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An *in-situ* reactivation study reveals a supreme stability of γ -alumina for the oxidative dehydrogenation of ethylbenzene to styrene

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Ethylbenzene oxidative dehydrogenation over γ -alumina under *in-situ* conditions has revealed that the catalyst recovers fully the original conversion and selectivity under steady state conditions. In the transition state, the reactivated catalyst achieved faster the steady state conditions. This was supported by physico-chemical characterisation that revealed a pore widening due to the crystallite sintering during the reactivation, which has a beneficial effect. The excellent stability after the reactivation recycle, as well as along the run, show the good promise of this catalyst.

Styrene (ST) also known as ethenylbenzene (IUPAC), vinylbenzene, phenylethene, phenylethylene, cinnamene, styrol, Diarex HF 77 or styrolene is an important intermediate in the chemical industry. Styrene is produced at industrial scale by a process called direct dehydrogenation of ethylbenzene (EB). Steam is used as heating carrier due to the high temperature required, 580-630 °C, and the process is catalyzed over a K-promoted Fe₂O₃ catalyst which is highly selective to styrene.^{1,2} The conversion per pass is low due to the equilibrium restriction; this implies a high recycle stream in the process involving expensive compression costs. Alternative routes to overcome the equilibrium limitations have been sought out.

The use of oxidants such as O₂^{2,3} is a very attractive driver for this purpose. Oxidants help to shift the reaction by H₂ oxidation into H₂O. In the case of CO₂ the equilibrium is still present but more favourable, while with O₂ the equilibrium is

broken. Therefore, by feeding O₂ the equilibrium conversion can be as high as full conversion. Many types of catalysts have been investigated for the oxidative dehydrogenation of EB. Two families of active materials have been identified; carbon-based⁴⁻¹⁶ and oxide-based materials, such as alumina.¹⁷⁻²¹ For the latter, it was found that the mild acidity of the alumina promotes the formation of a special type of coke deposits from ethylbenzene, that contains the active and selective sites for this reaction. Therefore, the *operando* alumina catalyst is in fact a coked-alumina hybrid that is formed after the first hours under the reaction conditions.²²⁻²⁴ One of the poorly described features of this type of catalysts is the stability, not only under reaction conditions but against reactivation cycles. The scope of this work is to investigate the reactivation of a γ -alumina catalyst for the ethylbenzene oxidative dehydrogenation under *in-situ* conditions in the reactor bed. An *ex-situ* reactivation method, coupled with physico-chemical characterisation, was firstly undertaken to guide ourselves into a preliminary feasibility study.

The catalyst performance is given in Figure 1. The γ -alumina (GA-F) was compared to a MWCNT as reference standard. The tests were carried out under identical and industrially relevant conditions, meaning a high EB concentration and reduced O₂ partial pressure. The EB conversion, ST and CO_x selectivities and ST yield are plotted as a function of the time on stream (TOS). The behaviour of both catalysts is different; γ -alumina performs better at high temperature while MWCNT excels at low temperature. In their optimal temperature they both render quite comparable results in terms of EB conversion and ST selectivity. For both catalysts, the selectivity to benzene/toluene and heavy condensates are much lower than CO_x/ST and independent of the applied reaction conditions. The selectivity to CO_x is inversely coupled to ST (Fig. 1-b and 1-c). This is because ST and CO_x are produced in parallel reaction pathways.

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^d European Bioenergy Research Institute (EBRI), School of Engineering and Applied Science, Aston University, Aston Triangle, Birmingham, B4 7ET, United Kingdom. Electronic Supplementary Information (ESI) available: Experimental methods, N₂ physisorption of the spent and fresh γ -aluminas; TGA patterns of the spent γ -aluminas; XRD patterns of fresh, spent and reactivated (GA-CR5) catalysts. See DOI: 10.1039/C8CY00748A.

