



The Phenomena of Spreading of Hydrotalcite Sol on A Porous Silica Surface Governed by Marangoni Effect

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Abstract

Wetting phenomena plays a crucial role in a wide range of technological applications. Spreading of liquids on solids involving phase change is encountered in many areas ranging from biological systems to industrial applications such as coatings, printing, painting and spraying. The fundamental study on wetting of membrane precursors namely hydrotalcite sols on a porous silica surface with different types of precursor material was successfully carried out. Relationship between the contact angle of a hydrotalcite droplet on silica surface and the Marangoni effect was also investigated. The presence of PVA in hydrotalcite sols was found to influence the rheological properties of the sols significantly, resulting in higher viscosity and ultimately leading to lower contact angle on solid surfaces. The degree of hydrotalcite's philicity on a substrate was improved by the addition of PVA solution. In this study, the spreading of a liquid droplet on a solid surface controlled by a surface tension gradient, due to Marangoni effect was found to drive better spreading of the liquid droplet. Marangoni Number, Ma was found to be proportionally related with the surface tension of the sols but inversely proportional to contact angles of the sols. Marangoni forces that decreased the contact angle, promoted spreading of hydrotalcite droplets on the selected glass substrates.

Keywords: contact angle, hydrotalcite, marangoni effect, spreading, wetting evolution

1. Introduction

Inorganic membranes have been extensively studied for decades and used in many applications due to their stability at high-temperature and high-pressure. They exhibit good chemical stability, high-mechanical resistance, long life, good defouling properties, high surface area and porosity to enable high flux. Sol-gel method is considered to be the most practical method for fabrication of porous ceramic membranes. Membrane synthesis by sol-gel method enables production of uniform pore size, high purity membranes at ambient conditions. Successful development of a uniform film requires that a liquid precursor be wetted and spread effectively on a solid substrate. Poor precursor spreading on the substrate surface usually results in defective films that suffer peelings of flakes, delamination, craters and pinholes. In many cases, surfactants are used to reduce defects and enhance the spreading since they are known to have the ability to reduce the surface tension of a particular liquid and induce a surface tension gradient.

In the previous work to prepare inorganic membranes, polyvinyl alcohol (PVA), polyvinyl butyral (PVB), or polymethyl metacrylate (PMMA) were used as surfactants to enhance spreading of the liquid membrane precursor in order to produce a thin film on a porous alumina

substrate successfully (Othman and Kim, 2007a; Othman and Kim, 2007b; Othman *et al.*, 2006). Although surfactants could help in reducing cracks, they could also render the membrane to curl and warp as the membrane dries and ages possibly due to the phobicity of the precursor material and other unidentified causes. The phenomenon of membrane warping was observed in mesoporous Al_2O_3 and Pd- Al_2O_3 asymmetric composites during preparation of Pd-alumina membrane (Othman and Kim, 2008a).

The phenomena of spreading and warping in membrane preparation could be governed by the Marangoni effect (Ganesan and Zebin, 2006). The Marangoni effect (sometimes also called the Gibbs-Marangoni effect) is the mass transfer on, or in, a liquid layer due to surface tension differences. The spreading is controlled by a surface tension gradient, which forms when a drop of surfactant solution is placed on a solid surface. The proposed model suggests that, as the spreading front stretches, the surface tension increases (concentration of surfactant becomes lower) at the front relative to the top of droplet, thereby establishing a dynamic surface tension gradient. The driving force for spreading is due to Marangoni effect, the higher the gradient, the faster the spreading. Few reports addressed the Marangoni effect of trisiloxane ethoxylates on polystyrene

surface (Nikolov *et al.*, 2002) in order to increase wettability of herbicide on leaf surfaces and spreading behaviour of volatile drop on a hot surface (Sefiane, 2006; Tseng *et al.*, 2004).

The phenomena of spreading governed by Marangoni effect are not well understood. The presence of Marangoni effect in membrane synthesis and development has not been reported so far, nor the explanation of the phenomena of wetting of sol precursors on a porous solid substrate. Therefore, in this paper fundamental study on a liquid spreading of a liquid precursor droplet with different sizes and different types of precursor material is performed. This is to be able to describe the phenomena of spreading of a sol precursor droplet and warping of membrane.

