





Semi-Hydrogenating Zintl-Phase Catalysts AeTr₂ (Ae = Sr, Ba; Tr = Ga)

Daniel Lesse / New Mexico Highlands University

ABSTRACT

A Zintl-phase can be defined as a substance comprised of 1st through 3rd group elements, along with post-transition metals. Zintl-phases are known to possess some interesting properties. The property we are interested in is the ability of electron-deficient Zintl-phases to absorb hydrogen. Another substance which has this ability is the Lindlar catalyst. This catalyst is used in the hydrogenation reduction of phenylacetylene to make styrene, a popular monomer used to make a variety of plastics, rubbers, and expanded foam products. The Lindlar catalyst is rich in Pd, making it not only expensive, but also unsustainable. The ACS claims there is an undeniable risk to future supply. Therefore, it is in the best interests of humanity to develop new species of catalysts free of valuable transition metals. For the purposes of the following research, we focus on Zintl-phase hydrogenation catalysts, and explore the likelihood that they can replace conventional catalysts in the near future.

I. Background and Introduction

Zintl-phases are defined as substances comprised of elements from groups 1-3, in addition to post-transition metals. Electron deficient Zintl-phases, such as SrGa₂, have the ability to absorb hydrogen¹. Lindlar catalyst is also a well-known hydrogenation catalyst due to the hydrogen absorbing properties Pd. This of observation leads to the rational design of new species of hydrogenation catalysts free of transition metals.

Styrene (C_8H_8), commonly synthesized through the reduction of phenylacetylene (C_8H_6) under hydrogen with Lindlar catalyst², is widely used in the industrial production of synthetic rubber, plastics, and expanded foam products. This process is most popularly accomplished with the use of catalysts containing expensive transition metals, particularly palladium². The discovery and utilization of catalysts free of Pd remains an important goal of solid-state chemists, not only due to the potential financial impact, but is also directly driven by the limited supply of those metals. According to the American Chemical Society, Pd resources are limited, and at risk of being eventually depleted.



Figure 1: Zintl-phase elements shaded red.

Using Lindlar catalyst under H_2 , phenylacetylene readily hydrogenates at 70°C and 1 bar pressure². This hydrogenation causes the reduction of the C-C triple bond (alkyne) to become a double bond (alkene) as the carbon atoms gain two hydrogen atoms³, forming the styrene molecule².

A potential difficulty in this process is the over-hydrogenation of the phenylacetylene to ethylbenzene², an undesirable impurity which causes decreased integrity in styrene products. This is due to the mechanistic effect on the reactivity of the active species of the coordination polymerization⁴. Overhydrogenation is controlled through the poisoning of the Lindar catalyst with lead, selectively blocking facets on the surface of the particles and limiting its ability to hydrogenate. However, poisoning also creates problems. Lead is toxic, creating hazardous workplace conditions.



Figure 2: Reduction of phenylacetylene to styrene and over-hydrogenation, using SrGa₂ in place of Lindlar catalyst.

Dr. Joshua Goldberger and Kelsey Hodge of The Ohio State University's Center for Emergent Materials have been exploring the ability of electron deficient Zintl-phase compounds to perform hydrogenation catalysis, similar to the Lindlar catalyst, under mild conditions. While results are inconsistent thus far, the data does look promising. Using BaGa₂ under hydrogen, with n-butanol as a 100% solvent. а conversion from phenylacetylene styrene to and ethylbenzene has been recorded in only ten hours, reports Hodge. This signifies very strong catalytic ability, and the potential to outperform Lindlar catalyst.



Figure 3: Side view of the SrGa₂ lattice. Sr is depicted in red, Ga in blue. (.cif file courtesy of Springer Materials⁵)

The hydrides of these compounds are not likely to have the ability to catalyze, however. For the formation of $AeTr_2H_2$ from $AeTr_2$ -type $AeGa_2$, hydrogen is added to a three-bonded, sp2-hybridized E- entity, which changes into sp3-hybridized after binding to H³, as shown in figure 4.

Once hydrogenated, the compounds have all active sites occupied, and are not likely able to facilitate the diffusion of hydrogen atoms across the surface of the catalyst, according to Hodge. However, electron-deficient Zintl-phase compounds free of hydrogen show strong potential for adsorbing hydrogen atoms onto their surfaces. Once this happens, the hydrogen atoms can diffuse across the surface of the catalyst and bind with the phenylacetylene, converting it to styrene under mild conditions.



Figure 4: SrGa₂H₂. The teal H atoms occupy all active sites, rendering the substance incapable of catalysis. (.cif file courtesy of Springer Materials¹)

Difficulties with this type of research mostly involves the considerable time commitment to each step of the process. The furnace program for the synthesis for a reasonable pure product is about sixty hours long. XRD analysis is about a threehour process. In addition, the product is air sensitive, quickly forming oxides when exposed to oxygen. In addition, the product is also water sensitive. Contact with water is known to destroy catalytic ability. If a desired level of purity is achieved, setting up a sample to test for catalysis is a multistep process, in addition to the average catalysis time of 24 hours before results can be analyzed. In addition to the time constraints, the high number of variables in the process create difficulty when trying to isolate problems.

