INFLUENCE OF THE SYNTHESIS CONDITIONS OF γ-ALUMINA ON ITS HYDROCARBONS AND WATER ADSORPTION PROPERTIES

Solange Borrego, Matthieu Lagauche, Karin Barthelet, and Elsa Jolimaître

IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

Abstract: The surface properties of γ-alumina can be modulated by its synthesis conditions. Since water adsorbs dissociatively on the surface of γ-alumina, its surface state will depend also on the water partial pressure of the atmosphere. However, those surface properties have never been clearly correlated to the adsorption properties of γ-alumina. Adsorption is the first step of every catalytic cycle, and thus this could be interesting information to get, being the objective of this study. To reach this objective, different γ-alumina samples were synthesized: a reference one, one that differed in the nature of the synthesis gas, and another one that differed in the boehmite morphology. They were all characterized in terms of water adsorption and, for the reference sample, of hydrocarbons adsorption by thermogravimetry. The adsorption isotherms for the reference sample (obtained from boehmite Pural SB3 decomposed under air) could only be obtained through adsorption measurements, which were simulated by a model based on DFT, and by a normal-like distribution model, with good fittings. Changing the synthesis gas from air to nitrogen resulted in an unstable sample. On the other hand, starting from a boehmite with proportionally less edges lead to a sample with less adsorption capacities, suggesting that edges are important adsorption sites for water. Finally, a preliminary hydrocarbons adsorption study was conducted on the first sample, showing that ethylene adsorbs more than ethane, and that its adsorption capacity increases with the decrease in hydroxyl content. In particular, desorbing the last hydroxyl seems to free a specific site that has now to be identified.

Introduction

Transition aluminas are metastable crystalline phases which have a very important role in the chemical and refining industry, being used in processes as diverse as ammonia production, hydrocracking, and catalytic reforming as heterogeneous catalysts and supports. γ-alumina is a low-temperature transition phase, and the aluminum oxide used the most as a support in the chemical industry due to its attractive qualities: very high porosity, surface area, acid/base characteristics, and relative inexpensiveness.

The precursor of γ-alumina is boehmite (AlOOH). The boehmite calcination to form transition aluminas involves short-range rearrangements of atoms in the crystal structure (topotactic transformation); thus the cubic packing of oxygen sub lattice of boehmite is maintained in the γ-alumina (Figure), with the microscopic morphology of the boehmite precursor having a major influence on the characteristics of the obtained alumina.
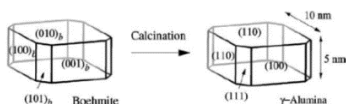

Figure 1 – Topotactic transformation of boehmite into γ-alumina [1].

The surface and structure of γ-aluminas have been a subject of study since the 1960s, aided by technologies such as infrared spectroscopy [2–5], nuclear magnetic resonance spectroscopy [3,4,6], and x-ray diffraction [4,6,7]. It is known that the surface properties of γ-alumina are related to local microstructure and surface chemical composition, and can be manipulated in order to govern the acid-basic reactions and the dispersion of active phases on the support. There is wide experimental evidence that all of these properties are dependent on the preparation step [8].

γ-aluminas have an elaborate and heterogeneous surface, due to the presence at the surface of coordinatively unsaturated (*cus*) cations, with the coordination number of aluminum being tetrahedral (Al^{IV}) or octahedral (Al^{VI}) [4,5,9], with variable amounts of pentahedrally coordinated aluminum (Al^{V}) also being reported [2,3,10,11]. In addition, there are also at the surface oxygen vacancies to ensure electrical neutrality.

The most abundant component at the surface of γ-alumina is made up of water, that can adsorb by two means: undissociated (H_2O), or dissociated in the form of hydroxyls (OH^-); this adsorption occurs to compensate the surface unsaturation present at the uppermost layer due to the presence of coordinatively unsaturated cations and anions [12]. The hydroxyls at the surface of γ-alumina have a major influence on its chemical and electrochemical properties, and as such any process that modifies the hydroxyls coverage on γ-alumina, such as

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the temperature of calcination, can have an effect on the surface state [8].

The surface hydroxyls have been studied by several techniques, such as IR spectroscopy, and modeled by DFT. Many authors agree to distinguish hydroxyls in function of the coordination number of the aluminum they are bonded to, and the number of aluminum neighbors.

The existence of Lewis acid sites (*cus* cations) and basic sites (oxide anions) at the surface of γ-alumina allows rehydroxylation by interaction with water, with these sites being converted into surface hydroxyls. The presence of water has, then, an influence on the surface state and thus on the adsorption sites. It can also be supposed that it will compete in some cases with hydrocarbons.

All studies on rehydration of γ-alumina agree that water is initially chemisorbed and then physisorbed. Chemisorption has been evidenced in particular thanks to calorimetric measurements done by Coster *et al.* [13]: these authors consider as irreversible adsorbed quantity the one non-desorbed by a simple decrease of the pressure. They even proposed that chemisorption of water could be represented as a two-step process for γ-alumina under atmospheric conditions [13] (Figure Error! No text of specified style in document.), involving:

1. non-dissociative adsorption of water on *cus* cations, where there is a transfer of electron density to a Lewis acid site;

2. dissociative chemisorption of water and modification of surface aluminum coordination with the hydroxyl group bonded to the aluminum atom, which means that the two-coordinate oxygen atom adjacent to the aluminum site is protonated.
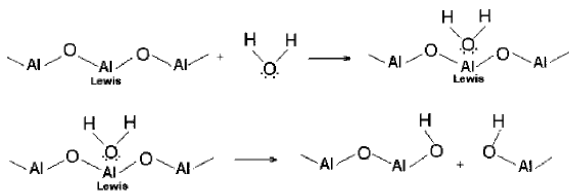

Figure Error! No text of specified style in document. – **Two-step process of the interaction between water and the surface of γ-alumina [13].**

As such, chemisorbed water is not in molecular form and involves more than one type of site. On the contrary, physisorbed water involves molecular water, with hydrogen bonding to hydroxyl groups on the activated alumina surface. Depending on the pore size and relative pressure, there could also be capillary condensation within the smaller pores.

Since water is dissociatively chemisorbed, this phenomenon provokes an extensive surface reconstruction. Nuclear magnetic resonance studies done by Coster *et al.* [10] show that reconstruction by water chemisorption favors Al^{VI} at the expense of both Al^{IV} and Al^{V}, with about 60% of the surface aluminum being likely to change coordination when going through hydroxylation.

