Effect of Acetic Acid Concentration on the Alumina Properties

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Abstract

Alumina support were prepared by pressing using alumina as main material, and adding proper bonding-agent. the influence of peptizator on the properties of alumina support, such as surface area, Side crushing strength and surface acidity was investigated. The results show that peptizator can improve the side crushing strength, but have small effect on the surface area of alumina in a certain range when peptizator was in a certain range. However the excess acetic acid will destroy the alumina particle structure, increasing catalyst internal stress, which not only reducing the strength of the catalyst, but also reducing the surface area and surface acidity of alumina support; the results of characterization showed that the size of alumina support particle and stacking mode of agglomerate was changed with the adding of peptizator, meanwhile the number of co-ordinatively unsaturated surface tetrahedral sites aluminum atoms was also altered, then the various of properties of alumina support are changed.

Keywords

Alumina; Peptizing Agent; Acetic Acid.

1. Introduction

Increasing environmental restrictions on petroleum products to limit the sulphur level in fuels necessitated new generation hydrodesulfurization (HDS) catalysts.[1] Previous study clearly showed that the support nature play an important role in the catalytic behaviour of HDS catalysts.[2-4] And enhancing dispersion of the catalytic metal-sulfide is one of the approaches to modify the HDS catalyst. The moulding process effected the activity of catalysts,so the moulding is an important step in production of catalysts used for industry[5]. Most research is focused on alumina-supported catalysts[6]. One of the notable features of alumina support is its excellent mechanical strength. However, intensive researches have shown that rather strong chemical interactions exist between the alumina and the transition metal oxides of precursor[7]. Some of the interaction species are very stable and may prevent complete sulfidation thus decreasing the catalyst HDS activity. The common methods of alumina production are by injection, extrusion, spray, gel-forming and press-moulding. It is used extensively in producing of industrial catalysts with the features simple, high efficientive and low cost in press-moulding.

In present work, the alumina was produced by press-moulding with the sucrose as the binding agent. In order to improve and optimize the forming technology with the further aim of enhanced the activity of alumina as support of hydrodesulfurization catalysts, the objectives of this study are to determine effect of peptizing agent on the alumina properties,

2. Experimental

2.1 Reagents and procedure

Reagents used in this work included alumina powders, sucrose and acetic acid. The alumina was milled to pass a 300 mesh screen and then dried at 110^{o}C for 2h. Alumina powders with 25wt.% sucrose as binder was ingredients in a large bowl and stir gently until well mixed, followed by adding different concentration acetic acid as the peptizing agent was added and kept under stirring 15min. A wet paste was obtained and kept in a closed glass vessel for 24 h at room temperature to maintain moisture and allow homogenization of the mixture. After that, the paste was shaped into cylinder in a laboratory-type mould. After being dried at 105^{o}C in air for 3 h, the shaped samples were transferred to a tubular oven and further calcined in flowing N_2 (75 ml/min), where the temperature was increased

10ºC/min and remained at 600 ºC for 2 h. The calcined samples with 0,50vol.%,60vol.%,70vol.% acetic acid were denoted as Al_2O_3 1,2,3,4 separately.

2.2 Analysis

The side crushing strength (SCS) of the AAC was measured by using an YHKC-2A grit compressive strength instrument (Yinhe plant in Jiangyan, China). BET surface area and pore size distribution of the supports Al_2O_3, AC and AAC were determined by using a ST-03A (Laidi appearance Co. in Beijing, China) adsorption analyzer. The X-ray diffraction (XRD) patterns of the catalysts were investigated with a Rigaku D8-FOCUS diffractometer using nickel-filtered Cu Kα radiation scanning 2θ angles ranging from 10º to 80º. Fourier-transformed infrared (FTIR) spectra were measured using the KBr method on a Fourier-transform infrared spectrometer (Bruker Nicolet-5700) and recorded in the range of 4000–500 cm^{-1}.

3. Results and Discussion

The crushing strength is an important factor in which determine that if the hydrodesulfurization catalysts can be used in industry [8]. In order to avoid the pressure drop increased with the catalyst crumble in transport, inserted and used, the higher crushing strength is inquired. The crushing strength of hydrogen catalysts depends on the support. An appropriate amount of peptizing agent is needed in alumina molding to achieve higher crushing strength and macropores for DBTs sulfur compounds in petroleum[9]. The acetic acid is selected as petizing agent in present work. Table 1 shows the side crushing strength of alumina with different concentration acetic acid.

Table1. The side crush strength of alumina

Acetic acid vol.%	0	50	60	70
SCS(N/mm)	160.4	165.4	182.6	173.3
$S_{BET}(m^2/g)$	138	122	80	50
Pore size(nm)	3.9	4.2	3.8	4.3

The side crushing strength of the alumina with 60 vol.% acetic acid is 182.6 N/mm, much higher than 128N/mm of the alumina employed, indicating that an addition of acetic acid increased the mechanical strength of the alumina in moulding, moreover the side crushing strength is increasing with the acetic acid concertration increased when the concentration is less than 60vol.%. Therefore, the alumina is expected to be a mechanically enhanced support for commercial HDS catalysts but the acetic acid concentration is not too higher.

Table 1 shows the pore size of the Al_2O_3 1,2,3,4. The Al_2O_3 exhibited a mesoporous character with a dominant pore size around 4.0 nm, larger than Al_2O_3 (1.7 nm) which employed with no dealing with acetic acid, which is mainly the contribution of the secondary pores formed by the combination of primary particles. Moreover, the decomposability of sucrose during calcination could render a high interparticle void volume. The BET surface area of alumina is decreasing with the acetic acid concentration increased indicating a reduction of micropores because of the incorporation of acidic solution and hydrothermal treatment during the production of the alumina.

