Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Mechanisms of Absorption and Desorption of CO_2 by Molten $NaNO_3$-promoted MgO

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1. Preparation of different $NaNO_3$ promoted MgO-based CO_2 absorbents and their characterization data

Three different $NaNO_3$/MgO samples were prepared and compared for the CO_2 absorption capacity.

(1) Preparation of MO samples starting with MgO: MgO and $NaNO_3$ were mixed through ball-milling with acetone using a rotation speed of 60 rpm for 24h and heat-treated for 3h at 450°C in air.

(2) Preparation of MH sample starting with $Mg(OH)_2$: $Mg(OH)_2$ and $NaNO_3$ were mixed through ball-milling and heat-treated for 3h at 450°C. $Mg(OH)_2$ was obtained by reacting $MgSO_4 \cdot 7H_2O(aq)$ with NaOH(aq). After the precipitation reaction is completed after 24 h, the precipitate was collected by filtration and heat-treated.

(3) Preparation of MCH sample starting with $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$: $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ and $NaNO_3$ were mixed through ball-milling with acetone for 24h and heat-treated for 3h at 450°C.

All of the three samples are composed of MgO and $NaNO_3$ according to their XRD patterns without any other phase (Figure S1(a)). The SEM images show some differences among the three samples (Figure S2(b)). The particles in MH sample are the smallest (50-100 nm) and are the most homogeneous in size. MO and MCH samples are composed of larger particles (> 80 nm) and are similar to each other in particle size and the size distribution. However, the image of MCH indicates that the particles in MCH are fused to one another while those in the other two samples appear to be separated from one another. Probably, the fused parts are constituted of $NaNO_3$. However, the exact nature of the fusion cannot be determined by the SEM images only.

As shown in Figure S2 the sample prepared by the method (3) showed the largest CO_2 absorption capacity. That this sample showed the largest capacity seems reasonable considering that decomposing $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ while in contact with molten $NaNO_3$ may result in intimate contact between $NaNO_3$ and MgO to be formed. However, why the decomposition of $Mg(OH)_2$ in the presence of $NaNO_3$ produces the lowest absorption capacity is not clear. Probably, the temperature of OH group loss is lower than the melting point of $NaNO_3$. Further studies are needed. All of the powder absorbent samples in the present study were, therefore, prepared by the method (3).

