The Effect of Temperature on the Carbonation Reaction of CaO with CO_2

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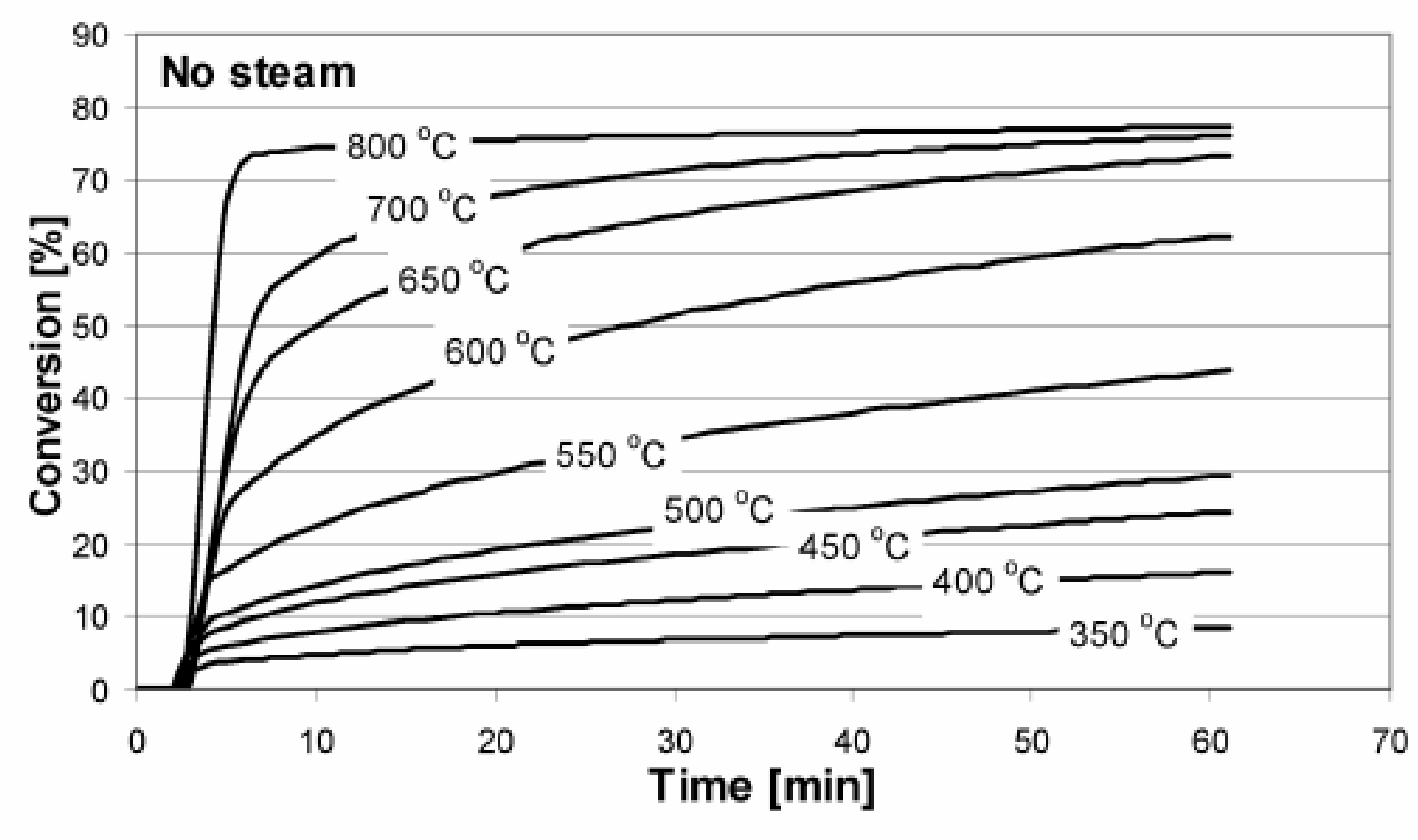
4 The effect of temperature on $CaCO_3$ surface morphology in high CO_2 concentration atmosphere

5 Conclusion

1. Introduction

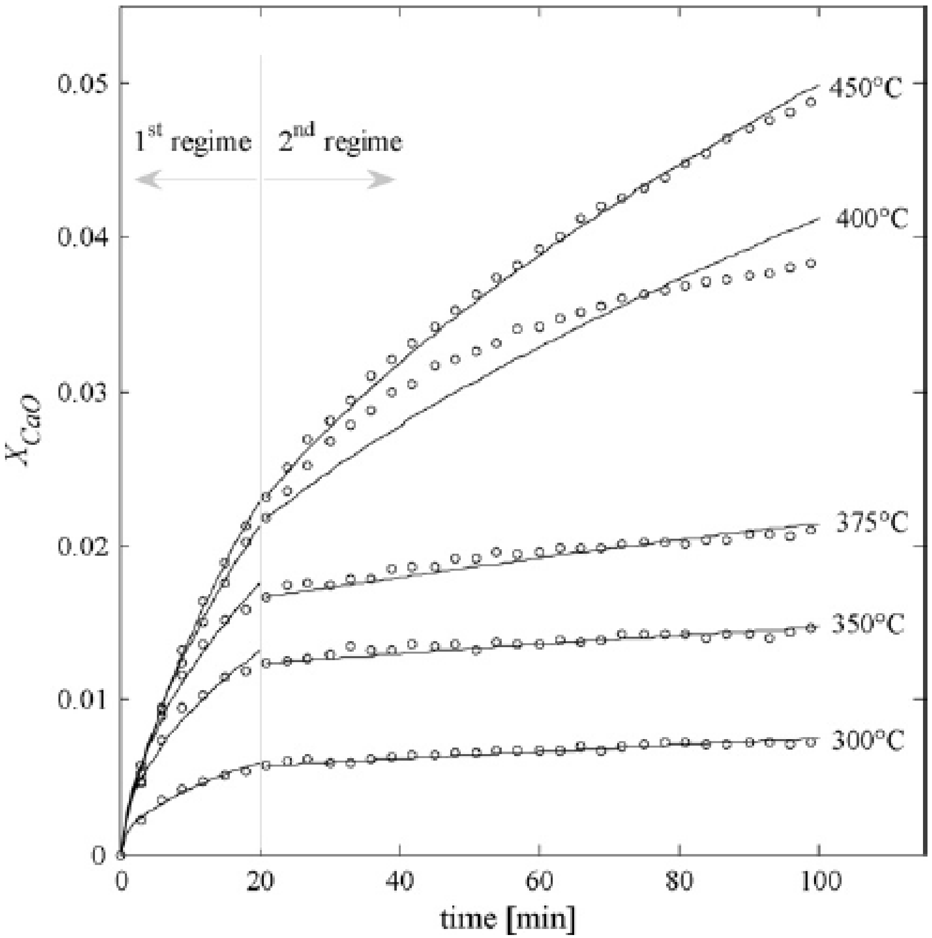
Vasilije Manovic and Edward J. Anthony. Ind. Eng. Chem. Res. in Press

Kelly Rock lime (300-425 um, 20vol% CO_2



The CaO conversion (also for the CaO conversion in the fast reaction stage) will increase with temperature increasing

