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## An *in situ* reactivation study reveals the supreme stability of $\gamma$ -alumina for the oxidative dehydrogenation of ethylbenzene to styrene†

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Ethylbenzene oxidative dehydrogenation over  $\gamma$ -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 the steady state conditions faster. This was supported by the physico-chemical characterisation that revealed pore widening due to crystallite sintering during the reactivation, which has a beneficial effect. The excellent stability after the reactivation recycle, as well as along the run, shows the great 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 on an industrial scale by a process called direct dehydrogenation of ethylbenzene (EB). Steam is used as a heating carrier due to the high temperature required, 580–630 °C, and the process is catalyzed over a K-promoted Fe<sub>2</sub>O<sub>3</sub> catalyst which is highly selective to styrene.<sup>1,2</sup> 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 O<sub>2</sub><sup>2,3</sup> is a very attractive driver for this purpose. Oxidants help to shift the reaction by H<sub>2</sub> oxidation into H<sub>2</sub>O. In the case of CO<sub>2</sub> the equilibrium is still

present but more favourable, while with O<sub>2</sub> the equilibrium is broken. Therefore, by feeding O<sub>2</sub> 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-based<sup>4–16</sup> and oxide-based materials, such as alumina.<sup>17–21</sup> For the latter, it was found that the mild acidity of alumina promotes the formation of a special type of coke deposit from ethylbenzene, which 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 few hours under the reaction conditions.<sup>22–24</sup> One of the poorly described features of this type of catalyst is its stability, not only under reaction conditions but against reactivation cycles. The scope of this work is to investigate the reactivation of a  $\gamma$ -alumina catalyst for ethylbenzene oxidative dehydrogenation under *in situ* conditions in a 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 Fig. 1. The  $\gamma$ -alumina (GA-F) was compared to a MWCNT as a reference standard. The tests were carried out under identical and industrially relevant conditions, involving a high EB concentration and reduced O<sub>2</sub> partial pressure. The EB conversion, ST and CO<sub>x</sub> selectivities and ST yield are plotted as a function of the time on stream (TOS). The behaviour of both catalysts is different;  $\gamma$ -alumina performs better at high temperature while the MWCNT excels at low temperature. In their optimal temperature, they both give 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 that to CO<sub>x</sub>/ST and independent of the applied reaction conditions. The selectivity to CO<sub>x</sub> is inversely coupled to ST (Fig. 1b and c). This is because ST and CO<sub>x</sub> are produced in parallel reaction pathways.

A comparison of two steps at 450 °C (second and fourth stages) reveals that both catalysts deactivate at 2% for the

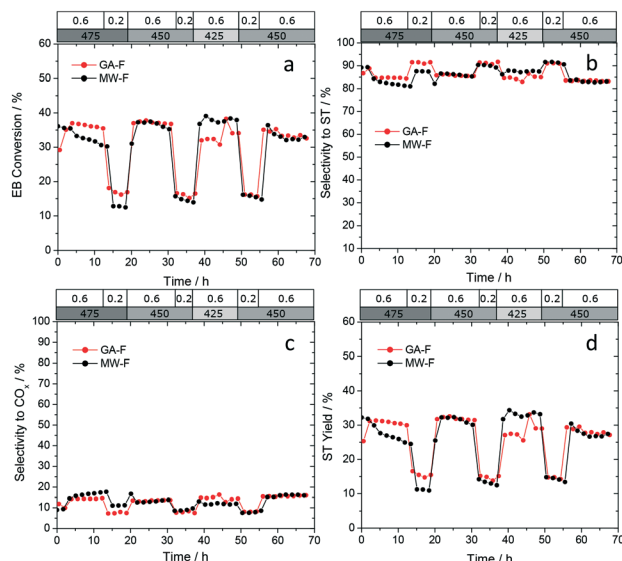
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† Electronic supplementary information (ESI) available: Experimental methods, N<sub>2</sub> physisorption of the spent and fresh  $\gamma$ -aluminas; TGA patterns of the spent  $\gamma$ -alumina; XRD patterns of fresh, spent and reactivated (GA-CR5) catalysts. See DOI: 10.1039/c8cy00748a