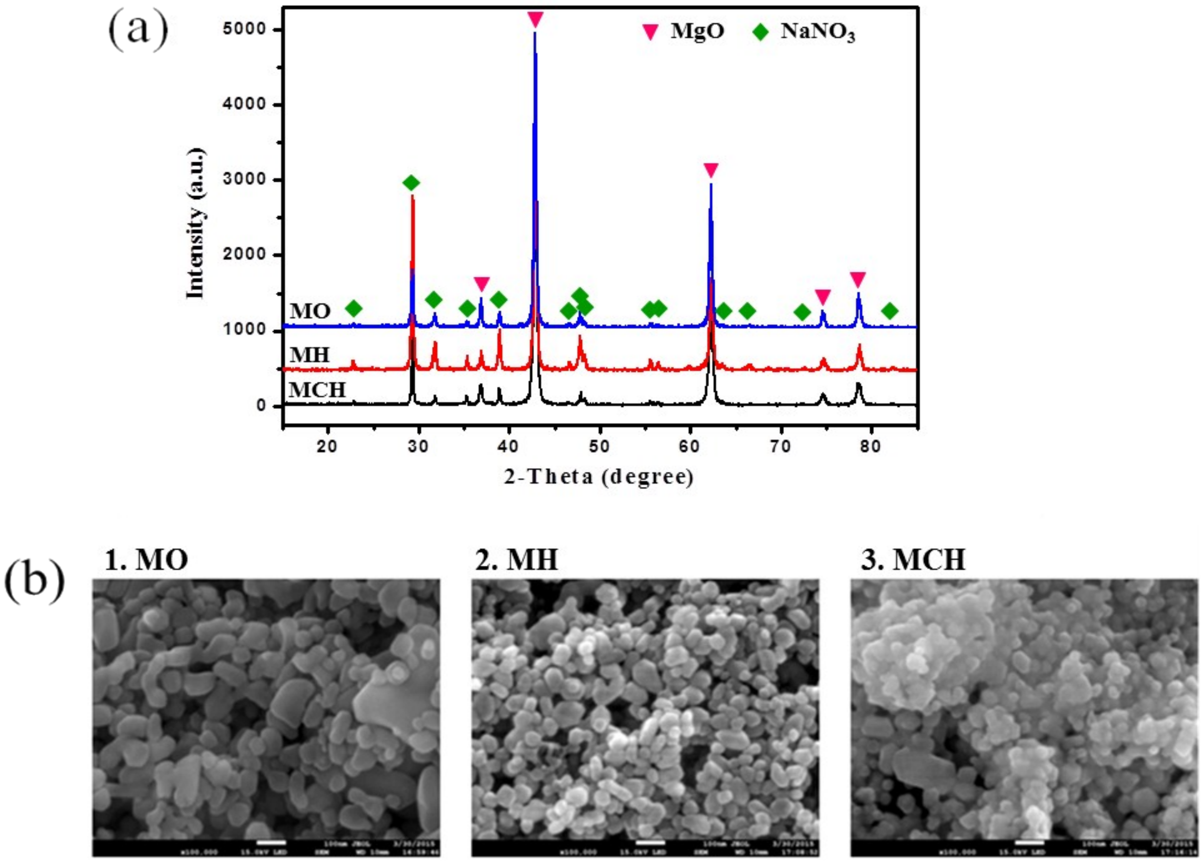


Figure S1. (a) X-ray diffraction patterns and (b) SEM images of MCH, MH, and MO

samples. Sample names are defined in the previous page.

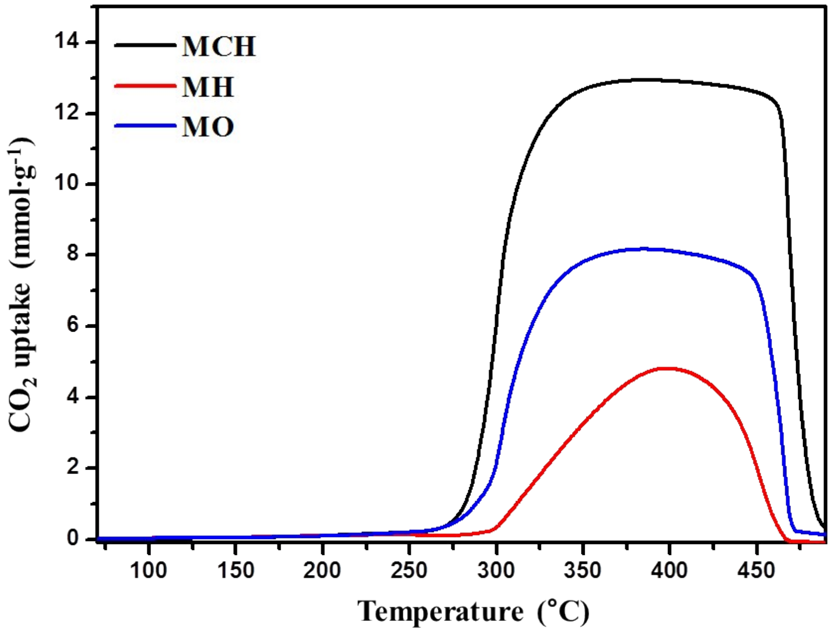


Figure S2. TSA curve of $NaNO_3$/MgO absorbent made different synthesis method. $NaNO_3$/MgO = 0.30, CO_2 100%, 1 atm.