1. Introduction



V. Nikulshina, M.E. Galvez, A. Steinfeld. Chemical Engineering Journal, 129 (2007) 75–83

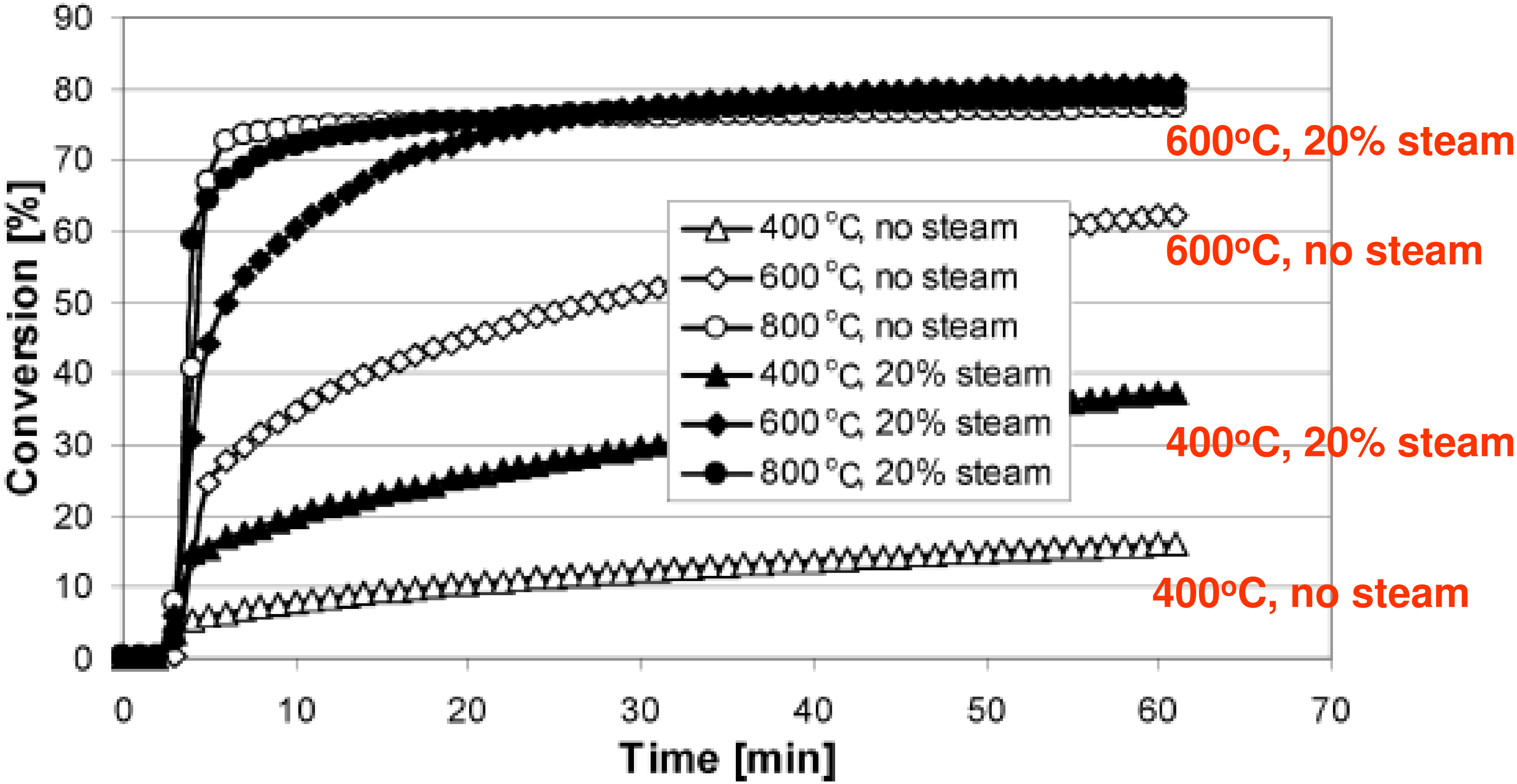
Experimentally measured extent of the carbonation of CaO as a function of time for the isothermal runs in the range 300–450°C with synthetic air containing 500 ppm CO_2.

Even for low CO_2 concentration such as 500 ppm CO_2 in air, the effect of temperature on the carbonation reaction is similar, i.e., CaO conversion increases with temperature increasing.

1. Introduction

Vasilije Manovic and Edward J. Anthony. Ind. Eng. Chem. Res. in Press

Kelly Rock lime (300-425 um, 20vol% CO_2, 20vol % steam



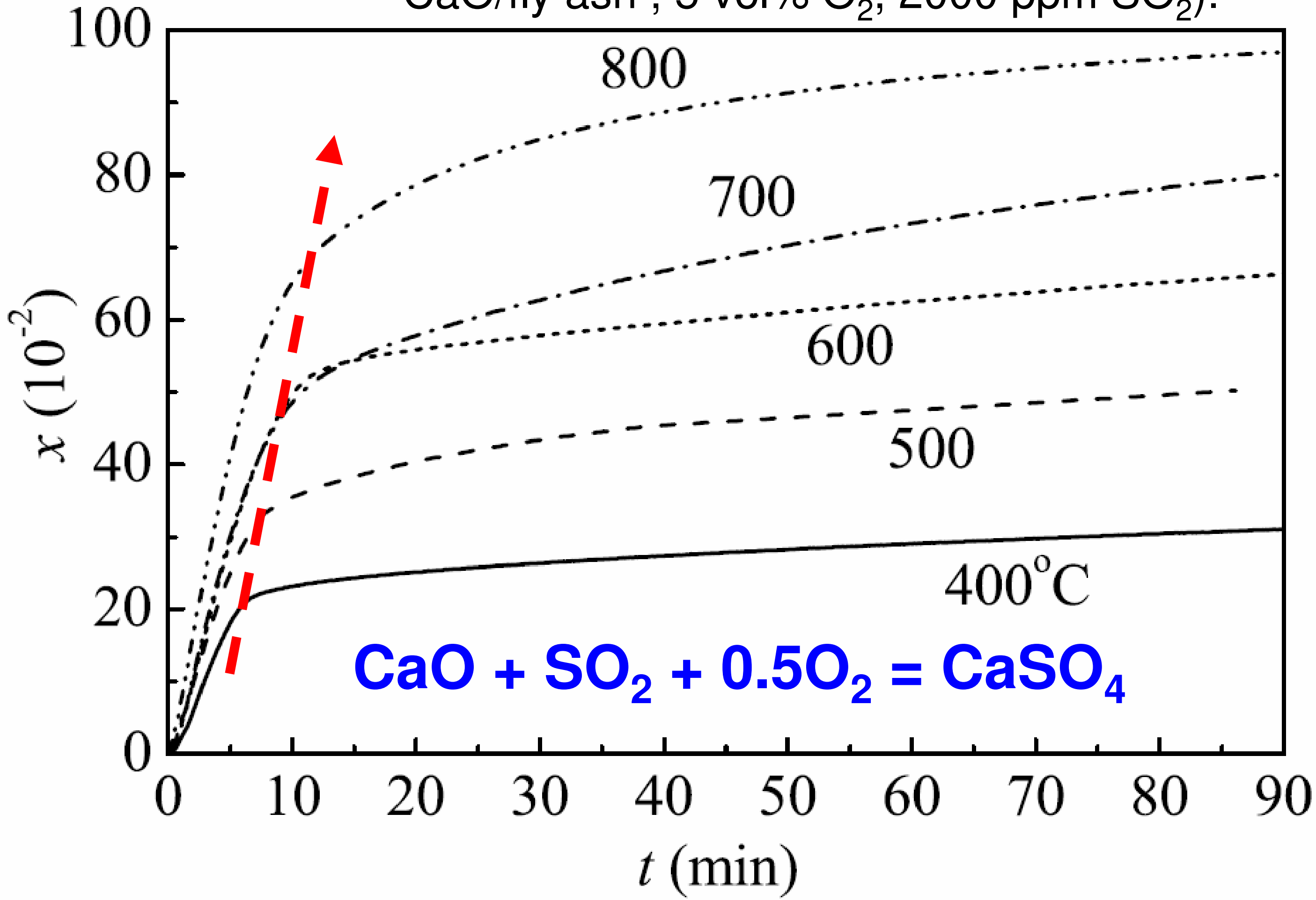
Addition of steam will enhance significantly the CaO conversion.

