</td>
<td>0.043:0.097</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>0.022:0.048</td>
<td>0.022:0.049</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>0.015:0.032</td>
<td>0.014:0.032</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>0.011:0.024</td>
<td>0.011:0.024</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>0.009:0.019</td>
<td>0.086:0.019</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>0.007:0.016</td>
<td>0.007:0.016</td>
</tr>
</tbody>
</table>

Table S5. Experimental conditions in microreactor system (3 ml volume) including flow rates of HMTS and olefins in different residence time.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.100:1.900</td>
<td>0.940:2.060</td>
<td>0.910:2.090</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>0.094:0.206</td>
<td>0.091:0.209</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>0.047:0.103</td>
<td>0.046:0.105</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>0.031:0.069</td>
<td>0.030:0.070</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>0.024:0.052</td>
<td>0.023:0.052</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>0.019:0.041</td>
<td>0.018:0.042</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>0.016:0.034</td>
<td>0.0150.035</td>
</tr>
</tbody>
</table>

Table S6. Experimental conditions in microreactor system (6 ml volume) including flow rates of HMTS and olefins in different residence time.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.200:3.800</td>
<td>1.880:4.120</td>
<td>1.820:4.180</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>0.188:0.412</td>
<td>0.182:0.418</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>0.094:0.206</td>
<td>0.091:0.209</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>0.063:0.137</td>
<td>0.061:0.139</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>0.047:0.103</td>
<td>0.046:0.105</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>0.038:0.082</td>
<td>0.036:0.084</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>0.031:0.069</td>
<td>0.050:0.070</td>
</tr>
</tbody>
</table>
Table S7. Experimental conditions in microreactor system (9 ml volume) including flow rates of HMTS and olefins in different residence time.

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-</td>
<td>0.282:0.618</td>
<td>0.273:0.627</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>0.141:0.309</td>
<td>0.138:0.315</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>0.093:0.207</td>
<td>0.090:0.210</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>0.072:0.156</td>
<td>0.069:0.156</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>0.057:0.123</td>
<td>0.054:0.126</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>0.048:0.102</td>
<td>0.045:0.105</td>
</tr>
</tbody>
</table>

Table S8. Experimental conditions in microreactor system (12 ml volume) including flow rates of HMTS and olefins in different residence time.

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>3.760:8.240</td>
<td>3.640:8.360</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>0.376:0.824</td>
<td>0.364:0.836</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>0.188:0.412</td>
<td>0.182:0.418</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>0.126:0.274</td>
<td>0.122:0.178</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>0.094:0.206</td>
<td>0.092:0.210</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>0.076:0.164</td>
<td>0.072:0.168</td>
</tr>
<tr>
<td>60</td>
<td>-</td>
<td>0.62:0.138</td>
<td>0.60:0.140</td>
</tr>
</tbody>
</table>