Synergy between structure direction and alkalinity toward fast crystallization, controlled morphology and high phase purity of ZSM-12 zeolite

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ABSTRACT

Aiming for a control of the morphology and phase purity of the final product, two commercially available organic templates, supplying tetraethylammonium (TEA^+) and methyltriethylammonium ($MTEA^+$) cations in the synthesis mixture, were used for the hydrothermal synthesis of ZSM-12 zeolite. As key factors, alkalinity and water content of the synthesis mixture and silicon and aluminum source types were comprehensively studied using these two organic templates. All the products obtained were characterized by powder XRD, SEM, N_2 physisorption, ^{29}Si and ^{27}Al-MAS solid state NMR and TGA techniques. Using TEAOH organic template and organic Si and Al sources along with the proper adjustment of water and sodium hydroxide contents in synthesis mixture, mono-sized polycrystalline particles of ZSM-12 with high crystallinity and purity were synthesized. Alleviating TEAOH drawbacks, $MTEA^+$ organo-cation in the hydroxide form was used which led to the formation of mono-sized ZSM-12 single crystals. When using MTEAOH organic template, hydroxide ion and Na^+ contents and the type of Al source were found to be playing major roles toward nucleation and growth of ZSM-12 crystals. Owing to increased alkalinity of the synthesis mixture, MTEAOH also promoted faster crystallization over a wide-range of Si/Al ratio (30 to ~infinity). The discrete mono-dispersed synthesized crystals possessed a well-defined cubic morphology with no impurities.

1. Introduction

The growing demands for zeolites as one of the best available porous catalysts and adsorbents [1] have encouraged many researchers to either introduce new types of zeolitic material or innovate and optimize the synthesis conditions of the existing frameworks [2,3]. To date, more than 200 frameworks are known [4,5] among which some, such as ZSM-12, have recently attracted more attention due to their exceptional pore topologies. ZS**M-TW**elve (MTW) is a high-silica zeolite (Si/Al >10) which was first invented by Mobil Research and Development scientists, Rosinski

and Rubin in 1974 [6]. Later on, using more sophisticated techniques, the structural characteristics of ZSM-12 were discovered [7,8]. In general, ZSM-12 framework owns a mono-dimensional non-interpenetrated pore structure with well-defined 12-membered ring channels run in the [0 1 0] direction. The framework topology has monoclinic symmetry (C2/m) with unit cell parameters of a = 2.4863 nm, b = 0.5012 nm, c = 2.4328 nm, and β = 107.7° [9]. The elliptic ring opening has free diameters of ~5.6 × 6 Å, which is very narrow for a zeolite with 12-membered ring, for instance FAU-type aperture is almost 7.5 Å wide [10]. This exceptional pore size is more comparable to that of 10-membered ring zeolites, such as MFI and TON zeolites, which are extensively used in chemical industries. Searching alternatives for 10-membered ring catalysts with higher catalytic performances, ZSM-12, as a most interesting candidate, presents surface properties similar to those zeolites with medium-size pores along with many other features. First, the slightly larger pore size allows ZSM-12 to accommodate bulky intermediate species, enhancing catalytic

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efficacy in some applications, as discussed by Wang et al. [11] in a publication entitled "0.3 Å makes the difference". Second, single file diffusion within the 1D straight channels of ZSM-12 provides trapping ability of small molecules between strongly adsorbed large molecules. This appealing property was exploited to capture small un-burned hydrocarbons along with larger ones from automotive exhaust during cold-start period [12]. Finally, non-interconnecting linear channels of ZSM-12 hinder catalyst deactivation by carbonaceous deposits, providing superior catalytic stability in a variety of hydrocarbon conversion reactions [13–16]. Regarding all these beneficial properties, ZSM-12 is becoming the focus of numerous catalytic studies searching for an optimized shape-selective catalyst, especially for reactions occurring in petroleum refining such as isomerization, alkylation, hydroisomerization, hydrocracking and oligomerization [15–28].

The great performance of ZSM-12, provided by its intricate channel system, can be further improved by optimizing other characteristics of the zeolite, besides its textural properties, including framework acidity, phase-purity and crystal size and morphology. Especially, crystal size and morphology are of great importance in controlling selectivity and deactivation of a zeolite catalyst [29,30]. It was demonstrated for many zeolite catalysts other than ZSM-12 that larger crystals suffer from faster deactivation [28,31–33]. Furthermore, zeolites with 1D channel system, including ZSM-12, have a high crystal aspect ratio (length-to-width ratio) which creates mass transfer issues inside their long micropores. Therefore, controlling the size and morphology of ZSM-12 crystals promises improved catalytic performances [28]. The pivotal role of ZSM-12 size and morphology was recently demonstrated for the hydroisomerization of n-hexadecane [29]. This study showed that the ZSM-12 microcrystals with small dimensions exhibited higher isomer yield and selectivity towards monobranched products. Moreover, considering the importance of nanozeolite in catalysis and separation [34], further size reduction of ZSM-12 is believed to immensely enhance their performance. Despite numerous reported works on ZSM-12 synthesis [35–38], there are still no routes toward synthesizing nano-ZSM-12 particles from organic template-containing or template-free gels.