Steam promotes carbonation through enhancement of solid state diffusion in the product layer. But for the enhancement in fast reaction stage?

1. Introduction

YuRan Li et al. Fuel 86 (2007) 785–792.

CaO/fly ash , 5 vol% O_2, 2000 ppm SO_2).



$CaO + SO_2 + 0.5O_2 = CaSO_4$

For CaO sulphation reaction, the temperature effect is also similar, i.e., CaO conversion increases with temperature increasing, especially for the first fast reaction stage.

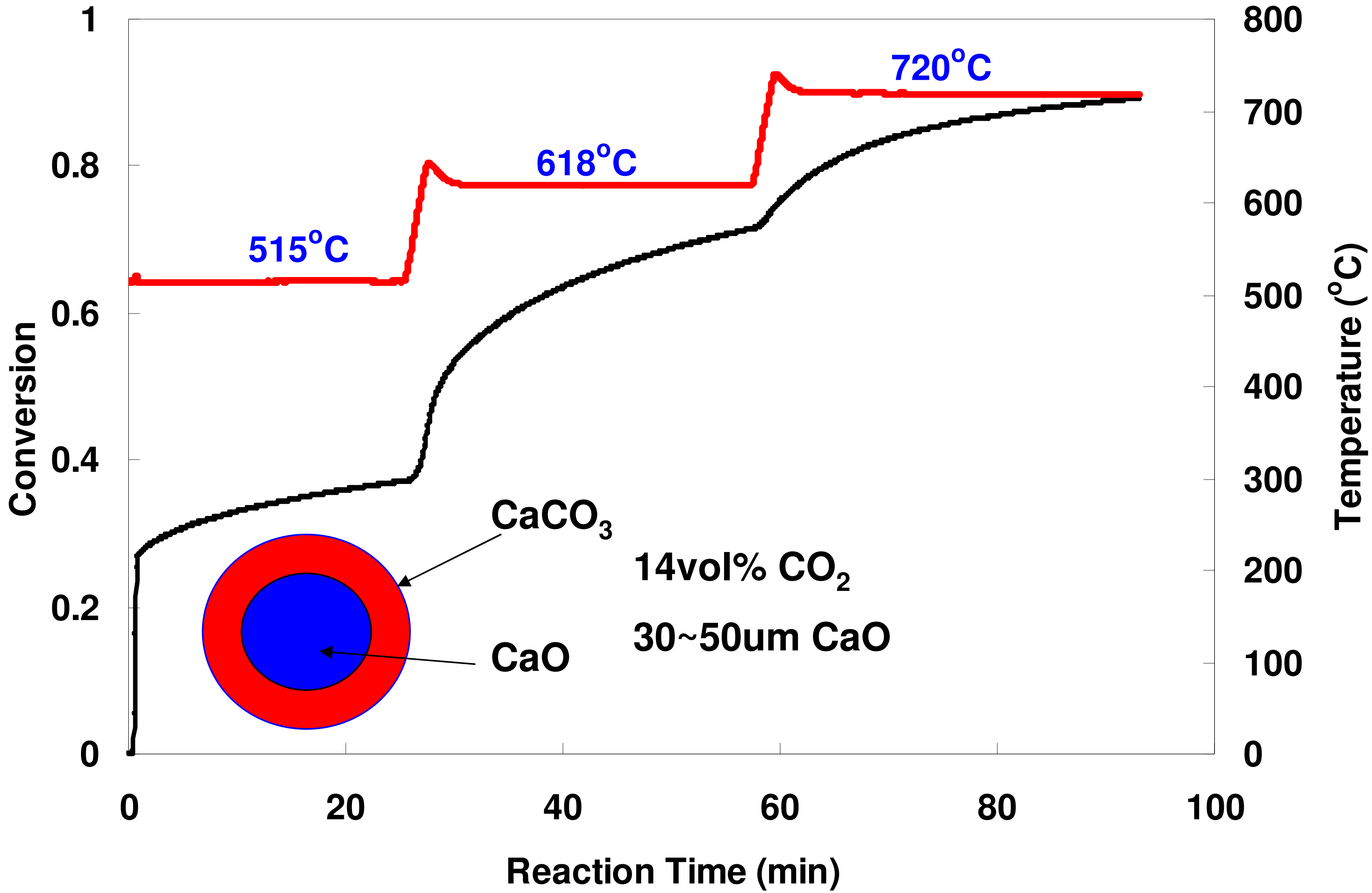
1. Introduction - Summary

The effect of temperature on the gas-solid non-catalytic reaction is a classical topic. The effect of reaction temperature on the gas-solid reaction rate can be understood according to collision theory or activated complex theory. However, the mechanistic implications of the effect of temperature on the solid conversion extent are less well known and quite complex.

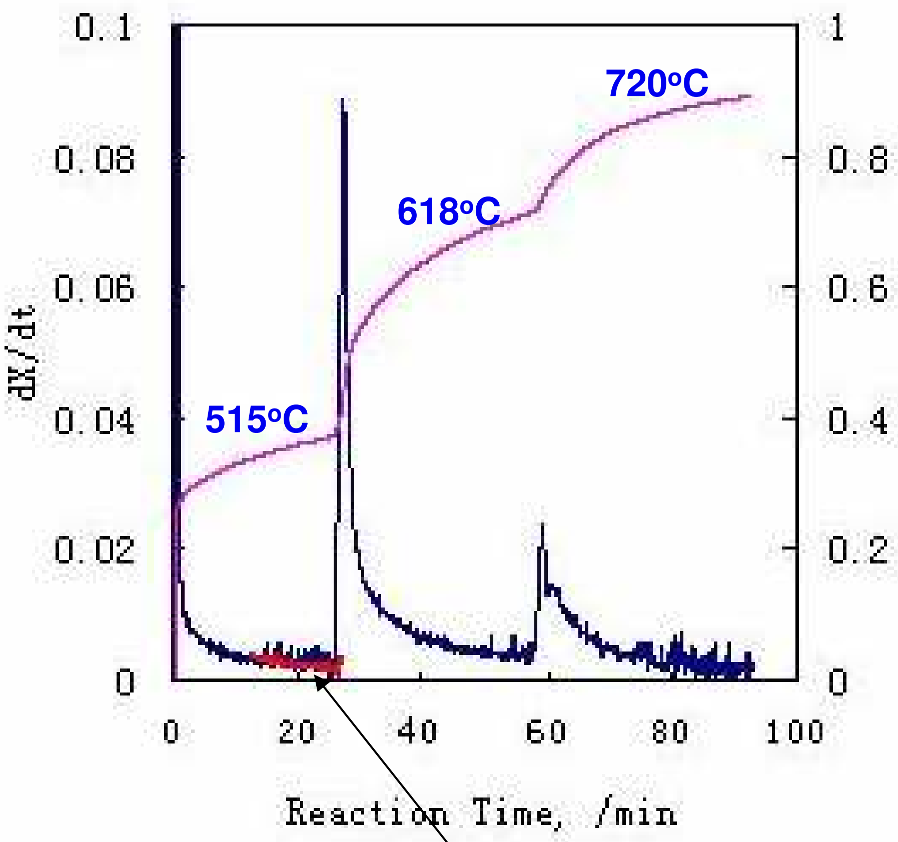
Why the solid conversion extent (in the fast reaction stage) increases with the temperature increasing?

