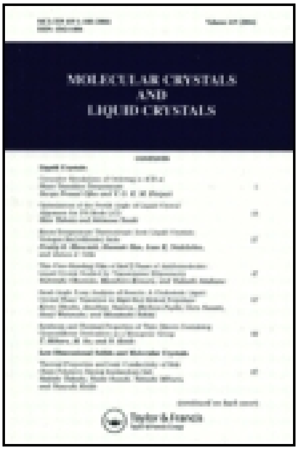

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REACTION OF METAL CHLORIDE GRAPHITE INTERCALATION COMPOUNDS WITH AMMONIA

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Abstract The reaction of metal chloride-GIC with ammonia has been examined from the kinetic, thermodynamic and structural points of view. This reaction, which is widely reversible between two values of the ammonia/metal chloride ratio, can be used for the chemical storage of thermal energy or cold generation. The reaction rates have been found to be larger than those of non graphitic metal chlorides. The diffraction studies show that the final compounds are inclusion compounds rather than GIC. This structure allows an easy transfer of the ammonia molecules between inside/outside graphite crystallites.

INTRODUCTION

In order to study the process of the chemical storage of thermal energy, it appears that the absorption reaction of ammonia by the metallic chlorides, intercalated in graphite, is a very attractive technique.[1]

MCl_x metal chlorides react with ammonia according to:

$$MCl_x + 2\,NH_3 \rightleftharpoons MCl_x(NH_3)_2 \qquad (1)$$

$$MCl_x(NH_3)_2 + 4\,NH_3 \rightleftharpoons MCl_x(NH_3)_6 \qquad (2)$$

Only the second reaction is reversible within the useful temperature range.

$MnCl_2$, $MgCl_2$, $CoCl_2$, $NiCl_2$ and $CuCl_2$ graphite intercalation compounds (GIC) have been used in place of pure chlorides to improve the mass and thermal transfers of the reactive powder. The studied reaction is usually as follows (except for copper chloride, for which the fixed ammonia molecules are successively 2, 3.33 and 6)[2]:

$$C_n\,MCl_x(NH_3)_2 + 4\,NH_3 \rightleftharpoons C_n\,MCl_x(NH_3)_6 \qquad (3)$$

From a thermodynamic point of view, reaction (3) releases about 50 kJ per NH_3 mole, as much as in the case of pure chlorides, but the kinetic curves show a real increase in the reaction rate.

EXPERIMENTAL TECHNIQUES

The GICs were prepared according to the usual methods based on the gas-solid reactions within a 400-600°C temperature range under chlorine pressure. Madagascar natural graphite powder (granulommetry ∅ 40 to 100µm) was used as starting material.

We selected the following compounds :

First stage GICs : $C_{5.4}MnCl_2$[3], C_7MnCl_2[3], $C_5(MgCl_2)_{0.8}(CoCl_2)_{0.2}$[4], $C_{5.2}CoCl_2$ [4], C_7CuCl_2 [3],

Second stage GICs : C_7MgCl_2 [4], $C_{11}NiCl_2$ [3].

The experimental device used to observe or to follow the reaction between the GIC and ammonia is simply constituted of two stainless steel parts connected by a tube through which the ammonia gas can flow in both directions. The first part is the reactor. It contains a certain amount of GIC powder. In the case of the *in situ* reaction observed by means of neutron diffraction, the reactor walls are sufficiently thin to let the neutrons in. The second part contains the liquid ammonia. It can be cooled to keep the pressure of the ammonia gas constant within the 0 -10 bars range.

Structure and reaction kinetics were studied by neutron diffraction, X-ray diffraction and scanning electron microscopy.

Neutron diffraction measurements were performed using the multidetection D1B diffractometer (λ = 2.52 Å) at the Institut Laüe-Langevin (ILL) HFR in Grenoble (France). Data were recorded over an 1 h period (time scale of 5 mn per spectrum). Data proccessing was performed with standard computing programs [5] available at the ILL.

X-ray diffraction was performed using the CuKα radiation (λ = 1.542 Å) in a Philips diffractometer.

The external surface of the GIC powder grains was observed by scanning electron microscopy.

KINETIC

No distinction can be made between reaction (1) and reaction (2) during the first contact of the metal chloride-GIC with ammonia. In general, these reactions are completed only after several absorption-desorption cycles, depending on the powder granulommetry : fine-grained products (< 40 µm) rapidly and completely react. This also depends on the ammonia diffusion rate : the second stage GIC reacts more quickly than the first stage, which is denser than the second. In the case of the $CuCl_2$-GIC, the reaction rapidly leads to a stoichiometric saturation, essentially because copper chloride crystallizes in chains (and not in a lamellae as the other chlorides).This allows the free circulation of the ammonia molecules in microscopic channels between the graphite planes and the chloride chains.