Isotherms of water adsorption on alumina are usually of type II [14,15] (Figure 3).
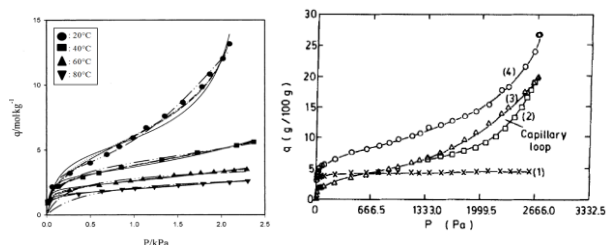
(a) Alumina activated at 320 °C during 12h [14]
(b) Isotherm at 26 °C on γ-alumina activated at 350°C under vacuum, (4) experimental and (1) to (3) simulated [15]

Figure 3 – Water adsorption isotherms on γ-alumina.

At low water partial pressures, the slopes of the isotherms are very high, which confirms that water adsorption is favorable in that area.

To simulate these isotherms, Ruthven *et al.* [16] divided the adsorption isotherm (4), a Type II isotherm, in many isotherms:

- Isotherm (1) corresponds to chemisorption, tending to a fixed q value of ~4 g/100 g, and is a Type I isotherm modeled by a Langmuir isotherm;

- Isotherms (2) and (3) correspond to physisorption phenomena in adsorption and desorption, with a hysteresis loop that corresponds to capillary condensation, and are modeled by a BET isotherm.

Ruiz *et al.* [15] have one of the few studies available on ethane and ethylene adsorption on γ-alumina, showing a relationship between the surface coverage and the standard enthalpy, at 30°C (Figure). The adsorption enthalpy decreases with the surface coverage until reaching a value of 10 kJ/mol; this variation indicates the surface sites are not all equivalent. Ethylene presents a higher adsorption enthalpy, probably due to the interaction of the π-bond with the surface, and that difference is accentuated at low surface coverage. It seems that adsorption is more favorable for unsaturated hydrocarbons, in comparison with their linear equivalents.
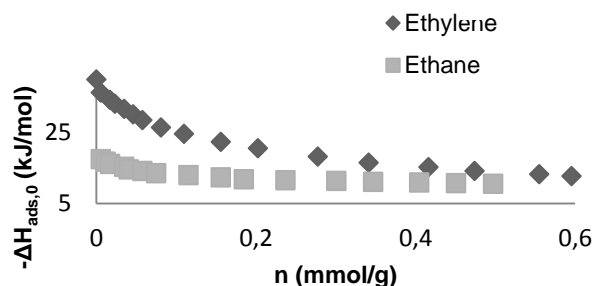

Figure 4 – Adsorption enthalpies for ethane and ethylene for various surface coverage's at 30°C.

The adsorption enthalpies of these hydrocarbons (up to -40 kJ/mol for ethylene and -17 kJ/mol for ethane) on γ-alumina are much lower than the adsorption enthalpy of water, so it can be supposed that for an ethane/ethylene it is physisorption. Water would probably compete with the hydrocarbons. However, there are no studies available that validate this assumption.

To sum up, even though adsorption is the first chemical step of any catalytic cycle, and potentially a limiting one, there are not many studies available on hydrocarbons adsorption on γ-

alumina. What is known is that the nature of the adsorbate, and the water content in the surrounding gas have a considerable impact on this adsorption. In particular, at low water partial pressures, water adsorption is very favorable, and there could be competition with hydrocarbons. As such, it is necessary to study water adsorption on γ-alumina in order to understand the changes in the surface state, which can have an influence on hydrocarbons adsorption.

To conclude, although γ-alumina is largely used as a catalyst support in the chemical industry, due to its textural properties, and acid/base characteristics, there is no well-established correlation between these properties and the activity of catalysts, neither between them and their adsorption capacities. To try to investigate this, different samples of γ-alumina are synthesized by varying the structure of the initial boehmite, the water partial pressure in the surrounding gas, and the type of gas. The influence of these synthesis conditions on the surface structure is studied by measuring the corresponding isotherms of water adsorption. Finally, these surface states will be correlated with their adsorption capacities of hydrocarbons.

Methods

Various samples of γ-alumina are synthesized under different conditions (Figure 5), namely:

- the type of boehmite (Pural SB3 or Disperal 40);
- the type of gas (air or nitrogen);
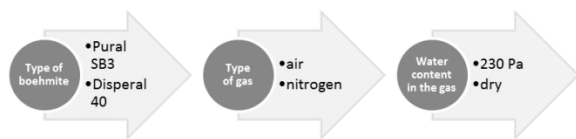- the water content in the gas (dry or from the gas network at 230 Pa of water).

Figure 5 – Scheme for the synthesis conditions of γ-alumina.

The two boehmites present different characteristics, the most important one being the ratio between the edges and plans (Figure 6): since the transformation of boehmite to γ-alumina is a topotactic one, that is, the crystallographic structure is maintained from reagent to product, it is interesting to compare the difference in adsorption properties and surface structure that brings about. It is worth noting that BET specific surface area for Pural SB3 is 326 m²/g, while for Disperal 40 it is 100 m²/g. Both boehmites have almost no impurities (< 0,01%).
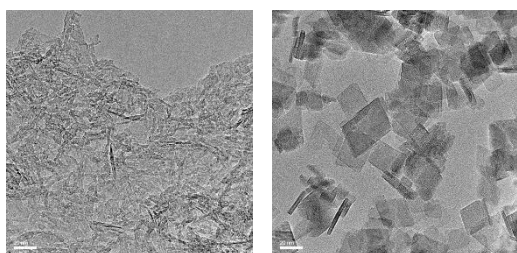

Figure 6 – TEM for boehmites Pural SB3 (on the left), and Disperal 40 (on the right).

The type of gas used (air or nitrogen) has different amounts of oxygen, that can lead to different oxygen defects on the samples synthesized. On the other hand, the water content in the gas (dry or 230 Pa) has the potential to create different defects and acid sites at the surface of the samples.

A classical methodology is applied to synthesize the samples of γ-alumina: the reaction takes place in a U-reactor, where 5 g of boehmite go through the following temperature program:

1. The temperature goes from 20 to 120°C at a constant rate of 5°C/min, and there is a 3h plateau whose aim is to remove most of the water;
2. The temperature goes from 120 to 650°C at the same constant rate, reaching a 6h plateau;
3. The temperature goes back to room temperature.

