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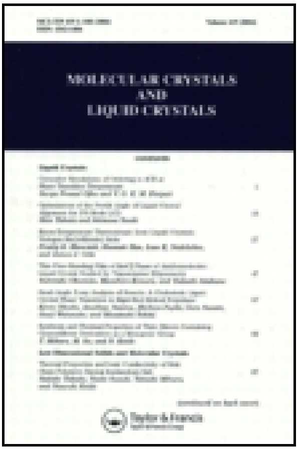

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Solid State Interaction of Butyl Halides with Magnesium

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Solid State Interaction of Butyl Halides with Magnesium

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The Mg – n-BuCl, Mg – n-BuBr and Mg – n-BuI systems by electrical conductivity, gas chromatography (GC) and UV-spectral method was investigated. The systems were obtained by chemical vapour deposition (CVD) method.

Keywords: solid state; magnesium; butyl halide

INTRODUCTION

The electrical conductivity measurement is a perspective method of investigation of intermolecular interaction and regulation of properties of low temperature chemical systems during their formation. However, there are some difficulties dealing with the fact that conductivity depends on their parameters [1]. Particularly, in early studies devoted to low temperature reactions in metal - butyl halid vapour co-condensates the connection of conductivity with the presence of particles containing unpaired electrons was found. The effects of radical-ion concentration in Mg-alkylhalid systems and the nature of halid were also presented. The result of ESR study of alkylhalid confirmed the radical-ion presence. The scheme of the reaction reported in [2] and Figure 1.

DESCRIPTION OF EXPERIMENT

The electrical conductivity of magnesium – butyl halides films obtained by the co-condensation of alkyl halides and metal vapours on the surface cooled down to 130 K was investigated. The developed technique allows

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us to measure resistivity of the sample in region 10^8 — 10^{12} Ohm under the temperatures between 130-300 K.

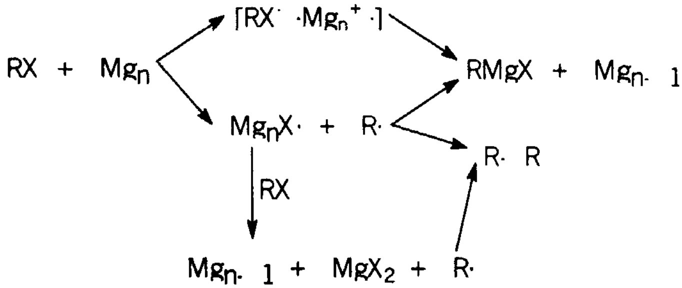

FIGURE 1. The scheme of low-temperature interaction between Mg nanoparticles and alkylhalides. It is shown the possibility Grignard reactive formation and alternative (Wurtz) reaction.

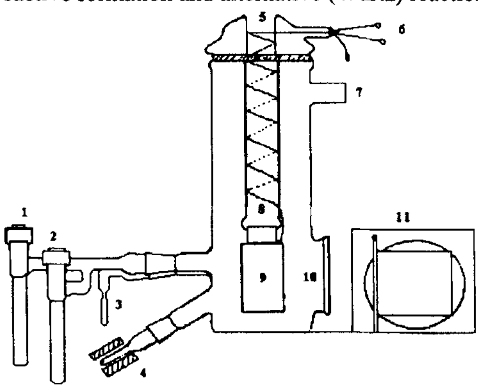

FIGURE 2. Chromatography cryostat.
1 - the evaporator of alkyl halide; 2 - the evaporator of H_2O; 3 - the tube for GC; 4 - the evaporator of metal; 5 - the capacity filled liquid N_2; 6 - the capacity for contacts; 7 - to the pump; 8 - the glass finger, cooled liquid N_2; 9 - the Cu-cube, cooled liquid N_2; 10 - The KBr window; 11 - the system of mirrors for IR-method.

The measurements were carried out during preparation and following heating of the samples. The typical results of these experiments are presented at Figures 3a), 4a), 5a). The technique used in our study was described in [3]. The products of interaction were investigated by GC method (Figure 3b), 4b), 5b)). All parameters, except the nature of halid, were constant.

The scheme of cryostat is presented at Figure 2.

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DISCUSSION

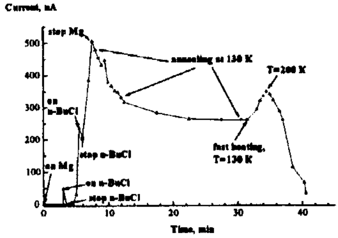
The typical time dependencies of current during the reagent condensation and annealing are presented at Figures 3a), 4a), 5a). The dramatic increase of current during the condensation of Mg is presented at all of the plots. The current is diminished from maximum to zero during the butyl halide condensation. This is because the metal is in the agglomerated state on the layer. The process of cluster formation was described at [1,2]. It resulted from the excess of energy of condensing atoms. The estimated film thickness is about 50 nm, but the real structure of condensate includes a great number of touching clusters posses different grade. Butyl halide condensation on this island film firstly destroys the thin contacts between metal clusters. It leads to decrease of current. If the thickness of the contacts is more than 1 nm, then change of current is unique for each system.

