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Properties of negatively charged ruthenium clusters in molten sodium chloride

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Abstract

Negatively charged ruthenium clusters dispersed in molten NaCl are studied with density functional theory and molecular dynamics. The Ru clusters are charged by adding additional Na atoms to the molten salt. We consider Ru_6^{m-} and $2\text{Ru}_3^{m/2-}$ clusters ($m = 0, 2, 4$) and investigate the importance of size, charge, and molten NaCl electrolyte on the stability of the small Ru clusters. Generally, the Ru clusters are not stable in the few atom limit compared to Ru atoms in bulk metallic Ru. However, charging the clusters, increasing their size, and solvating them in molten NaCl reduces the energy cost substantially. Neutral Ru_6 suspended in NaCl is relatively unreactive towards N_2 adsorption, but when charged, the clusters are predicted to be very active for both molecular and dissociative N_2 adsorption.

1. Introduction

Metal nanoparticles suspended in molten salt media^{1–3} can be obtained by reducing their corresponding cations (as halides or oxides) in a mixture with a non-reducible molten salt using hydrogen gas,⁴ or an alkali metal.^{5–7} The reduction potential of alkali metal dissolved in molten alkali halide salts is so large that the alkali atoms ionize to alkali ions and solvated electrons.^{8–11} Consequently, it may be possible to obtain negatively charged metal nanoparticles suspended in molten alkali halide salts by adding alkali metals to a molten salt that already contains metal nanoparticles in oxidation state 0. To our knowledge this has not been explored experimentally.

Such negatively charged metal particles could potentially function as a Lewis base catalyst and be useful in industrial applications.¹² Base catalysts facilitate the formation of negative ion intermediates.¹³ Heterogeneous base catalysts often work by donating electrons to intermediates adsorbed on the surface, and one way to modify the activity is to charge the catalyst particles and thereby affect their ability to donate electrons. Examples are zeolites doped with alkali metal,^{14,15} supported metal clusters promoted with alkali metal,^{16,17} and metal clusters supported on electrides¹⁸ (i.e. salts where electrons serve as anions).

In this study we use *ab initio* molecular dynamics (AIMD) to investigate the stability of negatively charged ruthenium clusters in molten sodium chloride and their ability to stabilize negatively charged adsorbates/intermediates. The study builds on a recent study from our group, where the reactivity of solvated electrons was investigated in molten alkali chloride.¹⁹ When we add the Ru clusters to the molten NaCl containing solvated electrons, the electrons move to and negatively charge the Ru clusters. We specifically study Ru₃ and Ru₆ clusters in molten NaCl containing $m=0, 2$, and 4 solvated electrons ($m e^-(\text{solvated}) + m \text{Na}^+ + 45 \text{NaCl}$), which result in charged cluster systems of the form Ru_{*n*}^{*m*-} + $m \text{Na}^+ + 45 \text{NaCl}$. In this way, we construct four

cases with Ru clusters of different charges and sizes, namely: (i) $\text{Ru}_6 + 45\text{NaCl}$, (ii) $\text{Ru}_6^{2-} + 2\text{Na}^+ + 45\text{NaCl}$, (iii) $\text{Ru}_6^{4-} + 4\text{Na}^+ + 45\text{NaCl}$, and (iv) $\text{Ru}_3^{2-} + 2\text{Na}^+ + 45\text{NaCl}$. The Ru_6^{m-} clusters in system (i), (ii), and (iii) are compared to $2\text{Ru}_3^{m/2-}$ to gain insight into the stability of clusters with different sizes and charges. N_2 adsorption on all four clusters is used to probe the reactivity of the clusters.

We find that the Ru clusters with three or six atoms are not stable compared to Ru metal. This is understandable as ruthenium metal has a high cohesive energy.²⁰ However, Ru_6 is roughly the largest clusters we can investigate with AIMD, when we want the cluster to be solvated in the molten salt. Nevertheless, the stability is affected by molten NaCl, the cluster charge, and its size. This insight will be useful when attempting to synthesize negatively charged Ru clusters in the nanometer range. It is also possible that very small Ru clusters will be kinetically stable against agglomeration because of their own negative charge or the charge of their solvation shell.

