

# HYDROGEN- GENERATING COMPOSITION ON MAGNESIUM BASE

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## Introduction

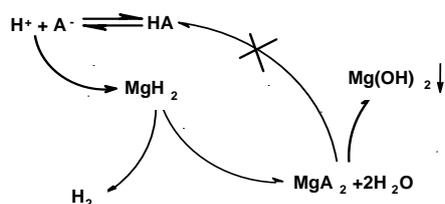
An interaction of light metals or its hydrides with proton-containing compounds is esteemed as one of the most simple and accessible methods of hydrogen production for a feed of autonomous and portative sources of electrical energy. However on route of creation of such hydrogen generators there are considerable technical difficulties. An unsolved problems mass and heat transfer and provision of regulable on demand evolution of high-clean hydrogen are a basic from it. Furthermore, hydrolysis of suitable for this aim solving metal hydrides such as  $MgH_2$ ,  $AlH_3$ ,  $BeH_2$  is difficult by low water solubility of formed hydroxides (-lg  $K_{sp}$  value for  $Mg(OH)_2$ ,  $Be(OH)_2$  and  $Al(OH)_3$  are equal 11.15, 21.2 and 32.0 respectively). In the present work hydrogen production by interaction of magnesium or magnesium hydride with proton-containing compounds is studied.

## Results and Discussion

In  $MgH_2$  hydrolysis



a rate of hydrogen evolution is very low and full hydrogen evolution does not descend even in two day. It, apparently, is connected with diffusion limitation induced by low water solubility of magnesium hydroxide as  $1.9 \text{ mg} \cdot \text{l}^{-1}$  at  $21^\circ\text{C}$  formed on reaction (1).



The hydrogen evolution is impossible in process wherein magnesium hydride interacts with HA acid that return in start state constantly by hydrolysis as the magnesium salts are not hydrolyzed at normal conditions [1].

For regulable and completely controlled hydrogen evolution by interaction of magnesium hydride with other reagent it is necessary, that formed product was well water-soluble. Such reagent can be the compound dissociating in water with proton formation or Brønstedt acid.

A compounds with alkalinity are not applicable for this problem solution, as  $Mg(OH)_2$  is alkali-insoluble. Reagents with high vapor pressure over solution, as hydrochloric, nitric or acetic acids or salts hydrolyzed with their formation (as iron, aluminium or zinc chlorides) are unusable in this reaction also.

The solid organic acids with minimum molecular weight, well water soluble and water-soluble magnesium salts formed are preferable to clear hydrogen production by interaction of magnesium hydride with acids. A few organic acids as glycolic, malonic, citric or succinic acids or its anhydrides that are converted into respective acids by water interaction conform with these regulations. Environmental safety of these acids and its magnesium salts are important too.

The citric acid is tribasic but  $HA/MgH_2=2$  molar ratio is need for full completion of reaction with  $MgH_2$  over a low  $K_a$  value on second and third dissociation stages ( $pK_2=4.761$ ;  $pK_3=6.40$  as against to  $pK_1=3.13$ ). The citric acid is well water-soluble as 133 g per water 100 g and the hydrogen evolution rate may be regulated by dosed water supply.

The dissociation constants of sulphuric acid on first and second stages are equal  $pK_1<0$ ,  $pK_2=1.94$ . Magnesium sulfate is well water-soluble as  $355 \text{ g} \cdot \text{l}^{-1}$  at  $20^\circ\text{C}$  and vapor pressure of sulphuric acid is less than it for water. The experiments show that sulphuric acid reacts with magnesium hydride as dibasic without diffusive limitations concerned with salts water solubility.



The determining factor for full interaction of magnesium hydride on equation (2) is sulphuric acid concentration. The calculation show that on equation (2) 98 g of  $H_2SO_4$  (1 mole) produces 120 g of  $MgSO_4$  (1 mole) dissolving in  $120:355 = 0.338 \text{ l}$  of water wherefrom for reaction without diffusive limitations concerned with insolubility of magnesium sulfate in this media is need acid concentration  $\leq 22.5 \text{ wt.}\%$ . At water deficit i.e. at acid concentration  $>22.5 \text{ wt.}\%$   $H_2$  evolution ceases after the introducing of last portion of the counted quantity of  $H_2SO_4$  solution and renews after a dilution of a suspension by water alone or is gentle by a strong solution of sulfuric acid. This result indicates the possibility of regulable  $H_2$  evolution

by dosed supply of aqueous solution of  $H_2SO_4$  to magnesium hydride.

For usability magnesium hydride after mixing with fluoroplastic-42 or  $SiO_2$  aerosol (5-15 wt.%) may be formed to tablets at pressure equal of 100-150  $N \cdot cm^{-2}$  and sulfuric acid is mixed with  $SiO_2$  aerosol (10-15 wt.%) to a dust. In this case the rate control of  $H_2$  evolution can be regulated by dosed water supply or tablets disposition concerning solution of sulfuric acid in the device for example similar to a Kipp gas generator [2].

Magnesium metal produces 1  $H_2$  mole per Mg mole in the interaction with proton-containing compounds.

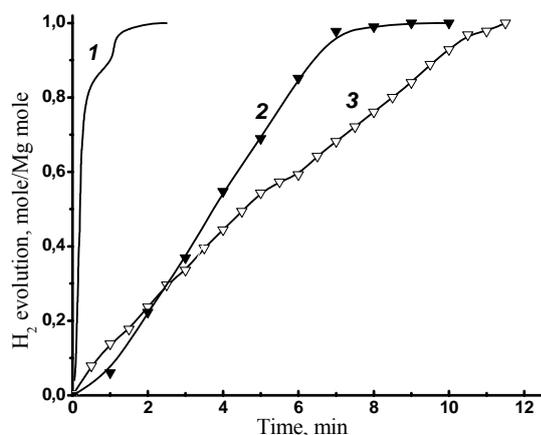


Fig. 1.  $H_2$  evolution curves in interaction magnesium with citric acid (3:2 mol.) at one-fold (1) and dosed (2, 3) water introduction. The introduction time symbolize as triangle.

Magnesium metal like to magnesium hydride not interacts with water because of formation of water-insoluble  $Mg(OH)_2$ . The citric acid use as proton-containing compound has shown, that in this case as against to reaction of  $MgH_2$  the citric acid interacts as tribasic. The regulated hydrogen evolution in this case is reached by dosed supply of water or solution of citric acid (Fig. 1).

### Conclusions

The possibility of production of high-clear hydrogen with need hydrogen pressure as result of irreversible reaction of magnesium or magnesium hydride with proton-containing compounds is important advantage of this process. Magnesium hydride is synthesized by magnesium hydrogenation and for its production at least of 1  $H_2$  mole/Mg mole is required. Carbothermic reduction of magnesium oxide is the main production method of magnesium. The magnesium hydride price is significant (at least in 4-5 times) more than magnesium. The hydrogen production by metallical magnesium interaction with organic acids is justified economically.

### References

1. Tihonov V.N. // Analytical chemistry of magnesium. "Analytical chemistry of elements" series. Moscow. Nauka publisher. 1973. P. 10.
2. Patent RU2345829 Russia (01.11.2006).