Fabrication of functionally graded 3A/5A zeolites by electrophoretic deposition

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Functionally graded zeolites of molecular sieve type 3A and 5A are deposited by electrophoretic deposition (EPD) from acetone suspension with 8% volume concentration of n-butylamine as particle charging agent. The EPD characteristics of both 3A and 5A suspensions are studied. Functionally graded zeolite 3A/5A deposits are obtained at 200 V DC. Energy dispersive X-ray dispersion (EDX) analysis results confirm the graded structure. The deposited zeolites are also analysed by scanning electron microscopy (SEM). The factors influencing the deposition process are discussed.

Keywords: Electrophoretic deposition (EPD), Functionally graded materials (FGM), Powder processing, Scanning electron microscopy (SEM)

Introduction

Functionally graded materials (FGMs) are composites whose structure is tailored with respect to spatial locations. Owing to the tailored composition, material properties of FGM can be also spatially customised. Various techniques, such as powder stacking and sintering,[1] electrophoretic deposition (EPD), sedimentation, vapour deposition, etc. have been employed to produce FGMs. Among these techniques, EPD is a convenient method to fabricate both graded coatings and 3D parts.[2–5] By in process changing the concentration of constituents in the deposition suspension, smooth (step less) FGM can be conveniently obtained by EPD.[6,7] The thickness of an EPD deposit can be easily controlled.

Zeolites have good gas adsorption capability. Zeolites have been well recognised for their unique ability to adsorb and separate gases, catalyse chemical reactions and selectively exchange cations in solutions. These properties result from their uniform, well defined pore structure which promotes the adsorbents' chemical interactions that occur at discrete sites within their lattice. Because these chemical interactions (in adsorptive or catalytic processes) either generate or require heat, the application of zeolites for exo- or endothermic processes is often limited by heat transfer into or from these insulator-like aluminosilicates.

Functionally graded material composites provide a new and unique approach in managing heat transfer and maintaining temperature uniformity in either adsorptive or catalytic applications of these molecular sieves. In addition, the layering of different zeolites' types may provide unique opportunities to perform selective separation and catalysis in the same reaction. Layering of other adsorbents/catalysts such as alumina or silicas may also be possible using EPD technology, although this work is beyond the scope of the present paper.

The EPD of zeolite thin films has been investigated by several researchers.[8,9] The usage of water and organic solvents, such as isopropyl alcohol (IPA), acetylacetone (AcAc), has been investigated.[10,11] Owing to the hydrolysis of water, gas bubbles are formed in the deposit if water is used as the suspension media. Therefore, organic solvent was preferred. In contrast to previous studies, in this research, the authors used acetone and n-butylamine as solvent to deposit zeolite particles successfully. Moreover, the authors demonstrated the possibility to fabricate zeolite FGM by EPD, which is the first attempt of this kind.

Experiments

Suspension preparation

Molecular sieves type 3A ($0{\cdot}6K_2O:0{\cdot}40Na_2O:1Al_2O_3:2{\cdot}0\pm 0{\cdot}1SiO_2:xH_2O$) and 5A ($0{\cdot}80CaO:0{\cdot}20Na_2O:1Al_2O_3:2{\cdot}0\pm 0{\cdot}1SiO_2:xH_2O$) (both from Sigma-Aldrich, USA) were used to deposit FGM by EPD. The powder was first baked for 24 h in a vacuum baking furnace (Precision Inc.) under 100°C to remove the adsorbed water. The baked powders' and unbaked powder's behaviour was completely different during EPD: without baking, for the same experimental conditions, there was no deposition. After baking, the powders were mixed with acetone and 8% volume concentration n-butylamine in a planetary ball mill for 2 h to make the suspension homogeneous. After that, the suspension was further dispersed in an ultrasonic cleaner.

