

**Selective Growth of CaCO₃ Polymorphs on
Aluminum Surface: Effect of Mg²⁺ ions**

By

Niranjana Sreelal

IISER Pune



Advisor

Dr. Amitava Pramanik

Unilever R & D Bangalore, 64 Main Road, Whitefield,

Bangalore 560066, INDIA

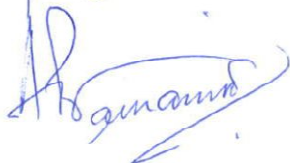
Certificate

This is to certify that this dissertation entitled “**Selective Growth of CaCO₃ Polymorphs on Aluminum surface: Effect of Mg²⁺ ions**” towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by **Niranjana Sreelal** at **Unilever R & D Bangalore, 64 Main Road, Whitefield, Bangalore 560066, INDIA** under the supervision of **Dr. Amitava Pramanik, Principal Scientist, SSG Functional Materials, Unilever R & D Bangalore, 64 Main Road, Whitefield, Bangalore 560066, INDIA** during the academic year 2014-2015.

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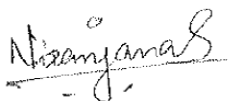


Declaration

I hereby declare that the matter embodied in the report titled “**Selective Growth of CaCO₃ Polymorphs on Aluminum surface: Effect of Mg²⁺ ions**” are the results of the investigations carried out by me at *Unilever R & D Bangalore, 64 Main Road, Whitefield, Bangalore 560066, INDIA* under the supervision of *Dr. Amitava Pramanik, Principal Scientist, SSG Functional Materials, Unilever R & D Bangalore, 64 Main Road, Whitefield, Bangalore 560066, INDIA* and the same has not been submitted elsewhere for any other degree.

Date:

Signature:

A handwritten signature in black ink, appearing to read "Nishant", written over a horizontal line.

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Abbreviations

FTIR	:	Fourier Transform Infrared
FESEM	:	Field Emission Scanning Electron Microscopy
EDX	:	Energy Dispersive X- Ray
XRD	:	X-Ray Diffraction
ICP-OES	:	Inductively Coupled Plasma Optical Emission Spectroscopy
g	:	Grams
mL	:	Millilitres
M	:	Molar
M. Wt.	:	Molecular Weight
ppm	:	Parts Per Million
h	:	Hours
min	:	Minutes
nm	:	Nanometer
µm	:	Micrometer

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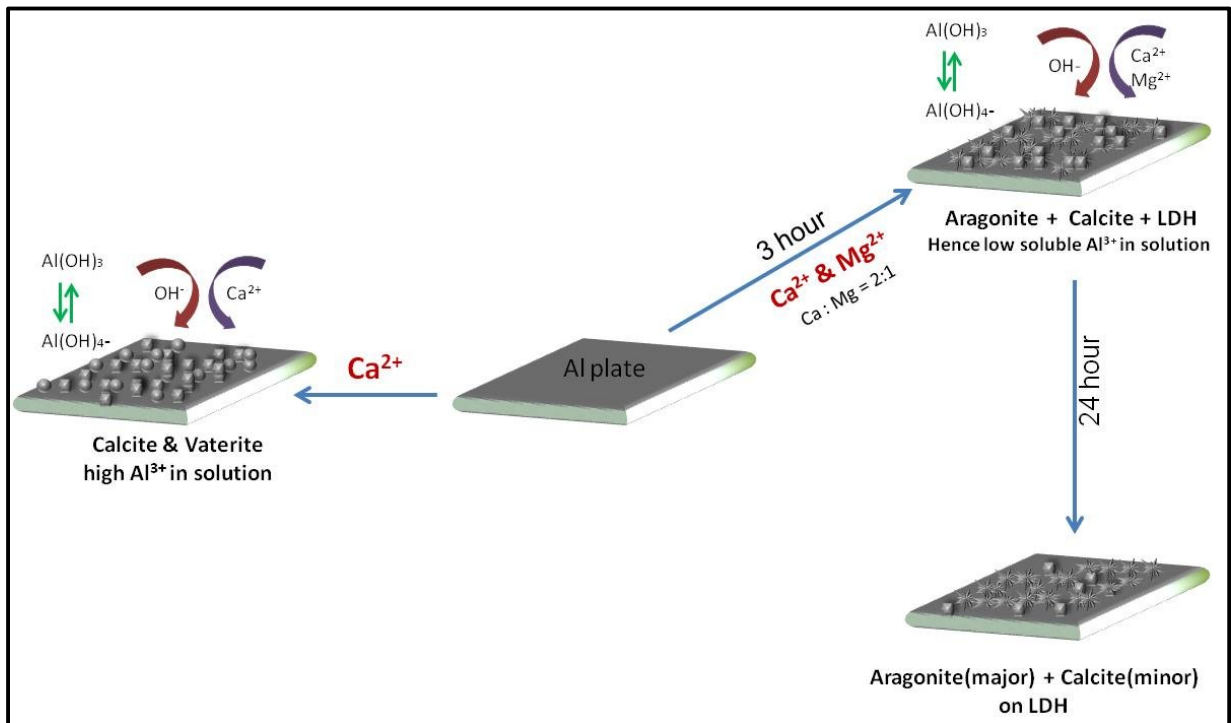
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Table 1: Synthesis of CaCO_3 on Al plates under different reaction conditions.