It is worth noting the difference in color obtained for the samples synthesized under air and nitrogen: the former are white powders, while the latter are gray powders with diverse tones.

Afterwards, different and complementary methods are used in this work to characterize as well as possible all the samples obtained:

- X-Ray diffraction (XRD) to identify the structure of the alumina and to characterize its morphology;
- Measurement of N_2 adsorption isotherms at 77 K to assess the specific surface areas of the γ-alumina samples synthesized;
- Infrared (IR) spectroscopy to identify the nature of the surface hydroxyls present in the different samples, which appear in the 3800-3500 cm⁻¹ zone, as well as their chemical environment (the coordination of the neighboring aluminum atoms). Depending on the morphology, it is expected there will be peaks with different intensities related to the intensity of each crystallographic face;
- Nuclear magnetic resonance (NMR) spectroscopy to study the nature and chemical environment of the surface hydroxyls present in the γ-alumina samples synthesized;
- Ultraviolet-visible (UV-Vis) to identify the amount and type of defects found in the different samples.

Through thermogravimetry, a common technique that consists on measuring the mass variation of a sample following a certain temperature profile at a given controlled atmosphere, and relating that variation with, for instance, the adsorption or desorption of components found in the gas, it is possible to determine the adsorption and desorption isobars of water and hydrocarbons on differently synthesized γ-aluminas.

For the desorption isobars of water on γ-alumina, a sample (~75 mg) is put in the thermobalance at a certain partial pressure of water (1, 20, 500, 1000 or 1400 Pa) with a nitrogen flow of 4 NL/h, being left to stabilize at room temperature until the local mass variation become negligible. A temperature program is then applied to the sample, going from 100 to 600°C in increments of 100°C (Figure 1). For each temperature, the sample is also left to stabilize until the local mass variation is insignificant.
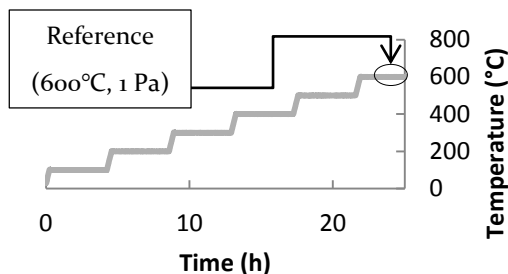
Figure 1 – Temperature program used for the desorption experiments.

For the adsorption isobars of water on γ-alumina, the methodology used is equal, except for the temperature program, which is reversed: it goes from 600 to 100°C in increments of 100°C (Figure 2.).
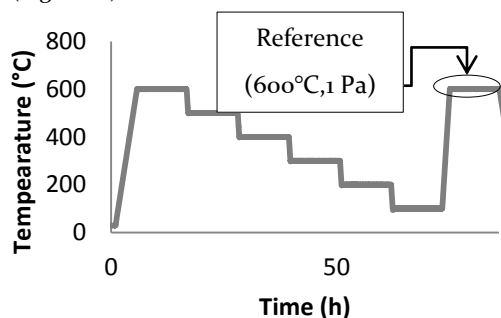

Figure 2 – Temperature program used for the adsorption experiments.

It is necessary to establish a relative reference to allow the correlation of adsorption and desorption results at different partial pressures of water. That reference is chosen at 600°C and 10 ppm of water; at these conditions, an approximation is made: the surface of γ-alumina does not present any hydroxyl groups. At this temperature, that is lower than the thermal decomposition temperature of boehmite to obtain γ-alumina, it is assumed the sample is thermally stable. On the other hand, this partial pressure of water is the lowest one the thermobalance allows.

In order to obtain reproducible results, the stabilization time for the samples synthesized under air must be at least 2 h (after which the mass loss is 0,006 OH/nm²/h) and for the ones synthesized under nitrogen at least 15 h (after which the mass loss is 0,03 OH/nm²/h). The duration of the plateaus is adjusted to ensure their stabilization.

To determine the number of surface hydroxyls, it is necessary to calculate the difference between the mass loss at the adsorption plateau and the reference plateau, which was chosen at a water partial pressure of 1 Pa and 600°C, where it is assumed the surface of the sample is devoid of hydroxyls.

When the mass variation for different partial pressures of water and temperatures is known, it is possible to determine the number of hydroxyl groups at the surface of γ-alumina by applying (1). Therefore, the hydroxyl groups for different synthesis conditions are quantitatively obtained, and can be correlated to the quantity of hydrocarbons adsorbed.

$$OH/nm^2 = \frac{Dm \times N_A \times 2}{1000 \times M_{H_2O} \times S_{BET} \times 10^{18}} \quad (1)$$

Where:
Dm – Mass variation associated with water (mg/g);
N_A – Avogadro's number (6,02 x 10²³ (1/mol);

2 – Water dissociates to form two hydroxyls;
M_{H_2O} – Water molar mass (18 g/mol);
S_{BET} – Specific surface area of the sample (m²/g).

The protocol used to study the ethylene adsorption on γ-alumina is in Figure 3. An alumina sample is placed in the thermobalance (~ 60 mg) and put in equilibrium at the water partial pressure necessary to reach the hydroxylation rate wanted, under a nitrogen flow rate of 4 NL/h. The sample undergoes several activation-adsorption-desorption cycles:

- Activation at 100°C and stabilization during 2 h;
- Decrease of temperature till 30°C, followed by injection and adsorption of ethylene until the mass is stable;
- Desorption under nitrogen at 30°C;
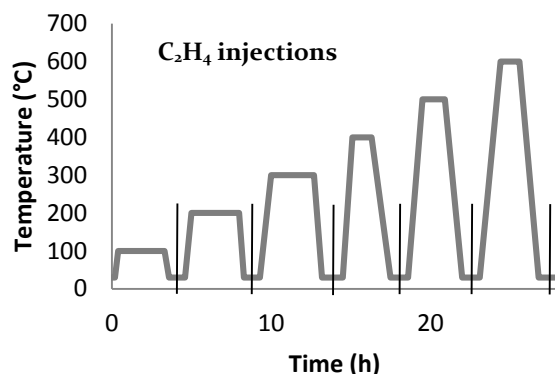- Activation at 200°C and stabilization during 2 h;
- etc. till 600°C.

Figure 3 – Ethylene adsorption at fixed surface coverages.

These cycles have the advantage of greatly limiting rehydroxylation, ensuing precise results about the evolution of the behavior of the surface in function of the surface coverage. The alumina is reactivated in an atmosphere whose water content is controlled before each adsorption. Furthermore, the adsorption temperature is fixed at 30°C since it allows adsorption in great quantities, and the mass variations are then measured with more precision. Finally, the duration of the stabilization plateaus at different temperatures is minimized: the more temperature, the less time the mass needs to stabilize.

