

# Preparation of alumina with different precipitants for the gas phase dehydration of glycerol and their characterization by thermal analysis

Dirleia S. Lima<sup>1</sup> · Oscar W. Perez-Lopez<sup>1</sup>

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#### Abstract

Mesoporous aluminas were prepared using different precipitants at different pH of precipitation and evaluated in the gas phase dehydration of glycerol. Samples were characterized by thermal analysis techniques (TGA, NH<sub>3</sub>-TPD and TPO), specific surface area measurements, XRD and SEM. The gas phase dehydration of glycerol was performed in a fixed bed quartz tubular reactor at 773 K using a 10% glycerol aqueous solution. Thermogravimetric analysis has revealed the temperature regions of decomposition for the prepared alumina catalyst precursors. The specific surface area and the crystallinity of the samples were dependent on both the pH and the used precipitating agent. Samples precipitated with NaOH presented higher density of acid sites than the samples prepared with Na<sub>2</sub>CO<sub>3</sub>, regardless of precipitation pH. The catalytic properties of the prepared aluminas are mainly related to the specific surface area and to acidic characteristics. Conversions of glycerol above 85% were obtained for all samples. The selectivity for glycerol dehydration was strongly related to the amount and strength of acid sites. The best result for dehydration was obtained for samples prepared with NaOH and precipitated at pH=5. These results are related to the higher specific surface area, greater amount of acid sites and the higher ratio of weak acid sites. TPO revealed the amount of carbon deposited on the catalysts. Samples that showed higher carbon formation also showed a higher production of light olefins, indicating that the formation of carbon is related to the formation of these byproducts. NH<sub>3</sub>-TPD has shown the ratio of different acid sites on the surface of alumina samples that makes possible to estimate the correlation between the acidity and the catalytic properties.

Keywords Dehydration of glycerol · Acrolein · Alumina synthesis · Co-precipitation · Acid strength

# Introduction

Glycerol is an alcohol obtained as a byproduct of biodiesel production via the transesterification reaction of vegetable oils and animal fats [1]. One way of adding value to residual glycerol is through glycerochemistry, which studies the different chemical routes through which it is possible to recover this low-quality glycerol and transform it into other products. Among the existing catalytic chemical routes, dehydration, oxidation, hydrogenolysis, etherification, acetylation, halogenation and steam reforming of glycerol are the most important [2].

An interesting product that can be obtained through glycerol conversion is acrolein, which is currently produced by the oxidation of propylene with a catalyst-based process on bismuth molybdate [3, 4]. The production of acrolein from sustainable and renewable resources is recent. However, the main obstacle to such industrial application (large scale) is the economic issue related to the cost of refined glycerol [4]. Crude glycerol from biodiesel production usually contains water. The direct use of this glycerol without the removal of water is an advantage in the catalytic reaction to obtain acrolein, in addition to bringing economic and environmental benefits since it makes its purification unnecessary and also minimizes industrial water consumption. A promising way of converting this aqueous crude glycerol solution is by dehydration, which leads to the production of high-value chemicals such as acrolein and hydroxyacetone, according to reaction (1) [5]:

Oscar W. Perez-Lopez perez@enq.ufrgs.br

<sup>&</sup>lt;sup>1</sup> Laboratory of Catalytic Processes - PROCAT, Department of Chemical Engineering, Federal University of Rio Grande do Sul (UFRGS), Ramiro Barcelos Street, 2777, Porto Alegre, RS CEP 90035-007, Brazil



Acrolein obtained from these processes can be used as feedstock to produce acrylic acid and its derivatives, while hydroxyacetone is an intermediate for the production of propanediols and can be employed to obtain acetic acid [6, 7].

Several solid acid catalysts have been tested for gas phase dehydration of glycerol [8]. Some of them are: ion exchange resins, sulfates, phosphates, heteropoly acids supported on silica, alumina, active carbon and zeolites [9]. Although widely used, the microporous nature of zeolites often has transport limitations, particularly when large molecules are involved, which adversely affects the catalytic performance [10]. Pathak et al. [11] concluded that the acidity of the catalyst has a great effect on the conversion of glycerol to the yield of liquid products: acetaldehyde, acrolein, formaldehyde and acetone. In the dehydration of glycerol, zeolites and heteropoly acids are the mainly used catalysts [4]. However, while most of these catalytic systems lead to high selectivity for acrolein with high total glycerol conversion, few maintain their catalytic properties for more than 5 to 10 h. Catalyst deactivation occurs mainly due to the extensive deposition of coke on its surface [12].

