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Special Issue Volume 3 Issue 1, pp. 210 - 223

Date of Publication: 17th May, 2017

DOI-https://dx.doi.org/10.20319/mijst.2017.s31.210223

PYROMETALLURGICAL METHOD FOR THE RECOVERY OF ALUMINUM FROM Fe$_2$O$_3$/α-Al$_2$O$_3$ CATALYST

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Abstract

In this study we report an investigation on the recovery of iron and aluminum oxides by roasting Fe$_2$O$_3$/Al$_2$O$_3$ catalyst with KHSO$_4$ under different operation conditions such as temperature, KHSO$_4$/catalyst mass ratio (K/C) and reaction time. It was found that 79.67% of Al$_2$O$_3$ and 96.94% of Fe$_2$O$_3$ were dissolved after 7h at 600°C and K/C= 36. After the separation of Fe(III) and Al(III) in aqueous solution by a pH-controlled precipitation method, the resulting Al(OH)$_3$ was dehydrated to γ-AlOOH (pseudo-boehmite) by heating at 105°C while γ- η and α-Al$_2$O$_3$+θ residues were obtained after calcination at 500-950 and 1200°C respectively.

Keywords

Pyrometallurgy, Fusion, Dissolution, Alpha alumina, Recovery, Phase transformation.

1. Introduction

Nowadays, economical and environmental requirements impose the development of effective methods for the recovery of valuable metals from secondary sources. A variety of industries are responsible for the release of heavy metals into the environment through their solid wastes (Hannef and Akintug, 2016). Among them, spent catalysts are classified as hazardous materials by the environmental protection agency (EPA) as they may be spontaneously
combustible and release toxic gases. Furthermore, spent catalysts have been proven to contain high amounts of heavy metals that can be leached by water.

The recovery of useful materials from corresponding industrial wastes has been the subject matter of a large amount of research work which aims to produce high purity products meeting the requirements of the market (Ngo and Tran 2017). However, the recovery of hard dissolving compounds such as the constituents of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst fails to be extensively studied. $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst is used in several industrial chemical reactions such as in dehydrogenation of ethylbenzene (Wang et al., 2017), in ethylene oxidation (Ahn and Lee 2002) and in the selective reduction of $\text{NO}_x$ (Ellmers et al., 2015). Two main processes are used for the recovery of metals and metal oxides. The wet process known as hydrometallurgical method is the more conventional technique that has been developed a long time ago in which acid solutions such as $\text{HCl}$, $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, citric and oxalic acids have been used under different operation conditions (Kim et al., 2017; Tuncuk and Akcil 2016; Chen et al., 2015; Tanong et al., 2016). However, these processes found little practical application when mineral phases are extremely stables such as silicates (zircon, tourmaline, oxinite, topaze, etc.) or oxides (corundum, rutile, aluminous spinels, etc.) for which wet method gives only low dissolution efficiency. The dry process called pyrometallurgical method is based on mixing some chemical products in solid form with the sample and heating at high temperatures to form products easily soluble into water (Busnardo at al., 2007; Kar et al., 2005; Trpčevská et al., 2015). The most used products are $\text{LiBO}_2$ at $\sim 900^\circ\text{C}$, $\text{Na}_2\text{CO}_3$ and $\text{K}_2\text{CO}_3$ at $\sim 850$ and $\sim 900^\circ\text{C}$ respectively, $\text{NaOH}$ at $\sim 600^\circ\text{C}$, $\text{KHSO}_4/\text{K}_2\text{S}_2\text{O}_7$ at $\sim 300-600^\circ\text{C}$. These products can dissolve almost all rocks and minerals which are highly stables.

In the literature, studies are generally focused on the improvement of the dissolution efficiency of minerals. However, no research was found dealing with the reformation of metal oxides after their dissolution and separation from the other components. This study was focused first, on the optimization of the operation conditions in order to separate the constituents of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst by roasting it with $\text{KHSO}_4$. Roasting with $\text{KHSO}_4$ was chosen because it is less corrosive than alkaline fusion with $\text{NaOH}$ or $\text{Na}_2\text{CO}_3$. The obtained product after fusion reaction was treated to separate both components by a pH controlled precipitation method. The
second objective of this work was to study the phase transformation (with XRD analysis) of the purified aluminum during calcination at different temperatures.

