Studies of Molten-Salt-Catalysed
Coal Gasification

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Introduction

The research which was carried out was an investigation into the mechanism of the well-known and widely-reported alkali metal carbonate catalysed reaction of carbaceous materials with CO_2 and H_2O .

The basic premise of the proposal was that the particular alkali metal ion was unimportant but rather it was $\text{CO}_3^{=}$ which was relevant. Hence, it was desirable to evaluate the concentration dependence of the gasification reaction upon $[\text{CO}_3^{=}]$ since the stoichiometric reaction known as the Boudouard reaction¹

could as well be expressed in terms involving $\text{CO}_3^{=}$:

This must be particularly important since the overall gasification process proceeds both with solid catalyst (i.e. when it is below the carbonate m.p.) as well as when the catalyst is molten and ionic species are present. The use of the molten salt for study allows one to capitalize on a solid-state electrolyte-based oxygen sensor to investigate the thermodynamic activity of $\text{O}^{=}$.

during the reaction and hence infer $\text{CO}_3^=$ dependence even in non pure carbonate systems.²

Two molten salt systems were proposed for study with CO_2 and H_2O :

- A. The pure carbonate melts and—
- B. Melts in which $\text{CO}_3^=$ could be produced at lower concentrations relative to pure melt.

The pure carbonate melts included the appropriate binary and ternary eutectic mixtures to permit a study of lower temperature molten materials; the solvent system was the LiCl-KCl eutectic in which $\text{CO}_3^=$ could be dissolved as a slightly stable complex and in which for example $\text{S}_2\text{O}_2^=$, B_2O_3 and V_2O_5 could be dissolved establishing as well a variety of buffered $\text{O}^=$ concentrations. These $\text{O}^=$ equilibria would be coupled with control of CO_2 pressure so that the equilibrium $\text{CO}_3^= \rightleftharpoons \text{CO}_2 + \text{O}^=$ would allow $\text{CO}_3^=$ to be fixed for given CO_2 pressure.

Results

The solid state electrolyte sensor system utilizing gold electrodes was found to be a suitable oxygen sensor for use in pure carbonate melts. Gold film electrodes were unstable but a heavy gold wire contact proved stable in molten carbonates. The oxygen activity has been measured in pure Na_2CO_3 (mp 858°C) in

the 58%Na, 42%K binary eutectic (mp 710) and in the 43%Li, 51%Na 25%K ternary eutectic (mp 397°C). In each melt the measured value of $O^=$ is described quantitatively by the partial pressure of O_2 which would be in equilibrium with the $O^=$ in the melt. These pressure values are in the range of .01 to .05 atm for all three melt systems. The temperature dependence is not strong. More importantly, however, the value of P_{O_2} does not seem to follow the equilibrium behavior reported to hold in melts and usually expressed as

$$P_{CO_2} a_{O^=} = \text{constant}^3 \quad a_{O^=} = \text{activity of oxygen} = a_{O_2}$$

since the passage of either CO_2 or He through the melt does not significantly alter the measured a_{O_2} .

When carbonaceous material is introduced into these single component and binary eutectic melts through which CO_2 is passing, there is an immediate and very large decrease in the oxygen activity (Fig. 1). These initial studies were carried out in an open Al_2O_3 crucible but samples of the gaseous atmosphere above the melt were aspirated to a gas chromatograph and show the presence of CO. The lower melting ternary system was studied over the range 500° to 700°C. There is a significant difference in behavior as a function of temperature. At 500°C the presence of carbon has little effect on a_{O_2} measured and no CO could be detected. At 600°C, the oxygen activity began to decrease but only the change seen at 700°C was consistent with the other pure melts.

A quantitative gasification rate measurement was not possible in the open crucible but a closed tank reactor has been built and tested, although no extensive data were obtained.

The removal of the solid carbon from the carbonate melts produced a strikingly slow return of the oxygen activity to its initial value (compared with the speed of the initial decrease). The rate of the return was a function of the nature of the gas used to purge the melt; He caused a more rapid return than CO_2 and with no purge the return was very slow. An example for the binary eutectic is shown in Fig. 1.

It should be noted that the oxygen activity in the melt during reaction, although quite low, was still orders of magnitude larger than that characteristic of the gaseous equilibrium between CO , CO_2 , C and oxygen.

It has been pointed out that KOH is nearly as effective a catalyst as K_2CO_3 . We have investigated molten KOH from the melting point (400°C) to 700°C . Even with a CO_2 purge the oxygen activity remained equilibrated with air (over periods of hours) and over the entire temperature range the introduction of carbonaceous material had no effect on the activity. Additionally, no CO was detected using the aspirator procedure.

Tests of the H_2O driven reaction in an open crucible proved to be unreproducible and were abandoned until the closed reactor was available.

A study of the LiCl-KCl eutectic (mp 352°C) with 2% Li_2CO_3 dissolved in it showed that the relatively high oxygen activity in the range 400-600°C was sharply lowered by introduction of carbonaceous material. Without carbonate in the melt, no effect of carbon on the $\text{O}^\ominus$ activity was observed.

A controlled atmosphere fused salt reactor has been built and tested. The analysis of the product and effluent streams is with the gas chromatograph, the sampling value for which is "on line" to the reactor. (Fig. 2) A flow system has been set up to permit a variety of gases to be introduced into the melt (Fig. 3). The electrode is a dipping sensor and is mechanically stable when the melt cools and solidifies. The reactor is equipped with a carbon introduction port to allow solid pieces to be inserted and removed from the melt or to allow a powder slurry reaction to be studied (to increase the available surface area).

