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# Tetramethoxysilane as a convenient silicon source for phase control of cubic SBA-1 mesostructures

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## Abstract

The critical role of silica precursors in the synthesis of the cubic SBA-1 mesophase under strongly acidic conditions at different synthesis temperatures has been investigated. The undesirable phase selection in the synthesis of SBA-1 that occurred at high temperatures can be prevented when the conventional silica source tetraethoxysilane (TEOS) is replaced by tetramethoxysilane (TMOS). The presence of higher concentration of methanol due to the faster hydrolysis rate of TMOS, which effectively serves as cosolvent to maintain the high surface curvature of surfactant micelles, is a key factor for preservation of the cubic SBA-1 mesostructure at synthesis temperature higher than 313 K.

*Keywords:* Mesoporous SBA-1; Silica precursors; Tetramethoxysilane; Phase selection

## 1. Introduction

The discovery of the M41S family of mesoporous materials has stimulated the studies of cooperative assembly of inorganic cluster ions and surfactant species in liquid crystal-like structures due to their potential use as prospective catalysts, adsorbents, and templates for the synthesis of nanostructures [1]. Among the various mesoporous materials, the cubic SBA-1 mesostructure (*Pm3n*) is very unique and interesting because of its cage-type pore structure with open windows [2,3]. The conventional synthesis of SBA-1 is based on the $S^+X^-I^+$ pathway, where $S^+$ denotes the cationic surfactant, $X^-$ the acid anion, and $I^+$ the inorganic (silica) species, under strongly acidic conditions and at low synthesis temperatures, e.g., at 273 K, using cetyltriethylammonium bromide (CTEABr) and tetraethoxysilane (TEOS) as the surfactant and the silica source, respectively. The use of the large headgroup surfactant CTEABr to ensure a small value of surfactant packing parameter ($g < 1/3$) is essential for the preferential formation of the cubic SBA-1 mesophase. However, the synthesis temperature employed is a crucial factor for determining the final form of the mesophase. Kim and Ryoo [4] have optimized the synthesis procedures for the formation of the cubic SBA-1 mesostructure. According to their studies, a cubic SBA-1 mesophase was favored at a low temperature of 273 K, while a phase selection of the mesophase from cubic SBA-1 to hexagonal SBA-3 occurred at temperatures higher than 313 K. The low-temperature synthesis condition leads to a very low cross-linking degree of the silica framework, which make the as-synthesized SBA-1 unstable towards washing with water [4,5]. Therefore, there is a need to raise the synthesis temperature for SBA-1 in order to enhance the stability of SBA-1. We have recently demonstrated that the use of additives such as D-fructose allows a successful synthesis of stable SBA-1 at synthesis temperatures higher than 313 K without any undesirable phase selection [6]. In the absence of any additives, however, precise control of the phase behavior in the synthesis of SBA-1 at high synthesis temperatures (e.g., above 293 K) is still difficult because of the fast kinetics of the silica condensation in the strongly acidic media employed.

Besides temperature, the small amounts of ethanol, formed by the hydrolysis reaction of TEOS, has been pointed out as an

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important driving force for the phase change of MCM-type mesoporous materials to occur in basic media [7]. Recently, the roles of alcohol as both cosolvent and cosurfactant in mesoporous silica synthesis have been suggested and discussed [8–17]. Since the structure of SBA-1 corresponds to the micellar structure with a high surface curvature, any additives as cosurfactant or cosolvent, accompanied by temperature change, may easily affect the final form of the mesophase. Therefore, it is of great importance to have control of the phase behavior in the formation of SBA-1 in order to facilitate its widespread applications. Herein we report that the formation of well-ordered SBA-1 at high synthesis temperatures can be simply achieved when the conventional silica source TEOS is replaced by tetramethoxysilane (TMOS). In the present work, the hydrolysis and condensation behaviors of the silica precursors were identified to play a critical role in the self-assembly of surfactant–silica composites for the final form of the mesostructure.

