



Activity of titania and zeolite samples dosed with triethylamine



Caitlin Baker^a, James L. Gole^{a, b}, Jonathan Brauer^c, Samuel Graham^b, Jianzhi Hu^d, Jeff Kevin^e, Andrew D. D'Amico^e, Mark G. White^{f, *}

^a School of Physics, Georgia Institute of Technology, Atlanta, GA 30332, USA

^b School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

^c Department of Microbiology and Plant Biology, University of Oklahoma, Norman, OK, USA

^d Pacific Northwest National Laboratory, Fundamental Sciences Division, Richland, WA 99352, USA

^e Micromeritics Instrument Corporation, Norcross, GA 30093, USA

^f Dave C. Swalm School of Chemical Engineering, Mississippi State University, Mississippi State, MS 39859, USA

ARTICLE INFO

Article history:

Received 4 July 2015

Received in revised form

3 August 2015

Accepted 17 August 2015

Available online 28 August 2015

Keywords:

Titania

Zeolite Y

Triethylamine

Nanocolloid

Microcrystalline

ABSTRACT

Certain properties of titania and the ammonium- and proton-form of Y zeolites silica/alumina = 5.2 were explored before and after treatment by triethylamine (TEA). The effect of the triethylamine upon the physical and chemical properties of both titania and the zeolite were characterized by physical and chemical adsorption methods. BET surface area data showed enhanced surface area of the TEA-treated nanotitania over the untreated nanotitania; whereas, the TEA-treated zeolite showed a considerable decrease in surface area compared to the untreated zeolite. A lower bound on the exothermic heat release from the sol–gel generated TiO₂ nanoparticle–TEA interaction has been evaluated. Temperature programmed desorption (TPD) of the TEA-treated Y zeolite showed that weakly adsorbed TEA left the surface between 150 and 300 °C; strongly adsorbed TEA decomposed to ethylene and ammonia at higher temperatures. Methanol adsorption isotherms and temperature-programmed, surface reaction (TPSR) were used to understand further the Zeolite–TEA interactions and correlations were made to CO₂ adsorption. XPS, IR, and Raman spectroscopies, powder XRD, and ²⁷Al MAS–NMR spectroscopy were used to characterize the changes attending the TEA adsorption. Pre-adsorbed, triethylamine decorated acid sites so as to neutralize these sites for the reaction of methanol to dimethyl ether. Carbon monoxide and formaldehyde, products of the methanol probe reaction, were observed – suggesting that basic sites are present in this treated zeolite and titania.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Recently, we discussed the catalytic activity of nitrogen and metal ion doped titania, comparing the activity of nanotitania to a commercial catalyst [1,2]. The goal of these studies was to convert Lewis acid sites to basic sites employing a relatively simple nitration process at the nanoscale [1–3]. Titanium oxide nanocolloids were treated with alkyl amines, such as triethylamine in solution. It was apparent that N species were added to the colloid before the system was converted to its oxide. Titania has been identified by many authors as an effective catalyst for the deoxygenation of oxygenates, such as those found in pyrolysis liquids [4]. Most of these demonstrations were established either in model catalysts, such as

single crystals of titania, or in low surface area versions of titania (<10 m²/g). We attempted to develop nano-colloidal titania having surface areas >150 m²/g so as to improve the catalytic activity. These higher activity catalysts would be of interest in practitioners who want these catalysts. In addition, we attempted to incorporate nitrogen atoms into titania so as to open up the reaction manifolds to decarboxylation and dehydration which have been shown to be effective pathways to remove O atoms from oxygenates. We show here our attempts to extend this approach to treating already formed oxides to determine if this technique will be effective with a similar TEA-treatment for Y zeolites.

Zeolites represent low-density, aluminosilicates and play an important role in a variety of petrochemical processes where they are used as molecular sieves, selective adsorbents, and catalysts [5–11]. Zeolites are known to play an important role in petroleum refining and chemicals production [1]. The singular properties of zeolites are closely correlated to their physical structure, which

* Corresponding author.

E-mail address: white@che.msstate.edu (M.G. White).

consists of fully, corner-connected (Al,Si)O₄ tetrahedra as well as surface-based octahedral sites and results from their ability to form cavities and channels of various sizes. These are usually occupied by charge-balancing cations, which can include H⁺, Na⁺, and Fe⁺², as well as solvent molecules.

For active molecular sieves and catalytic surfaces, there has been considerable interest in the design and synthesis of extra-large zeolite pores [12] and in the formation of basic sites in the normally acidic zeolite lattice (for example, tetrahedral AlO₄⁻ sites which bind a proton for charge neutrality) [13]. In complement to the generation of high pore volumes, it is desirable to demonstrate that the rigidity of the complex zeolite structure can be altered, perturbing but not destroying its intrinsic character. The modification of the properties of zeolites has been done using a variety of methods [13,14]. In particular, amine-treatment of zeolites has been used in an effort to enhance the CO₂ storage capacity of zeolites [15]. An important modification of a typical zeolite, such as zeolite Y, with acidic catalytic sites would result if these sites can be converted to basic sites capable of binding and *converting* a reactant at the activating site [11]. It has been suggested that these basic sites could be nitrogen-based [12,16].

