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Review

The effect of organic additive in Mg/graphite composite as hydrogen storage materials

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ABSTRACT

Among the metals that form hydrides, Mg and Ti are the lightest materials; however, they are covered with passive layer of oxides and hydroxides and require activation treatment under high temperature (>300 °C) and hydrogen pressure (>3 MPa) before being used for storage and transport applications. It is well known that addition of small amounts of graphite to Ti or Mg, lead to a dramatic change in the kinetics of mechanically induced (ball milling) hydrogen sorption and significantly stimulates the Ti–hydrogen interaction. Imamura et al. in a series of publications in this journal confirmed that the magnesium/graphite (Mg/C) composite formed by mechanical milling with the organic additives not only show improved hydriding–dehydriding properties of magnesium but also additional hydrogen uptake other than that due to the magnesium component. Among the organic additives (benzene, cyclohexene, cyclohexane, and tetrahydrofurane) which were tried by Imamura et al. tetrahydrofurane was the most promising. Tetrahydrofurane required only 1 h of ball milling and the least amount of volume used during ball milling was needed compared to the other additive. The objective of this publication is to suggest a mechanism for the effect of tetrahydrofurane. The role of THF is possibly due to the value of the mw/ε (mw is the molecular weight and ε is the dielectric constant) for THF being in the range in which the solvent provide a medium where complex formation between Mg molecules and the solvents is maximum. This can happen when halide impurities undergo chemical transformations to form Grignard type reagents (organomegnesium halides). Thus the values of mw/ε can be used as an initial guide to select the proper solvent.

Contents

1. Introduction

Among the metals that form hydrides, Mg and Ti are the lightest materials; however, they are covered with passive layer of oxides and hydroxides and require activation treatment under high temperature (>300 °C) and hydrogen pressure (>3 MPa) before being used for storage and transport applications. It is well known addition of small amounts of graphite to Ti or Mg, lead to a dramatic change in the kinetics of mechanically induced (ball milling) hydrogen sorption and significantly stimulates the Ti–hydrogen interaction. From 1987 to 2007, Imamura et al. from Japan published many articles in this journal about the effect of organic additives on the efficiency of Mg–Graphite composite prepared by ball milling for hydrogen storage. In 2007 Imamura admitted that the organic additives have proven to play important roles in the formation process of nano-composite with mechanical milling, which are not fully understood yet [1–6] (Fig. 1).

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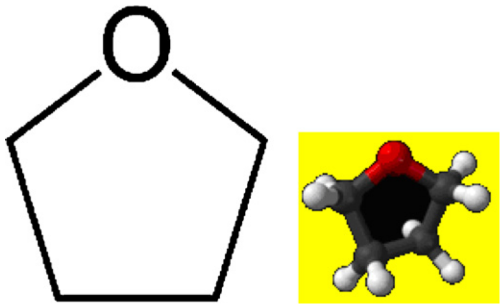


Fig. 1. The structure of tetrahydrofurane. The large red atom at the top is oxygen, white is hydrogen while the black are carbon. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Imamura et al. in a series of publications in this journal confirmed that the magnesium/graphite (Mg/C) composite formed by mechanical milling with the organic additives not only show improved hydriding–dehydriding properties of magnesium but also additional hydrogen uptake other than that due to the magnesium component. Among the organic additives (benzene, cyclohexene, cyclohexane, and tetrahydrofurane) which were tried by Imamura et al. tetrahydrofurane was the most promising. Tetrahydrofurane required only 1 h of ball milling and the least amount of volume used during ball milling was needed compared to the other additive. The objective of this publication is to suggest a mechanism for the effect of tetrahydrofurane

2. The dielectric constant ε

The dielectric constant of a solvent is a relative measure of its polarity. For example, water (very polar) has a dielectric constant of 80.10 at 20 °C while n-hexane (very non-polar) has a dielectric constant of 1.89 at 20 °C [7]. This information is of great value when designing separation, sample preparation and chromatography techniques in analytical chemistry. Solvents with a dielectric constant of less than 15 are generally considered non-polar. THF is an aprotic solvent with a dielectric constant of 7.6.

3. The ratio $\mu_\varepsilon = \mathrm{mw}/\varepsilon$

The ratio of the molecular weight of a compound mw to the dielectric constant ε should be given more importance vis-a-vis the dielectric constant of the organic additive alone [10]. This is because for aprotic solvents such as THF the stability constants β_j ($j = 1, 4$) decrease with increasing values of the dielectric constants up to a certain value and then increase sharply for value of ε around 45. It is shown by Khan et al. [10] that values of the stability constants β_j ($j = 1, 4$) for metal complex formation (e.g. copper chloro complex) in the organic solvent is highly dependent on the ratio of the molecular weight of the solvent (the organic additive) divided by the dielectric constant (e.g. μ_ε). The stability constants β_j values are high (metal such as Mg ions are able to form organic complex much more easily) if the values of μ_ε around 9–20. At higher values of μ_ε between 30 and 60, the values of stability constants for metal complex formation is very low. The values of stability constants β_j for metal complex formation increases again for μ_ε greater than 60. It is interesting that Khan et al. [10] observed that the values of the stability constants β_j ($j = 1, 4$) for the formation of organomegnesium halides is higher for higher values of *j*. This was only valid when the values of μ_ε is in the range from 9 to 20. Table 1 give the values of μ_ε for all solvents used by Imamura and his collaborators in his various publications in this journal. It is interesting that the results of Khan et al. [10] about the values of μ_ε applied to copper chloro complex in various aprotic solvents also seem to hold for magnesium carbon composite in THF.

