Journal of Catalysis 308 (2013) 142–153

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Tailoring zeolite morphology by Charge Density Mismatch for aromatics processing

Robert W. Broach, Edwin P. Boldingh, Deng-Yang Jan *, Gregory J. Lewis, Jaime G. Moscoso, Jeffery C. Bricker

UOP LLC, a Honeywell Company, 25 East Algonquin Road, Des Plaines, IL 60017, USA

ARTICLE INFO

Article history:
Received 12 March 2013
Revised 23 May 2013
Accepted 30 May 2013
Available online 20 July 2013

Keywords:
Charge Density Mismatch (CDM)
UFI
Mordenite
UZM-5
UZM-14
Zeolite
Nano
Crystal morphology
Aromatics alkylation
Aromatics transalkylation

ABSTRACT

Nano-crystalline zeolites UZM-5 and UZM-14 were synthesized via the Charge Density Mismatch (CDM) approach and were shown to have distinct morphologies that significantly impact aromatic alkylation and transalkylation reactions. UZM-5 has surface structure features and thin plate morphologies favorable for catalyzing the alkylation of benzene with ethene. The alkylation activity depends on the crystallinity and morphology, which affect acidity and access to surface cups and internal pores. Nano-crystalline mordenite, UZM-14, was characterized in terms of crystallite length in the direction of the 12-MR channels, mesoporosity, and accessibility of acid sites. Aromatics transalkylation performance was shown to correlate with mesoporosity and crystallite length along the pore direction. This was rationalized in terms of decreased diffusion path length in the micropores and improved accessibility of feed molecules to acid sites in the interior of the zeolite crystals.

1. Introduction

Zeolites have been utilized as catalysts and adsorbents in refining, petrochemical and emission control industries over the last few decades. The pursuit of zeolite research is driven by the recognition of their effectiveness in catalytic and separation applications, ease of separation from the product, and environmental friendliness. It is generally understood that zeolite selection is primarily based on matching the structure and active site density of the zeolite with the reaction chemistry of the conversion processes. It has also long been recognized that utilization of active sites is dictated by the mass transfer process through a hierarchy of micro–meso–macropores of the catalysts and adsorbents. In the overall mass transfer process, it is also understood that the morphology of the zeolite plays a significant role, impacting the activity, stability, and selectivity. The desire to attain high utilization of zeolitic active sites explains in part the significant effort going into the research of the nano-zeolite synthesis. While there are many successful examples of nano-zeolite synthesis, it is observed that there is still a need for a systematic and cost-effective approach for maximizing utilization of zeolitic active sites on a commercial scale. Zeolite synthesis based on the Charge Density Mismatch (CDM) approach has yielded new structures and new compositions of existing structures. The CDM-based syntheses often yield zeolites of small-crystallite dimensions ranging from about 500–20 Å, the latter comparable to one unit cell size. This unique feature is inherited from the underlying synthesis chemistry, enabling us to attain specific structures with controlled morphology. In this paper, the importance of the morphology of two CDM-derived UOP Zeolitic Materials (UZM) is illustrated in two aromatic conversion processes.

2. UZM synthesis: Charge Density Mismatch (CDM) concept

Exploratory zeolite synthesis in the 1990s was dominated by the template concept, inspiring the synthesis of ever more complicated organoammonium-based structure directing agents (SDA) with the goal of designing a hand in glove fit between the SDA and the zeolite pore system. Work by Zones, Davis, Corma, and others yielded beautiful structures, but the large SDAs were very expensive and produced high Si/Al ratio zeolites [1]. UOP has a broad interest in zeolites not only for catalysis, but also for adsorbent applications, all of which often require zeolites with

---

* Corresponding author.
E-mail address: deng-yang.jan@honeywell.com (D.-Y. Jan).

0021-9517/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcat.2013.05.034

significant framework charge density, i.e., low Si/Al ratios. UOP decided to pursue a new approach to zeolite synthesis in which two or more common, economical SDAs are used to crystallize a single zeolite structure. The strategy developed to accomplish this goal of SDA cooperation is called the Charge Density Mismatch (CDM) Approach [2,3].

Several criteria are required for a zeolite synthesis which orchestrates a cooperative interaction between two SDAs to crystallize a single zeolite. First, the reaction should take place in solution, so that both SDAs have access to all of the aluminosilicate species. A cooperative effect would be difficult to control and achieve if one SDA was mostly tied up in a solid gel phase, while the other was mostly in solution. Second, the SDAs are competing to balance framework charge on the zeolite. This suggests that there should be a significant amount of charge on the zeolite framework to be synthesized; otherwise, SDA concentrations will overwhelm their requirement in charge balancing, making the competition difficult to control. Third, one has to avoid a disproportionation in which each SDA separately crystallizes a different zeolite. To gain control over this aspect of condensation and crystallization of zeolites, we started with a reaction mixture that could not crystallize, the CDM reaction mixture. The CDM reaction mixture is a low Si/Al ratio aluminosilicate solution that has the potential to form a highly charged zeolite framework. The charge density mismatch is obtained by including a low charge density SDA, such as tetraethylammonium cations (TEA^+) or tetrapropylammonium cations (TPA^+), in the reaction mixture. The driving force for condensation and crystallization of zeolitic networks is the formation of a charged aluminosilicate network. Under typical synthesis conditions, the large, low charge density SDA cannot efficiently balance the high charge on the potential zeolite framework that would form in a manner that provides stabilization; hence, crystallization does not occur. Inherent in a CDM reaction mixture is a barrier to zeolite crystallization.