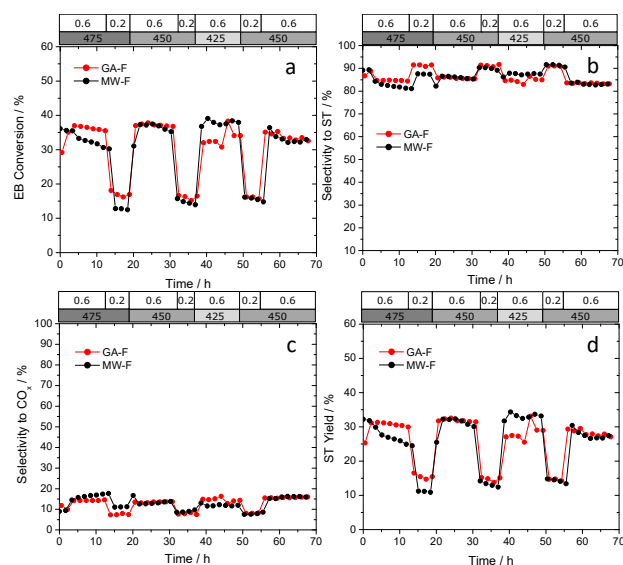


Figure 1. Comparison between γ -alumina and MWCNT. Time on stream EB conversion (a), selectivity to ST (b), selectivity to CO_x (c), ST yield (d) at various temperatures (475, 450, 425, and 450 °C) and O₂/EB=0.6 and 0.2 (vol.); GHSV of 3000 l/h; 10 vol. % EB.

A comparison of two steps at 450 °C (second and fourth stages) reveals that both catalysts deactivate in 2% for MWCNT and 5% for γ -alumina. A well-known fact for this decay is the intense coking that decreases the surface area, but also make the deposited coke more graphitic and defunctionalized, leading to worse active sites.²² Since the coking continues unlimitedly,²³⁻²⁴ and there is not an easy way to control it *in-operando*, such coke build-up needs to be controlled by a reactivation procedure *in-situ*.

The coke burning profiles were evaluated by temperature programmed oxidation (TPO) on the spent γ -alumina (Figure 2-a). The TPO pattern of the spent γ -alumina starts at 375 °C and ends at 520 °C with a maximum at 460 °C in a single process. The reactivation temperature was deduced from this pattern to be 450 °C, at which the rate of oxidation is half of the maximum rate. In this way, excessive heat released from the coke burning is prevented, and therefore exerting minimal side effects on the catalyst structure and texture.

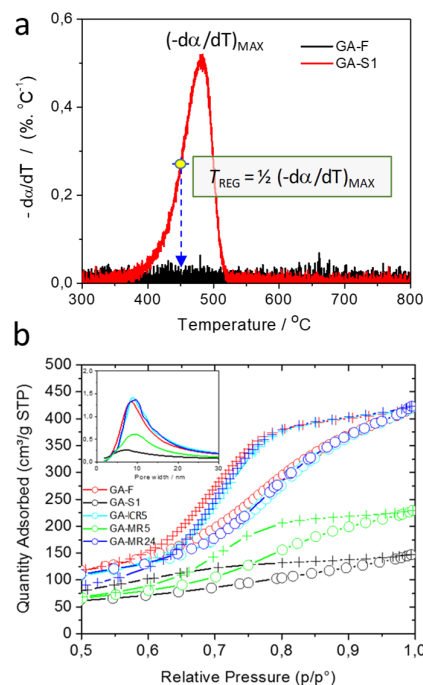


Figure 2. A) Oxidation rate patterns (TPO) for the fresh (reference) and spent γ -alumina. $\alpha = (W_0 - W)/W_0$; where W_0 is the initial weight. Conditions: synthetic air, 100 ml/min, heating rate of 3 °C/min. The temperature of reactivation (T_{REG}) was defined as the temperature at which the oxidation rate is half of the maximum, as indicated in the graph. B) Nitrogen sorption isotherms at -196 °C for the fresh, and regenerated γ -alumina. Inset: BJH pore size distribution.

