

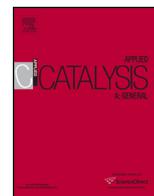


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Contents lists available at ScienceDirect

Applied Catalysis A: General

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



Reaction-dependent heteroatom modification of acid–base catalytic cooperativity in aminosilica materials

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ARTICLE INFO

Article history:

Received 4 August 2014
Received in revised form 27 October 2014
Accepted 31 October 2014
Available online xxx

Keywords:

Cooperative catalysis
Aminosilica
Heteroatom
Brønsted acid
Lewis acid

ABSTRACT

The effects of heteroatom substitution on the cooperative catalytic activity of a series of bifunctional acid–base aminosilica catalysts are probed in aldol and nitroaldol condensations. Three M^{3+} (B, Al, and Ga) and three M^{4+} (Ti, Zr, and Ce) heteroatoms are incorporated into different samples of SBA-15 silica and then grafted with aminosilanes to produce bifunctional acid–base catalysts. The catalytic activity of each material is measured in the aldol condensation of 4-nitrobenzaldehyde with acetone at 50 °C and the nitroaldol condensation of 4-nitrobenzaldehyde with nitromethane at 40 °C and compared to the catalytic activity of a heteroatom-free aminosilica catalyst. The heteroatom substitutions produce catalysts with larger amounts of strong Lewis acid sites compared to the heteroatom-free aminosilica catalyst. We rationalize these results in the context of the physical (e.g. surface area, pore diameter, particle size) and chemical properties (e.g. total number and strength of acid sites) of each material and the proposed catalytic mechanisms of the two reactions. The increase in the number of strong Lewis acid sites of each heteroatom material decreased its activity in the aldol condensation, though four heteroatom substitutions (B, Al, Ga, and Ti) increased the catalytic activity of the aminosilica catalyst in the nitroaldol condensation. The results suggest that inclusion of a small amount of Lewis acid sites in aminosilica materials can increase the cooperative catalytic activity of the materials in the nitroaldol condensation. The results also suggest that inclusion of Lewis acid sites in aminosilica materials decreases the cooperative catalytic activity of the materials in the aldol condensation.

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1. Introduction

Cooperative catalytic activity can be achieved in a variety of ways and can be defined as the interaction between two distinct catalytic sites to achieve a rate of reaction that is greater than the rate achieved with a single component [1]. Such reactions can be achieved with bifunctional catalysts that contain two distinct functional groups, most commonly an acid and a base, that are spatially separated such that the functional groups do not interfere with each other, yet can interact with a substrate(s) cooperatively to increase the rate of reaction. The two distinct catalytic units can individually activate substrates or act in concert to enhance the reaction, among other modes of cooperative activation [1]. The design of bifunctional catalysts most often relies on combining simple, inexpensive catalytic elements on chemically functionalizable materials to enable cooperative interactions [2,3]. Examples of cooperative acid–base catalysts include homogeneous

organocatalysts [4–8], polymeric systems [9], carbon quantum dots [10], and silica-immobilized systems [11–19]. The facile ability to separate and recycle heterogeneous catalysts from reactive fluids makes them attractive targets for incorporating acid–base cooperativity in new materials. While the results from homogeneous catalysts can be used as a basis for designing heterogeneous catalysts, incorporating cooperative catalytic elements is considerably more challenging in heterogeneous systems such as those based on silica supports because the silanols present on the surface, which act as organic functional group anchoring points or as weakly acidic cooperative partners, are typically not uniformly distributed [20–26]. Despite the complexity of silica-based catalysts, numerous studies demonstrate the ability to design materials that exhibit cooperative interactions, providing considerable insights into optimizing such catalysts. Early indications that silanols could act cooperatively with amines were unambiguously defined through experiments using thermally cleavable protecting groups and capping the surface silanols with trimethylsilyl groups using hexamethyldisilazane (HMDS) [27–31]. More recently, immobilizing amines with different linker lengths demonstrated that spatial positioning of the amines with respect to the location of surface silanols was

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crucial to optimizing the amine–silanol cooperativity [3,19]. While many types of acidic species including sulfonic, phosphoric, and carboxylic acids have been used as cooperative partners [11,12,18], it was recently demonstrated that weaker acidic species, such as silanols, provided more favorable cooperative interactions in the form of superior catalytic activity for the aldol condensation of 4-nitrobenzaldehyde with acetone in comparison to carboxylic acids and other stronger acids [18]. Another study revealed that shorter alkyl tethers (e.g. methyl and ethyl) limited cooperative interactions, whereas alkyl linkers longer than propyl exhibited the same catalytic rate for the aldol condensation of 4-nitrobenzaldehyde with acetone [19]. Additionally, the choice of solvent can impact the activity of the bifunctional catalyst. A recent report demonstrated that primary amines tethered to silica were more active for the aldol condensation of acetone and 4-nitrobenzaldehyde in water than in hexane because water shifted the equilibrium in favor of the aldol product and prevented the amine from forming an imine with 4-nitrobenzaldehyde, which inhibited the reaction [32].

In an interesting finding, it was recently shown that the observed trend for the alkyl linker lengths differs depending on the specific reactions. For the nitroaldol (Henry) condensation of 4-nitrobenzaldehyde with nitromethane, the rate of reaction steadily increased with increasing alkyl linker length on SBA-15 silica with a pore diameter of 6.5 nm [3]. Furthermore, that study also demonstrated that changing the pore diameter of the silica varied the catalytic activity by as much as an order of magnitude for the nitroaldol condensation, while also shifting the distribution of optimal amine linker lengths, providing another method for tuning the amine–silanol cooperative interactions [3].