Results and discussion

Water adsorption/desorption on reference sample: The reference sample is synthesized by the thermal decomposition of Pural SB3 at 650°C for 6h under air with a water partial pressure of 230 Pa. The size of the grains obtained is in the 5-80 µm range, while the specific surface area is 228 m²/g. The corresponding XRD spectra show that the alumina obtained is a γ-alumina, with coincident theoretical and experimental diffraction rays.

The water desorption measurements for the reference sample are obtained (Figure 10) for the water partial pressures of 1, 20, 500, 1000, and 1400 Pa, using as reference a plateau at 600°C at a water partial pressure of 1 Pa, where it is considered that the surface of the sample is completely dehydrated (no more hydroxyls).
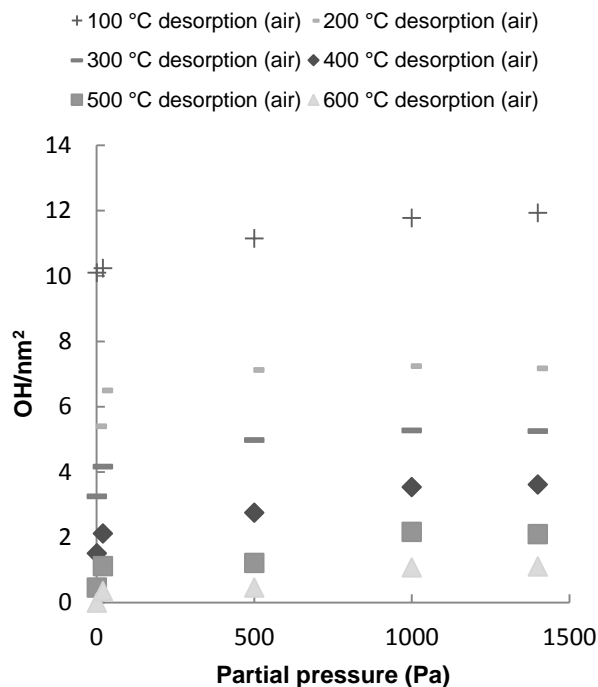
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Figure 10 – Water desorption isotherms obtained for the reference sample.

For low water partial pressures (1-20 Pa), the amount of surface hydroxyls increases linearly with a pronounced slope that depends on temperature, until, at high water partial pressures (500-1400 Pa), this amount reaches a plateau, also depending on temperature, with little change in the maximum values. Before going further in the interpretation, some points have to be verified.

To verify the thermic stability of the sample, the same desorption program is used with a key change: a pretreatment at a certain temperature (600 or 450°C) for 5 h precedes the usual temperature program. From them, it is possible to ascertain that the pretreatment step does not seem to heavily influence the water desorption on this sample, especially for higher temperatures.

To verify if the desorption isotherms correspond to equilibrium states, that is, if desorption and adsorption lead to the same surface coverage at the same temperature and water partial pressure, two experiments are carried out at 1400 Pa. The sample is first heated to 100 or 400°C, then heated to 600°C (hydroxyls are desorbed), and after that, cooled down again to 100 or 400°C (hydroxyls are readsorbed).

The values obtained for desorption and adsorption at the same temperature and water partial pressure (100 or 400°C and 1400 Pa, respectively) are not equivalent. Figure 11 puts in evidence the disparity between the surface coverage reached by desorption (3,63 OH/nm² at 400°C and 12,36 OH/nm² at 100°C) and adsorption (2,17 OH/nm² at 400°C and 7,80 OH/nm² at 100°C). The values differ by more or less 40%.
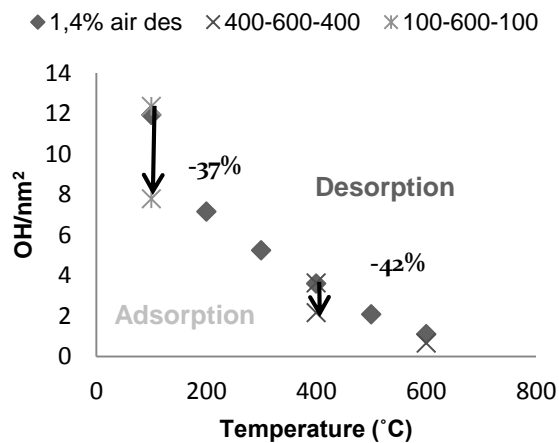
Figure 11 – Results for the 400-600-400°C and 100-600-100°C experiments, and comparison with the water desorption isobar at 1400 Pa.

This phenomenon is observed for all temperatures, as shown by the comparison between the points obtained by water desorption and adsorption in Figure 12.
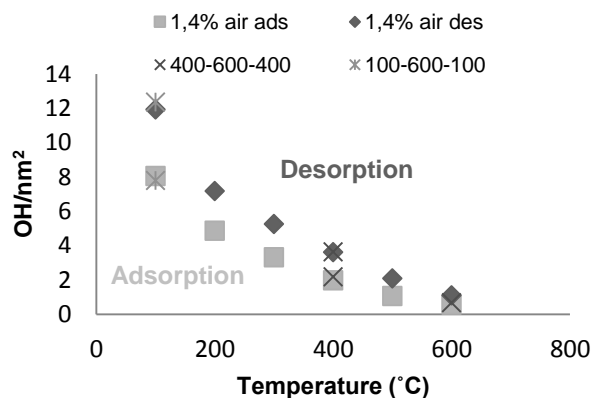
Figure 12 – Water desorption and adsorption isobars at 1400 Pa for the reference sample.

The points from the two return experiments, at 400-600-400°C and 100-600-100°C, are concordant with the values obtained from the complete experiments of progressive desorption or adsorption. On the other hand, two adsorption/desorption cycles are also run in order to check the reproducibility and reversibility of the adsorption and desorption measurements. From them, it is possible to conclude that the adsorption/desorption cycles are reproducible and reversible.

There are several hypotheses that could explain this disparity between the values obtained for adsorption and desorption.

