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Influence of calcination parameters on the properties of alumina as a catalyst support

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Abstract. The preparation history of Al_2O_3 strongly determines its properties for the application as a catalyst support. The interaction of calcination heating rate and temperature and its influence on the structural, textural, and acidic properties of alumina were studied. Commercial γ-alumina was calcined at 800°C, 900°C, 1000°C, 1050°C, 1100°C, and 1150°C by 2.5°C/min, 5°C/min, and 10°C/min. By increasing temperature up to 1050°C, transition aluminas (γ, δ, and θ) were reported, but the heating rate accelerated phase transformation and changed the amount of each phase in the samples. At 1100°C and 1150°C, α-alumina appeared. Mesopore alumina with different surface areas (265-126 m^2/g) was synthesized at calcination temperature from 800°C to 1050°C; when temperature reached 1100°C, the surface area decreased drastically and was around 14 m^2/g. Interaction of heating rate on the temperature had minimal effect on the surface area of samples, but considerable effect on the acidic properties. The intensity of acidic properties was affected by heating rate with nonlinear profiles. By increasing the heating rate, the ratio of Al cations occupied tetrahedral per octahedral sites and defect of crystal structures increased, so the surface acidity of aluminas was increased.

1. Introduction

The nature of support is an important parameter that influences the activity, selectivity, and lifespan of a catalyst; so, the support choice in the preparation of catalyst is considerable. The surface properties of the support influence the characters of active sites, while they can display a synergistic effect on the performances of the catalyst [1,2].

Alumina is widely used as the catalyst support and adsorbent in the chemical and petrochemical processes due to surface area, pore volume, pore sizes, structures, and acid/base characters. Aluminium oxide can exist in several phases, i.e. γ-, η-, β-, χ-, κ-, δ-, θ-, and α-alumina. Alpha-alumina is the thermodynamically stable and well-crystallized alumina and is usually obtained at high temperatures. The other phases are called transition or metastable phases [3].

Differences in crystalline structure may result in changes in physical and chemical properties of aluminas as the support [3,4]. The alumina phases have two broad categories of oxygen anions arrangements, a Face-Centered Cubic (FCC) or a Hexagonal Close-Packed (HCP). The Al_2O_3 structures, based on FCC packing of oxygen, include γ (cubic), δ (monoclinic), and θ (either tetragonal or orthorhombic), whereas the Al_2O_3 structures, based on HCP packing, are represented by α (trigonal), κ (orthorhombic), and χ (hexagonal) phases [5-7].

The sequence of phases formed and temperatures

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required for each phase transformation depend on the starting materials (alumina precursors), synthesizing route, and thermal treatments [8,9].

Alumina obtained from boehmite is usually used as a catalyst support due to its favor in textural properties with a wide range of surface areas (from 2-500 m^2/g), porosities, crystalline structures, and surface acidity [10,11]. The approximate temperatures required for the phase transformations in the crystallization sequences are [9,12]:

$$\text{Boehmite} \rightarrow \gamma(300-500^\circ\text{C}) \rightarrow \delta(800^\circ\text{C})$$
$$\rightarrow \theta(900^\circ\text{C}) \rightarrow \alpha(\geq 1200^\circ\text{C}).$$

Water between the crystal planes of boehmite is removed by heat treatment, and small pores, which originate in spaces within the particles, are formed and distinct crystal structures are appeared [11,13].

The calcination conditions impact on the properties of aluminas, such as structural, textural, and acidity characteristics. The calcination variables, such as temperature, time span, and heating rate interact with each other and influence the complexity of physical and chemical phenomena that occur during the thermal treatment of alumina precursors [14,15].

In many papers, the effect of calcination temperature on the final properties of aluminas has been investigated and reported, extensively [8,10,16,17], but the heating rate has been less imperceptible as an experimental variable. The effect of time span on textural properties is not statistically significant at calcination temperature; but it is sufficient for thermal stabilization of alumina [10,15].

In this study, different aluminas were prepared by calcining at various conditions. The end-temperature and heating rate were considered as calcination parameters and their effect on the properties of alumina were investigated.

2. Experimental

2.1. Materials and methods

Commercial spherical γ-Al_2O_3 (BET: 210.13 m^2/g and pore volume: 0.53 cm^3/g) was supplied from Sasol Co.