Due to its mechanical and physical properties, alumina can be used as a catalyst or a catalytic support for numerous chemical processes. Among the different types of alumina used in catalysis,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is the most used as a catalytic support due to its mechanical stability, moderately high specific surface area, sintering resistance over a wide temperature range, and also for having a high degree of metallic dispersion [13]. Despite its properties, alumina has been used on a smaller scale in this process, mainly as the support [8, 12, 14, 15].

Industrially, alumina is mainly obtained by the Bayer process which involves the extraction of alumina from bauxite using a hot sodium hydroxide solution under high pressure. Gibbsite is precipitated from the solution at temperatures between 338 and 343 K and calcined to produce alumina [16]. On the other hand, there are different methods of synthesis of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> reported in the literature [17–24]. One of these methods is the continuous co-precipitation [13], which allows obtaining a structure with more homogeneous crystals. Some of these studies evaluate the influence of calcination temperatures to obtain these materials, but it is known that other parameters, such as medium pH and choice of precipitating agent, also have a great influence on the synthesis process. It is therefore very important that these factors are also evaluated.

In this context, the objective of the present work is the preparation of aluminas by the continuous precipitation method, varying the pH of precipitation and the nature of the precipitating agent, and its application in the dehydration of glycerol.

### Experimental

#### **Catalyst preparation**

The catalysts were prepared using the continuous precipitation method. A solution of aluminum nitrate  $(Al(NO_3)_3)$ and different precipitating solutions  $(Na_2CO_3, NaOH and KOH)$  were used. The precipitation was performed in a CSTR (Continuous Stirred-Tank Reactor) jacketed reactor by mixing the aluminum nitrate solution (0.5 M) with the alkaline solution (1 M) containing the base, at fixed temperature and pH (333 K and  $7.0\pm0.1$  or  $5.0\pm0.1$ , respectively). The precipitated material was collected and submitted to crystallization at 333 K for 4 h. Subsequently, it was vacuum-filtrated and washed with deionized water until a conductivity lower than 50  $\mu$ S was reached. The material was oven-dried at 353 K for 12 h. Finally, it was calcined at 873 K for 6 h with a heating rate of 10 K min<sup>-1</sup> and an air flow rate of 50 mL min<sup>-1</sup>.

#### **Catalyst characterization**

Thermogravimetric analysis (TG) was performed in a thermobalance (TA Instruments, SDT-Q600) to evaluate the thermal events due to heating. Totally, 10 mg of uncalcined sample was heated to 1073 K with a heating ramp of 10 K min<sup>-1</sup> under 100 mL min<sup>-1</sup> of air flow [25].

The XRD diffractograms of the samples were obtained using a Bruker D2 Phaser X-ray diffractometer with Cu-k $\alpha$ radiation [26]. Scanning electron microscopy (SEM) was performed on an EVO MA10—Carl Zeiss equipment using backscattered electrons at 10 kV, with samples coated with a thin gold film prior to the SEM analyses.

The specific surface area of the catalysts was obtained from nitrogen adsorption/desorption measurements. Previously, the samples were pre-treated at 573 K for a period of 3 h under vacuum. The analysis was performed on a Quantachrome analyzer, model NOVA 4200e. The specific surface area of the samples was determined by the BET (Brunauer–Emmett–Teller) multi-point method [27, 28]. The pore volume, average pore diameter and pore size distribution were calculated with the BJH (Barrett–Joyner–Halenda) method using the desorption data.

The acidity of the catalysts was determined by temperature-programmed desorption of ammonia ( $NH_3$ -TPD), performed in a SAMP3 multipurpose analysis system equipped with a thermal conductivity detector (TCD). First, the samples were pre-treated at 373 K with 30 mL min<sup>-1</sup> of He for 30 min. The ammonia adsorption step was performed at 373 K for a period of 30 min using 30 mL min<sup>-1</sup> of a mixture containing 5 vol % ammonia in He [26, 28–30]. After that, a purge with He was performed for 30 min. Then, the temperature was raised to 1023 K with a heating ramp of 10 K min<sup>-1</sup> under He flow.

The amount of carbon deposited on the catalysts after the reaction was determined by temperature-programmed oxidation (TPO) in a thermobalance (TA Instruments Q600). A 10 mg sample was heated under an air flow rate of 100 mL min<sup>-1</sup> at a rate of 10 K min<sup>-1</sup> until 1023 K [26, 30, 31].