Electrophoretic deposition suspension study

In order to control the deposition of zeolite FGM, the EPD kinetics has to be determined experimentally. The voltage was 200 V, and particle loading of 5A type zeolite was 20 g L^{-1}. For 3A type zeolite, two different particle concentrations were investigated: 20 and 40 g L^{-1}. The EPD was conducted for different time

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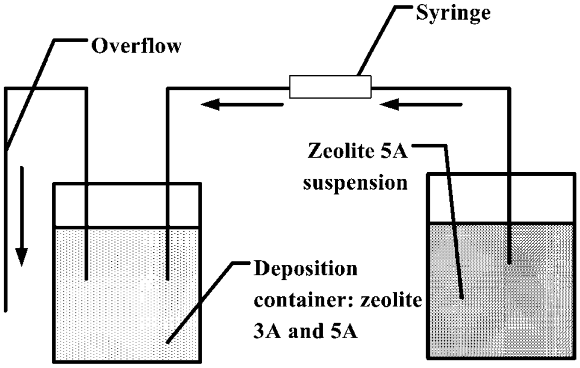


1 Set-up to deposit zeolite FGM by EPD

periods with different deposition parameters, and then the deposits were dried and weighted. In order to identify the influence of the conductivity on the deposition rate, the conductivity of the suspension was measured by using a conductivity meter (Fisher Scientific Inc.).

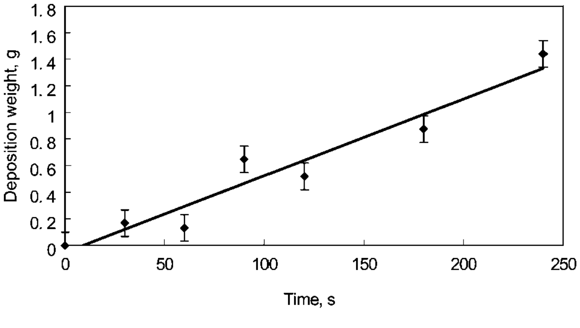
The EPD experiments were conducted in a glass beaker with magnetic stirring. Two vertically arranged stainless steel electrodes with 4 cm^2 surface area were separated at a fixed 20 mm distance. The electrodes were cleaned in acetone and then dried under air gun. A DC power supply (Dankar DK-22-4) was connected to the electrodes.

Electrophoretic deposition of graded zeolites

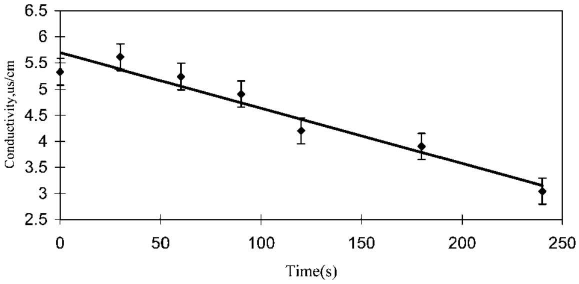
The constant voltage of 200 V was used in EPD of the FGM based on zeolites type 3A and type 5A. The experimental set-up is shown in Fig. 1. A magnetic stirrer was used to stir the suspension during EPD. Two suspensions of zeolite type 3A and 5A were prepared as described above. The particle concentration in both suspensions was 20 g L^{-1}. In order to obtain FGM, 30 mL suspension containing zeolite type 5A was continuously added by a syringe into the initial zeolite 3A suspension during EPD process. The total deposition time was 5 min. After deposition, the deposits have been dried at room temperature for 24 h in air.

Characterisation

After drying, the deposits thickness and microstructure have been characterised by scanning electron microscopy (SEM). The graded composition was analysed by energy dispersive X-ray dispersion (EDX) along the thickness direction of the deposit. The thickness of the deposit was measured by the cross-section micrograph analysis.



2 Zeolite type 5A deposition kinetics



3 Zeolite type 5A suspension conductivity

Results and discussion

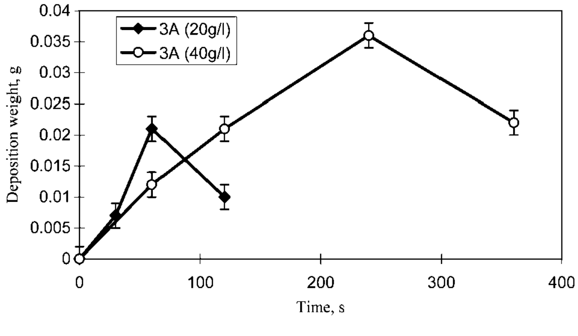
Electrophoretic deposition characteristics study

