Synthesis and Characterization of Cl_3Zr-O-Si-$(O)_3$-(bulk silica gel)

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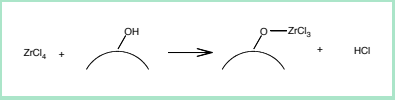
Abstract

Synthesis of $ZrCl_3$ bound to silica gel through an oxygen-zirconium bond has been attempted via the following reaction.
$ZrCl_4$ + H-O-Si-$(O)_3$-(bulk silica gel) -> Cl_3Zr-O-Si-$(O)_3$-(bulk silica gel) + HCl
Dried silica gel was reacted with $ZrCl_4$, evolving HCl and producing a surface bound metal compound. Mass balance, a weight gain of 14%, indicates that some zirconium is bound. A method to determine zirconium content in the synthesized compound was developed by detecting a xylenol orange-zirconium complex of digested samples via UV-Vis spectroscopy, but measurements were not reproducible. Instead, a protocol was successfully developed to detect zirconium content via inductively coupled plasma (ICP)-MS, which calculates the compound to contain approximately 7% zirconium by weight, corresponding to about 0.76 mmol Zr bound per gram of synthesized compound. The current evidence suggests that a $ZrCl_3$ is bound to the surface through a bridging oxo group. Further confirmation of this structure will be obtained from measuring the moles of HCl evolved in the reaction, providing the stoichiometry of the reaction, via titration of the HCl generated with KOH. The supported zirconium complex will be reacted with 1,1'-bi-2-naphthol (or suitable derivative) to obtain chiral Lewis acid catalysts.

Introduction

Synthetic routes to single-enantiomer production have been widely studied and can be achieved by various means. Asymmetric synthesis, specifically the use of enantiospecific catalysts, can prevent formation of the unwanted enantiomers. Chiral Lewis acid catalysts can be used to catalyze enantiospecific formation of carbon-carbon bonds. Moreover, use of heterogeneous catalysts have a number of advantages over homogeneous catalysts including ease of separation from products and greater reusability.

Synthesis of a Lewis acid surface bound heterogeneous catalyst containing zirconium trichloride bound to silica gel through an oxygen-zirconium bond has been attempted. We have a number of ways to characterize synthesized compounds, including IR, solid state NMR and elemental analysis. Yet, none of these methods can quantify zirconium content. Determination of zirconium content has been widely performed with xylenol orange (XO). In acidic solution, XO forms a 1:1 colored complex with zirconium, which can be monitored by a UV-Vis spectrophotometer. Measurements, however, could not be replicated. As inductively coupled plasma (ICP) MS has low detection limits and can be used rapidly to determine elements present, an alternate method to determine zirconium content in synthesized products was developed.



Scheme 1. Synthesis of Cl_3Zr-O-Si$(O)_3$-(bulk silica gel)

Experimental

Synthesis of Cl_3Zr-O-Si$(O)_3$-(bulk silica gel)
Suspend silica gel in toluene under nitrogen
Dissolve $ZrCl_4$ in acetonitrile in glovebox
Heat silica gel and toluene until gently boiling
Add $ZrCl_4$ acetonitrile solution dropwise to the silica gel and toluene
Apparatus is set up to collect HCl generated in reaction by bubbling gas evolved through a bubbler into a test tube of distilled water
After addition is complete, heat the reaction for 4 more hours
Filter reaction mixture under nitrogen
Wash the solid product with acetonitrile, followed by pentane
Dry under vacuum

Zirconium Analysis
Digest sample for 20 hr in conc. HNO_3
Vacuum filter digest and rinse filter with conc. HNO_3
Use filtrate to determine zirconium content

UV-Vis Spectroscopy
Calculation of molar absorptivity of XO-Zr complex
Make a 7.12*10-4 M XO stock solution. Cover bottle with aluminum foil.
Perform five 1:1 serial dilutions of a 1:2 XO to Zr (5.48 *10^{-4} M Zr) solution in 2M HNO_3. Cover all volumetric flasks used with aluminum foil.
Measure absorbance of each serial dilution via UV-Vis spectrophotometer
Perform linear regression of absorbance at λmax vs concentration of XO with the y-intercept set to 0 to obtain the molar absorptivity of the XO:Zr complex at λmax (ε_{536} avg) using Beer's law
Determination of Zirconium content
Dilute filtrate from digest by 1:50 in distilled water 4 times
For the last dilution, add XO stock solution in slight excess of 1:1 XO-Zr complex formation in 2 M HNO_3
Measure absorbance of the last dilution via UV-Vis spectrophotometer
Using ε_{536} avg, calculate zirconium content in sample

