Electronic Supplementary Information

High catalysis of $MgCl_2$ in hydrogen generation via hydrolysis of Mg-based hydride prepared by hydriding combustion synthesis

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Experimental

Magnesium (99.72 wt.%, -325 mesh) and nickel (99 wt.%, 2-3 μm) in molar ratio of Mg:Ni = 99:1 were chosen to prepare Mg-based hydride for the high content of MgH_2, which was determined by our previous optimization experiments. The powders mixed with acetone by an ultrasonic homogenizer, and then they were completely dried in air at 326 K. The powders were directly heated in HCS reactor without any compressive treatment. The powders were heated up to 853 K under 2.0 MPa hydrogen pressure and then held at this temperature for 1h. During the cooling period, the powders were kept at 613 K for 10 h. Part of the HCS products were mechanically milled in 50 mL stainless steel vial with stainless steel balls (ball to powder ratio of 20:1) at 400 rpm under 0.1 MPa Ar atmosphere for 1.0 h. The HCS and HCS+MM products were used directly for hydrolysis experiments.

The hydrolysis reactions were carried out in a flask reactor with three openings (one for water supply, one for pH-electrode or thermocouple and the other for hydrogen exhaustion). To keep the reaction temperature at 303 K, the reactor was immersed in water bath agitated by a magnetic stirrer (Scheme S1). Mg-based hydride of 0.5 g was reacted in 20 mL solution. The 0.5 mol L^{-1} $MgCl_2$ solution was stirred for more than 1 hour to ensure that $MgCl_2$ was dissolved in water in our experiment (the solubility of $MgCl_2$ in water at 303 K is 55.8 g/100 mL [1]). The generated hydrogen was flowed through silica gel before being measured by a flow meter (ADM 2000E, Agilent Technologies). Each reaction was repeated at least three times and had good reproducibility with a relative error not exceeding ±3%.

The reaction solution was filtrated by membranes with pore size of 1.2 μm in Buchner funnel. The deposited solid by-product was washed by pure water and filtrated three times, and then the by-product was dried to a constant weight at 323 K. After being complemented to 20 mL with pure water and stirred fully, the filtrate was used directly for the cyclic kinetic measurements of hydrogen generation via hydrolysis in $MgCl_2$ solution.

The crystal structure of samples was examined by X-ray diffraction (XRD) with Cu Kα radiation (40kV and 35mA) using an ARL X'TRA diffractometer. The elemental compositions of the samples were analyzed by energy dispersive X-ray spectroscopy (EDS, EDAX Inc.).The pH value of the solution was measured with pH meter from Mettler-Toledo, using a calibrated LE409 electrode.

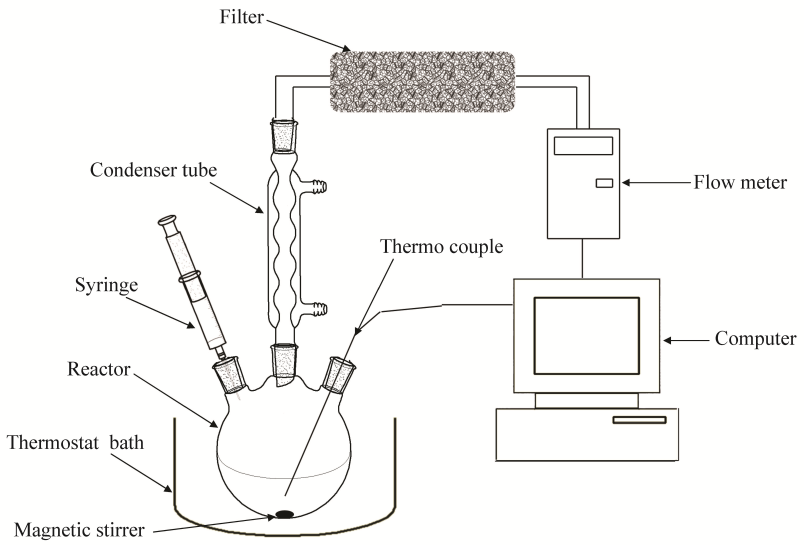
Reference:

[1] J.D. Speight, in *Lange's handbook of chemistry*, McGraw-Hill, New York, sixteenth edn., 2005, pp. 1.322

Characterization of samples

Figure S2, ESI† shows the XRD patterns of the Mg-based hydride prepared by HCS and the deposited solid by-product of hydrolysis of the Mg-based hydride prepared by HCS+MM in 0.5 mol L^{-1} $MgCl_2$ solution after 30 min. The single-phase of $Mg(OH)_2$ is shown in the XRD pattern of Fig. S2(a), ESI†, indicating that MgH_2 and Mg almost reacted completely. Fig. S2(b), ESI† shows a mixture of MgH_2 and Mg, and it indicates that there is about 4 wt.% unhydrided Mg remained in the HCS product obtained by the Rietveld analysis. It should be pointed that there was a small amount Ni in the Mg-based hydride as the original chemical composition was $Mg_{99}Ni$ before hydriding. However, the amount of Ni is under the XRD analysis sensitivity. The nickel and unhydrided Mg remained in the HCS product is consistent with the difference between the measured hydrogen yield and the theoretical value.