γ-Al_2O_3 was calcined by 3 levels of heating rate, i.e. 2.5°C/min, 5°C/min, and 10°C/min; and by 6 levels of end-temperature, i.e. 800°C, 900°C, 1000°C, 1050°C, 1100°C, and 1150°C. The remaining time was 3 h at end-temperature.

2.2. Characterization

The X-Ray Diffraction (XRD) pattern of calcined Al_2O_3 support was carried out by using a X-ray diffractometer (Model GNRMPD 3000) with Cu-Kα radiation at 40 kV and 30 mA. The mean crystal size of Al_2O_3 support was estimated by the half-width of the corresponding XRD peaks using Scherrer equation [18].

The BET surface areas of the products were determined by N_2 physisorption using a sorption analyzer, Quantachrome Nova 2200. The BET measurements, nitrogen adsorption-desorption isotherms, and pore structure analysis were conducted at 77 K. The pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) method for mesopores and Density Functional Theory (DFT) for micropores.

The water-displacement method was used for measuring pore volume of macropores. In this method, dry sample was weighted, then immersed in water at 70°C for 1 h. The sample was cooled to ambient temperature. The difference between weights of saturated sample in air and dry sample was that of water displacement in pores. The pore volume was calculated by using water density [19].

Temperature-Programmed Desorption (TPD) of NH_3 was performed in BELCAT A. Adsorption was carried out at 60°C in a mixture of NH_3 (2.5 mL/min) and He (47.5 mL/min) flow for 1 h. The product was then exposed to He for 30 min at 60°C to remove all the physically adsorbed species before starting the temperature program. The samples adsorbed ammonia at 60°C, and heated up to 700°C at heating rate 10°C/min. Desorption signals were monitored by using a TCD spectrometer. The amount of acid sites on the catalyst surface was proportional to desorption amount of ammonia.

3. Results and discussion

The X-ray diffraction patterns of samples calcined between 800°C to 1150°C by 5°C/min heating rate are shown in Figure 1. Different transition aluminas (γ, δ, and θ) were obtained at 800°C and 900°C that were confirmed according to the International Centre for Diffraction Data (ICDD). The strongest diffraction peak of γ-alumina is at the 2θ value of 45.8°(ICDD card No. 10-0425). The first strongest diffraction peaks of δ and θ are at the same 2θ value of 67.3°. The second strongest diffraction peak of δ-alumina is at the 2θ value of 45.5° (ICDD card No. 4-0877) and for θ-alumina is at the 2θ value of 45.0° (ICDD card No. 11-0517). By increasing the temperature up to 1000°C, γ-alumina disappeared and at the dominant phases, δ-alumina was formed; the broad peak means poor crystallization of the samples. At 1050°C, two transition (δ and θ) aluminas were formed and at 1100°C, crystal phase of α-alumina was obtained. The sharp XRD lines were observed for samples that were calcined at 1100°C and 1150°C, indicating appearance of a well crystallized alpha alumina.

In Figure 2, the effect of heating rate on the formation of transition alumina at 1050°C is shown.

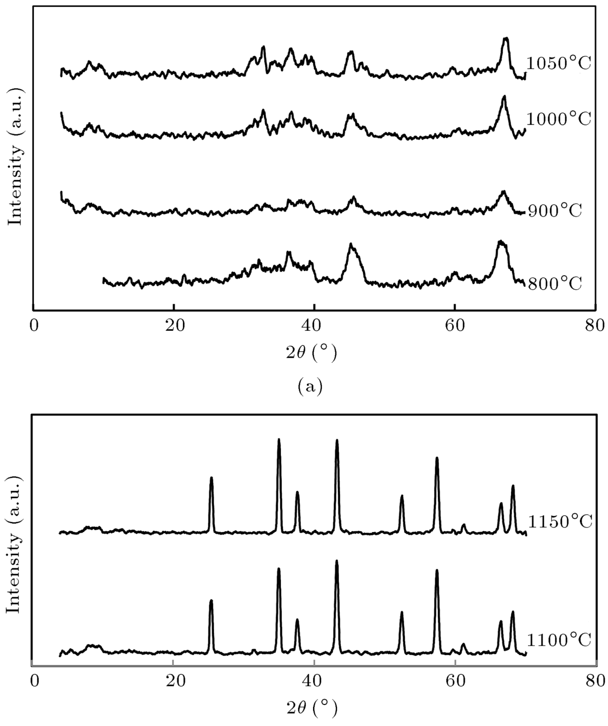


Figure 1. XRD patterns of calcined alumina at (a) 800°C-1050°C, and (b) 1100°C and 1150°C by 5°C/min.

