STUDIES ON THE EFFECT OF CATALYSIS AND DESTABILIZED AGENT ON THE HYDROGEN STORAGE PROPERTIES OF MAGNESIUM HYDRIDE AND MIXED COMPLEX HYDRIDE

NURULJANNAH BINTI JUAHIR

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April 2016

Main supervisor : Mohammad bin Ismail, Ph.D.

School : School of Ocean Engineering

Solid state hydrogen storage is an interesting method for storing hydrogen compared to compressed and liquefied hydrogen storage due to its favourable safety considerations and high gravimetric capacity. Among the solid state hydrogen materials, MgH_2 and $NaAlH_4$ are materials that have potential to be used as hydrogen storage material. The purpose of this study is to improve the hydrogen storage properties of MgH_2 and $NaAlH_4$ by modifying it with catalyst or destabilized with other hydrides. For MgH_2, the hydrogen sorption properties of MgH_2 can be improved by addition of catalyst (Co_2NiO) prepared by ball milling. The onset desorption temperature showed improvements, as well as dehydrogenation and rehydrogenation kinetics due to the formation of active species of Mg-Co alloy and $Co_{1.29}Ni_{1.71}O_4$ during the heating process. Apart from using catalyst, destabilization concept has been introduced to improve the hydrogen storage properties of MgH_2. A MgH_2-Li_3AlH_6 (4:1) destabilized system was prepared by ball milling to investigate the destabilization effect between MgH_2 and Li_3AlH_6. It was found that the formation of intermediate phase of $Li_{0.92}Mg_{4.08}$ and $Al_{12}Mg_{17}$ during dehydrogenation process was due to the destabilization of MgH_2 by Li_3AlH_6 and this intermediate phase plays a critical role in the enhancement of the hydrogen sorption properties of

MgH_2-Li_3AlH_6 destabilized system. From the result obtained, it was found that the optimize composite in this system was a composite with molar ratio of 4:1. In order to improve the hydrogen sorption properties of MgH_2-Li_3AlH_6 destabilized system, K_2TiF_6 catalyst was added into the composite. The formation of in-situ species of Al_3Ti, LiF and TiH_2 during the ball milling or heating process was responsible in improving the sorption properties of MgH_2-Li_3AlH_6 destabilized system. Besides MgH_2, the hydrogen storage properties of $NaAlH_4$-$Mg(BH_4)_2$ (2:1) composite with and without addition of 5 wt.% TiF_3 was also investigated in this study. It was found from X-ray diffraction (XRD) pattern, $NaAlH_4$ and $Mg(BH_4)_2$ peaks were absent and new peaks of $NaBH_4$ and $Mg(AlH_4)_2$ dominated the XRD pattern after ball milling. This result indicated that the solid state reaction between the components of $NaAlH_4$ and $Mg(BH_4)_2$ mixture was completed during the milling process. The dehydrogenation process of $NaAlH_4$-$Mg(BH_4)_2$-TiF_3 composite can be divided into three stages. It is believed that the formation of Ti-containing and F-containing species during the ball milling or the dehydrogenation process might be actually responsible for the catalytic effects, and thus, further improved the dehydrogenation and rehydrogenation of the TiF_3 added $NaAlH_4$-$Mg(BH_4)_2$composite system.

Abstrak tesis yang dikemukakan kepada senat Universiti Malaysia Terengganu sebagai memenuhi keperluan ijazah Sarjana Sains.

