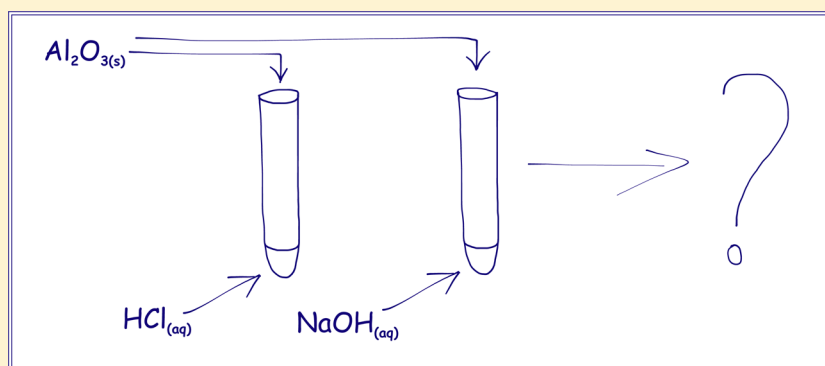


Obtaining and Investigating Amphoteric Properties of Aluminum Oxide in a Hands-On Laboratory Experiment for High School Students

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S Supporting Information

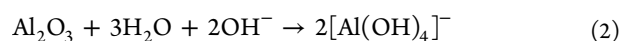
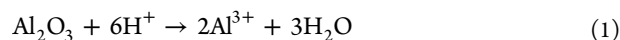


ABSTRACT: The aim of this laboratory exercise is to present a high school hands-on laboratory experiment, focused on obtaining and investigating the properties of various polymorphic forms of aluminum oxide. Amphoterism plays a key role when discussing the law of periodicity and periodic changes of acid–base properties of elements and their compounds. In many school syllabuses, that issue is based on third period elements, so the amphoteric substances are aluminum, aluminum oxide, and aluminum hydroxide. Although demonstrating those properties for aluminum and aluminum hydroxide is relatively simple, the same reactions for alumina can be quite problematic. It is due to the fact that aluminum oxide exists in several polymorphic forms, and only one of them reacts with acids and bases. Moreover, the commercially available aluminum oxide materials are usually nonamphoteric. The exercise describes preparation of various polymorphic forms of aluminum oxide by thermal decomposition of aluminum hydroxide, and tests for its acid–base properties. The experiment can be used as a separate activity, or as a part of a larger scenario considering the properties of third period oxides. It was successfully conducted with over 100 high school (K–11) students studying chemistry at standard and higher level according to the International Baccalaureate Diploma Programme.

KEYWORDS: High School/Introductory Chemistry, Laboratory Instruction, Inquiry-Based/Discovery Learning, Acids/Bases, Solids, Synthesis

INTRODUCTION

Aluminum, aluminum oxide, and hydroxide are described as substances with amphoteric properties. Demonstrating those properties plays a key role when discussing periodic changes of acid–base properties of elements and their compounds. In the case of aluminum and aluminum hydroxide, the properties may be demonstrated by carrying out simple experiments.^{1,2} Unfortunately, presenting the amphoteric properties of aluminum oxide is more complicated. It should react according to the following reactions:²



Unfortunately, not all polymorphic forms of aluminum oxide have these amphoteric properties.² It can exist in the following

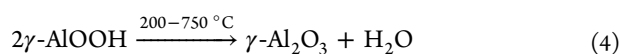
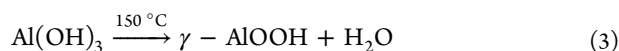
phases:³ γ , δ , κ , ρ , η , θ , χ , α , and only the γ - Al_2O_3 is amphoteric.⁴ Other polymorphic forms exhibit basic properties, so they react with acids only (eq 1). Among nonamphoteric phases, the α phase is the most stable, and the other are metastable.^{5,6} In α - Al_2O_3 structure, oxygen ions are hexagonally close-packed, and the aluminum atoms occupy two-thirds of the octahedral sites: each aluminum atom is surrounded by six oxygen atoms in an octahedral interstitials, and each oxygen atom is surrounded by four aluminum atoms.⁷ γ - Al_2O_3 has defected spinel regular structure, in which 21(1/3) of the 16 octahedral and 8 tetrahedral positions are occupied at random by Al^{3+} ions.^{8,9}

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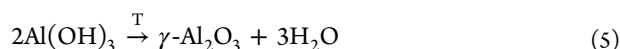
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Aluminum oxide is of great industrial importance. It is used in the industry as an adsorbent, catalyst support.⁴ However, its use is related rather to the highly developed specific surface area and high thermal stability rather than to its amphoteric properties. For this reason, commercially available aluminum oxide materials are mainly the α phase ones.^{5,10}