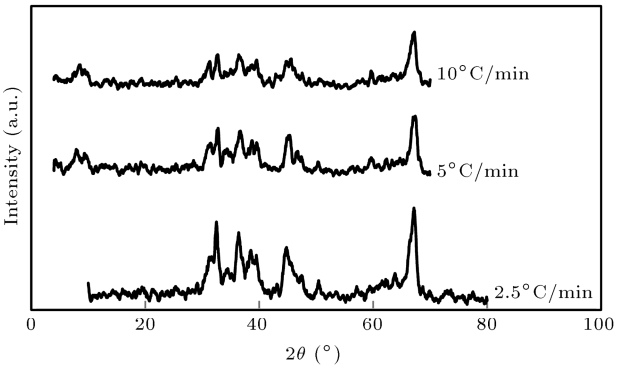


Figure 2. XRD patterns of calcined alumina at 1050°C by using 2.5°C/min, 5°C/min, and 10°C/min.

Diffraction patterns of other samples were omitted, since they were similar to those shown in Figures 1 and 2.

Estimated phase percent and crystal size of each transition alumina that was indicated in XRD patterns is given in Table 1.

All γ, δ and θ transition aluminas were existent in those samples that calcined by 2.5°C/min heating rate and end temperature up to 1050°C. By increasing the temperature, the crystal sizes decreased and the density of aluminas increased, as the vacant space in alumina structure decreased [12]. But, γ alumina was detected only at 800°C and 900°C at 5°C/min heating rate and was not reported by increasing the heating rate up to 10°C/min. Therefore, the phase transformation was accelerated by increasing heating rate. Crystal sizes did not change, significantly, as crystal structures changed permanently. The structures with lower grade of crystallite and defect crystal planes were formed at 5 and 10°C/min in comparison to 2.5°C/min heating rates.

The changes of the crystal structure from FCC to HCP appeared when the transition aluminas were converted to α-alumina. The variation in coordination is caused by the transformation of aluminium tetrahedrons to octahedrons, which is only finalized at temperatures higher than 1100°C [20]. By comparing crystal sizes between 1100 and 1150°C, i.e. α-alumina, it can be concluded that the crystals were grown and partial sintering happened at 2.5°C/min heating rate, but the crystal sizes did not significantly change at 5°C/min, and 10°C/min. Therefore, the calcination heating rate can affect the sintering properties of aluminas [21].

This phase transition sequence is the same as the transition alumina sequence obtained from boehmite source, while the γ phase is changed to δ and θ and finally, α phase is formed. In fact, the structural alumina system from one extreme to another will turn out to be quite important for the definition and understanding of some transition phase properties [22].

The N_2 adsorption-desorption isotherms and pore size distribution curves calculated by BJH method for samples prepared by 5°C/min heating rate are shown in Figures 3 and 4, respectively.

Isotherms of calcined samples at 800°C to 1050°C were similar to type IV of IUPAC classification, which was related to mesopores. The hysteresis loops were H2 type of IUPAC [23]. The monolayer adsorption occurred around a relative pressure of 0.69 for these samples. So, the proportion of micropores to mesopores was constant by increase in calcination temperature. Adsorption-desorption isotherms of samples at 1100°C and 1150°C were the same as type III of IUPAC that is for macropores. Therefore, it confirmed that α-alumina was formed. As isotherms of other heating rates were similar to those in Figure 3, they were omitted.