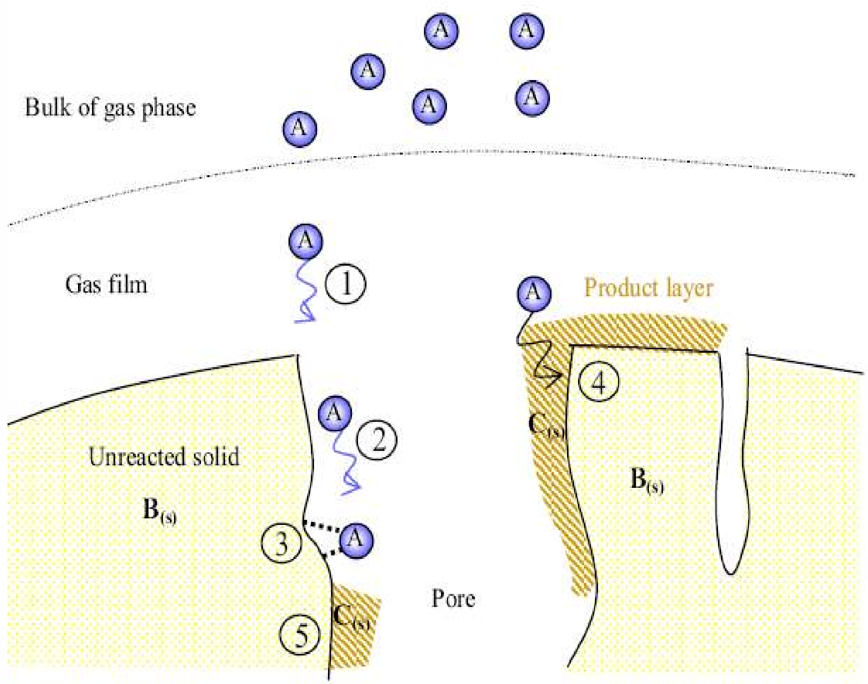
Why the addition of steam can enhance the solid conversion?

2. The effect of temperature on the carbonation reaction of CaO with CO_2



2. The effect of temperature on the carbonation reaction of CaO with CO_2





(1) External diffusion, not important; (2) pore diffusion $\sqrt{T / M_{CO_2}}$ **1.1 times**

(3) Product layer diffusion

***D*e is calculated with experimental data at 618°C**

2. Temperature effect on the carbonation - Summary

Temperature increasing will lead to

(1) reaction rate constant increasing;

(2) pore diffusion coefficient increasing;

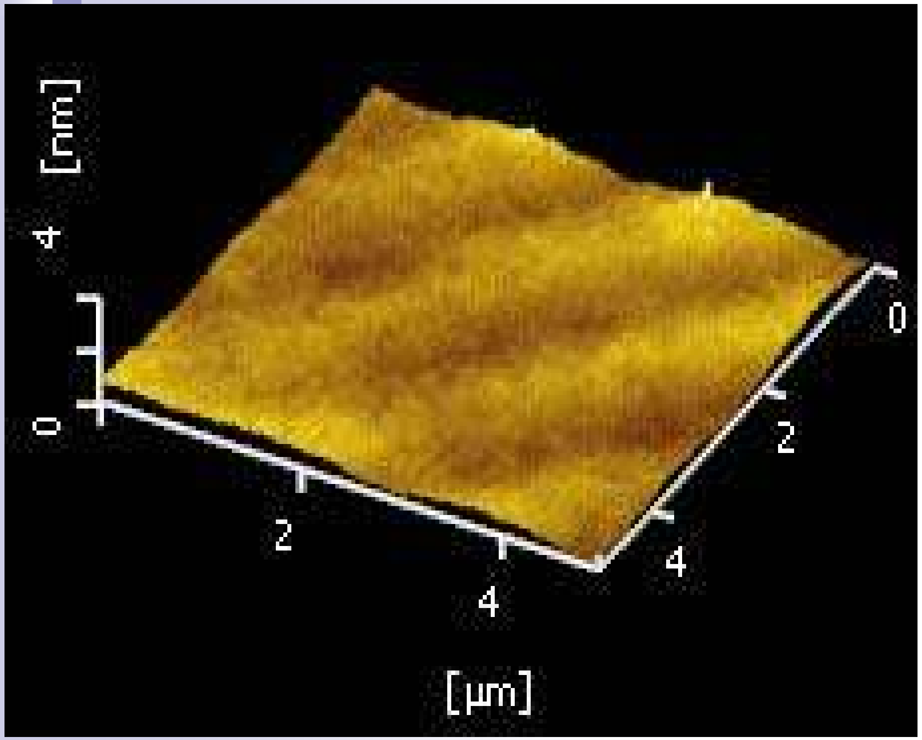
(3) product layer diffusion coefficient increasing.

When the reaction goes into product layer diffusion controlled stage, all these factor together are not enough to make the carbonation reaction happens fast again.

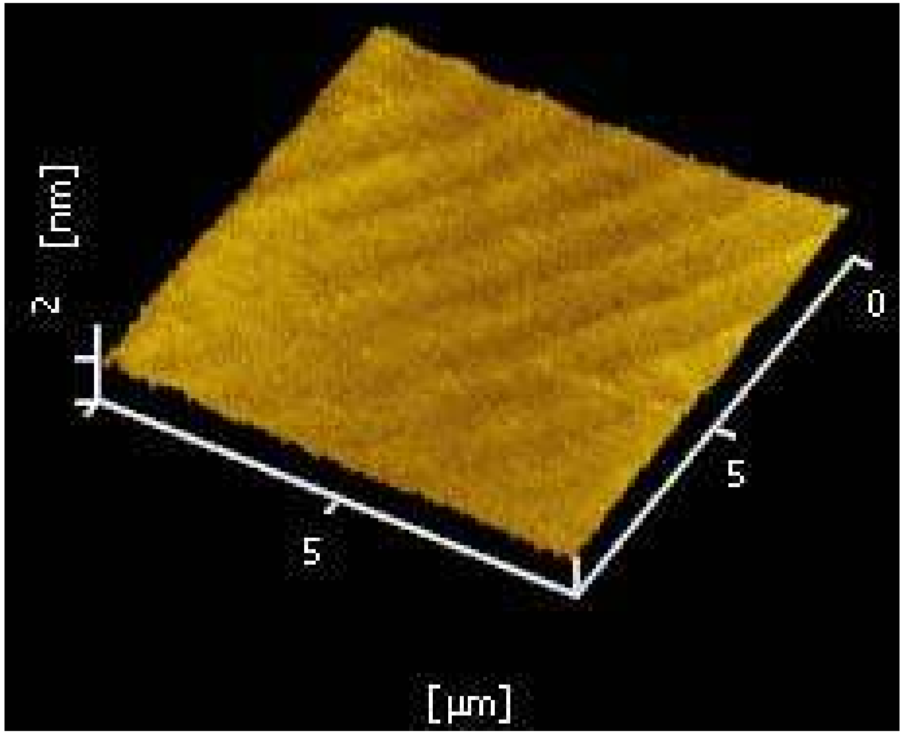
What mechanism will make this phenomenon happen?

