

Second Youth of a Metal-Free Dehydrogenation Catalyst: When γ -Al₂O₃ Meets Coke Under Oxygen- and Steam-Free Conditions

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Supporting Information

ABSTRACT: The role of carbonaceous deposits (coke) formed in dehydrogenation catalysis has been extensively investigated over the last few decades mainly with respect to the deactivation of metal-based and metal-free heterogeneous catalysts. Although much less emphasized, coke deposits grown on selected metal oxides have also been described as active and selective phases for alkene dehydrogenation under an oxidative or non-oxidative atmosphere. This work describes the straightforward preparation of "coked" γ -Al₂O₃ composites and their catalytic performance in the ethylbenzene (EB) direct dehydrogenation (DDH) to styrene (ST) under steamand oxygen-free conditions. The study unveils the effective potentiality of a catalytic system already known to the



scientific community but never employed for EB DDH under severe conditions, close to those commonly used in industrial plants (600 °C, 10 vol % EB/He, GHSV = 3000 h⁻¹). Such a simple catalytic system has revealed a significant stability on longterm trials (≥ 150 h) and markedly high ST selectivity ($\geq 97\%$) along with process rates (λ up to 16.3 mmol_{ST} g_{cat}⁻¹ h⁻¹) that are the highest claimed so far for related carbon systems at work in the process. Furthermore, the outlined performance of our composites in DDH is close to that claimed for classical iron-based industrial catalysts operating in the presence of a large amount of steam. γ -Al₂O₃ precoking with an aliphatic C-source has shown additional beneficial effects on the ultimate γ -Al₂O₃@ C performance in DDH. These findings pave the way for the development of cheap and durable dehydrogenation catalysts. They rewrite (in part at least) the role of coke in a challenging heterogeneous process while offering important hints to the comprehension of the reaction mechanism promoted by plain C-sites.

KEYWORDS: γ-Al₂O₃@coke composites, metal-free catalysis, ethylbenzene direct dehydrogenation, catalytically active coke, heterogeneous catalysis

INTRODUCTION

The annual styrene (ST) global demand is rapidly approaching (by 2020) 35 million tons per year, 1 and more than 70% is industrially produced by catalytic dehydrogenation (direct dehydrogenation, DDH) of ethylbenzene (EB) using multipromoted iron oxide catalysts in the presence of large excesses of steam as diluent.^{2,3} In spite of the protocol efficiency, the catalyst undergoes a series of chemicomechanical stresses that limit its lifetime on stream, thus making an already high energy-demanding transformation less and less sustainable. The rapid catalyst deactivation due to leaching of the metal active phase or structure collapse under severe reaction

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conditions together with the active sites' passivation due to the generation of coke deposits represent the main weak points of this catalytic technology. Anyhow, high ST selectivity and EB conversions are generally obtained under high temperatures $(600-650 \ ^{\circ}C)$ in combination with large excesses of steam as a cofeed that alleviate catalyst coking and provide heat to compensate the catalyst temperature loss due to the endothermic process.⁴ Overall, the requested energy and water inputs for running the process are huge.⁵ In recent years, selected nanocarbon structures in the form of plain C-networks or light-heterodoped systems (mainly N-doped materials) have shown excellent catalytic performance and distinguished anticoking properties in the EB DDH under steam-free conditions.6 ¹¹ Such a discovery has largely boosted fundamental research on carbon-based catalysts, hence setting the way toward the improvement of industrially relevant catalytic technologies.¹²⁻¹⁵ Oxygen cofeed streams (oxidative dehydrogenation conditions, ODH) are generally preferred with carbon-based catalysts at work.¹⁶⁻²³ Indeed, oxygen-rich environments make the process more attractive from a thermodynamic viewpoint (exothermic), allow the transformation to take place under milder temperature conditions, and offer reasonable hints to the comprehension of the mechanistic role played by these metal-free sys-tems.^{4,11,13,15,16,23,24} However, catalysts operating under ODH conditions also suffer from serious drawbacks that limit the process efficiency and catalyst lifetime on stream (e.g., reduced selectivity due to ST overoxidation, reduced catalyst efficiency under high EB concentrations due to catalyst's coke passivation, and dangerous operative conditions due to the use of a potentially explosive cofeed).²³

"Catalyst coking" in heterogeneous DH catalysis has been extensively studied over the last few decades mainly with respect to its detrimental deactivation effect under DDH and ODH conditions. With the exception of rare examples,¹⁰ all metal or metal-free catalysts engaged in the process largely suffer from deactivation by coke deposits. This phenomenon is even more pronounced when the applied operative conditions are closer to those of industrial plants. As a result, costly and energy-demanding regeneration treatments of the catalytic systems in oxygen-rich streams are periodically required to burn out all undesired coke deposits and restore the pristine catalyst performance.

