

Temperature-Dependent Evolution Study of Sulfated Metal Catalysts Using FTIR Spectroscopy

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21 July 2017
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Abstract — Sulfated metal oxide catalysts have many industrial applications, including the conversion of ethanol to ethylene, which allows for a more environmentally safe method to produce ethylene. Current catalysts used to facilitate those reactions are either environmentally destructive, costly or exceptionally precarious to handle. However, there is limited research in infrared spectroscopy of these catalysts, which can shed light on some important properties. This paper presents the methods, goals and purposes for examining the structure and bonds of the sulfates on the metal oxides. Fourier Transform Infrared Spectroscopy (FTIR) was used to obtain spectra for sulfated zirconia and a sulfated aluminum-tin catalyst with a ratio of 1 Al:4 Sn. Background and sample scans were taken for varying sets of parameters. The number of scans, optical velocity and number of scans were changed. This research can provide a set of parameters ideal for studying these catalysts which contributes to future examination of sulfated metal oxide configurations. From this study, it was concluded that the water physisorbed to the catalyst surface evaporates as temperature increases, and that data allowed the deduction that optimal temperature to use those catalysts in order to maximize efficiency and lower cost is 150°C. Also, the preferred set of parameters are 0.1581 cm/s for optical velocity, and 128 scans.

I. INTRODUCTION

Currently, reactions that pertain to organic compounds and hydrocarbons are facilitated using acid catalysts, which are acids that decreases the time a reaction takes to occur [11]. However, those catalysts are homogeneous, which requires distillation in order for them to be reused as they are dissolving into the solvent as the reaction continues, and that process of separating the catalyst from the solvent not only consumes an exorbitant amount of energy, but it is costly and not environmentally sound. On the other hand, sulfated metal oxide catalysts are economical and environmental, as well as non-corrosive as opposed to their highly acidic homogeneous

counterparts [3]-[14]. An example of a reaction that these catalysts will facilitate is the dehydration of ethanol into ethylene. While ethanol is a product of cane sugar, ethylene is derived from natural gas, and as the world shifts from fossil fuels to green energy sources, these catalysts will contribute to that transition.

As the idea of using sulfated metal oxides in order to replace currently unfeasible or expensive catalysts becomes more appealing, scientists are beginning to research the structure and reactivity of those oxides. To facilitate that analysis, the research team utilizes FTIR spectroscopy to study the configuration of sulfated zirconia and aluminum-tin [1]-[12]. The data obtained from the FTIR spectra will provide a more in-depth approach to analyzing the structures of sulfated zirconia in order to build a foundation for future researchers interested in the development of commercially feasible catalysts.

In order to utilize sulfated zirconium dioxide to its full capacity as a heterogeneous catalyst, the configuration of the SO_4^{2-} on the surface of the ZrO_2 must be known. The research team determines the types of sulfur-oxygen bonds present on the catalyst surface, using spectra taken from the FTIR spectrometer, which will contribute to the ascertainment of the structure of the sulfate ions on the surface as well as the availability of each configuration.

II. BACKGROUND

A. Sulfated Zirconia

Sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) is a metal oxide that has been treated with a solution that contains sulfate ions (SO_4^{2-}), such as H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ [1]. Initially, ZrO_2 is a weak acid, but after being impregnated with a sulfate solution, it

becomes a superacid. A property of this sort of acid is having a Hammett acidity function—the extended and more advanced version of the pH scale—larger than -11.93. Superacids, like sulfated zirconia, have several properties, including the ability to decompose or oxidize alkanes [12]. Zirconium is found in the compound FMSZ (iron, manganese, sulfur, zirconium) and enables the conversion of ethane to be possible for temperatures below 300°C [3].

This sulfated metal oxide was chosen to be evaluated because of its similarities to other previously studied catalysts like sulfated titania, which is also another superacid [1]-[15], and the sparsity of research devoted to this specific catalyst.

B. Sulfated Aluminum-Tin Oxide

Sulfated aluminum-tin oxide, similar to sulfated zirconia, is a solid acid catalyst. However, the sulfur species present on the support metal may differ from sulfated zirconia in concentrations and structure. The difference in molecular weight, coupled with the variations in sulfur group composition may allow for distinct applications of each of these catalysts [5].

C. FTIR Spectroscopy

In Fourier Transform Infrared Spectroscopy, infrared light is shined through the sample and records the amount of absorption. The spectrometer also measures the vibrational frequencies of the bonds in the form of wavenumbers, which can be used to detect the effects of intermolecular interactions [13]. For this specific study, FTIR is being used to investigate the type of sulfur-oxygen bonds present on the surface of the sulfated zirconia and sulfated aluminum-tin catalysts. The results also contribute to the determination of the structure and location of the sulfate ion in the sulfated metal oxides [2].

