Electronic Supplementary Information

Halogen type as a selectivity switch in catalysed alkane oxyhalogenation

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Table S1. Fitting parameters of $^{151}$Eu Mössbauer spectroscopic measurements at 78 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>Oxidation state</th>
<th>$\delta$ / mm s$^{-1}$ $^a$</th>
<th>$\Delta E_Q$ / mm s$^{-1}$ $^b$</th>
<th>$\Gamma$ / mm s$^{-1}$ $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$_2$O$_3$</td>
<td>Precursor</td>
<td>Eu$^{3+}$</td>
<td>0.88 (2)</td>
<td>−3.50 (2)</td>
<td>3.10 (1)</td>
</tr>
<tr>
<td></td>
<td>Fresh</td>
<td>Eu$^{3+}$</td>
<td>0.62 (2)</td>
<td>2.50 (2)</td>
<td>2.64 (9)</td>
</tr>
<tr>
<td>EuOCl</td>
<td>EOC</td>
<td>Eu$^{3+}$</td>
<td>0.78 (1)</td>
<td>1.50 (2)</td>
<td>2.70*</td>
</tr>
<tr>
<td></td>
<td>POC</td>
<td>Eu$^{3+}$</td>
<td>0.65 (1)</td>
<td>2.10 (2)</td>
<td>2.84 (6)</td>
</tr>
<tr>
<td>EuOBr</td>
<td>Fresh</td>
<td>Eu$^{3+}$</td>
<td>0.81 (2)</td>
<td>2.50 (3)</td>
<td>2.70 (1)</td>
</tr>
<tr>
<td></td>
<td>EOB</td>
<td>Eu$^{3+}$</td>
<td>0.79 (2)</td>
<td>2.70 (2)</td>
<td>2.50 (1)</td>
</tr>
<tr>
<td></td>
<td>POB</td>
<td>82% Eu$^{3+}$</td>
<td>0.63 (1)</td>
<td>2.90 (1)</td>
<td>2.49 (7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18% Eu$^{2+}$</td>
<td>−13.93 (8)</td>
<td>4.70 (4)</td>
<td>2.70*</td>
</tr>
</tbody>
</table>

$^a$ isomer shift; $^b$ electric quadrupole splitting; $^c$ experimental line width; * parameters kept fixed during fitting; the standard deviation for each parameter is shown in brackets.
Fig. S1 Temperature-programmed reduction with $\text{H}_2$ of the fresh $\text{EuOCl}$ and $\text{EuOBr}$ catalysts.
Fig. S2 Selectivity to product $j$ as a function of the alkane conversion in the oxychlorination of a) ethane and b) propane and in the oxybromination of c) ethane and d) propane over the catalysts. The selectivity to the olefin and to the alkyl halide is shown in Figure 1 of the main manuscript. The dotted grey lines denote the yield of product $j$ and the different symbols refer to the reaction temperature.
Fig. S3 Selectivity to product $j$ as a function of the ethane conversion in the oxybromination of ethane over CeO$_2$. The dotted grey lines denote the yield of product $j$ and the different symbols refer to the reaction temperature.
Fig. S4 Selectivity to product $j$ as a function of the propane conversion in the a) oxychlorination and b) oxybromination of propane over CeO$_2$. The dashed grey lines denote the yield of product $j$ and the different symbols refer to the reaction temperature.
Fig. S5 High-resolution transmission electron micrographs of the fresh EuOCl catalyst and after the oxychlorination of ethane (EOC) and propane (POC).
**Fig. S6** High-resolution transmission electron micrographs of the fresh EuOBr catalyst and after the oxybromination of ethane (EOB) and propane (POB).
Fig. S7 a) O 1s and b) C 1s core level spectra of the EuOCl and EuOBr catalysts after ethane oxychlorination (EOC) and oxybromination (EOB), respectively. The solid, dashed, and dotted lines represent the raw data, background, and fits of the different contributions, respectively.
Fig. S8 Selectivity to product $j$ as a function of the alkane conversion in the oxidative dehydrogenation of ethane (a, b) and propane (c, d) over the catalysts. The dotted grey lines denote the yield of product $j$ and the different symbols refer to the reaction temperature.
Fig. S9 Reagent conversion and product selectivity in the gas-phase chlorination of a) ethane and b) propane and in the bromination of c) ethane and d) propane.
Fig. S10 Arrhenius plots of the different reactions investigated in this study.
Fig. S11 Selectivity to product $j$ as a function of the alkyl halide conversion in the dehydrochlorination of a) $\text{C}_2\text{H}_5\text{Cl}$ and b) $\text{C}_3\text{H}_7\text{Cl}$ and in the dehydrobromination of c) $\text{C}_2\text{H}_5\text{Br}$ and d) $\text{C}_3\text{H}_7\text{Br}$ over the catalysts (solid symbols) and over inert quartz particles (open symbols). The dotted grey lines denote the yield of product $j$ and the different symbols refer to the reaction temperature.
**Fig. S12** Selectivity to product $j$ as a function of the alkyl halide conversion in the dehydrochlorination of a) $\text{C}_2\text{H}_5\text{Cl}$ and b) $\text{C}_3\text{H}_7\text{Cl}$ and in the dehydrobromination of c) $\text{C}_2\text{H}_5\text{Br}$ and d) $\text{C}_3\text{H}_7\text{Br}$ over the catalysts in the presence of $\text{HX}$ and $\text{O}_2$. The dotted grey lines denote the yield of product $j$ and the different symbols refer to the reaction temperature.
Fig. S13 Selectivity to product $j$ as a function of the alkyl halide conversion in the dehydrochlorination of C$_2$H$_5$Cl over EuOCl in the presence of O$_2$. The dotted grey lines denote the yield of product $j$ and the different symbols refer to the reaction temperature.
**Fig. S14** Selectivity to carbon oxides as a function of the olefin conversion in the oxidation of a, b) \( \text{C}_2\text{H}_4 \) and c, d) \( \text{C}_3\text{H}_6 \) over the catalysts. The dotted grey lines denote the yield of product \( j \) and the different symbols refer to the reaction temperature.