II. Methods

Strontium digallide was synthesized using a box furnace, with samples held under vacuum. The synthesis was achieved by combining appropriately massed samples of +99% pure Sr and +99% pure Ga, at a 1:2 stoichiometric ratio. The Sr,

which was stored under mineral oil and always handled in an argon rich environment due to its air-sensitive nature, was mechanically cleaned prior to massing. The mineral oil covered Sr was repeatedly and vigorously wiped with Kim wipes, prior to having the pre-existing oxide layer removed. Once the surface was free of all perceivable oil, the oxide layer could be scraped away with a bladed tool. SrO appears as a dark grey layer covering the outer surface of the Sr. This layer, once removed, reveals the shiny, metallic surface of clean strontium. Once an adequate amount of clean Sr was obtained, both elements were placed into an alumina crucible and vacuum-sealed inside a quartz tube measuring approximately 1.8cm in diameter. The sample was then placed inside a furnace and brought up to 1073K, at a rate of 2.7°C per minute. This temperature was held for 12-48 hours, before being allowed to return to room temperature over an eight-hour period.

The resulting sample was then returned to an argon-filled glove box where it was ground fine (particulate size $10-30 \mu$ m) and prepared for analysis using x-ray diffraction (XRD). Initial scans showed the presence of an unknown side phase, so preparations were made to run more syntheses. Variables such as furnace temperature, maximum temperature, and length of time held at maximum temperature, and crucible conditions could all be controlled and tested.

To test catalytic ability, a sample of SrGa₂ was placed inside a 10mL, argonfilled round-bottom flask. This flask was then transferred out of the glove box to a fume hood. A phenylacetylene (C₈H₆) solution was then prepared at 3mol% catalyst with tetrahydrafuran as solvent (C₄H₈O) and the pre-massed sample of SrGa₂. The contents of the flask were then allowed to react at 40°C under H₂ for twenty hours. The solution was then filtered and analyzed via high pressure liquid chromatography (HPLC) to determine the rate of conversion of phenylacetylene into styrene.

III. Results and Discussion

SrGa₂ was Initial synthesis of conducted by combining the required elements under vacuum and running a furnace program of 800°C for 12 hours before an eight-hour ramp-down back to room temperature. Upon removal from the furnace, the quartz tube was observed to be coated with a dark brown substance, which was determined to be from strontium escaping from the crucible and becoming fused with the inner surface of the quartz tube. This sample was later ground and analyzed using x-ray diffraction and determined to contain some quantity of Sr_{2.85}Ga_{8.45}, an undesirable side-phase. It was decided that a purer phase of the desired SrGa₂ would be necessary before further catalytic experiments could be run.



Figure 5: *HPLC results of SrGa2 sample containing approximately 10% Sr2.85Ga8.45. Conversion rate occurred at 0.7%/20hr. phenylacetylene to styrene. Amount considered negligible. Tall central peak is phenylacetylene. Arrow points to styrene peak.*

A series of syntheses were then conducted to eliminate the side phase. For the first attempt at purification, the furnace time at 800°C was increased by 12 hours. This increase resulted in impurity peaks on the XRD scan, and an apparent decrease in quantity, but a considerable amount was still observed. Next, a sample was prepared using a 10% excess of Sr. The furnace program remained unchanged. The result was an apparent increase in the amount of observed Sr_{2.85}Ga_{8.45}. For the next attempt, the furnace program was increased to 48 hours at 800°C, with no excess. The result showed fewer impurity peaks than previous trials. Encouraged by these results, three samples were prepared in tandem. The first was done with a 10% excess of Sr, the second with 25% excess of Sr, and the third with no excess, but the crucible was capped with an additional crucible resting directly over the top of the first. The capped sample did not show any appreciable improvement to the synthesis. The sample containing a 10% excess of Sr also showed a negligible amount of improvement. The sample containing a 25% excess of Sr, once analyzed with XRD, appeared to contain approximately 90% SrGa2. pure



Figure 6: Notable XRD scans of SrGa₂. Third line from top calculated to be 0.7% pure. (.cif files courtesy of Springer Materials¹)

The strontium-deficient impurity was possibly caused by a relatively large amount of Sr sublimating and fusing to the inner surface of the quartz-tube which lead to a shift in the stoichiometry.



Figure 7: 100% conversion of phenylacetylene to styrene and ethylbenzene, as reported by Hodge.

IV. Conclusions

Experimentation has shown a strong likelihood of eventual development of Zintl-phase hydrogenation catalysts. Although the SrGa₂ performed poorly, it

was not unexpected in such early trials, and in the time allotted for experimentation. Further experimentation needs to occur, not only in the hydrogenation stage, but also in the synthesis of the catalyst. Reproducible results need to be achieved before methods for preventing over-hydrogenation can be explored. Methods for removal of potential oxides from the surface of the catalyst would also be beneficial. Broadening the scope of materials to other electron deficient Zintl-phases would also increase the likelihood of developing a functional catalyst. In closing, it appears highly likely that a new species of catalyst will be developed to rival or even replace Lindlar's.

V. References

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