The EPD kinetics of zeolite 5A is shown in Fig. 2. The results indicate that the deposition kinetics of zeolite type 5A agrees with Hamaker's law[12]

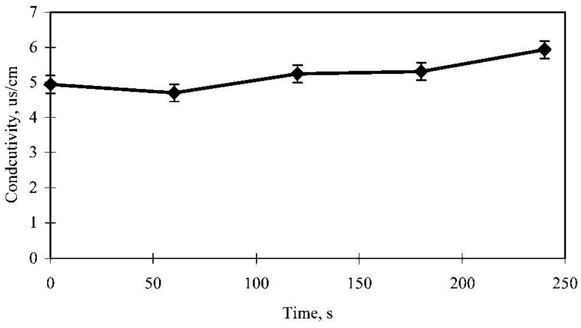
$$\frac{dY}{dt}=f\mu EcA$$

where Y is the yield (kg), t is the time (s), μ is the electrophoretic mobility ($cm^2 V^{-1} s^{-1}$), E is the electrical field strength ($V m^{-1}$), c is the solids loading ($kg m^{-3}$), A is the area of deposition electrode and f is a factor of deposition effectiveness, which is always <1.

The change in the conductivity of the suspension is shown in Fig. 3. It indicates that the conductivity dropped as the deposition proceeded (a common phenomenon in EPD: the conductivity decreases with the growth of the thickness of the deposit; this trend is apparently enhanced in the present procedure by the different conductive abilities of 3A and 5A zeolites). The kinetics of zeolite type 3A with two particle loadings, which are 20 and 40 g L^{-1} respectively, are plotted in Fig. 4. The kinetics results of zeolite type 3A show that there was a peak value of the deposition weight; after that, the deposition weight drops. The reason is that as deposit thickness and weight increase, the adhesion force to hold the deposit together cannot compensate the gravity force of the deposit; as a result, some part of the deposit 'slips' back to the slurry. This has been observed in the experiment of zeolite 3A EPD but not in 5A. The conductivity of the suspension during EPD of zeolite type 3A is shown in Fig. 5. The conductivity of zeolite type 3A remains stable compared to zeolite type 5A. The structure difference between these two particle species might be the reason of the different kinetics and the conductivity change during EPD.



4 Zeolite type 3A deposition kinetics



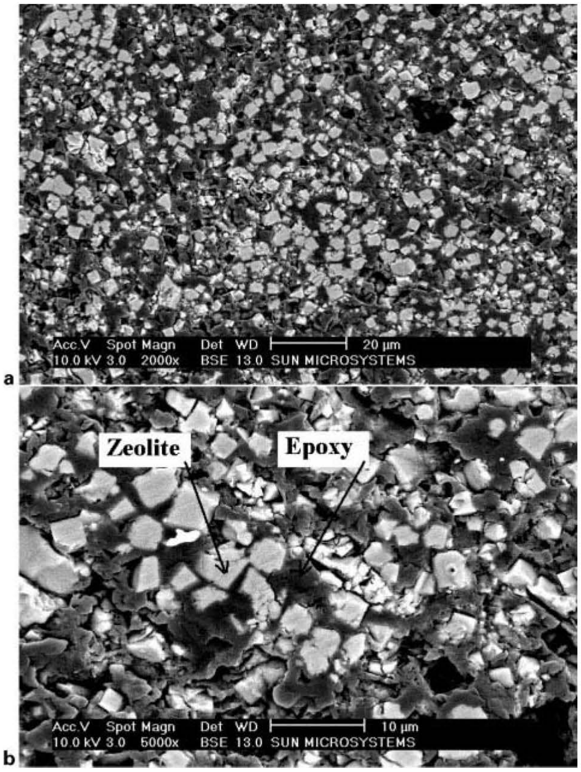
5 Zeolite type 3A suspension conductivity

Deposit characterisation

The deposits were smooth and uniform. There were no cracks observed in the deposits after drying. Figure 6 shows the cross-section SEM image of the deposited FGM. One can see large scale pores between grains of zeolite (containing nanosize pores). The adsorption capability of zeolites is determined by intrinsic nanoscale pores and should not be effected by the mesoscale porosity. The measurement of adsorption capability is an object of further investigations, while the present work is concentrated on the feasibility of the fabrication of functionally graded zeolite deposits. Figure 7 shows the EDX analysis result of the deposit to confirm the composition of the deposit. The ratio of Na to Ca concentration is shown in Fig. 8. From Fig. 8, it is clear that the concentration of Ca increased along the thickness direction, which means that the concentration of zeolite type 5A increased. Therefore, the composition of resultant deposit is a graded structure.