Air Oxidation of XO
Take spectra of XO solution
Bubble air through XO stock solution for 6min and for another 25min, take spectra after 6min and after 25min of bubbling
Calculate percent difference between absorbance values at λmax, 430nm

Zirconium Analysis, continued
Determination of Zirconium content via ICP-MS
For each run, from Zr standard solution, make 4 standards containing 25.0ppb, 12.5ppb, 6.25ppb and 3.13ppb Zr or 50.0ppb, 25.0ppb. 12.5ppb, and 6.25ppb Zr in 2% HNO_3 by volume via 1:1 serial dilutions
Dilute filtrate by a 1:4*10^5 dilution in 2% HNO_3
Measure mean intensity and use the outputted standard curve equation (from linear regression) to calculate the concentration of Zr in the diluted sample
Calculate the %Zr by wt from the original sample

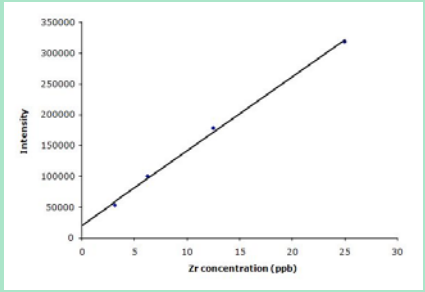


Figure 2. Calibration curve for zirconium analysis via ICP-MS.

Table 1. Zirconium content calculated from ICP-MS analysis for different synthetic runs.

run	%Zr by weight	moles Zr per gram of compound
1	6.79	0.74
2	7.20	0.78

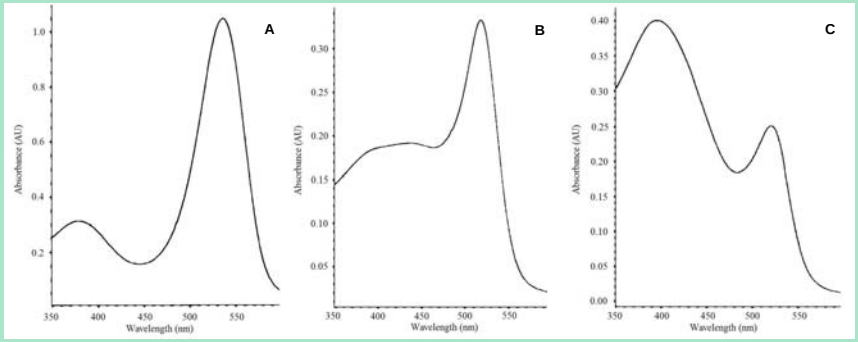


Figure 1. A, absorbance spectrum of 1:2 XO-Zr in 2M HNO_3 standard 1, B, absorbance spectrum of XO-Zr in 2M HNO_3 from the 20 hr digest, C, absorbance spectrum of XO in 2M HNO_3 standard 1.

Results and Discussion

From the calibration curve for 1:2 XO-Zr, average molar absorptivity is 1.98*10^4 M^{-1}*cm^{-1} at λmax, 536nm. Surprisingly, the percent of Zr calculated from the digest filtrate was 1790%. From a standard curve, XO in 2M HNO_3 has a significant absorbance at 536nm with an average molar absorptivity value of 1.42*10^4 M^{-1}*cm^{-1}. The inflated percent of Zr in the sample is likely due to excess XO in the solution.

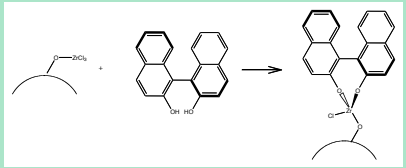
To analyze the XO-Zr complex and excess XO in the digest filtrate as a mixture, the determination of molar absorptivity of XO in 2M nitric acid at its λmax, 395nm, was attempted. Two XO standard curves, however, resulted in 13.6% differences in molar absorptivity values at 395nm. Bubbling air through an XO solution gave negligible differences in absorbance values after 6 and 25 min of bubbling, implying that air oxidation was not causing the fluctuation in absorbance at 395nm for XO.

ICP-MS runs detect about 7% Zr by wt or an average 0.76mmol Zr bound per gram of synthesized compound. This result, in addition to an average weight gain of 14%, suggests that $ZrCl_3$ is bound to the silica gel surface through a zirconium-oxygen bond.

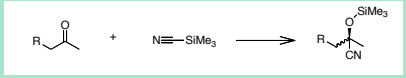
Future Work

-Determine amount of HCl generated during the reaction by titrating the HCl evolved with KOH

-React surface bound zirconium complex with 1,1'-bi-2-naphthol (BINOL) or derivative



Scheme 2. Synthesis of (binol)-ClZr-O-Si-$(O)_3$-(bulk silica gel)



Scheme 3. Silylcyanation reaction

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