

Unusual Phase Inversion Behavior in an Emulsion Polymerization System Caused by Ammonia

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Porous carbon with pores and porewalls was prepared by the polymerization of an O/W emulsion of Span 80-Tween 80/liquid paraffin/water-resorcinol-formaldehyde (R/F) with NaOH. However, a different kind of carbon material which comprises spherical or intertwined worm-like particles was fabricated by using ammonia as the catalyst. Inferential evidence indicates that the O/W emulsion undergoes a phase inversion caused by ammonia; whether the phase inversion leading to a W/O emulsion or a transition structure depends on the R/F concentration within the aqueous phase.

Emulsions are disperse systems, which generally consist of emulsifier and at least two immiscible or slightly miscible phases, a hydrophobic phase (oil phase) and a hydrophilic phase (aqueous phase).¹ Emulsion polymerization is a type of reaction which usually starts within an emulsion incorporating water, monomer, and emulsifier. Recently it has been very useful for the preparation of porous polymer (or carbon) materials with well-characterized surface properties or colloidal polymer particles with narrow size distribution. For example, Mock et al. prepared polystyrene particles by seeded emulsion polymerization.² Menner et al. obtained open porous polymer through high internal phase emulsion (HIPE) polymerization.³ Compared to the great attention given to various parameters to affect the emulsion properties, such as the hydrophile-lipophile balance (HLB) value, phase inversion temperature (PIT), oil/aqueous phase level, component ratio, monomer properties, and additive, however, less effort has been devoted to catalysts.⁴⁻⁶ Besides, a phase inversion caused by only changing the catalyst in a polymerizing emulsion system has been little reported previously.

In our previous study, porous carbon with common pores and porewalls was prepared by the polymerization of an O/W emulsion system of Span 80-Tween 80/liquid paraffin/water-resorcinol-formaldehyde (R/F) with NaOH.⁷ In this work, however, monolithic carbons comprising spherical or highly intertwined worm-like particles were obtained by using ammonia as the alternative catalyst. These carbons are a entirely different kind of products compared to the porous carbon mentioned above. Samples were prepared basically according to the procedure described in ref 7 except that the catalyst was changed to ammonia. The carbons denoted as PC1, PC2, and PC3 correspond to 71.4, 35.7, and 29.8% R/F mass fraction within the aqueous phase, respectively. For comparison, a sample denoted as PC4 was prepared with an R/F concentration of 35.7 wt % in the presence of NaOH.

Figure 1 shows SEM photographs of the prepared carbon materials. Sample PC1 comprises definitely spherical particles with the diameters between 1–5 μm . The particles are fused

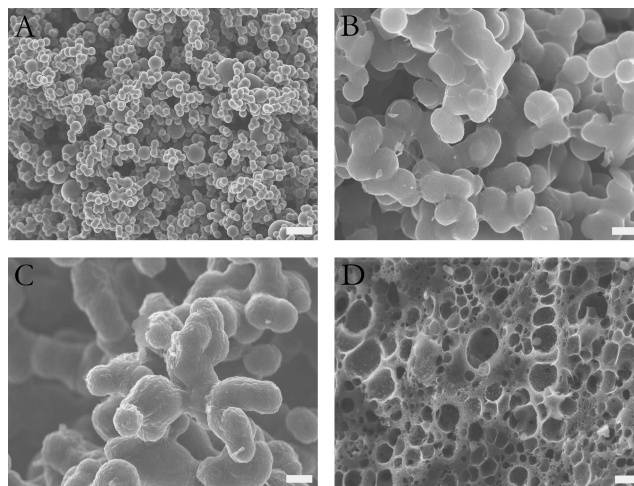


Figure 1. SEM images of PC1 (A), PC2 (B), PC3 (C), and PC4 (D). The scale bars for A, B, C, and D is 10, 1, 2, and 3 μm , respectively.

