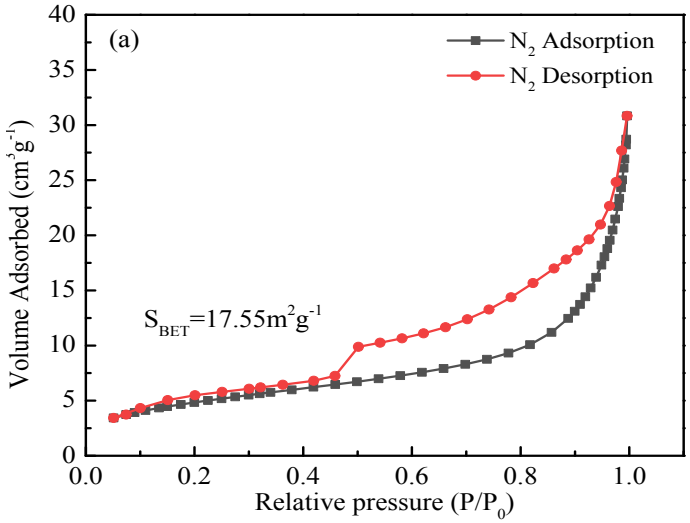
1. BET analysis

The N_2 adsorption-desorption isotherms and pore size distribution diagrams of $CaCO_3$ prepared under optimal reaction conditions are shown in Fig. 1. Fig. 1(a) shows that the N_2 adsorption-desorption isotherm of $CaCO_3$ is of type IV according to the IPUAC classification having H_3 type hysteresis loop in the latter half part (P/P_0 is 0.5~1.0), indicating that the product has a typical mesoporous structure [1]. Moreover, from Fig. 1(b), the pore size distribution is mainly concentrated between 30-50 nm, which is caused by the cavity formed by the hollow microsphere $CaCO_3$ stacking together, which is consistent with the TEM analysis. The BET surface area of the prepared $CaCO_3$ was 17.55 $m^2 \cdot g^{-1}$, which is 3 time higher than that of the ordinary precipitated $CaCO_3$ (about 5 $m^2 \cdot g^{-1}$) [2], which could be highly beneficial for applications of the fabricated $CaCO_3$ in painting industry.



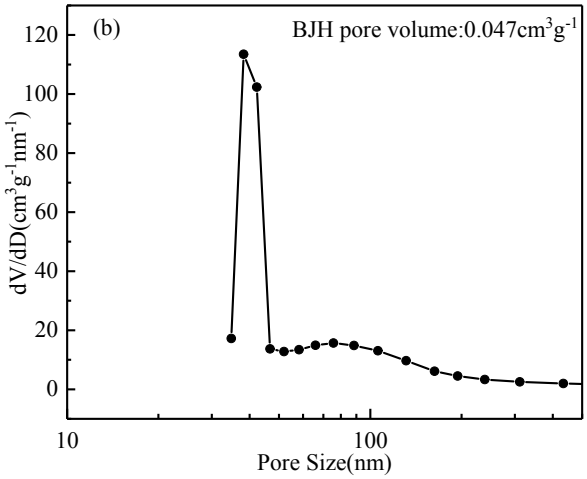


Figure 1(a)**.** Nitrogen adsorption-desorption isothermal curves, and (b) pore diameter distribution of micro-nano hierarchical hollow microspheres $CaCO_3$ obtained

2. TG analysis

Fig.2 (A and B) shows the weight loss curves of $CaCO_3$ prepared without EDTA and with EDTA where the experiments were conducted at 10 °C·min^{-1} heating ramp from ambient to 800 °C temperature under nitrogen atmosphere. The curves can be split into three phases of weight loss i.e. the first stage is the removal of a small amount of free water in the $CaCO_3$ (A-B or A-C); the second stage shows the thermal decomposition of $CaCO_3$ with and without EDTA (C-E or B-D). The initial decomposition temperature (C, B) of the samples with and without EDTA was 686 °C and 676 °C respectively with a corresponding weight loss of 34.45% and 46.11% at the end of the decomposition (E, D). This was attributed to the decomposition of organic matter in EDTA and releases volatile, thus resulted in a lower weight loss percentage [3,4]. Moreover, the obtained hollow sphere with EDTA has a higher specific surface area and a higher proportion of surface molecules, which leads to

significant surface effects and aggravates the tendency of $CaCO_3$ to decompose [5].

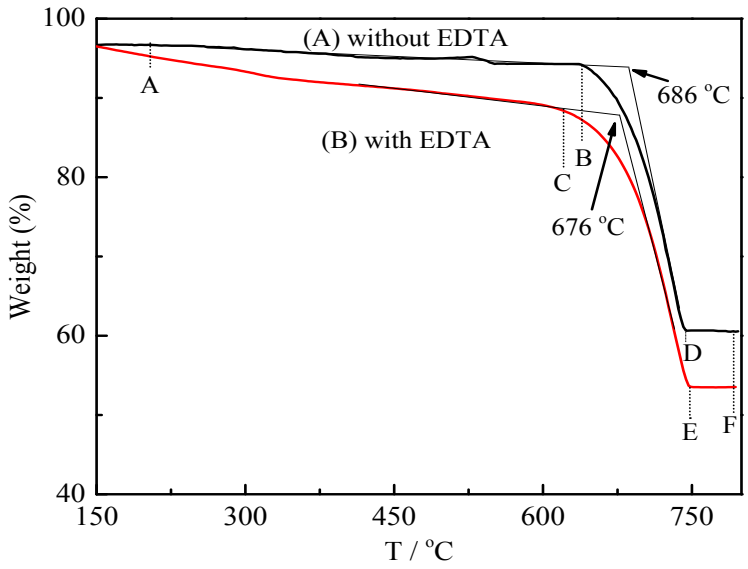


Figure 2. TG diagram of micro-nano hierarchical hollow microspheres $CaCO_3$ under optimal reaction conditions: (A) without EDTA; (B) with EDTA.

1. H. Bodhisatwa, D. A. Wood, V. Vishal, A. K. Varma, D. Sakha and A. K. Singh, *Fuel*, 2018, **220**, 837-848.
2. L. N. Schultz, M. P. Andersson, K. N. Dalby, D. Müter, D. V. Okhrimenko, H. Fordsmand and S. L. S. Stipp, *Journal of Crystal Growth*, 2013, **371**, 34-38.
3. P. K. Hou, R. Li, Q. F. Li, N. Lu, K. J. Wang, M. L. Liu, X. Cheng and S. Shah, *ES Materials & Manufacturing*, 2018, **1**, 57-66.
4. R. J. Das, S. Vupputuri, Q. Hu, Y. Chen, H. Colorado, Z. H. Guo and Z. Wang, *ES Materials & Manufacturing*, 2018, **8**, 46-53.
5. Y. Gao, Y. D. Sun, H. F. Zou, Y. Sheng, X. Q. Zhou, B. W. Zhang and B. Zhou, *Materials Science and Engineering B*, 2016, **203**, 52-58.