Scheme 1: Mechanistic interpretation of the CaCO_3 growth on Al plate

Abstract

Aragonite, a hitherto unobservable polymorph by room temperature synthesis has been grown successfully on metallic aluminum surface, following a room temperature carbonation technique. Soluble Al species are detected in the bulk medium due to leaching from the plate surface under the alkaline reaction condition. In addition, when Mg^{+2} ions are present in the medium, it got precipitated as layered double hydroxide (LDH) by combining with the Al^{3+} ions on the metallic plate. In presence of Mg^{+2} ions, the polymorph selection is retained and the relative proportion of aragonite polymorph grown on the aluminum surface progressively increases with time of reaction. Based on these observations and characterization tools, a unified mechanistic approach on stabilization of meta-stable aragonite polymorph on aluminum surface is proposed.



Selective Growth of CaCO₃ Polymorphs on Aluminum Surface: Effect of Mg²⁺ ions

1. Introduction

Crystallization is a multi-step complex process initiated by nucleation followed by subsequent growth. This process is influenced by changes in reaction parameters such as temperature, pressure, solvents, additives etc.¹ A material may crystallize in more than one crystal form or phase depending on the crystallization environment.² In such cases, the material is said to exhibit polymorphism; a phenomenon in which the same material exists in different crystal structures. Polymorphs may have varied morphologies, stabilities and physical properties but their chemical identity remains the same. Ostwald's rule³ predicts that the least stable polymorph crystallizes first and then gets transformed to thermodynamic more stable ones. This is due to the fact that polymorphs with lowest energy is stable compared to its other counterparts, thus if the metastable polymorph is formed in a kinetically controlled environment, it tends to transform to stable polymorphs with progress in reaction time provided it gets the activation energy. The mechanism of such transformations by two step dissolution followed by re-crystallization process i.e., dissolution of unstable polymorph and growth of stable polymorph is well reported in literature.^{4,5}

Polymorphic transformation of inorganic materials are well studied, which can be influenced by modulating changes in the synthetic step.^{6,7} CaCO₃ is one of the most abundant naturally occurring minerals on earth which occurs as rocks, marbles, lime stones, seashells and coral.^{8,9} It is known to exist in both crystalline and amorphous form and exhibits polymorphism.¹⁰ The three common polymorphs of anhydrous CaCO₃ are calcite, vaterite and aragonite.¹¹ Out of these, calcite is most stable and most abundant polymorph while vaterite is least stable at ambient conditions.¹² Aragonite polymorph is generally obtained by high temperature synthesis and occurs naturally in mollusks and seashells.¹³ Transformation of one polymorph to another can be achieved by varying the reaction conditions such as temperature, pressure, pH, reaction time and additives. Additives such as polymers¹⁴, inorganic particles, insoluble matrices¹⁵ or

ions^{16,17} typically act as habit modifiers and can affect both morphology and polymorph selectivity. Such transformations and stabilization of a specific polymorph over the other have strong influence in bio-mineralization of materials.^{18,19,20}

Ground water contains dissolved salts of calcium and magnesium which contribute to its hardness. Hard water leads to lime scale formation on the containers/ vessels in which water is stored, due to precipitation of CaCO_3 by reaction of calcium salts present in the water with the dissolved bicarbonate or the atmospheric carbon dioxide. This are domestic nuances as utensils become tarnished in households, while it poses more serious hazard in industries, where scale formation in boilers²¹ damages the surfaces, requires more energy input for heating water and also causes serious accidents.^{22,23,24}

Since polymorph control is relatively facile in CaCO_3 , suitable controlling of deposition or growth of appropriate polymorph should reduce tarnishing of metal surfaces, owing to the differential solubility of one polymorph over the other. This coupled with their morphological differences is an area of active research.¹⁰

In this work, we have studied polymorph stabilization of CaCO_3 on Al surfaces by room temperature carbonation technique. The results were analyzed using different characterization techniques like XRD, FT-IR, SEM and ICP. Based on the polymorph selectivity we propose a mechanism for such transformation on Al surface. This work paves the way to devise rational strategies for making household surfaces less affected by scaling.

2. Experimental Section

2.1 Materials

Calcium chloride [$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, A.R grade], magnesium chloride [$\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, A.R grade], ammonium carbonate [$(\text{NH}_4)_2\text{CO}_3$, A.R grade] and aluminum plates (Al, Purity: 99.99%, Thickness: 0.25 mm) were purchased from Sigma-Aldrich and used without further purification. Distilled water was used for all experiments having the following characteristics; pH ~ 7.1 , electrical conductance $2 \times 10^{-6} \text{ S cm}^{-1}$, total dissolved salt $<0.5 \text{ mg/L}$ and turbidity $<0.1 \text{ NTU}$ at 25°C .

