



Thermodynamic complexity of sulfated zirconia catalysts



Naiwang Liu^{a,b}, Xiaofeng Guo^c, Alexandra Navrotsky^{b,*}, Li Shi^{a,*}, Di Wu^{d,*}

^aState Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

^bPeter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California, Davis, One Shields Avenue, Davis, CA 95616, United States

^cEarth System Observations, Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM 87545, United States

^dThe Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99163, United States

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ABSTRACT

A series of sulfated zirconia (SZ) catalysts were synthesized by immersion of amorphous zirconium hydroxide in sulfuric acid of various concentrations (1–5 N). These samples were fully characterized by X-ray diffraction (XRD), thermogravimetric analysis and mass spectrometry (TGA-MS), and aqueous sulfuric acid immersion and high temperature oxide melt solution calorimetry. We investigated the enthalpies of the complex interactions between sulfur species and the zirconia surface (ΔH_{SZ}) for the sulfated zirconia precursor (SZP), ranging from -109.46 ± 7.33 (1 N) to -42.50 ± 0.89 (4 N) kJ/mol S. ΔH_{SZ} appears to be a roughly exponential function of sulfuric acid concentration. On the other hand, the enthalpy of SZ formation (ΔH_f), becomes more exothermic linearly as sulfur surface coverage increases, from -147.90 ± 4.16 (2.14 nm^{-2}) to -317.03 ± 4.20 (2.29 nm^{-2}) kJ/mol S, indicating formation of energetically more stable polysulfate species.

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1. Introduction

Heterogeneous catalysis plays a critical role in modern chemical industry. Unless the catalytic active components are stabilized through subtle, thermodynamically favorable interactions on a substrate they are generally not robust for industrial applications [1]. Well-known examples include supported metal nanoclusters [2] and dispersed super-acidic moieties [3]. Thus, knowing the strength of interactions and bonding between molecular-level active catalytic species and support materials is of great importance for understanding and optimizing parameters for successful catalyst synthesis and operation.

Because of its very strong surface acidity, sulfated zirconia (SZ) has been applied extensively in the chemical industry as an acid catalyst [4]. Applications include isomerization [5], hydrocracking [6], alkylation [7,8] and oligomerization of hydrocarbons [9]. Numerous experimental (spectroscopy, diffraction and microscopy) [10–14] and computational (density functional theory and molecular dynamics) [15,16] studies have been performed to explore the specific binding, surface assembly and/or structure, and catalytic activity of SZ. However, few studies have investigated the energetics of SZ materials, including sulfur species – zirconia

interactions in aqueous solutions during catalyst precursor (SZP) synthesis (enthalpy of immersion of zirconia in sulfuric acid), the material phase evolution during calcination, and the energetics of formation of the as-made SZ catalyst.

In this context, calorimetry is a powerful tool to probe the interactions and bonding energetics on surfaces or at interfaces. Recently, we have performed a series of systematic thermochemical studies on small molecule – surface interactions using immersion, solution and/or gas adsorption calorimetry [17–21]. In addition, the bonding energetics of CO₂ [22,23], CH₄ [24], water, ethanol [25], N,N-dimethylformamide (DMF) and N,N-diethylformamide (DEF) [26] was also investigated for various metal–organic frameworks (MOFs). Most of these bonding or interaction enthalpies were found to be functions of adsorbate molecule coverage.

Here, we take a similar approach to evaluate interactions in the SZ catalyst. Combining sulfuric acid immersion calorimetry, high temperature oxide melt solution calorimetry, and thermogravimetric analysis and mass spectrometry (TGA-MS), we determined the magnitude of sulfur species – zirconia surface interactions (enthalpy of immersion) under SZP synthesis conditions at room temperature. Additionally, we identified two groups of energetically distinct sulfur species adsorbed on the SZP surface. Further, we quantified the enthalpies of SZ formation (ΔH_f) from constituent oxides. These energetics were determined, interpreted and discussed as functions of sample treatment temperature, sul-

* Corresponding authors.