Aluminum oxides may be obtained in the reaction of thermal decomposition of aluminum hydroxide.⁷ The latter may exist as bayerite α -Al(OH)₃ or gibbsite γ -Al(OH)₃, but the polymorphic structure of hydroxide does not have significant influence on the final product phase composition.⁶ Both of the forms heated to about 150 °C release water and create an intermediate product which is γ -AlOOH (eq 3) boehmite.¹¹ When heated further to the temperature of above 200 °C, boehmite decomposes into γ -Al₂O₃ (eq 4).¹²



These reactions may be summarized as follows:



γ -Al₂O₃ heated to a temperature of about 750 °C is converted into a mixture of θ and δ phases, and at a temperature above 1200 °C, it creates the α phase.^{10,12} There are also other aluminum minerals like α -AlOOH diasporas, which, during calcination, form α -Al₂O₃ directly.⁹

The rich polymorphism of alumina hinders the preparation of materials with the desired properties. The aim of this article is to present a simple method for obtaining amphoteric and nonamphoteric aluminum oxides, and to provide test procedures for the verification of their acid–base properties.

EXPERIMENTAL DETAILS

Preparation of γ -Al₂O₃

The γ -Al₂O₃ can be obtained through the calcination of aluminum hydroxide in the temperature range of 200–750 °C. The process may be carried out in a laboratory furnace or in a laboratory dryer. The high yield can be achieved during the calcination of the sample weighing approximately 3.5 g at 250 °C for 30 min. It is advised to keep the samples' geometric surface relatively large; therefore, the use of an evaporating dish instead of a crucible is recommended. The obtained product should be stored in a desiccator due to its hygroscopic properties.

It is also possible to obtain comparable dehydration conditions using a Bunsen burner. In such case, the heating should be carried out in a crucible, and the sample weight should not exceed 1.5 g. Decomposition time is approximately 2.5 min. However, obtaining recurrent results requires optimization of the method to the conditions and equipment in a particular laboratory. It is suggested to adjust the intensity of the burner's flame and the height of the crucible over the flame using a pyrometer. The temperature measured inside the crucible should be in the range of 400–500 °C. Overly excessive heating and local overheating lead to the formation of nonamphoteric phases and nonstoichiometric oxides.

Preparation of α -Al₂O₃

Typical laboratory burners allow for the heating of materials to a maximum temperature of approximately 1000 °C. Such temperature allows for the decomposition of aluminum

hydroxide into a mixture of θ and δ phases.⁵ Obtaining the α -Al₂O₃ requires a temperature above 1200 °C.^{12,13} School laboratories are often not equipped with furnaces that reach such high temperature. For that reason, an alternative procedure for high temperature calcination in a microwave oven is presented below.¹⁴

The technique involves carbon as a microwave radiation susceptor (granular activated carbon, diameter 1–4 mm). It reaches a temperature of 1283 °C in a microwave in approximately 1 min.¹⁵ The susceptor is placed in the AST vessel (in German: Die Aktivkohle-Suszeptor-Tiegel). It can be made of a clay flowerpot and refractory mortar. A crucible with the sample is placed in the AST vessel. The space between the crucible and the vessel wall should be filled with carbon as shown in Figure 1.

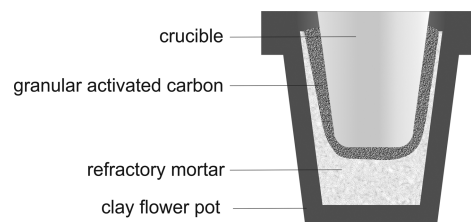


Figure 1. AST element construction in cross section.

The AST vessel should be placed in the microwave oven in the area where the radiation intensity is the highest, the so-called hot spot. The location of the hot spot can be found using moistened thermosensitive paper (e.g., fax machine paper). Paper should be placed in the oven at the height of the reaction crucible (e.g., on a polystyrene pad), and the oven should be turned on for a few seconds.

With the use of a 300–400 W microwave power (it can be 1000 W microwave oven set on one-third of power), a 0.5 g sample of Al(OH)₃ should be calcined for approximately 3 min. This leads to decomposition yield close to 100%. Using the same method and heating parameters allows for inducing the phase transition of γ -Al₂O₃ into α -Al₂O₃.

Similar to when using a Bunsen burner, too intense or overlong heating may lead to the formation of nonstoichiometric oxides. In some cases, the temperature inside the AST can even rise above 2054 °C and melt the aluminum oxide.¹⁶

Examination of the Acid–Base Properties of Aluminum Oxide

Testing the acid–base properties of the obtained Al₂O₃ materials may be based on a trial using HCl and NaOH solutions. It is advised to use 0.001 mol/dm³ solutions of acid and base mixed with indicators: methyl orange and phenolphthalein, respectively. About 2 cm³ of the acid or alkaline solution should be placed in a test tube, and then a pinch of the tested oxide should be added. If there is no sign of reaction, the test tube content should be gently heated.