2.2 Methods

2.2.1 Syntheses

Growth and polymorphic transformation of CaCO_3 on Al plates and in the bulk solution was studied using room temperature carbonation technique. $\sim 2.5 \text{ cm} \times 2 \text{ cm} \times 0.25 \text{ mm}$ sized Al plates were dipped in a solution containing CaCl_2 and MgCl_2 for different reaction times in an air-tight desiccator in presence of 5g of $(\text{NH}_4)_2\text{CO}_3$ which acted as the source of NH_3 and CO_3^{2-} .²⁵ After the desired reaction time the Al plates were washed with copious amount of distilled water followed by acetone and dried in air. The particles formed in the bulk solution was also filtered separately, washed with water and dried in air.



Figure 1: Reaction vessel for synthesizing CaCO_3 by room temperature carbonation process.

Table 1: Synthesis of CaCO_3 on Al plates under different reaction conditions.

Sample	Ca^{2+} (mM)	Mg^{2+} (mM)	Time (h)
1	10.0	0.0	3
2	6.5	3.5	3
3	10.0	0.0	6
4	6.5	3.5	6
5	10.0	0.0	24
6	6.5	3.5	24

2.2.2 Characterization

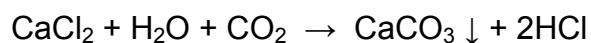
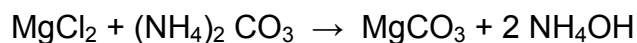
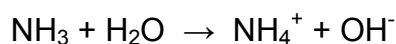
The morphology of the particles deposited on Al plates were investigated using a scanning electron microscope (SEM, Hitachi S-4700) equipped with an accelerating voltage of 10 kV. Samples were mounted on holey carbon tape and imaged after gold sputter to make them conductive. The powder X-ray diffraction pattern of samples was obtained on a Rigaku Ultima IV diffractometer using $\text{Cu K}\alpha$ ($k = 1.54 \text{ \AA}$) radiation with a

step size of 0.05/s and 2 θ angle ranging from 20 to 60 degrees. Room temperature Fourier Transform infrared spectroscopy measurements were performed in a Perkin-Elmer FT-IR spectrophotometer in the diffused reflectance mode. ICP-OES was done by taking an aliquot of 200 μ L from the bulk solution and diluting it to 10ml in 0.1% nitric acid.

3. Results and Discussion

3.1 Synthesis and polymorph stability

The growth of CaCO₃ on Al plates was studied by room temperature gas diffusion technique using (NH₄)₂CO₃ and CaCl₂/ MgCl₂ as reagents. In this process, slow decomposition of (NH₄)₂CO₃ results in release of NH₃ and CO₂ gas. Owing to the slower process which enables formation of well-defined crystals of CaCO₃, gas diffusion technique was preferred against the conventional double decomposition precipitation. Here ammonia acts as the source of alkalinity while CO₂ acts as the source of carbonate. As the reaction proceeds, the pH of the medium increases slowly, resulting in the formation of CaCO₃ polymorphs both in the bulk solution and on the Al plates. The chemical reaction for the formation of CaCO₃ is as follows:



In this work we studied two contrasting scenarios, condition 1 where the solution contained only Ca⁺² ions and condition 2 where Ca⁺² and Mg⁺² were both present. In the second case the ratio of Ca⁺² to Mg⁺² was maintained at 2, which is representative of hard water generally found in natural ground water. The growth of particles on the Al

plate was monitored over different intervals of time. Figure 2 shows the comparative polymorph stabilities of CaCO_3 on Al plates after 24 hour reaction.

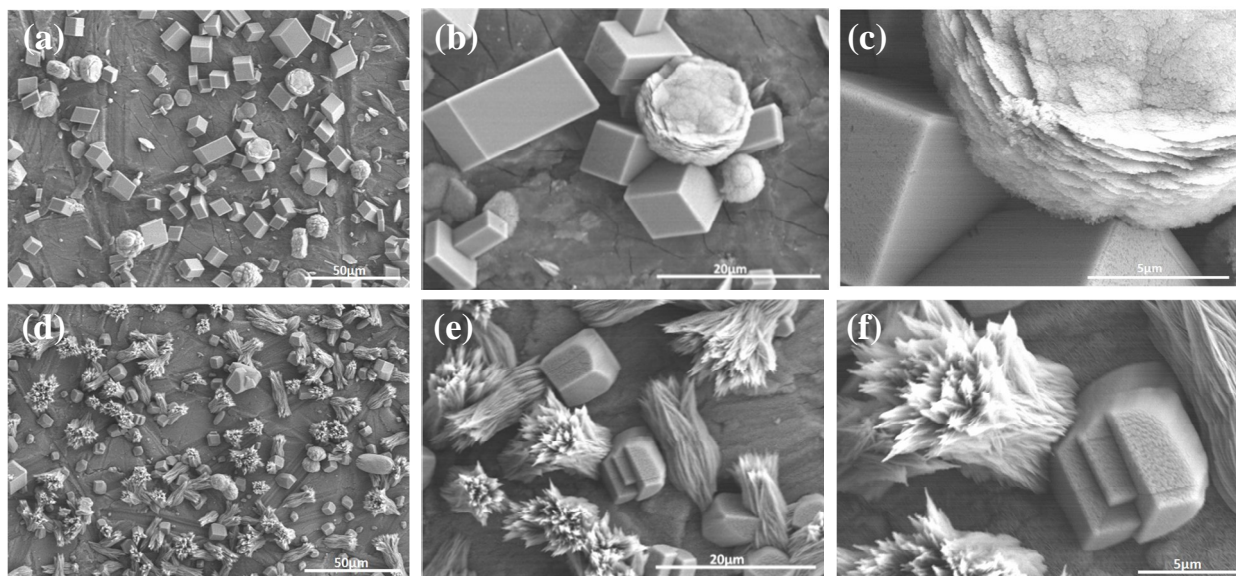


Figure 2: SEM micrographs of CaCO_3 particles grown on Al plate after 24 h reaction in (a-c) 10 mM Ca^{+2} and (d-f) 10 mM 2:1 $\text{Ca}^{+2}/\text{Mg}^{+2}$.

