



Short Communication

Hydrothermal degradation of model sulfonic acid compounds: Probing the relative sulfur–carbon bond strength in water



Jason M. Anderson^a, Robert L. Johnson^b, Klaus Schmidt-Rohr^b, Brent H. Shanks^{a,*}

^a Chemical and Biological Engineering Department, Iowa State University, Ames, IA 50011, USA

^b Department of Chemistry, Iowa State University, Ames, IA 50011, USA

ARTICLE INFO

Article history:

Received 22 January 2014

Received in revised form 17 March 2014

Accepted 18 March 2014

Available online 25 March 2014

Keywords:

Sulfonated carbon

Hydrothermal stability

NMR characterization

ABSTRACT

Development of heterogeneous catalysts for the biorenewable industry requires hydrothermal degradation resistance. However, the relationship between hydrothermal stability and the immediate electronic hybridization of the carbon atoms adjacent to the sulfonic acid active group is not fully known. We systematically tested model compounds containing sulfonic acid groups linked to aromatic, alkane, or cycloalkane carbon atoms. We subjected them to hydrothermal conditions. The compounds' structural integrity was monitored with solution NMR. The aromatic-sulfonic acid compounds degraded readily, while the hydrolysis of the alkyl sulfonic acid linkages was negligible. Therefore, hydrothermally stable sulfonic-acid catalysts need sulfonic acid attached via alkyl linkers.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Development of heterogeneous catalysts for transforming carbohydrate and other biomass-derived feedstocks into higher-value chemicals will require catalyst materials that are stable in the condensed phase. Carbohydrates are quite reactive or non-volatile relative to hydrocarbons, and even when catalysts can be used in gas phase reactors the results of the resulting conversions can have poor selectivity and rapid coke formation [1,2]. Even more challenging are aqueous-phase reactions since water under hydrothermal conditions (typically pressurized at 120–250 °C) [3,4] is physically destructive to a large number of materials, including silica, metal oxides such as gamma alumina, zeolites and numerous functionalized polymers [5–7]. Metal oxides are by far the most widely used support materials in the petroleum industry, while carbon and polymer resins have found only limited applications. Carbon is quite resistant to hydrothermal breakdown and shows promise to be a viable support material and a catalyst for hydrothermal reactions. It can also be produced at relatively low cost from a wide variety of feedstocks including lignocellulosic materials and carbohydrates.

The use of solid carbon-based acid catalysts with sulfonic acid functionality is a promising approach to replace sulfuric acid used in numerous applications including cellulose hydrolysis, sugar dehydration, and transesterification of biodiesel. These materials can be produced in a simple two-step process using glucose or carbohydrate pyrolysis at temperatures ranging from 350 to 550 °C followed by sulfonation [8,9] with fuming sulfuric acid or sulfur trioxide. Electrophilic aromatic substitution has been the predominant mechanism forming the C–SO₃

bond and these treatments result in a nearly complete removal of alkyl carbons, and minor additional polycondensation [10]. Sulfonated carbon materials produced using this method have sulfonic-acid groups linked to aromatic carbons and are highly acidic due to the electronegativity of the aromatic system [10]. While these materials have been demonstrated to have excellent activity, their hydrothermal stability is less certain. In recent studies, a spectrum of carbon materials, produced at a range of temperatures, was sulfonated, and tested for hydrothermal stability [10,11]. All readily lost activity through hydrolysis and leaching of sulfur, which clearly indicated that these materials are not sufficiently stable for long term use in a reaction system. Given the difficulty of characterizing the location of sulfur in the chemical structures that were synthesized, it was not possible to draw conclusions about the effects of the local structure on sulfonate stability, including the influence of adjacent groups and carbon hybridization, and temperature at which degradation occurred [11,12]. The literature suggests that bonding of S to aliphatic C would be more stable [13], but a systematic comparison of hydrothermal stability has not been published. The current work sought to investigate these effects by using model compounds that simulate various bonding environments that could exist on a carbon surface.

The molecule types chosen for stability analysis included sulfonic acid groups bonded to aromatic, saturated cyclic, and straight chain aliphatic structures. It has been proposed in the literature that an increase in electron-withdrawing functional groups near an aromatic-bound sulfonic acid would lead to an increased stability of the carbon–sulfur bond [14]. To test this hypothesis, we compared trimethylbenzene sulfonic acid, trinitrosulfonic acid, and benzenesulfonic acid, which represent electron donation, withdrawal, and the control case, respectively. To compare alicyclic versus aromatic rings, cyclohexane and

* Corresponding author.

E-mail address: bshanks@iastate.edu (B.H. Shanks).

benzene sulfonic acid were included in the study. Linear aliphatic compounds were also investigated. The chain length dependence, important for silica attachments [15,16], was explored with butane sulfonic acid and octane sulfonic acid. The study of the degradation behavior of all these sulfonic acids enabled us to make specific comparisons about stability of the carbon–sulfur bond and its dependence on its immediate chemical environment.

2. Experimental

2.1. Materials

The trimethylbenzene sulfonic acid, trinitrosulfonic acid, benzenesulfonic acid, cyclohexane sulfonic acid, sodium butane sulfonate, sodium octane sulfonate, and deuterium oxide were purchased from Sigma-Aldrich. Hydrochloric acid was purchased from Fisher Scientific. All chemicals were used without further purification. The starting compounds were acidified if they were in the salt form by adding an equivalent molar amount of HCl to the salt.