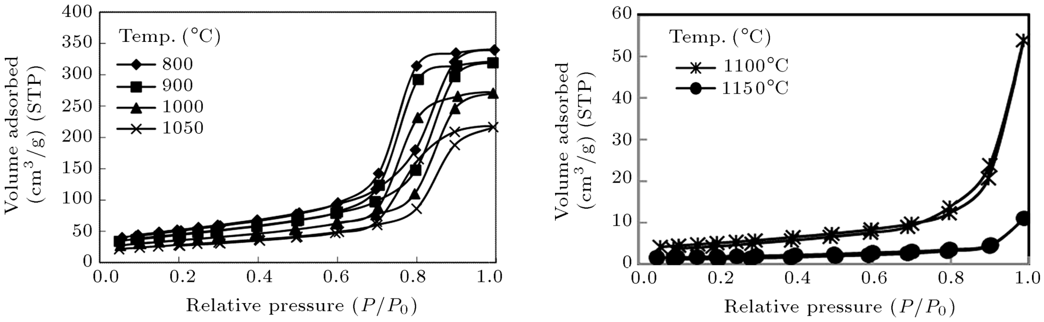
The pore size distributions of some calcined samples using BJH method based on desorption data are shown Figure 4. The maximum pore size that can readily be measured is around 100 nm. The pore size distributions were the same and average pore diameter was around 9 nm by increasing calcination temperatures from 800°C to 1050°C. The broad distribution between 2 nm to 100 nm was indicated for samples at 1100°C and 1150°C, because they had major pores larger than 100 nm.

Figure 5 shows the effect of calcination temperature and heating rate on the specific surface areas of the alumina supports that were measured by BET method.

Table 1. Estimated phase percent and calculated crystal sizes of alumina.

Heating rate	***T***	**Phase (%)**				**Crystal size (nm)**			
(°C/min)	**(°C)**	γ	δ	θ	α	γ	δ	θ	α
2.5	800	50	28	22	-	25.6	38.2	40.6	-
	900	48	28	24	-	24.1	25.1	31.4	-
	1000	41	31	28	-	23.1	11.2	16.4	-
	1050	24	26	40	-	23.9	11.7	18.5	-
	1100	-	-	-	100	-	-	-	23.8
	1150	-	-	-	100	-	-	-	29.9
5	800	50	28	22	-	15.2	22.7	22.11	-
	900	46	28	26	-	44.45	36.44	18.14	-
	1000	-	100	-	-	-	12.2	-	-
	1050	-	51	49	-	-	19.1	17.7	-
	1100	-	-	-	100	-	-	-	28.4
	1150	-	-	-	100	-	-	-	27.4
10	800	*	*	*	*	-	11.63	-	-
	900	*	*	*	*	-	21.3	12.5	-
	1000	*	*	*	*	-	12.08	13.8	-
	1050	*	*	*	*	-	11.4	26.3	28.3
	1100	-	-	-	100	-	-	-	27.5
	1150	-	-	-	100	-	-	-	25.6

*: Not determined.



(a) (b)

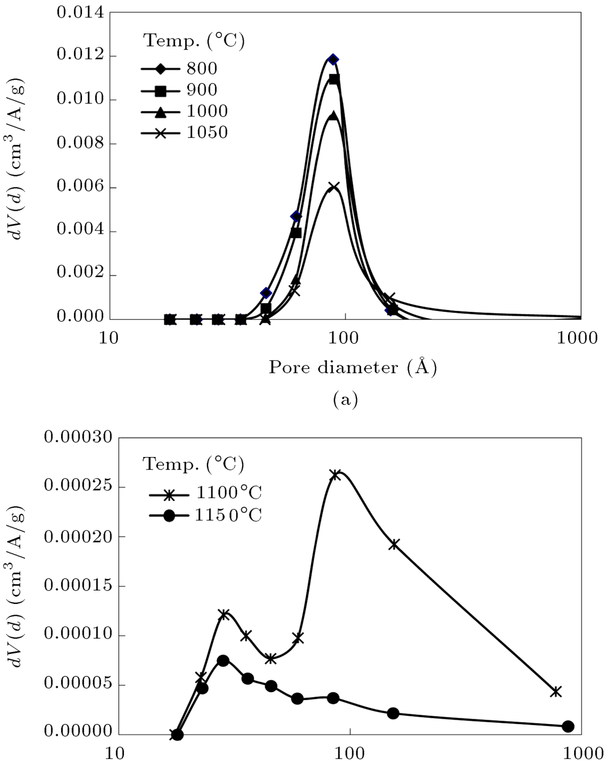
Figure 3. Adsorption-desorption isotherms of alumina calcined at 800°C-1150°C by using 5°C/min.