RESULTS

The results presented below have been obtained by students who performed the experiment under the authors' supervision.

Calcination in a Laboratory Furnace

A 3.48 g sample of aluminum hydroxide was placed in a laboratory furnace preheated to 250 °C. The sample was calcined at constant temperature for 0.5 h. The yield of the

process based on the weight lost was 99.8%. The product reacted with acid and base.

Calcination Using a Bunsen Burner

A 1.21 g sample of aluminum hydroxide was placed in a crucible and heated on a Bunsen burner. The temperature of the crucible was adjusted using a pyrometer to 450 °C. The heating was continued for 2.5 min. The yield of the process was 99.3%. The obtained product was reactive with acid and base.

Calcination in a Microwave

A 0.36 g sample of aluminum hydroxide was placed in a crucible in accordance with Figure 1 and heated in a 1000 W microwave oven set on one-third of its maximum power for 3 min. The yield of the process was 99.5%. The preparation was reactive with acid, but it did not react with base.

The same heating procedure was used to calcine the previously obtained aluminum oxide preparations. The sample of the oxide obtained in a laboratory furnace (at 250 °C) weighed 0.20 g, and as a result of heating in a microwave oven, the weight loss was 0.04 g. The sample of the oxide obtained using the burner weighed 0.19 g, and the weight loss was 0.02 g. Both preparations react with acid, but they do not react with base.

HAZARDS

Aluminum hydroxide $\text{Al}(\text{OH})_3$ and aluminum oxide, Al_2O_3 , are not classified as dangerous.

DISCUSSION

This experiment was carried out with the participation of upper secondary school students (K–11) studying chemistry at standard and higher level according to the International Baccalaureate Diploma Programme. The described synthesis and test for Al_2O_3 is part of a larger scenario considering the properties of third period oxides. Working in groups, the students first obtain aluminum oxide using one of the described methods (worksheet presented in Appendix A). Then, each of the groups investigates the properties of Na_2O , MgO , Al_2O_3 , SiO_2 , P_4O_{10} , and SO_2 oxides in reactions with water, acid, and base (worksheet presented in Appendix B); aluminum and sulfur oxides are prepared by the students, and the rest is delivered by the teacher. At this stage the concept of amphotericism is introduced, with the students learning how to distinguish between acid–base properties and being acidic or basic anhydride.

After the laboratory part, the students discuss the obtained results and write down the chemical equations. The properties of aluminum oxides obtained by the various groups are different and depend on the synthesis method applied. The groups that use a laboratory furnace (at 250 °C) always obtain an amphoteric preparation, while the groups conducting calcination using microwaves always obtain a basic product. The groups conducting calcination using a Bunsen burner may obtain various results, depending on the intensity and heating time. The conducted discussion creates an opportunity for the introduction of the polymorphism concept and broadening the knowledge on the crystalline structure of matter and phase transitions within the solid state. The discussion is followed by an experiment in which the students carry out a phase transformation of the obtained amphoteric Al_2O_3 into non-amphoteric form using a microwave oven and test acid–base properties of products.

Decomposition of aluminum hydroxide should be complete; otherwise, the result can be influenced by what remains from a reactant. The process's yield can be calculated based on weight loss and it should reach 98–100%. The X-ray powder diffraction analysis of the obtained materials showed that the described procedures do not lead to single phase products; fortunately, the mixed phases obtained allow reproducible results to be gained.

The achievements of the students involved in the pilot implementation of the described experiment ($n = 36$) were compared to the results obtained in the previous year ($n = 28$). All the students participated in a standard level chemistry course, and groups and tests level were comparable. The most significant change was observed in the ability to determine the chemical properties of third period elements and their compounds and writing appropriate chemical equations. It resulted in a better average test score, i.e., 4.54 (scale 1–7, 7-excellent) for the group taking the experiment, as compared to 4.18 for the group that did not take it; the most frequent grade was 4 in both cases. For the students who completed the investigation, formative assessment feedback was also analyzed and compared to the outcomes of the previous investigation. The results show that the level of 14 students (39%) in the assessment rubric improved (3-level rubric,¹⁷ the most frequent change was from the first to the second level). Additionally, basing on the student-provided feedback, it can be stated that the form of guided inquiry supports the students in proceeding to the expected direction during the entire investigation process; moreover, the experiment was well received by all the students and no gender bias was observed. It can be concluded that during the described investigation the students not only gained chemical knowledge and learned laboratory techniques, but they also developed soft skills such as debating with peers, forming coherent arguments, working collaboratively, etc.

