Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

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

SiO_2-stabilized γ-Al_2O_3 extrudates (Albemarle Catalysts BV, denoted as GA-F) was employed. The extrudates were crushed and sieved into a 212-425 μm 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. O_2/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% O_2). Regeneration was finished after 6 hours, when no more CO_2 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 N_2-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 CuKα radiation, λ=1.54056 Å. The spectra were recorded with a step size of 0.02° for 3 s accumulation time, in the 2θ 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/l/h. The EB liquid evaporated in a α-Al_2O_3 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 (CO_2, H_2, N_2, O_2, 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 O_2/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-Al_2O_3) 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

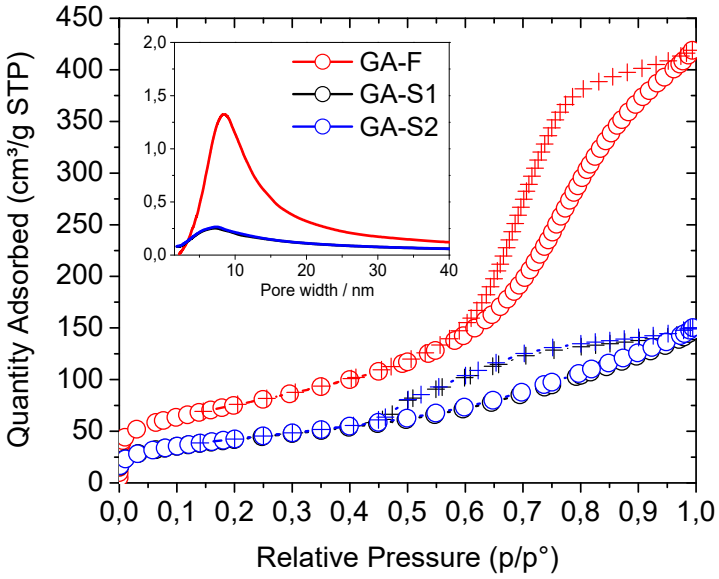

Figure S-1. Nitrogen sorption isotherms at -196 °C for the fresh and spent **Alumina materials**. Inset: BJH pore size distribution.

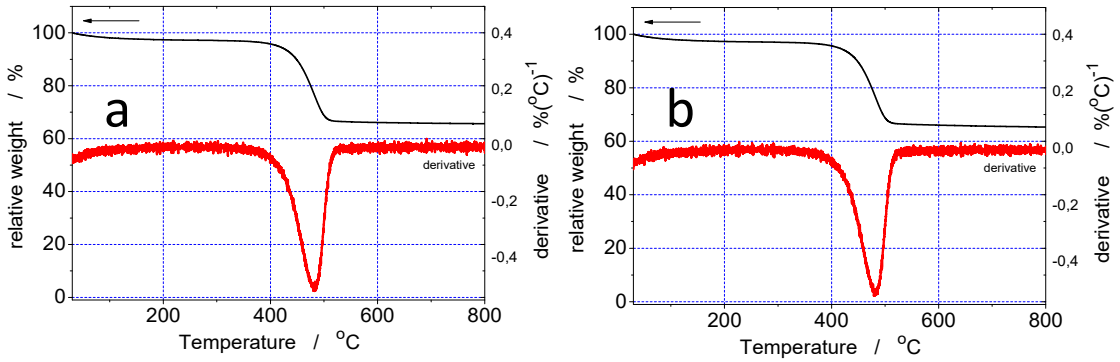

Figure S-2. TGA curves of two spent γ-alumina. Conditions: synthetic air, 100 ml/min, heating rate of 3 °C/min: **A**) GA-S1 and **B**) GA-S2.

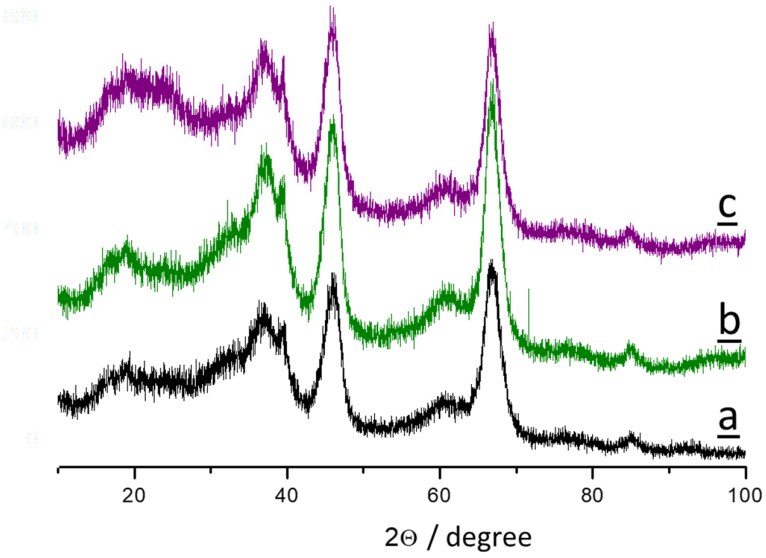

Figure S-3. XRD patterns. **A)** GA-F; **B)** GA-CR5; **C)** GA-S1 with γ-alumina structure [2].

3. Literature of the Supporting Information

[1] C. Nederlof, F. Kapteijn, M. Makkee, Applied Catalysis A: General 417–418 (2012) 163-173.

[2] L. López Pérez, S. Perdriau, G. ten Brink, B.J. Kooi, H.J. Heeres, I. Melián-Cabrera, Chem. Mater. 25 (2013) 848−855.