## 2. Experimental

### 2.1. Materials synthesis

In a typical synthesis, the silica source, namely TEOS or TMOS (both from Aldrich), and HCl were first mixed with distilled water at room temperature to obtain a homogeneous solution. The surfactant CTEABr, synthesized according to a previous published procedure [2,3], was then added into the solution. The reaction was then conducted at a pre-determined synthesis temperature in the range 273–363 K under vigorous stirring for 4 h. Thereafter, the reaction mixture was subjected to short hydrothermal treatment at 373 K for 1 h, as suggested by Vinu et al. [5]. The precipitate was filtered (without washing) and dried at 343 K overnight. The molar composition of the reaction mixture was 1 CTEABr : 5 Si : 230 HCl : 3500 $H_2O$. TMOS and TEOS were used as the silica sources, respectively, and the corresponding materials obtained were denoted as

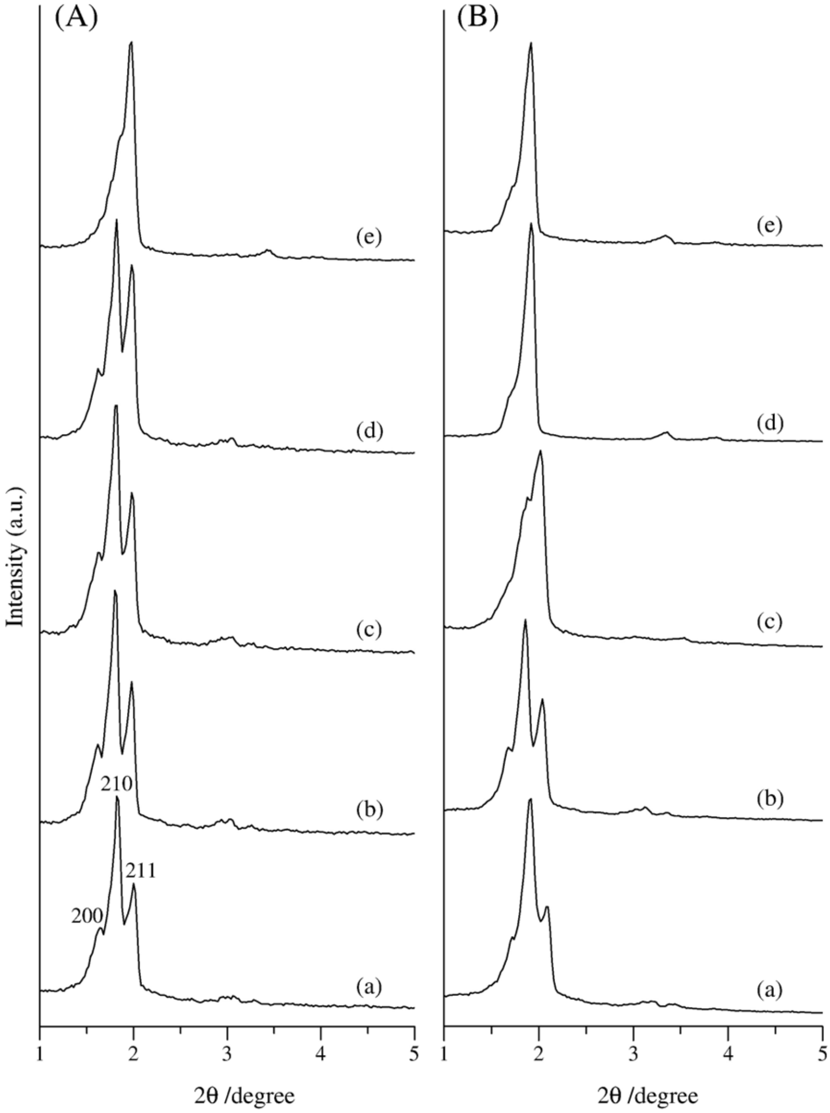

Fig. 1. Powder XRD patterns of as-synthesized (A) M-SBA-T and (B) E-SBA-T samples, synthesized at different temperatures, $T$ = (a) 273, (b) 293, (c) 323, (d) 343, and (e) 363 K.