E-mail addresses: anavrotsky@ucdavis.edu (A. Navrotsky), yushi@cust.edu.cn (L. Shi), d.wu@wsu.edu (D. Wu).

furic acid concentration, and sulfur species coverage. These measurements provide thermodynamic insights for sulfation of zirconia surfaces in both catalytic material synthesis and applications.

2. Materials and methods

2.1. Synthesis of sulfated zirconia (SZ)

Zirconium hydroxide (Z) was synthesized via a sol-gel method. Ammonium hydroxide solution (~25% v/v) was dripped into zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) aqueous solution kept at 60 °C under vigorous stirring until the pH reached 8.0. This solution was aged at room temperature for 12 h followed by filtration. The precipitation, zirconium hydroxide, was collected and washed 5 times to maximize chloride ion removal. The dried zirconium hydroxide powder was then subjected to sulfation immersion/impregnation for 1 h, in which sulfuric acid solutions of different concentration from 1 to 5 N were used. After another round of filtration and drying, we obtained the sulfated zirconia precursor (SZP). The final product, sulfated zirconia (SZ) was achieved through calcination of SZP at 650 °C in air for 2 h. For clarity, the final treatment temperature is marked after each sample name in the tables. Hence, the zirconium hydroxide, sulfated zirconia precursor and sulfated zirconia were denoted with temperature labeled as Z-25, SZP-25 and SZ-650.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were collected using a Bruker-AXS-D8 Advance diffractometer (Bruker, AXS, Inc., Madison, WI) operated at 40 kV and 40 mA (Cu K α , $\lambda = 0.15406$ nm). Data were acquired in the 2θ range of 20–70° (step size 0.02° and 1 s per step). The sample phase distribution and crystallite size were quantified by Rietveld refinement using JADE 6.1 software.

The Brunauer-Emmett-Teller (BET) surface areas were measured using a Gemini 2360 instrument (Micromeritics, Norcross, GA). Prior to BET analysis, samples were degassed at 200 °C under vacuum for 12 h. All the measurements were triplicated to ensure reproducibility.

2.3. Thermogravimetric analysis and mass spectrometry (TGA-MS)

Thermogravimetric analysis (TGA) was carried out using a Netzsch STA 449 instrument (Netzsch, Selb, Germany). About 20 mg sample was pressed into a pellet and heated from 30 to 1000 °C (10 °C/min) under argon flow (40 mL/min). The evolved gas was introduced into a mass spectrometer (Cirrus-2, MKS Instruments UK Ltd., Crewe, UK) through a capillary tube heated at 100 °C. Each TGA-MS analysis was corrected by recording a baseline with empty platinum crucible. The mass spectrometer was calibrated using calcium oxalate monohydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), which has known water content.

2.4. Immersion calorimetry

The immersion enthalpies of zirconia in sulfuric acid solutions (1–5 N) were measured using a Setaram C80 microcalorimeter (Setaram Instrumentation, Caluire, France) equipped with a custom-made dropping tube. Each sample was hand-pressed into a pellet (about 10 mg), weighed on a microbalance, and dropped from room temperature into the solution at 25 °C. The drop resulted in a heat effect (calorimetric peak) associated with the reaction between the solid sample and the solution. Immersion calorimetry on each sample was repeated at least eight times to ensure reproducibility, which is shown as error bars (2 standard

deviations of the mean) in the figures. Prior to immersion calorimetry, samples were outgassed at 200 °C overnight to maximize removal of adsorbed species.