The first hypothesis is that the surface structure changes; it could, for example, undergo sintering, which would be catalyzed by the presence of water [17]. Indeed, the first temperature in the adsorption program is 600°C, which is lower than the temperature of transition to δ-alumina, but close to the conditions of dealumination. However, since there is the same quantity adsorbed for the pretreated and the non-pretreated samples at 600°C, it seems that no sintering occurs at that temperature. This is also confirmed by a very low decrease of the specific surface area (from 228 to 207 m²/g) after treatment at 600°C. Therefore, sintering is not a viable explanation for

the difference between the adsorbed quantities reached by desorption and adsorption.

Then, the possibility of occurrence of capillary condensation is studied, in which case a hysteresis loop would appear. To study this hypothesis, the Kelvin equation (2) is applied to this system from 20 to 300°C at a water partial pressure of 1400 Pa. The values for the surface tension of water are from reference [18]. The Kelvin radii obtained in function of the show that, for temperatures higher than 100°C, capillary condensation does not occur in the pores of this sample. As such, this is not a viable explanation for the different adsorbed quantity from adsorption and desorption experiment.

$$ln\frac{p}{p^0} = \frac{2\gamma V_m}{rRT} \qquad (2)$$

Where:

p – Vapor pressure (Pa);
p_o – Saturation vapor pressure (Pa);
γ – Surface tension (J/m²);
V_m – Molar volume of the liquid (m³/mol);
r – Radius of the droplet (m).

Finally, it is considered that the measurements obtained by desorption cannot correspond to equilibrium points. This implies that some hydroxyls are very difficult to desorb, that is to say their desorption activation energy is very high and far higher than that of adsorption. In that case, desorption would be a slower phenomenon than adsorption, and a very long time would be needed to reach the equilibrium. Moreover, the probability of two hydroxyls meeting to form water gets lower the longer the sample is dehydrated; this could also influence the slowing down of desorption. To verify this hypothesis, it is necessary to extract the desorption activation energy from the experimental data.

Dima and Rees [19] have developed an equation which establishes a relationship between the desorption activation energy and the surface coverage, using the data from a water desorption isobar. For that, the authors considered that desorption is a first-order reaction, and that there is no readsorption during desorption. After some mathematical treatment, the authors obtain equation (3), where the function p is given by (4).

$$\frac{\sum_i ln\theta_i \cdot p\left(\frac{E}{RT_i}\right)\sum_i p\left(\frac{E}{RT_i}\right)T_i e^{-E/RT_i}}{\sum_i p^2\left(\frac{E}{RT_i}\right)} - \sum_i ln\theta_i T_i e^{-E/RT_i} = 0 \qquad (3)$$

$$p(x) = \frac{\exp(-x)}{x} + \int_x^\infty \frac{\exp(-u)}{u}du \qquad (4)$$

Where:

θ_i – Surface coverage (g/g);
T_i – Temperature (K);
R – Ideal gas constant (8,32 J/(mol.K));
p – Partial pressure of the gas (Pa);
E – Activation energy for desorption (kJ/mol).

This equation is applied to the values obtained for the desorption experiments at 1, 20, 500, and 1400 Pa. After a numerical approximation of function p, the results are reported in Figure 13. The points obtained by Hendrisken et al. [20] result from the measurement of the heat of adsorption by calorimetry, and are used as the first values for Solver.
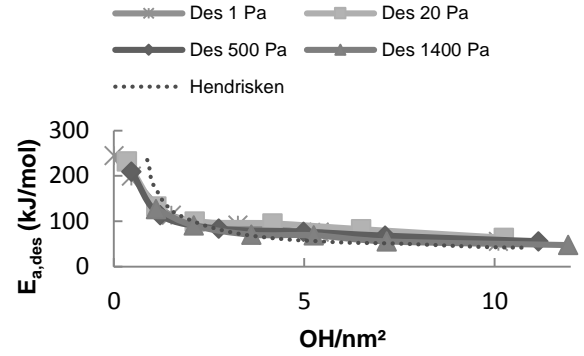

Figure 13 – Influence of the surface coverage on the desorption activation energy of the reference sample.

Calculations of desorption activation energy in function of surface coverage by hydroxyl lead to curves close to the experimental points of Hendrisken. Thus, they can be considered as quite accurate ones.

These curves show that the desorption activation energy depends on the surface coverage whatever the water partial pressure, becoming particularly high for the almost dehydrated surface. This confirms that the surface of the alumina is heterogeneous with different types of adsorption sites. For high surface coverage, the activation energy is close to the vaporization enthalpy of water (40,7 kJ/mol at 100°C [49]), but for low surface coverage, it becomes very high (> 100 kJ/mol). Thus, the last hydroxyls are very difficult to desorb, and as such, it is probably difficult to reach an equilibrium by desorption. This activation energy seems to be independent from the water partial pressure, since all the curves tend to the same one, considering there was an approximation made.

To try to determine if these remaining hydroxyls can be associated with one or several specific types of hydroxyls, the sample is heated at different temperatures and characterized by IR spectroscopy. It is submitted to the same temperature program used to verify the equilibrium, that is, two 400°C plateaus separated by a 600°C plateau. However, the water partial pressure is 20 Pa due to technical constraints. The spectra obtained are drawn in Figure 4: the top line corresponds to the spectrum of the solid heated to a 400°C plateau, after desorption of some water molecules, and the bottom line to the one of the previous solid heated to 600°C and back to 400°C, after adsorption of water.
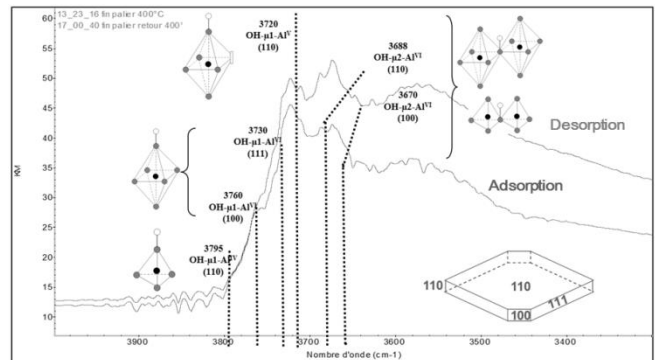

Figure 4 – IR analysis of a 400-600-400°C experiment at 20 Pa for sample #1 after desorption from ambient to 400°C (top line) and after the 400-600-400°C temperature program (bottom line).

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The quantities of types of hydroxyls in the two 400°C plateaus are different, which confirms that some hydroxyls are non-desorbed by performing desorption. Indeed, several bands are lower in the second spectrum. However, the variation of the bands ratio cannot be interpreted, because each hydroxyl type has probably its specific molar attenuation coefficient, which is temperature-dependent, and these coefficients are unknown.