The textural properties of the fresh and spent γ -alumina were investigated by N₂-physisorption (Figure S-1 in the Electronic Supporting Information). The isotherm of the fresh γ -alumina has a type IV with hysteresis H1,²⁵ which represents cylindrical pore geometry of solid particles with pore size uniformity and pore connectivity. It is well known that the pore shape for γ -alumina is not cylindrical but from the textural point of view it behaves as having opened cylindrical pores. The hysteresis of the spent catalyst changes to H2 type with a closure point at 0.45 relative pressure. Hysteresis H2²⁵ occurs in solids where the pores have narrow necks and wide bodies or when the porous material has interconnected pores. Since the fresh γ -

Table 1. Thermogravimetric data and textural parameters derived from N₂ adsorption at -196 °C.

Material	Treatment	TGA (wt.%) ^a	η_{TGA}^R (%)	S_{BET} (m ² /g) ^c	V_T (cm ³ /g) ^c	ΔS_{BET}^R (%)
GA-F	As-received	3.9	100	272	0.639 (9.4)	100
GA-S1	Spent catalyst, 60 h	31.5	-	154	0.231	-
GA-S2	Spent catalyst, 60 h	31.7	-	152	0.232	-
GA-CR5	<i>Ex-situ</i> , 450 °C air, 5 h ^e	3.9	100 ^b	259	0.646 (9.9)	95
GA-MR5	<i>Ex-situ</i> , 450 °C, 1 %O ₂ , 5 h ^f	5.8	93 ^b	160	0.341 (-) ^d	- ^d
GA-MR24	<i>Ex-situ</i> , 450 °C, 1 %O ₂ , 24 h ^f	3.8	99 ^b	256	0.650 (10.2)	94

a) Determined by TGA weight loss between 200-800 °C; b) Spent GA-S1 was employed for the regeneration study; c) between parentheses are the geometrical pore size determined as $4 \cdot 10^3 \cdot V_T / S_{\text{BET}}$ (in nm); d) Not calculated because of the low reactivation efficiency based on TGA; e) using an open-air box furnace; f) using a tubular flow furnace.

alumina does not have such interconnectivity effect at 0.45 relative pressure, the pore neck restrictions are ascribed to the coking. The pore size distribution curves of the spent sample is broader, less intense and shifts slightly towards lower pore sizes. This also indicates pore blockage (Fig. 2-b, inset).

Quantitative data showed that the specific surface area decreased from 272 (GA-F) to 152–154 m²/g (spent, Table 1) which is ~44% lower. The spent material was analysed twice (*i.e.* two samples of the same batch; samples GA-S1 and GA-S2) to ensure that the sample is homogeneous in terms of coke content. The textural results were quite close to each other. As an additional evidence, the TGA for both spent samples provided comparable patterns, see TGA and DTGAs patterns in Figure S-2 (Electronic Supporting Information). The weight losses have an absolute difference of 0.2 wt.% (Table 1).

An *ex-situ* reactivation method was first studied to shed light on the calcination feasibility, in two variants: conventional under ambient air and in a tubular furnace with low oxidant concentration; *i.e.* 1%O₂/Ar. Following reactivation, the materials were characterized by TGA and N₂ physisorption. The isotherms and pore size distribution curves of the conventionally reactivated material (GA-CR5) were nearly identical to the fresh γ -alumina (Figure 2-b). The reactivation efficiency was estimated in two ways, via TGA and textural analysis. The TGA-based efficiency was complete with 100% coke removal (Table 1). Whereas the BET efficiency was of 95%. This small reduction comes from the bigger pores that are formed by sintering of the crystallites after the regeneration; the average pore size changes from 9.4 nm (GA-F) to 9.9 nm (GA-CR5) after the regeneration. XRD confirmed that the overall γ -alumina structure is preserved during the reaction (GA-S1) and after reactivation (GA-CR5), Fig. S-3 (Electronic Supporting Information).

A mild reactivation was investigated for two processing times, 5 and 24 h. At 5 h the TGA efficiency was 93%, meaning that more time would be required to remove the coke. This result is consistent with the BET value, leading to a BET efficiency of 59%. Therefore, a prolonged experiment was

carried out at 24 h. The coke removal was then nearly complete with 99% for the TGA efficiency, and 94% BET recovery. The latter is ascribed to the larger pore size after the reactivation, 9.4 for the fresh into 10.2 nm for the GA-MR24. In both reactivation procedures, the pore volume increased slightly.