Early attempts to produce basic sites in zeolites included the ion exchange of group I A and II A cations. Here, the goal was to replace the Na ions normally used to balance the framework negative charge with ions of increasing electro-positivity so as to realize the benefits of these strong Brønsted bases [14]. Zeolites have also been decorated with strong Lewis bases as an alternate approach to create basic sites, *e. g.*, zeolite beta was dosed with ammonia at 300 °C in an attempt to develop basicity in this zeolite by developing a nitride surface species [15]. Aluminosilicates and aluminophosphates have also been treated with ammonia at higher temperatures to develop surface basicity [16]. Organic bases have been grafted to zeolites in another attempt to confer basicity to acidic zeolites [17]. Alkyl amines have been used to develop surface species onto silicon [18], and titania [19,20]. We demonstrate here our attempts to change the properties of a titania nanocolloid and a crystalline, zeolite Y, using a treatment with triethylamine, completed at a temperature slightly elevated from room temperature. In particular, we compare and contrast the effectiveness of the TEA treatment to alter the properties of a loosely-assembled nanosized colloid of titania with the properties of a fully-crystallized, rigid, zeolite Y.

2. Experimental

2.1. Catalyst preparation

TiO₂ nanocolloids were formed by hydrolysis of Ti (IV) tetraisopropoxide. 250 mL of doubly ionized water and 80 mL of acetic acid were combined in a one-liter flask as the mixture was cooled to 0 °C in an ice bath under vigorous stirring. Ten milliliters of 2-propanol followed by 3.7 mL of Ti[OCH(CH₃)₂]₄ were added to a dropping funnel fixed to the flask as this solution was added slowly and drop-wise, under a dry nitrogen atmosphere, again with vigorous stirring. Continued stirring of the initial mixture for 24 h produces a clear colloidal solution. This clear solution can also be maintained under refrigeration for several months. For the present experiments, the nanocolloid ranged in size from 10 to 20 nm [1]. Spherical particles of this size having a density of anatase (3.74 g/cm³) generate an external surface area (Supplemental Information) of 80–150 m²/g which includes some of the observed surface areas for the titania nanocolloids of 150–180 m²/g, *vide infra*. Given these results, we conclude that some porosity is present in the nanocolloids shown here. The TiO₂ nanocolloid was treated directly using triethylamine (TEA) in order to form TiO_{2-x}N_x [1,2]. The

reaction was found to take place readily and appeared complete within several seconds accompanied by heat release and the formation of a yellowish, partially opaque, mixture. XPS studies indicate the presence of 4–8% nitrogen in the surface region of the nitrated samples.

The inordinately-high heat release of the triethylamine reaction with the titania nanocolloid prompted us to characterize further this event by estimating the enthalpy of the reaction, ΔH_{TEA/titania}, in the small, 2 mL bottle depicted in Fig. S1 (Supplemental Information). A thermocouple system was attached to the bottle under black electrical tape and the temperature rise as a function of reaction time was recorded. A prescribed quantity of TiO₂ nanocolloid, aqueous solution (0.0933 g titania, and balance water to give a total mass of 0.204 g) was mixed with TEA (1.58 g). The maximum temperature rise was 16 °C for the reactants and bottle.

As a control experiment to the TEA-treatment of the titania nanocolloid, we used zeolites as sources of a microcrystalline, rigid metal oxide: the ammonium form of the zeolite, NH₄Y, and the proton form of the zeolite, HY, both having a silica/alumina ratio of 5.2. These materials were obtained from Zeolyst Products with the commercial designations of CBV 500 and CBV 600, respectively. The total aluminum ion concentration in these samples was estimated to be 4.83 mmol/g zeolite, from a consideration of the silica/alumina ratio provided by the vendor. Two methods were used to contact the NH₄Y and HY zeolites with the triethylamine (TEA). By method A, 5 g of zeolite was stirred in a 5 cm³ triethylamine solution, which corresponds to 35.9 mmol of triethylamine, at 48 °C for 45 min and dried at 73 °C. By method B, the zeolite was contacted with TEA at 48 °C for 30 min in an open container with stirring, followed by heating at 73 °C in a closed container for 30 min, and then cooled to 48 °C in an open container with subsequent drying at 48 °C. Treated samples were labeled NH₄YN and HYN followed by A or B to distinguish between treatment methods. No significant heat release was observed by either treatment method. A second control sample was established by heating a NH₄Y zeolite at 400 °C for 12 h to convert it to the acidic form, labeled H-400 °C.

A variation of treatments A and B was developed in which the H-form of the Y zeolite (CBV 600) was treated by method A and method B. These samples are designated Z2, and Z3, respectively.

2.2. Surface area

The specific surface areas were obtained using the nitrogen vapor adsorption technique at 77 K. Data were recorded on the ASAP 2420, ASAP 2020 Accelerated Surface Area and Porosimetry Systems, and the 3FLEX Surface Characterization Analyzer at Micromeritics Instruments, Corporation (Norcross, GA). Samples were prepared at temperatures ranging from 50 °C to 400 °C on the ASAP 2420. Most samples achieved a maximum surface area with an optimal preparation temperature of 300 °C. Prior to testing, the samples were pretreated in two preparation stages. The samples were first degassed on a SmartPrep 065 at 250 °C under nitrogen flow for 1 h. The second stage of preparation was performed on the ASAP 2420 where the samples were degassed under vacuum at 300 °C, the optimal preparation temperature, for 4 h.

2.3. Temperature programmed desorption, TPD, and methanol temperature programmed surface reaction, TPSR

Methanol and CO₂ adsorption isotherms over the zeolite were collected at 50 °C after pretreatment at 90 °C and 600 °C (TPSR) for methanol and 90 °C and 475 °C for CO₂. Methanol is a probe reaction that characterizes the samples for acidity and basicity from a consideration of the products generated over each sample, *vide*

Download English Version:

<https://daneshyari.com/en/article/72234>

Download Persian Version:

<https://daneshyari.com/article/72234>

[Daneshyari.com](https://daneshyari.com)