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EVALUATION OF AMMONIA-SALT MIXTURE REACTIONS

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1. ABSTRACT

This work investigated ammonia-salt reaction using TGA. Three samples were prepared containing $BaCl_2$, $BaBr_2$ and a 50:50 molar ratio of $BaCl_2$ and $BaBr_2$. The results confirmed the existence of a binary salt mixture with sorption characteristics different from the individual salts. The mixture did not appear to form several obvious complex compounds with ammonia, but instead underwent sorption over a large temperature range in a similar way to physical adsorption. This suggests that salt mixtures are a promising candidate for use in heat pumping and thermal storage applications.

2. INTRODUCTION

Reversible reactions between halide salts and ammonia have been successfully exploited in recent years for heat pumping, thermal transformation and thermal storage applications. However, there are only a limited number of candidate salts whose reactions occur within the low (-20°C to 200°C) temperature range, constraining the operating conditions of any technologies. Experimental and theoretical studies over the past three decades have focused overwhelmingly on reactions between single salt-chlorides and ammonia [1], with very little attention paid to salt mixtures [2]. Salt mixtures present the opportunity to tune the sorption operating conditions of ammonia-salt reactions and expand the range of pressures and temperatures over which sorption reactions can occur, increasing the applications of heating and cooling technologies that use these reactions.

3. METHDOLOGY

Several salts, such as $BaCl_2$, undergo a single ad-/desorption reaction, whereas others, such as $BaBr_2$, form several complex compounds with ammonia and therefore have several successive ad-/desorption reactions over a temperature range. Literature sources [3] indicate that $BaBr_2$ and NH_3 undergoes four reversible adsorption and desorption reactions in quick succession over a relatively small temperature range:

$$BaBr_2 + NH_3 \leftrightarrow BaBr_2 \cdot NH_3 \qquad (1)$$
$$BaBr_2 \cdot NH_3 + NH_3 \leftrightarrow BaBr_2 \cdot 2NH_3 \qquad (2)$$
$$BaBr_2 \cdot 2NH_3 + 2NH_3 \leftrightarrow BaBr_2 \cdot 4NH_3 \qquad (3)$$
$$BaBr_2 \cdot 4NH_3 + 4NH_3 \leftrightarrow BaBr_2 \cdot 8NH_3 \qquad (4)$$

whereas $BaCl_2$ and NH_3 undergoes only one reaction:

$$BaCl_2 + 8NH_3 \leftrightarrow BaCl_2 \cdot 8NH_3 \qquad (5)$$

Samples were prepared using a wet impregnation technique that deposited salt onto the surface of expanded natural graphite (ENG) discs. ENG was chosen as it has an excellent thermal conductivity (26 $W \cdot m^{-1} \cdot K^{-1}$ in-plane and 8 $W \cdot m^{-1} \cdot K^{-1}$ through plane) and a low density and large void volume (ρ = 150 $kg \cdot m^{-3}$), therefore enabling excellent heat and gas mass transfer. Three samples were prepared: one containing only $BaCl_2$, one

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containing $BaBr_2$ and one containing a 50:50 molar ratio of $BaCl_2$ and $BaBr_2$. TGA experiments were then undertaken using a thermogravimetric instrument, a Rubotherm Magnetic Suspension Balance. The instrument separates the sample environment from the balance via a magnetic coupling, allowing for a controlled gaseous environment (in this case ammonia gas) to surround the sample. The pressure was controlled by linking the sample chamber to a receiver containing liquid ammonia. A diagram of the TGA experimental setup is shown in Figure 1. During each test, the pressure was set to a constant value whilst the sample temperature was increased and decreased in small steps of 1°C.