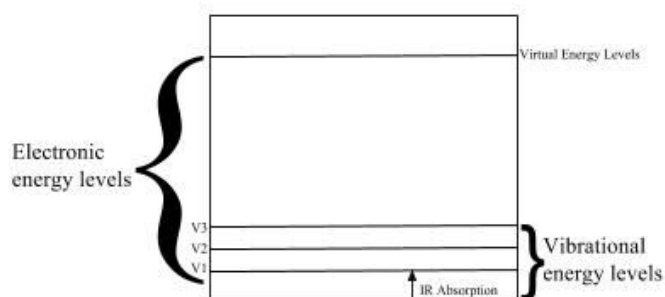


Fig. 1 Model of the vibrational energy levels in which each spectrum obtained represents in contrast to the energy levels in which electrons become excited (electronic energy levels).



Fig. 2 FTIR spectrometer used in Rutgers University's Chemical and Biochemical Engineering Department.

D. FTIR Spectroscopy Parameters

Aperture: Aperture essentially describes the amount of light that is allowed to hit the detector (a simple analogy would be to a camera) [2].

Resolution: Resolution describes the precision of the instrument in distinguishing between peaks. A higher resolution indicates that the spectrum is obtained in larger wavenumber intervals, meaning that it is less precise [2].

Number of Scans: This parameter indicates how many times the instrument will scan the indicated wavenumber range. A larger number of scans means that more values are averaged for the final spectrum. This usually means that the results will be more precise given that the curve will be smoother. However, the downside is that it takes longer to generate the spectrum [2].

Optical Velocity: Optical velocity indicates how fast the moving mirror in the instrument moves. This affects how long the scan takes to complete and how much light is transferred to the detector. At higher optical velocities, the shutter loses a significant number of photons when closed, reducing the precision of the data and increasing the signal-to-noise ratio [2].

Temperature: Temperature was controlled via an external heating plate connected to the FTIR spectrometer. As the current flowing through the resistor increases, the heat dissipated increases, along with the temperature of the sample and air [2].

D. Peaks of Sulfur Oxygen Bonds

In order to determine the configurations of the sulfate species on the metal oxide surface, each peak observed on the spectra returned by the IR spectrometer needed to be translated into a certain wavenumber and then assigned to a specific sulfur-oxygen bond. Ranges of wavenumbers and position of peaks therefore can be related to potential configurations of the sulfate on the surface of the metal, as seen in Table 1.

TABLE I
WAVENUMBERS OF BONDS PRESENT IN SULFATED METALS

Wavenumber (cm ⁻¹)	Functional group
984	V _{as} (S-O) (tridentate) ^[7,8]
999-1006	V _s (S-O)(bidentate) ^[9]
1034-1036	V _{as} (S-O) (tridentate) ^[7,8]
1061-1085	V _s (S-O) (bidentate or polymeric)
1133-1146	V _{as} (S-O)(bidentate) ^[9]
1210	V _s (O=S=O) (bidentate bridge) ^[9]
1280-1300	V _s (O=S=O) (bidentate chelating)
1357-1386	V _{as} (S=O)(tridentate) ^[7]

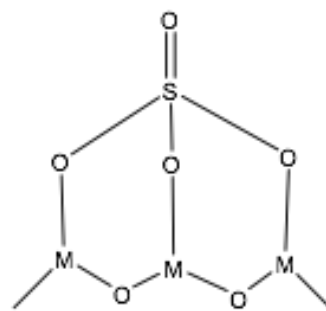


Fig. 5 Proposed structure of a tridentate sulfated group on metal oxides.

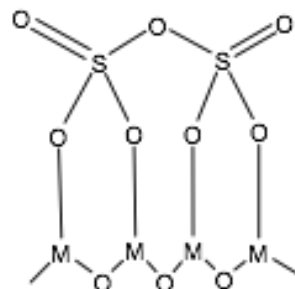


Fig. 6 Proposed structure of a polymeric sulfated group on metal oxides.

Bidentate sulfated groups are a type of the potential species present on the catalyst surface that have two oxygens bonding to the metal itself. Chelated bidentate have one metal atom in that group, as seen in Fig. 3 and Fig. 4 depicts a bridged bidentate that has two metal atoms [10]. Tridentate sulfated groups, on the other hand, have three oxygens bonded to three different metal atoms, as shown in Fig. 5. Lastly, a polymeric sulfated group is comprised of two sulfur atoms chained to a single oxygen atom, illustrated by Fig. 7.

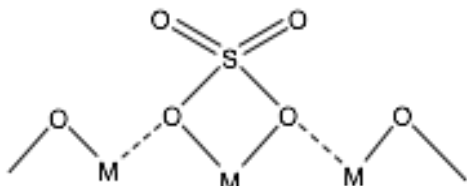


Fig. 3 Proposed configuration of a chelating bidentate sulfated group on a metal oxide.

