

Purification of the alumina precursor and precise impurity measurements with spectrophotometric method

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The activated carbon's enormous capacity to absorb and retain significant quantities of many organic compounds has led to its use as a purifying medium. An anion is adsorbed onto the activated carbon, and the metal ion interacts with the anion, effectively being absorbed by an adsorbate. Observation of the metal ion adsorption, displayed that complex organic agents and pre-absorbed anions can affect the amount of adsorption. In this study, we have tried to improve the purity of alumina precursor using activated carbon for 1.5 hr by stirring at 200 rpm at 82 °C.

Key words: Alumina, Aluminum isopropoxide, Activated carbon, Hydrolysis, Spectrophotometer.

Introduction

Aluminum isopropoxide (AIP) is a significant precursor for preparing high-purity aluminum related materials and alumina. Alumina is becoming a more attractive material for the technological industry, especially in microelectronics as substrate and there are many impurities such as Fe, Ti, V, Ca, Mg, Si, Mn, Cu, Pb, Na, Cr and Zn in AIP and α -alumina. Among the impurities, iron and silicon are the key trace impurities, which dramatically affect the optical and other intrinsic properties of alumina-containing materials, such as an abnormal grain growth of alumina stimulated by SiO₂ [1]. Therefore, it is important to precisely measure the impurities quantitatively and to remove trace impurities from AIP or α -alumina. An efficient elimination of trace impurities from aluminum isopropoxide has been reported recently, including the inter-metallic compound method in metals or alloys [2], forming the high boiling point organic compound by chelate organic ligands [3], carbothermal reduction [4], and vertical zone melting method [5]. There are several methods which have been used for determination of impurities in the alumina precursor such as X-ray fluorescence spectrometry [6], secondary ion mass spectrometry (SIMS), spark source mass spectrometry, ICP-AES [7-10], however these methods need high cost techniques and it is hard to determine any single element, separately. In this study, we presented a method to remove the impurities in aluminum isopropoxide by activated carbon at its

optimal condition. The spectrophotometric method was used to determine the trace amounts of elements such as Fe, Ti, Ca, V, Cu, P, Si, Ni and Zn in the synthesized alumina precursor samples. Beer's law is obeyed in the concentration range of 0.01-10 $\mu\text{g mL}^{-1}$ of the measured elements in all methods used. Interfering effect of various cations and anions was also investigated. The impurity measurement method's validity was checked by comparing the results obtained with inductively coupled plasma (ICP) analysis.

Experimental

Instrumentation

The determination of impurity metal ion concentration was carried out by T-60 UV-VIS spectrophotometer equipped with 1.0 cm quartz cell and the pH of the solution was controlled with a Thermo, Orion 920A + digital pH meter. The results have been checked by Perkin-Elmer Optima 5300 DV inductively coupled plasma optical emission spectrometer.

Procedure of purification

Aluminum isopropoxide (AIP) was purified with activated carbon for 1.5 hr by stirring at 200 rpm at 82 °C (Fig-1). The purified AIP was obtained by the filtration and vacuum distillation at 10 mmHg and at ~ 140 °C. By using chelate reagent, the content of impurity element in a sample can be conveniently and highly accurately determined spectrophotometrically without being affected by any interfering substances.

Determination of impurities

A highly selective and very sensitive spectrophotometric

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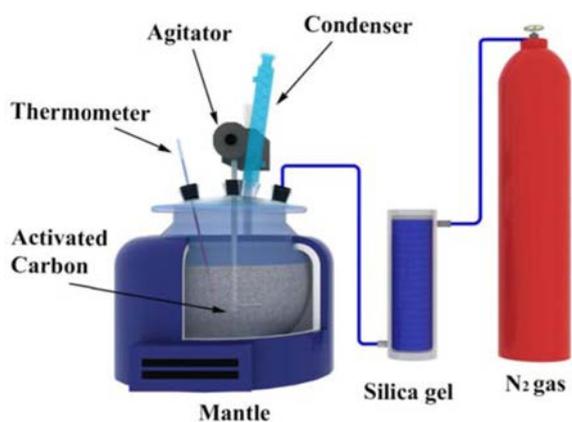


Fig. 1. Schematic diagram of AIP purification apparatus with activated carbon.

