

Preparation of a large pore alumina-based HDM catalyst by hydrothermal treatment and studies on pore enlargement mechanism

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Abstract

The changes occurring in the alumina phase during hydrothermal treatment of γ -alumina in the presence and absence of additives such as P, F, phenol and acetic acid, were investigated with a view to understand the mechanism of pore widening in γ -alumina under hydrothermal conditions. The results showed that the formation and growth of boehmite into large crystallites by rehydration of γ -alumina was responsible for pore enlargement. As a part of the study, a wide pore Ni-Mo/ γ -alumina was prepared by hydrothermal treatment procedure and its performance in vacuum residue hydroprocessing was evaluated. The catalyst showed a remarkably high activity for hydrodemetallization and asphaltenes conversion reactions in vacuum residue hydroprocessing. Distribution of the deposited metals within the catalyst pellet was more uniform for this catalyst compared to that of a conventional HDM catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pore enlargement in alumina; Hydrothermal treatment; Hydrotreating catalyst preparation

1. Introduction

Many important catalysts used in the petroleum refining industry are based on alumina supports. In alumina supported catalysts, the active catalyst components remain dispersed to a large extent within the pores of the support. The pore size of the alumina support, therefore, plays an important role in influencing the activity of the catalyst, particularly for reactions involving large molecules.

Recently research on the preparation of alumina supports with wide pores has been stimulated by renewed interest in the upgrading of petroleum heavy cuts and residues by hydroprocessing by alumina-

based Co-Mo and Ni-Mo catalysts. The residues contain high concentrations of undesirable heteroatoms (e.g. S, N, V, Ni) bound to large macromolecular structures some of which have molecular diameters in the range 2–10 nm [1]. Catalysts used in residual oil hydrotreating processes deactivate predominantly by pore blockage due to metals deposition [2]. To avoid rapid catalyst deactivation by metal deposits, multiple reactor fixed-bed hydrotreating units with graded catalyst systems having different pore sizes are used [3,4]. A large pore HDM catalyst designed to maximizing metals removal and to provide a large capacity for metals accumulation is recommended for use in the first reactor. In effect, this will protect the more active, narrow pore more active—high surface area HDS and HDN catalysts that follow in the other reactors in series from metals contamination.

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Several methods such as the use of pore forming additives, controlling alumina precursor (e.g. boehmite) crystallite size during precipitation and aging, thermal sintering, etc. have been reported in the literature for preparing large pore of alumina supports [5,6]. Pore size control of γ -alumina supports by low temperature hydrothermal treatment has been the subject of some investigation in our laboratory [7,8]. The results of the previous studies showed that pores could be widened selectively with greater than 70% of the total pore volume in the desired pore size range by low temperature hydrothermal treatment. However, the mechanism of pore enlargement under such mild hydrothermal conditions was not clearly established in the study. In the present work, further studies were conducted to secure a better understanding of the mechanism of pore widening under low temperature hydrothermal treatment conditions and to have a more effective control over the process. In addition, a large pore Ni-Mo/ γ -alumina was prepared by hydrothermal treatment and its performance in hydrotreating Kuwait vacuum residue was evaluated.

2. Experimental

Pure γ -alumina (surface area 185 m²/g, pore volume 0.5 ml/g), and fluorine and phosphorous containing γ -aluminas were used in the study. For hydrothermal treatment experiments a 500 ml autoclave was used. The autoclave was first loaded with about 100 ml distilled water, and then a 20 g sample of the alumina was loaded in a basket and placed in the autoclave above the surface of the water. The autoclave was then heated to different temperatures in the range 150–300 °C. The heating time varied between 1 and 8 h. In a few experiments, 25% phenol/water or 25% acetic acid/water solution was used instead of pure water. Following the treatment, the autoclave was cooled rapidly, the alumina sample was dried at 110 °C, and then calcined at 400 °C for 1 h and at 500 °C for 3 h. Treated alumina samples were characterized before and after calcination. A mercury porosimeter (Quantochrome Autoscan 60) was used to determine pore size distribution. A Quantasorb adsorption unit was used for BET surface area measurements. X-ray diffraction (XRD) analysis of the samples was performed using an X-ray spectrometer

