Evaluation of Durability of Hybrid Silica with Ethylene Chains

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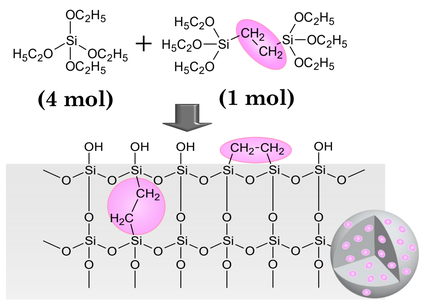
Silica-based reversed-phase columns have been widely used since the 1970s. Silica has the advantage of being mechanically strong and able to withstand high pressures, but conventional silica C18 has limited use under alkaline conditions and is only durable up to pH 8. In the 2000s, hybrid silica with ethylene chains bonded to the inside or surface of silica was developed, and patent applications were filed for these technologies. Currently, these technologies are freely available, and it is expected that these hybrid silica packings will be available on the market.

In this study, we evaluated the durability of so-called hybrid silica with ethylene chains bonded to the inside and surface of silica, and hybrid C18 bonded with C18 and end-capped. The amount of hybrid silica dissolved was measured when an alkaline mobile phase of pH 11.5 was passed through the column, and the hybrid C18 bonded with C18 and end-capped was also evaluated in the same way. The durability of hybrid silica under alkaline conditions greatly differed depending on the method of introducing and bonding ethylene chains to silica, with a difference of 100 to 1000 times the amount of dissolved silica. The difference in stability of hybrid C18 under alkaline conditions was smaller than that of hybrid silica alone, suggesting that the effect of end-capping on durability is greater than that of hybrid silica.

2 types of hybrid silica gel

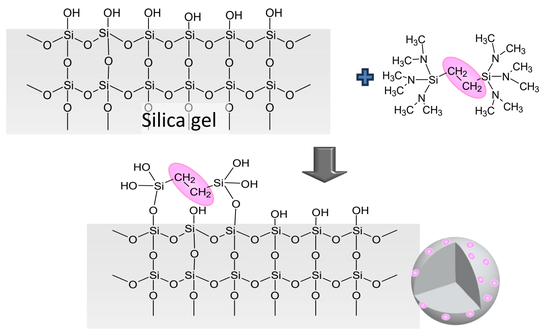
1. Hybrid ①

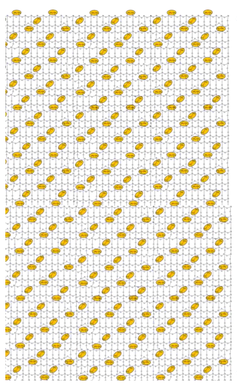
Ethylene cross-linked silica gel



2. Hybrid ②

Ethylene chains bonded to the silica gel surface



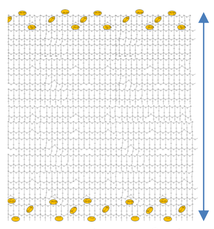


12.5 nm, 125 Å
Thickness of silica skeleton

Hybrid ①
Fully hybrid silica

%C: 7%

(180 m²/g)



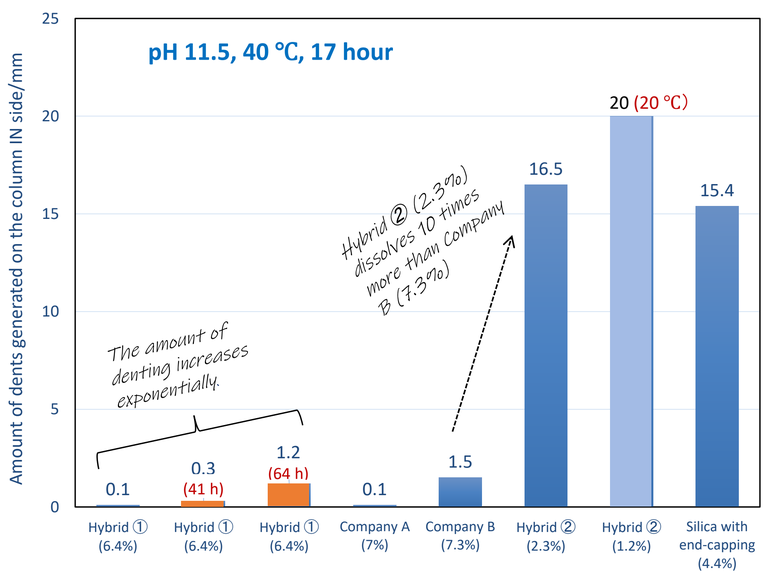
6.6 nm, 66 Å
Thickness of silica skeleton