In the Mg – n-BuCl (see Figure 3a)) system the gradual diminution of current followed by its stabilisation while keeping at 130 K was found. After that the current stabilised. We consider such current behaviour as a result of BuCl diffusion to the surface of clusters.

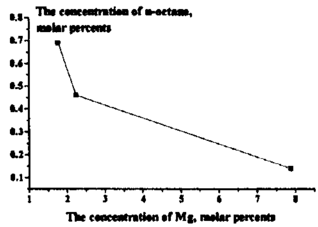
The annealing leads to the spontaneous rise of current with maximum at 200 K. Possibly it is connected with the formation of electron-traps lower by energy than Fermi level. Ion-radical pares can play the role of these electron-traps. The existence of ion-radical pares in these systems was fixed in previous works by ESR [2]. The decrease of conductivity during further heating may deals with the following transformation of these pares.

In the experiments of the chromatography series the co-condensates were hydrolysed. The products of hydrolysis were established by GC method. The results of GC analysis of system Mg – n-BuCl are presented at Figure 3b)). These results show that the quantity of

Wurtz-reaction products after hydrolysis decreased if the concentration of metal in the co-condensate was increased.



a)



b)

FIGURE 3a). The time dependence of Mg - n-BuCl system electroconductivity during the reagents condensation and annealing at 130 K.
on Mg/n-BuCl - The beginning of Mg/n-BuCl vapour condensation.
off Mg/n-BuCl - the end of metal vapour condensation fast heating - heating of the sample (v=7K/min)

FIGURE 3b). The dependence of concentration n-octane at products of hydrolysis the system Mg - n-butylchloride (the result of GC) from the concentration of Mg at co-condensate.

The systematic diminution of current during the maintaining of Mg – n-BuBr co-condensate at constant temperature was found. Literature data show that the activity of n-BuBr is higher than one of n-BuCl [2]. Moreover, the mechanism of reaction between Mg and n-BuBr is more radical. We could not find the stabilisation of resistance while the maintaining and a rise of current during the heating. The results of experiments (see Figure 4a)) confirm our hypothesis.

The GC analysis of this system shows that the quantity of n-octane (the product of Wurtz reaction) at the hydrolysed co-condensate doesn't depend on Mg concentration (see Figure 4b)). On the other hand the specific yield of n-octane (calculated per one atom of Mg) is diminished when the concentration of Mg in co- condensate increases. So the specific activity of Mg decreases also.

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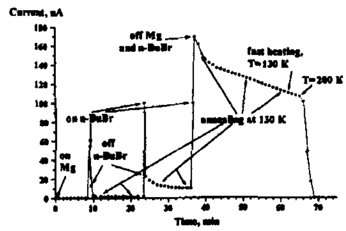
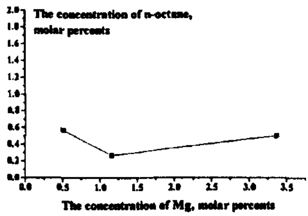


a)



b)

FIGURE 4a). The time dependence of Mg - n-BuBr system electroconductivity during the reagents condensation and annealing at 130 K.

FIGURE 4b). The dependence of concentration n-octane at products of hydrolysis the system Mg - n-butyl-bromide (the result of GC) upon the concentration of Mg at co-condensate.

The full stabilisation of current was found in Mg – n-BuI system after the quick decrease (see Figure 5a)). This fact can be explained by two factors:

1) The activity of n-BuI is much more than n-BuBr and n-BuCl (Conductivity decrease).
2) The big quantity of n-octane is formed. The molecules of n-octane cover the surface of clusters and the reaction stops.

The increase of current was not found during the heating, so the mechanism of this reaction is radical. The linear increase of concentration of n-octane in the products of hydrolysis depending on concentration of Mg in co-condensate was stated by GC method (see Figure 5b)). Though the specific yield of n-octane is diminished like in other systems. This fact can be explained by the rise of size of metal clusters.

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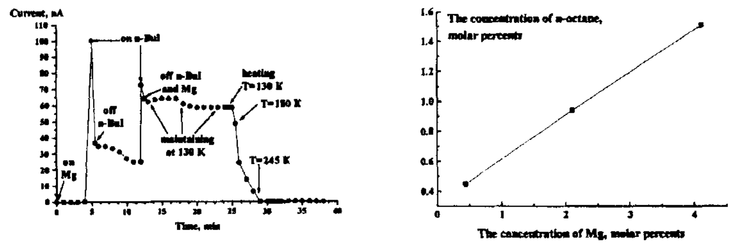

a) b)

FIGURE 5a). The time dependence of Mg - n-BuI system electroconductivity during the reagents condensation and annealing at 130 K.

FIGURE 5b). The dependence of concentration n-octane at products of hydrolysis the system Mg - n-butyliodide (the result of GC) upon the concentration of Mg at co-condensate.

CONCLUSIONS

The unique reactivity dependence of Mg nanoparticles as function of particle grade and nature of halides was found. The possibility of correlation between electrical conductivity and mechanisms of model (Mg – butyl halide) systems was carried out at the first time.

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