HYDROTHERMAL STABILITY OF ALUMINUM BORATE

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Aluminum borate with Al to B ratio of 10 was treated with water steam at 750 ° C for up to 48 h. It was found that steam would change the pore size distribution and the surface area of the aluminum borate. It did not possess superior hydrothermal stability under severe conditions. This can be ascribed to high surface instability of transition materials especially for boron compounds. However, even when only a small amount of boron is incorporated into the alumina structure, the surface area of such material can be increased.

1. Introduction

The hydrothermal treatment of fresh resid hydrodesulfurization (RDS) catalyst is important because the catalytic activity of the catalyst in its fresh state is an inadequate measure of its performance. During operation in a commercial RDS plant, the catalyst is deactivated by thermal and hydrothermal degradation. Under equilibrium conditions, the catalyst inventory of the units is called the equilibrium catalyst and this type of catalyst has an activity level substantially below that of fresh catalyst. Therefore, the determination of the catalytic activity of a catalyst is more meaningful if the fresh catalyst is first artificially deactivated.

Alumina is the most widely used catalyst support in industry. Hydrotreatment of residue oils is generally carried out over alumina supported catalysts containing combinations of cobalt and molybdenum salts or nickel and molybdenum salts (Ohtsuka [5]; Stanislaus et al. [6]).

A recently presented result (Chen et al. [1]) described a new hydrodesulfurization (HDS) catalyst of aluminum borate (AB) supported cobalt-molysulfide, and showed that it is more active than the conventional CoMo/Al_2O_3 catalyst in RDS reaction. If it were commercialized, the first problem to be faced is that of deactivation of catalyst resulting from hydrothermal condition. It is, therefore, of great interest to investigate the effect of hydrothermal treatment on aluminum

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borate support. It is known that water steam generated by the RDS process may alter the pore structure of the catalyst or support. A commercial alumina was also included for comparison. The objective of this study is to access the hydrothermal stability of aluminum borate.

2. Experimental

The aluminum borate support with the Al to B ratio of 10 was prepared from common solutions of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) and boric acid (H_3BO_3) using an ammonium hydroxide solution as a precipitant. A well-stirred container was charged with distilled water as buffer. The two solutions previously described were slowly added into this distilled water with a controlled rate of addition in order to maintain the pH of the solution at a constant value of 8.0 ± 0.1. The resulting precipitate was filtered, washed with distilled water and dried overnight at 373 K. Dry clump aluminum borate and appropriate distilled water were well grinded. The mixture was extruded. The diameter of extrudate was 1/16 in. The wet extrudate was dried in air at room temperature and then calcined at 773 K for 5 h. A commercial alumina support from United Catalyst Incorporation was included for comparison.

Dried samples were placed in a verticle-type quartz reactor tube, and temperature was controlled with a West 2050 PID controller. The catalyst bed was held between two quartz wool plugs. A simplified schematic diagram of the hydrothermal treatment apparatus is shown in fig. 1. The sample was treated with air-diluted water steam at variable contact periods varying from 4 to 48 h. The water stem flow rate was maintained at 1000 μl/min and the reaction tempera-

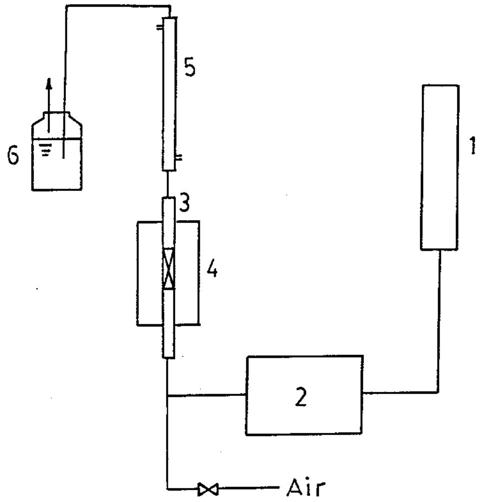

Fig. 1. Hydrothermal treatment apparatus.

ture kept at 750 ° C. In order to give the concentration profile of water steam and the heat flux profile of the system a more homogeneous distribution, appropriate air was used as a carrier gas in this study. These deactivation conditions are generally used in testing the hydrothermal stability of cracking catalysts (Sterte et al. [7]), and these are also testing standard of material for hydrothermal stability of ASTM (700 ° C to 850 ° C).