Hybrid ②
Partially hybrid silica

%C: 2.5%

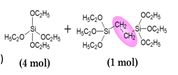
(340 m²/g)

Comparison of durability of hybrid silica gel under alkaline conditions



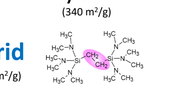
Durability test conditions (pH 11.5)
Column dimension: 100 x 2.1 mm
Mobile phase: 50 mM potassium phosphate pH 11.5
Flow rate: 0.1 mL/min
Temperature: 40 ℃
Elution time: 17 h
(The carbon loading of the ethylene chain is shown in parentheses.)

Hybrid ① (6.4%)
Company A (7%)
} **Full hybrid** (185 m²/g)

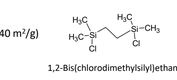


Company B (7.3%) ? Full or partial hybrid

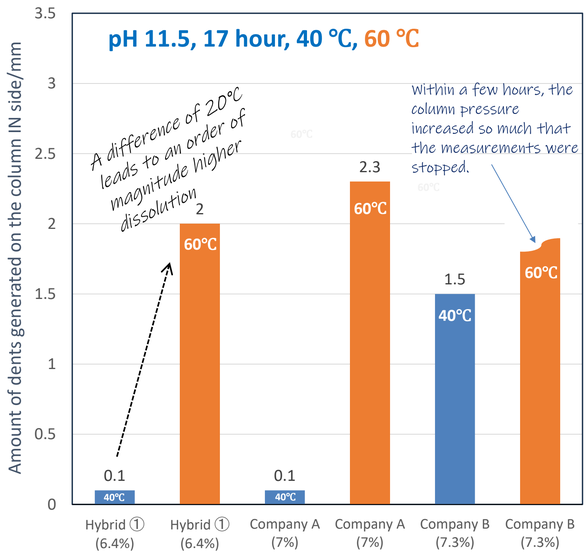
Hybrid ② (2.3%)
Hybrid ② (1.2%)
} **Partial hybrid** (340 m²/g)



Silica with only end-capping (4.4%) **No hybrid** (340 m²/g)



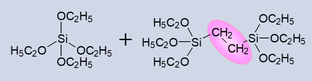
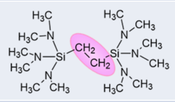
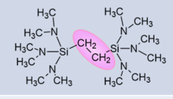
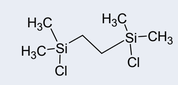
1,2-Bis(chlorodimethylsilyl)ethane



Durability test conditions (pH 11.5)
Column dimension: 100 x 2.1 mm
Mobile phase: 50 mM potassium phosphate pH 11.5
Flow rate: 0.1 mL/min
Temperature: 40 ℃ and 60 ℃
Elution time: 17 h

- When comparing the amount (speed) of silica dissolution when an alkaline mobile phase was passed through hybrid silica, Hybrid ② showed a value 100 to 1000 times higher than Hybrid ①.
- The amount of silica C18 dissolved in an alkaline mobile phase increases exponentially over time, and this was also the case for hybrid silica (Hybrid ①).
- When the temperature difference was 20℃, the amount of silica dissolved was about 10 times different, and a 10℃ temperature increase caused the amount of silica dissolved to increase by about three times.

