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# Microwave assisted growth of SAPO-34 on β-SiC foams for methanol dehydration to dimethyl ether

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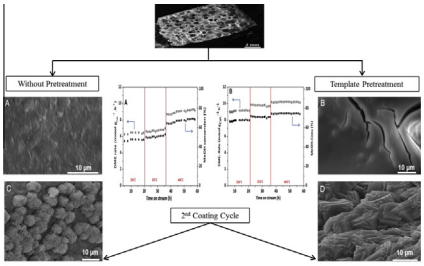
## HIGHLIGHTS

- Microwave-assisted synthesis was applied to control the growth of SAPO-34 on SiC.
- Multi coating steps were required to obtain full coverage of SAPO-34 crystals.
- Full coverage of SAPO-34 on SiC foams was obtained after 2 times of coatings.
- Template pretreatments of SiC foams improved the loading of SAPO-34 crystals.
- The SAPO-34/SiC foam showed enhanced activity and stability in methanol dehydration.

## GRAPHICAL ABSTRACT




SAPO-34/SiC catalyst

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## ABSTRACT

SAPO-34 layers were successfully grown on β-SiC foam with medium specific surface-area, using microwave-assisted hydrothermal synthesis method (MAHyS) for applications as a structured catalyst. Preliminary investigations on SAPO-34 phase purity were conducted to select the appropriate concentrations and protocol to grow pure SAPO-34 on SiC foams. SAPO-34/SiC foam composite was obtained via microwave-assisted synthesis route. X-ray diffraction (XRD) was used to confirm the formation of the composite. Microwave irradiation time, number of coating cycles and pretreatment of the SiC support with zeolite precursor and the template solution were studied to optimize the growth and coverage of SAPO-34 crystals on the SiC foam surface. SAPO-34 crystals with cubic morphologies having 7 μm average size were obtained after 6 h microwave irradiation at 180 °C. However, multi coating steps were required to obtain full coverage of SAPO-34 crystals. Template pretreatments of the host material (SiC foams) significantly improved the loading of crystals on the support surface. Full coverage of SAPO-34 on SiC foams was obtained after 3 times of coatings, which is mostly attributed to the template layer formed on the foam surface that induced the heterogeneous nucleation on the support. The SAPO-34/SiC foam structured catalyst exhibited excellent selectivity and stability in methanol dehydration to dimethyl ether, which was carried out in a fixed bed reactor.



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## 1. Introduction

Zeolites are known for their high catalytic activities which enabled them to be widely used in different chemical reactions. In the large scale industrial applications, zeolites are packed in fixed bed reactors in a form of extruded pellets or powdered microgranules. This design suffers from the mass and heat transfer limitations, high-pressure drop of the reactant stream passing through the bed and fouling caused by impurities. Furthermore, zeolites are mostly synthesized in a powder form which further calls for filtration for their separation from the synthesis medium. For industrial applications the zeolite powder was further mixed with inorganic binders prior to the extrusion process. The presence of inorganic binders is very likely to reduce the catalyst efficiency by blocking the access to the active sites and also to increase the diffusion problems. It is of interest to develop new synthesis methods allowing the production of zeolites with controlled macroscopic shape for subsequent catalytic applications.

Recently, the application of structured catalysts is gaining more attention, with numerous zeolite/substrate composite materials developed, for a wide range of applications. Structured catalysts are a promising alternative to fixed bed catalytic reactors providing several considerable aspects: enhanced hydrodynamic, better heat and mass transfer and easy access to the catalyst active centres. Zeolites have been successfully grown on different host materials including stainless-steel [1,2], honeycombs [3,4], glass [5] and ceramic foams [6–8]. Silicon carbide, synthesized by a gas–solid reaction [9–11], has been reported to be a suitable ceramic support for different catalytic processes [11–13]. The SiC possesses several advantages such as good intrinsic thermal conductivity, medium to high surface area (10–100 $m^2/g$), large pores, controlled macroscopic shape, and chemical inertness. The high chemical inertness of the SiC allows it to be efficiently employed in the structured zeolite synthesis without facing problems of chemical dissolution during the course of the hydrothermal synthesis. SiC foams are promising substrates for zeolite growth, and have been intensively studied for their chemical stability, mechanical strength and high thermal conductivity [14]. Coating of different zeolites such as ZSM-5 [15,16], Beta zeolite [17] and silicalite [18]) on SiC foams has been reported and has shown superior performances in certain reactions [17,19]. The advantages of using SiC foam structure are the following: (i) high external surface area which significantly improve the external mass transfer rates, (ii) high porous structure which leads to an extremely low pressure drop even at high gaseous space velocity, and (iii) the foam structure plays a role of static mixer allowing the good mixing of the gaseous or liquid reactant through the foam. The detailed characterization of the pressure drop through the foam structure can be found in Ref. [20].