#### **Catalytic activity**

The catalytic activity of the samples was evaluated by the conversion of glycerol in a tubular quartz micro-reactor. Approximately, 0.1 g of catalyst (32-42 mesh of granulometry) was disposed in a fixed bed supported by quartz wool. The reactor was heated under nitrogen flow at a rate of 10 K min<sup>-1</sup>. Nitrogen was fed by a mass flow controller (Sierra Instruments), and a solution of glycerol in water  $(10\% \text{ w w}^{-1})$  was fed through a syringe-type pump (KD Scientific) at a flow rate of 0.4 mL h<sup>-1</sup>. The catalytic tests were carried out at a temperature of 773 K during 5 h. The gaseous products of the reaction were analyzed every 1 h by online gas chromatography (Varian 3600cx) using a Porapak Q packed column at 473 K and nitrogen as the carrier gas. Flame ionization (FID) and thermal conductivity (TCD) detectors were used. The liquid products of the reaction were continuously condensed and collected every 1 h of reaction for further analysis on a Varian 3600cx gas chromatograph [26, 30].

## **Results and discussion**

#### **Catalyst characterization**

Table 1 presents the prepared samples, the nomenclature adopted for each sample and also the results obtained for the BET specific surface area, average pore diameter and pore volume. It is observed that among the influences of the precipitating agent, the sample synthesized with KOH (A7AP3) resulted in the highest specific surface area (432 m<sup>2</sup> g), whereas the sample prepared with Na<sub>2</sub>CO<sub>3</sub> resulted in the

 Table 1
 Samples nomenclature, preparation conditions, BET specific surface area, average pore diameter and pore volume

| Catalyst | Precipitant                     | pН  | $S_{\rm BET}/{\rm m}^2~{\rm g}^{-1}$ | D <sub>p</sub> /nm | $V_{\rm p}/{\rm cm}^3~{\rm g}$ |
|----------|---------------------------------|-----|--------------------------------------|--------------------|--------------------------------|
| A7AP1    | Na <sub>2</sub> CO <sub>3</sub> | 7.0 | 48                                   | 3.83               | 0.126                          |
| A7AP2    | NaOH                            | 7.0 | 277                                  | 3.84               | 0.479                          |
| A7AP12   | $Na_2CO_3 + NaOH$               | 7.0 | 323                                  | 9.22               | 0.489                          |
| A7AP3    | КОН                             | 7.0 | 432                                  | 3.84               | 0.660                          |
| A5AP1    | Na <sub>2</sub> CO <sub>3</sub> | 5.0 | 389                                  | 3.82               | 0.367                          |
| A5AP2    | NaOH                            | 5.0 | 359                                  | 3.80               | 0.235                          |



Fig. 1 Mass variation obtained during the TG analysis

lowest specific surface area (48 m<sup>2</sup> g). The pH of precipitation had also a significant influence on the specific surface area of the obtained material. Samples prepared at pH 5 presented a larger specific surface area than the samples prepared at pH 7 independently of the used precipitating agent. Samples prepared at pH 5 have a higher specific surface area than those prepared at pH 7 due to the type of precipitate formed. In the case of precipitation performed at pH 7, the precipitate formed is poorly crystallized leading to the formation of a pseudo-boehmite. For precipitation at pH 5, an amorphous precipitate is obtained which gives a microcrystalline boehmite of greater specific area. In addition, the sample with larger specific surface area (A7AP3) also presented the largest pore volume.

Figure 1 shows the mass variation for the prepared samples during the thermogravimetric analysis (TGA). It can be observed that, with the exception sample A7AP12, all samples had the highest percentage of mass loss up to 473 K of heating. This initial loss is linked to the removal of water molecules from the material. The decomposition for the samples prepared with sodium carbonate occurred around

573 K, whereas for the samples prepared with hydroxide the decomposition extends to higher temperatures, above 673 K.

Figure 2 shows the nitrogen adsorption–desorption isotherms for all samples. It is observed that all samples presented type IV hysteresis (according to IUPAC classification) which is characteristic of a mesoporous material, as was also observed in other studies [32, 33].