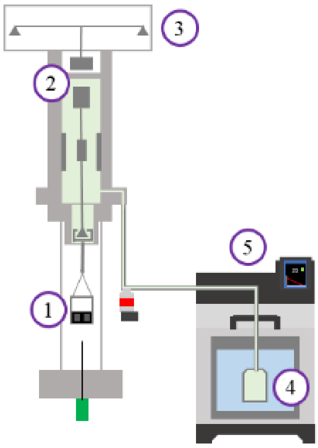

Fig. 1. TGA apparatus showing (1) bucket containing samples, (2) magnetic coupling, (3) balance, (4) receiver containing liquid ammonia and (5) temperature-controlled bath. Not to scale.

4. RESULTS

Each sample was tested over several pressures and a temperature range sufficient to ensure full adsorption and desorption. Figure 2 shows one of the isobaric adsorption and desorption curves of $BaBr_2$ at 700 kPa, clearly showing three of the four reactions. Figure 3 shows the results of all three samples at 700 kPa, clearly indicating that a mixture of $BaCl_2$ and $BaBr_2$ has formed that has different sorption characteristics to the individual salts. The mixture largely appears to undergo ad-/desorption across a continuous temperature range, similar to physical adsorption such as that seen in carbon-ammonia reactions. Adsorption occurred at a lower temperature than desorption and the mixture also displayed reaction hysteresis.

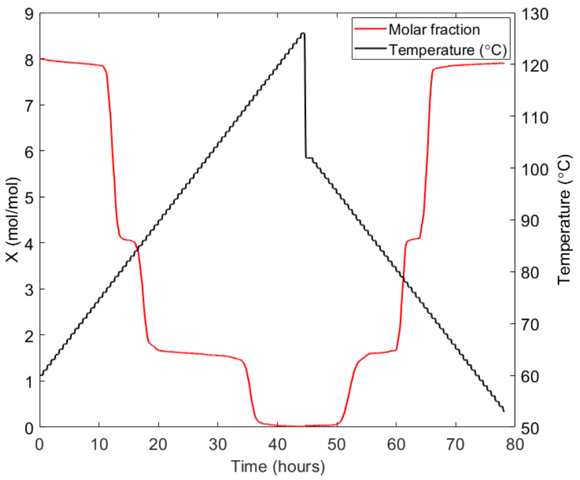

Fig. 2. Isobaric adsorption and desorption curve of $BaBr_2$ at 700 kPa.

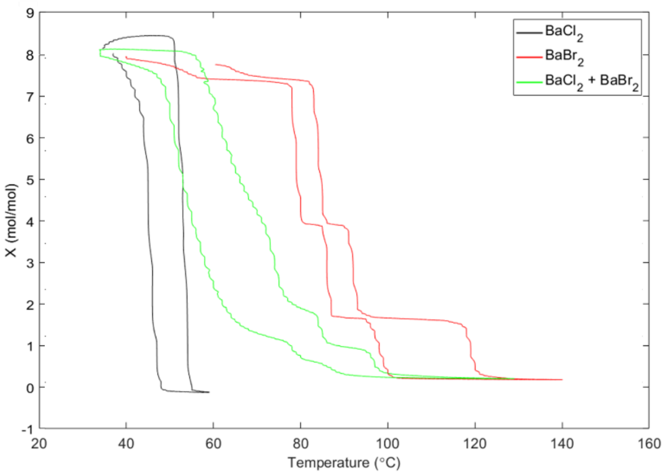

Fig. 3. Ammonia sorption for $BaCl_2$, $BaBr_2$ and a 50:50 molar mixture of $BaCl_2/BaBr_2$.

5. CONCLUSIONS

This work has used TGA to characterise $BaCl_2$-NH_3 and $BaBr_2$-NH_3 reactions and has also confirmed the existence of a binary salt mixture with sorption characteristics different from the individual salts. The mixture does not appear to form several obvious complex compounds with ammonia, but instead undergoes sorption over a large temperature range in a similar way to physical adsorption, although it retains the reaction hysteresis seen with individual halide-ammonia salt reactions. This suggests that salt mixtures are therefore a promising candidate for use in heat pumping and thermal storage applications.

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