Figure 1 shows, for example, the advancement of reaction (3) for different ammonia pressures. The kinetic rates depend on this pressure, but, in fact, they depend on the equilibrium drop, that is to say the difference between the equilibrium pressure and the actual pressure. The same phenomenon is observed as regards temperature : the reaction rates also depend on the equilibrium drop, the difference between the equilibrium temperature and the actual temperature. Nevertheless, in the latter case, the reactor temperature increases a lot during the reaction –which is highly exothermic– and the reaction rate slows down.

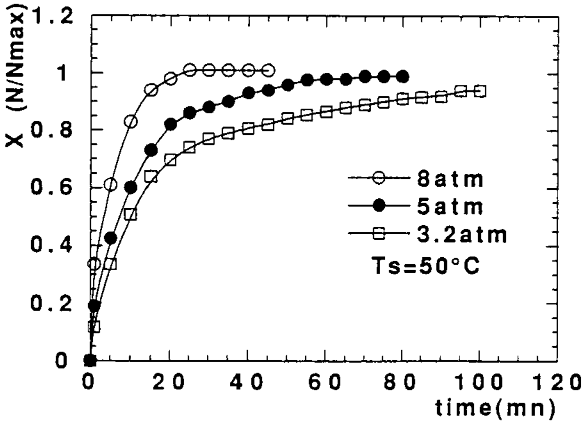

FIGURE 1 Advancement curves for reaction (3) in the case of C_7MgCl_2.

Another method of following the kinetics of the reaction is by *in situ* diffraction . This was achieved with a neutron beam penetrating the metallic walls of the reactor. A three dimensional plotting-diagram of reactions (1) + (2) is shown in figure 2. We can observe the fast disappearence of the (00l) lines of the binary GIC, with the appearence of the (hkl) lines of the metal chloride ammines.

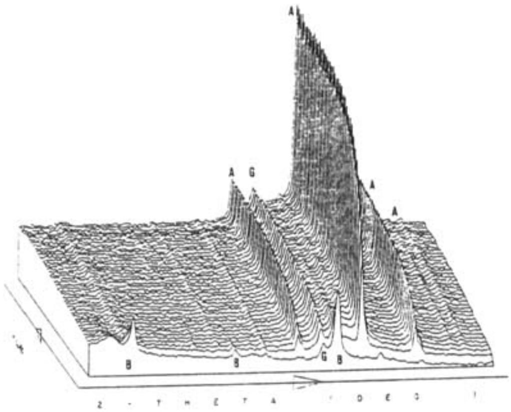

FIGURE 2 Neutron diffraction spectra evolution for the first reaction of C_7MnCl_2 with ammonia (B : (00ℓ) binary compound lines, G : (002) graphite line, A : (hkℓ) ammine lines)

THERMODYNAMIC

The reactions of fixation of the ammonia molecules are very energetic. The first two molecules which fix (according to reaction 1) yield approximatively 80kJ per ammonia mole ^{2,6}. This reaction is reversible only at a high temperature (for exemple, 300°C under a pressure of five bars of ammonia in the case of $MnCl_2(NH_3)_{0-2}$), so it is not useful for chemical storage of thermal energy.

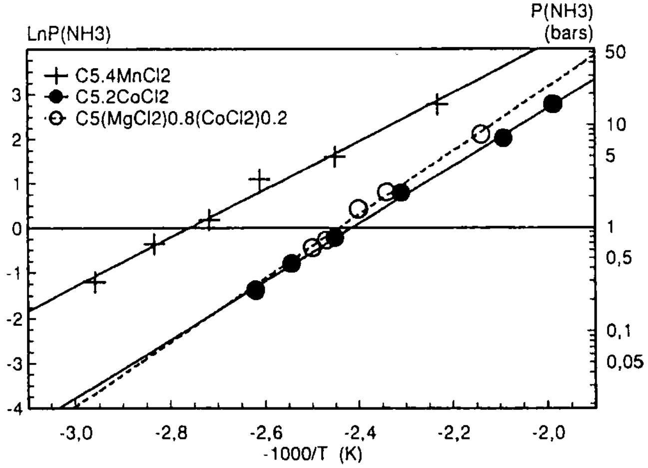

FIGURE 3 Clapeyron diagram of reaction (3) for several GICs. The enthalpy values are : 45.0 kJ ($C_{5.4}MnCl_2$), 53.7 kJ ($C_{5.2}CoCl_2$) and 59.2 kJ ($C_5(MgCl_2)_{0.8}(CoCl_2)_{0.2}$)

The last four ammonia molecules release only 45 to 60 kJ per mole, but this reaction is reversible in a temperature region which is really practical for the energy storage (for exemple, 120°C in the case of $MnCl_2(NH_3)_{2-6}$).