Based on the good promise of the above results, that showed complete coke removal and satisfactory recovery of the BET with a limited sintering, most likely associated to the heat of the combustion during the burning, an *in-situ* approach was implemented. This consisted of applying a reactivation step after a catalytic run. For this, the EB feed was switch off. In this way the O₂ would be able to combust the coke rendering the catalyst surface clean of coke for the next catalytic cycle. The results are presented in Figure 3. Both conversion and selectivity in the second run returned to the values of the original test. In fact the second test showed a faster steady state operation that is ascribed to the wider pore size that enables a faster deposition of the active/selective ODH coke.

Conclusions

Reactivation of a coked γ -alumina from EB ODH was investigated in several variants. *Ex-situ* regeneration studies provided a good understanding of the effect of the regeneration conditions on coke removal and texture. Both rendered good results with complete coke removal and a small depletion of the BET surface area due to the sintering of the crystallites. This depletion had, however, a positive effect when the reactivation was carried out *in-situ*. It led to achieving the steady state conditions faster. Under steady state conditions, the performance was nearly identical to the first run, showing the good stability of γ -alumina during an *in-situ* thermal reactivation. Along the run, the catalyst was remarkably stable as well.

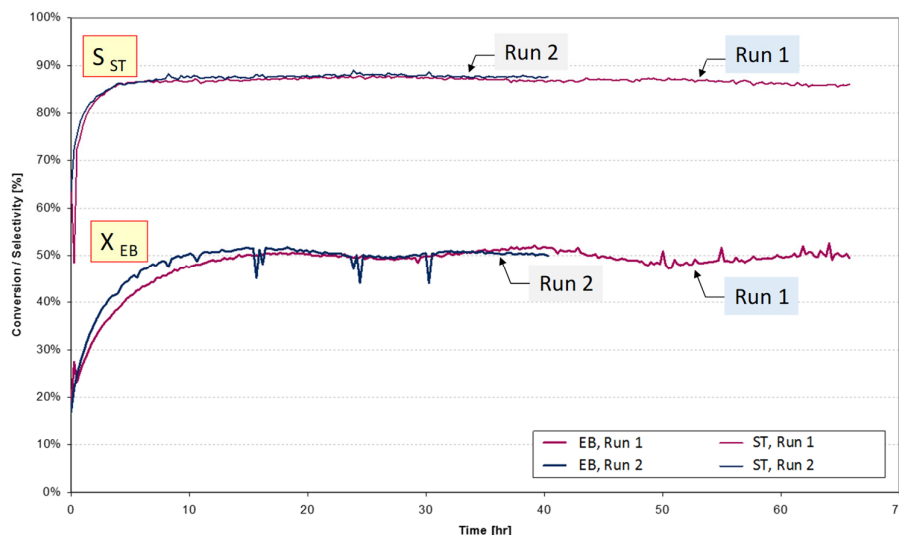


Figure 3. Time on stream EB conversion and ST selectivity for γ -Alumina with an intermediate *in-situ* regeneration. Conditions: 300 mg Al₂O₃, 6 mL/min He, 450 °C, O₂:EB = 0.7, WHSV = 0.7 g/(h g cat).