The specific surface areas decreased by increasing the calcination temperature. This is attributed to the changes in the size of alumina crystal, caused by the destruction of some small pores. When temperature increases from 800°C to 1050°C, the surface area, however, decreases quickly; but, the pore diameter remains unchanged. Then, both the surface area and the pore diameter drop as the pore structure collapses with increasing temperature to 1100°C [10].

The specific pore volumes calculated by BJH method for mesopores and DFT method for micropores and estimated with water displacement for macropores are shown in Figure 6. By increasing temperature, specific pore volume decreased. The average proportion of DFT and BJH pore volumes for samples at end-temperature up to 1050°C was around 0.25. This means that micropores were changed commensurate with mesopores.

For samples calcined at 1100°C and 1150°C, micro and mesopore volumes drastically decreased. Sintering of particles may occur during the heat treatment, which could reduce pore volume after calcination at higher temperatures. Sintering may also be responsible for decreasing surface area and increasing pore size, which is signified by the collapse of porous structure characteristics of the low-temperature phases and the consequent diminishing of the surface area [16].

The pore size distribution, shapes of N_2 adso-



(b)

Figure 4. Pore size distribution of alumina calcined at (a) 800°C-1050°C, (b) 1100°C and 1150°C.

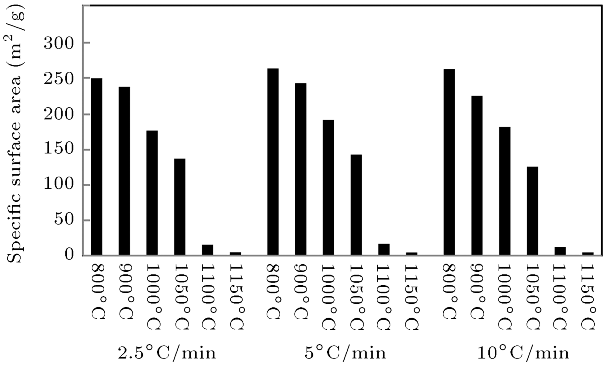


Figure 5. Effect of calcination temperature and heating rate on the surface area.

rption-desorption isotherms, and hysteresis loops are basically similar at different heating rates, but only differ in quantity.

Textural properties of alumina are the key parameters of the catalyst support usage. Calcination conditions had different effects on the surface area and porosity. Surface area and pore volume were less influenced by increasing heating rate, but the calcination temperature had a strong influence on the surface area due to changes in crystal structures and densification of transition aluminas; but, it had a moderate effect on the pore volumes [10,14,24].

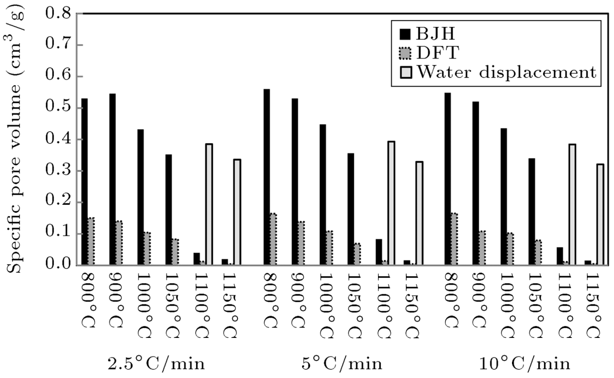


Figure 6. Specific pore volume measured by BJH method for mesopores, DFT for micropores, and water displacement for macropores at different calcination temperatures and heat rates.