To get more quantitative information, a H^1 NMR analysis is performed in a similar way to the IR study. In Figure 5, the top line corresponds to the spectrum of the solid at the end of the first 400°C plateau (after desorption of water from ambient temperature), while the middle line corresponds to the spectrum of the solid at the end of the last 400°C plateau (after adsorption of water from 600°C). The bottom one corresponds to the spectrum obtained by subtracting the two previous ones.
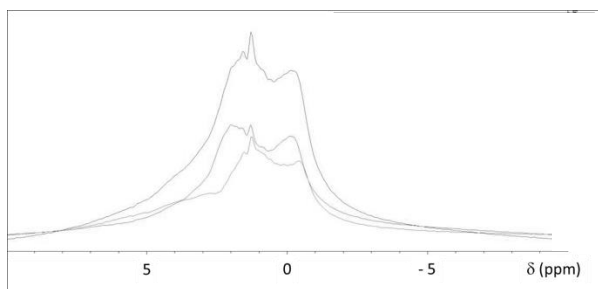

Figure 5 – H^1 NMR spectra for the 400-600-400°C experiment for the reference sample (middle line for the spectrum of the solid after adsorption, and top line for the spectrum of the solid after desorption).

Taoufik *et al.* [22] suggest some attributions to the peaks, in particular that the ones with negative chemical shifts correspond to terminal hydroxyls, while the ones with positive chemical shifts correspond to bridged/tribridged hydroxyls.

In accordance with the IR spectra following the same temperature program, the NMR spectra show that the quantities of hydroxyls in the two plateaus are different (lower for the sample after adsorption from 600 to 400°C), but the ratios between the different types of hydroxyls seem to be maintained. This indicates that there are always at least two different types of hydroxyls desorbed at the same time, as is the case where to desorb a water molecule, a terminal hydroxyl has to combine itself with a hydrogen from another hydroxyl. The latter is more probably a bridged or tribridged hydroxyl, so that after the hydrogen departure, the oxygen will still have a correct coordination number. Consequently, it is not possible to attribute a specific type of hydroxyl to the ones that have difficulty desorbing: in other words, the remaining hardly desorbed hydroxyls can be any type of hydroxyl, but probably with different probabilities depending on the family.

The adsorption isotherms obtained through adsorption experiments are shown in Figure 6. These isotherms do not tend to the same plateau, and as such, there are different adsorption sites involved in the adsorption phenomenon, which is in agreement with previous results. The points at high partial pressures and low temperatures seem higher than expected, but this could be due to the fact that there is physisorption happening at these conditions, making the stabilization difficult.
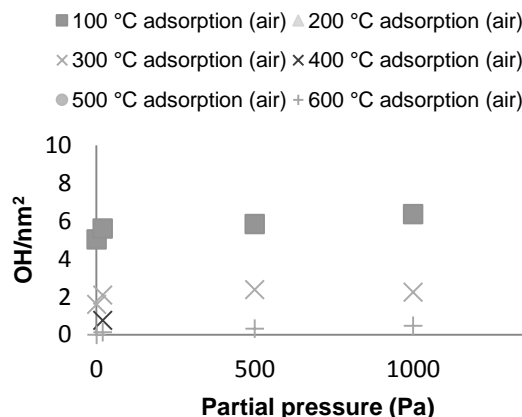

Figure 6 – Water adsorption and desorption isotherms for sample #1.

To confirm the accuracy of the adsorption points, it is necessary to compare them to simulated isobars. Since there are many adsorption sites involved, the models that can be used are, for instance:

- based on Density Functional Theory (DFT);
- Langmuir multisite;
- Statistical models.

Starting with Density Functional Theory, quantum chemistry calculations are performed [23,24] on periodic models depicting the system as a unit cell repeated along the 3 directions of space [25], with the VASP code [26,27]. Alumina surface models for the γ-alumina (100) and (110) orientations are adapted from Digne *et al.* [28,29] and Wischert *et al.* [30] and reoptimized at a up-to-date level of theory (GGA functional *plus* dispersion corrections). [31] Adsorption energy of water for growing water coverage are estimated, taking into account possible dissociation of the water molecule into hydroxyl groups. Analysis of surface vibrational modes enables the quantification of approximate enthalpic and entropic terms (harmonic approximation), leading to the estimation of adsorption enthalpy and Gibbs free energy at the desired temperature and water partial pressure, assuming an ideal gas behavior for gaseous water [32].

The curve that is obtained based on DFT can be seen in Figure 7 in comparison with the adsorption experimental points at a water partial pressure of 1400 Pa. The tendency of the curve and the experimental points is similar, although there is a gap between the values themselves. This can be linked to a problem of the definition of the reference state. In this study, at a water partial pressure of 1 Pa and 600°C, the surface of γ-alumina is considered completely dehydrated. Yet, there will be always some hydroxyls at the surface at these conditions, which are considered in the simulated model. Consequently, a correction is applied to the experimental points that improve the correspondence between experiments and calculations, but a difference is maintained. This point will have to be investigated. However, the difference seen at 100°C is probably because the simulated model does not take into consideration the physisorption phenomenon, which happens more strongly at this temperature, contrary to the experiments. As such, this model fits the adsorption experimental values for this sample in a satisfactory, if lacking, way.
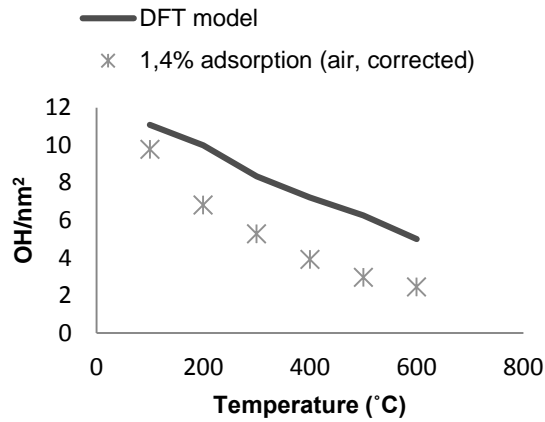
Figure 7 – Comparison between the experimental points for adsorption at 1400 Pa and the model based on DFT.

The Langmuir multisite model is also taken into consideration to simulate the experimental values. However, to apply this model, it is necessary to know the number of adsorption sites and, for each of them, the maximum adsorbed quantity, the adsorption enthalpy and entropy. These parameters could be extracted from the simulated model based on DFT, but it would be a very onerous work, and as such this model is not considered.