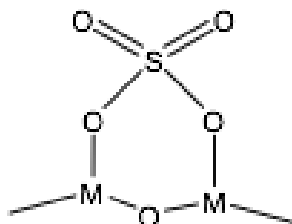


Fig. 4 Proposed configuration of a bridged bidentate sulfated group on the metal oxide.

III. PROCEDURE

A. Running the FTIR Spectrometer

The FTIR spectrometer, as seen in Fig. 2, was used to obtain the spectra of SO₄²⁻/ZrO₂ catalyst at different temperatures with varying parameters. Certain bonds were identified on the spectra of the samples by inspecting the placement of the peaks on the graphs. The changes in the wavenumbers as the temperature increased were observed and those variations were indicative of the types of interactions between H₂O and SO₄²⁻.

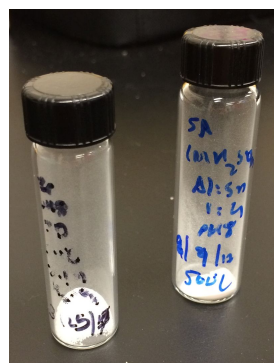


Fig. 7 The left vial contains sulfated zirconia, and the right vial contains sulfated aluminum tin oxide.

After finishing the scans of the sulfated zirconia, further spectra of the SO₄²⁻ on the surface of sulfated aluminum-tin (SO₄²⁻/Al-Sn) catalyst were collected. The optical velocity and number of scans were uniform throughout the entire scanning of the SO₄²⁻/Al-Sn, and they were chosen according to the

SO₄²⁻/ZrO₂ spectra. By increasing the temperature of the catalysts, the evolution of the sulfate species on the catalyst surface could be ascertained.

B. Parameters Used for Sulfated Zirconia and Sulfate Aluminum-Tin

Sulfated zirconia (SO₄²⁻/ZrO₂) was the first sample to be tested, and all parameters were tested excluding resolution and aperture, which were kept at 4 wavenumbers and 100%, respectively. The varied parameters are seen in Table 2.

TABLE II
PARAMETERS USED FOR SULFATED ZIRCONIA

Temperature	Optical Velocity	Number of Scans
25°C	0.1581, 0.3165, 0.4747	16, 32, 64, 128
50°C	0.1581, 0.3165, 0.4747	16, 32, 64, 128
100°C	0.1581	16
150°C	0.1581, 0.3165, 0.4747	16, 32, 64, 128
200°C	0.1581	16
250°C	0.1581	16

For sulfated aluminum-tin, the temperature at which the sample was tested varied, while optical velocity and number of scans were kept constant at the preferred set of parameters that were determined after analyzing the spectra from sulfated zirconia.

IV. RESULTS AND ANALYSIS

A. Spectra of Sulfated Zirconia

By varying optical velocity and number of scans, as seen in Table 2, the best set of parameters to run spectra on were determined. The temperature range allowed the researchers to evaluate how the presence of moisture on the surface of the catalyst affected the sulfur-oxygen bonds, and how the configurations of the sulfate species and the properties of the metal would change with temperature increases.

The different optical velocities and the graphs the spectra returned are displayed together in Fig. 8. The spectrum with an optical velocity of 0.4747 exhibited the most noise, which is the effect of the velocity of the moving mirror. The less noise results in a clearer graph with more defined peaks. Though an optical velocity of 0.3165 has less interference from the surroundings than 0.4747, best results were obtained with an optical velocity of 0.1581 cm/s returned the most continuous spectrum with the least noise. The optimal optical velocity, therefore, is 0.1581 cm/s.

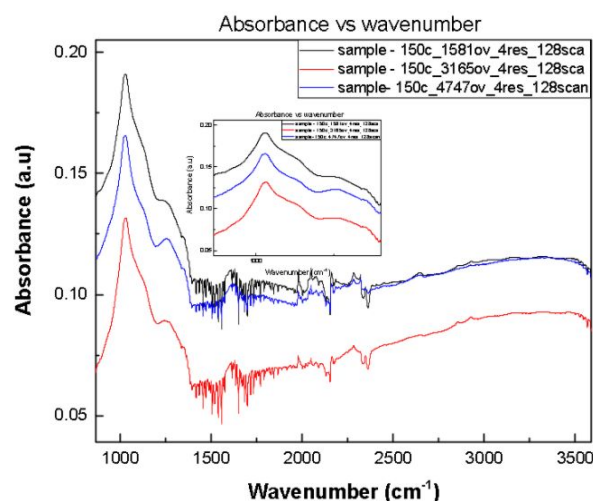


Fig. 8 FTIR spectra of sulfated zirconia at 150°C with constant scans and different optical velocity.

