CHAPTER 5

ABILITY OF CARBON AEROGEL AS A HYDROGEN STORAGE MATERIAL

5.1 Dehydrogenation Temperature of Pure CA and CA-Mg at Different Concentrations

The desorption behaviours of pure CA and CA-Mg samples as hydrogen storage materials were observed using TPD analysis over a wide temperature range at different concentrations of Mg^{2+}. Figure 5.1 presents the TPD curves of CA and CA-Mg samples (0.002, 0.004, 0.006, 0.008, 0.01 mol) from room temperature to 500 °C with a ramp rate of 10 °C min^{-1}. Initially, the samples were treated with hydrogen gas as the TPD system released hydrogen gas at 50 °C for the adsorption process, followed by a dehydrogenation process where the TPD system was observed by increasing the temperature from room temperature to 500 °C. It can be clearly seen that hydrogen desorption occurred in pure CA and CA-Mg samples, where different initial dehydrogenation temperatures were observed due to the presence of Mg^{2+}.

The pure CA began to release hydrogen gas at 367.81 °C, whereas the initial dehydrogenation temperature of CA-Mg increased first at 377.22 °C (0.002 mol) and 377.33 °C (0.004 mol), then decreased to 372.69 °C (0.006 mol), and finally to 346.76 °C (0.008 mol). However, at 0.01 mol, the dehydrogenation temperature increased back to 411.15 °C due to the different contribution of micropore volume for each sample, as shown in Table 4.4 (Chapter 4). The summary of dehydrogenation temperatures of CA and CA-Mg samples from room temperature to 500 °C after being treated with hydrogen gas at 50 °C for 60 minutes are tabulated in Table 5.1.

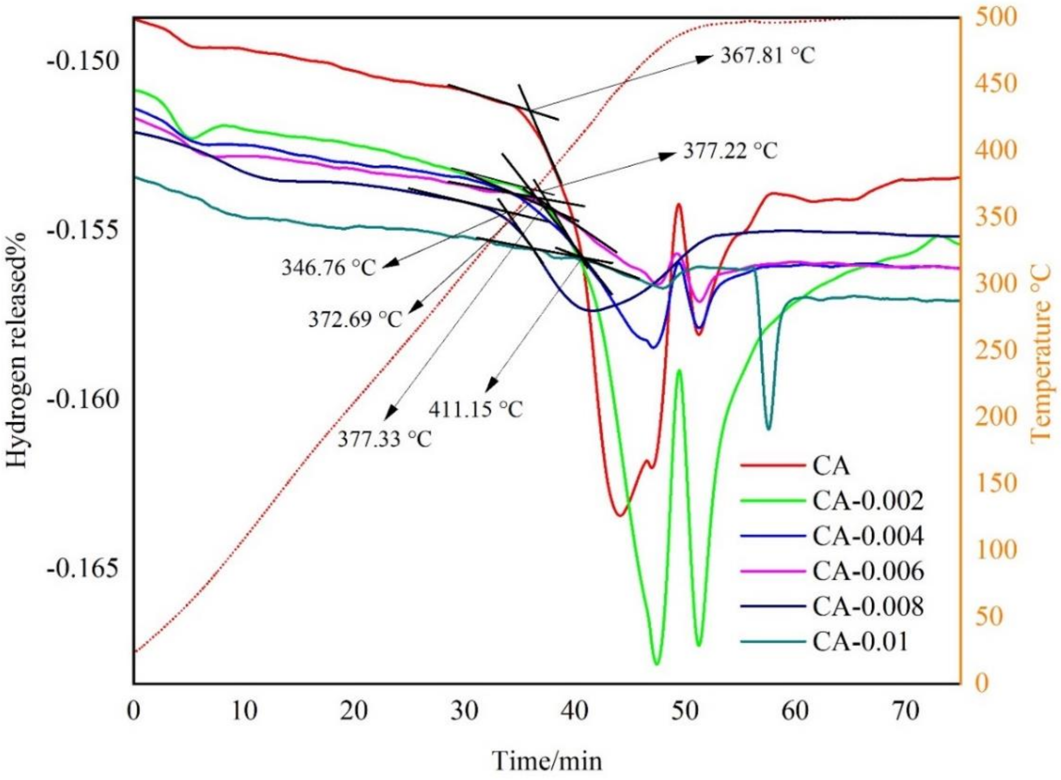

Figure 5.1: TPD Curves of Pure CA and CA-Mg Samples from Room Temperature to 500 °C with The Ramp Rate of 10 ºC min^{-1}