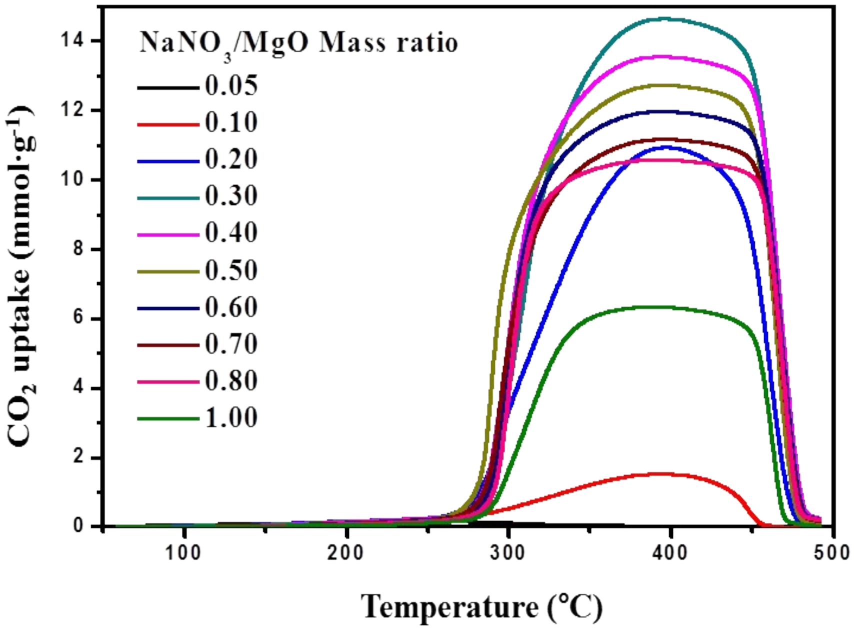


Figure S3. Plots in Figure 2(a) in the conventional CO_2 absorption capacity scale.

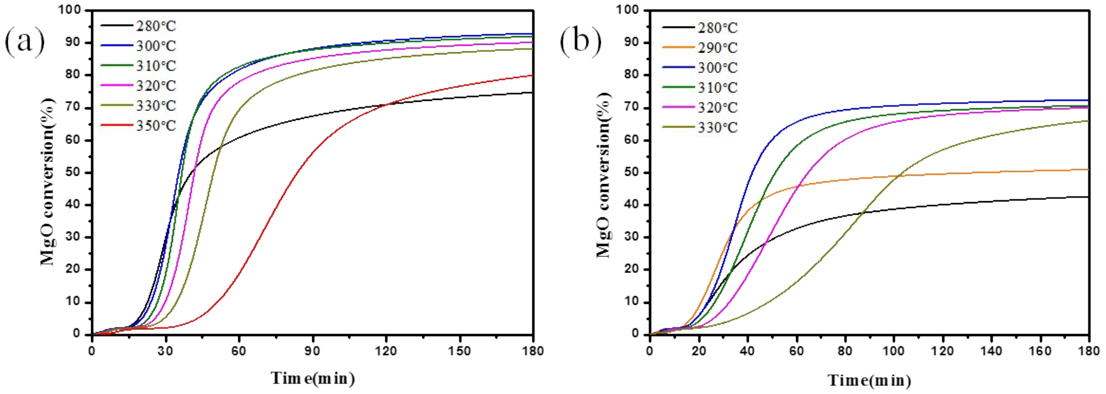


Figure S4. CO_2 absorption isotherms of $NaNO_3$/MgO absorbents at variouis temperatures: (a) 0.30 $NaNO_3$/MgO and (b) 1.00 $NaNO_3$/MgO.

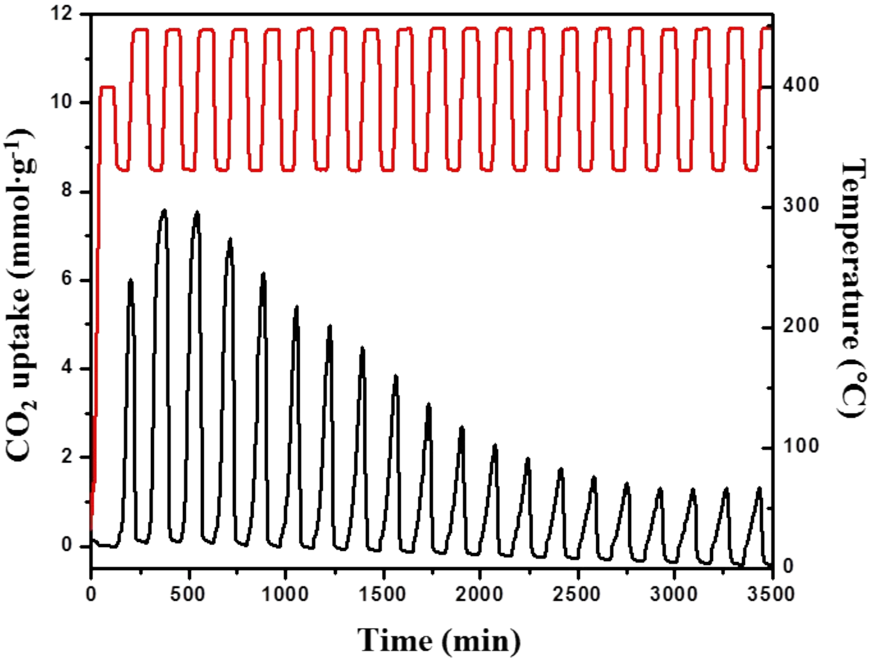


Figure S5. Cycling data of 1.00 $NaNO_3$/MgO under 100% CO_2 condition. (Absorption at 330°C; desorption at 450°C)