Each sulfonic acid was placed into a Parr reactor at 160 °C at a 100 mmol/g concentration in D₂O for initial hydrothermal treatment and it was also used to verify safety of the chemical (some compounds created significant pressures when heated). The trinitrobenzenesulfonic acid caused the greatest safety concerns as it needed to be vented during the hydrothermal testing to ensure safe operating conditions. If the compound did not generate pressure, it was subsequently placed in Altech glass vials for testing at 130 °C and 100 °C. In this way, all the compounds were tested at the three different temperatures. Samples were taken at time points of 0 (when the Parr reactor reached the desired temperature, ramp rate of 10 °C/min), 1, 6, 12, 18, and 24 h. Solution NMR was used for species identification.

Since the sulfonic acids with a benzene backbone generated a solid via carbonization, elemental analysis was done on both the liquid filtrate and the solid to determine the amount of sulfur in each. To prevent the solids from interfering with solution NMR, the resulting sample was filtered with a 0.2 μm filter before analysis. The filtrate and solids were analyzed via elemental analysis, ICP-AES, and XPS to determine the amount and oxidation number of sulfur left in each phase.

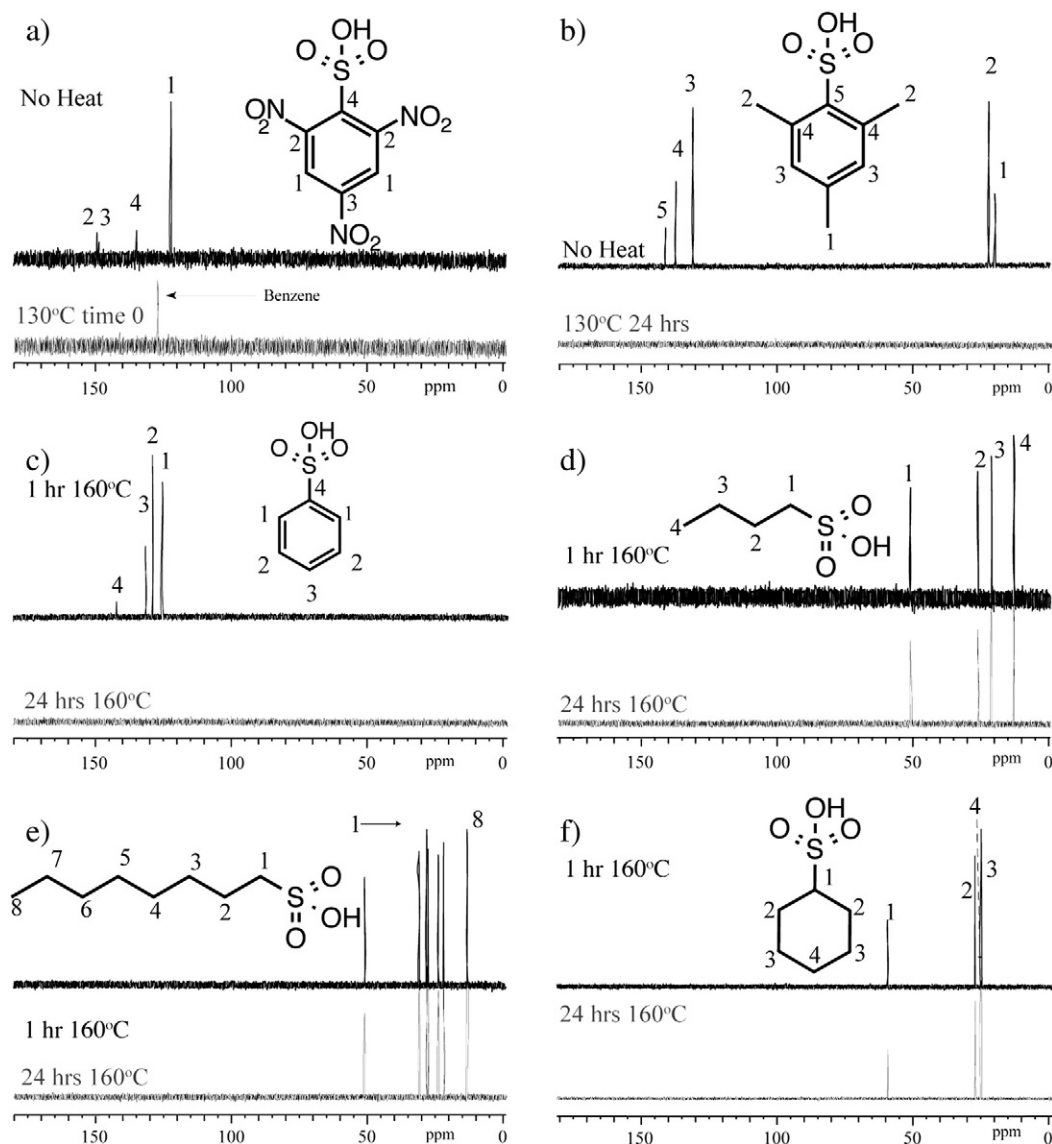


Fig. 1. Solution ¹³C NMR spectra of (a–c) aromatic sulfonic acid compounds and alkyl sulfonic acid molecules (d–f). The black spectrum (top) is from the un-transformed molecule and the red (bottom) is the spectrum showing breakdown at the mildest condition (if any).

Download English Version:

<https://daneshyari.com/en/article/49603>

Download Persian Version:

<https://daneshyari.com/article/49603>

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