SUMMARY

Amphoterism plays a key role while discussing the law of periodicity and periodic changes of the acid–base properties of elements and their compounds. Typically, at high school level the law of periodicity is discussed based on third period elements and their compounds. Because aluminum oxide exists in several polymorphic forms, demonstration of its amphoteric properties is problematic. Using the described procedures, teachers can easily prepare amphoteric samples of alumina and present sufficient experiment or prepare guided inquiry students' exercise focused on the investigation of chemical properties of third period oxides. Students can also synthesize aluminum oxide on their own. This creates an opportunity to introduce the concepts of polymorphic phase, phase transfers in a solid state, various techniques of calcination and the relation between temperature of calcination, and chemical properties of the obtained preparation. Such an approach stimulates students to analyze any unexpected results, conduct discussions, and form coherent arguments.

REACTANTS

Aluminum hydroxide, $\text{Al}(\text{OH})_3$, CAS: 21645-51-2, Sigma-Aldrich.

■ ASSOCIATED CONTENT**📄 Supporting Information**

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00314.

Appendix A: experimental procedures (PDF, DOCX)

Appendix B: worksheets (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

■ REFERENCES

- (1) de Lima, K. M.; da Silva, Á. R.; de Souza, J. P.; das Neves, L. S.; Gasparotto, L. H. Determination of Al Content in Commercial Samples through Stoichiometry: A Simple Experiment for an Advanced High-School Chemistry Olympiad Preparatory Course. *J. Chem. Educ.* **2014**, *91* (9), 1473–1476.
- (2) Tesh, K. F. The use of potassium alum in demonstrating amphotericism. *J. Chem. Educ.* **1992**, *69* (7), 573–574.
- (3) Macêdo, F.; Bertran, C. A.; Osawa, C. C.; Iaponeide, M. Kinetics of the $\gamma \rightarrow \alpha$ -alumina phase transformation by quantitative X-ray diffraction. *J. Mater. Sci.* **2007**, *42* (8), 2830–2836.
- (4) King, R. B. *Encyclopedia of Inorganic Chemistry*, 1st ed.; John Wiley & Sons, Inc.: Chichester, 1994; pp 108–110.
- (5) Tonejc, A.; Stubicar, M.; Tonejc, A. M.; Kosanović, K. Transformation of γ -AlOOH (boehmite) and Al(OH)₃ (gibbsite) to α -Al₂O₃ (corundum) induced by high energy ball milling. *J. Mater. Sci. Lett.* **1994**, *13* (7), 519–520.
- (6) Llusar, M.; Pídol, L.; Roux, C.; Pozzo, J. L.; Sanchez, C. Templated Growth of Alumina-Based Fibers through the Use of Anthracenic Organogelators. *Chem. Mater.* **2002**, *14* (12), 5124–5133.
- (7) Bailer, J. C.; Emeléus, H. J.; Nyholm, S.; Trotman-Dickenson, A. F. *Comprehensive Inorganic Chemistry*, X ed.; Pergamon Press: Oxford, 1973; pp 1035–1036.
- (8) Samain, L.; Jaworski, A.; Edén, M.; Ladd, D.; Seo, D. K.; Garcia-Garcia, F.; Häussermann, U. Structural analysis of highly porous γ -Al₂O₃. *J. Solid State Chem.* **2014**, *217*, 1–8.
- (9) Wells, A. *Structural Inorganic Chemistry*, 4th ed.; Oxford University Press: Oxford, 1984; pp 457–458.
- (10) Bodaghia, M.; Mirhabibi, A.; Zolfonun, H.; Tahriri, M.; Karimi, M. Investigation of phase transition of γ -alumina to α -alumina via mechanical milling method. *Phase Transitions* **2008**, *81* (6), 571–580.
- (11) Stacey, M. H. Kinetics of decomposition of gibbsite and boehmite and the characterization of the porous products. *Langmuir* **1987**, *3* (5), 681–686.
- (12) Day, M. K.; Hill, V. J. The Thermal Transformations of the Aluminas and their Hydrates. *J. Phys. Chem.* **1953**, *57* (9), 946–950.
- (13) Youn, H.; Jang, J.; Kim, I.; Hong, K. Low-Temperature Formation of alpha-Alumina by Doping of an Alumina-Sol. *J. Colloid Interface Sci.* **1999**, *211* (1), 110–113.
- (14) Lühken, A.; Bader, H. J. Hochtemperaturchemie im Haushalts-Mikrowellenofen. *CHEMKON* **2001**, *8* (1), 7–14.
- (15) Mingos, D. M.; Baghurst, D. R. Applications of Microwave Dielectric Heating Effects to Synthetic Problems in Chemistry. *Chem. Soc. Rev.* **1991**, *20* (1), 1–47.
- (16) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 95th ed.; CRC Press: New York, 2014; pp 4–45.
- (17) *Chemistry. First Examinations 2009. Diploma Programme Guide*; International Baccalaureate Organization: Cadriff, 2007; pp 23–24.