Table 5.1: Initial Dehydrogenation Temperature of CA and CA-Mg Samples from Room Temperature to 500 °C After Being Treated with Hydrogen Gas at 50 °C for 60 Minutes

Samples	**Adsorption Temperature (°C)**	**Initial dehydrogenation Temperature (°C)**
CA	50	367.81
CA-0.002	50	377.22
CA-0.004	50	377.33
CA-0.006	50	372.69
CA-0.008	50	346.76
CA-0.01	50	411.15

5.2 Rate of Hydrogen Desorption

Pure CA and CA-Mg samples had shown a significant TPD curve, especially in terms of hydrogen released during TPD analysis (Figure 5.2). The rates of hydrogen desorption in the pure CA and CA-Mg samples were almost the same when Mg^{2+} was at a concentration of 0.002 mol, but the CA-Mg sample was in favour because it desorbed hydrogen gas the most. In TPD analysis, the nature of sample did not influence the result but totally depending on the surface feature of the sample (Huang et al., 2021). Based on Figure 5.2, the CA-Mg sample showed that Mg^{2+} had enhanced the surface feature of the sample because it was able to desorb hydrogen gas the most compared to pure CA. Besides, the CA-Mg sample was able to adsorb hydrogen gas the most at 50 °C and desorb at 377.22 °C. Thus, the CA-Mg sample at 0.002 mol was the best candidate for hydrogen storage material.

In terms of percentage hydrogen released, pure CA and CA-Mg showed a significant TPD curve, which both consisted of two desorption peaks as shown in Figure 5.2. The first desorption of pure CA occurred after 44 minutes at 0.163% and the second desorption occurred after 7 minutes at 0.158%. For CA-Mg at 0.002 mol, the first desorption took 47 minutes at 0.168% and the second desorption took 4 minutes at 0.167%. Even after the second desorption, CA-Mg released the most hydrogen compared to CA. When compared to pure CA, CA-Mg has the most efficient method of releasing hydrogen, with second desorption taking only 4 minutes.

This happened due to the different contribution of micropore volume in each sample, as shown in Table 4.4 (Chapter 4). The contribution of micropore volume decreased as the concentration of Mg^{2+} increased. The increase in concentration of Mg^{2+} has led to the formation of mesopores in the CA-Mg sample, which is the main feature for hydrogen storage materials. This has been indicated by BET analysis that the addition of Mg^{2+} can enhance the hydrogen desorption behaviour of pure CA, depending on the concentration of Mg^{2+}. As a result of the highest hydrogen desorption amount, 0.002 mol of Mg^{2+} can be considered the optimum condition for synthesising CA as hydrogen storage materials.

