



Fabrication of pore window in ordered mesoporous silica by spatial control of functional groups



Man Park^{a,*}, Jun Hyung Kim^a, In-Keun Shim^b, Jin-Ho Choy^c

^a Soil Science Lab., College of Agriculture and Life Science, Kyungpook National University, Daegu 702-701, South Korea

^b School of Chemistry and Molecular Engineering, Seoul National University, Seoul 151-747, South Korea

^c Center for Intelligent NanoBio Materials, Division of Nanoscience and Department of Chemistry, Ewha Womans University, Seoul 120-750, South Korea

HIGHLIGHTS

- Rod-shaped MCM41 crystals are multifunctionalized topographically.
- A functional pore window is fabricated around pore entrance.
- Location of pore window is confirmed by the distribution of window-complexed Pb species.
- The pore window could be bestowed with lock-and-key function.

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ABSTRACT

Great difficulty has been found in controlling the spatial distribution of functional organic groups grafted onto ordered mesoporous silicas even though it plays a decisive role in many applications. Topographical multifunctionalization of rod-shaped MCM41 crystals has been accomplished in this study through selective surface fluorination and subsequent step-wise grafting of organic groups, leading to fabrication of a functional pore window on pore entrance surface. Distinctive fabrication of functional organic window around pore entrance was visualized by the distribution of window-complexed Pb cations in a narrow band within a distance of about 10–60 nm from both vertical crystal edges, pore entrances. Its unique function was clearly illustrated by interfacial property of the MCM41 crystals with both a guest molecule and a substrate surface. In particular, its lock-and-key function was successfully demonstrated by pH-dependent locking and unlocking of pore opening. Therefore, this study would contribute substantially to selective and precise manipulation of surface functionality in ordered mesoporous silica materials for tailor-making of diverse delivery vectors and nanoreactors.

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1. Introduction

Frameworks and surfaces of ordered mesoporous materials have been modified with a variety of functional components for both enhancement and exploration of activity, selectivity, and stability [1–6]. In particular, a great deal of effort has been made to functionalize ordered mesoporous silica materials (OMS) with various organic functional groups because hybridization of OMS with organic groups could offer remarkable new properties and multifunctional nature [5–10]. It is also known that organic groups could be tailored topographically as well as multiply [11–16]. However, great difficulty has been found in controlling their spatial

distribution on OMS crystals even though it plays a decisive role in many applications.

Typical rod-shaped OMS crystals have three distinctive surfaces: external, internal, and pore entrance surfaces. Several attempts have been made to modify these surfaces separately, including step-wise functionalization [11], modification of pore opening through chemical vapor deposition of silica precursors [12], selective modification of the internal surface versus the whole surface [13], coumarin-modified MCM-41 [14] and spiropyran-modified one [15] for photo chemically controlled drug delivery system, pH-responsive carrier system based on carboxylic acid modified SBA-15 [16] and polyamine modified MCM-41 [17,18], and site-selective functionalization with sequential co-condensation approach [19]. Unfortunately, nearly all of them are confined to differentiation between external and internal surfaces although pore entrance surface governs the interaction with guest molecules. In

* Corresponding author. Fax: +82 53 953 7233.

E-mail address: manpark@knu.ac.kr (M. Park).

fact, none of them are satisfactory in elaborately controlling the spatial distribution of functional groups on pore entrance surface. Its selective functionalization would lead to fabrication of the pore window which regulates passage of guest molecules, interaction between pores and substrate materials, and even sequential multifunctionalization of internal surfaces.

Spatial manipulation of organic groups on rod-shaped OMS crystals has been attempted in this study through controlling reactivity of surface silanol groups (Fig. 1). Post-grafting of organic groups, a typical route of selective modification, depends exclusively on the exposed silanol groups of OMS crystals. In general, as-synthesized rod-shaped crystals expose only the silanol group of external surface because the silanol group of internal surface are tightly covered by packed templates. Simple fluorination of the as-synthesized crystals can lead to selective deactivation of the silanol groups of external surface [20–22]. Both the fluorinated external surface and most of the template-packed internal surface could hardly participate in subsequent grafting reaction. And subsequent grafting would result in localized attachment of organic groups only on pore entrance surface because the templates packed in the pores could be removed gradually from pore entrance to pore inside in a controlled rate [22]. Thus, the organic group selectively grafted on pore entrance surface act as a functional pore window. The silanol groups of internal surface still remain intact to be further functionalized. This study has successfully demonstrated the distinctive topographical multifunctionalization which leads to fabrication of a functional pore window in rod-shaped OMS crystals. Its precise location and unique function

are also clearly illustrated by interfacial property of the OMS crystals with both a guest molecule and a substrate surface.