2.5. High temperature oxide melt solution calorimetry

The drop solution enthalpies of all samples in molten sodium molybdate ($3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$) at 703 °C were measured using a custom-made Tian-Calvet twin microcalorimeter. The detailed methodology was described elsewhere [27]. Sample pellets (~5 mg) were hand-pressed and dropped from ambient conditions into the solvent in a platinum crucible in the hot calorimeter. The calorimetric assembly was flushed using oxygen (50 mL/min) to maintain oxidizing environment and the solvent was bubbled with oxygen (0.5 mL/min) to promote sample dissolution and to propel evolved gases. All samples were degassed at 200 °C overnight before calorimetric measurement. The calorimeter was calibrated using the known heat content of high purity alpha alumina (Alfa Aesar, 99.997%). The thermodynamic cycles used to derive the enthalpy of SZ formation (ΔH_f) are listed in Table 1.

2.6. Catalytic activity test

An alkylation reaction in which olefins react with aromatics leading to reduced olefin concentration in aromatic liquids (Scheme 1) [31] was employed to test the catalytic activity of SZ treated in different conditions. Alkylation was carried out in a fixed bed tubular micro-reactor equipped with a constant flow pump to enable precise flow rate and temperature control. Catalyst (SZ, 2 mL) was loaded into the micro-reactor, the spare space of which was filled with quartz sand (space filler). The tests were performed at 1.0 MPa with a liquid hourly space velocity (LHSV) of 30 h⁻¹ [32]. Bromine Index is an indicator of olefin content in aromatics. According to ASTM standard D 2710-92, it is defined as the amount of bromine (mg) consumed by 100 g of hydrocarbon. The inlet and effluent liquids of the fixed bed tubular micro-reactor were monitored by a Bromine Index Analyzer (OSC 971KK 101, Ogawa Seiki Co., Ltd., Tokyo, Japan). The olefin conversion rate, X , was calculated as $X = (N_i - N_o)/N_i \times 100\%$, in which N_i and N_o correspond to the bromine index of the inlet and effluent liquids, respectively. The specific olefin and aromatic compounds involving in the alkylation reactions and their contents are listed in Table 2 [32].

Table 1
Thermodynamic cycles for enthalpies of SZ formation, ΔH_f .

Reaction formula ^a	Reaction enthalpy
$\text{ZrO}_2 \cdot x\text{SO}_3 \cdot y\text{H}_2\text{O}$ (tetragonal/ads/ads, 25 °C) \rightarrow ZrO_2 (sol, 703 °C) + $y\text{H}_2\text{O}$ (g, 703 °C) + $x\text{SO}_3$ (sol, 703 °C) ^b	ΔH_{ds}
ZrO_2 (tetragonal, 25 °C) \rightarrow ZrO_2 (sol, 703 °C)	ΔH_1^c
H_2O (ads, 25 °C) \rightarrow H_2O (g, 25 °C)	ΔH_2^d
H_2O (g, 25 °C) \rightarrow H_2O (g, 703 °C)	ΔH_3^e
SO_3 (g, 25 °C) \rightarrow SO_3 (sol, 703 °C)	ΔH_4^f
SO_3 (ads, 25 °C) \rightarrow SO_3 (g, 25 °C)	ΔH_f
$\Delta H_f = \Delta H_{ds} - \Delta H_1 - \Delta H_2 - \Delta H_3 - \Delta H_4$	

^a “g”, “ads” and “sol” denote “gas”, “adsorption” and “in sodium molybdate solution”, respectively.

^b Ref. Majzlan et al. [28] and Drouet and Navrotsky [29].

^c ΔH_{ds} and ΔH_1 ($\Delta H_1 = 27.06 \pm 0.71$ kJ/mol ZrO_2 [30]) are drop solution enthalpies of sulfated zirconia (SZ) and nanophase tetragonal zirconia obtained using high temperature oxide melt solution calorimetry, respectively.

^d ΔH_2 is enthalpy of H_2O adsorption on sulfated zirconia surface.

^e $\Delta H_3 = 25.65$ kJ/mol H_2O [30].

^f ΔH_4 is drop solution enthalpy for SO_3 , and it cannot be determined directly experimentally but has been calculated from the formation enthalpies of SO_2 and O_2 . According to previous work, $\Delta H_4 = -217.02 \pm 4.17$ kJ/mol [28].

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