In the gas phase, the adsorption energy of a N_2 molecule to a Ru_6 cluster is similar to adsorption at step sites on the $\text{Ru}(0001)$ surface. When the Ru_6 cluster is moved from the gas phase to the molten NaCl, it loses most of its reactivity, but becomes reactive again when it becomes negatively charged. A scaling relation exists between the molecular adsorption and dissociative adsorption energies of N_2 which holds for Ru clusters in the gas phase, Ru clusters in molten NaCl, and Ru clusters charged by solvated electrons. The single exception is the Ru_3^{2-} cluster in molten NaCl, which binds molecular $^*\text{N}_2$ more weakly than expected. The $^*\text{N}_2$ and 2N^* species always become negatively charged when adsorbed on the Ru clusters.

2. Computational details

The computational details follow closely the approach used in the recent study about solvated electrons in molten alkali chloride salts from our group.¹⁹

The molten NaCl containing Ru_x clusters is modeled as free standing films with 45 NaCl units and a thickness of roughly 20 Å. The computational cells are 12 Å × 12 Å parallel to the molten salt films and 40 Å in the perpendicular direction. The systems are studied with constant temperature AIMD using VASP.^{21–24} The MD simulations utilize density functional theory (DFT) calculations with plane wave basis sets (350 eV energy cutoff) and Γ -point sampling of reciprocal space. The DFT exchange-correlation effects are approximated by the PBE functional²⁵ and the D3 van der Waals correction.²⁶ The DFT calculations use the PAW method and include 1, 5, 7, and 8 valence electrons for every Na, N, Cl, and Ru atom, respectively. Spin polarization is included in all calculations and the spin is fixed to the singlet spin state. Fixing the spin to the singlet state is an approximation, since small Ru clusters can be ferromagnetic;²⁷ however our MD simulations are conducted at 1100 K, which is likely above the Curie point of our clusters. The 1100 K is also a little above the melting point of NaCl (1074 K).²⁸ The temperature is controlled by a Nosé thermostat,²⁹ the motion of the atoms is treated classically and time evolution is propagated with 1 fs time steps.

The internal energy, $\langle E \rangle_t$, of a given system is calculated as the time average kinetic energy (K) and DFT energy (E_{DFT}) from the MD simulation.

$$\langle E \rangle_t = \frac{1}{t-t_0} \int_{t_0}^t E_{\text{DFT}}(\tau) + K(\tau) d\tau \quad (1)$$

The initial part of each MD simulation ($t < t_0$) is disregarded to equilibrate the system before internal energy sampling is conducted. The t_0 value for each simulation is chosen such that any

initial internal energy transient is removed. As the Ru_x clusters (with and without $\text{*N}_2 / 2\text{N*}$) are initially placed at the vacuum molten NaCl interface, t_0 roughly coincides with the time it takes for the molten NaCl to properly solvate the cluster. The molten salt systems are subsequently sampled for 11 to 19 ps. The t_0 values and sampling times ($t-t_0$) for the individual molten salt simulations are listed in Supporting Information (Table S1). The Supporting Information also contains movies showing the full trajectories of the MD simulations with Ru clusters in molten NaCl.

We have calculated reaction energies as internal energy differences. For example, the adsorption energy of a N_2 molecule, E_{ad} , adsorbed on Ru_n^{m-} is calculated as the internal energy of the system with adsorbed N_2 ($\langle E_{\text{N}_2 + \text{Ru}_n^{m-}} \rangle_t$), minus the internal energy of the Ru_n^{m-} cluster alone in the molten salt ($\langle E_{\text{Ru}_n^{m-}} \rangle_t$), minus the internal energy of the N_2 molecule alone in the gas-phase ($\langle E_{\text{N}_2(\text{g})} \rangle_t + \frac{3}{2}k_B T$). The $3/2k_B T$ term is added to the internal energy of the gas-phase molecule because the center-of-mass motion is not included in the MD simulation.

$$E_{\text{ad}} = \langle E_{\text{N}_2 + \text{Ru}_n^{m-}} \rangle_t - \langle E_{\text{Ru}_n^{m-}} \rangle_t - \left(\langle E_{\text{N}_2(\text{g})} \rangle_t + \frac{3}{2}k_B T \right) \quad (2)$$

In the Supporting Information we have plotted cumulative reaction energies as a function of sampling time (running averages) (Figure S1 and Figure S2). These plots also show the degree of internal energy convergence for the individual AIMD simulations.