(Philips PW 1410) operated at 30 kV and 20 mA with Cu K α radiation. The hydrothermal treatment procedure described above was used to prepare a large pore Ni-Mo/ γ -alumina. Hydrotreating performance tests were conducted with 50 ml catalyst in a fixed-bed reactor using Kuwait vacuum residue as feedstock under the following conditions: LHSV = 2 h⁻¹; H₂/oil ratio = 1000; pressure = 120 bar; temperature = 440 °C. The feedstock contained 5.2 wt.% sulfur, 0.44 wt.% nitrogen, 94 ppm vanadium, 26 ppm nickel, 9.2 wt.% asphaltenes and 19.2 wt.% CCR and had an API gravity = 6.8. Feed and product samples were analyzed by standard procedures. A first order kinetic equation was used to determine the HDN rate constant. The rate constants for HDS, HDM and asphaltenes conversion (HDAs) reactions were determined using the following standard *n*th order kinetic equation with *n* = 2 for HDS, 1.5 for HDM, and 2 for HDAs.

$$k = \frac{\text{LHSV}}{n-1} \left(\frac{1}{S_p^{n-1}} - \frac{1}{S_f^{n-1}} \right)$$

where *S_f* is sulfur content in feed (wt.%) *S_p* the sulfur content in product (wt.%).

Relative volume activities (RVAs) of the catalyst for various reactions were determined from the rate constants using the following equation:

$$\text{RVA}_{\text{sample}} = \frac{k_{\text{sample}}}{k_{\text{standard}}} \times \text{RVA}_{\text{standard}}$$

A conventional HDM catalyst was used as the standard reference catalyst with an RVA = 100.

3. Results and discussion

Initial studies were focused on the effect of hydrothermal treatment in pore enlargement of pure γ -alumina. The results presented in Fig. 1 show that pore widening in γ -alumina occurs as a result of hydrothermal treatment and the shift in the pore size to the larger range increases with increasing temperature confirming our earlier findings [7,8]. The next set of experiments was designed to investigate the mechanism of pore enlargement in γ -alumina supports under hydrothermal treatment conditions. For this purpose, a series of hydrothermal treatment

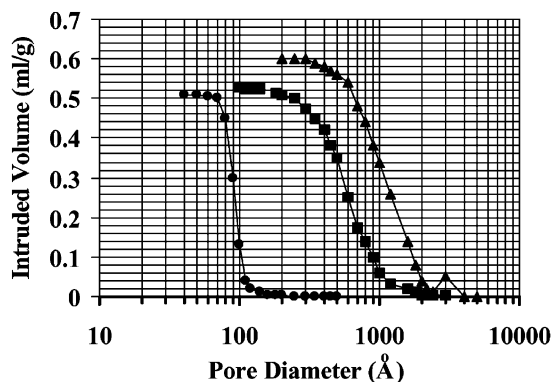


Fig. 1. Effect of hydrothermal treatment on pore enlargement of γ -alumina. (●) Untreated γ -alumina; (■) treated at 200 °C; (▲) treated at 300 °C.

experiments were conducted on pure γ -alumina as well as on F and P containing γ -aluminas and the changes in pore size distribution of different aluminas were examined after the treatment. The results are presented in Fig. 2(a) and (b). A large shift in the pore size to the higher range is noticed for pure γ -alumina (with no F or P) after hydrothermal treatment, whereas in the F and P containing aluminas no appreciable widening of pore size occurs upon hydrothermal treatment under similar conditions. These results indicate that in γ -alumina containing F or P, the pore enlargement that occurs under hydrothermal treatment conditions is suppressed.