2. Experimental

The catalyst used in this study was a 5%Fe₂O₃/α-Al₂O₃ (n/n) with a particle size of 100μm. The present study was carried out on a fresh sample in order to avoid interferences with impurities that may affect the dissolution results. The BET surface area of the sample was 21m²/g and its XRD diffraction pattern is shown in Fig. 1. X-ray diffraction patterns were obtained with a X'Pert Pro MPD, Philips diffractometer using CuKα radiation (λ = 1.5406 Å) in step mode between 20° and 80° with scanning speed of 0.02°/s. Identification of the crystalline phases was done by the Joint Committee for Powder Diffraction Standards (JCPDS) file of the instrument. The pH measurements of the solutions were performed using HANNA 931401 pH-meter.

KHSO₄ (99%, Riedel-de Haën) was used as fusion reagent for both Fe₂O₃ and Al₂O₃ while NaOH (99%, Alfa Aesar) was used as precipitation agent. Distilled water was used for all solution preparations and rinsing. In this study, the influences of KHSO₄/catalyst mass ratio (12, 24 and 36), temperature (400, 500 and 600°C), and reaction time (2, 4 and 7h) were investigated. Fusion tests were carried out in 100ml-capacity crucibles which were placed in a furnace at different temperatures for a given reaction time. During fusion tests, aluminum and iron oxides were transformed into metal sulfates according to the following reactions (Busnardo et al., 2007):

\[
\text{Al}_2\text{O}_3 + 6\text{KHSO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{K}_2\text{SO}_4 + 3\text{H}_2\text{O} \quad (1)
\]

\[
\text{Fe}_2\text{O}_3 + 6\text{KHSO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3\text{K}_2\text{SO}_4 + 3\text{H}_2\text{O} \quad (2)
\]

Both forms Al₂(SO₄)₃ and Fe₂(SO₄)₃ are soluble into water. After completion of fusion test, the product was cooled down and a volume of hot distilled water (100°C) was added to the roasted sample under stirring for 30min after which the mixture was filtered. Fe³⁺ and Al³⁺ ions were analyzed in leach liquor with volumetric method. The percentage of dissolutions of iron and aluminum oxides were calculated from the following equation:

\[
\text{(3)}
\]
The experiments were run in duplicate, and errors for each experiment were below 5%.

3. Results and Discussion

3.1 Effect of variables on the dissolution of iron and aluminum oxides

The X-ray diffraction analysis of the sample before reaction with KHSO₄ shows that corundum (α-Al₂O₃) was the major component (Fig.1) whereas hematite (α-Fe₂O₃) was the minor component.

![X-ray diffraction pattern of Fe₂O₃/α-Al₂O₃ catalyst](image)

According to the stoichiometry, 6 mol of KHSO₄ are necessary to react with 1mol of alumina or iron oxide corresponding to 8:1 and 5:1 mass ratios respectively. Generally, in any dissolution operation, stoichiometric amount of a leachant does not show the optimal level of recovery. Furthermore, fusion conducted near the stoichiometric (KHSO₄/catalyst) mol ratio risks to decrease yield due to losses of KHSO₄ that may be transformed into SO₃ at high temperatures according to the following reaction (Busnardo et al., 2007):

\[
2 \text{KHSO}_4 \rightarrow \text{K}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + \text{SO}_3
\]  

(4)

Therefore, it is necessary to use an excess of the leachant so as to compensate such losses. In the first experiment, the reaction was carried out in three crucibles at 400°C. Each crucible contained a definite mass ratio of KHSO₄/catalyst (12:1- 24:1 and 36:1). The amount of the
catalyst used was 0.5g. The same experiment was conducted after that at 500 and 600°C. The crucibles were held at each temperature for 7h.

![Figure 2: Effect of temperature and K/C mass ratio on the dissolution of iron (a) and aluminium (b) oxides](image)

The results (Fig. 2a, b) show that increasing the reaction temperature from 400 to 500°C did not affect the dissolution efficiencies of both metal oxides regardless of K/C used, whereas a clear improvement was observed at 600°C where 96.94% and 79.67% were registered with Fe₂O₃ and Al₂O₃ respectively at 600°C and K/C=36. In order to study the effect of reaction time, the crucibles were held in oven at 600°C for 2, 4 and 7h. The experiments were carried out with the same K/C mass ratios: 12-24 and 36 (Fig. 3a, b).