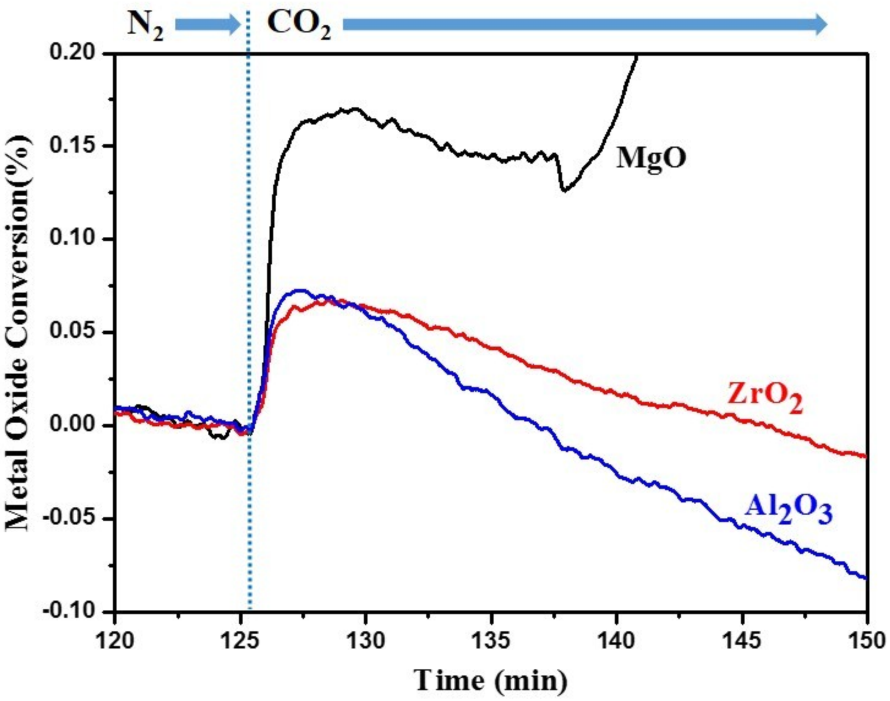


Figure S6. Adsorption test of MgO, ZrO_2, Al_2O_3 powder with $NaNO_3$.

2. Measurement of MgO solubility in molten $NaNO_3$

In order to estimate the solubility of MgO in $NaNO_3$, we adopted the method described by gravimetric analysis. This method appears to be a general practice in measuring the solubility of a solid compound in a high temperature molten salt. 0.7 g of high purity MgO (Aldrich, 99.999%) lumps (> 2 mm) was placed in an alumina crucible. 2.8 g of $NaNO_3$ was place on top of MgO and the crucible was heated to 450°C in a box furnace. The crucible was covered with a lid to prevent contamination. Small aliquots (~10 mg each) were taken from the molten $NaNO_3$ at various points of time for samples for ICP-AES. The sampling was done by draining the top part of the $NaNO_3$ solution. Care was taken to avoid any undissolved MgO particles in the samples. Three or four samples were taken at each point of time. The contents of the samples were determined.

