Supporting Information

How to control selectivity in alkane oxidation?

Xuan Li,¹,² Detre Teschner,¹,³ Verena Streibel,¹ Thomas Lunkenbein,¹ Liudmyla Masliuk,¹
Teng Fu,¹ Yuanqing Wang,¹,² Travis Jones,¹ Friedrich Seitz,¹ Frank Girmsdies,¹
Frank Rosowski,²,⁴ Robert Schlögl,¹,³ Annette Trunschke¹,*

¹Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195
Berlin, Germany

²UniCat-BASF Joint Lab, Technische Universität Berlin, Sekr. EW K 01, Hardenbergstraße 36, 10623 Berlin,
Germany

³Department of Heterogeneous Reactions, Max-Planck-Institut für Chemische Energiekonversion, Stiftstraße 34-36,
45470 Mülheim a. d. Ruhr, Germany

⁴BASF SE, Process Research and Chemical Engineering, Heterogeneous Catalysis, Carl-Bosch-Straße 38, 67056
Ludwigshafen, Germany

kobelinxju@gmail.com
teschner@fhi-berlin.mpg.de
streibel@stanford.edu
lunkenbein@fhi-berlin.mpg.de
liumasliuk@fhi-berlin.mpg.de
teng@fhi-berlin.mpg.de
yqwang@fhi-berlin.mpg.de
trjones@fhi-berlin.mpg.de
seitzfr@fhi-berlin.mpg.de
girgsdie@fhi-berlin.mpg.de
frank.rosowski@basf.com
acs@fhi-berlin.mpg.de
trunschke@fhi-berlin.mpg.de
Supporting information

Figure S1. XRD patterns and results of Rietveld refinement exemplarily shown for pH6.3@12h with short rod-like particles (AR=1.5) (top) and pH9.9@12h with elongated rod-like particles (AR=5.1) (bottom).

Figure S2. XRD patterns of used catalysts (see Table S1 for results of refinement).
Table S1. Crystallite size and aspect ratio calculated from anisotropic fitting in Rietveld refinement of the XRD patterns

<table>
<thead>
<tr>
<th></th>
<th>as synthesized</th>
<th>aspect ratio</th>
<th>after catalysis</th>
<th>aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH6.3@12h</td>
<td>27.5</td>
<td>28.1</td>
<td>40.8</td>
<td>1.0</td>
</tr>
<tr>
<td>pH6.7@12h</td>
<td>27.8</td>
<td>27.1</td>
<td>46.2</td>
<td>1.0</td>
</tr>
<tr>
<td>pH8.0@12h</td>
<td>28.7</td>
<td>25.4</td>
<td>66.1</td>
<td>1.1</td>
</tr>
<tr>
<td>pH9.1@12h</td>
<td>26.6</td>
<td>21.3</td>
<td>53.6</td>
<td>1.2</td>
</tr>
<tr>
<td>pH9.9@12h</td>
<td>23.9</td>
<td>17.5</td>
<td>58.1</td>
<td>1.4</td>
</tr>
<tr>
<td>pH9.9@24h</td>
<td>22.5</td>
<td>18.6</td>
<td>49.9</td>
<td>1.2</td>
</tr>
<tr>
<td>pH9.9@48h</td>
<td>23.3</td>
<td>21.8</td>
<td>47.5</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Figure S3. Intensity of the main peak at 3366 cm$^{-1}$ in the infrared spectra in Figure 9 (main text) as a function of the Mn/W ratio determined by XPS (Table 2 in the main text).
Figure S4. Profiles of temperature-programmed oxidation after thermal pre-treatment of the catalysts in Ar at T=673 K.

Figure S5. Initial consumption rate of propane as a function of oxygen defect concentration measured by temperature-programmed oxidation (Figure S4, Table 2 in the main text).

Table S2. Intensity of NEXAFS Mn L\textsubscript{2,3} edges in TEY mode (Fig. 12 in the main text)

<table>
<thead>
<tr>
<th>Intensity /a.u.</th>
<th>(I_{L_3}) at 640.0 eV</th>
<th>(I_{L_2}) at 652.3 eV</th>
<th>Branching ratio of (L_3/L_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH6.3@12h</td>
<td>8.39</td>
<td>2.03</td>
<td>4.13</td>
</tr>
<tr>
<td>pH9.9@12h</td>
<td>8.03</td>
<td>2.02</td>
<td>3.98</td>
</tr>
</tbody>
</table>
Figure S6. FT-IR spectra of the catalyst pH9.9@12h at 673 K at a flow rate of 5 ml/min, temperature of 673 K and gas composition as described in the legend.