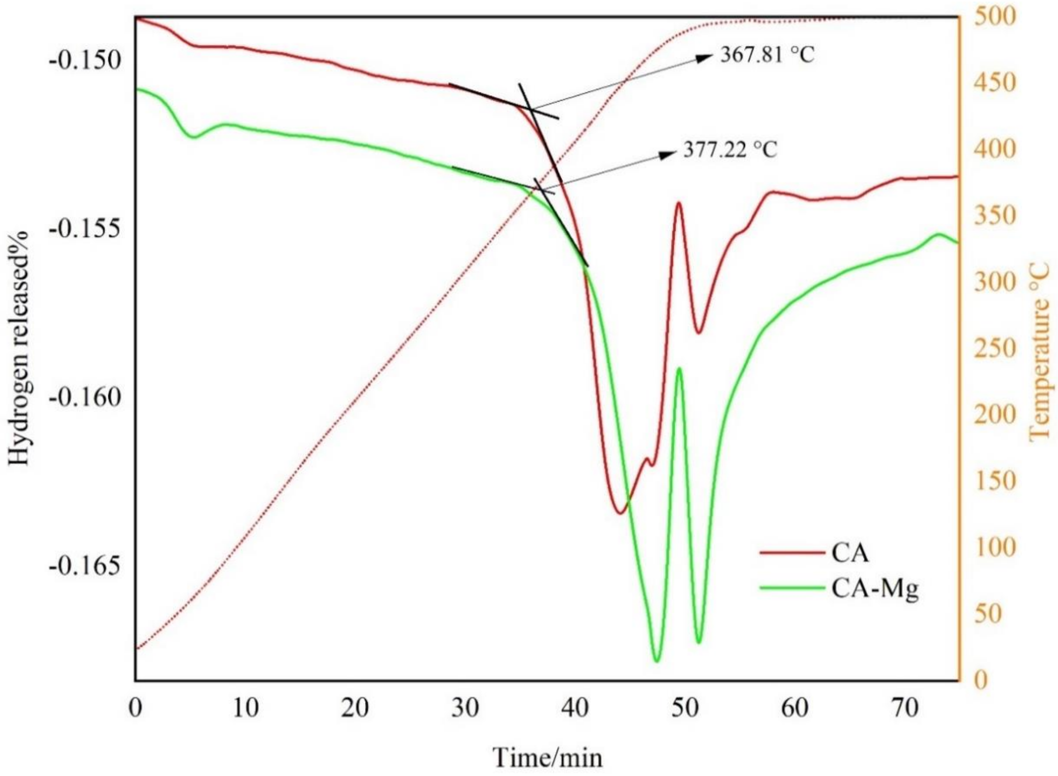

Figure 5.2: Comparison TPD Curve of Pure CA and CA-Mg (0.002 mol) Samples from Room Temperature to 500 °C with The Ramp Rate of 10 °C min^{-1}

Using pure CA as a reference sample in determining the optimum adsorption temperature of hydrogen, pure CA was treated with hydrogen at 30 °C, 50 °C, 70 °C and 100 °C subsequently. The effect was studied beforehand to analyse its contribution to the rate of hydrogen desorption, as shown in Figure 5.3. Pure CA desorbed hydrogen the most when being treated with hydrogen at 70 °C and showed that adsorption of hydrogen occurred rapidly at 70 °C but Mg^{2+} had a great influence as an enhancer where it can made CA-Mg desorb hydrogen the most when being treated with hydrogen at 50 °C as shown in Figure 5.2. Pure CA took 44 minutes for the first desorption to take place when being treated with hydrogen at 50 °C but it took 53 minutes for the first desorption to happen when being treated with hydrogen at 70 °C. Even though the percentage of hydrogen released was the highest (0.167%) at 70 °C, it was time consuming. With the Mg^{2+} enhancement, the time can be reduced to 47 minutes, the adsorption temperature to 50 °C and the percentage of hydrogen released maintained at 0.167% until 0.168%. This is a great achievement for the synthesis process of a CA-Mg (0.002 mol) sample as hydrogen storage materials.

