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Supplementary Material:

Surface-active ionic liquids in catalytic water splitting

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Contents

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1 Reaction profiles

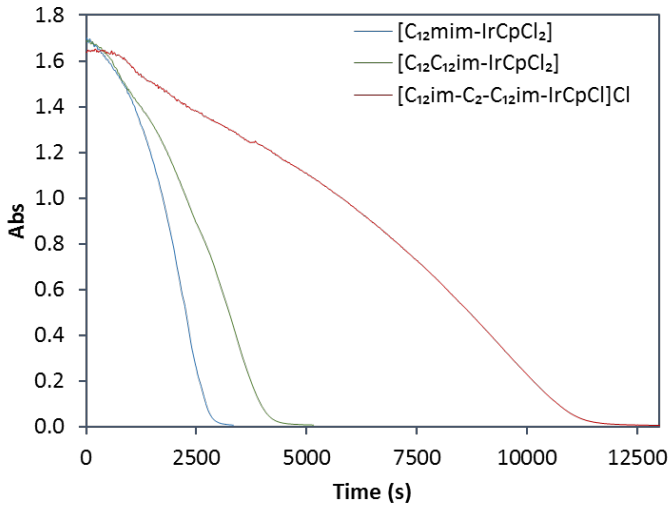

Figure S1 Representative kinetic profiles for the three new catalysts at concentration of $2\,\mu$M and CAN $3\,$mM in HNO_3 $0.1\,$M

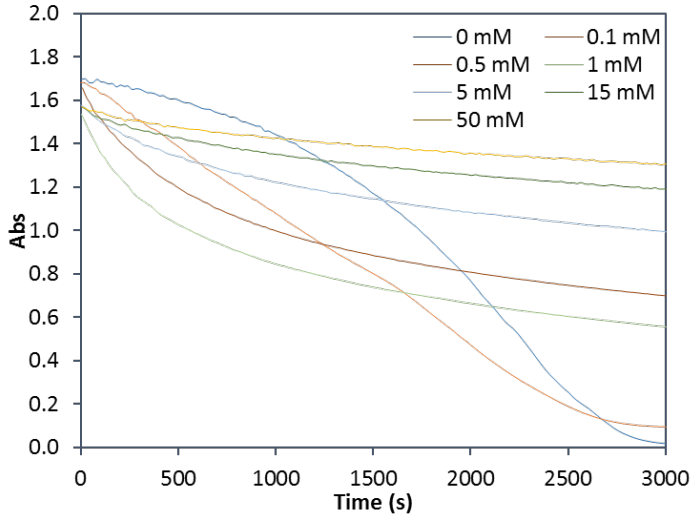

Figure S2 Reaction profiles for catalyst **2** $2\,\mu$M and CAN $3\,$mM with different concentrations of additional $[C_{12}mim]Cl$ in HNO_3 $0.1\,$M

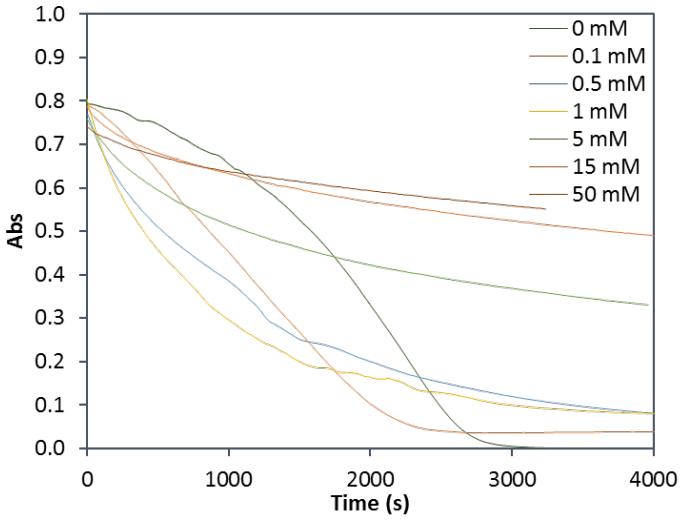

Figure S3 Reaction profiles for catalyst **2** $2\,\mu$M and CAN 1.5 mM with different concentrations of additional [C_{12}mim]Cl in HNO_3 0.1 M