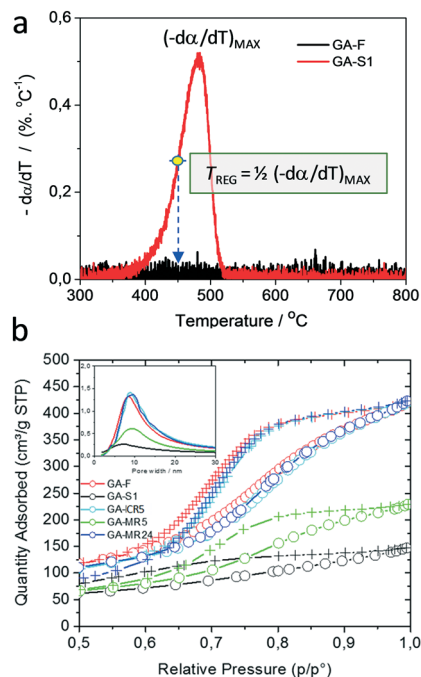


**Fig. 1** Comparison between  $\gamma$ -alumina and a MWCNT. Time on stream vs. EB conversion (a), selectivity to ST (b), selectivity to  $\text{CO}_x$  (c), and ST yield (d) at various temperatures (475, 450, 425, and 450 °C) and  $\text{O}_2/\text{EB} = 0.6$  and 0.2 (vol.); GHSV of  $3000 \text{ l l}^{-1} \text{ h}^{-1}$ ; 10 vol% EB.

MWCNT and 5% for  $\gamma$ -alumina. A well-known reason for this deactivation is the intense coking that not only decreases the surface area, but also makes the deposited coke more graphitic and defunctionalized, leading to poorer active sites.<sup>22</sup> Since the coking continues unlimitedly,<sup>23,24</sup> and there is no 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  $\gamma$ -alumina (Fig. 2a). The TPO pattern of the spent  $\gamma$ -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 coke burning is prevented, therefore exerting minimal side effects on the catalyst structure and texture.

The textural properties of the fresh and spent  $\gamma$ -aluminas were investigated by  $\text{N}_2$ -physisorption (Fig. S-1 in the ESI†). The isotherm of the fresh  $\gamma$ -alumina is type IV with hysteresis H1,<sup>25</sup> which represents the cylindrical pore geometry of solid particles with pore size uniformity and pore connectivity. It is well known that the pore shape of  $\gamma$ -alumina is not cylindrical but from a textural point of view it appears to have open cylindrical pores. The hysteresis of the spent catalyst changes to an H2 type with a closure point at 0.45 relative pressure. Hysteresis H2<sup>25</sup> occurs in solids where the pores have narrow necks and wide bodies or when the porous material has interconnected pores. Since the fresh  $\gamma$ -alumina does not have such an interconnectivity effect at 0.45 relative pressure, the pore neck restrictions are ascribed to coking. The pore size distribution curve of the spent sample is broader, less intense and shifted slightly



**Fig. 2** a) Oxidation rate patterns (TPO) for the fresh (reference) and spent  $\gamma$ -aluminas.  $\alpha = (W_0 - W)/W_0$ ; where  $W_0$  is the initial weight. Conditions: synthetic air,  $100 \text{ ml min}^{-1}$ , and heating rate of  $3 \text{ °C min}^{-1}$ . The temperature of reactivation ( $T_{\text{REG}}$ ) is defined as the temperature at which the oxidation rate is half of the maximum, as indicated in the graph. b) Nitrogen sorption isotherms at  $-196 \text{ °C}$  of the fresh and regenerated  $\gamma$ -aluminas. Inset: BJH pore size distribution.

towards lower pore sizes. This also indicates pore blockage (Fig. 2b, inset).