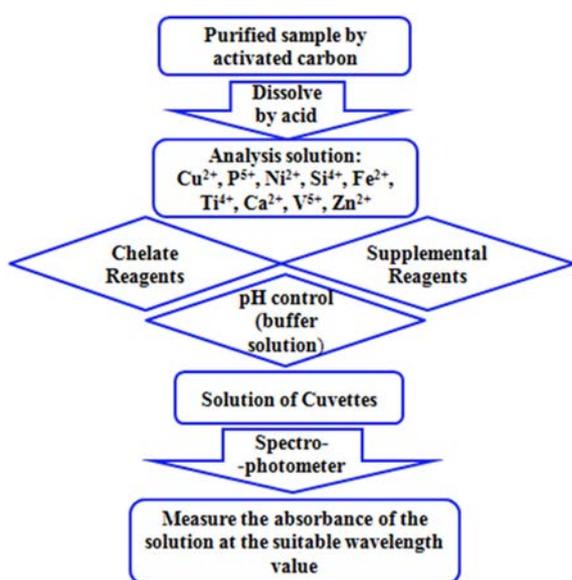


Fig. 2. General procedure for determination of impurities.

method was used to determine the trace amounts of elements such as Fe, Ti, Ca, V, Cu, P, Si, Ni and Zn in the synthesized alumina samples (Fig-2). Beer's law is obeyed in the concentration range of $0.01\text{--}10\ \mu\text{g mL}^{-1}$ of the measured elements in all methods used.

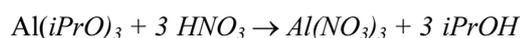
The silicon could form silicon molybdenum yellow complex with molybdate at pH 0.9 using ammonium molybdate as a color developer. With sulfuric acid increasing the acidity, the complex was reduced to silicon molybdenum blue complex by ascorbic acid. The maximum absorption wavelength of silicon molybdenum blue complex is 813 nm [11]. The procedure in the application of 2,9-dimethyl-1,10-phenanthroline involves formation of the cuprous chelate, in which 2 molecules of the substituted phenanthroline coordinate with each cuprous ion not interfered with by large amounts of iron at 454 nm. The limit of identification is 0.03 microgram of copper or 1 part of copper in 1,660,000 parts of aqueous solution after extraction with n-hexyl alcohol [12]. Bismuth together with phosphate and

molybdate forms a very stable complex in acid medium which turns blue "molybdenum blue" by reduction with ascorbic acid. The sensitivity of the proposed method is 0.0078 ppm (aqueous solution) and 0.0066 ppm (MIBK) [13]. 2-hydroxy-3-methoxy-benzaldehyde thiocarbazono reacts with Nickel (II) in aqueous solution at pH 4.0-8.0 and at room temperature to form a yellow colored ML (1 : 1) complex with absorption maximum at 410 nm [14]. Zinc (II) reacts with 3-hydroxybenzylaminobenzoic acid and forms a light yellow colored complex at pH 5.0. The complex has a maximum absorbance at 460 nm. The complex is stable for more than twelve hours [16].

Results and Discussion

Determination of impurities with spectrophotometer

The samples were prepared by hydrolysis of an AIP with 10-20% nitric acid, boiling down of the resultant isopropyl alcohol and decomposition of the excess nitric acid, and dilution of the resultant solution with an appropriate amount of deionized water [7].



Then, we determined the amount of impurities including Fe, Ti, Ca, V, Cu, P, Si, Ni and Zn using their characteristic chelate reagent for each element. The color of the sample changed linearly with the concentration of each impurity element. All the measurement results has been shown in Table-1, respectively, using the standard calibration lines (Fig-3) which have been obtained with the known impurity concentrations of each elements.

After the purification of AIP, it was distilled repeatedly as mentioned above; the impurity level could be reduced as shown in Table-1, respectively.

Determination of impurities with ICP-OES analysis

The determination of impurity metal ion concentration was carried out by T-60 UV-VIS spectrophotometer and Perkin-Elmer Optima 5300 DV inductively coupled plasma optical emission spectrometer. The degree of purification achieved in the alumina precursor powder after 1.5 h with activated carbon, the impurities such as

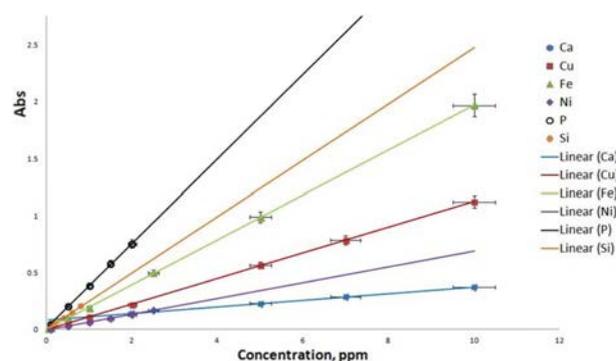


Fig. 3. Calibration graph of impurity elements in aqueous solution.

Table 1. The comparison results of spectrophotometric and ICP analysis.