Another way to develop a representative and user friendly model exists, using statistical models. In his thesis, Xia [33] developed several adsorption models, with one that represents well the experimental data (Figure 8): the normal-like distribution model, given by (5). The location parameter is approximately equal to the adsorption enthalpy, which is calculated using the Dima and Rees approach. The scale parameter is fitted using the model and experimental values. Finally, the standard variation of entropy is obtained by DFT calculations.

$$\theta = \frac{exp\left(\frac{T\Delta s^0 + \epsilon_c}{\epsilon_v}\right)\left(\frac{p}{p^0}\right)^{RT/\epsilon_c}}{1 + exp\left(\frac{T\Delta s^0 + \epsilon_c}{\epsilon_v}\right)\left(\frac{p}{p^0}\right)^{RT/\epsilon_c}} \quad (5)$$

Where:
θ – Overall coverage;
Δs^o – Standard variation of entropy (kJ/mol);
ϵ_c – Location parameter;
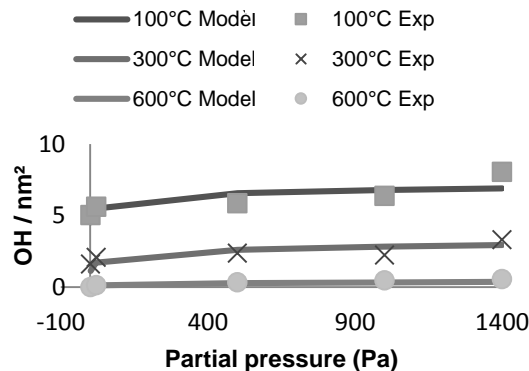ϵ_v – Scale parameter.

Figure 8 – Comparison between the experimental water adsorption isotherms for the reference sample and the normal-like distribution model.

Considering this good representation of the experimental data by the model, it is possible to conclude that the adsorption measurements can be simulated by this model. However, some points, especially at high partial pressures and low temperatures, deviate from the experimental ones. This could also be explained taking into account this kind of model is designed for chemisorption only; as such, there may be physisorption occurring at these conditions.

Thanks to this study, a procedure has been successfully set up to determine accurate water adsorption isotherms. Models for desorption curves and adsorption isotherms have also been developed so that it is now possible to extract important information, such as the adsorption enthalpy.

The same methodology will now be applied to the other samples prepared during this study.

Water adsorption/desorption on sample synthesized under nitrogen: This sample is synthesized by the thermal decomposition of Pural SB3 at 650°C for 6h under nitrogen with a water partial pressure of 230 Pa. The specific surface area of this sample is 233 m²/g. The XRD spectra show that the alumina obtained is a γ-alumina, with coincident theoretical and experimental diffraction rays.

The only significant difference this sample has in comparison with the reference sample is its color, which is gray. To explain this, two hypotheses are formulated.

First, without oxygen in the synthesis gas, there could be some carbonaceous residue in the alumina, but by a CHONS analysis, it is verified that none of the samples contain an important carbon content (0,03% for this sample, and 0,06% for the reference one).

Secondly, it could be envisaged that some defects have been created because of the lack of oxygen in the system. This type of defects should be detectable by UV-vis analysis [34]. The UV-vis spectra of both samples synthesized under air (bottom line) and nitrogen (top line) are drawn in Figure 9. The characteristic band gap at 4,5 eV indicates the samples are γ-aluminas. However, it is clear the type of defects are dissimilar: the sample synthesized under nitrogen has more oxygen gaps, that can create defects at the surface, as well as center-F defects that are non-existent in the sample synthesized under air, creating a difference in charge that may be responsible for new types of defects.
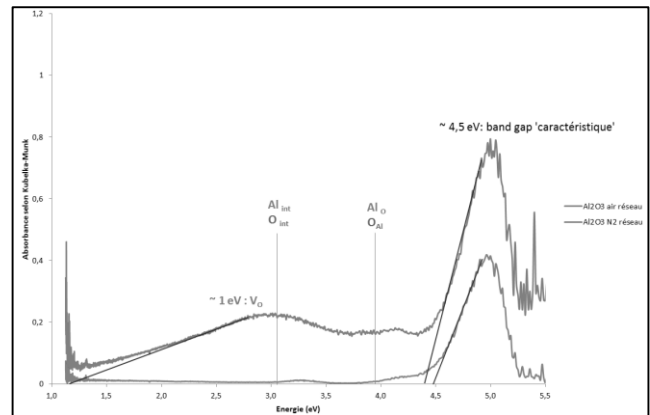

Figure 9 – UV-vis analysis of samples synthesized under nitrogen (top line) and air (bottom line).

A study of the influence of a pretreatment step at 600°C on this sample is also done, where it can be seen that, unlike the

sample synthesized under air, the pretreatment has a non-negligible effect on the desorption isobar, especially at low temperatures, with the pretreated sample having a lower surface coverage than the non-pretreated one.

This implies that some oxygen gaps have been filled during the pretreatment, resulting in a sample that adsorbs less. Yet, as the pretreatment is done under nitrogen, the only explanation is that the atmosphere contains traces of oxygen that are enough to fill these vacancies. If this is true, the same kind of phenomena is expected to happen during the synthesis of alumina, with more or less vacancies being generated depending on the synthesis time. At the limit, the sample would have no oxygen vacancies if the synthesis time is long enough.

As such, an alumina is synthesized under nitrogen atmosphere during 12 h, twice the usual time, and the recovered powder is white, instead of gray. Consequently, the alumina synthesized under nitrogen is not a stable sample, since it continuously changes under atmosphere, and it would be too difficult to be sure of its surface state. Thus, it has been decided to give up nitrogen as a synthesis gas.

Water adsorption/desorption on sample with different boehmite morphology: This sample is synthesized by the thermal decomposition of Disperal 40 at 650°C for 6h under air with a water partial pressure of 230 Pa. The XRD spectra show that the alumina obtained is a γ-alumina, with coincident theoretical and experimental diffraction rays. The corresponding BET specific surface area is about 100 m²/g.