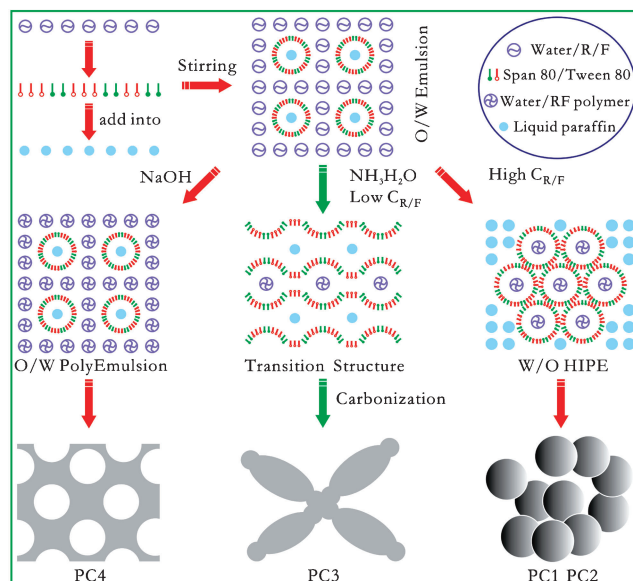
instead of independent (Figure 1A). With the decrease of aqueous R/F concentration, the particles gradually became sphere-like and intertwined worm-like shapes, as shown in Figures 1B and 1C. While carbon materials prepared with NaOH as a catalyst are porous materials with pores and porewalls, independent of the R/F concentration in water. Figure 1D shows a typical SEM image of the porous carbon. The pores show dimensions similar to particles in samples PC1, PC2, or PC3.

In our previous study, an O/W emulsion with water plus R/F in the external phase and liquid paraffin in the internal phase were formed in the mixed water/oil system, which was determined by phase dilution.⁸ The droplet structure of this emulsion was not changed by NaOH and finally porous carbon PC4 was prepared. However, a completely different kind of carbon material was obtained in this study. Because the base increases instability of the emulsion which is a thermodynamically unstable system and the emulsion has relatively rapid polymerization speed, the emulsion type is difficult to be verified by phase dilution or electric conductivity after the addition of catalyst. However, it could be inferred from the morphologies of the resultant carbons that the emulsion system does not keep an O/W structure in the presence of ammonia; otherwise final products similar to PC4 would be obtained. Besides an O/W emulsion type, there are two other possibilities for the system: no emulsion (i.e., the original emulsion was completely destroyed by ammonia) or W/O emulsion. If there was not any emulsion formed, carbons comprising spherical or worm-like particles would unlikely be formed. Besides, only R/F polymer and consequent nonporous carbon rather than materials

possessing porosity would be prepared if original emulsion structure were completely destroyed by ammonia. In a non-emulsion system, generally it is difficult to prepare carbons with porosity by simple polymerization of R/F or other organic precursors without any pore-forming agent.⁹ On the other hand, basically equivalent particle and pore size between PC1 (or PC2) and PC4 implies that the emulsion was to be reconstituted rather than destroyed. Therefore, the first case of no emulsion formed could be excluded, and the only possibility left for the emulsion system is that the original O/W emulsion undergoes a phase inversion toward a W/O one induced by ammonia. The inverted emulsion is a W/O HIPE because its internal phase (water plus R/F) takes more than 80 vol%. HIPEs were first defined by Lissant as emulsions containing a dispersed phase volume of 70% or greater.¹⁰ By polymerization and carbonization of aqueous R/F in the HIPE, carbons comprising spherical particles were prepared. The fact that the particles were fused can be explained in the same way as the products obtained from open porous polymerized HIPEs.³ The removal of the oil or aqueous phase which takes the role of template causes pore throats in that HIPEs and fused spheres in this case. However, sample PC3, in contrast to PC1 and PC2, should be the product of an in situ polymerized emulsion with a transition structure between O/W emulsion and W/O HIPE because the particle shape matches the characteristics of this system. As evidenced by these structural and experimental results, it is concluded that the O/W emulsion undergoes a phase inversion induced by ammonia, whether the inversion leads to a W/O HIPE or a transition structure dependent on the R/F concentration in the aqueous phase, as shown in Scheme 1.

