



Direct aldol and nitroaldol condensation in an aminosilane-grafted Si/Zr/Ti composite hollow fiber as a heterogeneous catalyst and continuous-flow reactor



Yingxin He, Abbas Jawad, Xin Li, Marktus Atanga, Fateme Rezaei, Ali A. Rownaghi*

Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO 65409-1230, USA

ARTICLE INFO

Article history:

Received 20 May 2016

Revised 1 July 2016

Accepted 2 July 2016

Keywords:

Cooperative catalysis

Bifunctional acid–base catalysts

Aminosilane-grafted Si–Zr–Ti/Torlon composite hollow fibers

Aldol and nitroaldol condensations

Continuous-flow reactor

ABSTRACT

A proof-of-concept study for a new type of continuous-flow reactor based on porous aminosilane-grafted Si–Zr–Ti/Torlon composite hollow fibers was considered for aldol and nitroaldol condensations of aromatic aldehydes with acetone and nitromethane. These novel hollow fiber reactors consist of bifunctional groups in fiber wall that make them bifunctional catalysts for cooperative interactions (i.e., acid–base catalysis). In this study, the effects of reactant flow rate, reaction time and temperature, and electron-donating and electron-withdrawing groups of para-substituted benzaldehyde derivatives on the catalytic activity of aldol and nitroaldol condensation reactions were systematically investigated. The yield of products was found to be dependent on the cooperative interactions of acid–base pairs, para-substituted benzaldehyde, and reaction conditions such as temperature and contact time. Moreover, relatively high yields of ca. 100% were obtained at higher flow rates for primary aldol and nitroalcohol products, while benzylideneacetone and nitrostyrene yields were higher at longer contact times. The obtained results indicate that the aminosilane-grafted Si–Zr–Ti/Torlon composite hollow fibers provide a new platform as flow reactors for heterogeneously catalyzed reactions that may facilitate the ultimate scale-up of practical fiber catalysts for the synthesis of complex organic compounds.

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1. Introduction

The aldol and nitroaldol condensation reactions are essential steps in C–C bond formation for organic synthesis, production of complex molecules in the fine chemical and pharmaceutical industries, and development of biomass conversion schemes [1–4]. Aldol and nitroaldol condensation reactions are industrially catalyzed by homogeneous catalysts that typically have short lifetimes and require further separation from reaction mixtures [5–8]. The short catalyst lifetime and relatively high energy requirement for recycling are drawbacks of homogeneous catalysts that limit their use in industrial applications. Fortunately, insights from homogeneous catalysts can be applied to development of more robust heterogeneous catalysts that integrate acid and base sites into a single support material. The design of bifunctional catalysts that combine basic sites with acidic sites usually relies on incorporating inexpensive elements into chemically functionalizable materials to enable simultaneous activation of both electrophilic and

nucleophilic reaction partners [2,5,6,9]. Bifunctional catalysts that contain two distinct catalytic sites can act as cooperative catalysts for achieving higher reaction rates than those achieved using either of the catalytic species independently [9–11].

The incorporation of silanol groups (weak acid sites) next to amine sites (base sites) was previously shown to increase the overall rate of aldol condensation and other important C–C coupling reactions such as Knoevenagel [12,13], Claisen–Schmidt [14,15], Michael addition, and Henry (nitroaldol) condensations [5,6]. The use of amine-functionalized mesoporous silica (e.g., SBA-15 and MCM-41), zirconia (ZrO₂), and titania (TiO₂) has been studied in aldol condensation by several research groups [5,9,11,14,16–20]. These materials exhibited improved activity as bifunctional catalysts for aldol condensation [2,5,6,9]. An alternative method is to engineer the surface silanol groups by introducing new types of hydroxyl species such as titanols [21] or Brønsted acid sites (such as unsaturated Zr⁴⁺ species) that are stronger than silanols or Lewis acidic sites [11,22]. Higher activity and selectivity could be obtained on catalysts having two or more functionalities on the surface. Vermoortele et al. [23] showed that amine-functionalized UiO-66-NH₂ metal–organic frameworks (MOFs) with Lewis acid Zr sites and Brønsted base –NH₂ sites are more

* Corresponding author.

E-mail addresses: rownaghia@mst.edu, ali.rownaghi@gmail.com (A.A. Rownaghi).

active and selective than bare UiO-66 for the cross-aldol condensation reaction of heptanal with benzaldehyde to form jasminaldehyde. It has been shown that primary, secondary, and tertiary amines with various alkyl linker lengths exhibit totally different catalytic activities in the aldol condensation reaction, due in part to significant differences in the ability to form imine species as key intermediates for this reaction, and in part to differences in the degree of amine sites deactivation, which dramatically affects catalyst activity [5,24,25].