These previous studies have mainly focused on modifying the organic components of the catalytic moieties and the physical dimensions of the silica support, though the chemical modification of the silica framework may also have positive effects on the activity of cooperative catalysts. Additionally, these previous studies primarily used the surface silanols as the acidic component of the cooperative interactions, but the inherent heterogeneity of the distribution of silanols present on the surface makes controlling the number of protic species with which the amines interact difficult. An alternative method to modify the properties of the silanol-covered surface is the incorporation of heteroatoms in the silica matrix. M^{3+} elements will typically introduce a Brønsted acid site that is a stronger acid than the silanols, while M^{4+} elements will introduce new types of hydroxyl species such as titanols [33] or even Lewis acidic sites in the case of coordinatively unsaturated Zr^{4+} species [34,35] and tetrahedrally coordinated Ti sites [36]. At present, studies of the effects of heteroatom substitution on cooperative acid–base catalysts have been limited mainly to Al substitution for C–C coupling reactions and one-pot cascade reactions [13,37–48]. In this study, we examine the effects of heteroatom substitution with materials with similar pore diameters, similar organic (amine) loadings, and approximately 5 mol% heteroatom substitution. More specifically, we investigate the effects of heteroatom substitution for two well-studied model reactions (aldol vs. nitroaldol couplings), showing these reactions are differently affected by the incorporation of heteroatoms into the silica framework.

2. Experimental

2.1. Materials

Pluronic P123 block copolymer ($EO_{20}PO_{70}EO_{20}$, $M_n \sim 5800$), tetraethyl orthosilicate (TEOS, 98%), tetramethyl orthosilicate (TMOS, 98%), aluminum isopropoxide ($Al(O^iPr)_3$, 98%), titanium tetraisopropoxide ($Ti(O^iPr)_4$, 98%), cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99%), zirconium oxychloride octahydrate

($ZrOCl \cdot 8H_2O$, 98%), ammonium fluoride (NH_4F , 98%), and nitromethane (96%) were obtained from Sigma-Aldrich. Acetone (99.5%), aqueous ammonia (28 wt% NH_3), and 4-nitrobenzaldehyde (99%) were obtained from Alfa Aesar. Toluene (99.5%) and hexane (98.5%) were obtained from BDH. Ethanol (100%) was obtained from Koptec, (3-aminopropyl)triethoxysilane (99%) was obtained from Gelest, 1,4-dimethoxybenzene (99%) was obtained from TCI, and 12.1 M HCl was obtained from EMD. Deuterated chloroform (99.8%) was obtained from Cambridge Isotope Laboratories, Inc.

2.2. Synthesis of SBA-15 and heteroatom-substituted SBA-15

All SBA-15 materials were prepared according to previous reports [18,19,37,49–55]. The details of the synthetic procedures are in the Supporting Information.

2.3. Grafting of organosilanes on SBA-15 materials

For each heteroatom material and bare SBA-15 silica, a 500 mg sample was dried under vacuum at 100 °C overnight prior to functionalization. The flask containing the 500 mg sample was purged with UHP nitrogen and mixed with 12.5 mL of anhydrous toluene and 58.5 μ L of (3-aminopropyl)triethoxysilane (or 67.2 μ L of (5-aminopentyl)triethoxysilane synthesized in a Parr reactor from the reaction of 5-bromopentyl triethoxysilane with ammonia) [19]. The solution of toluene and silane was injected via syringe through the rubber septum of the flask, at which point the mixture was magnetically stirred at room temperature for 24 h. Next, the mixture was heated to 80 °C and stirred for another 24 h. The solid was washed and filtered with 100 mL each of toluene, hexane, and ethanol, sequentially. The material was dried under vacuum at 100 °C overnight and stored in a labeled container for later use. Amine-functionalized heteroatom materials follow the same naming convention, X-A#-SBA-15, in this manuscript, where X refers to the heteroatom and A# refers to the number of carbon atoms in the alkylamine linker (A1 for aminomethyl, A3 for aminopropyl, A5 for aminopentyl). The amine-functionalized SBA-15 without heteroatom substitution is called A3-SBA-15 throughout the manuscript.

2.4. Materials characterization

Nitrogen physisorption experiments were performed on a Micromeritics Tristar 2030 at 77 K. All samples (approximately 100 mg each) were degassed under vacuum overnight at 110 °C prior to the physisorption measurements. The surface area of each material was determined using the Brunauer–Emmett–Teller (BET) method and the total pore volume and pore diameter were determined using the Broekhoff–de Boer method with the Frenkel–Halsey–Hill (BdB–FHH) modification using the data from the adsorption isotherm [56]. Scanning electron microscopy (SEM) images were recorded on a Hitachi scanning electron microscope (SEM SU 8010) using an acceleration voltage of 5 kV. A thin layer of gold was sputtered onto each sample prior to scanning. Ammonia temperature-programmed desorption (TPD) experiments were performed on a Micromeritics Autochem II 2920. Approximately 125 mg of each sample was placed into a quartz U-tube and dried under a flow of He at 10 mL/min at 500 °C for 1 h. Each sample was cooled to 50 °C, at which point NH_3 (2000 ppm in He) flowed over the sample at a rate of 25 mL/min for 1 h. The sample was held at 50 °C, while the tube was purged with He for 30 min to remove weakly adsorbed NH_3 . The desorption experiment started at 50 °C and increased to 500 °C in a He flow of 10 mL/min with a temperature increase of 10 °C/min. The desorbed NH_3 was measured by a thermal conductivity detector (TCD). All samples containing organosilanes were sent to Atlantic Microlab (Norcross, GA) for

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