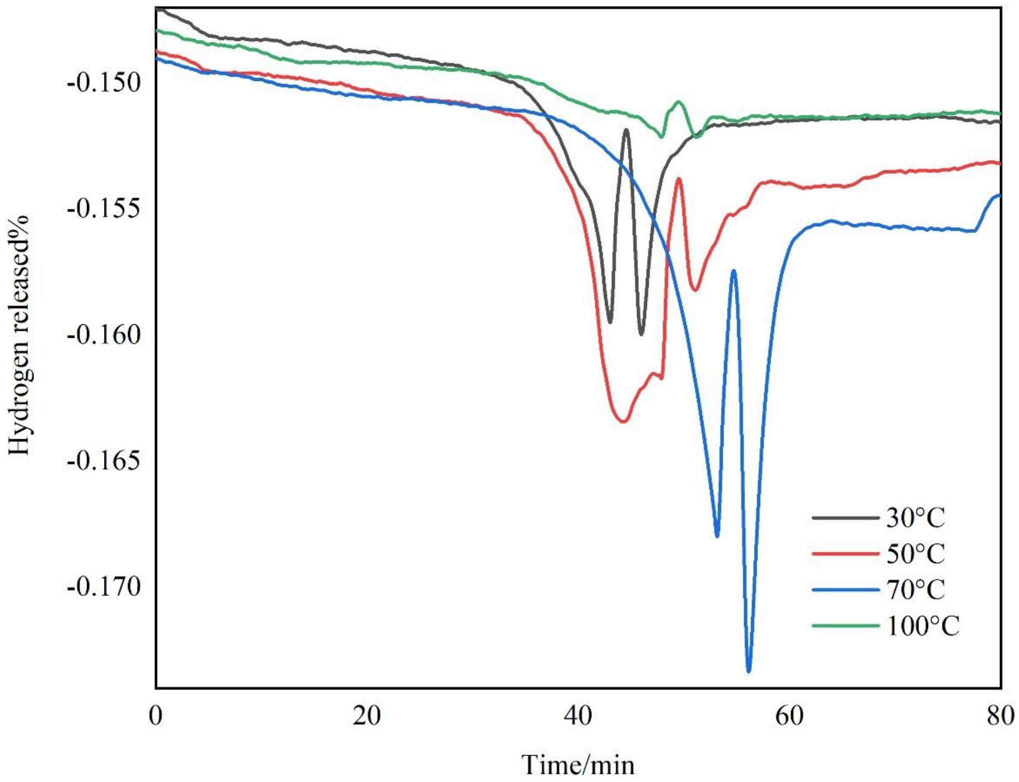

Figure 5.3: Effect of Adsorption Temperature of Hydrogen towards Rate of Hydrogen Desorption of Pure CA

5.3 Carbon Aerogel as a Hydrogen Storage Material

The occurrence of crosslinking reactions between CMC and several metal ions was well represented in this research. From a preliminary study of several metal ions (Mg^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}) as a crosslinking agent, Mg^{2+} showed an outstanding role as a crosslinking agent where it formed a better CMC-Mg aerogel with a spongy structure due to the efficient crosslinking reaction between CMC and Mg^{2+}. The CMC-Mg sample's crosslinked network structure was shown to be the best starting material for the synthesis of CA as hydrogen storage materials. During the carbonisation of CA, Mg^{2+} helped to reduce the weight loss of CA even though the concentration of Mg^{2+} kept increasing as compared to the other metal ions, as shown in Table 4.1 (Chapter 4). The FTIR spectra of CA-Mg samples in Figure 4.3 (Chapter 4), proved that Mg^{2+} played a big role in promoting complete carbonisation of CA because most of the functional groups that exist in CMC-Mg were decomposed during carbonisation. CMC-Mg samples were decomposed into CA and MgO as shown in Figure 4.4 (Chapter 4) where XRD patterns of CA-Mg indicated the characteristics of a highly crystalline compound, which explained the disappearance of the OH peak in the FTIR spectra.

In terms of concentration, 0.002 mol of Mg^{2+} produced the best surface feature of CA because it can desorb hydrogen gas the most during TPD analysis and had the highest rate of hydrogen desorption compared to pure CA. In BET analysis, the morphology of CA-Mg can be analysed based on the N_2 adsorption/desorption isotherm. The hysteresis loop pattern of the isotherm was observed, confirming the presence of mesopores, which are the main feature of hydrogen storage materials. In this case, the CA-Mg represented ink-bottled shape pores, while pure CA represented a narrow slit-shaped pore, as shown in Figure 5.4.