After contrasting spectra with alternating number of scans, it was deduced that the number of scans has a limited effect on the graphs, as seen in Fig. 9. However, it can be reasoned that with more scans in one reading, more data points can be collected and will result in better signal to noise ratios.; that logic allowed the research team to conclude that for the optimal graph, 128 scans should be used. It is important to note, however, that if a reaction, or any sample that changes over time, is being analyzed, the number of scans can be decreased to adjust the time in which the spectrometer returns the spectra. On the other hand, it is not recommended that the optical velocity be increased, despite the decrease in return time, because of the rapid deterioration in the quality of the spectra. The 0.1581 cm/s for preferred optical velocity was chosen from Fig. 8, and the 128 scans was established at optimal number of scans because of the logic that the larger the number of scans, the more data and the better the spectra. In conclusion, the optimal optical velocity and number of scans to use are 0.1581 cm/s and 128 scans.

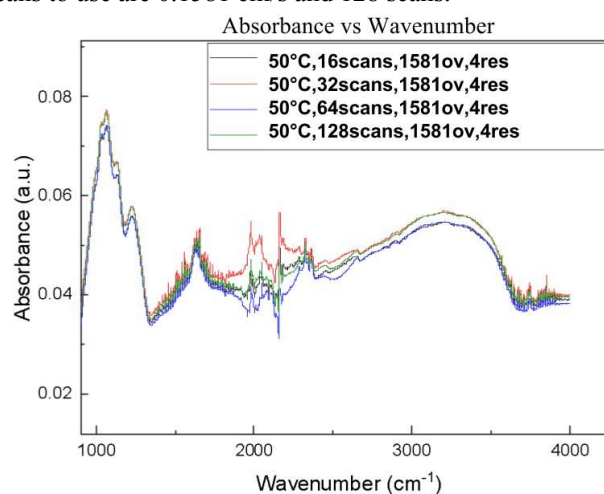


Fig. 9 FTIR spectra of sulfated zirconia at 50°C with constant optical velocity and differing number of scans.

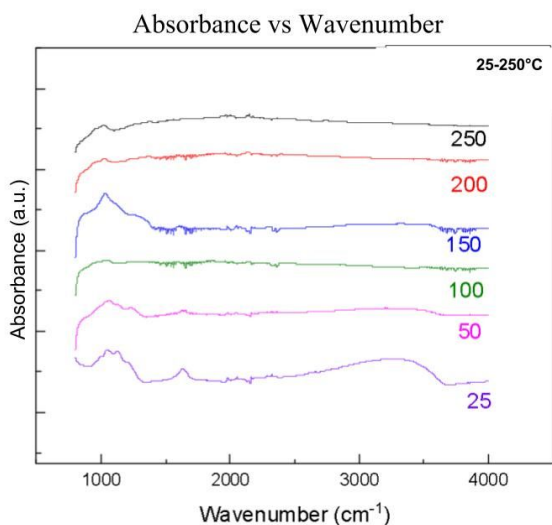


Fig. 10 FTIR spectra of sulfated zirconia at optimal optical velocity and number of scans, with varying temperatures.

Using the optimal parameters, Fig. 10 is the compilation of all the spectra of $\text{SO}_4^{2-}/\text{ZrO}_2$ at a range of temperatures. In the 25°C spectrum, a large peak is seen between 3000 cm^{-1} and 3500 cm^{-1} [6], and that is indicative of the presence of water bonded to the sulfate on the surface of the zirconia. Although the sample of sulfated zirconia was calcined, at room temperature, the moisture in the air easily bonds to the oxygens of the sulfates on the zirconia, and results in a hydrated sample. As the temperature increases, the peak for water diminishes in intensity with respect to the magnitude of the sulfur-oxygen bond present at around 1000 cm^{-1} . Also, the peak that represents the sulfur-oxygen bond shifts right as the temperature increases. That shift indicates that the water that evaporated was bonded to the oxygen, because when water adsorbs to it, the bond's vibration is hindered by the additional anchor and therefore the wavenumber would be lower than it should be.

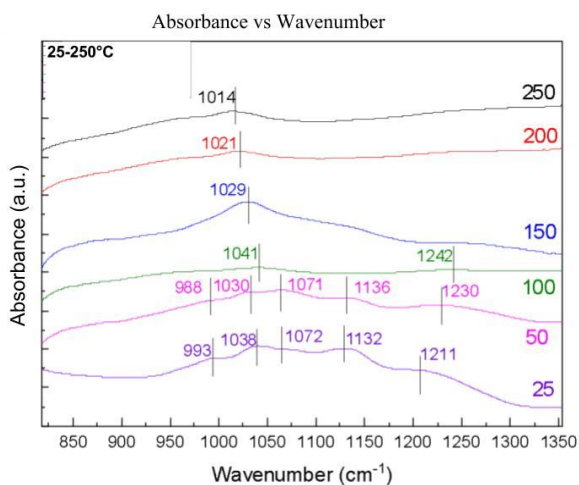


Fig. 11 FTIR spectra of sulfated zirconia at optimal optical velocity and number of scans, with a range of temperatures.