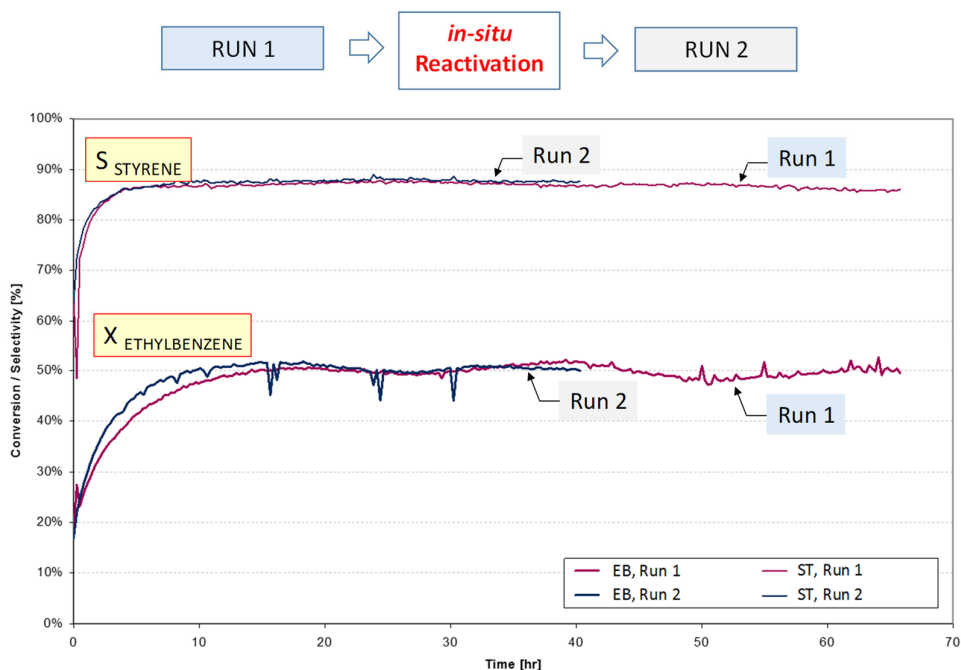
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Supporting information

An *in-situ* reactivation study reveals a supreme stability of γ -alumina for the oxidative dehydrogenation of ethylbenzene to styrene

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1. Experimental methods

1.1. Materials

SiO₂-stabilized γ -Al₂O₃ extrudates (Albemarle Catalysts BV, denoted as GA-F) was employed. The extrudates were crushed and sieved into a 212-425 μ m fraction used for the catalytic tests, regeneration and characterization studies.

1.2. *Ex-situ* reactivation

Two regeneration protocols were carried out on the spent catalyst, mild and conventional. The mild regeneration (denoted as MR) was carried out in a quartz-tube housed tubular oven (Nabertherm RT 50/250-11). The sample was loaded in a flat quartz crucible that was placed horizontally at the centre of the furnace's isothermal heating zone. Regeneration took place at 450 °C in 1% vol. O₂/Ar at a heating rate of 3 °C/min and held for 5 and 24 h. The conventional regeneration (denoted as CR) was done in the in LT9/11 Nabertherm box furnace at 450 °C in air at a heating rate of 3 °C/min and held for 5 h. Fresh, spent and regenerated materials with their codes and treatments are given in Table 1.

1.3. *In-situ* reactivation

The sample is regenerated in between experiments at the reaction conditions by switching off the EB feed. Only the ethylbenzene feed is removed from the reactant mixture during the regeneration, giving a diluted air mixture (0.9 vol% O₂). Regeneration was finished after 6 hours, when no more CO₂ could be measured on-line.

1.4. Characterization methods

The organic content of the fresh and spent catalysts was quantified by thermogravimetric analysis (TGA) on a Mettler-Toledo analyzer (TGA/SDTA851e). The weight loss was monitored from 30 to 1000 °C at a heating rate of 10 °C/min using a flow of synthetic air of 100 mL/min NTP. The oxidation rate patterns (TPO) were obtained with the same technique making use of the TGA derivative patterns.

The textural properties were analyzed by N₂-physisorption at -196°C using a Micromeritics ASAP 2420. Fresh and regenerated γ -alumina samples were degassed at 300 °C for 10 h under vacuum. Spent samples were degassed at 200 °C for 10 h to ensure that the coke deposited on γ -alumina is not altered during the degassing. The surface area (S_{BET}) was calculated with the conventional BET method. The pore volume (V_{T}) was calculated using the single point total desorption pore volume at the relative pressure 0.98. Pore size distributions were calculated using the BJH-model.