![Figure 3: Effect of the reaction time on the dissolution of iron (a) and aluminium (b) oxides](image)
Reaction time affected strongly the dissolution results of both metal oxides. In fact, after 2h of fusion reaction 45.34% of Fe$_2$O$_3$ and 22.47% of Al$_2$O$_3$ were dissolved at K/C=12. The efficiencies increased up to 92.32% and 75.05% respectively with the same K/C ratio after 7h. At higher K/C ratios (24 and 36) no great differences in dissolution efficiencies were observed after 4 and 7h especially in the case of aluminum oxide where it registered 75.44% after 4h and 79.67% after 7h with K/C=36. Both values are close indicating that K/C parameter plays less effect than temperature and reaction time. This was also observed in figure 2 where increasing K/C from 12 to 36 at fixed reaction time of 7h did not increase the dissolution efficiencies.

Alpha alumina was more difficult to dissolve; its decomposition kinetic was slow and probably needed more elevated temperature and longer reaction time to reach higher percentage of dissolution. But this is not of a great interest because of the high energy consumption.

### 3.2 Precipitation of Fe$^{3+}$ and Al$^{3+}$

Ones the fusion tests were undertaken and the insoluble metal oxides were transformed into soluble salts, the further step was to separate them in aqueous phase. The sample used was that obtained after fusion with KHSO$_4$ under the conditions: K/C=36, 600°C and 7h.

The pH of the obtained solutions after fusion tests was equal to 1. The separation was possible by choosing a pH interval in which one component could be precipitated while the second one remained in soluble form. The pH range in which iron is in solid form is wider than that of aluminum (Matjie et al., 2005). Thus, in a first step, NaOH at 2M was added in a dropwise manner to the aqueous solution containing soluble salts until the pH attained 8. At this pH value, the formation of a brown hydroxide precipitate was visually observed due to the reactions:

\[
\text{Al}^{3+} + 3\text{(OH)}^- \rightarrow \text{Al(OH)}_3^{3s} \quad (5)
\]

\[
\text{Fe}^{3+} + 3\text{(OH)}^- \rightarrow \text{Fe(OH)}_3^{3s} \quad (6)
\]

Both components were in solid form. At higher pH values (>9) aluminum hydroxide may redissolve again to form Al(OH)$_{4aq}^-$ according to the reaction:

\[
\text{Al(OH)}_3^{3s} + \text{OH}^- \text{(excess)} \rightarrow \text{Al(OH)}_{4aq}^- \quad (7)
\]

Therefore, the pH of the solution was increased further up to 12 and the mixture was heated in order to accelerate the dissolution of aluminum hydroxide. A red metal hydroxide
precipitate appeared indicating that iron remained in the solid form and that aluminum hydroxide was transformed into soluble form.

The precipitate (iron hydroxide) was, after that, separated from the solution by filtration. In a second step, the remaining solution containing soluble aluminum ions was treated to precipitate it by decreasing the pH up to 4 with the addition of sulfuric acid at 2M. A white gelatinous precipitate was then formed. The precipitate was withdrawn after centrifugation, dried at 105°C overnight and analyzed by XRD (Fig. 4). A part of the obtained solid was thoroughly washed several times with distilled water in order to remove residual K\(^+\), SO\(_4\)\(^{2-}\) and Na\(^+\) ions, dried at 105°C overnight and analyzed by XRD (Fig. 5). The obtained solid was exposed to repetitive calcinations (each for a period of 2h) at different temperatures (500, 950 and 1200°C) to produce aluminum oxide (Fig. 6a-c). The aim from varying the calcination temperature was to follow the phase transformation of aluminum hydroxide during heating.

Figure 4: X-ray Spectrum of Aluminum precipitate unwashed and dried at 105°C overnight.
Figure 5: X-ray Spectrum of Aluminum precipitate washed and dried at 105°C overnight

The metal recovery was focused on alumina because it was the main component of the catalyst. The result of X-ray powder diffractogram obtained for the dried alumina at 105°C before washing (Fig. 4) shows a very crystalline structure with a multitude of peaks due to the presence of crystallites containing potassium, sulfate and sodium. After washing with water and drying (Fig. 5) the X-ray spectrum shows broad lines indicating a poorly crystalline sample which could be assigned to the formation of pseudo-boehmite (γ-AlOOH) obtained upon the dehydration of Al(OH)₃.

According to Nguefack et al., 2003 the name pseudo-boehmite is used for solids resulting from different preparation conditions. Their diffraction peaks are broadened compared to those of well-crystallized boehmite. After calcination at 500°C, the obtained product was still an amorphous solid. The X-ray analysis shows two broad peaks indicated by ‘g’ characteristic of γ-alumina (Fig. 6a). The surface area of the solid was 213 m²/g. This high surface area indicated a high porosity of the product resulting from partial dehydration of the pseudo-boehmite.