In the first scenario, uniform deposits of calcite and vaterite particle were observed on the Al plates. The calcite particles were uniform with well defined edges and rhombohedral in shape while the vaterite particles ranged from spherical to pancake like structures. The presence of meta-stable vaterite polymorph was detected on the Al plates even after 24 hours of reaction. For the second scenario, we detected a mixture of calcite and aragonite particles. The calcite particles were distorted rhombohedra while the aragonite particles had flaky floret shapes, both being uniformly present on the Al plates. In addition to this we also observed plate like LDH structures on the surface of Al plates. These LDH particles were bound on the plate surface, resulting in the formation of a network plates with nanometer thickness over which CaCO_3 polymorphs grew with time. Figure 3 shows the high magnification SEM images of LDH network formed on Al plate. The chemical reaction for formation of LDH particles on Al plates in presence of Mg^{+2} ions can be described according by the following reactions:

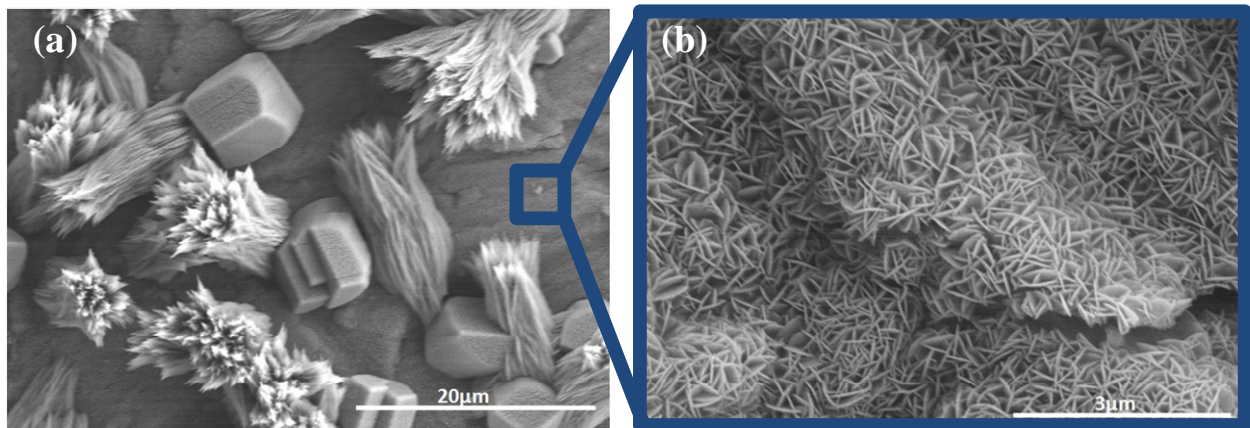
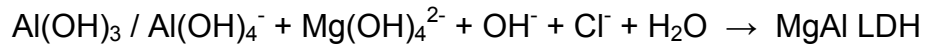
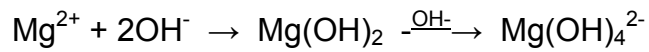
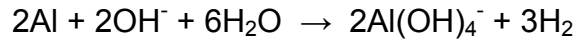


Figure 3: SEM micrographs showing polymorphic transformation of CaCO_3 particles grown in presence of 10 mM 2:1 $\text{Ca}^{+2}/\text{Mg}^{+2}$ on Al plate after (a) 48h and (b) LDH particles on the surface of Al plate.

In the second scenario, further investigation revealed that aragonite particles were preferentially formed compared to calcite and the relative proportion of aragonite increased with the time of reaction. Subsequently, the presence of soluble Al species was also detected in the bulk solution. Figure 4 shows the SEM images of particles formed on Al plates at different reaction times.