The metal contents of the aluminum borate support were determined by means of Inductively Coupled Plasma-Atom Emission Spectroscopy (Jarrell-ash 1100). The specific surface areas of the samples were measured by the traditional BET method with volumetric nitrogen adsorption (Micromeritics 2500). The pore size distribution was measured by nitrogen adsorption.

3. Results and discussion

The results from the hydrothermal treatment of alumina and aluminum borate samples are shown in figs 2 to 4. As shown in fig. 2, the deactivation curve can be subdivided into two distinct parts. The initial period is characterized by a rapid but continuously decreasing deactivation rate. In contrast, the final period or ultimate deactivation demonstrates a nearly constant deactivation rate.

It has been widely accepted that water modifies carbon, sulphur, vanadium and nickel deposited during the HDS and HDM of heavy crude oils. In addition, water will change the pore size distribution and surface area of catalyst or support. Fig. 2 also shows that the surface area of fresh commercial alumina support was 166 m^2/g. After 48 h deactivation at 750 ° C, it decreased to 104 m^2/g and lost 37% of its surface area. A similar situation also took place on aluminum borate support, it lost approximately 48% of the surface area of the

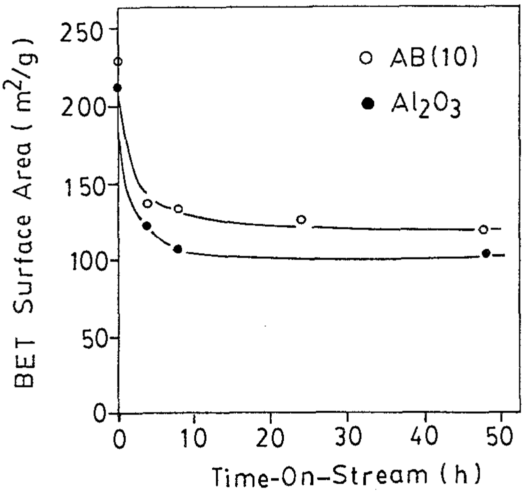

Fig. 2. Influence of hydrothermal treatment on BET surface area.

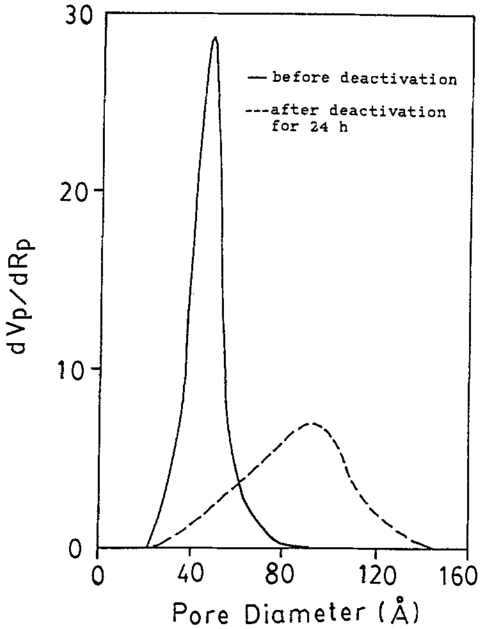

Fig. 3. Pore size distribution of aluminum borate catalyst before and after hydrothermal treatment.

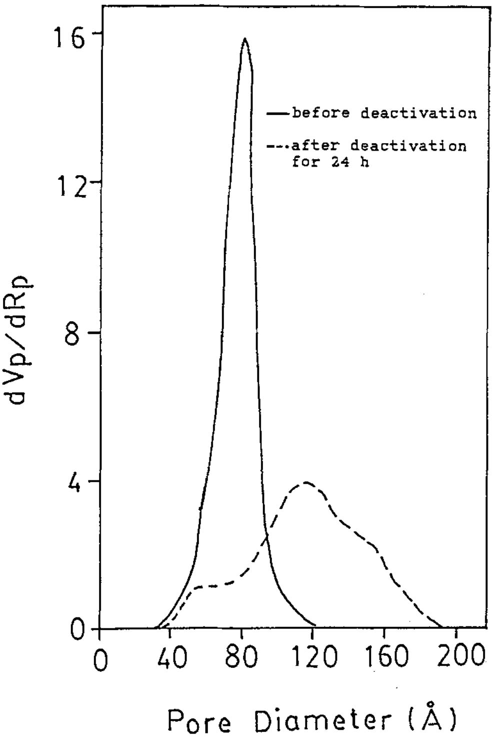

Fig. 4. Pore size distribution of alumina catalyst before and after hydrothermal treatment.

