Recycling and Utilization of Spent Hydroprocessing Catalysts

Meena Marafi [1]* and Antony Stanislaus [2]
Petroleum Research & Studies Center
KISR, P.O.Box 24885, Safat, Kuwait
*mmarafi@prsc.kisr.edu.kw

Introduction

Spent hydroproceesing catalysts constitute a major portion of the solid wastes generated in the petroleum refining industries. As these catalysts are hazardous wastes, land filling or other treatment methods for disposal are not preferable when all costs and liabilities are taken into account. Although the recovery of metals from spent catalysts have been reported in many studies, the recovery of alumina in the form of boehmite has received little attention in the earlier studies [1,2]. Boehmite is an important precursor for γ-alumina which is widely used as support in many industrially important catalysts. In the present work, studies were conducted with the objective of recovering alumina in the form of high purity boehmite after extracting the valuable metals from a decoked spent hydroprocessing catalyst that contained 8.8wt% MoO_3, 5.9wt% NiO, 17.4wt% V_2O_5, and the balance Al_2O_3.

Materials and Methods

The spent catalyst was roasted with sodium carbonate at 700°C for 2hrs to convert the MoO_3 and V_2O_5 to sodium molybdate and sodium vanadate which were subsequently dissolved in water and removed by filtration. The residue containing NiO and Al_2O_3 was digested with caustic soda in an autoclave at 250°C for 3hrs to dissolve the Al_2O_3 as sodium aluminate leaving NiO as residue. $Al(OH)_3$ was precipitated from the sodium aluminate solution by treating with CO_2. The $Al(OH)_3$ precipitate was washed thoroughly, and then subjected to hydrothermal treatment in a high pressure autoclave. The hydrothermally treated product was filtered, washed, dried at 110°C, and characterized by X-ray diffraction, surface area, pore volume and pore size distribution measurements.

Results and Discussion

XRD analysis of the hydrothermally treated material confirmed that it is 100% boehmite (Fig. 1). $Al(OH)_3$ transforms to boehmite (ALOOH) under hydrothermal conditions by the removal of 1 mole of H_2O per mole of $Al(OH)_3$ by dehydration. The effects of temperature (in the range 180-240°C) and duration (6-30hrs) of hydrothermal treatment on boehmite formation, its crystallinity, surface area and porosity were examined. The results presented in Table 1 show that increase in hydrothermal treatment temperature from 180 to 240°C increased the crystallinity of boehmite and reduced its surface area and pore volume. Increasing the duration of hydrothermal treatment from 6 to 30hrs also led to a substantial reduction in the surface area and pore volume. These changes in boehmite properties also affected the properties of γ-alumina prepared by calcinations of boehmite at 500°C (Tables 1). The pore size distribution data for the γ-alumina samples (Fig. 2) derived from the boehmite samples prepared at different temperatures show a bimodal pore size distribution in all samples. However, the amount of large pores increases with increasing temperature. The above results clearly show that high quality boehmite, that is suitable for the preparation of γ-alumina with high surface area (>240 m^2/g), large pore volume (> 0.75 ml/g) and mean pore diameter in the desirable range (100-110 A), could be recovered from spent hydroprocessing catalysts.

Significance

The recovery of boehmite for reuse from spent hydroprocessing catalyst wastes together with the extraction of valuable metals not only can add more economic value to the metal recovery process, but also can lead to total recycling of such hazardous spent catalysts without leaving the residual alumina for disposal.

Table 1. Effect of hydrothermal treatment temperature on surface area, pore volume and pore size of boehmite and γ-alumina.

Temp (°C)	Boehmite			γ-Al_2O_3		
	Surface Area (m^2/g)	**Pore Volume (ml/g)**	**Pore Dia (Å)**	**Surface Area (m^2/g)**	**Pore Volume (ml/g)**	**Pore Dia (Å)**
180	244.01	0.68	96.6	269.21	0.78	101.3
200	184.44	0.65	117.3	195.94	0.74	126.2
240	117.02	0.52	173.2	149.69	0.66	170.6

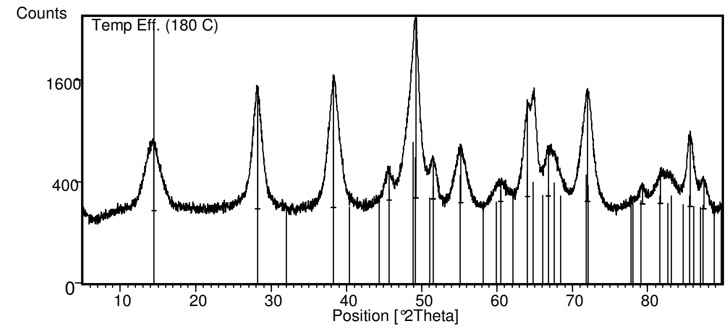

Figure 1. XRD pattern of boehmite prepared by hydrothermal treatment of $Al(OH)_3$ at 180°C for 20hrs

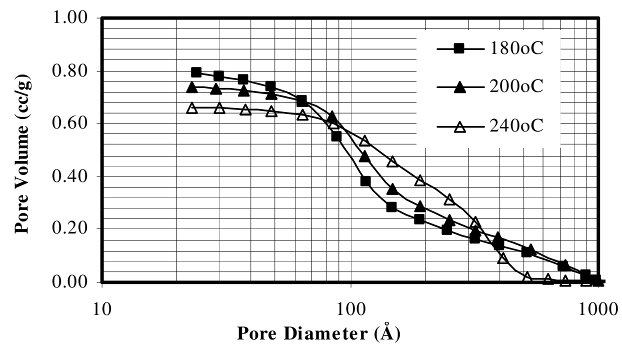

Figure 2. Pore size distribution of γ-alumina derived from the boehmite samples prepared under different hydrothermal treatment temperatures.

References

1. Furimsky, E. *Catal. Today* 30, 223 (1996).
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