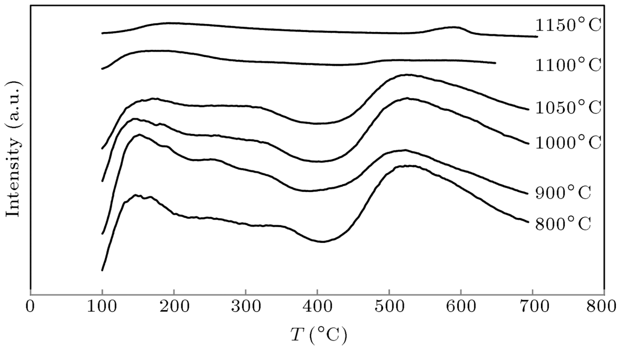


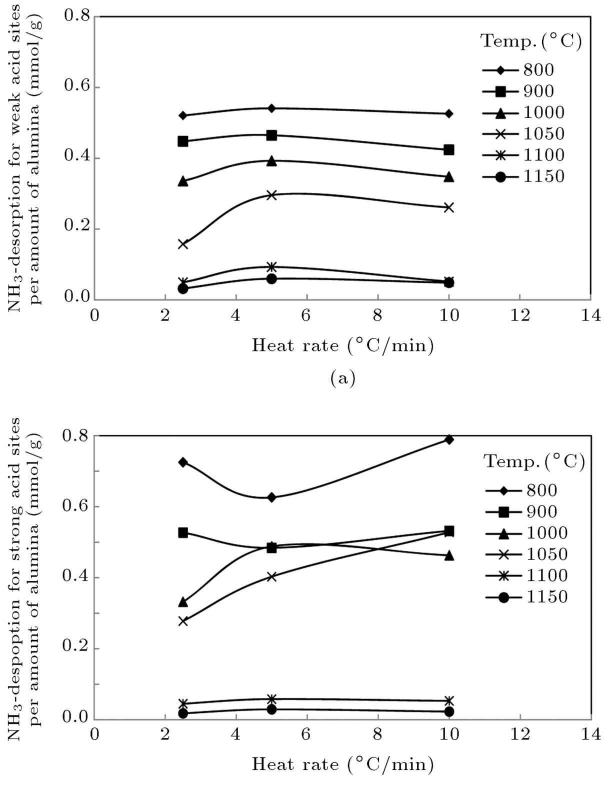
Figure 7. NH_3-TPD spectra of samples calcined at 800-1150°C by 5°C/min.

Temperature programmed desorption of ammonia (NH_3-TPD) is a technique to determine the surface concentration and strength of acid sites [25]. This technique was used to correlate acidic properties of alumina with calcination conditions.

NH_3-TPD profiles of samples calcined at different temperatures by 5°C/min heating rate are shown in Figure 7.

There are two peaks for every sample, which indicate the presence of two acid sites on these alumina mixing phases. The low temperature peak (around 150°C) could be attributed to weak acid sites, while the high temperature peak (around 550°C) could be associated with strong acid sites. For samples 1100°C and 1150°C, tiny peaks existed, which confirmed that α-alumina had low acidity in comparison with the other alumina phases. The decline in the acid site can be ascribed to the surface reconstruction. This may be attributed to the greater amount of low coordination surface aluminium ions due to more surface dehydroxylation [26].

The amount of desorbed ammonia, which is considered the same as the acid site concentration as s function of calcination condition, is shown in Figure 8. The aluminas contained a larger number of



(a)

(b)

Figure 8. Amounts of NH_3-desorption vs. calcination heating rate at 800 -1150°C for (a) weak and (b) strong acid sites.

strong acid sites than weak ones. The amounts of two types of acidic sites decreased by increasing calcination temperature and this dependency was linear, similar to the effect of temperature on the surface area of aluminas. The effect of temperature on the strong acid sites was drastic.

The removal of OH group during high temperature treatment creates coordinative unsaturated surface cations that are placed on the tetrahedral and octahedral Al coordination. The partly uncoordinated metal cations and oxide onions that lie on the surface of aluminas can act as acids and bases, respectively, according to the Lewis definition. The strongest acid sites are considered to be the tetrahedral Al ions, which are mainly located in crystallographically defective configurations and yield the reactive surface sites; they tend to be annihilated at high temperature [3].