2. Method

2.1. Hydrotalcite sol preparation

For sol gel method, appropriate ratios of aluminium tri-sec-butyrate ($C_{12}H_{27}AlO_3$) and magnesium methoxide $(CH_3O)_2Mg$ were mixed with hot ethanol, respectively. The Mg/Al atomic ratio in the solution was selected as 3:1. It would be wise to hydrolyze the alkoxides separately for approximately 30 minutes to optimize the hydrolyzation process of the solution, under vigorous stirring at 70-90°C to form sol. Then, 9.5ml 1M potassium carbonate (K_2CO_3) was added to the mixture, followed by peptization of the sol using molar composition of the alkoxide, acid and water at 1:0.07:100, and vigorous stirring until homogeneity.

For binder addition, polyvinyl alcohol (PVA) (4g PVA/100ml H_2O) was added. The peptized sol was allowed to cool steadily for prolongation of hydroxylation, alkoxilation or condensation. The solution was refluxed at 353 K up to 16 hours until the gel was formed. The sol was dried in fume cupboard overnight to form dried gel. 10 ml of the sol was poured into petri dish and dried at ambient temperature for 48 hours. The sol dried up and formed dried gel. The dried gel was calcined in programmable carbolite furnace for 24 hours.

The same procedures were repeated except the addition of PVA solution to prepare sol without PVA binder. The obtained sols were designated as HT_{sg-PVA} and HT_{sg} to represent Mg-Al hydrotalcite prepared by sol-gel

technique with PVA and without PVA, respectively.

2.2. Silica sol preparation

Silica was used as membrane support in this work. 8.4 ml of tetraethyl orthosilicate, $Si(OC_2H_5)_4$ and 75.7 ml of ethanol were added into 18 ml of deionized water and 97.9 ml of ammonia solution. The sol mixture was stirred rigorously for 2 to 4 hours. The hydrotalcite pellet disc was coated with silica sol using dip coating method for the preparation of membrane. The pellet was dipped into the silica sol for about 10 seconds for both surfaces. The coated support was dried at ambient temperature until the dried membrane layer was obtained. Then the dried coated membrane was calcined at 500°C.

3. Results and Discussion

Wetting is the ability of a sol or liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting is determined by a force balance between adhesive and cohesive forces. It is important in the bonding or adherence of two materials. Adhesive forces between liquid and solid cause a liquid drop to spread across the surface whereas, cohesive forces within the liquid cause the drop to ball up and avoid contact with the surface. The contact angle, θ , is an important parameter to quantify the wettability of solid surfaces. It is defined as the angle made by the intersection of the liquid/solid interface and the liquid/air interface. It can be alternately described as the angle between solid sample's surface and the tangent of the droplet's ovate shape at the edge of the droplet. A high contact angle indicates a low solid surface energy or chemical affinity. This is also referred to as a low degree of wetting. A low contact angle indicates a high solid surface energy or chemical affinity, which leads to a high or sometimes complete degree of wetting.

3.1. Effect of PVA on sol

The addition of PVA in this work was to promote better spreading of liquid membrane precursor and reduce cracks formation on a thin film. However, high viscosity of the sol as a result of excessive PVA addition could enhance the risk of cracks and lower adhesion of coating due to formation of aggregates at higher viscosity,

leading to the formation of easily detachable particles on the surface. Therefore, it was proposed that for dip coating technique, the sol was not to exceed the value of viscosity at approximately 50cP to prevent the absence of fluidity (Haas-Santo, 2001). The viscosity reading was taken at 30°C and spindle speed of 150 rpm with shear rate of 183.45s^{-1} using Brookfield rheometer. The viscosity of HT_{sg} sol was 30.292cP and HT_{sg-PVA} was 47.88cP.

Three different liquids/sols namely; HT_{sg}, HT_{sg-PVA}, and water, were dropped onto different hydrotalcite substrates with/out PVA and coated with silica layer. Differences in the contact angles for all sols on the substrates were observed and recorded. All sols were dropped carefully on to the respective substrate and contact angles were measured using an optical contact angle meter at ambient conditions. It was found that hydrophilicity of hydrotalcite pellet was improved after the addition of PVA solution in the substrate. Introduction of acid and PVA was known to not only peptize and strengthen the sol but also reduce the surface tension of the sol, by inducing a surface tension gradient facilitated by what is termed as a *Marangoni* mechanism. Marangoni defines that a sessile drop that has low surface tension tends to move to another drop that has relatively higher surface tension, thereby reducing the contact angle of the latter (Othman and Kim, 2008b). In this work, the Marangoni's effect was shown by the reduction of the contact angle of water on the substrate from 10.1° to 1.5°. When highly diluted solution with low viscosity was used to a substrate, a homogeneous, crack-free and continuous films were produced [Celik et al., 2006]. Reduction in contact angle as a result of diluted sols on a particular substrate was expected to enhance spreading or wettability of the sols on the substrate. The similarity of materials might as well contribute to better spreading and coating as observed in the previous work, in which, multi-step TiO₂ shell deposition was applied on silica cores (Lee et al., 2008).