Influence of suspension media and additives

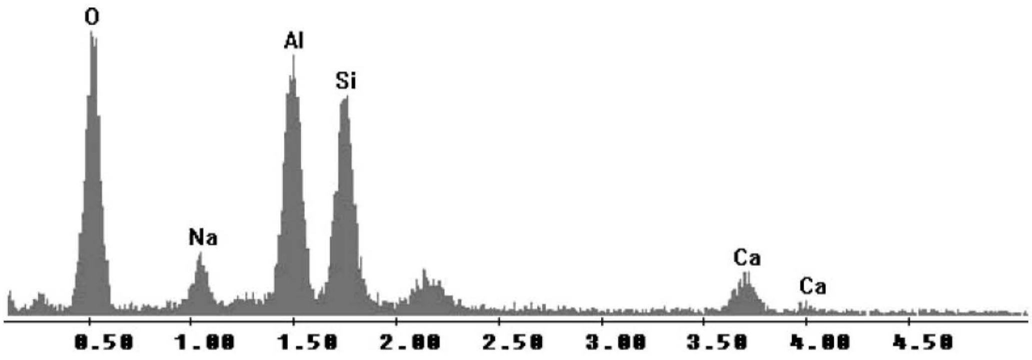
Suspension media is critical to the deposition procedure and deposit quality. Both water and organic solvents have been used for EPD. It is well known that the use of water can lead to several problems, such as the faster kinetics, which makes the control of the deposit thickness difficult, and the hydrolysis of water at low voltage ($\sim$5 V),[13] which promotes bubbling and pin holes. Although bubbling can be avoided through membrane method,[14,15] or using hydrogen adsorption electrodes,[16] it is more convenient to conduct EPD in organic solvent, especially for thin coatings. For thick coatings and 3D shaping, aqueous EPD is preferred because of the faster kinetics.



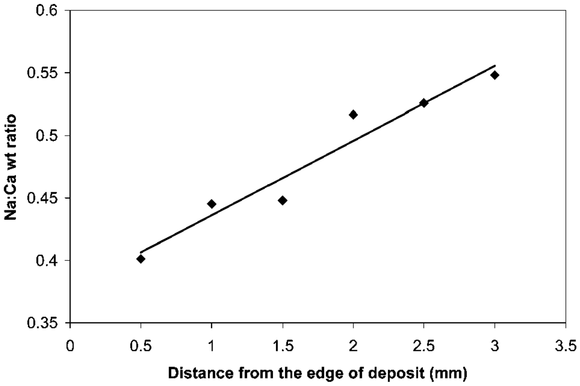
6 *a* cross-section mirograph of deposited zeolite and *b* enlargement of *a*

Particle charging influences the deposition rate significantly as indicated by Hamaker's law.[10] With the deposition proceeds, due to the built-up of the deposit, the resistivity of the suspension increases. Indeed, as the deposition progresses, the overall resistivity in the circuit increases due to the increase in the deposit thickness. As a result, the potential drop in the suspension is very large. The potential drop leads to the drop of deposition rate significantly. Consequently, the thickness of deposition is limited. A good example is the alumina–ethanol system stabilised by hydrochloric acid. The deposit resistivity is extremely high in this case and it is nearly impossible to fabricate millimetres thick deposits.[17] The experiments conducted in this research indicated that acetone and n-butylamine render satisfactory deposition rates. The 3 mm thick zeolite 3A deposit in the experiments was obtained within 5 min.