Heat treatment to 950°C resulted in a changed pattern to a well distinguished peaks corresponding to η-Al₂O₃ (Fig. 6b) and the sintering in surface area was found to be mild (164 m²/g). Tsuchida and Ichikawa 1989 and Tsuchida 1994 have found that amorphous alumina is the prerequisite for η-Al₂O₃ which agree with our results.
Heating to 1200°C enables the transformation of the sample to α-alumina with some residues assigned to θ-Al₂O₃ indicated by ‘t’ as shown in figure 6c. The BET surface area of the sample was 14m²/g.

It is reported that the amorphous aluminum hydroxide can be transformed into one of the various transitional alumina through the elimination of most of the water of constitution. This transformation leads to alumina with partially disordered structures (χ, κ, γ, δ, θ…etc.). As the calcination temperature increases, the structures become more ordered until the final transformation to the extremely stable corundum (α-Al₂O₃) form. However, there is still disagreement on the sequence of formation of transitional alumina phases, their structures and the mechanism of dehydration. In the literature, two major sequences are related for the crystalline transition of alumina (Jang et al., 2000). The first sequence is believed to be as follows: γ-Al₂O₃ (ca. 450°C), δ-Al₂O₃ (ca. 750°C), θ-Al₂O₃ (ca. 1000°C) and α-Al₂O₃ (1200°C). The second sequence: χ-Al₂O₃ (ca. 400°C), κ-Al₂O₃ (900°C) and α-Al₂O₃ (1200°C). In our case the sequence followed by aluminum hydroxide was: Pseudo-boehmite (105°C), γ-Al₂O₃ (500°C), η-Al₂O₃ (950°C) and α-Al₂O₃+θ residues (1200°C). Generally, only pure α-Al₂O₃ is detected at 1200°C.
Figure 6: X-ray analyses of Aluminum hydroxide calcined at 500°C (a), 950°C (b) and 1200°C (c) for 2h.

To the best of our knowledge, there are no literature reports regarding the dissolution of α-Al₂O₃ into soluble aluminum ions and their recombination once more into alpha alumina. However, it is reported that the phase transformation of aluminum hydroxide depends on a number of factors including precursor material, crystallite size, pressure, moisture, temperature applied during calcination and heating rate (Ingram-Jones et al., 1996). The presence of residual θ-Al₂O₃ at 1200°C is an indication that the final product was affected by the operations applied for the separation of Al₂O₃ from Fe₂O₃ and the different steps used such as washing, drying and calcination to produce the end product in pure form.

Alpha-alumina has several special properties such as hardness, chemical inertness, wear resistance and a high melting point. This method was applied because dissolving alpha alumina with other classical leachants such as HCl or H₂SO₄ was not effective (Boukerche et al., 2010, Larba et al., 2013). Alumina based ceramics was found to corrode under hydrothermal conditions because of the dissolution of the impurities existing at the grain boundaries such as MgO, CaO, SiO₂ and Na₂O₃ (Oda and Yoshio 1997; Genthe and Ausner 1992) while the dissolution of Al³⁺ in bulk material was found to be negligible (Curkovic et al., 2008). The alumina support used in
this study was a pure product which explains the fact that under moderate conditions (hydrothermal treatments with HCl or H₂SO₄ solutions) no dissolution was observed and even under drastic conditions like those tested in this work it was not totally dissolved.

It is worth-noting that under the conditions: K/C=12, 600°C and 7h the dissolution efficiencies registered 92.32% and 75.05% with Fe₂O₃ and Al₂O₃ respectively. When K/C increased to 36 the dissolution efficiencies slightly increased to 96.94% and 79.67% respectively after the same reaction time and temperature. Thus, it can be considered that the optimal amount of the roasting agent under the conditions used in this study is 12:1 which is more reasonable from economical point of view.

4. Conclusion

The pyrometallurgical process developed for the treatment of Fe₂O₃/Al₂O₃ catalyst allowed to recovery high percentage of both components. The optimal operation conditions were K/C= 12, T=600°C and t=7h. Both metal oxides were more sensitive to the variation of temperature and reaction time than to K/C mass ratio. The reformation of pure Al₂O₃ after its separation from Fe₂O₃ was possible. XRD analysis of the product calcined at different temperatures showed amorphous behavior till 500°C, at 950°C it was transformed to η-alumina and at 1200°C α+θ alumina was obtained. Alumina obtained at different temperatures may be reused as raw material in new processes such as coating, adsorbent, ceramic and as catalyst support. The method used in this study may be a useful alternative to landfill of hard dissolving compounds which are difficult to separate from other solid wastes with hydrometallurgical methods.
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