Morphological modification of a zeolite can be achieved by either modifying the classical solvothermal synthesis routes upon varying synthesis parameters, such as aging of the gel, introducing new organic templates, sources of silicon and aluminum, adjusting the synthesis temperature and composition of the starting gel [39,34] or post-treatment [40,41]. Looking for new methods, crystal-growth modifiers [42–45] and microemulsion techniques [46,47] are also proposed to control the size and morphology of a crystalline zeolite. These chemicals can be solvents, surfactants or polymers [48–51]. In contrast to other types of zeolites, controlling the size and morphology of ZSM-12 crystals has rarely been studied. For instance, the crystal growth behavior of ZSM-12 was recently investigated using various co-solvents and growth-modifier chemicals (e.g., PEG, Brij 35) [52,53]. Although these studies could successfully introduce a broader synthesis window for faster ZSM-12 crystallization, the size and morphology of the products did not show considerable improvements, compared to original synthesis using TEA+ organocation and all led to the formation of large aggregates of intergrown nanocrystals. Moreover, micro-emulsion technique might not be extended to the ZSM-12 synthesis conditions due to emulsion thermal stability issue at the high temperature used in hydrothermal synthesis of ZSM-12 [47,54]. Therefore, modifying the classical hydrothermal synthesis routes upon varying the synthesis parameters with no extra-additives would be much more appealing technique to control the ZSM-12 morphology. This technique was implemented for widely used zeolites, especially silicalite-1, leading to a full knowledge of its crystallization mechanism [55–57]. Unfortunately, the proposed size reduction methodology used for silicalite-1 zeolite, for instance, by using TEOS/organic template/water clear gel cannot be generalized and extended for other high silica zeolites, specifically ZSM-12 (TEOS: tetraethyl orthosilicate). Using six different organic templates, Cheng et al. [58] showed that such a synthesis mixture does not produce ZSM-12, not only at low temperatures (<100 °C) but also, at the conventional synthesis temperature, i.e. 160 °C.

High-silica zeolites such as ZSM-12 are mainly synthesized through hydrothermal treatment of an as-prepared gel. Using this classical technique, ZSM-12 microcrystals with different morphologies such as cubic, spherical, hexagonal, needle, rice-shaped crystals were reported [9,35,37,38,59,60]. This diversity is mainly attributed to the types of organic molecular templates used for the synthesis [61] which act as either structure-directing or pore-filling agents. Although organic template-free seed-assisted synthesis, proposed by Okubo and coworkers, has successfully produced ZSM-12 microcrystals with rod-like morphology, the final product suffered from pore blocking, aggregation and intergrowth and wide particle size distribution [36,62]. Moreover, it is not possible to synthesize pure silica zeolite using inorganic structure-directing agents [34]. All these show the pivotal role played by organic templates in ZSM-12 hydrothermal synthesis affecting the crystallization products in terms of crystalline phase, size and morphology [56,63,64].

In literature, there are many reports on the synthesis of ZSM-12 zeolites using various organic templates, starting with the work of Rosinski and Rubin who synthesized ZSM-12 zeolite using either a mixture of diethylsulphate and triethylamine or tetraethylammonium ions (hydroxide and bromide forms), all resulted in pure crystalline ZSM-12 [6]. Later on, several quaternary ammonium molecules, in the forms of hydroxides or halides of simple alkylammonium [29,35,37,38,65–67] and complex molecules such as cyclic and polycyclic N-heterocycles [68–77] were utilized. Because of the commercial availability and lower cost, simple quaternary ammonium molecules, i.e. MTEA+ and TEA+ cations, have extensively been used for ZSM-12 synthesis. Using methyltriethylammonium bromide (MTEABr) and tetraethylammonium hydroxide (TEAOH), ZSM-12 crystallization had thoroughly studied by Ernst et al. [37] and Gopal et al. [38], respectively. Initially, MTEABr was introduced as the best candidate, allowing faster crystallization at higher Si contents along with reaching lower Si/Al ratios (22.5 to infinity) while TEA+-based templates (at Si/Al < 60) was leading to some impurities such as ZSM-5 [37]. Reducing the cost of organic templates, two other forms of these organocations, i.e. MTEACl [66] and TEABr [35], were also proposed. Using one of these simple organic templates, the morphology of the final ZSM-12 product was also shown to be affected. For instance, ZSM-12 with an elongated cuboidal geometry (rice shaped) of crystallites with average length of 5 μm and a diameter of 1.5 μm were obtained using MTEABr [37,61] whereas cuboidal geometry of crystallites of size smaller than 2 μm was produced using TEABr organic template [35,61]. Such crystallization behavior was found to be highly reproducible by other researchers, even with slight changes [29].

Although zeolites such as ZSM-12 are highly selective to the type of organic templates being used, synthesis conditions are also playing a delicate role, i.e. one organic template, dedicated to ZSM-12 synthesis, may result in zeolites with different structures upon alternating the synthesis conditions. In addition to crystal phase, there is a strong correlation between the size and morphology of a specific zeolite and chemical sources and alkalinity of a synthesis mixture which can be controlled by organic template, water content and the base [37,78].