It was observed in the experiments that as the deposition proceeds, the thickness of the deposit became more non-uniform: the upper portion of the deposit is thinner than the lower portion of the deposit. This is



7 Energy dispersive X-ray spectrometry analysis of deposited structure



8 Ratio of Na to Ca weight concentration along thickness direction of deposit

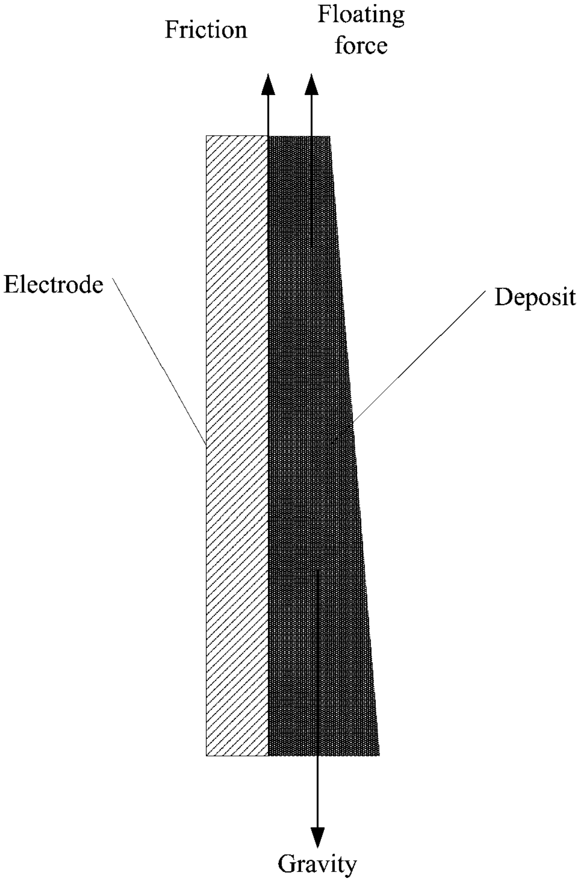
because the deposits slid towards the bottom of the electrode. This phenomenon was illustrated in Fig. 9. For thin deposits, the friction between the deposit and the electrode plus the floating force from the suspension is enough to hold the deposit. However, due to the increase in the deposit thickness, the gravity becomes higher than the friction and floating force. As a result, the thickness of the deposit becomes non-uniform. If the deposit time is shorter, the deposit does not have enough time to gain substantial thickness non-uniformity (the difference between the top and the bottom portions of the deposit). Therefore, in order to deposit thick deposits uniformly, large voltage was preferred to reduce the EPD time. However, the experiments indicated that large voltage caused the roughness of the deposit surface.

Suspension stability

Stable suspension is essential to create uniform deposits. The stability of suspension is a complex problem, which includes many interacting parameters. Generally, particle size, additives, suspension media and fluid conditions influence the stability of suspension. For example, the particles should not be excessively large; otherwise gravity will render rapid sedimentation.

Colloid suspension additives can help make the suspension stable and homogeneous. These additives include electrosteric stabiliser and electrostatic stabiliser. Electrostatic stabiliser increases particle charging which stabilises the suspensions. In some cases, such as when dealing with large particle sizes, chemical additives are not able to suspend particles, thus stirring was usually adopted. The experiments indicated that the addition of n-butylamine could not suspend the zeolite particles effectively. Particles have been partially sedimented. Therefore, magnetic stirring was necessary.

Particle agglomeration is another major problem. First, agglomeration causes the instability of the suspension. Second, if post-EPD consolidation such as sintering is required, the agglomeration can cause incomplete densification and defects in the final product. It was found that ultrasonic vibration could effectively break particle agglomeration. The suspension was mixed by magnetic stirrer and then put into the ultrasonicator for further processing. The visual inspection of sedimentation indicates that 15 min of vibration was enough to break agglomerates and make the suspension more stable.



9 Forces acting on deposit during EPD

Conclusions

The EPD of zeolite type 3A and type 5A particles was successfully conducted using acetone and n-butylamine. No cracks were formed after drying of the green deposit. By changing the composition of the suspension, the FGM based on zeolites type 3A and type 5A was successfully synthesised. The characterisation by SEM indicated that the particles were uniformly deposited. The analysis by EDX indicated the graded structure of the deposited zeolite materials.

Acknowledgements

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