Following three experiments will try to answer this question.

3. $MgO + SO_2 + 0.5O_2 = MgSO_4$



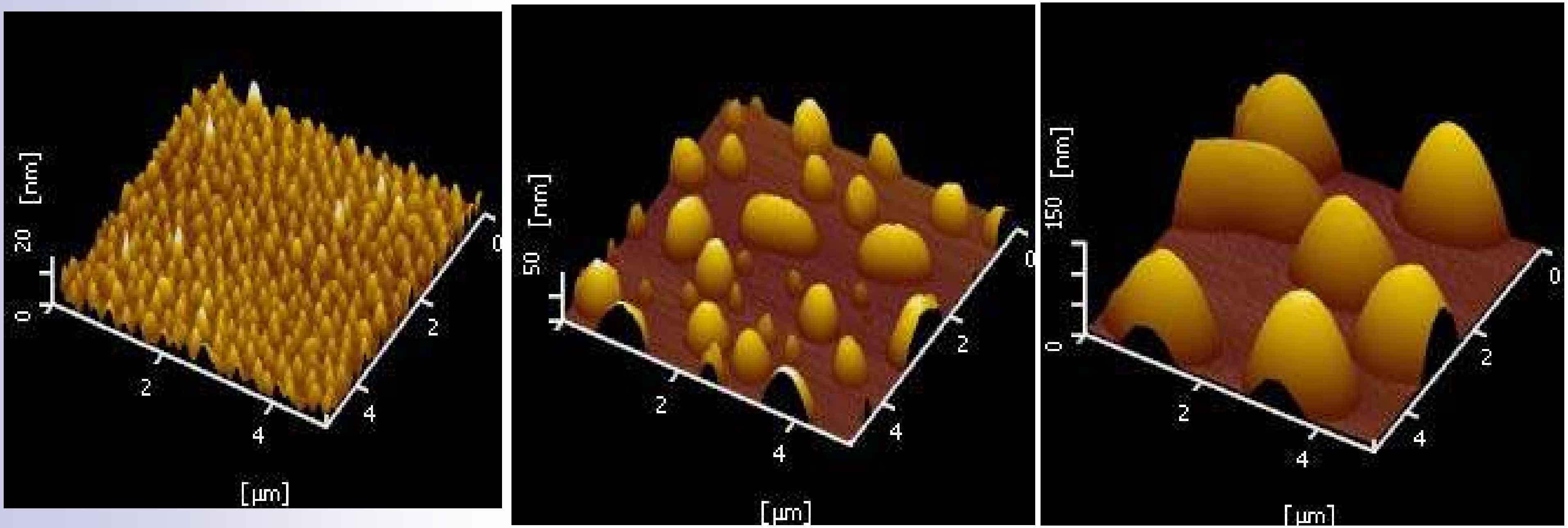
AFM image of a fresh single crystal MgO surface



AFM image of the single crystal MgO surface after exposing at 750°C for 20 min in pure N_2

MgO single crystal is still smooth and uniform without changing after it exposed at high temperature