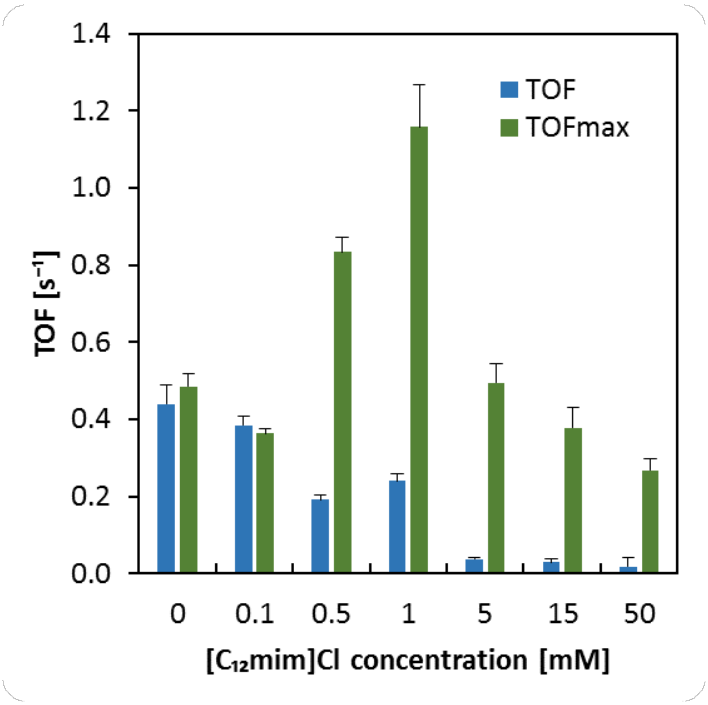

Figure S4 $TOF_{\langle t \rangle}$ and $TOF_{\max}$ for catalyst **2** $2\,\mu$M and CAN 1.5 mM with different concentrations of additional [C_{12}mim]Cl in HNO_3 0.1 M

2 Reaction kinetics

We assume that the depletion of the Ce^{4+} can be described by

$$[Ce^{4+}](t) = a_1 e^{-k_1 t} + \frac{a_2}{(1-b_2)+b_2 e^{k_2 t}} \tag{S1}$$

with the initial absorbance $a_0 = a_1 + a_2$. The first part on the right hand side is a first order reaction. The second part stems from an autocatalyzed reaction. a_1 and a_2 are the relative importance of the two processes. If, for example, a_1 is almost a_0, then the overall reaction follows first order, if a_2 is almost a_0 the reaction is determined by the autocatalyzed process. k_1 and k_2 are the corresponding rate constants in Hz. The parameter b_2 describes the position of the turn point of the logistic function.

Eq. (S1) can be reformulated

$$a_1 e^{-k_1 t} + \frac{a_2}{(1-b_2)+b_2 e^{k_2 t}} = a_1 e^{-k_1 t} + \frac{\tilde{a}_2}{1+e^{k_2 (t-t_0)}} \tag{S2}$$

using $\tilde{a}_2 = a_2/(1-b_2)$ and $t_0 = \ln\Big((1-b_2)/b_2\Big)$. Here, t_0 corresponds to the time when half of the second process had taken place.

2.1 Rationalization

A first order reaction can be described by

$$-\frac{d[Ce^{4+}]}{dt} = k_1 [Ce^{4+}]. \tag{S3}$$

Solving this differential equation yields the first part of Eq. (S1).

In principle, the differential equation of the pure autocatalytic part looks like

$$-\frac{d[Ce^{4+}]}{dt} = k'[Ce^{4+}] + k''[Ce^{4+}]\left([Ce^{4+}]_0 - [Ce^{4+}]\right) \tag{S4}$$

resulting in

$$[Ce^{4+}](t) = \frac{[Ce^{4+}]_0([Ce^{4+}]_0 \cdot k'' + k')}{k' e^{([Ce^{4+}]_0 k'' + k')t} + [Ce^{4+}]_0 k''} \tag{S5}$$

Substituing $k_2 = [Ce^{4+}]_0 k'' + k'$ and $k' = k_2 \cdot b_2$ one yields

$$[Ce^{4+}](t) = \frac{[Ce^{4+}]_0}{1-b_2+b_2 e^{k_2 t}} \tag{S6}$$

which is similar to the logistic function of Eq. (S1).