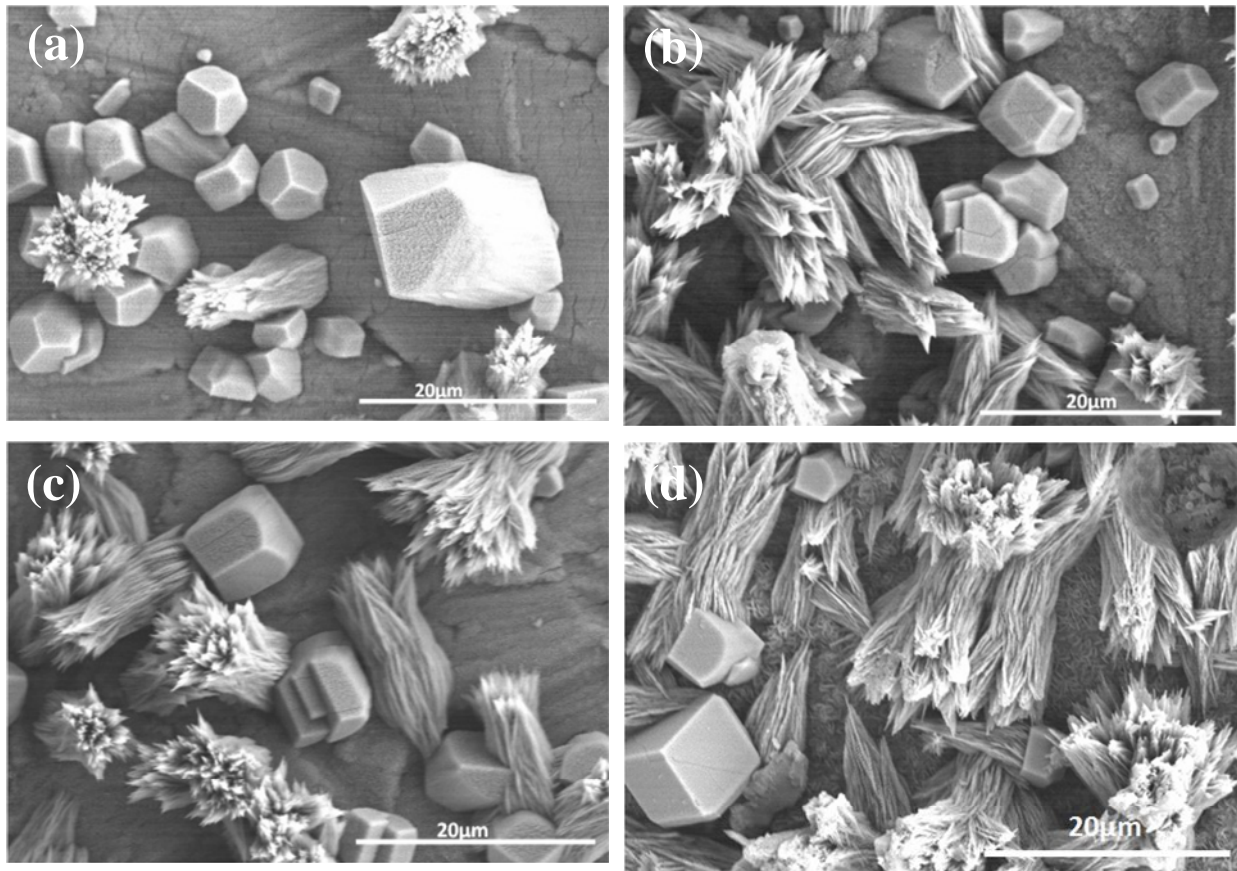


Figure 4: SEM micrographs showing polymorphic transformation of CaCO_3 particles grown in presence of 10 mM 2:1 $\text{Ca}^{+2}/\text{Mg}^{+2}$ on Al plate after (a) 3h; (b) 6h; (c) 24h and (d) 48h reaction.

Contrary to the Al plate surface, in the bulk solution no LDH particles were detected. As shown in Figure 5, a mixture of calcite and vaterite were formed in the Ca^{+2} based systems while for mixed Ca^{+2} and Mg^{+2} systems a mixture of calcite and aragonite particles were detected.

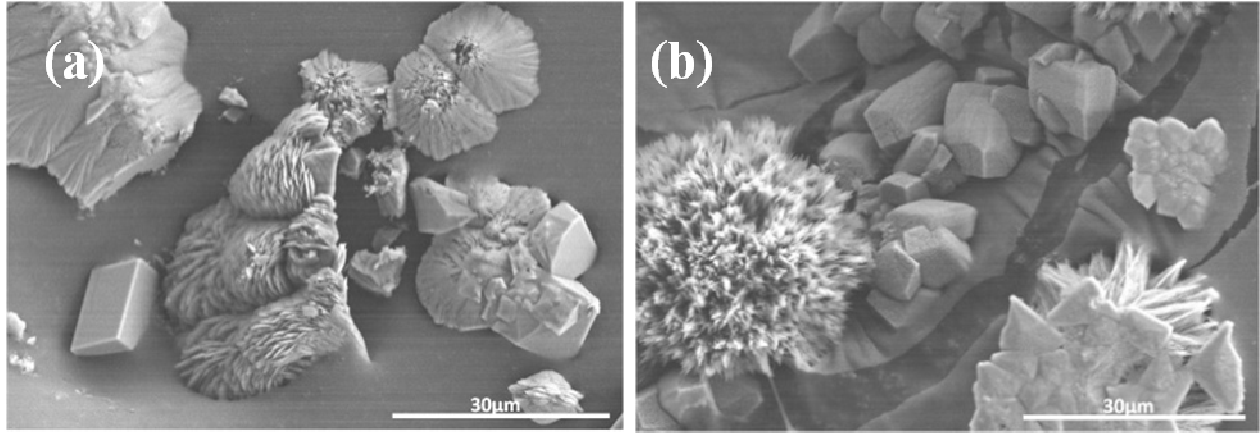


Figure 5: SEM micrographs showing polymorphic transformation of CaCO_3 particles grown in presence of (a) 10 mM Ca^{+2} and (b) 10 mM 2:1 $\text{Ca}^{+2}/\text{Mg}^{+2}$ in bulk solution after 24h reaction.