Figure 3 shows the pore size distribution results for all samples, whereas Table 1 shows the average pore diameter values. These results demonstrated that these materials are mesoporous. The A7AP3 sample exhibits a bimodal pore size distribution, which is in agreement with the high specific surface area for this sample. However, from Fig. 2f it is

observed that the A5AP2 sample showed a different behavior with a rapid uptake at a low relative pressure (0–0.4 bar), which indicates the presence of micropores in the structure. This result is confirmed by the pore size distribution shown in Fig. 3f, where the A5AP2 sample has a narrow pore distribution with most pores having diameters of less than 5 nm. A similar behavior was also observed in the material developed by Chang et al. [34]. In addition, the shape of the hysteresis indicates pores with narrow neck and broad body as presented by Cychosz and Thommes [35].

Figure 4 shows the results of the X-ray diffraction for the synthesized samples. With the exception of sample A7AP1, all samples presented reflections at 37.2°, 45.7° and 66.8°



Fig. 2 Nitrogen adsorption-desorption isotherms for samples calcined at 873 K: a A7AP1, b A7AP2, c A7AP12, d A7AP3, e A5AP1 and f A5AP2



Fig. 3 Pore size distribution for samples: a A7AP1, b A7AP2, c A7AP12, d A7AP3, e A5AP1 and f A5AP2



Fig. 4 X-ray diffractograms for samples calcined at 873 K

corresponding to transitional low-temperature alumina, indicating that the used method was effective to obtain the alumina materials [3, 13, 15, 21, 36]. The more amorphous structure for the A7AP1 sample may explain the fact that this material had a significant lower surface area than the other samples.

Figure 5 shows the SEM images for all the samples. There are differences in the morphology of the obtained materials. The A7AP1 sample has a smooth surface compatible with the low surface area and porosity of this material (Table 1). In Fig. 5b, d, micrographs of the A7AP2 and A7AP3 samples, respectively, it is noted that the grain was formed from overlapping flakes, which is a classical grain morphology of pure alumina materials. In the case of the A7AP12 (Fig. 5c) and A5AP1 (Fig. 5e) samples, each particle is an agglomerate of crystals, most of them platy, with sharp edges. This morphology is more evident for sample A5AP1. This peculiar shape can be compared to that of a lettuce. The A5AP2 sample (Fig. 5f) has a flat surface with the presence of very small pores which is in agreement with the pore size distribution presented in Fig. 3f.

Figure 6 shows the  $NH_3$ -TPD results for all the synthesized samples. A broad desorption peak is observed for all samples in the range of 423–723 K. The desorption of

ammonia in this temperature range demonstrates that these materials have weak and moderate acidity and no strong acid sites, which was also observed by Zhong et al. [19].

For a better analysis of the results, deconvolution of the obtained  $NH_3$ -TPD profiles was performed using the Gaussian method. The results of this deconvolution can be seen in Fig. 7 and the numerical data in Table 2.

The deconvolution results show the existence of two types of sites for all the samples. The weak acid sites are characterized by the peak in the lower-temperature region, between 483 and 513 K, and the moderate acid sites, represented by the peak at higher temperatures, above 573 K. It is noted that both the precipitating agent and the pH influenced the acidic properties of the obtained material. Among the materials prepared at pH 7.0, the A7AP2 sample had the highest density of total acid sites, these being predominantly weak acid sites. In addition, the acid strength of both types of sites was higher since the desorption temperatures in the deconvolution were higher. The A7AP1 sample had the opposite behavior, resulting in a lower density of total acid sites and a predominant presence of moderate acid sites. This same behavior was observed for the samples prepared at pH 5.0. in which the A5AP2 sample had a higher total acidity, consisting predominantly of weak acid sites, than the A5AP1 sample. It is evident that the precipitating agent used in the synthesis has influence on the acidity of the formed material. It was observed that the use of NaOH as a precipitant led to the formation of materials with a higher acidity than those obtained from Na<sub>2</sub>CO<sub>3</sub>.

#### **Catalytic activity**

Figure 8 shows the conversion of glycerol during 5 h of reaction at the temperature of 773 K for all the samples. The obtained glycerol conversion values were higher than 80% for all the samples during the time-on-stream.

