INTRODUCTION

Superficially porous particle (SPP) technology can achieve comparable separation efficiency while working at lower column backpressure with comparison to fully porous particles. In order to take the advantages of SPP technology and make it workable for high pH applications, superficially porous silica particles have been modified with organic-inorganic hybrid coatings to increase the high pH stability. However, the lifetime of the Hybrid SPP, especially the commonly used 2-3µm particles, is much shorter than the fully porous Hybrid particles.

In this work, we have studied the dissolution of superficially porous silica particles incorporating hybrid coatings and bonded phases under a high pH chromatographic testing condition to explore the column failure mechanism. Based on the experimental results, we have developed mathematical models to elucidate the shell and core silica dissolution rates of the Hybrid SPP under high pH testing condition, correlated the silica dissolution models with the corresponding chromatographic behavior, and determined the failure mode.

METHODS

High pH Chromatographic Testing Condition:

- Column Dimension: 2.1 x 50 mm
- Column Temperature: 60°C
- Flow Rate: 0.8 mL/min
- Mobile Phase: A. pH 10.5, Ammonium bicarbonate (10 mM); B. Acetonitrile
- Gradient: 5-95% B in 2.3 min. linearly, hold at 95% B for 0.7 min, return to 5%B in 0.5 min, hold at 5%B for 1.5 min.

Analyses of Packing Materials and Effluents:

- Quantification of bonded phase cleavage by carbon analysis
- Quantification of dissolved silica by weight loss measurements of dried column bed
- Flame atomic absorption on HF-digested concentrated effluents
- Examination of particle morphology by broad ion beam cutting (BIB) and scanning electron microscope (SEM)
- Quantification of dissolved core silica by Coulter technique

RESULTS AND DISCUSSION

Cleavage of Bonded Phase:

The relative % loss due to the cleavage of bonded phases from 5µm Hybrid SPP C18 A and B materials is shown in Figure 1. Considering 1% measurement uncertainty, Material A did not have significant loss of bonded phase up to 136 hours while Material B showed significant loss at 97 hours of testing. The results have demonstrated more stable bonding on Material A. For Material B, we have determined by chemical composition analysis that this material consists of 47.6% core silica, 30.6% shell silica, 18.0% BEH, and 3.8% bonded phase. At the end of 280 hours of testing, there was a total weight loss of 52.0%, 1.2% or less from bonded phase cleavage and the rest from silica dissolution.

Silica Dissolution and Chromatographic Performance:

The total silica loss determined from silica in effluents for Material B over 280 hours of testing was 91mg, and the total weight loss measured from dried column bed was 89mg. Reasonably consistent results were achieved by the two quantification methods. The experimental silica dissolution rates are plotted in Figure 2. The following mathematical models are created by fitting the experimental results:

\[ R_{\text{Si}} = \frac{dW}{dt} = a(1-e^{-bt}) \]

Two dissolution kinetics of amorphous silica in static systems have been reported, linear and exponential dependencies on chemical driving force (under-saturation), respectively, for amorphous phases in salt-free solutions and for crystal-like processes in electrolytes [ref. 1-3]. Although silica could be dissolved like crystals in the high pH buffer, dissolved silica was carried away by mobile phase, and saturation was never reached. Instead of the chemical driving force, accessible silica surface was the rate-limiting parameter. The dissolution rate of nano silica in shell could increase with rapid exponential decay and reached equilibrium (Model I). The dissolution rate of core silica increased exponentially at beginning (Model II). Particles with increased space between core and shell became compressible. Around 166 hours, significant channels formed, and fronting started (refer to Figure 3). From this point, the increase of accessible surface area (and thus silica dissolution rate) slowed down (Model III). As the compression increased, pressure increased gradually.

When the dissolution rate reached the maximum, the majority of cores could be separated from the shell completely (refer to Figure 4). Then, accessible surface area increased as core size decreased and core surface became smooth. Meanwhile, the space between core and shell increased. Around 256hrs, column pressure increased faster. The increase of accessible surface area suggested significant particle breakage [IV]. The splitting of peak indicated the formation of column void.

Comparison of Hybrid Materials:

As shown in Figure 6, Hybrid superficially porous particles are not as stable as Waters fully porous BEH particles that consist of the Hybrid throughout entire spheres. Smaller Hybrid SPP silica cores having larger accessible surface area per unit volume or column dissolved faster, and thus, faster failed. The high pH stability of Hybrid SPP materials also depends on coating technology.

CONCLUSIONS

- Although bonding chemistry can improve the high pH stability of column packing materials, the stability of base particles plays the key role.
- Shell silica and core silica have different dissolution kinetics. The dissolution models have been verified.
- The chromatographic performance of Hybrid SPP in the high pH testing changes with core silica dissolution, or the failure is due to the dissolution of core silica.
- Smaller Hybrid SPP fails faster if accessible core surface area per unit volume is larger for dissolution.
- Hybrid coating technology can impact the Hybrid SPP stability.
- Waters 1.7µm fully porous BEH particles are much more stable than 1.7 and 2.6µm Comp. E materials.

References:


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