3.2 Characterization

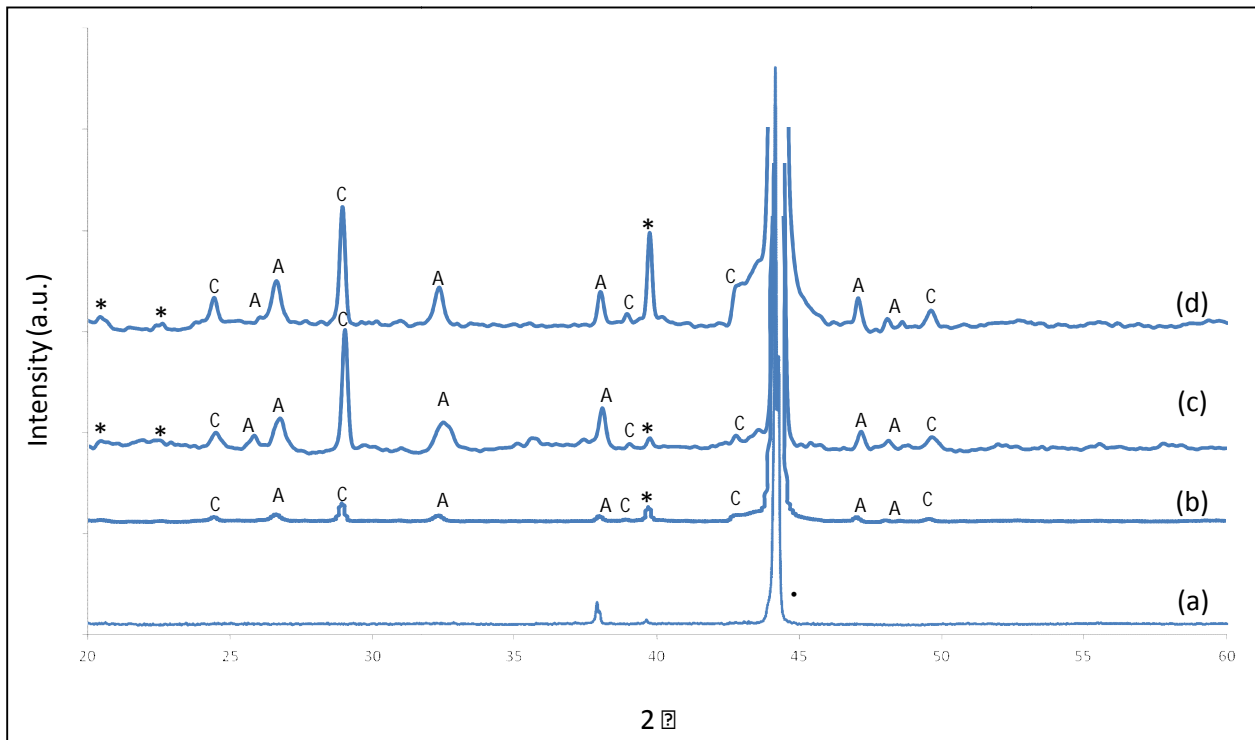


Figure 6: XRD profiles of (a) Al plate and (b-d) CaCO_3 particles grown in presence of 10 mM 2:1 $\text{Ca}^{+2}/\text{Mg}^{+2}$ after (b) 3h; (c) 6h; (d) 24h reaction respectively. Abbreviations: C, calcite; A, aragonite; *, peak for LDH; • Al plate.

The phase composition and polymorph selectivity on the Al surface was analyzed by powder X-ray diffraction technique. Figure 6 shows the relative composition of different polymorphs as a function of reaction time synthesized in the presence of mixed $\text{Ca}^{+2}/\text{Mg}^{+2}$ systems. Both calcite and aragonite phases were detected on the surface of Al plate and vaterite phase was absent in all cases. Also, weak peaks corresponding to LDH phase appeared as the reaction progressed. This clearly validated the formation of insoluble LDH particulate network on the surface of the plates. Moreover, the relative proportion of aragonite peaks increased compared to calcite as reaction progressed. This is consistent with our observations from the SEM studies where we demonstrated the increase in aragonite polymorph content compared to calcite on the Al plate surface as a function of time.

FTIR studies were conducted by scraping particles formed on the surface of Al plate to further validate the polymorph selectivity and polymorph stability. Figure 7 shows the comparative plot of CaCO_3 particles grown on Al plate in absence and presence of Mg^{+2} ions.