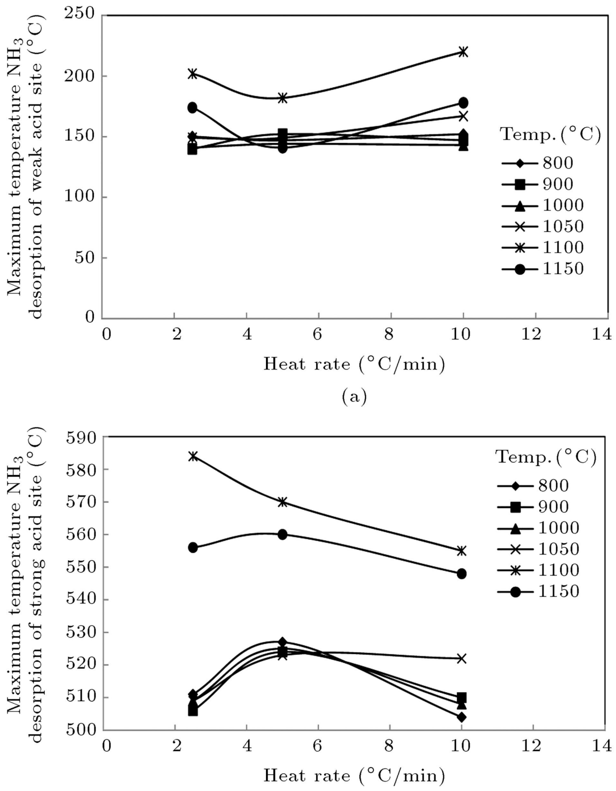
The XRD results confirmed that the calcination conditions had an intensive effect on the variation structures of aluminas. The existence of amorphous phases shows that the crystal defects the samples; therefore, it shapes acidic sites on the alumina surface.

The heating rate had influence on the concentration of acid sites; therefore, this profile was not linear. For the amount of weak acidic sites, it was convex; but, for strong acidic sites, it was convex up to 1000°C and concave at higher temperature than 1000°C, which can be seen in Figure 8. This indicated that heating rate had notable effect on the acidic properties of each alumina phase. This finding was confirmed by Ros et al. who modelled the effect of calcination properties on the physiochemical properties of transition aluminas; the concentration of acid sites varied with the square of heating rate. At low temperature, the concentration isotherms of strong acid sites presented a minimum, but at high temperature, they presented a maximum [14].

High heating rate, since samples were exposed to higher temperature for a shorter time, favored for formation of a larger amount of strong acid sites, as their formation occurred with low surface area loss [14].

The intensiveness of acid sites could be shown by maximum temperature of peaks. The first peak could be regarded as weak acid sites with maximum temperature around 150°C; so, heating rate did not have significant effect on the weak acidic intensity for transition aluminas.

For strong acid sites, maximum temperature was around 510°C to 525°C. The heating rate had influence on the intensity of strong acid sites of transition aluminas. The profiles were similar to those of quadratic function and convex form, as shown in Figure 9.



(a)

(b)

Figure 9. Maximum peak temperature at 800-1150°C for (a) weak and (b) strong acid sites.

After dehydroxylation during high temperature treatment, the surface develops Lewis acidity on the uncoordinated $Al^{\delta+}$ sites [14]. The intensity of the desorption peaks gradually decreases with the increase in calcination temperature, suggesting that less acidic sites are present in the samples [26].

With the definition of Lewis acidity, acidic supports are associated with a low electron-richness on the support oxygen atoms. It is found that a lower electron richness of the support oxygen atoms leads to a higher ionization potential of the active metal particles in catalysts. As the acidity of the support increases, the electron richness of the support O atoms decreases [27,28].

All calcination variables had influence on the alumina acidity. The most important element was the calcination temperature, a key factor that changed concentration of the acid site. The calcination temperature changed the transition alumina structure. Transition alumina was a mix of spinel forms with trivalent and divalent Al cations that occupied the tetrahedral or octahedral sites. The coordination of the unsaturated aluminium atoms was varied and dependent on the formed crystal plans [22,29]. Ratio of Al cations occupying tetrahedral per octahedral sites, surface crystal plane, and defect of crystal structure were affected by the acidity of alumina. The effects of the time at the final temperature and cooling temperature were not considered as these parameters were not statistically significant over the number of strong acid sites [10,25].

4. Conclusion

As investigated, the alumina crystal structures changed permanently by increasing temperature, but the heating rate accelerated the phase transformation. This acceleration caused shaping more defect crystal plane. The temperature had a strong effect on the surface area and a moderate one on the pore volume. The surface area decreased by increasing temperature due to change of alumina structure and densification. The heating rate had not notable interaction with temperature to change surface area.

The amounts of weak and strong types of acidic sites decreased by increasing calcination temperature and this dependency was linear, similar to the effect of temperature on the surface area of aluminas; but, the effect of temperature on the strong acid sites was drastic.

High heating rate, since the samples were exposed to high temperature for a short time, favored the formation of a larger amount of strong acid sites to create more surface defects. The strongest acid sites are considered to be the tetrahedral Al ions, which are mainly located at defective configurations of crystals.

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