For samples prepared at pH 7.0 with different precipitants, it is observed that the glycerol conversion is influenced by both the specific surface area and the acidity of the catalyst. The lowest conversion obtained for the sample A7AP1 can be related to the low specific surface area and also to the lower acidity, when compared to the other samples. In addition, the samples A7AP1 and A7AP12, which presented the lowest values of density of acid sites, were those that resulted in the lowest values of conversion, **Fig. 5** SEM images for the samples: **a** A7AP1 with magnification of 5000 X; **b** A7AP2 with magnification of 10,000 X; **c** A7AP12 with magnification of 5000 X; **d** A7AP3 with magnification of 10,000 X; **e** A5AP1 with magnification of 5000 X; and **f** A5AP2 with magnification of 5000 X



indicating that more acidic materials give better results in the catalytic conversion of glycerol, as it was also observed by Kim et al. [37]. It is observed that alumina prepared using NaOH (A7AP2) showed the best conversion of glycerol, maintaining approximately 99% in the first 3 h of reaction, and remaining with a conversion of approximately 97% at the end of 5 h of reaction. Samples prepared at pH 5.0 had higher specific area and higher acidity and, consequently, they showed a higher conversion than the respective samples prepared at pH 7.0. It may be further noted that the acidity of the materials has an important effect on glycerol conversion, which has also been observed by Pathak et al. [11].

These results can be considered promising considering that alumina is used as support in most of the works [12, 15]. In addition, the conversion values obtained in the present



Fig. 6 NH<sub>3</sub>-TPD curves for samples calcined at 873 K

work are approximate to those already reported in the literature. According to the work of Zakaria et al. [38], the conversion of glycerol to olefins resulted in conversion values of 77; 77.4 and 79.6% when Al<sub>2</sub>O<sub>3</sub> was used as a catalyst. Further, in the study performed by Haider et al. [39], total conversion in the glycerol dehydration was achieved using ceria and zirconia grafting onto alumina ( $\alpha$  and  $\theta$ - $\delta$  phases) as supports for silicotungstic acid, producing 85% selectivity to acrolein.

Figure 9 shows the average distribution of gaseous products obtained after 5 h of reaction. It is observed that the sample A5AP2 exhibited the highest values for acrolein (30%) and hydroxyacetone (40%), revealing high selectivity for glycerol dehydration; the remaining 30% are composed of light olefins and other products formed by secondary reactions. This result may be associated with the high density of acid sites of this material (Table 2), as well as to a larger amount of Lewis acid sites being converted to Bronsted acid sites under the reaction conditions interacting with vapor present in the system as already observed in other studies in the literature [15, 40]. These products were also obtained in the study of glycerol dehydration over Al<sub>2</sub>O<sub>3</sub> performed by Massa et al. [15], which obtained acrolein as the desired product and hydroxyacetone as the main byproduct. The explanation for this result was that the monodehydration of glycerol led to the formation of hydroxyacetone, and this process is catalyzed by Lewis acid sites. The A7AP1 sample also showed high selectivity for hydroxyacetone (40%). On the other hand, samples A7AP2 and A7AP3 were prominent in the formation of light olefins as byproducts, which were identified as ethylene and propylene, as shown in Fig. 9. In addition, the lower selectivity of the A7AP2 sample to acrolein may be due to a more severe coking due to the fact that this material presents acid sites with higher acidic strength [41]. The A5AP1 sample prepared with Na<sub>2</sub>CO<sub>3</sub> at pH 5.0 also showed good selectivity in the formation of hydroxyacetone and olefins.

By analyzing the conversion results (Fig. 8) together with the distribution of gaseous products (Fig. 9), all the samples showed good selectivity for the formation of acrolein and hydroxyacetone, the latter with values between 30 and 50%. Furthermore, the influence of the pH of the reaction medium, as well as the precipitating agent, on the yield of the products is observed. Among the samples prepared at pH 7.0, samples A7AP1 and A7AP12 presented the best results of acrolein and hydroxyacetone. For samples prepared at pH 5.0, the sample A5AP2 synthesized with NaOH as the precipitating agent presented the best dehydration products. In contrast, the samples A7AP2 (NaOH) and A7AP3 (KOH), which were prepared at pH 7.0, were also found to have a good yield in light olefins as byproducts of the reaction. Sample A5AP1, which was synthesized with Na<sub>2</sub>CO<sub>3</sub> at pH 5.0, also showed higher formation of these byproducts. Among the samples prepared with NaOH at different pH, the higher production of light olefins for the A7AP2 sample may be due to the fact that it has acid sites with higher acidic strength than the A5AP2 sample, because the desorption temperatures for A7AP2 were higher (Table 2).

#### Characterization after the reaction

Table 3, as well as Fig. 10, shows the results of the TPO analysis for all the samples after the reactions.