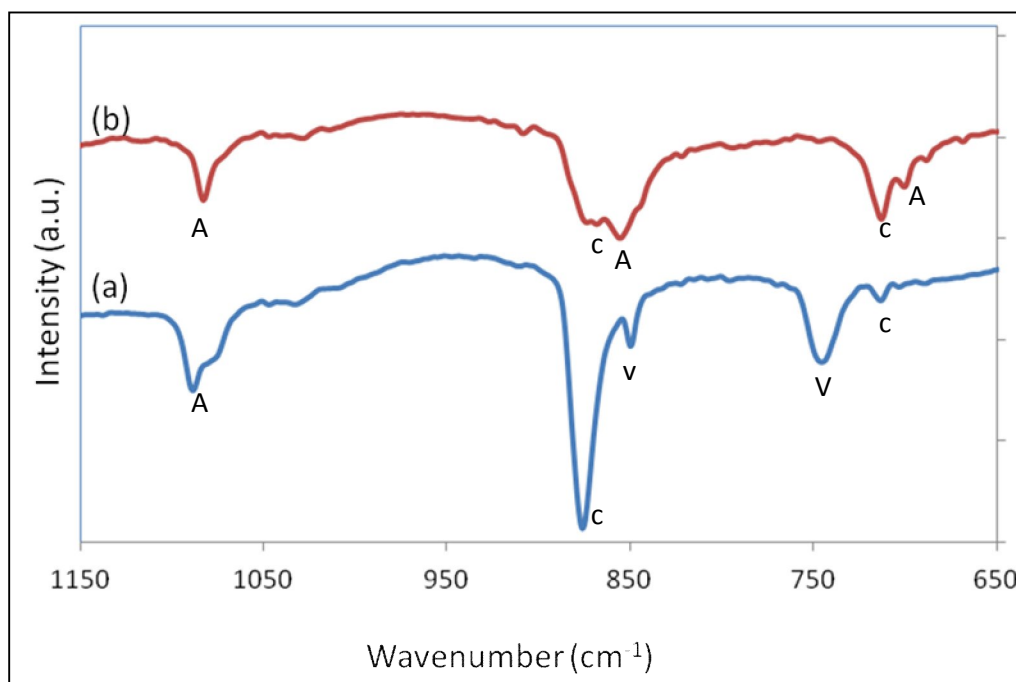


Figure 7: FTIR spectra of CaCO_3 particles grown on Al plate in presence of (a) 10 mM Ca^{+2} and (b) 10 mM 2:1 $\text{Ca}^{+2}/\text{Mg}^{+2}$ after 24h reaction respectively. Abbreviations: C, calcite; A, aragonite; V, vaterite.

Both the samples displayed two characteristic peaks at 712 and 876 cm^{-1} respectively indicating the presence of calcite phase. For sample (b) additional peaks at 700, 855, and 1083 cm^{-1} were detected, indicating the presence of aragonite phase along with its calcite counterpart. Whereas, the presence of vaterite particles along with calcite was confirmed for sample (a) owing to the strong peak at 746 cm^{-1} which was completely absent in sample (b).

3.3 Mechanistic insights on polymorphic transformation

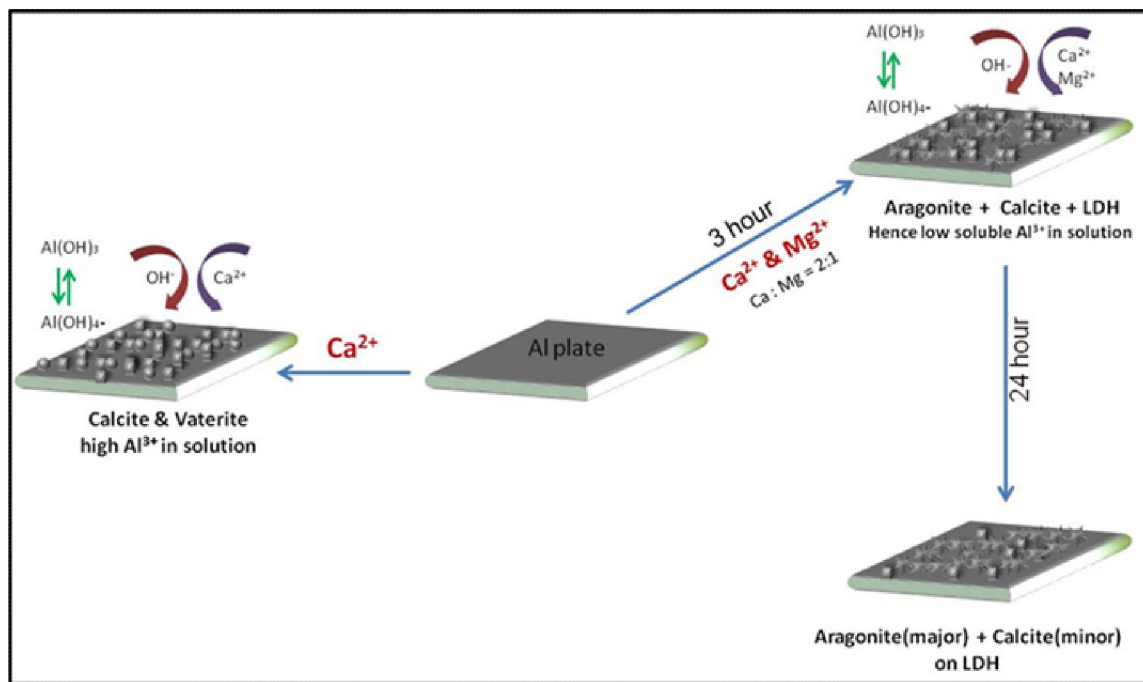
It has been well reported in literature that Mg^{+2} ions in solution stabilizes metastable polymorphs, particularly the aragonite form.^{16,26,27,28} As the pH of medium increases due to solubilisation of NH_3 in water, leaching of Al species such as $\text{Al}(\text{OH})_3$ or $\text{Al}(\text{OH})^{4-}$ starts from the surface of Al plate. The presence of dissolved Al species was confirmed by ICP analysis. In the presence of only Ca^{+2} ions in solution, the leached Al species are freely available in the medium and no LDH phase was observed. This may be due to the absence of relatively high pH (~13) required for formation of Ca-Al LDH and lower reaction temperature in our study, which did not facilitate the formation of such particles.²⁹ Consequently the concentration of Al species increased with time (~12.3 mg/L) compared to the scenario in which Ca^{+2} and Mg^{+2} were both present.