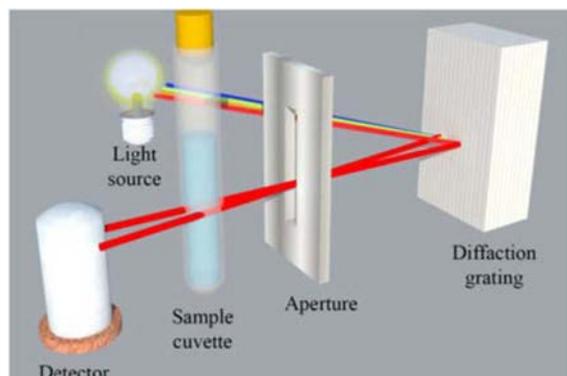
Element	Weight fraction of impurity in the sample, ppm			
	Single distillation		Double distillation	
	Spectrometer	ICP	Spectrometer	ICP
Ca	0.53	0.43	0.45	0.34
Fe	5.81	6.09	2.49	3.71
Cu	0.0	0.39	0.0	0.19
Zn	4.53	4.78	3.21	3.53
Cr	–	0.13	–	0.13
Ni	0.56	0.03	0.35	0.0
Si	0.96	11.62	0.96	6.32
P	0.0	0.0	0.0	0.0
Ti	1.36	0.51	0.84	0.29

Fe, Ti, Ca, V, Cu, P, Si, Ni and Zn were removed in its proportions, respectively (table-1).

Comparison of the impurity measurement techniques

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law. The advantages of the single beam design are low cost, high throughput, and hence high sensitivity, because the optical system is simple. The disadvantage is that an appreciable amount of time elapses between taking the reference (I) and making the sample measurement (I_0) so that there can be problems with drift. This was certainly true of early designs but modern instruments have better electronics and more stable lamps, so stability with single beam instruments is now more than adequate for the vast majority of application.

The analytical characteristics of ICP-OES make it a

**Fig. 4.** Schematic of a wavelength-selectable, single-beam UV-Vis spectrophotometer.

useful technique for metal determinations. It can measure about 70 elements in aqueous solutions. ICP-OES cannot measure H, He, C, N, O, F, Ne, Cl, and some other random elements. Total dissolved solids in solutions need to be less than 1.5%. Optimum working range for element concentrations is 0.5-100 ppm. It is possible to go both lower and higher, but responses may become non-linear. All sample solutions must be filtered and free of particulates, sediments, precipitates, etc.

There are several number of advantages of ICP-OES, it combines good quantitative multi element capability, wide linear dynamic ranges, good sensitivity, limited spectral and chemical interferences, low detection limits, in addition speed and ease of data handling and reporting with widespread instrument availability. Plasma excites all atoms in a sample, and you can choose wavelengths for each element and analyze multiple elements at once. The disadvantage is that the matrix matched standards have to be made for each element of interest, it is high cost. Table-2 summarizes the advantages and disadvantages of ICP-OES and other elemental analysis techniques. Elements such as Ca and Fe are difficult to determine by conventional Ar ICP-MS because of mass spectral interferences by argides.

Ceramic based samples, especially alumina is difficult to completely solubilize via acid digestion. Due to its extreme refractory character, a closed vessel microwave system have been used for decomposition of alumina. These vessels supported maximum temperature and

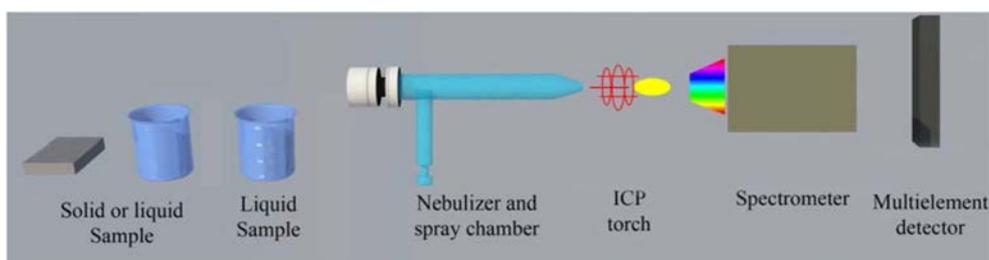
**Fig. 5.** Basic principle of ICP-OES analysis.

Table 2. Summary of elemental analysis techniques.