2.2 Turn over frequency of the autocatalyzed reaction

The time-dependent concentration of the product, [Ce^3](t), should be [Ce^{4+}]$_0$−[Ce^{4+}](t). Consequently, the rate $r(t)$ of Ce^{3+}-production is

$$r(t) = \frac{d[Ce^{3+}]}{dt} \simeq \frac{[Ce^{4+}]_0}{a_0} \cdot \frac{a_2 \cdot k_2 \cdot b_2 e^{k_2 t}}{(1-b_2+b_2 e^{k_2 t})^2} \tag{S7}$$

neglecting the first order reaction. The maximum rate r is reached at

$$t_{max} = \frac{\ln(1-b_2) - \ln(b_2)}{k_2} \tag{S8}$$

As a result, the maximum turn-over-frequency

$$TOF = \frac{r(t_{max})}{[cat]} = \frac{a_2 \cdot k_2 \cdot [Ce^{4+}]_0}{4(1-b_2) \cdot a_0 \cdot [cat]} \tag{S9}$$

2.3 Turn over frequency of the first order reaction

In the rare case, that the depletion of [Ce^{4+}] follows a first order reaction without the autocatalyzed process, i.e. $a_1 \simeq a_0$ and

$$r(t) = \frac{d[Ce^{3+}]}{dt} \simeq \frac{[Ce^{4+}]_0}{a_0} a_1 \cdot k_1 \cdot e^{-k_1 t}, \tag{S10}$$

the turn-over-frequency has its maximum value at $t = 0$:

$$TOF = \frac{[Ce^{4+}]_0 \cdot a_1 \cdot k_1}{[cat] \cdot a_0} \tag{S11}$$

The last value can also be gained from a Taylor-series expansion of the [Ce^{3+}](t)

$$\begin{aligned}
[Ce^{3+}] &= [Ce^{4+}]_0(1-\frac{a_1}{a_0}e^{-k_1 t}) && \text{(S12)}\\
&= [Ce^{4+}]_0(1-e^{-k_1 t}) && \text{(S13)}\\
&\simeq [Ce^{4+}]_0\left(1-(1-k_1 t+\ldots)\right) && \text{(S14)}\\
&\simeq [Ce^{4+}]_0 \cdot k_1 \cdot t && \text{(S15)}
\end{aligned}$$

since $a_1 = a_0$ is the initial assumption of this rare case. The slope of Eq. (S15) is $[Ce^{4+}]_0 \cdot k_1$ which has to be divided by [cat] to get the turn-over-frequency.

2.4 Mean reaction time

Since the maximum TOF might not be appropriate to characterize the efficiency of a catalyst in a chemical reaction as the time spent at the maximum TOF level does not enter the efficiency considerations. A lower maximum TOF level mantained over a longer period of time may result in a faster reaction overall.

As alternative property to characterize the promotion of the chemical reaction due to the catalyst or reaction conditions, one may look at the average reaction time

$$\langle t\rangle = \int_0^\infty \frac{[Ce^{4+}](t)}{[Ce^{4+}](0)}dt \qquad \text{(S16)}$$

Here, $[Ce^{4+}](t)$ is the time-dependant concentration of Ce^{4+} and $[Ce^{4+}](0)$ its initial value. Integrating eq. (S1) yields

$$\langle t\rangle = \frac{1}{a_1+a_2}\left[a_2\frac{\ln(b_2(e^{k_2 t}-1)+1)-k_2 t}{(b_2-1)k_2} - \frac{a_1 e^{-k_1 t}}{k_1}\right]_0^\infty \qquad \text{(S17)}$$

For longer times t the first part of the right hand side can be simplified to $a_2 \ln b_2/\big((b_2-1)k_2\big)$. As result, eq. (S17) is

$$\langle t\rangle = \frac{\frac{a_2 \ln b_2}{(b_2-1)k_2}+\frac{a_1}{k_1}}{a_1+a_2} \qquad \text{(S18)}$$

The turn-over-frequency at the mean reaction time is

$$TOF\left(\langle t\rangle\right) = \frac{[Ce^{4+}]_0}{(a_1+a_2)[cat]}\cdot\left(a_1 k_1 e^{-k_1\langle t\rangle} + \frac{a_2 b_2 k_2 e^{k_2\langle t\rangle}}{\left(1-b_2+b_2 e^{k_2\langle t\rangle}\right)^2}\right) \qquad \text{(S19)}$$

3 SAXS measurements

SAXS measurements were performed using a Bruker Nanostar (Bruker AXS) equipped with microfocus X-ray source (Incoatec ImS High Brilliance) with CuK_α radiation with a wavelength of 0.1542 nm, a pinhole camera and a 2D-position sensitive detector (Vantec 2000). The samples were filled into glass capillaries (1.5 mm diameter, 10 μm wall thickness, from Hilgenberg). Scattering patterns were recorded for 6 hours, azimuthally integrated and corrected for background scattering from the capillary. The integrated intensity is shown in Fig. S5 in dependence on the scattering vector $q=(4\pi/\lambda)\ \sin\Theta$, with 2Θ being the scattering angle (black line). The red line is a fit with a core-shell model as in ref. 25 of the paper. Additionally, a power-law term was added to describe the strong intensity increase towards low q-values. The fit results in a core radius of 0.75 nm, a shell thickness of 2.1 nm and a value of 0.035 for the scaled medium contrast γ.