2. Experimental

2.1. Synthesis of rod-shaped MCM41

Sodium hydroxide (0.25 g) and hexadecyltrimethylammonium bromide (0.825 g) were dissolved in 200 ml of distilled water, and then 4 ml of tetraethoxyortosilicate was added with vigorous stirring [23]. After the mixture was further stirred for 1 h, it was aged at 90 °C for 3 days. The resulting solid was filtered, washed, and dried at 100 °C for 1 day.

2.2. Spatial control of grafting

One gram of as-synthesized MCM41 crystals was suspended in 0.1 M NaF solution (100 ml) and stirred at 80 °C for 2 h to fluorinate external surface [21,22]. The reaction product was washed with deionized water, dried under an ambient atmosphere, and finally dehydrated at 120 °C for 6 h under N₂ environment. The resulting surface-fluorinated MCM41 was kept in a sealed bottle. A pore window on pore entrance surface was constructed by suspending the surface-fluorinated MCM41 in a solution of either 3-(2-aminoethylamino) propyltrimethoxysilane or aminopropyltrimethoxysilane in ethanol (0.9 μmole/10 ml ethanol) and refluxing the mixture for 3 h. The resulting white solid was washed with absolute ethanol, and refluxed in a solution of 50 ml absolute

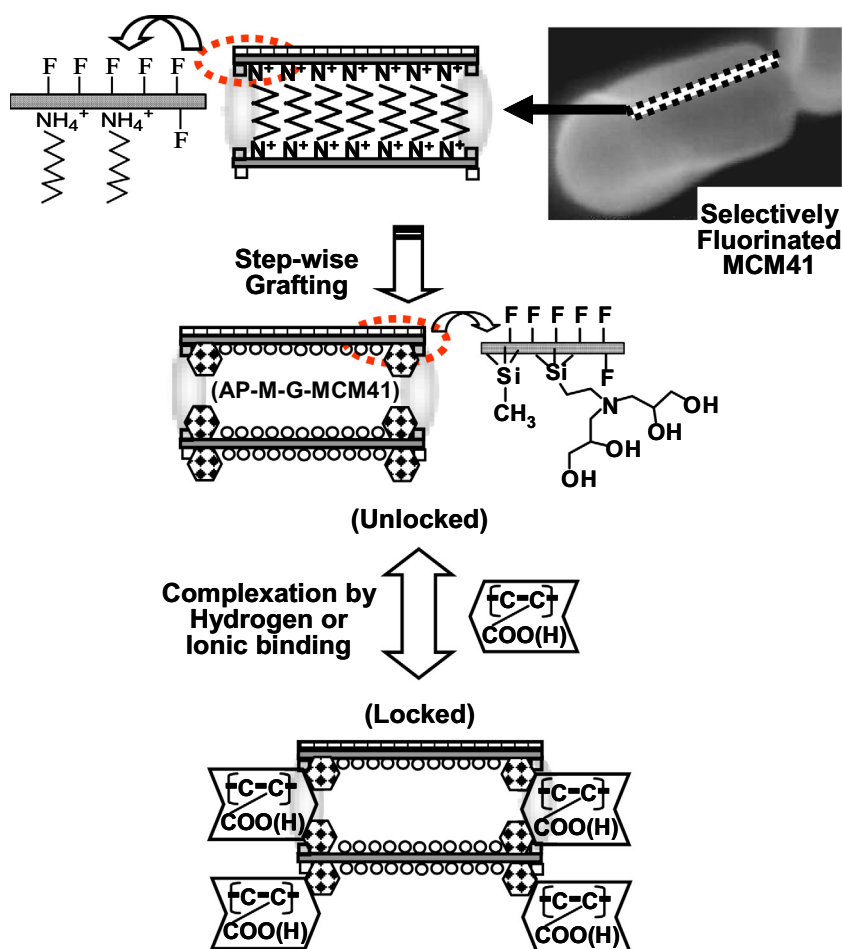


Fig. 1. Illustration of selective spatial control on organic functionalization.

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