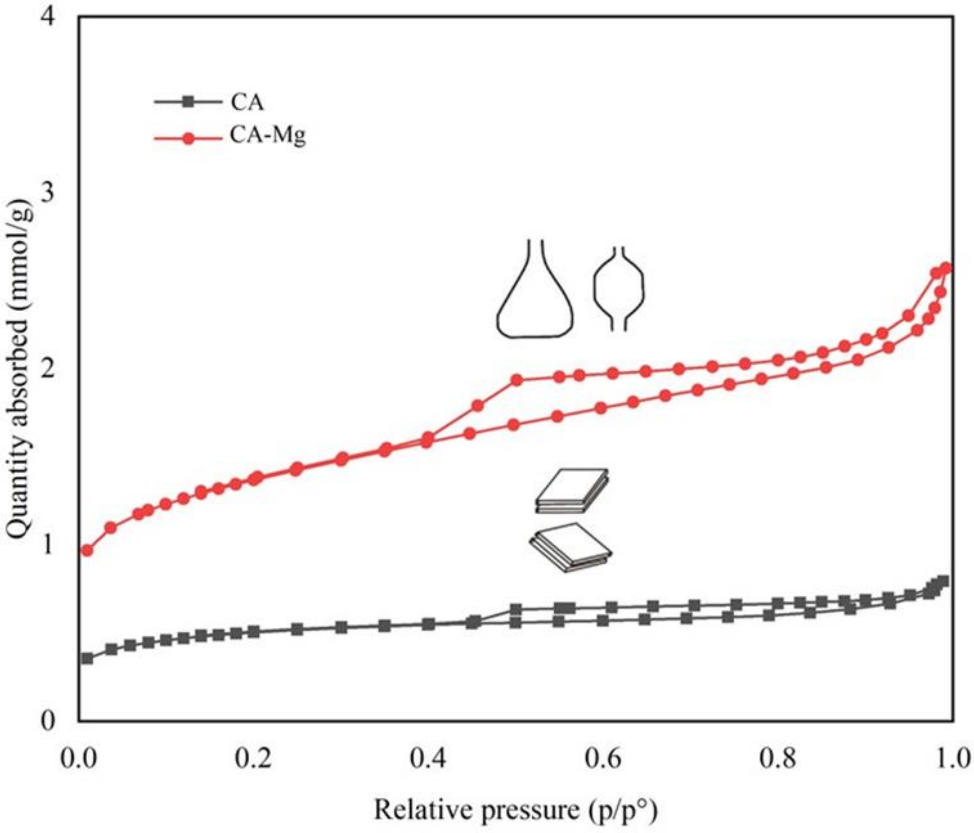

Figure 5.4: N_2 Adsorption/Desorption Isotherms of CA and CA-Mg (0.002 mol) Samples with Related Pore Shape

The morphology of pure CA and CA-Mg (0.002 mol) can be clearly observed from a FESEM image (Figure 5.5), which shows significant changes. Mg^{2+} played an important role as a crosslinking agent for CMC and led to the formation of a well-developed CA structure. Therefore, CA-Mg at 0.002 mol was proven to have the best features as a candidate for hydrogen storage materials.

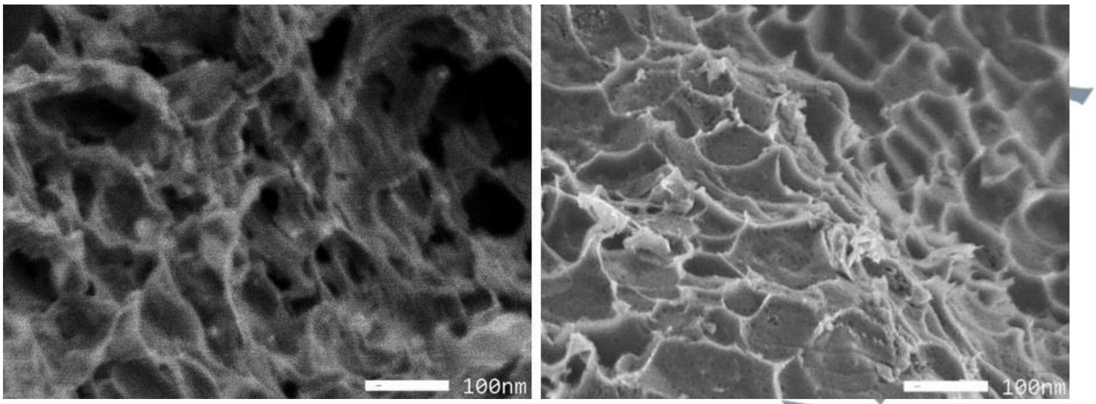

Figure 5.5: FESEM Image of Pure CA and CA-Mg (0.002 mol) Samples

5.4 Conclusion

Hydrogenation was proven to occur on the surface of the pure CA and CA-Mg samples based on TPD analysis. At 0.002 mol, the CA-Mg sample released the most hydrogen gas at 0.168% compared to other concentrations where the initial dehydrogenation temperature was 377.22 °C. The presence of mesopore contributed to the better morphology of CA for hydrogen adsorption. The FESEM image clearly shows the changes in morphology of CA, proving whether CA was better with or without Mg^{2+} enhancement. A well-developed structure of CA-Mg was observed compared to pure CA due to the crosslinked network structure of Mg^{2+} which led to the development of a better pore structure. A slit-shaped pore obtained was also a suitable pore shape for hydrogen storage materials because it could provide a better adsorption site for hydrogen gas.