An important part of this study is the effect of solvated electrons on the stability of Ru_3 and Ru_6 clusters and the clusters reactivity towards a N_2 molecule. We have therefore calculated atomic Bader charges^{30–32} to track the location of these electrons. Bader charges are calculated

for atomic configurations taken with 1 ps intervals along the MD trajectories and the average values reported.

3. Results and Discussion

3.1 Stability of Ru_n^{m-} clusters. Ru has a high cohesive energy and we find that the clusters of three or six Ru atoms are not stable compared to Ru metal. However, moving the Ru clusters between gas phase and molten NaCl media and changing the charge and size of the clusters affects the stability significantly (Table 1).

Formation of a gas phase Ru_6 cluster from Ru metal requires 20.8 eV, while breaking the Ru_6 cluster into two gas phase Ru_3 clusters adds an additional 8.0 eV. The energy required for cluster formation is significantly lowered when the clusters are solvated in molten NaCl. Forming a Ru_6 cluster in molten NaCl from bulk Ru requires 14.7 eV, while breaking Ru_6 into two Ru_3 in the molten NaCl requires an additional 6.1 eV. The molten NaCl stabilizes two Ru_3 clusters more than the Ru_6 cluster, but not nearly enough to favor 2Ru_3 over Ru_6 .

In molten NaCl containing solvated electrons the Ru_6 cluster becomes negatively charged (formally written as reaction eq 3).

The solvated electrons are very reactive,¹⁹ but surprisingly, moving two solvated electrons to Ru_6 and forming Ru_6^{2-} (Bader charge on Ru_6^{2-} is -1.37 *e*) does not lower the energy cost (14.8 eV, Table 1) compared to formation of the neutral Ru_6 in molten NaCl (14.7 eV) (Bader charge on Ru_6 is -0.34 *e*). Transferring four solvated electrons and forming Ru_6^{4-} does lower the energy cost substantially (13.1 eV) (Bader charge on Ru_6^{4-} is -2.17 *e*).

In addition to Ru_6 , Ru_6^{2-} , and Ru_6^{4-} , we have also considered 2Ru_3 , 2Ru_3^- , and 2Ru_3^{2-} to obtain the energy required to break Ru_6^{m-} clusters into $2\text{Ru}_3^{m/2-}$ as a function of charge (Table 1). These MD simulations are initialized by placing one $\text{Ru}_3^{m/2-}$ cluster at the upper surface and the other $\text{Ru}_3^{m/2-}$ cluster at the bottom surface of the molten NaCl film. We originally had the preconception that highly negatively charged Ru clusters would be prone to breaking into two clusters in order to lower the total electron-electron repulsion. However, the results in Table 1 show that electron-electron repulsion is not very important as the reaction energies for $\text{Ru}_6 \rightarrow 2\text{Ru}_3$, $\text{Ru}_6^{2-} \rightarrow 2\text{Ru}_3^-$, and $\text{Ru}_6^{4-} \rightarrow 2\text{Ru}_3^{2-}$ only decrease a little with increasing charge (6.1 eV, 5.6 eV, and 5.7 eV, respectively).