Figure S3, ESI† shows the EDS pattern of the deposited solid by-product after hydrolysis of Mg-based hydride in 0.5 mol L^{-1} $MgCl_2$ solution for 30 min. The main elements in the sample were magnesium and oxygen. There was a small amount of nickel (0.9 at.%) and chloride (0.5 at.%), which indicates that there might be tiny amount of residue consisting of chloride in the deposited by-product.



Scheme S1 Schematic diagram of the apparatus for the hydrolysis reaction in this study

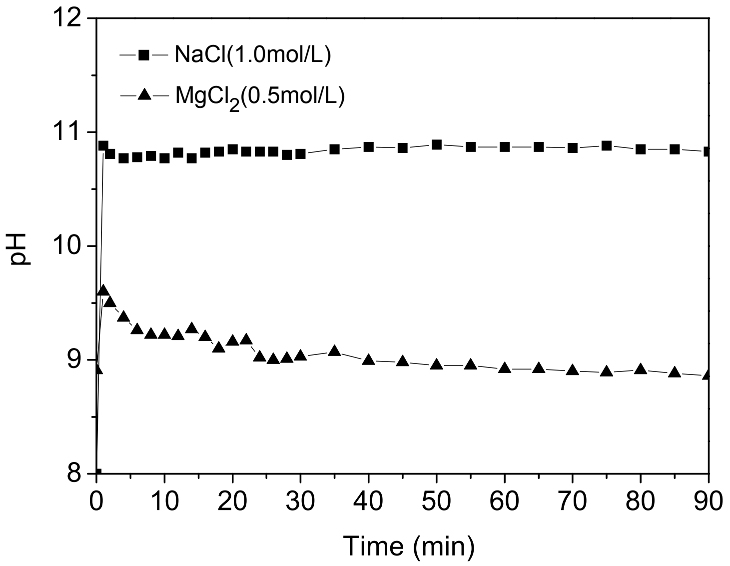


Fig. S1 pH value changes in the hydrolysis of Mg-based hydride prepared by HCS in $MgCl_2$ solution and in NaCl solution with the same molarities of Cl^- at 303K

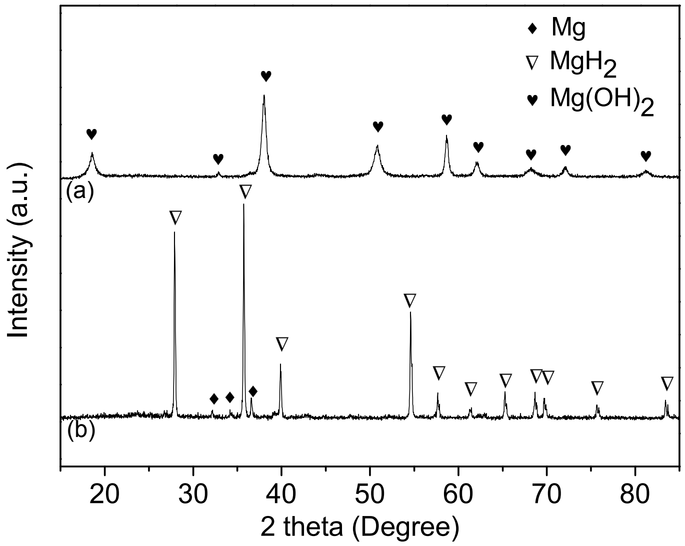


Fig. S2 XRD patterns: (a) Deposited solid by-product after hydrolysis of Mg-based hydride prepared by HCS+MM in 0.5 mol L^{-1} $MgCl_2$ solution for 30 min and (b) Mg-based hydride prepared by HCS method.

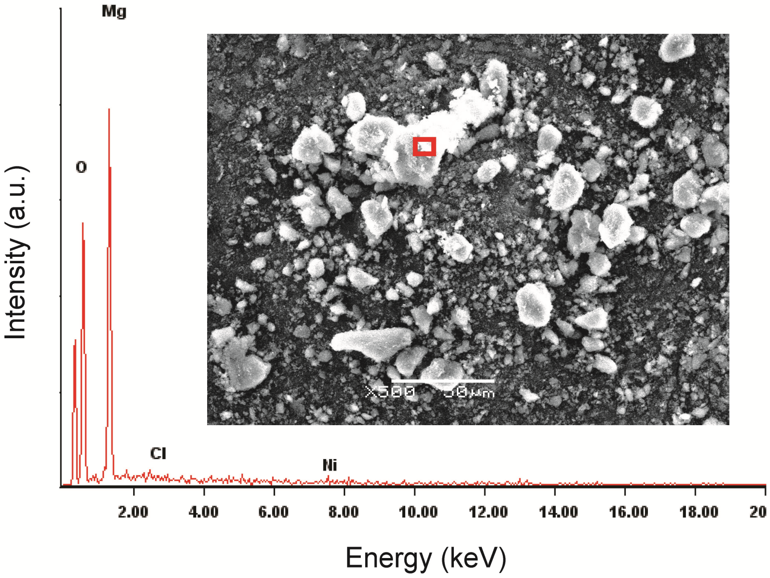


Fig. S3 EDS pattern of the deposited solid by-product after hydrolysis of Mg-based hydride prepared by HCS+MM in 0.5 mol L^{-1} $MgCl_2$ solution for 30 min