The adsorption and desorption measurements for sample #5 are obtained at a water partial pressure of 1400 Pa, and can be seen in Figure 10.
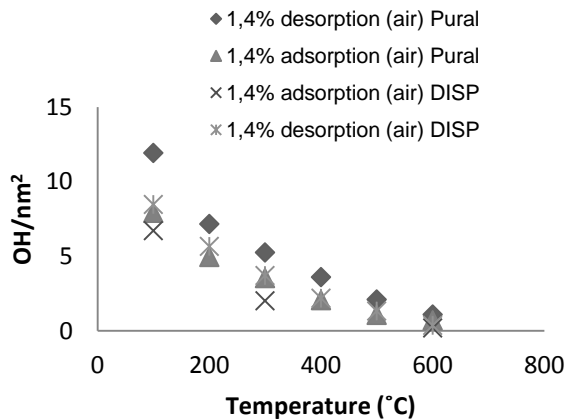

Figure 10 – Adsorption isobar for the sample synthesized from Disperal 40 at a water partial pressure of 1400 Pa.

It is apparent that this sample results in an alumina that adsorbs less than the reference sample, which was synthesized from Pural SB3, this difference being constant even at 600°C. This could be due to the fact that alumina from Disperal 40 has proportionally less edges than Pural SB3, which could be high energetic sites. By IR spectroscopy, it would be probably possible to get more precise information, but at the time of writing of this report, these analyses are in progress.

On the other hand, for the alumina from Disperal 40, the adsorbed quantities at 600°C obtained by desorption and adsorption experiments are almost identical and very close to zero. This seems to indicate that at this temperature and water

partial pressure, the water is all desorbed from the surface of the sample, which is different from what happens to the reference one. This shows that the last desorption sites are less energetic than those of the reference. To confirm this, it is necessary to proceed to the estimation of the desorption activation energy for this sample, as it was done for the reference.

Hydrocarbons adsorption on reference sample: Due to lack of time, only the reference sample, alumina synthesized from Pural SB3 under air, has been tested in hydrocarbons adsorption. Ethane and ethylene are used in this work, since they are simple molecules that differ only in a double bond, as well as being relatively inexpensive.

The adsorption of ethylene is done at 30°C according to the program described in the Methods. The alumina is activated at temperatures from 100 to 600°C in 100°C increments under a nitrogen flow of 4 NL/l containing 1 Pa of water. Even if the desorption experiments do not reach a thermodynamic equilibrium, the stabilization state is sufficiently stable to use the desorption experiments to set up the hydration state of the sample before adsorbing hydrocarbons on them. Between each activation plateau, the alumina is submitted to a similar nitrogen flow, though this time containing an ethylene partial pressure of 0,25 bar. The results obtained can be seen in Figure 11. For comparison, there is a desorption point obtained for ethane during preliminary tests.
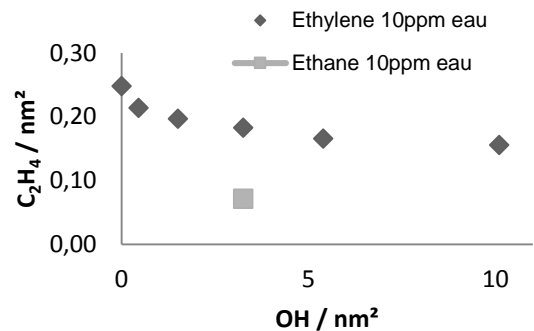

Figure 11 – Ethylene and ethane adsorbed on sample #1 in function of the surface coverage.

First, at the same surface coverage, ethylene adsorbs more than ethane. This goes with literature in the sense that adsorption is more favorable for unsatured hydrocarbons, in comparison with their linear equivalents [35].

Secondly, the quantity of adsorbed ethylene increases as the number of surface hydroxyls decreases; in other words, the more dehydroxylation, the more hydrocarbons adsorption is favored. Looking at ethylene adsorption at very low surface coverage, the shape of the curve also indicates that desorption of the very last hydroxyls may create more specific sites for ethylene adsorption. Nonetheless, the nature of the sites needs now to be identified.

Conclusions and future work

In this work, different γ-alumina samples were synthesized by varying their synthesis conditions. A reference sample was synthesized from boehmite Pural SB3 under air with a water partial pressure of 240 Pa. To compare the influence of the synthesis gas, another sample was synthesized in a similar fashion to the reference, but using nitrogen instead of air. Unfortunately, it lead to an unstable sample. To compare the influence of the boehmite morphology, another sample was synthesized similarly, but using boehmite Disperal 40, which has a lower ratio of edges and plans compared to Pural SB3. As such, it was possible to obtain different γ-alumina surfaces.

For the reference sample, a procedure was successfully set up to determine accurate water adsorption isotherms. Indeed, its hydration and dehydration were extensively studied, leading to the conclusion that the last hydroxyls are very strongly linked to the surface and need a high activation energy to be desorbed. Thus, the only way to reach adsorption equilibrium points was to proceed to adsorption experiments, which was reinforced by the good adjustment of adsorption isotherms by different models, one based on DFT calculations, and another statistical one. Moreover, although desorption experiments do not correspond to an equilibrium, their modelisation lead to the enthalpy of adsorption. Thanks to IR and ^{1}H NMR analyses, it was shown that the last desorbed hydroxyls correspond to different types of hydroxyls. This suggests that to desorb one water molecule, the needed hydroxyl and hydrogen come from two different types of hydroxyls, with the hydrogen coming probably from a bridged hydroxyl.

For the use of a boehmite with a lower ratio between the edges and plans, it was possible to see that this resulted in a sample that has a lower number of adsorption sites, since the edges correspond to high energetic adsorption sites. The sites in this sample were also less energetic than the reference, since it was possible to remove all the water at the surface at a water partial pressure of 1400 Pa and 600°C.

As such, it was possible to synthesize two different γ-alumina surfaces with different water adsorption properties, and to correlate them with the synthesis conditions.

The study on hydrocarbons adsorption on γ-alumina was also started on the reference sample. It was found that ethylene adsorbs more than ethane at the same conditions. Also, ethylene adsorption depended on the surface coverage of γ-alumina, increasing with its decrease. At very low surface coverage, the shape of the isotherm seemed to indicate that there is the formation of more specific sites, since ethylene adsorption increased more in that area.

Regarding the very encouraging results obtained by this study, this work has to be continued. First, the sample synthesized from Disperal 40 has to be analyzed by IR and ^{1}H NMR spectroscopies to try to identify the types of surface hydroxyls missing compared to the sample synthesized from Pural SB3. Then, its hydrocarbons adsorption adsorption capacities have to be determined. By comparing all these results with those of the sample synthesized from Pural SB3, some links could probably be established between surface state and adsorption of hydrocarbons. Afterwards, it would also be interesting to consider obtaining another γ-alumina surface, maybe by using another boehmite.

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