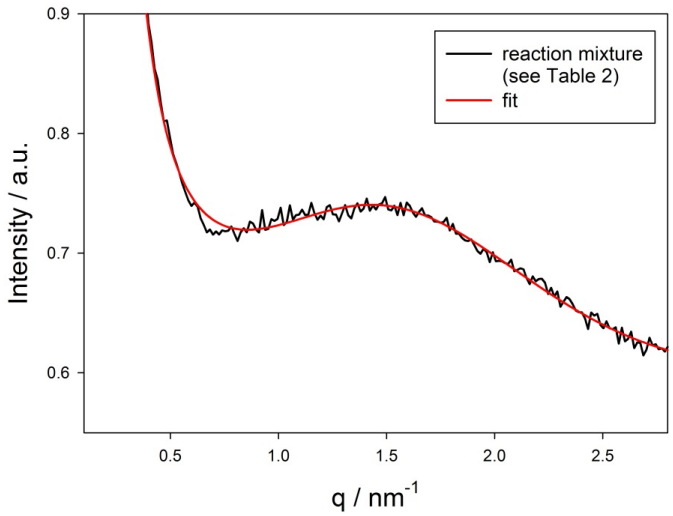

Figure S5 SAXS intensity for the reaction mixture (as described in Table 2 of the paper), black line, together with fit from the core-shell model, red line

4 Ionic liquid stability

Stability experiments were done in 10 mL screw cap vials equipped with magnetic stirrer and thermostat at 25° C. 20 μl of stock solution in acetonitrile of the catalyst 2 were added to 2 ml of HNO_3 0.1 M Milli-Q water solution containing 50 μM of C_{12}mim-Cl. Afterwards 1 ml of freshly prepared cerium ammonium nitrite stock solution in HNO_3 0.1 M in Milli-Q water and 1 ml of HNO_3 0.1 M in Milli-Q water were added to the vials, respectively. After one hour, the aqueous phases were extracted with dichloromethane 5 times. The combined organic phases were dried on Na_2SO_4, filtered, and evaporated in vacuo. The ionic liquid stability against oxidation was proven by comparing the ^{1}H NMR spectra of the two reactions.

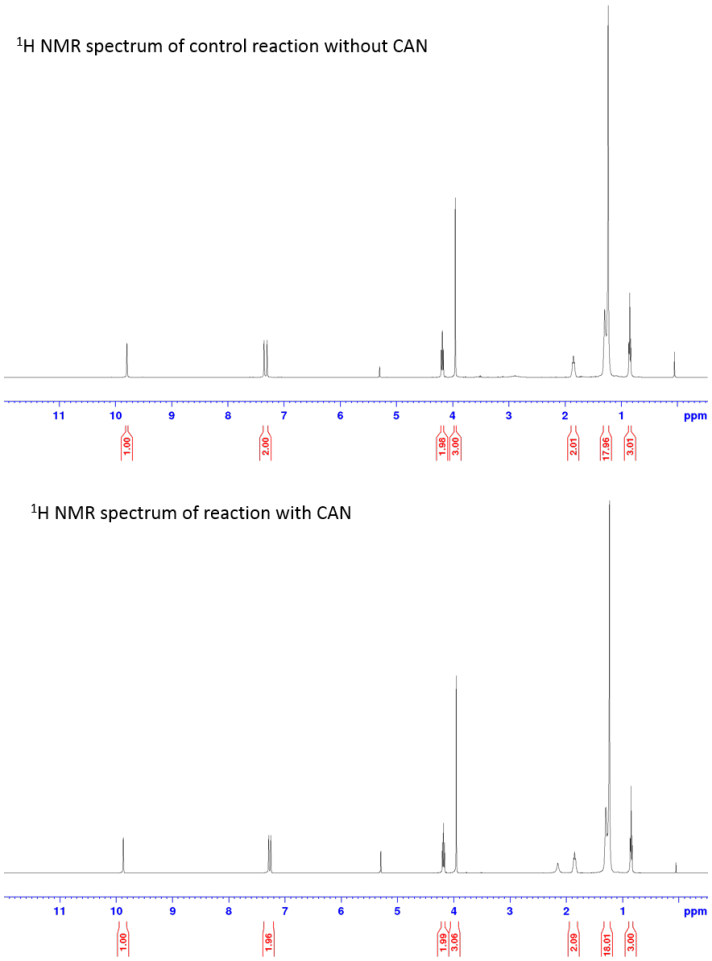

Figure S6 Proof of ionic liquid stability under oxidative conditions