In Fig. 11, a large difference in absorbance can be seen between the different temperatures, and that is caused by the inconsistency of the contact between the anvil of the spectrometer and the sample.

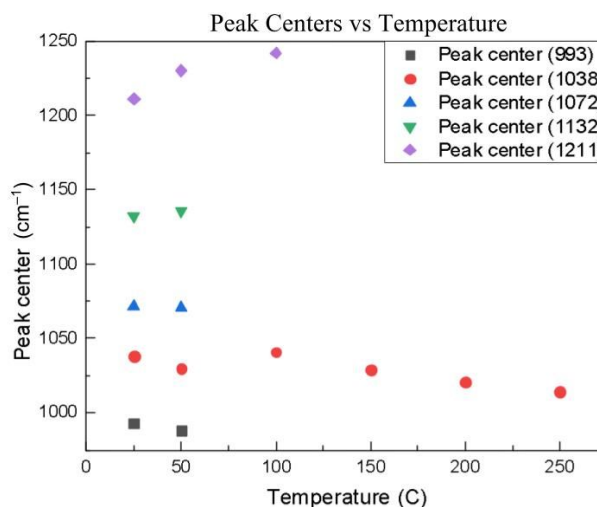


Fig. 12 Differences of how the peak centers change as temperature increases.

After examining the different spectra of $\text{SO}_4^{2-}/\text{ZrO}_2$, peaks and their wavenumbers were determined, and how each changed as temperature increased was graphed in Fig. 12. All of the assignments from wavenumber and peak to bonds are listed in Table 4. Many of the peaks were no longer exhibited as the temperature increased, which led the research team to believe that the properties of the sample changed dramatically along with the temperature. The blue plotted points have a wavenumber that can be assigned to an O–S–O bond and as temperature went beyond 50°C, it is possible that that peak merged with another vibrational mode. Since an increase in temperature also resulted in the dehydration of the sample, it was postulated that peaks that shifted right were the representatives of bonds that were affected by the presence of water. For example, the peak center that is represented by the purple points shifted up from 25°C to 100°C has the wavenumber range of the sulfate configuration depicted in Fig. 5. Then, that peak either merged with another peak or disappeared entirely as the temperature increased beyond 100°C, which could be because of the changes in the structure of the surface sulfate species in accordance to temperature. A close up view of how the peak changed can be found in Fig. 13.

TABLE IV
ASSIGNMENTS OF BONDS TO WAVENUMBERS FOR SULFATED ZIRCONIA^A

Wavenumber (cm ⁻¹)	Functional group	Wavenumbers Present in Our Spectra
984	$V_{as}(\text{S-O})$ (tridentate) ^[7,8]	988 (50°C)
999-1006	$V_s(\text{S-O})$ (bidentate) ^[9]	993 (25°C)

Wavenumber (cm ⁻¹)	Functional group	Wavenumbers Present in Our Spectra
1034-1036	V _{as} (S-O) (tridentate) ^[7,8]	1038 (25°C), 1030 (50°C), 1041 (100°C), 1029 (150°C), 1021 (200°C), 1014 (250°C)
1061-1085	V _s (S-O) (bidentate or polymeric)	1072 (25°C), 1071 (50°C)
1133-1146	V _{as} (S-O)(bidentate) ^[9]	1132 (25°C), 1136 (50°C)
1210	V _s (O=S=O) (bidentate bridge) ^[9]	1211 (25°C), 1230 (50°C), 1242 (100°C)

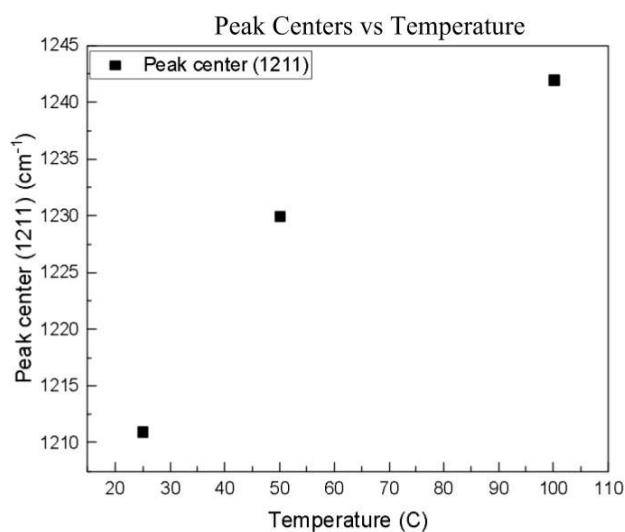


Fig. 13 Temperature-dependent changes in wavenumber for a specific peak found in the spectra of sulfated zirconia.