Table 1
The values for dielectric constant ε and μ_ε at room temperature [10].

	THF	Benzene	Cyclohexane	Cyclohexene
ε_r	7.6	2.3	2.0	18.3
μ_ε	9.49	34	42.3	4.5

4. The Grignard mechanism

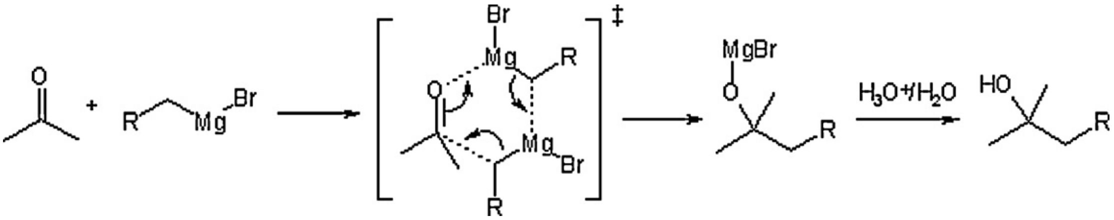
The Grignard reaction is the addition of an organo-magnesium halide (Grignard reagent which is assumed to form during ball milling in the presence of chloride or bromide impurities) to a ketone or aldehyde, to form a tertiary or secondary alcohol, respectively. THF or diethyl ether is often used as solvents for Grignard reagents because of the oxygen atom's ability to coordinate to the magnesium ion component of the Grignard reagent. In addition, the oxygen atom has no acidic hydrogen that can undergo an acid–base reaction with the Grignard reagent. Victor Grignard (University of Nancy, France) was awarded the 1912 Nobel Prize in Chemistry for the discovery of such reagents. In a reaction involving Grignard reagents, it is important to ensure that no water is present, which would otherwise cause the reagent to rapidly decompose. This indicate that indeed, it is the effect of dielectric constant which play a major rule since the dielectric constant of water is very high compared to THF. Thus, most Grignard reactions occur in solvents such as anhydrous diethyl ether or tetrahydrofuran, because the oxygen of these solvents stabilizes the magnesium reagent. This is the reason why it may be preferable for such reactions to be carried out in nitrogen or argon atmospheres. Many methods have been developed to initiate sluggish Grignard reactions. Mechanical methods include crushing of the Mg pieces in situ, rapid stirring, and sonication of the suspension. These methods weaken the passivating layer of MgO, thereby exposing highly reactive magnesium to the organic halide which may be formed during ball milling of THF [8]. This is similar to the ball milling of magnesium/carbon composite in the presence of THF.

5. The effect of the stability constant for metal complex formation

Grignard reagents are formed via the action of an alkyl or aryl halide on magnesium metal. The reaction is conducted by adding the organic halide to a suspension of magnesium in an ether, which provides ligands required to stabilize the organo-magnesium compound. Typical solvents are diethyl ether and tetrahydrofuran. It is assumed that alkyl or aryl halide is formed during ball milling due to the presence of halide impurities such as chlorides, bromides and/or iodides. Thus in the presence of THF the stability constants β_j for chloro- or bromo-magnesium organic complex formation is higher than in other solvents as was shown by comparing the values of μ_ε for the different solvents shown in Table 1. Oxygen and polar solvents such as water or alcohols are not compatible with Grignard reagents. The reaction proceeds through single-electron transfer (no complex formations). Finally it is known that Grignard reagent is very useful for forming carbon–heteroatom bonds [9].

6. Reaction mechanism

The addition of the Grignard reagent to the carbonyl typically proceeds through a six-member ring transition state [8].



However, with hindered (e.g. in the presence of oxygen or water) Grignard reagents, the reaction may proceed by single-electron transfer.

7. Conclusion

THF was the best solvent in Imamura work, probably because of the ability of the ether oxygen in THF to coordinate to Mg ions to form various organo-magnesium halides complex. It is assumed those alkyl or aryl halides are formed during ball milling. The alkyl or aryl halides react with magnesium powder to form organo-magnesium halides. Furthermore the stability constants β_j for organo-magnesium halides formation in THF was much higher than in other solvents. This is because the value of μ_ε for THF was about 10. At this value of μ_ε the stability constants β_j for complex formation was shown previously to be high and increases with increasing j values from 1 to 4. More experimental verifications are needed to confirm that indeed μ_ε can be an indicator for the ability of metal (Mg or Cu in THF) to form organo-metal complex. Furthermore this work indicates that halide impurities may be the culprit for the improved hydrogen storage in mechanically activated Mg/C composites and in the presence of THF. Finally the values of μ_ε must be calculated for any compound before it can be used as organic.

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