Discussion

These observations enable one to distinguish between several mechanistic proposals for the catalytic process and to discuss the role of KOH in the process.

There are essentially two types of mechanisms suggested for the reaction of C with CO_2 .⁵ The first is based upon the observed volatilization of alkali metal from carbonate catalysed systems and proposes that a possible mechanism consists of the 3-step sequence

with the first step being rate limiting. (A significant loss of free metal from the catalyst is less likely in a molten salt as M is typically soluble.) If reaction (1) does occur then the large observed decrease in oxygen activity would have to be associated with consumption of $\text{O}^=$ by M via a reaction such as $\text{M}_2\text{O} \Rightarrow 2\text{M}^+ + \text{O}^=$. With (1) rate limiting, M_2O would be equilibrated. The inconsistency becomes clear when the second class of proposals which are "electrochemical" in nature are discussed. The first, that of Jalan & Rao,⁵ is a version of the first proposal:

In this case two sites are required so that the redox couple can be formed. The observation that oxygen activity falls with reaction (and does not fall when no CO production occurs) is not obviously consistent with this proposal. This can be seen for

if one eliminates the metal ion in this mechanism, the second and third steps may be written in the form

The process represented by (5) has been carried out by Lorenz & Janz by imposition of an appropriate potential in an electrochemical cell but would not lead to a loss of O^- activity in the melt. Further, it is not clear that (6) actually occurs.

The third proposal (due to Wagner⁶) (which is consistent with our proposal) is also electrochemical but does not involve the metal ion:

This mechanism allows for the rapid reduction of O^- when C is introduced and CO is produced. A lack of CO production implies no reduction in O^- , as observed. It suggests also that KOH would intrinsically not be catalytically active with CO_2 but depends upon conversion to K_2CO_3 to become effective.

The notion of adsorbed CO (on C) and a subsequent release of CO does not explain the very slow return of O^- activity to its initial value prior to reaction, nor the differences in rate observed between a He and CO_2 purge. It is possible that CO is being purged out of the melt and the mass transport across

the purge bubble boundary dominates the rate rather than a reversal of a chemical equilibrium. A crude estimate of the ratio of the rate of diffusion into the He bubble relative to a CO_2 bubble suggests a factor of 3 to 4 which is larger than that observed. Only a careful chemical analysis will enable one to detect CO in the purge gas. This was not possible using the aspiration technique. Thus, the observation of the very low O^- activity during reaction does not seem to be consistent with metal cation involvement. The Wagner type mechanism seems to be more appropriate. The argument that Li_2CO_3 is a more effective catalyst than K_2CO_3 must be in the main a reflection of the lower m.p. (Fig. 18. ref. 1) and lower temperature for liquid film formation. The observation that KOH is as effective as K_2CO_3 is not borne out by molten salt studies. In an impregnated or mechanically mixed system the rate of conversion of KOH to K_2CO_3 by CO_2 is adequate to mask any induction period but in the melt system, the total conversion to K_2CO_3 by bubbling CO_2 through the melt was negligible for a period of several hours. Hence, it was not possible to produce K_2CO_3 in significant quantities and hence no O^- activity change was observed when carbon was introduced into the melt. (The binary eutectic at its m.p., 710°C , exhibits a very great decrease when carbon is introduced.)

The fact that Na_2CO_3 decompose to Na_2O and CO_2 at the m.p. could explain a large O^- activity in pure melts (via $\text{Na}_2\text{O} \rightleftharpoons 2\text{Na}^+ + \text{O}^-$) but when CO_2 is present the mechanisms which propose metal cation involvement consume Na^+ and hence are not likely to decrease O^- .

The ternary eutectic has 43% Li_2CO_3 and yet it is not effective catalytically at temperatures significantly lower than that of the binary eutectic. This too suggests that it is not the Li salt per se but the ability to produce $\text{CO}_3^{=}$ in a liquid film (i.e. a lower m.p.) which accounts for its superior behavior. The data of McKee indicates a similar result.⁷

Conclusions

A measurement of the properties of the gasification catalyst itself, which has been made for the first time, provides several insights into the mechanism which were not previously obtainable other than as speculation.

The measurement of the oxygen activity in the melt systems demonstrates that for the CO_2 based gasification

- a) The mechanisms which involve the metal or metal cation in a significant way are inappropriate.
- b) The effectiveness of solid KOH and Li_2O must be in their ready conversion to carbonates.
- and c) Therefore, the increased activity of Li_2CO_3 relative to K_2CO_3 is a result of the m.p. being lower permitting more effective dispersion of the catalyst over the carbon surface rather than an intrinsic difference due to differences between Li^+ and K^+ .

It is interesting to note that in other catalytic systems in which alkali metal cations have an effect on the catalytic activity of another material (e.g. $\text{Li}_2\text{S}_2\text{O}_7$ vs $\text{K}_2\text{S}_2\text{O}_7$ on V_2O_5 for oxidation of benzene to maleic anhydride⁸) the Li salt is typically a poison!

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OXYGEN ACTIVITY RECOVERY

FIGURE 1

FIGURE 3

FIGURE 4