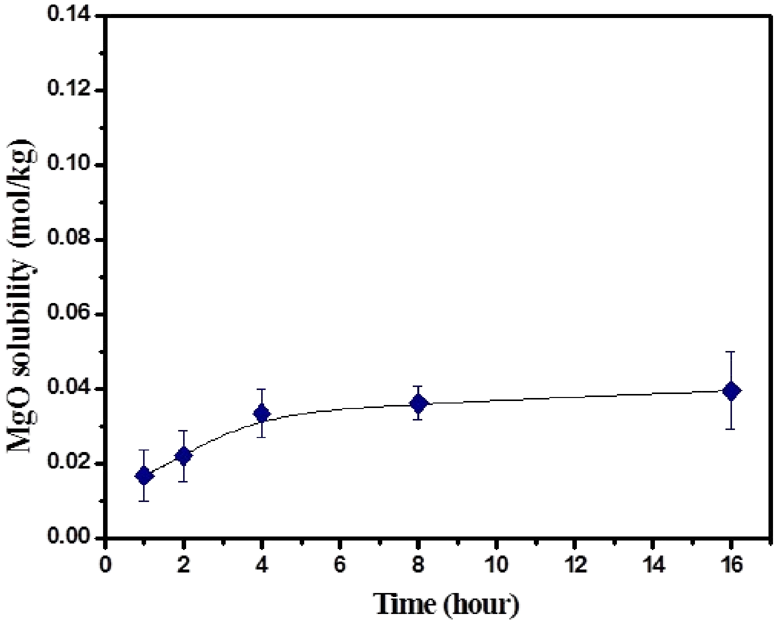


Figure S7. MgO solubility variations in $NaNO_3$ at 450°C

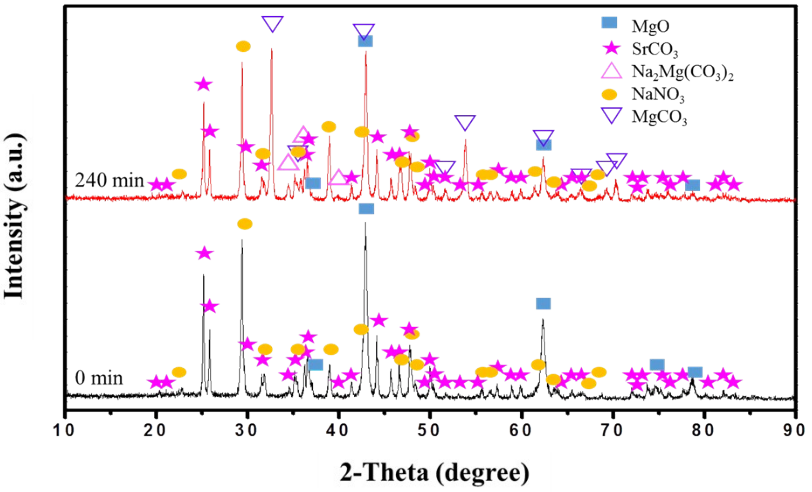


Figure S8. Before and after X-ray diffraction patterns of isothermal CO_2 absorption of $NaNO_3$/MgO absorbent with $SrCO_3$ at 330°C under 100% CO_2.

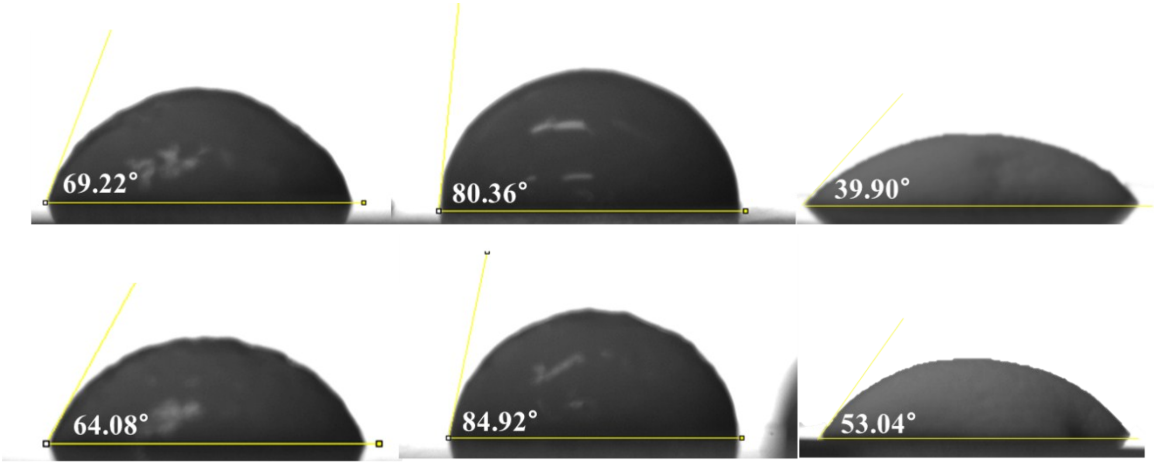
3. Considerations on the ‘contact angle measurement’ of a molten nitrate salt on a

surface.