3. $MgO + SO_2 + 0.5O_2 = MgSO_4$

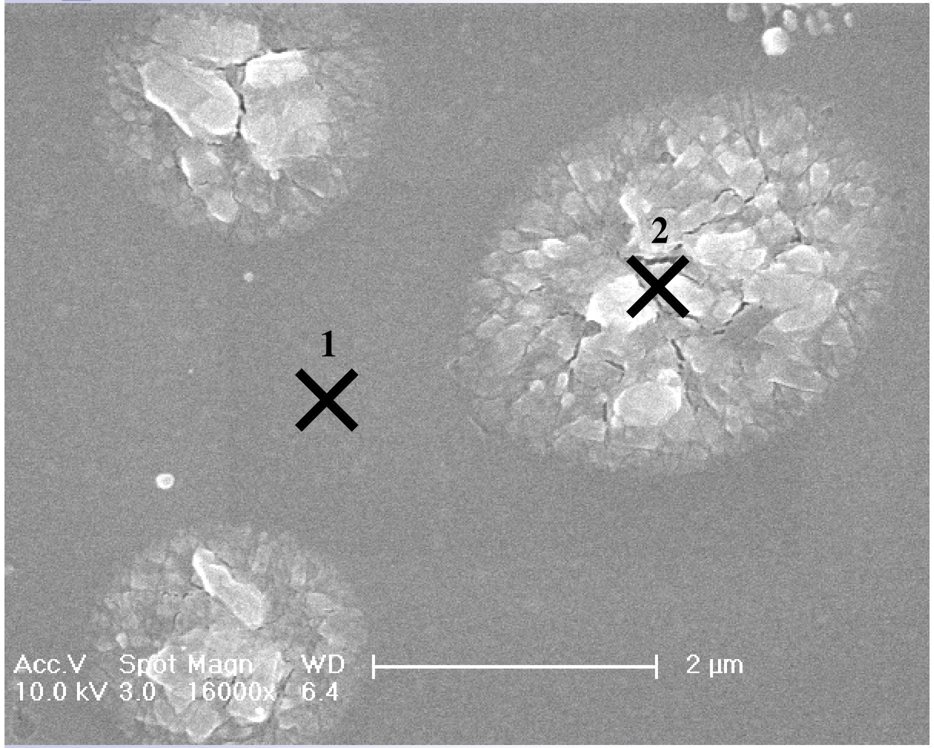


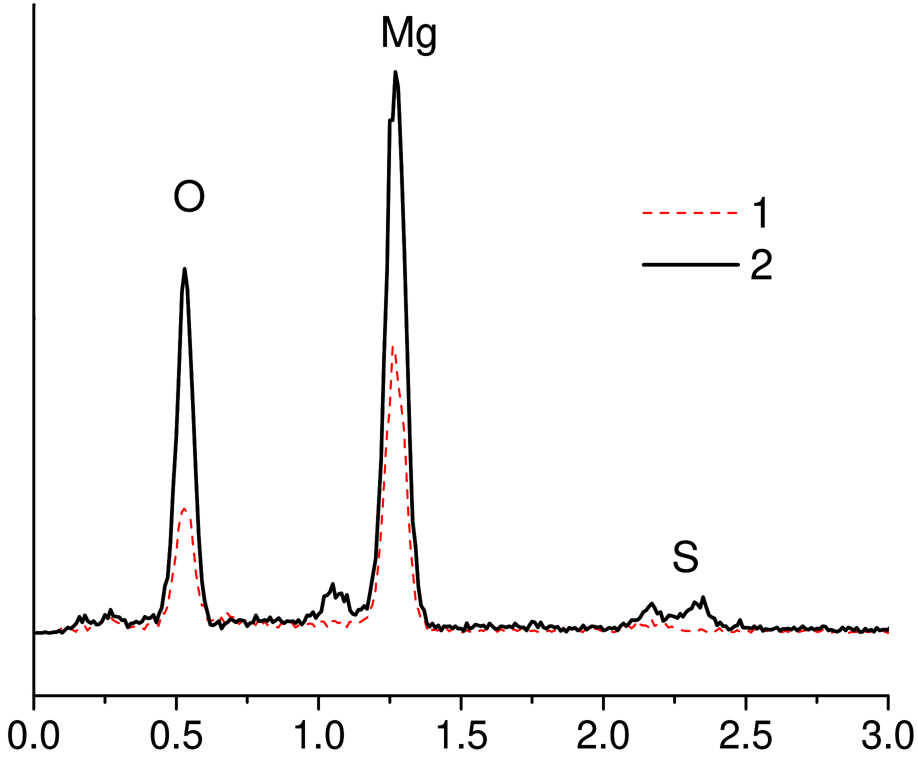
550°C 650°C 750°C

AFM images of single crystal MgO surfaces reacting with 200 ppm of SO_2 and 5 vol% O_2 with the rest of pure N_2 for 10 min with different sulfation temperature

(1) Product is island shape, (2) not uniformly distribute on the surface, and (3) product size increases with temperature increasing, more fresh surface available

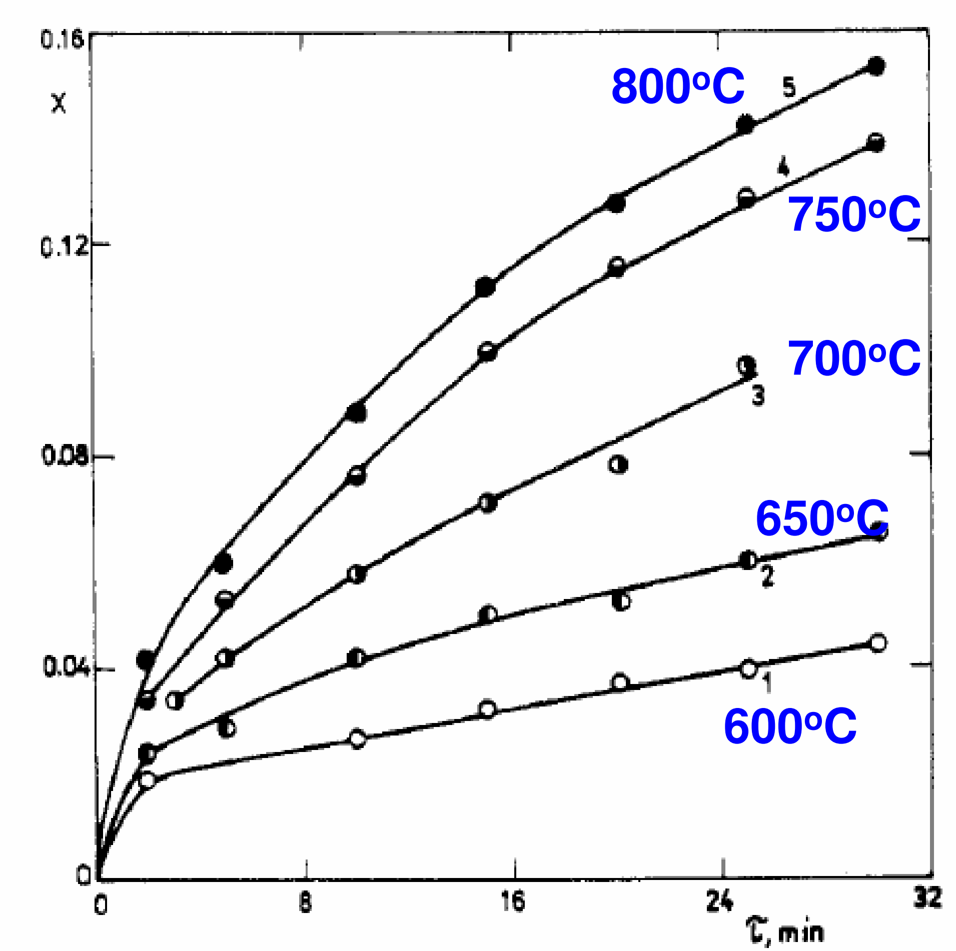
3. $MgO + SO_2 + 0.5O_2 = MgSO_4$





The sulfur element on the island is much higher than that obtained in its surrounding, which indicated that the island is $MgSO_4$

3. $MgO + SO_2 + 0.5O_2 = MgSO_4$

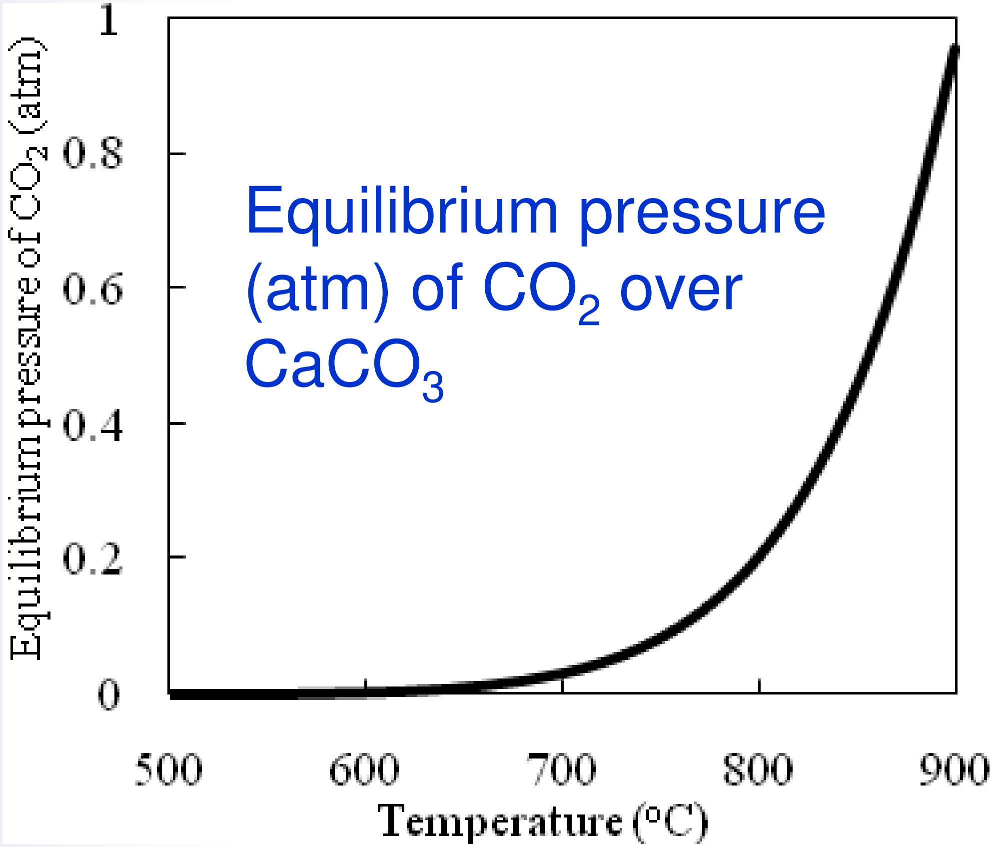


Effect of the sulfation temperature and exposure time on the conversion, Particles **0.565** mm calcined at ***850°*C;** magnesite JE; concentration of ***SO_2*,** **0.3%** by volume.