Table 1. Stability of Ru clusters compared to Ru(s). Listed are the reaction energies to form Ru_6^{m-} (ΔE_I) and the reaction energies to form $2\text{Ru}_3^{m/2-}$ (ΔE_{I+2}) from 6Ru(s) and m solvated electrons:

$\text{Ru}_6^{m-} / 2\text{Ru}_3^{m/2-}$	Reaction media	ΔE_I	ΔE_{I+2}
$\text{Ru}_6 / 2\text{Ru}_3$	gas phase	20.8 eV	28.8 eV
$\text{Ru}_6 / 2\text{Ru}_3$	molten NaCl	14.7 eV	20.7 eV
$\text{Ru}_6^{2-} / 2\text{Ru}_3^-$	molten NaCl	14.8 eV	20.3 eV
$\text{Ru}_6^{4-} / 2\text{Ru}_3^{2-}$	molten NaCl	13.1 eV	18.8 eV

3.2 Interactions between Ru_n^{m-} clusters and NaCl. In order to understand the interactions between molten NaCl and Ru clusters of different charge and size, we have constructed radial distribution functions ($g(r)$) from the MD trajectories of $\text{Ru}_6 + 45\text{NaCl}$, $\text{Ru}_6^{2-} + 2\text{Na}^+ + 45\text{NaCl}$, $\text{Ru}_6^{4-} + 4\text{Na}^+ + 45\text{NaCl}$, and $\text{Ru}_3^{2-} + 2\text{Na}^+ + 45\text{NaCl}$ (Figure 1). We note that the MD simulation for $\text{Ru}_3^{2-} + 2\text{Na}^+ + 45\text{NaCl}$ is different from the one conducted for the system with 2Ru_3^{2-} discussed in section 3.1.

In the $\text{Ru}_6 + 45\text{NaCl}$ simulation (Figure 1a), $g(r)$ for Ru-Cl has a sharp peak at 2.4 Å, which shows that the inner solvation shell around Ru_6 mainly consists of Cl^- ions. The area of the peak ($r < 3$ Å, Table 2) correspond to 0.98 Cl^- neighbors per Ru atom and visual inspection of the atomic configurations show that each Ru atom binds a single Cl^- ion. The Ru- Cl^- interactions are partially covalent in nature, which moves electrons to the Ru_6 cluster and results in a -0.34 e Bader charge on Ru_6 (Table 2). Further away from the Ru atoms there is a broad Ru-Na peak centered around ~ 3.5 Å. This is the clearest outer solvation shell and it constitutes 3.26 Na^+ neighbors per Ru atoms ($r < 4$ Å, Table 2). These Na^+ ions are likely situated here to stabilize the Cl^- ions in the inner solvation shell rather than the Ru_6 cluster itself. Similar oscillations in ionic concentration have been found in MD simulations of $\text{LiCl}(l)\text{-MgO}(s)$ interfaces³³ and $\text{KCl}(l)\text{-CdSe}(s)$ interfaces.³⁴ Finally, there are two peaks in $g(r)$ for Ru-Cl at ~ 4.5 Å and ~ 5.5 Å. These peaks correspond to the Cl^- ions in the inner solvation shell and their next nearest and third nearest Ru neighbors.

The radial distribution functions for $\text{Ru}_6^{2-} + 2\text{Na}^+ + 45\text{NaCl}$ (Figure 1b) indicate why moving two highly reducing solvated electrons to Ru_6 does not stabilize the energy of the cluster (Table 1). The Ru_6^{2-} cluster is negatively charged (Bader charge of -1.37 e , Table 2), which displaces Cl^- ions from the inner solvation shell resulting in a smaller peak at 2.4 Å in $g(r)$ for

Ru-Cl and a reduction to 0.67 Cl⁻ neighbors per Ru atom ($r < 3$ Å, Table 2). The energy penalty from being less solvated by Cl⁻ ions is only compensated for by a small increase in Na⁺ ions in the outer solvation shell (3.36 Na⁺ neighbors per Ru atoms ($r < 4$ Å)). The negative charge on the Ru₆²⁻ cluster weakens the solvation by the molten NaCl to such an extent that, at the end of the MD simulation, the Ru₆²⁻ cluster sits at the molten salt surface and is not fully wetted by the molten NaCl (Figure 1b). In the Supporting Information a movie of the full trajectory is provided.