With a view to understand the reason for the observed suppressive effect of F and PO_4 ions on alumina pore enlargement under hydrothermal treatment conditions, we examined the changes occurring to the γ -alumina phase upon hydrothermal treatment. The hydrothermally treated samples were dried at 110 °C and then examined by XRD. Fig. 3 shows the XRD patterns of γ -alumina before and after hydrothermal treatment. The XRD patterns of pure γ -alumina and F and P containing γ -aluminas after hydrothermal treatment are presented in Fig. 4. It is seen that in the case of pure γ -alumina (with no F or P), the hydrothermally treated sample contains mainly boehmite crystals indicating that the γ -alumina is transformed to boehmite upon hydrothermal treatment. Calcination of the hydrothermally formed boehmite at 450–500 °C results in the formation of γ -alumina. It appears that

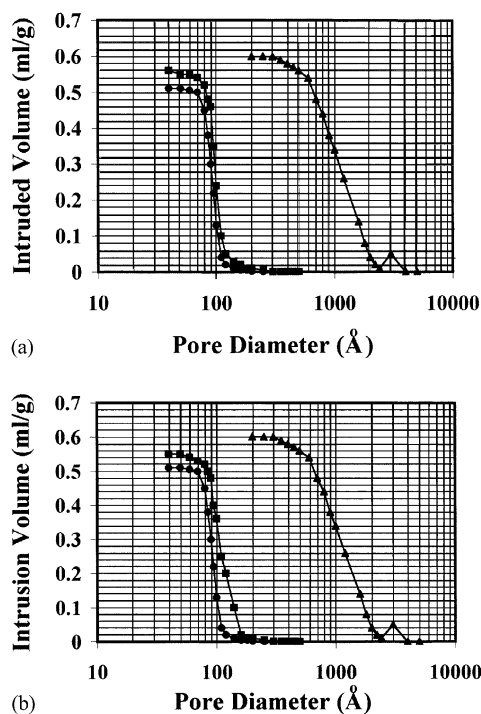


Fig. 2. (a) Effect of hydrothermal treatment on pore size distribution of fluoride containing γ -alumina. (●) Untreated γ -alumina; (■) 2% F- γ -alumina treated at 200 °C; (▲) pure γ -alumina treated at 300 °C. (b) Effect of hydrothermal treatment on pore size distribution of phosphorous containing γ -alumina. (●) Untreated γ -alumina; (■) 2% P- γ -alumina treated at 200 °C; (▲) pure γ -alumina treated at 300 °C.

the following sequence of steps lead to pore enlargement in γ -alumina.



The formation and growth of boehmite into large crystallites is probably responsible for the pore enlargement in hydrothermally treated alumina. The conversion of γ -alumina to boehmite under hydrothermal conditions essentially involves rehydration of γ -alumina by the uptake of 1 mol H_2O per mole of Al_2O_3 according to the above scheme.

Dissociative adsorption of water on to the anion vacancies of γ -alumina, and subsequent diffusion of the hydroxyl groups under the hydrothermal conditions may lead to the formation and recrystallization of boehmite with larger crystallites.

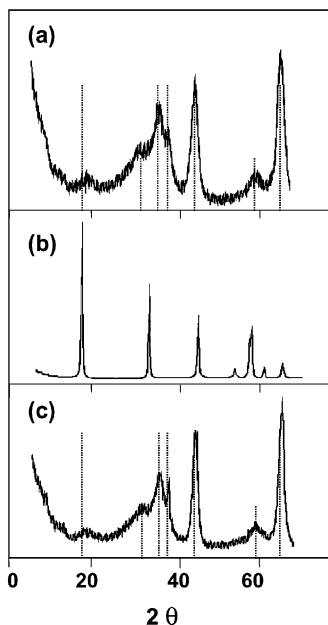


Fig. 3. XRD patterns of γ -alumina before and after hydrothermal treatment at 300 °C. (a) Untreated; (b) hydrothermally treated; (c) hydrothermally treated and calcined.