B. Spectra of Sulfated Aluminum-Tin

FTIR spectra of sulfated aluminum and tin were taken with a constant set of parameters with the exception of temperature, as indicated in Table 4. These ideal parameters were chosen because of their efficacy in producing clear spectra for sulfated zirconia. Fig. 14 shows all of the spectra of sulfated aluminum-tin taken. The prominent peak around 3500 cm⁻¹ indicates the presence of physisorbed water in the sample, since it is the symmetric stretching mode of water. The intensity of this peak diminishes with respect to the intensity of the sulfur-oxygen peak present at 1030 cm⁻¹, showing the evaporation of water at higher temperatures. As water evaporates, its characteristic vibrational modes become less apparent in the spectra.

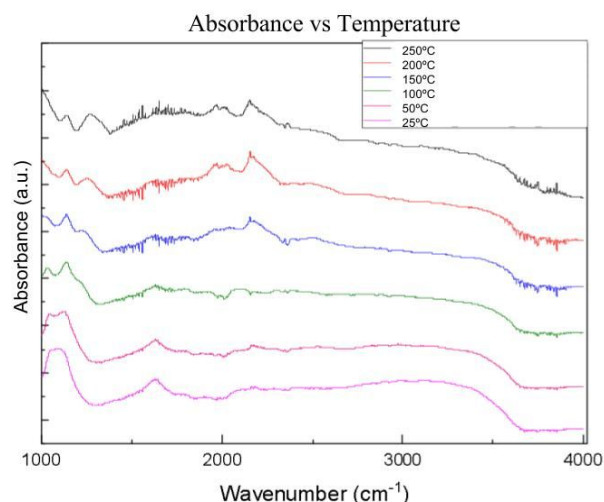


Fig. 14 FTIR spectra of sulfated aluminum-tin at optimal optical velocity and number of scans, with varying temperatures.

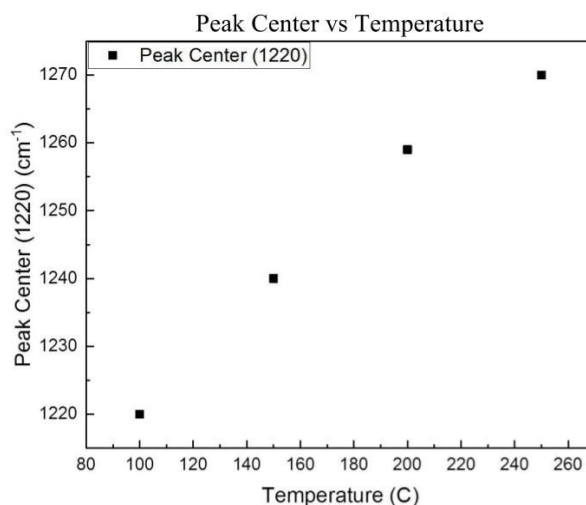


Fig. 15 Temperature-dependent changes in wavenumber for one peak found in the spectra of sulfated aluminum-tin.

At higher temperatures, the wavenumber of the S-O bond increased. It is postulated that this is due to the evaporation of water and decreased intermolecular hydrogen bonding. With less of this interaction from physisorbed water, the S-O bond was able to oscillate at a nearly unimpeded wavenumber. Fig. 15 indicates the quantitative shift in the wavenumber of the peak center with respect to temperature for the S-O bond.

Although there are many types of bonds (and therefore possible vibrational modes and wavenumbers) present in sulfated aluminum tin, we did not clearly observe all of them. Through the analysis of spectra, summarized in fig. 16, we were able to identify the species present in the sulfated aluminum-tin.

TABLE IV
ASSIGNMENTS OF BONDS TO WAVENUMBERS FOR SULFATED ALUMINUM-TIN^A

Wavenumber (cm ⁻¹)	Functional group	Wavenumbers Present in Our Spectra
984	V _{as} (S-O) (tridentate) ^[7,8]	967 (250°C), 970 (25°C, 50°C, 100°C, 150°C, 200°C)
1034-1036	V _{as} (S-O) (tridentate) ^[7,8]	1048 (100°C), 1047 (25°C, 50°C)
1133-1146	V _{as} (S-O)(bidentate) ^[9]	1142 (250°C), 1140 (25°C, 50°C, 100°C, 150°C, 200°C)
1210	V _s (O=S=O) (bidentate bridge) ^[9]	1270 (250°C), 1259(25°C, 50°C, 100°C, 150°C, 200°C)
1280-1300	V _s (O=S=O) (bidentate chelating)	1270 (250°C), 1259 (25°C, 50°C, 100°C, 150°C, 200°C)