The inner solvation shell for Ru₆⁴⁺ + 2Na⁺ + 45NaCl (Figure 1c) consists of 0.59 Cl⁻ neighbors per Ru atom ($r < 3$ Å, Table 2) and is only depleted slightly more than Ru₆²⁺ + 2Na⁺ + 45NaCl. The number of Na⁺ ions in the outer solvation shell is increased to 4.00 Na⁺ neighbors per Ru atom ($r < 4$ Å, Table 2). Therefore, adding the first two electrons to Ru₆ and forming Ru₆²⁻ significantly weakens the interactions with the molten NaCl, while adding the next two electrons and forming Ru₆⁴⁺ does not correspondingly weaken the interactions. This supports the observation that moving two solvated electrons to Ru₆ does not stabilize the cluster, while moving two additional solvated electrons to Ru₆²⁻ and forming Ru₆⁴⁺ does.

Finally, the radial distribution functions for Ru₃²⁻ + 2Na⁺ + 45NaCl are shown in Figure 1d. The Ru₃²⁻ cluster has more surface area per Ru atom and is therefore better solvated with 1.07 Cl⁻ neighbors per Ru atom in the inner solvation shell and 4.99 Na⁺ neighbors per Ru atom in the outer solvation shell. The increased surface area per Ru atom is probably why the molten NaCl media stabilizes 2Ru₃^{m/2-} clusters more than Ru₆^{m-} clusters, when compared to the energy difference between 2Ru₃ and Ru₆ in the gas phase (Table 1).

The atomic snapshots of Ru₆, Ru₆²⁻, and Ru₆⁴⁺ (Figure 1a, b, c) show that the three clusters have adopted the same atomic arrangement (triangular prism geometry), which is also

the most stable configuration for Ru_6 gas phase.²⁷ The smaller Ru_3^{2-} , Ru_3^- and Ru_3 clusters in the molten NaCl are found to change back and forth between linear configurations (as seen in Figure 1d) and triangular configurations in the MD simulations.

Figure 1: Radial distribution functions ($g(r)$) and atomic snapshots (at the end of the MD simulations) for (a) $\text{Ru}_6 + 45\text{NaCl}$, (b) $\text{Ru}_6^{2-} + 2\text{Na}^+ + 45\text{NaCl}$, (c) $\text{Ru}_6^{4-} + 4\text{Na}^+ + 45\text{NaCl}$, and (d) $\text{Ru}_3^{2-} + 2\text{Na}^+ + 45\text{NaCl}$. The radial distribution functions ($g_{A-B}(r)$) are defined such that the number of B neighbors (n_{A-B}) within r_{max} of each A species is given by $n_{A-B}(r < r_{\text{max}}) = \int 4\pi r^2 g_{A-B} \rho_{\text{tot}} dr$, where ρ_{tot} is the atomic density in the computational cell (total number of atoms divided by total volume). Na^+ ions (yellow) and Cl^- ions (green) within 3 Å of a Ru atom have increased radii in the atomic snapshots.

Table 2: Average number of Cl neighbors (within 3 Å) and Na neighbors (within 4 Å) of each Ru atom. Bader charge on the Ru_n^{m-} clusters.

System	$n_{\text{Ru-Cl}}(<3 \text{ Å})$	$n_{\text{Ru-Na}}(<4 \text{ Å})$	Bader charge on Ru_n^{m-} (e)

$\text{Ru}_6 + 45\text{NaCl}$	0.98	3.26	-0.34
$\text{Ru}_6^{2-} + 2\text{Na}^+ + 45\text{NaCl}$	0.67	3.36	-1.37
$\text{Ru}_6^{4-} + 4\text{Na}^+ + 45\text{NaCl}$	0.59	4.00	-2.17
$\text{Ru}_3^{2-} + 2\text{Na}^+ + 45\text{NaCl}$	1.07	4.99	-1.14

