Quantitative Sulfur Determination in SBA-15 Supported Sulfonic Acid Catalysts

Kaijin Li1, Alex Engler1, Yu Noda1, and Robert Rioux2,a
1Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802 USA
2Department of Chemistry, The Pennsylvania State University, University Park, PA 16802 USA
rioux@engr.psu.edu

Introduction
Catalyst supports and adsorbents are among the important applications that mesoporous silica materials impact, owing to their high surface area, large and symmetrical pore space, as well as high thermal stability even in the presence of water [1]. Reaction of suitable reagent with surface silanol (Si-OH) groups, one can achieve covalent grafting of ligands and functional groups onto mesoporous silica [2]. One such example is the grafting of thiol moiety; the thiol-grafted silica exhibited superior adsorption capacity of heavy metal ions compared with the original silica [3]. Mesoporous silica with supported sulfonic acids created by the oxidation of the grafted thiol [4], serve as viable solid acid catalysts for biomass-relevant conversion chemistry [5]. In order to precisely evaluate the efficiency of active sites of these grafted sulfonic acid catalysts, it is critical to quantitatively determine the different types of grafted surface functional groups (such as -SH, -SO2H, -OH, disulfides (S–S)) that exist on the catalyst surface after grafted thiol groups are oxidized to sulfonic acid groups. It is critical to determine the efficiency (extent and selectivity) of the surface oxidation of thiols to sulfonic acid groups since knowledge of the surface density of sulfonic acids enables rigorous normalization of the reaction rate, and work by Davis and co-workers have demonstrated that bifunctional thiol/sulfonic acid catalysts are more active and selective than sulfonic acid only catalysts [6]. Therefore, the determination of extent of grafted thiol oxidation is critical to determining the number of sulfonic acid groups and the possibility of cooperative catalysis. However, we still lack such comprehensive characterization technique developed for mesoporous silica-supported sulfonic acid catalysts.

This study provides a comprehensive set of analytical techniques for qualitatively characterizing the functional groups on the surface during the each step of the preparation of sulfonic acid grafted SBA-15 catalysts.

Materials and Methods
We employed the “post-oxidation” two-step preparation method to synthesize SBA-15 silica grafted sulfonic acid catalysts. In this method, the silica support was first treated with mercaptopropyltrimethoxysilane (MPTMS) for grafting thiol moieties, and then in the second step this grafted thiol groups were converted to sulfonic acid by oxidation in the treatment with H2O2 as an oxidant. A comprehensive characterization of samples at each preparation step was performed with titration with Ellman’s reagent for thiol content and acid-base titration for sulfonic acid content. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was also utilized to quantify the total sulfur content into the oxidation supernatant and the silica. Different grafting conditions and oxidation conditions were explored during preparation to investigate their influence on the composition of the surface functional groups.

Results and Discussion
Figure 1 is the result of sulfur determination in the grafted SBA-15 samples. Titration with Ellman’s reagent confirmed the successful grafting of thiol groups onto the SBA-15 surface with ~0.79 mmol/g. After the oxidation (A) process, treatment with 30 wt. % H2O2 at RT for overnight, no thiol was left on the surface. Acid-base titration of the solid sample detected ~0.31 mmol/g of acid, corresponding to ~39% of the initial sulfur grafted. On the other hand, ICP analysis of the used oxidation solution revealed the similar amount of sulfur (~39%) was leached out into the solution during the oxidation (A). The treatment with diluted H2O2 (0.5 wt. %) – “oxidation (B)” – was able to convert ~85% of –SH groups of the surface with substantially suppressed leaching (only <4%). However, it did not generate sulfonic acid, and ~81% of initially grafted sulfur as thiol remained unidentified. We hypothesize sulfur exists on the surface as disulfide or some weaker acids such as sulfinic acid, which could still be converted to sulfonic acid. Therefore, the second oxidation (C) with 30 wt. % H2O2 was carried out for this sample after (B), and the characterization result proved the presence of sulfonic acid (~32%), although the sulfur leaching remains to be the issue with this strong oxidation process.

Figure 1. Sulfur content in the thiol- and sulfonic acid-grafted SBA-15 catalysts determined with Ellman’s titration, acid-base titration, and ICP techniques.

Significance
The study established a quantitative multi-titration technique to determine the sulfur content of sulfonic acid grafted SBA-15, revealing a substantial leaching of grafted sulfur during the oxidation process. This demonstrated set of analysis techniques will be useful in improving the understanding of active sites of the sulfur grafted catalysts through their proper quantitation.

References