In this experiment, it was observed that when sol and substrate shared the same materials (PVA), it resulted in better ability of the sol to wet the substrate's surface. This is evident from the contact angle measurement made between HT_{sg} sol and HT_{sg-PVA} on the respective substrates such as shown in Table 1. The addition of PVA had effectively reduced the contact angle and hence increased the wetting ability.

Table 1. Contact angle of hydrotalcite sol on hydrotalcite pellet

Sols	Contact angle, θ	
	HT substrate without PVA	HT substrate with PVA
HT _{sg}	6.9	0.1
HT _{sg-PVA}	0.9	0.6
Water	10.1	1.5

3.2. Effect of silica coating on wetting

Silica coating is typically used for enhancement in hydrophilicity (reduction in hydrophobicity) of a particular material in many applications. Applications of silica coating in glass and Polyethylene terephthalate (PET) substrates are crucial to provide antifogging properties under a variety of temperature and high humidity conditions.

In this experiment, the effect of silica coating on different substrate was studied. A glass material was used as substrate and the results were compared to the coating of silica on hydrotalcite substrate. The phenomena of liquid wetting on silica-coating and uncoated substrate were also investigated. Figure 1 shows that contact angle of water was greatly reduced from 59.3° to 15.2° when the glass substrate was coated with silica.

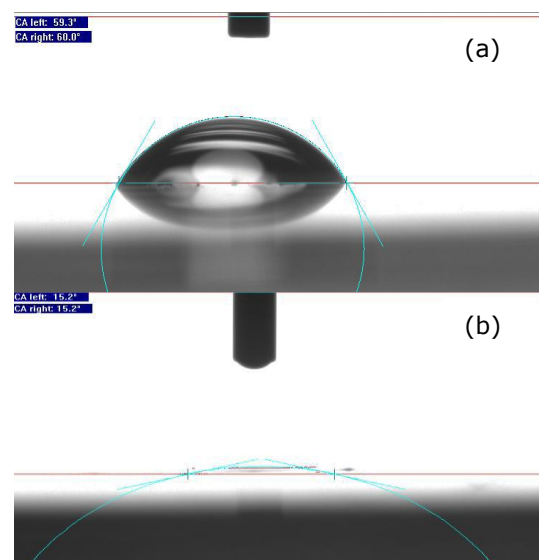


Figure 1. Contact angle of water on a glass substrate (a) Uncoated glass surface (CA=59.3) (b) Silica-coated glass surface (CA=15.2)

From the results, silica coating was able to reduce contact angle of water droplet on an impermeable glass substrate thereby, enhancing spreading ability (or greatly reducing hydrophobicity) of water on the

glass substrate. In terms of spreading ability and wettability of HTsg and HTsg-PVA sols on impermeable glass surface, it can be said that PVA improved wetting. This is shown by the contact angle of 40.9° and 35.4° for HTsg (hydrotalcite sol without PVA) and for HTsg-PVA (hydrotalcite sol with PVA), respectively. Silica layer reduced the contact angle further to 0° by increasing the wetting ability of the sols. The findings were then used to understand the microscopic coating of hydrotalcite sol on a nano-core silica substrate in order to prepare spherical hydrotalcite shell-silica core nano particles.

3.3. Marangoni effect

A solid substrate exposed to the atmospheric environment is almost invariably covered by a layer of fluid material. A drop, placed on a substrate which it wets, spreads out to form a film. A particularly important effect on the spreading kinetics of liquid is due to Marangoni forces induced by surface tension gradients. Marangoni forces drive spreading of liquid droplet on substrate and promote wetting ability of the droplet.