From Hartman M., Svoboda K., 1985.. Industrial and Engineering Chemistry Process Design and Development 24, 613-621.

The MgO sulfation behaviour is similar to that of CaO sulfation and carbonation, so above conclusion is assumed here to be suitable for the case of CaO with CO_2.

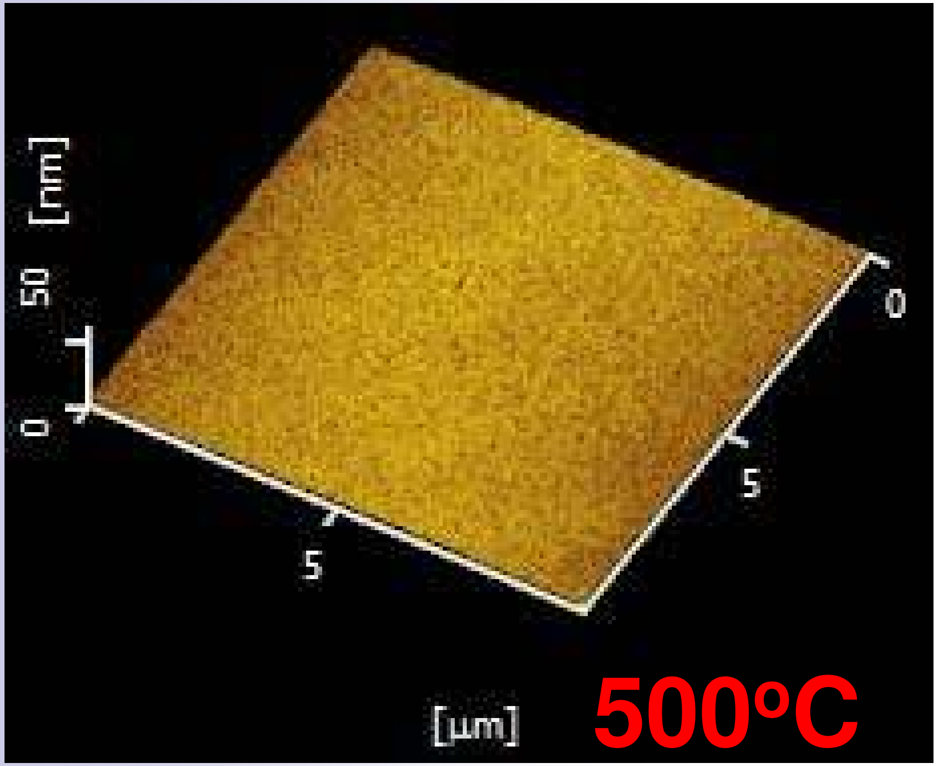
4. The effect of temperature on $CaCO_3$ surface morphology in high CO_2 concentration atmosphere

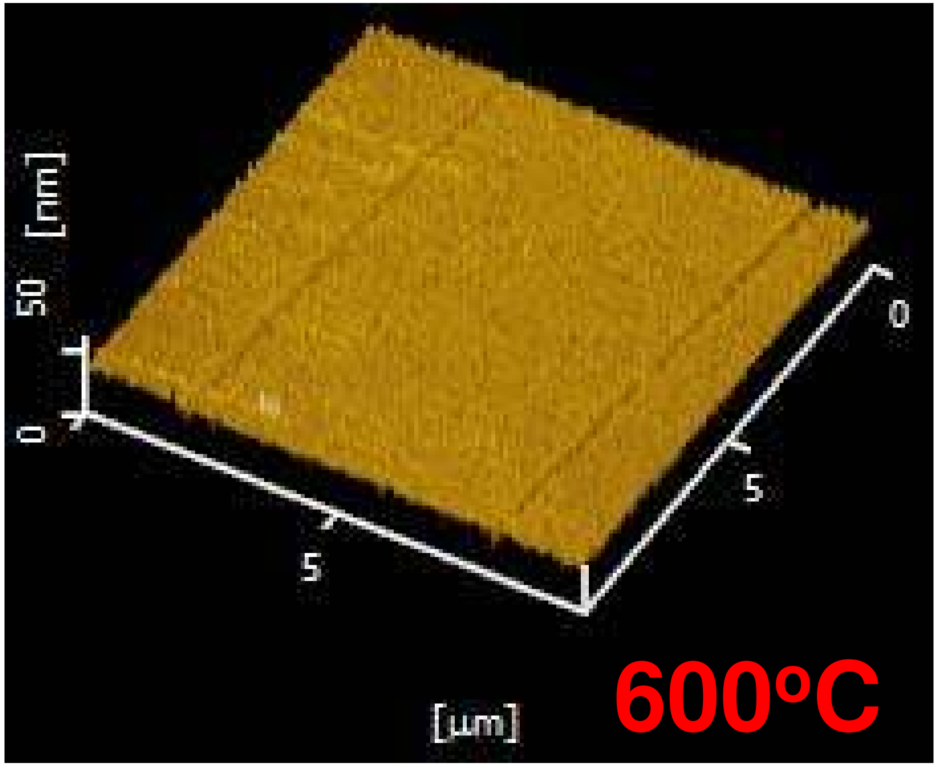


- **CO_2 concentration: 91vol. % with N_2 as the balance.**
- **Room temperature** $\xrightarrow{50^{o}C/min}$ **temperatures from 500°C to 700°C.**
- **Reaction time: 30 min.**