This is substantiated by the trends observed in the XRD patterns of F and P containing aluminas. The XRD data presented in Fig. 4 show that the γ -alumina phase in the F and P containing alumina samples do not undergo transformation to boehmite upon hydrothermal treatment. These results clearly indicate that the presence of P or F in γ -alumina inhibits its conversion to boehmite under hydrothermal conditions. F and PO_4 incorporated into γ -alumina are generally known to interact with the OH groups. Some of the anionic vacancies of γ -alumina are also likely to be filled with these ions during the impregnation step. It appears that the adsorption of water vapor on the anion vacancies of γ -alumina and its subsequent hydroxylation to boehmite are inhibited by the presence of F and PO_4 ions in γ -alumina. Anion vacancies and hydroxyl groups present in γ -alumina thus appear to play a key role in the hydrothermal transformation of γ -alumina to boehmite.

With a view to obtain further evidence to this proposition, we conducted a few additional hydrothermal treatment experiments using water mixed with some organic additives such as phenol and acetic acid which

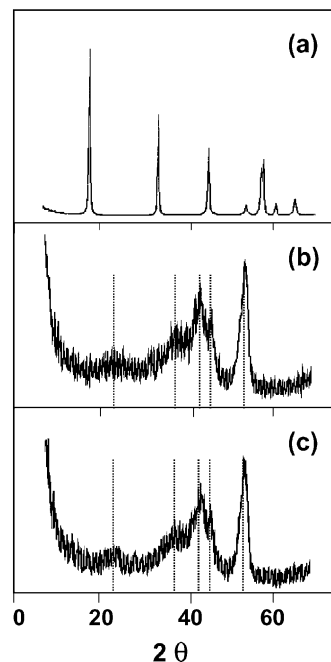


Fig. 4. Comparison between the XRD patterns of different aluminas after hydrothermal treatment at 300 °C. (a) Hydrothermally treated pure γ -alumina showing the formation of boehmite; (b) hydrothermally treated P containing γ -alumina; (c) hydrothermally treated F containing γ -alumina.

are known to react with the OH groups in alumina. The treated samples were characterized by XRD before and after calcination. The pore size distribution in the sample was also measured. Fig. 5 shows the pore size distribution of the alumina samples hydrothermally treated in the presence and absence of phenol. The pore size distribution of the fresh untreated γ -alumina (starting material) is also included in the figure for the purpose of comparison.

The presence of phenol (25%) in water during hydrothermal treatment is found to suppress the pore enlargement of alumina (Fig. 5(a)). A similar suppressive effect on pore widening is also noticed with acetic acid (Fig. 5(b)). The XRD results presented in Fig. 6 show that γ -alumina is completely converted to well-crystallized boehmite by hydrothermal treatment with pure water. The transformation of γ -alumina to boehmite is not complete when the hydrothermal experiments were conducted with phenol/water or acetic acid/water mixture. The boehmite

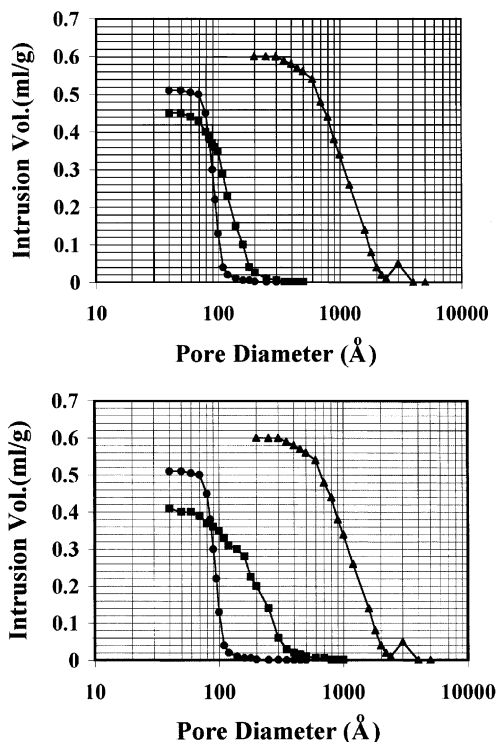


Fig. 5. (a) Effect of phenol on pore enlargement of γ -alumina by hydrothermal treatment. (●) Untreated γ -alumina; (■) hydrothermally treated with 25% phenol in water; (▲) hydrothermally treated with pure water. (b) Effect of acetic acid on pore enlargement of γ -alumina by hydrothermal treatment. (●) Untreated γ -alumina; (■) hydrothermally treated with 25% acetic acid in water; (▲) hydrothermally treated with pure water.

that is formed in the process is also not well-crystallized.