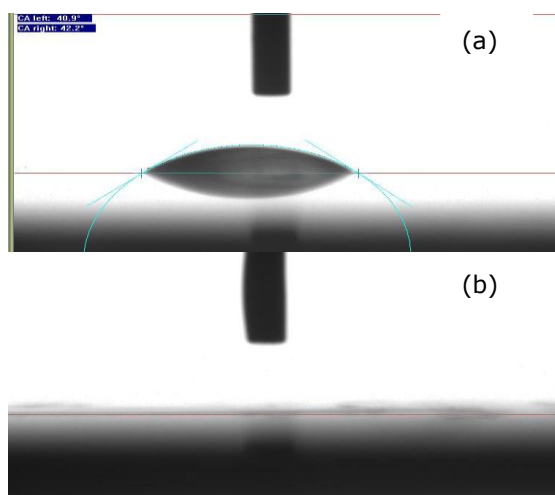


Figure 2. Contact angle of HTsg sol on a glass material a) Uncoated glass surface (CA= 40.9°) b) Silica-coated glass surface (CA= 0° , Ma= $+\infty$)

In this experiment, Marangoni Number, Ma was determined for all sols on both substrates and the significance of Marangoni Number to understand spreading of sols on the substrate was investigated. Marangoni Number was calculated using the equation:

$$Ma = \frac{\Delta\sigma \cdot h}{\mu \cdot D_{AB}} \quad (1)$$

Where :

$\Delta\sigma$ = surface tension of sols ($\text{kg} \cdot \text{m} / \text{m} \cdot \text{s}^2$)

h = height of pellet (m) = 0.002 m

μ = viscosity of sols ($\text{kg} / \text{m} \cdot \text{s}$)

D_{AB} = diffusivity of sols in substrate (m^2 / s)

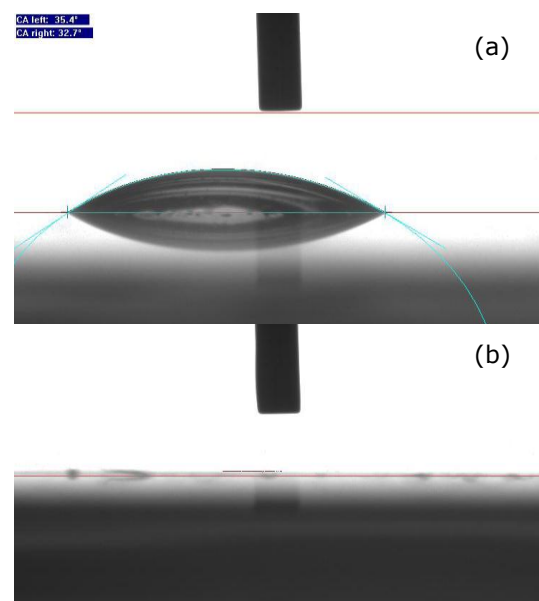


Figure 3. Contact angle of HTsg-PVA sol on a glass material (a). Uncoated glass surface (CA= 35.4°) (b). Silica-coated glass surface (CA= 0°)

From the results, Marangoni Number, Ma was found to be proportionally related with the surface tension of the sols on HT substrate such as shown in Table 2. As surface tension of sols increased, Ma increased as well. This is acceptable since Marangoni effect was induced by surface tension gradient. Higher surface tension would result in higher value of Ma.

Table 2. Marangoni Number on HT substrate

Sols	Surface Tension, σ (N/m)		Marangoni Number, Ma	
	HT _{sg} substrate	HT _{sg} -PVA substrate	HT _{sg} substrate	HT _{sg} -PVA substrate
HT _{sg}	1521.23	106.22	5.55×10^{13}	3.91×10^{12}
HT _{sg} -PVA	492.44	954.41	1.83×10^{13}	3.64×10^{13}
Water	3.88	3.75	1.18×10^{11}	1.14×10^{11}

4. Conclusion

Wettability of the sols on the substrate was enhanced by reducing the contact angle of the sol on a substrate. It was found that by adding an appropriate amount of PVA and in the presence of silica layer, the wettability of hydrotalcite sols was enhanced. A complete wetting of hydrotalcite sol was observed on silica-coated hydrotalcite substrates. Spreading of the liquid droplet was controlled by a surface tension gradient, formed when a drop of sol was placed on the solid surface or substrate. The presence of surface tension



gradient would induce Marangoni effect which drove spreading of the liquid droplet. Better wetting of liquid on a particular substrate was observed with larger surface tension gradient and higher Marangoni Number (Ma).

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