3.3 Reactivity of Ru_n^{m-} clusters probed by N_2 adsorption. In the final part, we study how the reactivity of the Ru clusters depends on the presence of the molten NaCl, cluster charge, and cluster size. We use molecular N_2 adsorption ($\text{N}_2(\text{g}) \rightarrow \text{*N}_2$) and dissociative N_2 adsorption ($\text{N}_2(\text{g}) \rightarrow 2\text{N*}$) as a probe for the reactivity. The adsorption energies are collected in Table 3, while the atomic structures of adsorbed *N_2 or 2N* at the end of the MD simulations are depicted in Figure 2. From Bader charge analysis we find that the adsorbed *N_2 molecule has a charge between $-0.7\ e$ and $-1.0\ e$ and that the two adsorbed N* species each have a charge of $\sim -1.0\ e$ (Table S2 in Supporting Information). The Bader charges on Ru_n^{m-} , *N_2 , and 2N* are connected to how well the species are solvated by the Cl^- and Na^+ ions, so we have also collected the number of ion neighbors in Table S3 in Supporting Information.

Figure 2: Atomic structures of adsorbed $*N_2$ and $2N^*$ on $Ru_3(g)$, $Ru_6(g)$, $Ru_6 + 45NaCl$, $Ru_6^{2-} + 2Na^+ + 45NaCl$, $Ru_6^{4-} + 4Na^+ + 45NaCl$, and $Ru_3^{2-} + 2Na^+ + 45NaCl$ at the end of the MD simulations. Na^+ and Cl^- ions within 3 Å of a N atom have increased radii.

N_2 adsorbs on the Ru_6 cluster in the gas phase with a molecular adsorption energy of -0.75 eV and a dissociative adsorption energy of -0.63 eV. The smaller $Ru_3(g)$ cluster is even more reactive, with molecular and dissociative adsorption energies of -1.14 eV and -1.60 eV, respectively. As a comparison, the adsorption energy of $*N_2$ and $2N^*$ on Ru(0001) terraces is -0.1 eV and -0.5 eV, respectively, while it is -0.8 eV and -0.8 eV on Ru(0001) step sites (those calculations were performed with the RPBE functional).³⁵ The gas phase Ru_6 cluster has a comparable reactivity to Ru(0001) step sites and it is believed that the step sites dominate in N_2 activation on Ru(0001) single crystals.^{36,37}

When the Ru_6 cluster is situated in the molten NaCl media it loses most of its reactivity due to the interactions between Ru_6 and Cl^- , which compete with the binding of $^*\text{N}_2$ or 2N^* to Ru_6 . The molecular and dissociative N_2 adsorption energies are therefore only -0.3 eV and -0.1 eV, respectively. Interestingly, charging the Ru_6 cluster with electrons and forming Ru_6^{2-} or Ru_6^{4-} make the clusters very reactive. The Ru_6^{2-} cluster in molten NaCl is found to be the most reactive cluster investigated with the most stable adsorption energies for both $^*\text{N}_2$ (-2.2 eV) and 2N^* (-3.4 eV). The reason Ru_6^{2-} is the most reactive cluster likely relates back to the small amount of Cl^- ions in the first solvation shell around the Ru_6^{2-} cluster prior to N_2 adsorption. When $^*\text{N}_2$ or 2N^* is adsorbed, they take electrons from the Ru_6^{2-} cluster such that the Bader charge on the cluster is changed from -1.37 e without adsorbents to -0.80 e with $^*\text{N}_2$ and 0.19 e with 2N^* . As the cluster becomes less negatively charged, the amount of Cl^- ions in the first solvation shell is increased from 0.67 Cl^- per Ru atom to 0.76 Cl^- per Ru atom with $^*\text{N}_2$ and 0.74 Cl^- per Ru atom with 2N^* . The $^*\text{N}_2$ and 2N^* species are hereby indirectly stabilized by the increased interactions between Cl^- and Ru atoms.