Powder X-ray diffraction (XRD) measurements were done on a Bruker D8 powder X-ray diffractometer using CuK α radiation, $\lambda=1.54056$ Å. The spectra were recorded with a step size of 0.02° for 3 s accumulation time, in the 2 θ angle range of 10-100°.

1.5. Catalytic tests

1.5.1 Micro-flow reactor

Screening catalytic tests were carried out in a six-flow parallel fixed bed reactor apparatus in down-flow operation, with reactors having an inner diameter of 4 mm. The reactors were loaded from top to bottom with a quartz wool plug, 10 cm glass beads (0.5 mm diameter) and 65 mm catalyst bed (0.80 ml) to ensure that the catalyst bed was located in the isothermal zone of the furnace. The glass beads had limited conversion which was less than 3% EB conversion under all applied conditions.

Each reactor gas feed had a flow of 36 ml/min (NTP) and consisted of a mixture of nitrogen, oxygen, and ethylbenzene. A liquid ethylbenzene flow of 1 g/h was evaporated (3.6 ml/min vapour at NTP) resulting in the 1:10 volume ratio of ethylbenzene and gas (10 vol.% EB) with a GHSV of 3000 l/h. The EB liquid evaporated in a α -Al₂O₃ filled tube in a synchronized flow with the gas feed. Pressure in the reactor system was 1.2-1.3 bars and an atmospheric outlet pressure drop was typically 0.2-0.3 bars.

The reactor outlet flows were analyzed using an online two channel gas chromatograph with a TCD (columns: 0.3m Hayesep Q 80-100 mesh with back-flush, 25m×0.53mm Porabond Q, 15 m × 0.53mm molsieve 5Å) for permanent gasses analysis (CO₂, H₂, N₂, O₂, CO) and a FID column (30 m × 0.53 mm, Df=3 mm, RTX-1) for hydrocarbon analysis (methane, ethane, ethene, benzene, toluene, ethylbenzene, styrene, and heavy aromatics). The catalytic test was carried out at various temperatures (475, 450, 425, and 450 °C) and O₂/EB = 0.6 and 0.2 (vol.). For all EB conversion data the oxygen conversion was 100%, unless otherwise is stated. All characterizations for the spent catalysts were done after the complete testing cycle of 70 h.

1.5.2 Single flow reactor

The single-flow catalytic test was carried out following the procedure described elsewhere [1].

1.6. Reactivation efficiency

The efficiency was defined as the corrected weight loss, relative to the bare alumina, from the TGA patterns as:

$$\eta_{TGA}^R = \left(1 - \frac{\Delta w_{800-200}^X - \Delta w_{800-200}^{bare\ alumina}}{\Delta w_{800-200}^{spent} - \Delta w_{800-200}^{bare\ alumina}} \right) \times 100 \quad (1)$$

where superscript 'x' refers to any material (*i.e.* spent, regenerated, fresh).

The recovery of the texture was defined using the BET surface areas as:

$$\Delta S_{BET}^R = \frac{S_{BET}^{reg.mat}}{S_{BET}^{fresh}} \times 100 \quad (2)$$

1.7. Materials nomenclature

The nomenclature used is the following; GA-suffix, where GA means *gamma*-alumina (γ -Al₂O₃) and the suffix is related to the treatment: **F** (fresh); **S** (spent after the reaction cycle); **CR** (conventional regeneration in a box furnace under atmospheric air) and **MR** (mild

regeneration); a number was added that corresponds to the duration in hours after reaching the 450 °C.