Fig. 1 presents the XRD patterns of Al_2O_3 which incorporation of acidic solution and H_2O respectively. The Al_2O_3 sample shows γ-Al_2O_3 at 2θ of 67, 45.8, 37.6, 39.5 and 19.4º [10]. It is noted that two alumina exhibit mainly γ-Al_2O_3 characters. The peptizing agent has no affection on XRD patterns of Al_2O_3.

Fig. 2 shows the FTIR spectra of the sufractant alumina. The strong peaks around 3400cm^{-1} for all the samples correspond to the stretching modes of hydroxyl groups and bridged hydroxyl groups [11]. In addition, the sharp bands at 1634 cm^{-1} result from the bending oscillation of -OH. The sharp bond around 1070 cm^{-1} for the alumina with 70 vol.% acetic acid is specified as the bending modes of hydroxyl groups in alcohol, water and Al–OH–Al groups [11], and is recognized as a characteristic of

boehmite or pseudo-boehmite [12]. This result is in good agreement with the XRD results mentioned above. Furthermore, the broad bond centered at 600 cm^{-1} is recognized as acharacteristic of γ-Al_2O_3 [11], which is consistent with that observed by XRD analysis.

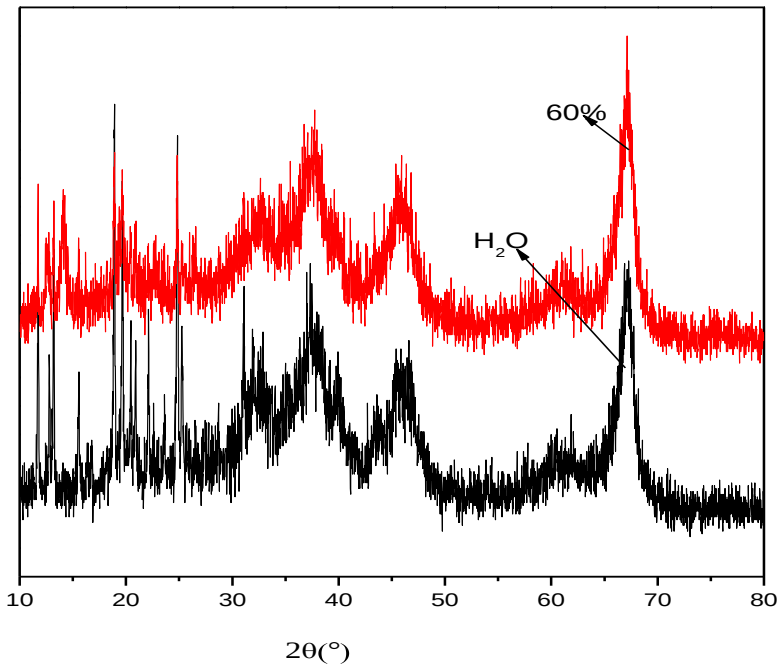

Fig. 1 XRD patterns of alumina

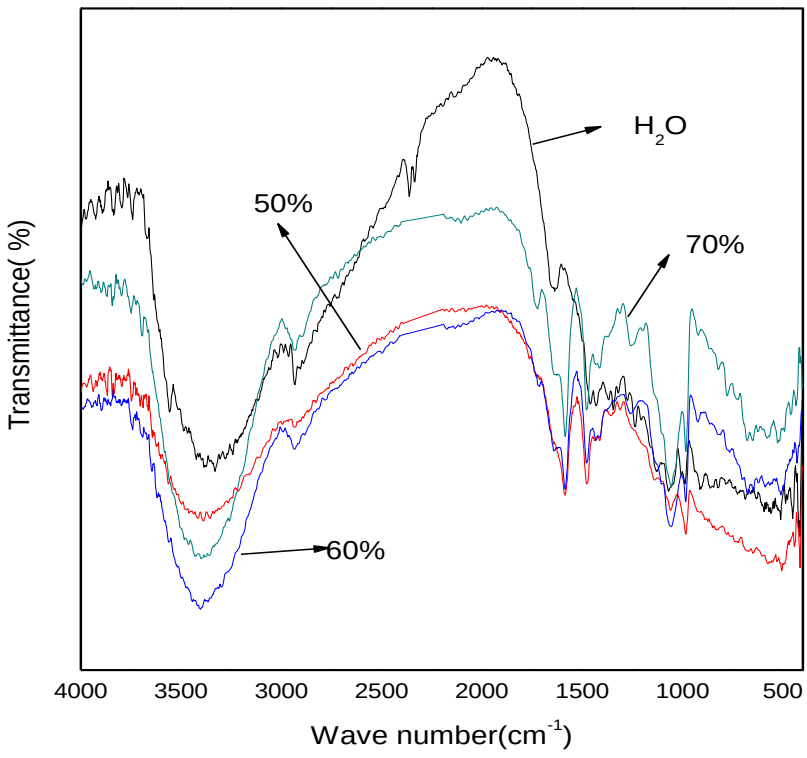

Fig. 2 FTIR spectra of different samples

4. Conclusion

The alumina properity was effected by peptizing agent which added in alumina moulding process. The side crushing strength of the alumina with 60 vol.% acetic acid is 182.6 N/mm, much higher than 128N/mm of the alumina employed. But the BET surface area of alumina is decreasing with the acetic acid concentration increased, so the acetic acid concentration should not too high. It is more acidic for alumina with higher acetic acid concertration and the phase of alumina is not affected by peptizing agent.

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