Some equilibrium curves, functions of the Clapeyron equation : $\ln P = - \Delta H/RT + \Delta S/R$ are given in figure 3. The enthalpy values of reaction (3) were obtained from their slopes.

STRUCTURAL STUDIES

Hex-ammine and di-ammine graphite compounds were studied by X-ray and neutron diffraction (figures 4 and 5). The spectra always present the lines of pure di- or hex-ammine of metal chlorides (in general, face-centered cubic for hex-ammine and tetragonal for di-ammine), and a broad and weak (002) line of graphite. In all cases, the initial GIC completely disapears.

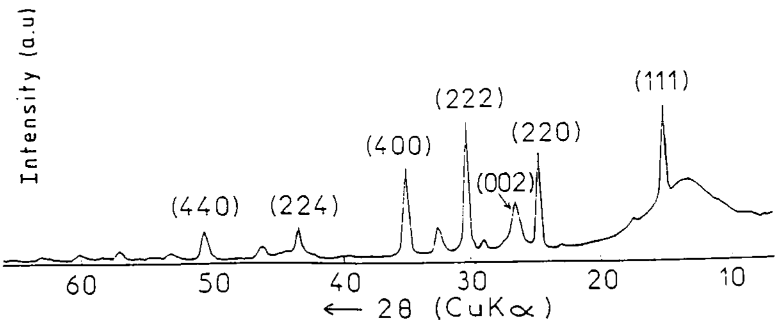

FIGURE 4a X-ray diffractogram of the $C_7MgCl_2(NH_3)_6$ compound. The indexation corresponds to this f.c.c. ammoniated compound, except for the (002) line of graphite.

Scanning electron microscopy shows that all the ammine salt has virtually remained among the graphite layers. The final compound is typically an inclusion compound, that is to say a compound which is weakly exfoliated, and within which the ammine crystallites are randomly distributed. The crystallites, as determined by the Scherrer method, are approximately 200 Å. The high rate of the reactions with ammonia may be explained by the low size of the reactive crystallite powder, and also by the comparatively large spaces between the graphite layers.

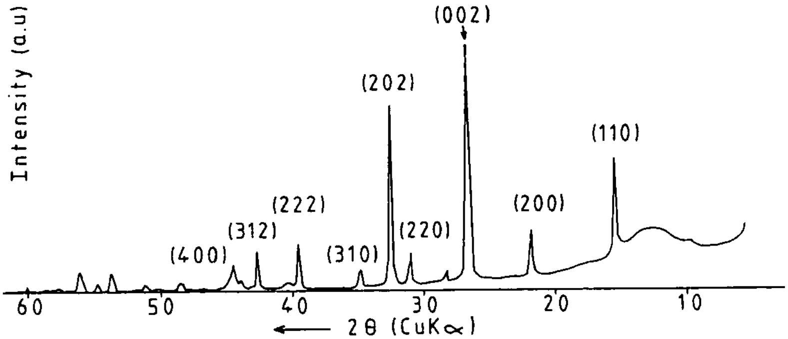

FIGURE 4b X-ray diffractogram of the $C_5(MgCl_2)_{0.8}(CoCl_2)_{0.2}(NH_3)_2$ compound. The indexation corresponds to a tetragonal compound, except for the (002) line of graphite.

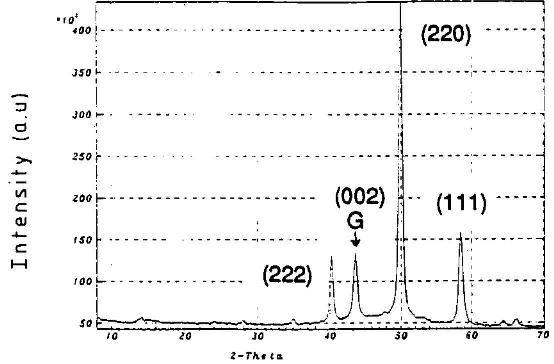

FIGURE 5 Neutron diffractogram of the $C_5MnCl_2(NH_3)_6$ compound (f.c.c. ammoniated compound + (002) graphite line)

CONCLUSION

Metal chloride GICs could be good candidates for the chemical storage of thermal energy. The use of graphite enhances the thermal transfer, but also avoids the agglomeration of ammine crystallites. This increases the mass transfer of ammonia molecules which can freely circulate between graphite planes and ammine grains.

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