2. Additional results

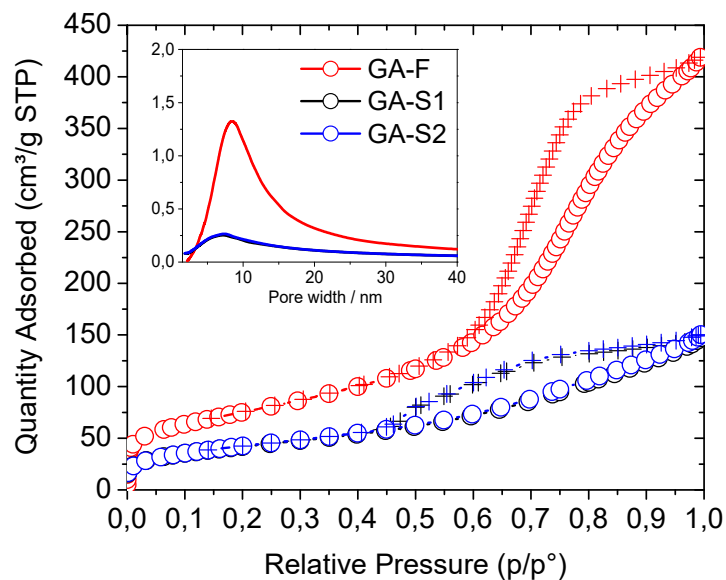


Figure S-1. Nitrogen sorption isotherms at -196 °C for the fresh and spent **Alumina materials**. Inset: BJH pore size distribution.

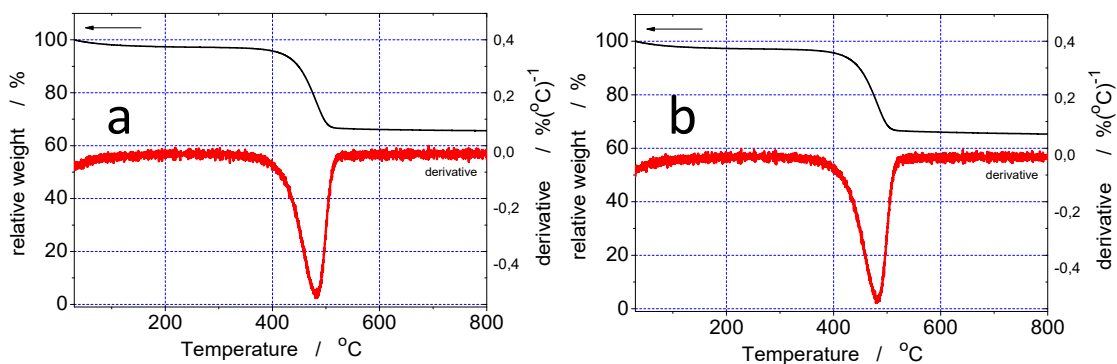


Figure S-2. TGA curves of two spent γ -alumina. Conditions: synthetic air, 100 ml/min, heating rate of 3 °C/min: A) GA-S1 and B) GA-S2.

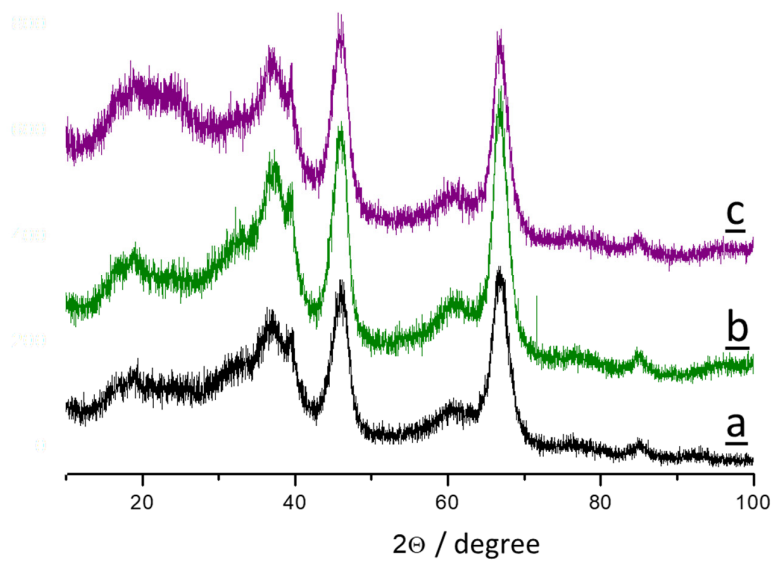


Figure S-3. XRD patterns. **A)** GA-F; **B)** GA-CR5; **C)** GA-S1 with γ -alumina structure [2].

3. Literature of the Supporting Information

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