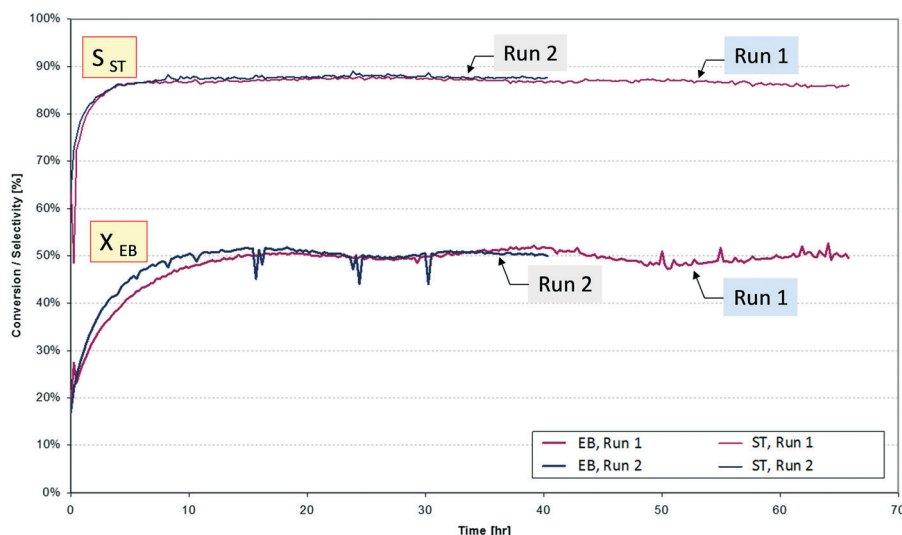
Quantitative data showed that the specific surface area decreased from 272 (GA-F) to 152–154  $\text{m}^2 \text{ g}^{-1}$  (spent, Table 1) which is  $\sim 44\%$  lower. The spent material was analysed twice (*i.e.* two samples of the same batch: samples GA-S1 and GA-S2) to ensure that the sample is homogeneous in terms of coke content. The textural results were quite close to each other. As additional evidence, the TGA for both spent samples provided comparable patterns; see TGA and DTGA patterns in Fig. S-2 (ESI†). 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 a low oxidant concentration; *i.e.* 1%  $\text{O}_2/\text{Ar}$ . Following reactivation, the materials were characterized by TGA and  $\text{N}_2$  physisorption. The isotherms and pore size distribution curves of the conventionally reactivated material (GA-CR5) were nearly identical to those of the fresh  $\gamma$ -alumina (Fig. 2b). 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 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)

**Table 1** Thermogravimetric data and textural parameters derived from N<sub>2</sub> adsorption at -196 °C

Material	Treatment	TGA <sup>a</sup> (wt%)	$\eta_{\text{TGA}}^{\text{R}}$ (%)	$S_{\text{BET}}^{\text{c}}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{\text{T}}^{\text{c}}$ (cm <sup>3</sup> g <sup>-1</sup> )	$\Delta S_{\text{BET}}^{\text{R}}$ (%)
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 <sup>e</sup>	3.9	100 <sup>b</sup>	259	0.646 (9.9)	95
GA-MR5	<i>Ex situ</i> , 450 °C, 1% O <sub>2</sub> , 5 h <sup>f</sup>	5.8	93 <sup>b</sup>	160	0.341 (—) <sup>d</sup>	— <sup>d</sup>
GA-MR24	<i>Ex situ</i> , 450 °C, 1% O <sub>2</sub> , 24 h <sup>f</sup>	3.8	99 <sup>b</sup>	256	0.650 (10.2)	94

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



**Fig. 3** Time on stream vs. EB conversion and ST selectivity for  $\gamma$ -alumina with intermediate *in situ* regeneration. Conditions: 300 mg Al<sub>2</sub>O<sub>3</sub>, 6 cm<sup>3</sup> min<sup>-1</sup> He, 450 °C, O<sub>2</sub>:EB = 0.7, and WHSV = 0.7 g h<sup>-1</sup> g cat<sup>-1</sup>.

after the regeneration. XRD confirmed that the overall  $\gamma$ -alumina structure is preserved during the reaction (GA-S1) and after reactivation (GA-CR5), Fig. S-3 (ESI†).

Mild reactivation was investigated for two processing times, 5 and 24 h. At 5 h, the TGA efficiency was 93%, indicating 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 for 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  $\gamma$ -alumina to 10.2 nm for GA-MR24. In both reactivation procedures, the pore volume increased slightly.

Based on the promise of the above results, which showed complete coke removal and satisfactory BET recovery with limited sintering, most likely associated with the heat of combustion during burning, an *in situ* approach was implemented. This consisted of applying a reactivation step after a catalytic run. For this, the EB feed was switched off. In this way, O<sub>2</sub> would be able to combust the coke rendering the catalyst surface free of coke for the next catalytic cycle. The

results are presented in Fig. 3. Both the 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 coked  $\gamma$ -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 gave good results with complete coke removal and 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  $\gamma$ -alumina during *in situ* thermal reactivation. Along the run, the catalyst was remarkably stable as well.

## Conflicts of interest

There are no conflicts to declare.

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