Hybrid silica gels used in this study

Name	Specific surface area	Pore diameter	Carbon loading	reagent
Hybrid ① (6.4%)	180 m²/g	15 nm	6.4%	
Hybrid ② (2.3%)	340 m²/g	12 nm	2.3%	Silica gel + 
Hybrid ② (1.2%)	340 m²/g	12 nm	1.2%	Silica gel + 
Silica with end-capping (4.4%)	340 m²/g	12 nm	4.4%	Silica gel + 

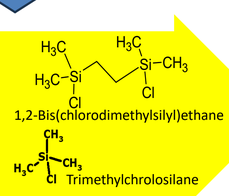
C18 bonding and end-capping

Hybrid silica gel
Hybrid① (6.4%), Hybrid② (1.2%)

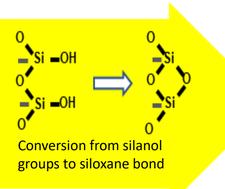
Particle size: 5 μm,

Bonding with Trifunctional C18

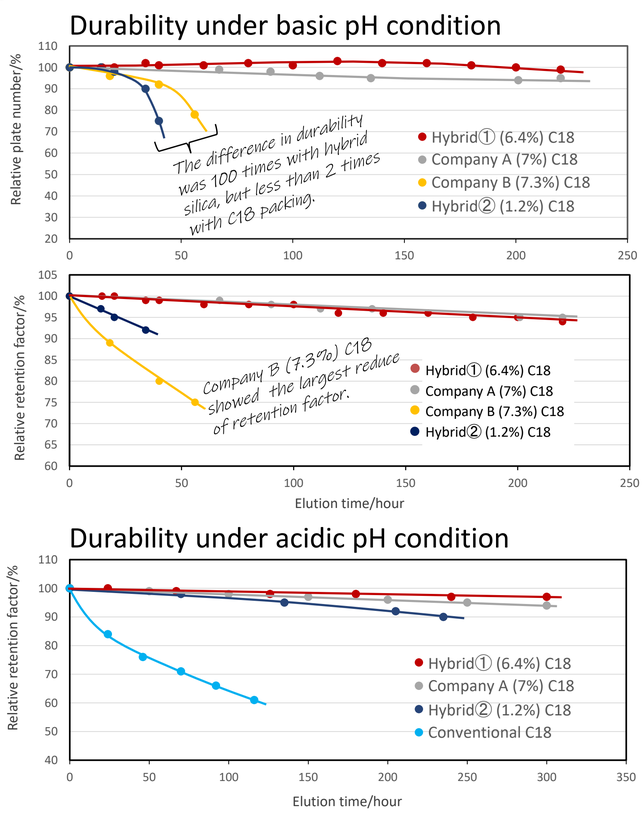
Double end-capping



Elevated temperature end-capping



Durability under acidic and basic pH conditions



Durable test condition
Column size: 150 x 4.6 mm
Mobile phase: Methanol/50mM potassium phosphate pH 11.5=10/90
Flow rate: 1.0 mL/min
Temperature: 40 ℃

Measurement condition
Mobile phase: Acetonitrile/water=70/30
Flow rate: 1.0 mL/min
Temperature: 40 ℃
Sample: 1 = Uracil (t_0), 2 = Butylbenzene

Durable test condition
Column size: 50 x 2.1 mm
Mobile phase: Acetonitrile/1.0% TFA pH 1=10/90
Flow rate: 0.4 mL/min
Temperature: 80 ℃

Measurement condition
Column size: 50 x 2.1 mm
Mobile phase: Acetonitrile/water =60/40
Flow rate: 0.4 mL/min,
Temperature: 40 ℃
Sample: 1 = Uracil (t_0), 2 = Butylbenzene

Conclusions

- ✓ It was confirmed that the durability of hybrid silica under alkaline conditions varies greatly depending on the method of bonding the ethylene chains.
- ✓ It was suggested that the durability of the C18 packing after C18 bonding and end-capping is greatly affected not only by the durability of the hybrid silica, but also by the surface treatment, especially end-capping.
- ✓ C18 using hybrid silica with ethylene chains bonded within the silica skeleton was found to have sufficient durability under mobile phase conditions from pH 1 to pH 12.