In order to assess the affinity of molten nitrate promoter to the surfaces of MgO and $MgCO_3$, we devised to measure its ‘contact angle’. Normally, the contact angle measurement is done with a water drop and the angle between the substrate surface and the surface of the flattened water drop is measured by a microscope to get the contact angle. In principle, a contact angle represents the equilibrium state between the cohesive force between water molecules and the adhesive force between water and the substrate surface. However, in general, contact angle measurement is done to compare two different surfaces. A larger contact angle means that the surface has lower affinity and a smaller contact angle higher affinity. We thought that the same principle holds even if the liquid is changed to a molten salt. No matter what the cohesive force and adhesive force are constituted, different contact angles can be interpreted as different degrees of affinity.

There are a few practical problems, however, in performing contact angle measurements with a molten salt. The liquid drop has to be small. In case of using water, the typical size is a few μL. If one is to use $NaNO_3$, a micropipette that can withstand heat above 308°C is required. For this reason, we chose to use a Li/Na/K triple eutectic nitrate with the melting point 120°C, which temperature or slightly higher the tips of commercial micropipettes can withstand. The consequent problem is whether the contact angle with the eutectic nitrate can be used in discussing the affinity to $NaNO_3$. Here, we simple assume that their affinities must show the same trend because both are alkali nitrates of the similar bonding nature. Another problem is the solidification of the molten salt drop during the optical measurement using a microscope. If one is to measure in the liquid state, the microscope has to be installed in an oven. Therefore, we assumed that the contact angle in the solidified drop is not much different from the value in the liquid state. In the least, for the purpose of telling which one between MgO and $MgCO_3$ is more attractive (or repulsive), we believe that there is a very slim chance for the observation made on $LiNO_3$/$NaNO_3$/KNO_3 is reverted on $NaNO_3$.

With these considerations, we believe that the different contact angles in Figure S9 on MgO and partially carbonated MgO can be translated into that MgO has a stronger affinity to molten $NaNO_3$ than $MgCO_3$ does.



Before CO_2 absorption After CO_2 absorption After regeneration

Figure S9. Optical pictures of MgO wafer treated with CO_2 after dropping molten (Li, Na, K)NO_3.

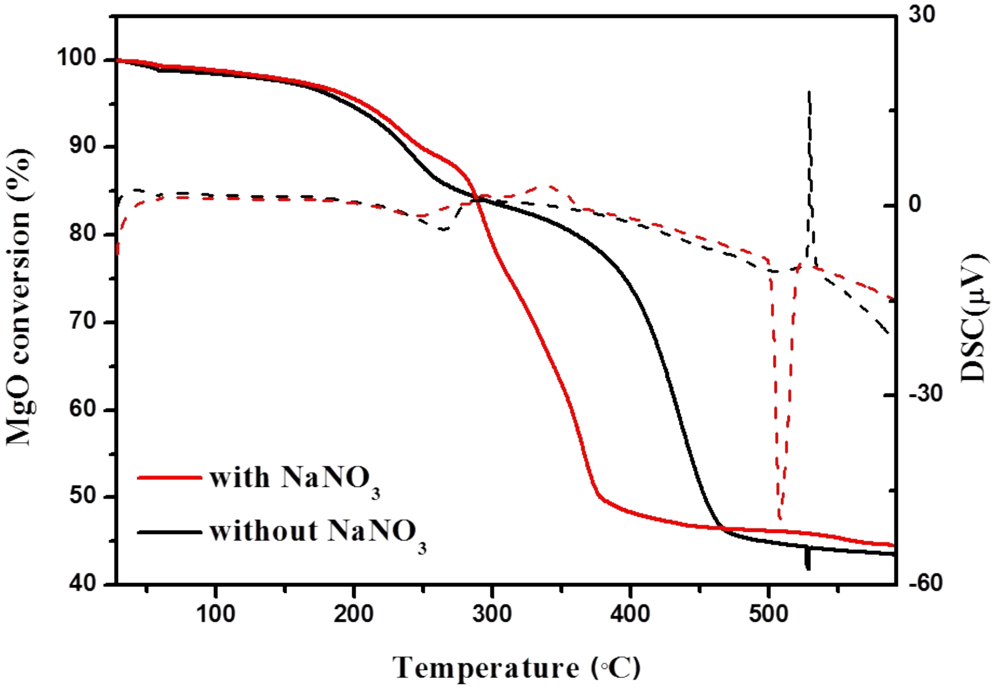


Figure S10. Decomposition behaviors of $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ with and without $NaNO_3$ as a function of temperature in 100% N_2.