Different methods have been developed for the fabrication of zeolite layers on solid surfaces including dip-coating [21,22], slurry-coating [23–25] and direct in-situ synthesis on supports [7,26–30]. The direct in situ growth on the support has an advantage over the dip and slurry coating because it yields in a full coverage of oriented crystals with strong adherence to the support surface which prevent subsequence active phase loss during the reaction.

SAPO-34 is a small pore size catalyst with a CHA framework recognized for the selective conversion of methanol to gasoline, olefin or dimethyl ether depending on the operating conditions. SAPO-34 crystals were already grown onto various supports as membranes for gas separation applications [31] and for heat pumping applications [32]. Rapid growth of SAPO-34 on α-alumina discs as membranes, using microwave irradiation technique was reported by Chew et al. [33]. Pop et al. [34] reported the use of SAPO-34 for methanol dehydration to dimethyl ether resulted in high activity.

Herein, we report the in situ growth of SAPO-34 on SiC foam supports using microwave irradiation method and the application of the resulting composite as structured catalyst for methanol dehydration to dimethyl ether. The novel SAPO-34/SiC composite is expected to provide a superior performance to the powdered form zeolite, by rendering easier access to the active sites and benefit from the open structure of SiC foams to significantly enhance the mass and heat transfer and reduce the pressure drop.

Prior to the growth of SAPO-34 on SiC foams, thorough investigation was conducted to identify the concentrations where pure SAPO-34 is obtained. Both microwave synthesis and conventional hydrothermal synthesis methods were utilized. Effect of template concentration, Si/Al ratio and water concentrations were studied. The influence of the synthesis duration and pre-treatment of the support with either the zeolite precursor slurry or the TEAOH template was also investigated. The catalysts were evaluated in the fixed-bed dehydration of methanol to dimethylether (DME) and the catalytic results were discussed at different temperatures for both the slurry pretreatment and template pretreatment methods. Also the catalytic activity and selectivity were compared for the powder SAPO-34 and the SAPO-34/SiC composite catalysts.

## 2. Experimental

### 2.1. Catalyst synthesis

A precursor solution was prepared by mixing phosphoric acid (85 wt.%) with deionized water and tetra ethyl ammonium hydroxide solution (TEAOH, 25 wt.% in water, Acros Organics) with continuous stirring for 30 min followed by drop-wise addition of colloidal silica (40 wt.% $SiO_2$ and 0.5 wt.% $Na_2O$, Snowtex-40, ST-40). To the above solution, aluminum isopropoxide (98 wt.% $Al(OC_3H_7)_3$) was added slowly and the solution was further stirred for 2 h. Hydrochloric acid (HCl, 37 wt.%) was used to maintain the acidity around the neutral range (6–8). The molar ratios of the resulting solution are presented in Table 1, where different parameters were varied for both hydrothermal and microwave syntheses.

Regarding the hydrothermal synthesis, the mixture was placed in a PTFE lined stainless steel autoclave and heated in a static oven at 200 °C for 24 h. The solid product was washed with distilled water, dried at 100 °C and subsequently calcined at 550 °C for 5 h under static air atmosphere in a tubular furnace to remove the organic template from the catalyst framework. In a typical microwave synthesis, 35 g of the precursor solution was transferred in a transparent PTFE autoclave (about 50 ml) and irradiated in a single autoclave microwave reactor (MicroSYNTH, Milestone, 800 W).

**Table 1**
Different concentrations for the synthesis of SAPO-34. *Note:* HY: hydrothermal synthesis, MW: microwaves assisted synthesis.

| Heating method | Parameter | $SiO_2$ | $Al_2O_3$ | $P_2O_5$ | TEAOH | $H_2O$ | HCl |
|---|---|---|---|---|---|---|---|
| HY, MW | $SiO_2/Al_2O_3$ | **0.2** | 1.0 | 1.0 | 2 | 110 | 0.7 |
| | | **0.4** | 1.0 | 1.0 | 2 | 110 | 0.7 |
| | | **0.6** | 1.0 | 1.0 | 2 | 110 | 0.7 |
| | | **0.8** | 1.0 | 1.0 | 2 | 110 | 0.7 |
| HY | TEAOH/ $Al_2O_3$ | 0.6 | 1.0 | 1.0 | **0.5** | 110 | 0.7 |
| | | 0.6 | 1.0 | 1.0 | **1.0** | 110 | 0.7 |
| | | 0.6 | 1.0 | 1.0 | **1.5** | 110 | 0.7 |
| | | 0.6 | 1.0 | 1.0 | **2.0** | 110 | 0.7 |
| HY | $H_2O/Al_2O_3$ | 0.6 | 1.0 | 1.0 | 2.0 | **70** | 0.7 |
| | | 0.6 | 1.0 | 1.0 | 2.0 | **90** | 0.7 |
| | | 0.6 | 1.0 | 1.0 | 2.0 | **110** | 0.7 |
| | | 0.6 | 1.0 | 1.0 | 2.0 | **130** | 0.7 |