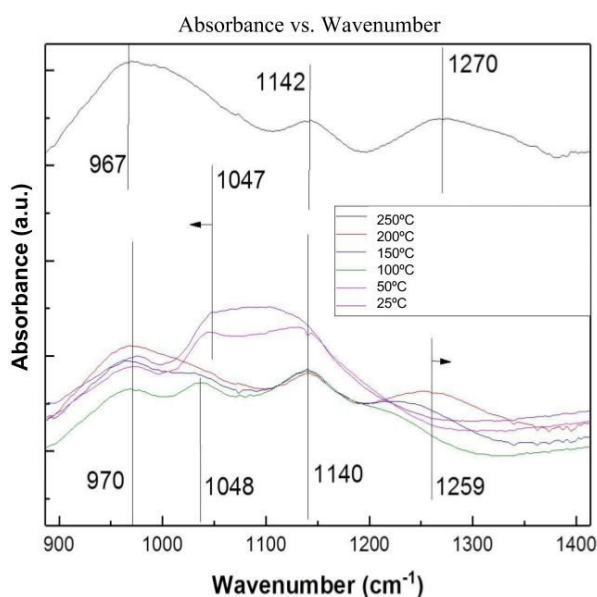


Fig. 16 Labeled peaks and temperature-dependent shifts for sulfated aluminum-tin.

C. Comparison of Sulfated Zirconia and Sulfated Aluminum-Tin

The sulfated aluminum-tin spectra provided evidence for how sulfate species might change using different metal oxide supports. The different chemical properties between the two compounds, such as composition of elements and atomic mass, should affect the sulfate species and how it is displayed in the spectra. With the help of targeted experiments and peak differences, it will be possible to determine the efficiency of the catalyst in terms of its reactivity and acidity. For example, future experiments may help to understand or tune the concentration of a particular type of configuration on the mixed metal oxide support of aluminum-tin, which might

work as a better catalyst than sulfated zirconia in certain reactions. Moreover, the spectra provide a foundation for future studies related to the active sites of the sulfated species.

At higher temperatures, the bonds were seen to either increase or decrease in wavenumber for each sulfated metal oxide. For example, the bonds seen in Fig 17. at 50°C are no longer visible at 150°C in Fig. 18. However, the sulfated aluminum-tin continued to show four peaks in the spectra. This demonstrated that, at 150°C, the zirconia experienced a structural reconfiguration while the aluminum-tin's structure remained intact. Similarities between the spectra allowed for the researchers to infer about what bonds were observed. The two spectra from Fig. 17 both have peaks at 1133 cm⁻¹. It is reasonable to assume that this peak is related to the O-S-O bond that occurs at 1147 cm⁻¹.

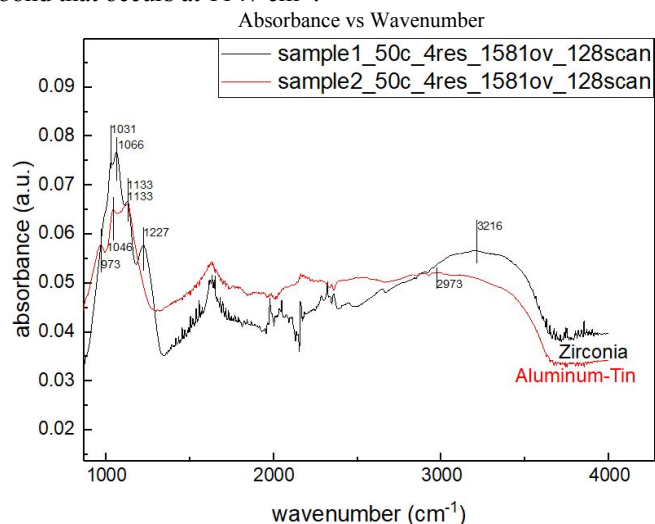


Fig. 17 Differentiating the spectra of sulfated zirconia and sulfated aluminum-tin at 50°C.

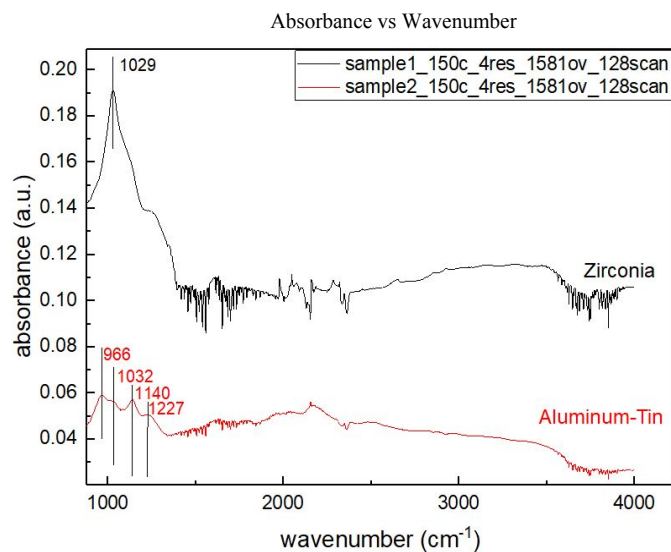


Fig. 18 Differentiating the spectra of sulfated zirconia and sulfated aluminum-tin at 150°C.