undeactivated sample. Therefore, as far as hydrothermal stability is concerned, aluminum borate is not as good as the alumina one. To be more specific, for providing support surface area for metal under severe hydrothermal conditions, both are not good.

Figs. 3 and 4 showed the changes of the pore size distributions before and after deactivation of aluminum borate and alumina samples, respectively. The aluminum borate sample has a rather narrow pore size distribution centered around a pore diameter of about 50 Å. By water steam treatment at 750 ° C for 48 h, the pore size distribution was shifted toward larger pore size with mean pore diameter of about 95 Å. This destruction effect of micropore diameter is attributed to high surface instability of transition aluminum borate especially for surface boron, which tend to envolve in the presence of water environment. Dobres et al. [2] reported that sintering begins in the aggregates of small micropores and subsequently spreads out to pores with a larger pore diameter. On the other hand, the alumina sample has a rather relatively broad pore size distribution centered around a pore diameter of about 80 Å in comparison with aluminum borate. The trend of the variation of the pore size distribution for the alumina sample was also obvious, but its extent was smaller than for aluminum borate. These results indicate that macroporous materials are more stable than microporous ones. This result is consistent with the report by Galiasso et al. [4].

Whereas a catalyst with a broad pore size distribution is also predicted to sinter more rapidly than that with a narrow pore size distribution (Flynn and Wankes [3]). Therefore, the pore size, the pore interconnection network, and the type of its distribution whether narrow or broad, unimodal or bimodal must be taken into account simultaneously in affecting the surface affecting area an the pore size distribution under water steam surroundings. Galiasso et al. [4] hypothesized that water is apparently adsorbed on certain Lewis acid sites of the catalyst, thus producing a partial rehydration of the alumina at temperature above 400 ° C and partial water pressure below 1 bar. The highly exothermal reactions generate significant water pressures in the micropores, which walls are weakened due to mechanical reasons and to a high surface reorganization capacity yielding more organized aluminas. This hypothesis was confirmed by XRD study, since the hydrothermal treatment increases crystallinity of the catalyst. A similar case may occur on aluminum borate and can be used to interpret the hydrothermal results.

It is worth mentioning that even though the aluminum borate support did not possess superior hydrothermal stability under severe conditions, the operated ultimate temperature in a typical run of RDS plant seldom exceeded 430 ° C. In addition, the temperature effect affects physical properties more than other factors, such as space velocity of steam, pressure of the system and so on, during the course of water steam treatment. In other words, the decrease of surface area and the change of pore size distribution will less severe under in situ practical operation conditions. This phenomena implies that the reduce of appropriate surface area to provide the raise of pore diameter is useful to enhance the HDS and HDM activity and stability since the pore diffusion always plays an important role in heterogeneous catalytic reactions. During HDS and HDM, coke and metal deposit were open to result in the pore mouth plugging especially for more heavier feedstock on the microporous catalyst. The investigation results showed that the CoMo/aluminum borate catalysts are more active than the conventional CoMo/alumina catalyst in RDS reaction (Chen et al. [1]). However, the average pore diameter of such catalysts were not larger than the commercial CoMo/alumina catalyst. The water steam which was generated by the RDS process may alter the pore diameter of aluminum borate catalyst and prevent the catalyst from pore plugging. The results in this study much strengthen the confidence that this type of catalyst is a very good candidate for RDS reaction.

4. Conclusion

The results of hydrothermal stability of alumina and aluminum borate in this study indicate that water destroys the micropores of the carriers and produces mesopores. It can be tentatively concluded that the larger the pore diameter and/or the narrower the pore size distribution, the higher the hydrothermal stability. In addition, even if only a little boron is incorporated into the alumina structure, the surface area of such material can be increased.

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