The mass loss up to 473 K is due to the removal of moisture and/or adsorbed volatile compounds, as shown in Fig. 10a. From 473 K, samples A7AP2 and A7AP3 showed a greater mass loss during the oxidation, which indicates higher carbon formation during the catalytic tests. This result may be related to high acidity, which provides more coking reactions as well as greater olefin formation. The A5AP2 sample, which had the best performance in glycerol dehydration, obtained the lowest carbon formation. This is due to its higher percentage of weak acid sites (57%) shown in Table 2. In addition, these results also show that the





 Table 2 Deconvolution of the NH<sub>3</sub>-TPD curves for the catalysts

| Catalyst | Temperature/K |          | Relative fraction of the total sites/% |                      | Total<br>acid sites/     |
|----------|---------------|----------|----------------------------------------|----------------------|--------------------------|
|          | 1st peak      | 2nd peak | Weak acid sites                        | Medium<br>acid sites | $\mu$ mol $g_{cat}^{-1}$ |
| A7AP1    | 481.8         | 573.2    | 42.9                                   | 57.1                 | 532.3                    |
| A7AP2    | 514.6         | 622.9    | 53.1                                   | 46.9                 | 756.9                    |
| A7AP12   | 489.2         | 585.4    | 47.6                                   | 52.4                 | 595.5                    |
| A7AP3    | 486.4         | 573.1    | 41.3                                   | 58.7                 | 720.3                    |
| A5AP1    | 497.0         | 590.4    | 43.3                                   | 56.7                 | 636.0                    |
| A5AP2    | 497.9         | 614.1    | 57.3                                   | 42.7                 | 855.1                    |

secondary reactions are responsible for the greater formation of coke during the process.

From the oxidation temperatures shown in Fig. 10b, it is observed that all samples formed graphitic carbon which oxidized at higher temperatures, except for samples A7AP1 and A7AP12. The sample A7AP1 led to the formation of light carbon, whereas the sample A7AP12 indicates the formation of light carbon and graphitic carbon.





Fig. 8 Conversion of glycerol versus reaction time

## Conclusions

Mesoporous aluminas with different properties were obtained by varying the precipitating agent and the pH of precipitation. The specific surface area, the crystallinity and the acidic properties of the samples were dependent on both the pH and the precipitating agent used.

The sample prepared with KOH had the largest BET area, whereas the sample prepared with  $Na_2CO_3$  had the

| Table 3 TPO results for all the samples after the real |
|--------------------------------------------------------|
|--------------------------------------------------------|

| Catalyst | Mass loss/% |                 | Total<br>mass | DTA peak<br>temperature/K |          |
|----------|-------------|-----------------|---------------|---------------------------|----------|
|          | Up to 473 K | 473 to<br>973 K | loss/%        | 1st peak                  | 2nd peak |
| A7AP1    | 3.3         | 14.7            | 18.0          | 575                       | 653      |
| A7AP2    | 2.1         | 21.8            | 23.9          | -                         | 739      |
| A7AP12   | 9.2         | 16.7            | 25.9          | 573                       | 739      |
| A7AP3    | 3.7         | 23.7            | 27.4          | _                         | 750      |
| A5AP1    | 1.7         | 18.5            | 20.2          | -                         | 744      |
| A5AP2    | 1.1         | 13.3            | 14.4          | _                         | 760      |

smallest specific surface area. Samples prepared at a lower pH resulted in materials with a higher specific area. All samples showed poor crystalline XRD pattern of transitional low-temperature alumina, except for the sample prepared with  $Na_2CO_3$  at pH=7, which was almost amorphous.

Samples precipitated with NaOH presented higher density of acid sites than samples prepared with  $Na_2CO_3$ , independently of precipitation pH, whereas the sample prepared with both precipitants showed an intermediate density of acid sites. The strength of acid sites was predominantly weak and moderate for all samples.

The catalytic properties of the prepared aluminas for the glycerol dehydration are mainly related to the specific surface area and to acidic characteristics. Conversions of glycerol above 85% were obtained for all samples. A lower







Fig. 10 Mass variation (a) and temperature difference (b) during the TPO analysis for samples after the reaction

glycerol conversion was obtained for samples with a lower surface area and lower density of acid sites. The selectivity for glycerol dehydration was strongly related to the amount and strength of acid sites. The best result for dehydration was obtained for the sample prepared with NaOH and precipitated at pH=5. These results are related to the higher specific surface area, greater amount of acid sites and the higher ratio of weak acid sites.

Samples that showed higher carbon formation also showed a higher production of light olefins, indicating that the carbon production is related to the formation of these byproducts. These results are related to the higher acidic strength of the medium acid sites.

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