Waste reduction and catalyst recycling have attracted intense research interest in recent years due to economic concerns for sustainable production of chemicals and pharmaceuticals [26]. The continuous-flow approach is a rapidly emerging technology that offers an interesting alternative to inherently less efficient batch processes. Homogeneous catalysis performed in a flow system has demonstrated successes in efficient mixing and heat control; however, the current flow systems suffer from some limitations including multistep transformation of unstable intermediates and low potential for catalyst recycling [27,28]. Heterogeneous bifunctional catalysis, on the other hand, offers options for catalyst separation and recycling and integration into a flow system. In contrast to homogeneous catalysts, however, performance of heterogeneous catalysts in a continuous-flow reaction system has been less explored as a result of lower catalytic efficiency and stereoselectivity than for their homogeneous counterparts [28,29]. Shibasaki et al. [28] prepared a series of Nd/Na heterogeneous catalysts by self-assembly of an amide-based chiral ligand and a multiwalled carbon nanotube and evaluated them for a nitroaldol reaction with high stereoselectivity to nitroalcohol in a continuous-flow system. In another study, Kobayashi et al. [30] synthesized β -nitrostyrene derivatives in a two-step continuous-flow reactor using heterogeneous catalysts. Asefa et al. [31] reported a facile method for continuous nitroaldol reaction in a fixed-bed reactor packed with primary and secondary amine-functionalized MCM-41 materials. These previous studies have primarily focused on evaluation of the physical properties of the support (mainly silica) or modification of organic constituents for tuning the amine-silanol cooperative interactions in a flow system to promote condensation reactions. Packing heteroatom bifunctional catalysts into an appropriate contactor such as a hollow fiber appears to be a promising approach for scaling up the continuous-flow process to practical sizes. Such novel configurations could function as flow reactors while catalyzing the aldol condensation reaction at the same time. The composite hollow fiber flow system not only confers advantages at the laboratory scale, but also offers excellent potential for large-scale production of valuable chemicals. This proposed system can potentially offer lower operational, maintenance, and capital costs, ease of installation, and a smaller footprint. Amine-functionalized polymeric hollow fibers composed of metal oxide particles embedded into a polymer matrix have recently been used for gas separation, namely separation and purification of CO₂ [32,33]. Such contactors offer advantages over traditional pellets or beads, due to a high surface-to-volume ratio, avoidance of particle attrition and low pressure drop, enhanced flow pattern reliability for scale-up, and the ability to control mass transfer resistances [32,34]. Of the advantages offered by hollow fiber-based continuous-flow technology, process intensification is a key feature, as composite hollow fiber-flow reactors can facilitate effective reactant interaction and mixing within the porous structure of the polymer matrix, transformation of unstable intermediates, and functionalization with various agents, while expanding the window of reaction conditions for a specific transformation.

Aldol condensation [35,36] and other reactions such as nitroaldol [28], Michael [26], Mannich [36,37], and Mizoroki-Heck [38] reactions have been investigated previously using flow platforms to promote these reactions [27,35,39–41]. However, to the best

of our knowledge, no catalytic investigations on the use of amine-functionalized composite hollow fiber reactors for these condensation reactions have been reported so far. In the present contribution, we demonstrate the applicability of aminopropyltriethoxysilane (APS)-grafted polyamide-imide (Torlon) hollow fibers (APS-grafted Zr-Ti-Si/PAI-HF) as a bifunctional heterogeneous catalyst in the cross-aldol and nitroaldol condensation of aromatic aldehydes with acetone or nitromethane under mild reaction conditions in a continuous-flow reactor.

2. Theory and background

Hybrid organic-inorganic functional groups can easily be immobilized into high-surface-area supports for applications in various gas separation and reaction processes [10,42]. Recent advances have led to the development of polymeric hollow fibers that comprise various inorganic fillers with different functional groups that can provide cooperative catalysis by controlling their spatial arrangements [32,43]. These hollow fiber catalysts are in fact pseudomonolithic materials comprising a porous polymer matrix with catalyst nanoparticles such as silica, zirconia, titania, zeolites, and MOFs embedded into the matrix. In this effort, we engineer hybrid organic-inorganic catalysts by tethering organic functional groups onto inorganic surfaces that can act together to provide catalytic activity and selectivity superior to what can be obtained from either nonfunctional materials or homogeneous catalysts. The silica, zirconia, and titania support surfaces grafted with aminosilanes provide a continuous range of weak acidic and basic bifunctional catalyst sites that play a significant role in the outcome of an acid-base catalyzed reaction. Here, we report that these hollow fiber catalysts can also be used in continuous-flow reactions for the production of large quantities of selective aldol or nitroaldol reaction products (Fig. 1). As schematically shown, in a hollow fiber reactor, the catalyst is immobilized and resides within the porous wall while the reagents are passed through the fiber shell and products are collected from the bore side, so in principle, no separation of the product from the catalyst is required. Also, by operating under optimum conditions to achieve high conversion, minimal separation of unreacted products is required. Furthermore, through this configuration the hollow fiber catalysts can easily be regenerated and reused. These advantages make the hollow fiber catalyst system the most convenient configuration to perform a reaction under continuous-flow conditions. It is anticipated that this catalytic hollow fiber reactor becomes an industrially viable substitute for the current commercial homogeneous catalytic systems for the aldol and nitroaldol condensation reactions involving soluble bases such as NEt₃, KH₂PO₄, Na₂CO₃, KOH, and NaOH [44,45].

3. Experimental

3.1. Chemicals and materials

Zirconia, titania, and silica (average particle size 100 nm, Sigma Aldrich), Torlon 4000T-HV, a commercially available polyamide-imide (PAI) (Solvay Advanced Polymers, Alpharetta, GA), poly(vinylpyrrolidone) (PVP) (average Mw 1300 K, Sigma Aldrich), N-methyl-2-pyrrolidone (NMP), and methanol (ACS Reagent, >98.5%, VWR) were used for polymer dope preparation and formation of the composite hollow fiber catalysts. 3-Aminopropyltrimethoxysilane (APS) (95%) was purchased from Gelest and used as the agent for grafting zirconia-, titania-, and silica-Torlon hollow fiber catalysts. Benzaldehyde (98%), 4-bromobenzaldehyde (99%), 4-nitrobenzaldehyde (99%), 4-methoxybenzaldehyde (98%), 4-hydroxybenzaldehyde (97%), ace-

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