In general, the emulsion structure could be affected by many factors such as HLB value, PIT, or oil/water phase ratio.^{11,12} One could achieve a phase inversion by changing the factors referred above, but it is unusual that the emulsion would phase invert by only changing the base catalyst from NaOH to ammonia considering that the other parameters in the emulsion are unvaried and that the change of the catalyst does not lead to a dramatic change in pH or temperature. Besides, it was found that the morphology of carbon materials is dependent on catalyst type instead of dosage. Thus, whether a base is strong or weak is not the reason causing the phase inversion behavior. We infer that there is something to do with intermolecular H-bond interaction. Ammonia could form H bonds with H₂O, R/F and surfactant molecules when it is added into the emulsion, which affects the cohesive energy parameters of oil/aqueous interface^{13,14} and finally leads to a structure transformation within the emulsion. Actually, HLB or PIT used for a phase inversion also could be ascribed to the change of interfacial cohesive energy.¹⁴ NaOH, however, did not have the ability to form H bonds. Thus, the emulsion retains an O/W type and the polymerization of which yields products with porous structure. To verify our assumption that it is the H-bond interaction that causes the phase inversion, we chose dimethylamine which also has the ability to form H bonds for the emulsion polymerization to prepare carbon materials. It was found that the resultant carbons have similar morphologies with those prepared with ammonia. This result preliminarily verified our presumption.

In summary, the O/W emulsion used undergoes a phase inversion induced by ammonia, whether the phase inversion leading to a W/O HIPE or a transition structure depends on the



Scheme 1. Schematic formation of carbon materials with different morphologies by using NaOH and ammonia respectively as the catalyst.

R/F concentration. The results are meaningful because they provide not only a simple way to control emulsion structure but also a technological potential of preparing carbons with various morphologies by emulsion polymerization.

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References

- 1 F. Wang, G. Xu, Z. Zhang, X. Xin, *Eur. J. Inorg. Chem.* **2006**, 109.
- 2 E. B. Mock, H. D. Bruyn, B. S. Hawkett, R. G. Gilbert, C. F. Zukoski, *Langmuir* **2006**, *22*, 4037.
- 3 A. Menner, R. Powell, A. Bismarck, *Macromolecules* **2006**, *39*, 2034.
- 4 A. Barbetta, N. R. Cameron, S. J. Cooper, *Chem. Commun.* **2000**, 221.
- 5 P. J. Dowding, B. Vincent, *Colloids Surf., A* **2000**, *161*, 259.
- 6 D. Nagao, N. Anzai, Y. Kobayashi, S. Gu, M. Konno, *J. Colloid Interface Sci.* **2006**, *298*, 232.
- 7 M. Liu, L. Gan, F. Zhao, H. Xu, X. Fan, C. Tian, X. Wang, Z. Xu, Z. Hao, L. Chen, *Carbon* **2007**, *45*, 2710.
- 8 D. Zhang, X. Song, F. Liang, Z. Li, F. Liu, *J. Phys. Chem. B* **2006**, *110*, 9079.
- 9 A. Léonard, N. Job, S. Blacher, J.-P. Pirard, M. Crine, W. Jomaa, *Carbon* **2005**, *43*, 1808.
- 10 K. J. Lissant, *J. Colloid Interface Sci.* **1966**, *22*, 462.
- 11 L. Chen, Y. Shang, H. Liu, Y. Hu, *J. Colloid Interface Sci.* **2006**, *301*, 644.
- 12 D. Morales, J. M. Gutiérrez, M. J. García-Celma, Y. C. Solans, *Langmuir* **2003**, *19*, 7196.
- 13 A. Beerbower, M. W. Hill, *Am. Cosmet. Perfum.* **1972**, *87*, 85.
- 14 W. Liang, *The Foundation of Emulsion Science and Technology*, Science Press, Beijing, **2001**, p. 60.