The Ru_6^{4-} cluster is also more reactive than the non-charged Ru_6 cluster in molten NaCl, with adsorption energies of -1.2 eV for $^*\text{N}_2$ and -1.9 eV for 2N^* . The Ru_6^{4-} cluster is more negatively charged than Ru_6^{2-} (Table 2), and it still has significant negative charge after $^*\text{N}_2$ adsorption (-1.90 e) and 2N^* adsorption (-0.51 e). This means that Ru_6^{4-} does not experience an increase of Cl^- ions in the first solvation shell (0.47 Cl^- per Ru atom with $^*\text{N}_2$ and 0.57 Cl^- per Ru atom with 2N^*) compared to before N_2 adsorption (0.59 Cl^- per Ru atom).

Table 3: Molecular ($E_{\text{ad}}(^*\text{N}_2)$, $\text{N}_2(\text{g}) \rightarrow ^*\text{N}_2$) and dissociative ($E_{\text{ad}}(2\text{N}^*)$, $\text{N}_2(\text{g}) \rightarrow 2\text{N}^*$) adsorption energies for N_2 on the Ru_n^{m-} clusters.

Ru_n^{m-} cluster	Reaction media	$E_{\text{ad}}(*\text{N}_2)$	$E_{\text{ad}}(2\text{N}^*)$
Ru₆	gas phase	-0.75 eV	-0.63 eV
Ru₃	gas phase	-1.14 eV	-1.60 eV
Ru₆	molten NaCl	-0.3 eV	-0.1 eV
Ru₆²⁻	molten NaCl	-2.2 eV	-3.4 eV
Ru₆⁴⁻	molten NaCl	-1.2 eV	-1.9 eV
Ru₃²⁻	molten NaCl	-1.1 eV	-3.3 eV
Ru₃	molten NaCl	-1.3 eV	-1.8 eV

In Figure 3, we have plotted the molecular $*\text{N}_2$ adsorption energy versus the dissociative 2N^* adsorption energy for all studied Ru clusters (the numbers reported in Table 3). It is seen that there is a clear scaling relation ($E_{\text{ad}}(2\text{N}^*) = a E_{\text{ad}}(*\text{N}_2) + b$) between molecular adsorption and dissociative adsorption energy pairs except for adsorption on Ru_3^{2-} . The reaction energies could have an error of up to ± 0.3 eV due to limited AIMD sampling (estimated from the cumulative reaction energies plotted in Figure S2). However, such an error would not significantly change the scaling relation or move Ru_3^{2-} on to the scaling line. Scaling relations between adsorption energies are well known,^{38–40} but it is somewhat surprising that the same scaling relation exist for adsorption on the Ru clusters in gas phase and adsorption on the Ru clusters in molten NaCl. It has been proposed that “electrolyte engineering” could be a way of breaking scaling relations,⁴¹ but since we find the same scaling relation with and without the molten NaCl reaction media, this approach may not be so promising.

Figure 3: Relation between $E_{\text{ad}}(*\text{N}_2)$ and $E_{\text{ad}}(2\text{N}^*)$ from Table 3. Red points represent gas phase Ru clusters, circles represent Ru_6^{m-} clusters, and triangles represent Ru_3^{m-} clusters. The fitted line $E_{\text{ad}}(2\text{N}^*) = 1.7 E_{\text{ad}}(*\text{N}_2) + 0.4 \text{ eV}$ indicates the existence of a linear scaling relation between molecular adsorption ($E_{\text{ad}}(*\text{N}_2)$) and dissociate adsorption ($E_{\text{ad}}(2\text{N}^*)$) for all energy pairs except for Ru_3^{2-} (not included in the fit).

In Figure 3, the energies for $*\text{N}_2$ and 2N^* adsorption on Ru_3^{2-} fall outside the general scaling relation. One possible explanation is that the $*\text{N}_2$ species in $*\text{N}_2 + \text{Ru}_3^{2-} + 2\text{Na}^+ + 45\text{NaCl}$ is not well solvated and therefore has less stable adsorption energy than expected from the adsorption energy of 2N^* in $2\text{N}^* + \text{Ru}_3^{2-} + 2\text{Na}^+ + 45\text{NaCl}$ (which is well solvated). This is supported by the observation that the N atoms in $*\text{N}_2 + \text{Ru}_3^{2-} + 2\text{Na}^+ + 45\text{NaCl}$ have the lowest number of Na^+ neighbors per N atom and one of the least negative Bader charges for a $*\text{N}_2$ species ($-0.69 e$). This data is presented in Table S2 and S3 in the Supporting Information.