Technique	Advantages	Disadvantages
AAS	Low detection limits	Few elements, time-consuming, matrix effects
NAA	Low detection limits	Few elements, requires access to reactor
SSMS	Low detection limits, multiple elements	Difficult quantification, surface-sensitive
WDXRF	Multiple elements, solid and liquid samples	Detection limits too high
ICP-MS	Low detection limits, multiple elements, isotope analysis	Matrix effects
ICP-OES	Low detection limits, multiple elements, limited spectral interferences	Liquid samples only, matrix effects
UV-Vis	Simple, Inexpensive	Slow-larger setup time, reagents tend to have short shelf life

pressure of 250 °C and 10 MPa, respectively [8]. Using this system, time and reagent consuming up until now, is a rather tedious analytical operation. Some paper reported that a time of up to 7 hours is required for microwave assisted dissolution of aluminum oxide samples. The analytical methods based on the slurry sampling technique; allow one to omit this critical step, as well to minimize blanks and sample contamination. Slurry sampling with electro-thermal atomization atomic absorption spectrometry (ETAAS) is already used for the determination of some metal impurities in aluminum oxide samples, but this technique allows the determination of single elements only, it is not very fast and the experimental conditions must be very individually optimized. The linear range of calibration in ETAAS is also very limited [9]. In this study, determination of impurities carried out via simple spectrophotometer and aluminum isopropoxide as alumina precursor have been analyzed. Dissolution of aluminum isopropoxide is much easier than digestion of alumina; it gave the chance to save time and the reagent consumption.

Preparation of high purity alumina

There are several papers that have reported being able to obtain a purified alumina. Tae-Soo Suh *et al.* [15] developed a purification method. First, the Na components, which were a major impurity included in aluminum hydroxide, were eliminated by an adsorption method using a silica powder (quartzite). Second, the exposed Na components which had been at the outer surface of alumina during the wet grinding procedure by a ball mill were also eliminated by washing with an aqueous solution of hydrochloric acid. The whole purification procedure of alumina was called the wash grinding method. The reduction ratio of Na₂O corresponding to the particle size of silica powders was reported to increased up to 90% in the case of a particle size of 0.32 mm, which is a relatively small particle size. Also, the degree of mixing is affected largely by the increase in the reduction ratio of the Na₂O component. Dulicina P.F.de Souza *et al.* [4] reported that sodium, silicon, iron, calcium and gallium as impurities in alumina were removed by carbothermal reduction (CRP) from alumina particles between 1100 and 1400 °C. Reduction of calcium and silicon oxides starts as low as 1200 and 1400 °C, respectively. The

Table 3. Purification with activated carbon on single distilled alumina precursor.

Element	Measured concentration, ppm		Degree of purification, %
	Before purification	After purification	
Ca	0.43	0.34	20.9
Fe	6.09	3.71	39.0
Cu	0.39	0.19	51.2
Zn	4.78	3.53	26.1
Cr	0.13	0.13	–
Ni	0.03	0.0	100
Si	11.62	6.32	45.5
P	0.0	0.0	–
Ti	0.51	0.29	43.1

starting material was a commercial aluminum hydroxide (gibbsite) and after conversion to α -alumina the impurities are located mainly in the bulk of the alumina particles. The gibbsite was milled to reach an average particle size of 0.3 μ m and then, carbon black and polyvinyl alcohol were added. The CRP experiments were performed in a 99.9% argon flow, which have produced a carbon monoxide partial pressure as a consequence of the presence of some oxygen in the argon gas. It was found that rates lower than 2.8 dm³/min decreased the rate of removal of iron and calcium. Sodium and silicon removal is decreased at lower argon flow rates. The degree of purification achieved in the alumina powder after 6 h of CRP showed sodium concentration reached the lowest level; iron oxide, silicon oxide and calcium oxide were removed in proportions of 90, 93% and 81%, respectively. There are some shortcomings in the above mentioned works; in wash grinding method, according to the author the sodium contents have been washed and purified at the outer surface of alumina; however sodium contents could be included at the inner part of alumina. It was only in relation to purification of sodium, other elements were not mentioned in that body of work. In carbothermal reduction process, EDS analysis shows that the impurity oxides were reduced by the CRP but the reaction products were not efficiently removed by the reduced argon flow.

In this study, the activated carbons have been used

for purification of alumina precursor as adsorbent material. In that case, more impurity elements could be eliminated than above mentioned methods and the purification process carried out at relatively low temperature. Table-3 shows the impurities before and after purification with activated carbon in alumina precursor, the average degree of purification is around 50%. The efficiency of purification has been increased on more contaminated samples.

Conclusions

We developed a procedure for the determination of impurities in aluminum isopropoxide by simple spectrophotometer using their suitable chelate reagent effect. In comparison with the high cost techniques such as ICP-OES or SSMS for metal ions determination, the spectrophotometric method in this study proved its potential to determine the trace impurity level precisely. It has confirmed that activated carbon could be one of the possible candidates for purification of alumina precursor. The higher efficiency appears to be a function of influent concentration. As influent concentration increases, so does removal.

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