4. The effect of temperature on $CaCO_3$ surface morphology in high CO_2 concentration atmosphere

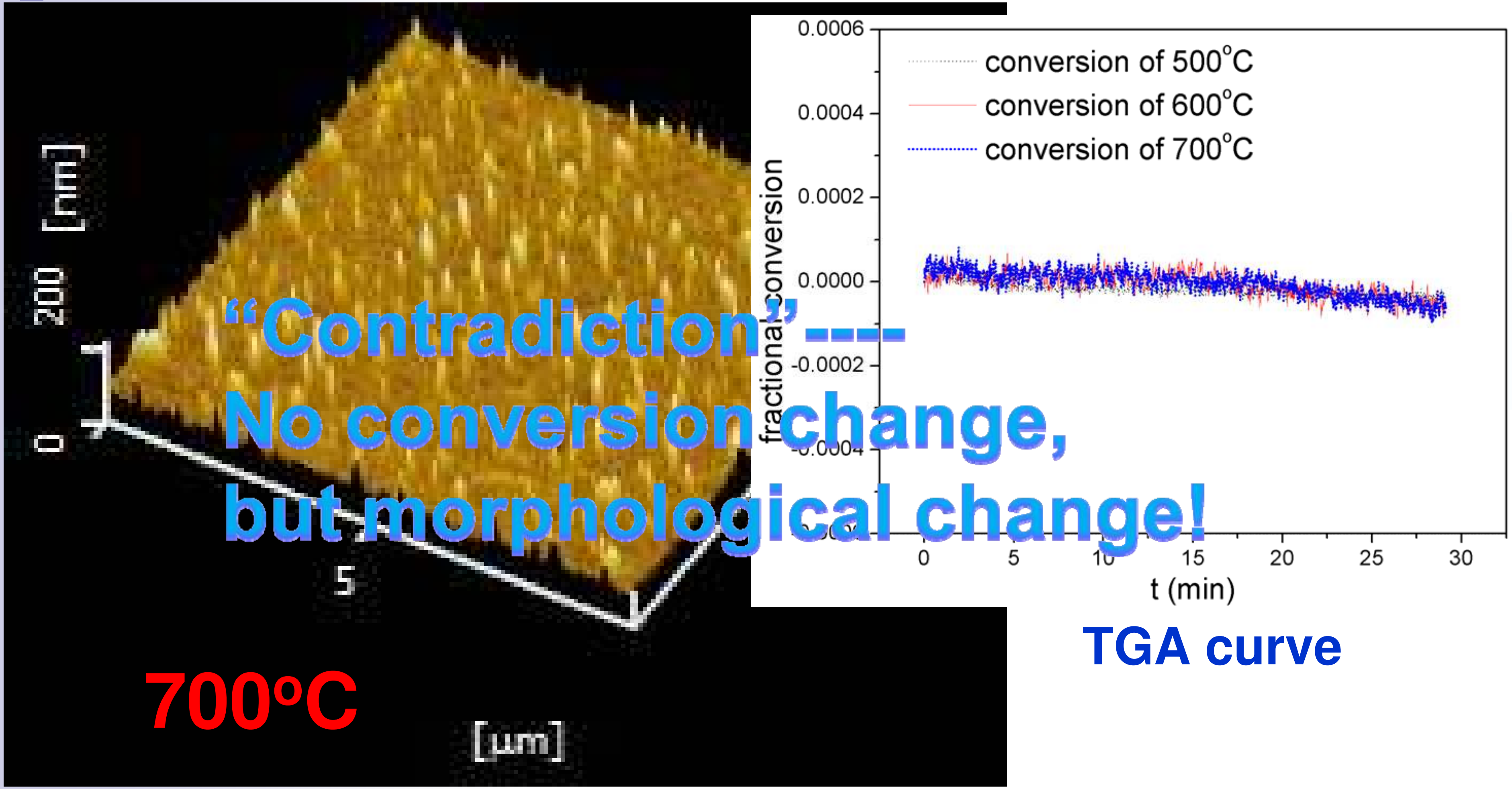
Morphological changes can be neglected.





AFM images of the $CaCO_3$ surfaces under 91vol.% CO_2 concentration for 30 min. N_2 as balance.

4. The effect of temperature on $CaCO_3$ surface morphology in high CO_2 concentration atmosphere



"Contradiction"----
No conversion change,
but morphological change!

700°C

TGA curve

AFM image of the $CaCO_3$ surface under 91vol.% CO_2 concentration for 30 min. N_2 as balance.

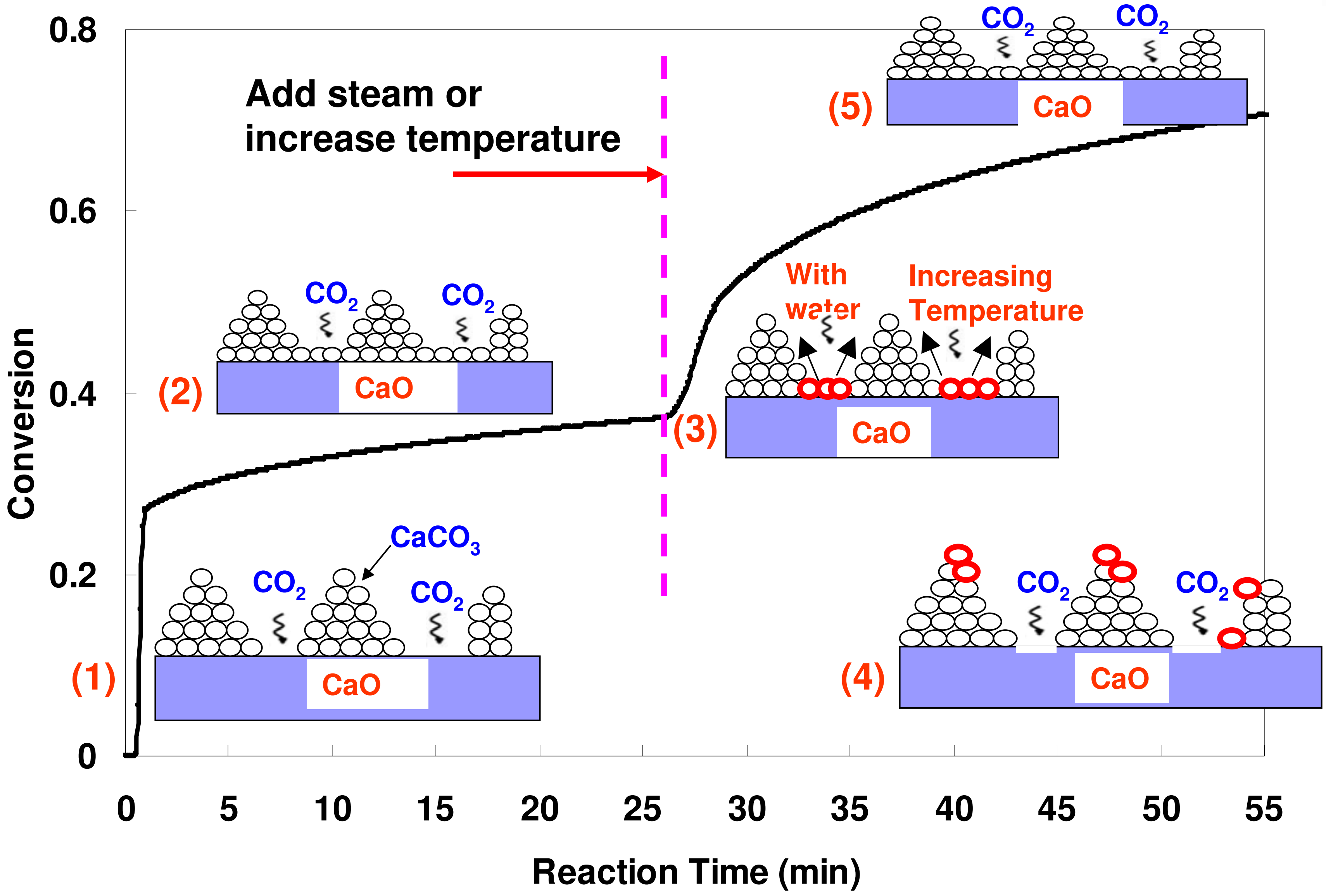
Summary for above three experiments

(1)Product is island shape, not uniformly distribute on the surface, and product size increases with temperature increasing, more fresh surface available

(2)The morphological changes of the $CaCO_3$ surface while there is no change in conversion may be the movement of $CaCO_3$ molecules or ions (CO_3^{2-}, Ca^{2+}) from one site to another to form islands and change the morphology, i.e., surface diffusion.

(3)Steam addition or temperature increasing accelerate the formation of larger size of product islands through enhancing the surface diffusion rate , more fresh surface available

5. Conclusion



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Thank You !

Any questions?