The surprising relation for $*\text{N}_2$ and 2N^* adsorption on Ru_3^{2-} compelled us to also consider $*\text{N}_2$ and 2N^* adsorption on a neutral Ru_3 cluster in molten NaCl. The AIMD simulations for $\text{Ru}_3 + 45\text{NaCl}$, $*\text{N}_2 + \text{Ru}_3 + 45\text{NaCl}$, and $2\text{N}^* + \text{Ru}_3 + 45\text{NaCl}$ were initialized

from the endpoint of the AIMD simulations for $^*\text{N}_2$ and 2N^* adsorption on Ru_3^{2-} , but with two Na atoms removed from the systems. The adsorption energies are -1.3 eV for $^*\text{N}_2$ and -1.8 eV for 2N^* (Table 3), which places the adsorption energies neatly on the scaling line in Figure 3. N_2 adsorption on the neutral Ru_3 cluster therefore emphasizes the strangeness of the Ru_3^{2-} case and indicates that both the size and the charge of the Ru_3^{2-} cluster is required to get the unusual behavior.

4. Summary

Ru_6 and Ru_3 clusters become negatively charged when they are suspended in a molten NaCl film containing solvated electrons. Furthermore, our results indicate that such charging will affect the stability and reactivity of small Ru clusters.

The interactions between the Ru clusters and the molten NaCl are very important for the stability of the clusters. The neutral Ru_6 cluster has an inner solvation shell of Cl^- ions and an outer solvation shell of Na^+ ions. The negative charge on Ru_6^{2-} reduces the number of Cl^- ions in the inner solvation shell and Ru_6^{2-} is therefore not stabilized by the solvated electrons. The inner solvation shell around Ru_6^{4-} is not depleted much further and Ru_6^{4-} is stabilized compared to Ru_6 and Ru_6^{2-} .

Suspending Ru_6 in molten NaCl decreases its reactivity for N_2 adsorption compared to Ru_6 in the gas phase; however, charging the Ru_6 cluster with two or four electrons restores high reactivity. The molecular and dissociative N_2 adsorption energies are connected by a scaling relation, which holds for both Ru clusters in the gas phase and charged Ru clusters in molten NaCl. The only exception is N_2 adsorption on Ru_3^{2-} in molten NaCl.

Compared to bulk Ru metal, the small Ru clusters are not stable; however, it may still be possible to synthesize small clusters from a ruthenium salt precursor (such as RuCl_3) and Na

metal as the reductant. In such a synthesis pathway the kinetic stability of the clusters against agglomeration will be important and then it may be beneficial to have negative charged clusters.

In our previous study of solvated electrons, we found that molten LiCl stabilizes negative species much better than does molten NaCl.¹⁹ However, here we have intentionally chosen molten NaCl instead of molten LiCl, because we wanted to prohibit formation of N^{3-} ions in the molten salt. Na_3N is thermally unstable whereas Li_3N is thermally stable.⁴² The same holds for NaH and LiH,⁴³ which would be important if hydrogen is included in the attempt to form ammonia. Ammonia synthesis would of course require molten salt eutectic mixtures with lower melting point than NaCl (1074 K).

Supporting Information

Movies showing the full trajectories of the MD simulations with Ru clusters in molten NaCl. Equilibration time (t_0) and sampling time ($t-t_0$) for the MD simulations. Average Bader charges on the Ru_n^{m-} clusters and adsorbed $*N_2$ or $2N^*$ species. Average number of Na^+ or Cl^- ion neighbors to each N atom or Ru atom. Plot of cumulative reaction energies as a function of sampling time for the formation Ru_6^{m-} and $Ru_3^{m/2-}$ clusters. Plot of cumulative adsorption energies as a function of sampling time for $*N_2$ and $2N^*$ adsorption.

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