Supplementary Information For

Enhanced Photothermal Reduction of Gaseous CO$_2$ over Silicon Photonic Crystal Supported Ruthenium at Ambient Temperature


Prof. P. G. O'Brien
Department of Mechanical Engineering, Lassonde School of Engineering
York University
4700 Keele Street, Toronto, Ontario, M3J 1P3, Canada

Dr. K. K. Ghuman,
International Institute for Carbon Neutral Research
Kyushu University
744 Motooka, Nishi-ku, Fukuoka, 819-0395, Japan

Dr. A. A. Jelle, Prof. D. D. Perovic, Prof. C. V. Singh, Prof. N. P. Kherani
Department of Materials Science and Engineering
University of Toronto
184 College Street, Toronto, Ontario, M5S 3E4, Canada

A. Sandhel, Dr. Jia Jia, Prof. G. A. Ozin
Department of Chemistry
University of Toronto
80 St. George St., Toronto, Ontario, M5S 3H6, Canada
Email: gozin@chem.utoronto.ca

Dr. T. E. Woods, Prof. C. A. Mims
Department of Chemical Engineering and Applied Chemistry
University of Toronto
200 College St., Toronto, Ontario, M5S 3E5, Canada

J. Y. Y. Loh, Prof. N. P. Kherani
Department of Electrical and Computer Engineering,
University of Toronto
10 King's College Road, Toronto, Ontario, M5S 3G4, Canada
Figure S1 SEM images of the Ru/SiO$_2$-o sample at (a) 4.9k, (b) 100k, and (c) 450k magnification, and of the Ru/i-Si-o sample at (d) 5k, (e) 300k, and (f) 600k magnification
Figure S2 Temperature profiles for reactions carried out under solar-simulated radiation from a 300 W Xe lamp at an intensity of 2,470 mW/cm$^2$ (24.7 Suns). When the lamp is turned on at the ~0.25 h point the temperature of the Ru/i-Si-o and Ru/SiO$_2$-o catalysts quickly increase to over 130 °C. The temperatures of these catalysts continue to rise at a slower rate and reaches ~150 °C at the 2 h point when the light is switched off. It should be noted that the thermocouple used for these measurements is located on the rear side of the silicon wafer that the photonic crystals are deposited on (the side that is opposite from the side with the photonic crystals and supported Ru). The actual temperature of the supported Ru is expected to be significantly greater than 150°C during photomethanation reactions. The temperature of the bare reactor, measured without a catalyst present and with the thermocouple placed out of the path of the incident light from the Xe lamp, did not exceed 50 °C after 2.5 h (black line).
Figure S3 Comparison of the XPS (a) Ru3d and (b) O1s peaks for the Ru/SiO$_2$-o (blue lines) and Ru/i-Si-o (red lines) measured before (dashed lines) and after (solid lines) the Sabatier reaction rate tests were performed.

The binding energy of the Ru3d$^{3/2}$ peak is in the vicinity of 284.5 eV, and the binding energy of the Ru3d$^{5/2}$ peak is closer to 280.5 eV. More specifically, the 3d$^{5/2}$ peak for metallic Ru lies between 279.96 eV and 280.3 eV, while the binding energy for ruthenium dioxide lies between 280.68 eV and 281.0 eV.[s1] The Ru3d$^{5/2}$ binding energy peak position for the Ru/SiO$_2$-o sample is located at 280.3 eV before and after the Sabatier reaction rate tests were performed, indicating the sputtered Ru is metallic. On the other hand, the Ru3d$^{5/2}$ binding energy peak position for the Ru/i-Si-o sample shifts from 280.3 eV before the reaction to 280.0 eV after the reaction. This indicates that under reaction conditions, in an H$_2$ environment under high intensity illumination, the Ru/i-Si-o sample is in a highly reduced state.

The Ru/SiO$_2$-o and Ru/i-Si-o samples exhibit a broad peak associated with ruthenium oxide (529.45 eV) and ruthenium hydroxide (530.75 eV) before testing. However, after the Sabatier reaction tests were run these intensity of these peaks diminishes while another peak located at approximately 532.4 eV arises, which can be attributed to adsorbed C/O species. [s2]
Figure S4 The ion mass 17 peak for photomethanation experiments carried out over the Ru/i-Si-o catalyst under solar simulated radiation produced from a 300 W Xe lamp with an intensity of 2,470 mW/cm² (24.7 Suns). These ion mass 17 peaks were acquired using an Agilent 7890A gas chromatographic mass spectrometer.

Figure S5 (a) photograph of custom built photoreactor set-up including a (i) stainless-steel batch reactor, (ii) Xe lamp, and (iii) $^{13}$CO$_2$ tank. (b) Photograph of the stainless-steel batch reactor including (i) gas inlet lines, (ii) heating band, (iii) thermocouple, (iv) pressure transducer, and (v) gas outlet line.
Table S1 Calculated bond lengths, Bader charges, and binding energies of adsorbed H$_2$ on neutral and charged Ru(0001) surfaces

<table>
<thead>
<tr>
<th>Surface charge</th>
<th>Bond length (Å)</th>
<th>Bader charge (e)</th>
<th>Binding energy, E$_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H1-Ru</td>
<td>H2-Ru</td>
<td>H1</td>
</tr>
<tr>
<td>[Ru(0001)]$^{-1.0}$</td>
<td>1.66</td>
<td>1.66</td>
<td>-1.36</td>
</tr>
<tr>
<td>[Ru(0001)]</td>
<td>-</td>
<td>-</td>
<td>-0.97</td>
</tr>
<tr>
<td>[Ru(0001)]$^{+1.0}$</td>
<td>1.76</td>
<td>1.76</td>
<td>-0.99</td>
</tr>
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References