D. Effect of Temperature on Physisorbed Water

In order to study the effect of physisorbed water, the peak between 3400-3500 cm^{-1} was analyzed in greater detail. The ratio of the area under this water peak to the area under S-O peaks was determined. Since the S-O peaks are found in the region between 900-1350 and converts from one form to another as a function of temperature, a direct ratio of intensity of water band to the intensity of a particular S-O band does not give comparable results. Therefore, the ratio of the area of water band and the area between 905-1344 cm^{-1} is used for comparing the effect of temperature on physisorbed water to merge the intensities of all sulfur peaks. This analysis is done for both catalysts and plotted in Figure 19. It was observed that the ratio falls sharply as a function of temperature from room temperature to 150 $^{\circ}$ C after which it plateaus. This indicates that at 150 $^{\circ}$ C, all the physisorbed water is ejected.

Since spectra for both samples show the evaporation of water, the minimum temperature that results in the most efficient catalyst that is not hindered by water can be established. As seen in Fig. 19, the ratio of the absorbance of water to the absorbance of the sulfur-oxygen bonds present decreases when temperature increases for both samples. However, the ratio for sulfated Al-Sn is never smaller than 1, unlike how the ratio for sulfated ZrO₂ reaches 0.5, and this indicates that the water physisorbed onto the Al-Sn surface did not evaporate as easily as the water on the zirconia did. Fig. 19 also demonstrates that at around 150 $^{\circ}$ C, both catalysts are functioning at their full potential without much interference from water.

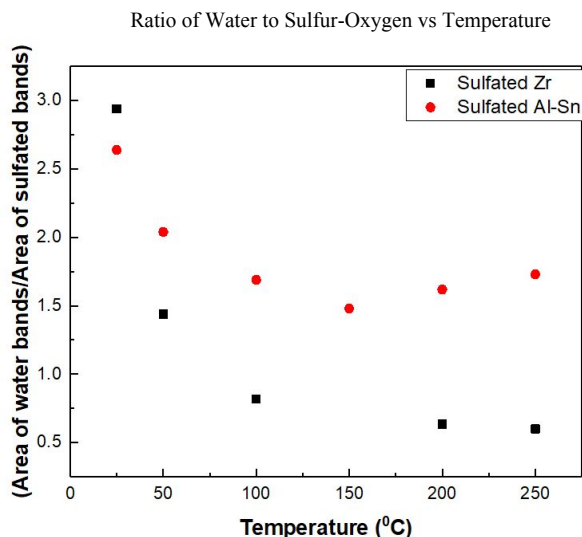


Fig. 19 A comparison of the vibration of water molecules to the sulfur-oxygen bonds in sulfated zirconia and aluminum-tin.

V. CONCLUSION

The study of both sulfated zirconia and aluminum-tin oxide catalysts resulted in the determination of optimal parameters and the bonds present in each catalyst, and the trend of certain

peaks and their wavenumbers as temperature increases. Despite the long return time of 0.1581 cm/s, the poor quality spectra returned by other optical velocities led us to use that setting. The other parameters, excluding temperature, had little to no effect on the derived spectra, so their values were trivial. In order to improve the spectra, the setting of 128 scans was chosen; for future non-time-dependent experiments this would be a favorable setting.

Temperature was found to affect the amount of water physisorbed onto all of the catalysts. The research team concluded this based on the change in wavenumber(s) associated with certain bonds. At higher temperatures, the wavenumbers associated with the S-O bond starts becoming more apparent, indicating less dampening caused by intermolecular hydrogen bonding. The wavenumber(s) did not increase without bound, however; they appeared to plateau at 1247 cm^{-1} as temperature was increased, which possibly signifies the natural vibration for an S=O bond. After examining how the intensity of the water peaks change relative to the intensity of the sulfur-oxygen bond peaks, it was concluded that the temperature in which each catalyst should be used in order to obtain the highest efficiency with the lowest cost is 150 $^{\circ}$ C.

ACKNOWLEDGEMENTS

This research project could not have been completed without the help of many, so the researchers would like to extend their gratitude to those that made it possible. The authors would like to thank Dr. Georgios Tsilomelekis for his guidance and support throughout this project. They would also like to recognize graduate students Pranav Ramesh and Shreyas Acharya for their assistance. The authors would like to thank Tiffany Yang, the Residential Teaching Assistant who oversaw the project. They also express thanks for Residential Teaching Assistant Jaimie Swartz for her assistance in the research process and in reviewing this paper as well as the other Residential Teaching Assistants for their hard work and dedication. In addition, they wish to express their appreciation toward the New Jersey Governor's School of Engineering and Technology, the Director, Dean Ilene Rosen, and the Associate Director, Dean Jean-Patrick Antoine, for providing the opportunity to conduct this research. They would also like to thank Rutgers University and the Rutgers School of Engineering. This project would not have been possible without the generous support of the State of New Jersey, NJ Governor's School of Engineering and Technology Alumni, Lockheed Martin, and Silverline Windows.

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