The crystallization barrier can be manipulated further by adjusting the hydroxide level. Higher hydroxide levels shift aluminosilicate speciation to smaller and more highly charged species, which enhance the mismatch and raise the barrier to crystallization. To crystallize a zeolite, one must break down this barrier. This must happen via cooperation of SDAs, since the CDM SDA cannot enable crystallization by itself and needs assistance. The barrier can be attacked via a perturbational approach, adding small amounts of high charge density SDAs (crystallization SDAs) like Li^+, Na^+, and TMA^+ to the reaction mixture that are better suited to stabilizing the highly charged zeolite framework. As the CDM SDA needs these crystallization SDAs to get the crystallization process started, the levels at which the crystallization SDAs are added are kept quite low, so that they do not dominate the crystallization (avoiding the above mentioned disproportionation) and need the CDM SDA to complete the crystallization. This results in the desired cooperation of SDAs.

There are several unique advantages offered by the CDM synthesis approach. It is essentially a two-step approach that separates the formation of a reactive aluminosilicate synthesis mixture from the process of inducing crystallization in the reaction mixture. The CDM SDA is usually the sole source of hydroxide and is decoupled from the crystallization SDAs, which are usually added as halide salts. Strict control over the concentration of the crystallization SDAs allows one to have great control over the rates and extent of condensation, often resulting in nanocrystals and crystals of unique morphologies [4]. Having a barrier to condensation and crystallization also helps to control the extent to which a reaction occurs. Most of the reaction mixture is in a solution state in a CDM reaction mixture. As the reaction proceeds, the solid products that form are not as highly charged as the aluminosilicate anions they came from. The species remaining in solution become even more highly charged, and thus, the barrier to condensation grows until the reaction finally stops. Recently, a study of the formation mechanism of UZM-9LS (a high silica zeolite with the LTA topology) from the reaction mixture 8 TEAOH:8 TEOS:$Al(OsecBu)_3$:0.5 TMACl:0.5 NaCl:240 H_2O gave a 20% yield after 18 days at 100 °C, and the rest of the reaction mixture remained in solution [5]. When the barrier to condensation in this same reaction mixture is attacked more harshly at 150 °C, the higher silica-containing and structurally related UZM-5 product (UFI topology) results [2]. The multiple SDA and perturbational aspects of the CDM approach have often revealed close relationships between structure and chemistry, such as between UZM-4 (BPH) and UZM-22 (MEI) [6]. Finally, the combinations of cheap SDAs employed in the CDM approach can yield zeolites with the same topology as those previously isolated using much more complicated structure directing agents, such as UZM-22 (MEI), which is derived from choline, Li^+ and Sr^{2+} vs. ZSM-18 (MEI) which has a complicated triquat SDA [6].

3. Alkylation

3.1. Alkylation background

Microporous materials play a key role in the current technology for producing petrochemical intermediates such as ethylbenzene (EB) and cumene [7–10]. The zeolites in general enable the alkylation processes to operate at very high efficiency under economic operating conditions, i.e., very low benzene to alkylation reagent ratios, high product yields, and long-lasting catalyst life. In reviewing the historic advancement of alkylation technology, it is observed that the microporous materials have evolved from MFI and modified Faujasite to zeolite BEA and MWW. The use of zeolites BEA and MWW is especially significant, because both zeolites have crystallite sizes in the nanometer range, as illustrated by their high external surface areas, typically greater than 100 m^2/g, which corresponds to less than 400 Å in a cubic morphology. The nanocrystallite morphology enhances the reaction to the primary alkylation for mono-alkylated product formation [11–14]. Furthermore, it minimizes the consecutive reactions for heavies formation, enabling long operating cycle.

UZM-5 (UFI) is a two-dimensional microporous material having a small pore opening (8-MR) and nano-thin plate morphology [15,16] with an external surface area typically in excess of 100 m^2/g. While the access of aromatics to the interior 8-MR channels is prohibited, there exists a structural possibility for facile hydrocarbon adsorption on the exterior surface of zeolite crystals. It was previously reported that UZM-5 showed xylene isomerization under sub-atmospheric pressures, which was attributed to the active sites on the exterior of the plates [17]. To explore the effectiveness of exterior active sites of UZM-5 and the influence of morphology, a series of UZM-5 samples were prepared and evaluated for EB alkylation.

3.2. Alkylation experimental

3.2.1. UZM-5 zeolite synthesis

The UZM-5 materials were prepared from a variety of reaction compositions falling within the following ranges 3–3.75 TEAOH:8–8.5 SiO_2:$Al(OH)_3$:0.5–0.55 NaOH:0.25–0.32 TMAOH:145–275 H_2O [18]. Typically, a CDM aluminosilicate solution is prepared by dissolving aluminum hydroxide (Pfaltz and Bauer) in TEAOH (35%, SACHEM), adding colloidal silica, (Ludox AS-40™, 40% SiO_2), and aging overnight in a stirred reactor at 95 °C. After the aging step, the solution is treated with an aqueous solution containing appropriate amounts of TMAOH (25%, SACHEM) and NaOH and digested in the stirred reactor at 125 °C for periods of