These results clearly demonstrate that phenol and acetic acid have a suppressive effect on the conversion of γ -alumina to boehmite under hydrothermal treatment conditions. It is possible that these reagents react with the OH groups originally present in the γ -alumina as well as with those formed by the adsorption of water vapor on the anion vacancies during the initial steps of hydrothermal treatment. In addition, some of the phenol and acetic acid molecules may compete with the H_2O molecules for adsorption on the anionic vacancies of γ -alumina. This would suppress the hydroxylation of alumina, its transformation to boehmite and the recrystallization or particle size growth of boehmite. Pore enlargement will, consequently, be inhibited.

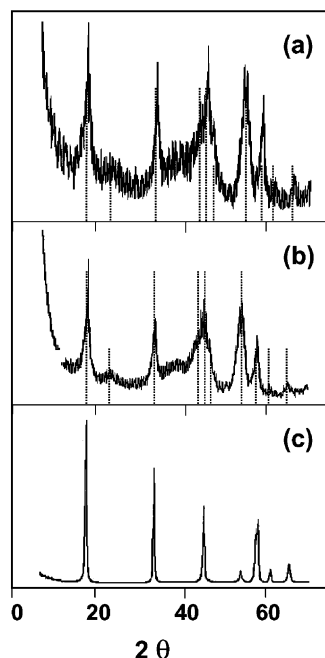


Fig. 6. Comparison between the XRD patterns of aluminas hydrothermally treated at 300°C in the presence and absence of organic reagents such as phenol and acetic acid: (a) 25% phenol in water; (b) 25% acetic acid in water; (c) pure water without phenol or acetic acid.

In the third set of experiments, a large pore Ni-Mo/ γ -alumina was prepared by hydrothermal treatment from a narrow pore Ni-Mo/ γ -alumina catalyst and its performance in residual oil hydrotreating was evaluated using Kuwait vacuum residue as feedstock. A comparison of the pore size distribution data for the catalyst before and after hydrothermal treatment is shown in Table 1. It is seen that a significant enlargement of the narrow pores has occurred as a result of hydrothermal treatment. Before hydrothermal treatment, the catalyst contained predominantly (61%) narrow pores with pore diameter less than 100 Å and about 25% mesopores with diameter in the range 100–500 Å. The amount of large pores having diameter >1000 Å was less than 8%. After treatment, the amount of large pores with diameter above 1000 Å has increased significantly from 7.6 to 43.7%. Remarkable increase is also noticed in the 500–1000 Å size pores. The amount of small pores (<100 Å) is negligibly small in the treated catalyst.

Table 1
Comparison of pore size distribution data of Ni-Mo/Al₂O₃ catalysts

Pore diameter (Å)	Before hydrothermal treatment		After hydrothermal treatment		Reference catalyst	
	Pore volume (ml/g)	Pore volume (%)	Pore volume (ml/g)	Pore volume (%)	Pore volume (ml/g)	Pore volume (%)
30–100	0.440	61.1	0.020	3.2	0.0615	9
100–250	0.112	15.5	0.061	9.7	0.218	31
250–500	0.070	9.7	0.166	26.4	0.110	16
500–1000	0.45	6.1	0.106	16.9	0.068	–
1000–3000	0.054	7.6	0.275	43.7	0.232	10
>3000	0.0	–	0.0	–	–	34
Total	0.721	100	0.628	100	0.69	100

The RVA of the hydrothermally prepared wide pore catalyst in promoting various reactions such as HDS, HDM, HDN, and asphaltenes conversion that occur during residual oil hydrotreating are compared with that of a reference hydrodemetallization catalyst of similar composition in Table 2. The RVAs were calculated using standard kinetics with reaction orders, $n = 2$ for HDS, 1.5 for HDM, 1.0 for HDN and 2.0 for asphaltenes conversion as shown in Section 2.

