

Synthesis of SAPO-34 catalysts *via* controlled crystal growth

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Introduction

SAPO-34 is a silicoaluminophosphate zeolite with 8-membered ring windows (~0.38nm) displaying chabazite structure. SAPO-34 is an efficient catalyst showing improved catalytic performance in reactions such as methanol conversion to olefins [1], oxidative dehydrogenation of propane [2], conversion of light alkenes [3]. Its catalytic properties are mainly attributed to its mild acidity [4], high thermal stability [5] and excellent shape selectivity [3]. In addition, due to its unique cage size and shape, SAPO-34 has been found to be suitable for *selective* formation of linear hydrocarbons by restricting the formation and diffusion of branched hydrocarbons [1]. Herein we report the successful synthesis of high surface area and small crystal size SAPO-34 with improved surface properties using crystal growth inhibitors.

Materials and Methods

Aluminum isopropoxide, phosphoric acid, and Ludox were used as the inorganic precursors. Tetraethylammonium hydroxide and dipropylamine were used as the primary and secondary templates. Polyethylene glycol, Brij-35 and methylene blue were employed as crystal growth inhibitors (CGI). In a typical synthesis, the inorganic precursors and H₂O were mixed and stirred for ~2hr. The templates and CGI were then added to the precursors in regular intervals. The final gel composition was 1Al₂O₃:1H₃PO₄:0.3SiO₂:1TEAOH:1.6DPA:77H₂O: xCGI, where 0.037 < x < 0.2. The gel was transferred to a teflon lined stainless steel autoclave after aging for 3 days and heated in conventional oven at 220°C for 24 hr. After the gel was cooled, it was centrifuged to separate the seeds from the gel and dried overnight at 60°C. The samples were calcined at 550°C for 5hrs to remove both the templates and CGI. The resultant SAPO-34 crystals were characterized using XRD, FTIR, SEM, BET, CHN analysis.

Results and Discussion

The formation of SAPO-34 nanocrystals requires conditions that favor nucleation over crystal growth in the initial stages of the process. CGI not only changes the alkalinity of the gel but also interact with reactive sites of the inorganic precursors in solution, shortening the nucleation period and thereby resulting in a larger number of smaller nuclei as shown in Figure 1. At this stage, CGI prevents the aggregation of these nuclei by adsorbing onto its surface and inhibits the growth of the crystals by separating the nuclei from the remained precursors. Then, the adsorbed CGI decomposed at high temperature in later stages of hydrothermal treatment. Therefore, a larger population of small nuclei after the induction period explains the formation of small crystals [6]. By using CGI, the surface area increased up to 40% as shown in Figure 2, which is attributed to smaller crystal size and incorporation of extra microporosity in the zeolite framework. Crystal size was also decreased significantly from ~1500nm to ~600nm as shown in Figure 3. The formation of typical chabazite structure

of SAPO-34 was confirmed by XRD (Figure 3d) and FTIR (not shown). It is also notable that SAPO-34 structure and crystallinity were not affected by employing the CGI because these cannot penetrate into the pores SAPO-34 due to their larger size. It is important to mention here from CHN analysis that more nitrogen is incorporated into the framework of SAPO-34, which not only changes the strength of acidity to favor the desired reaction rates but also increases the thermal stability. Catalytic performance studies of the synthesized SAPO-34 will be carried out for the selective oxidation of lower alkanes.

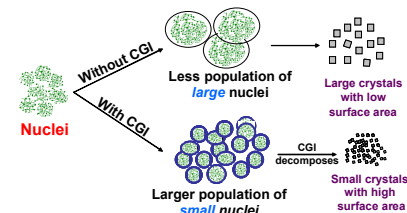


Figure 1: Synthesis route of SAPO-34 crystals using CGI

Significance

Due to its high surface area (up to 700m²/g), small crystal size (~600nm) with narrow particle size distribution, the synthesized SAPO-34 crystals represent attractive catalytic systems for selective alkane oxidation. It is anticipated that the reduction in crystal size and unique textural and structural properties of the synthesized SAPO-34 crystals will positively impact its catalytic properties.

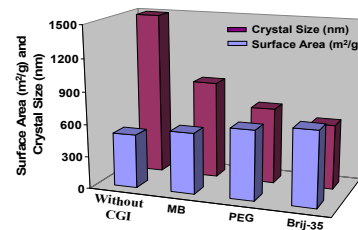


Figure 2. BET surface area and crystal size of the SAPO-34 crystals with and without CGI

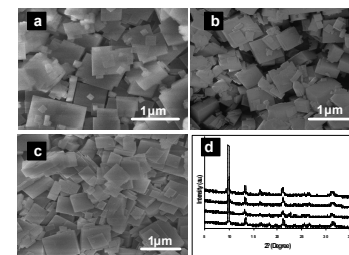


Figure 3. SEM images of the SAPO-34 crystals synthesized using a) PEG b) Brij-35 and c) MB as CGI; d) XRD of SAPO-34 synthesized with and without CGI [6]

References

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