KAJIAN TENTANG KESAN PEMANGKIN DAN AGEN PENYAHSTABILAN DALAM CIRI-CIRI PENYIMPANAN HIDROGEN MAGNESIUM HIDRIDA DAN KOMPLEKS HIDRIDA

NURULJANNAH BINTI JUAHIR

April 2016

Penyelia Utama : **Mohammad bin Ismail, Ph.D.**

Pusat Pengajian : **Pusat Pengajian Kejuruteraan Kelautan**

Penyimpanan hidrogen dalam bentuk pepejal adalah kaedah yang menarik bagi penyimpanan hidrogen berbanding dengan penyimpanan dalam bentuk mampatan dan cecair disebabkan oleh lebih selamat dan kapasiti gravimetrik yang lebih tinggi. Diantara bahan-bahan penyimpanan hidrogen dalam bentuk pepejal, MgH_2 dan $NaAlH_4$ adalah bahan-bahan yang mempunyai pontensi untuk dijadikan sebagai bahan penyimpanan hidrogen dalam bentuk pepejal. Tujuan kajian ini adalah untuk memperbaiki ciri-ciri penyimpanan hidrogen bagi MgH_2 dan $NaAlH_4$ diubahsuai dengan menggunakan pemangkin atau penyahstabilan dengan hidrida lain. Untuk MgH_2, ciri-ciri penyerapan hidrogen boleh diperbaiki dengan penambahan pemangkin Co_2NiO yang di hasilkan menggunakan kisaran bola. Suhu permulaan perlepasan hidrogen menunjukkan pembaikkan, begitu juga dengan pelepasan dan penyerapan kinetik disebabkan oleh pembentukkan spesies aktif Mg-Co alloy and $Co_{1.29}Ni_{1.71}O_4$ semasa proses pemanasan. Selain penggunaan pemangkin, konsep ketidakstabilan telah diperkenalkan untuk meningkatkan ciri-ciri penyerapan hidrogen dalam MgH_2. Satu sistem ketidakstabilan MgH_2-Li_3AlH_6 (4:1) telah disediakan dengan menggunakan kisaran bola untuk mengkaji kesan ketidakstabilan antara MgH_2 dan Li_3AlH_6. Telah didapati bahawa pembentukkan fasa pertengahan

$Li_{0.92}Mg_{4.08}$ dan $Al_{12}Mg_{17}$ semasa proses dihidrogenasi disebabkan oleh ketidakstabilan MgH_2 oleh Li_3AlH_6 dan fasa pertengahan ini memainkan peranan penting dalam meningkatkan ciri-ciri penyerapan hidrogen. Daripada keputusan yang diperolehi, didapati bahawa komposit yang optimum di dalam sistem ini adalah komposit dengan nisbah molar 4:1. Untuk meningkatkan lagi ciri-ciri penyerapan hidrogen sistem ketidakstabilan MgH_2-Li_3AlH_6, pemangkin K_2TiF_6 telah ditambah ke dalam komposit. Pembentukkan spieses *in situ* Al_3Ti, LiF dan TiH_2 semasa proses pengisaran bola atau proses pemanasan menyebabkan penambahbaikan dalam ciri-ciri penyerapan hidrogen sistem ketidakstabilan MgH_2-Li_3AlH_6. Selain MgH_2, ciri-ciri penyerapan hidrogen sistem $NaAlH_4$-$Mg(BH_4)_2$ (2:1) komposit dengan dan tanpa penambahan 5 wt.% TiF_3 telah dikaji dalam kajian in. Telah dijumpai daripada pembelauan sinar X, puncak $NaAlH_4$-$Mg(BH_4)_2$ telah tiada dan puncak baru $NaBH_4$ dan $Mg(AlH_4)_2$ menguasai corak pembelauan sinar X selepas pengisaran bola. Keputusan ini menunjukkan tindak balas pepejal diantara komponen campuran $NaAlH_4$ dan $Mg(BH_4)_2$ telah selesai semasa proses pengisaran bola. Proses pelepasan hidrogen $NaAlH_4$-$Mg(BH_4)_2$-TiF_3 komposit boleh dibahagikan kepada tiga peringkat. Dipercayai bahawa pembentukkan spesies Ti dan F semasa pengisaran bola atau proses pelepasan hydrogen bertangungjawab bagi kesan pemangkin, dan seterusnya, menambah baik pelepasan dan penyerapan system komposit $NaAlH_4$-$Mg(BH_4)_2$ yang ditambah TiF_3.