The results (Table 2) reveal that hydrothermally prepared wide pore catalyst is remarkably more active for HDM and asphaltenes conversion reactions. The RVA of this catalyst for HDM and asphaltenes conversion reactions are, respectively, 36 and 75% higher than that of the reference catalyst. However, its RVA for HDS is 15% lower than the reference catalyst. In addition to the higher HDM activity, the wide pore catalyst prepared in this work also showed better performance with regard to metals accumulation and distribution of the deposited metals (Fig. 7).

In the catalytic hydroprocessing of residual oil, the ability of the feedstock molecules to diffuse through

the catalyst particles to the active sites inside the pores is a key factor in determining the effectiveness of the catalyst [9]. The diffusion is predominantly determined by the pore size of the catalyst. Metal bearing compounds and asphaltenic materials that are present in the residual have low diffusivities due to their large molecular sizes. The incorporation of macropores or access channels into the catalyst can increase their effective diffusivities.

In the present studies, it is noticed that the prepared catalyst that has about 44% of its total porosity as macropores in the diameter range 1000–3000 Å and another 43% as large mesopores is substantially more active for promoting HDM and asphaltenes conversion reactions compared to that having very large (>3000 Å) macropores and smaller mesopores in the

Table 2
Comparison between the activities of hydrothermally prepared and conventional Ni-Mo/Al₂O₃ catalysts for different reactions in residual oil hydrotreating

Reactions	Relative volume activity (RVA)	
	Hydrothermally prepared catalyst	Reference catalyst
HDS	85	100
HDM	136	100
HDN	96	100
HDA _s	175	100

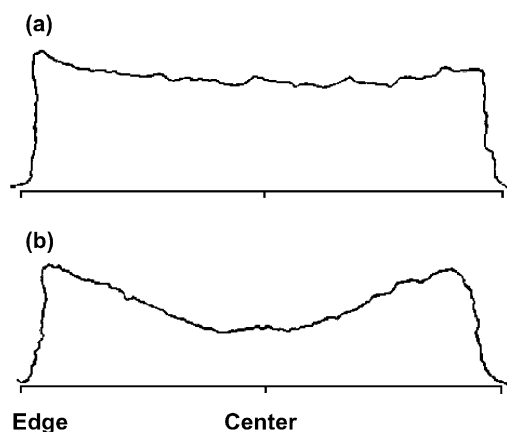


Fig. 7. Distribution profile of vanadium within the catalyst pellets. (a) Hydrothermally prepared wide pore catalyst; (b) conventional HDM catalyst.

range 100–250 Å. The reason for this difference in the activity between the two catalysts is not clear, even though the sizes of pores in both types of catalysts are large enough for unrestricted diffusion of large metal bearing molecules and asphaltenic materials. One possibility is that macropores larger than 3000 Å are not very effective for HDS and HDAs reactions. Another possibility is the increase in the degree of inter-connection between the two types of pores in the hydrothermally treated catalyst. This will improve diffusion, and hence increase catalyst's activity for HDM and HDAs. A more uniform distribution of the deposited vanadium throughout the pellet cross-section for this catalyst compared to the reference catalyst (Fig. 7) is in agreement with this.

4. Conclusions

In the present work, a series of experiments were conducted to secure a better understanding of the mechanism of pore widening in alumina supports under hydrothermal conditions. The results revealed that pore enlargement occurred as a result of rehydration of γ -alumina and its transformation to well-crystallized

boehmite. A wide pore Ni-Mo/ γ -alumina prepared by the hydrothermal treatment procedure showed remarkably high activity for hydrodemetallization and asphaltenes conversion reactions in vacuum residue hydroprocessing. Distribution of the deposited metals within the catalyst pellet was more uniform for this catalyst compared to that of a conventional HDM catalyst.

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