When Ca^{+2} and Mg^{+2} were present in the medium, considering the solubility product of CaCO_3 and LDH ($1.22 \times 10^{-8} \text{M}^2$ for vaterite, $4.61 \times 10^{-9} \text{M}^2$ for aragonite, and $3.31 \times 10^{-9} \text{M}^2$ for calcite and LDH $3.72 \times 10^{-10} \text{M}^2$ at 25 °C), it can be concluded that LDH would preferentially form compared to CaCO_3 . Moreover, the availability of Mg^{+2} ions at close proximity to the Al surface and the presence of soluble Al species in the medium results in the formation of LDH particles on the surface of Al plate. Since the reaction proceeds without being externally agitated, we believe that the generation of soluble Al species may be influenced by either or a combination of factors such as medium alkalinity and presence of Mg^{+2} ions in the vicinity of plates. Thus LDH particles

were formed only on the metal surface and absent in the bulk solution. As the Al species start leaching from the surface of the plate, it encounters relatively large concentrations of Mg^{+2} in its immediate vicinity, thereby spontaneously forming nuclei of MgAl LDH at the interface of the Al plate and bulk solution. With increase in time, the plate surface gets completely covered with LDH particles, thus reducing the availability of active site for further reaction, consequently the concentration of $Al(OH)_3$ or $Al(OH)^{4-}$ drops in solution. This has been proven from the ICP data which suggests a drop in the Al^{+3} concentrations with the progress of the reaction. The total soluble Al species were detected by ICP-OES as 0.31, 0.28 and 0.18 mg/L after 3, 6 and 24 hour reaction in the mixed Ca^{+2} /Mg^{+2} systems. Also, the structural integrity of the LDH plate network remained virtually unchanged with the time of the reaction. No depletion of Al^{+3} concentrations was observed for the Ca^{+2} systems.

It is known that Mg^{+2} ions at higher concentration favor the formation of aragonite particles in the medium¹⁴. In our reaction condition where the concentration of Ca^{+2} to Mg^{+2} ions is 2, it is expected that Mg^{+2} ions would be incorporated in the calcite matrix, resulting in the distortion of rhombohedral shapes of calcite. This arises due to lattice mismatch when Ca^{+2} ions are replaced by Mg^{+2} ions owing to the difference in their sizes. Moreover, considering the depletion of Mg^{+2} ions from the bulk solution at the initial stage of the reaction due to formation of insoluble LDH particles limits its ability to only affect lattice distortion of calcite particles during the precipitation of thermodynamically favorable calcite crystals at the start of the reaction. However, the depletion of Mg^{+2} ions in solution results in relative increase of Ca^{+2} ions in bulk solution. Sarkar et al¹⁴ has reported the role of Mg^{+2} ions containing insoluble LDH particles on the stabilization of aragonite phase which can be further influenced by the presence of surface hydroxyls and also modulating the surface charges on the LDH particles. LDH particles have surface bound hydroxyl groups which can exist as either protonated or deprotonated depending on pH of the medium. In alkaline reaction condition, there is high probability of these surface hydroxyls to remain deprotonated, which in turn can stabilize aragonite phase over calcite, though the precise mechanism for stabilization of such polymorphs is not known conclusively.³⁰ Moreover, it is also known that surface

charge density on materials can affect nucleation and eventually stabilize metastable polymorphs.³¹ Inorganic materials such as LDH, which has negative charge density at the current reaction condition (pH ~9) can aid in heterogeneous nucleation, thereby preferentially stabilizing the aragonite phase over calcite. This allows us to believe that with increase in time of the reaction, nucleation of CaCO_3 particles adopts in the aragonite polymorph compared to calcite and as such more amounts of aragonite polymorph is visibly observed to remain as stable polymorph on the surface of the immersed Al plate.



Scheme 1: Mechanistic interpretation of the CaCO_3 growth on Al plate

4. Conclusions

In this work selective growth of CaCO₃ polymorphs on Al plates was achieved using Ca⁺²/Mg⁺² salts and (NH₄)₂CO₃ as reagents by gas carbonation technique. In presence of Mg⁺² ions in the medium, LDH particles were formed on Al surface. The presence of Mg⁺² ions in solution coupled with substrate reactivity plays an important role in aragonite polymorph selectivity at room temperature over calcite polymorph with increasing reaction time. By suitably controlling the formation of desired polymorph on surfaces that are regularly used in household context, may aid in achieving superior and easier cleaning and reducing the tarnishing of surfaces. It may also throw light on devising rational strategies for making household surfaces less affected by scaling.

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