These features explain the moderate interest of the scientific community toward oxygen- and steam-free DDH conditions. Indeed, the accumulative character of coke deposits under non-oxidative conditions together with the endothermic nature of DDH reactions and the more elusive nature of the mechanism engaged by carbon-based catalysts under these conditions⁷ have resulted in a moderate number of scientific reports.^{6,8,26–33}

Looking beyond this scenario, it is still possible to take advantage of those phenomena that classically compromise the catalyst performance and to prepare highly efficient and cheap catalytic materials for the DDH process. For instance, the role of carbonaceous deposits (coke) formed on various inorganic supports and directly engaged as catalytically active sites for a given process has been known since a long time.³⁴ The first examples of "active coke" in catalysis have been described in the late twentieth century for EB^{35-39} and light alkane⁴⁰ ODH and more recently for *n*-butane,⁴¹ cyclohexane,⁴² and EB^{43} DDH. Although there are little doubts on the nature of active sites on "coked catalysts" in ODH, the same cannot be said for

systems at work under non-oxidative environments. While under the former conditions redox-active O-containing groups like ketones/quinones are unambiguously engaged in the dehydrogenation process,^{4,11,13,18,23,37} under non-oxidative environments it is reasonable to admit that C-defects/ vacancies in the coke structure are somehow the "active sites" for the alkane activation and conversion.^{4,32,34} Hence, the performance of coked catalysts is deeply influenced by the nature of coke, depending on the operating conditions used in its production⁴¹ (i.e., reaction temperature, C-source, and Cconcentration in the stream) and the nature of the substrate where it is grown.

In this contribution, we describe the straightforward preparation of durable dehydrogenation systems based on "coked or pre-coked γ -Al₂O₃ trilobs" for the highly efficient and selective EB DDH to ST under steam- and oxygen-free environments. Although "coked Al₂O₃ and coked mixed metaloxide" have already received a great deal of attention as catalysts^{37,41-45} in alkane DDH and ODH and great efforts have also been devoted to the study of nature of coke deposits and their beneficial effects in catalysis, 41,43,44,46-48 much less work has been addressed to unveil the real potentialities of these systems for the EB DDH under non-oxidative and industrially relevant conditions. Earlier evidence of the active role played by "coked metal oxides" in alkane DDH were anticipated in a Monsanto patent⁴⁵ where the inventors first forecasted the non-innocent action of carbonaceous deposits on the process as well as their paramagnetic nature due to the presence of unpaired electrons, likely involved in the dehydrogenation path. Despite really encouraging outcomes listed in the quite dated Monsanto invention, to date there is only one report from the literature of "coked γ -Al₂O₃" in a ⁴³ The short-term EB dehydrogenation under a N₂ atmosphere.⁴ authors showed that alumina became active and selective faster for the process under non-oxidative conditions (N_2) instead of using CO_2 as cofeed. They also showed that the coked catalyst reached its optimal performance after 10 h on stream before starting its deactivation. With the present study, we demonstrated that a radically different end of the story was possible. Indeed, previous studies on "coked alumina" as a catalyst in EB DDH under non-oxidative conditions have missed the real potentialities of the system. Herein we have unveiled that a "second youth" for the coked γ -Al₂O₃ catalyst in DDH under rigorous non-oxidative and industrially relevant conditions was possible (600 °C, [EB] = 10 vol % in He, GHSV = 3000 h^{-1}). Indeed, the system offers markedly high stability on long-term trials (≥ 150 h) along with constantly high ST selectivity (\geq 97%) and the highest process rates reported so far in the literature (λ up to 16.3 mmol_{ST} g_{cat}⁻ h^{-1}) for related carbon-based catalysts at work in the process.

RESULTS AND DISCUSSION

 γ -Al₂O₃@C^{EB} Synthesis and Characterization. The adopted reaction scheme for the in situ generation of coke on γ -Al₂O₃ is that classically used for the DDH catalytic run in a fixed-bed continuous flow reactor. To this aim, 300 mg of γ -Al₂O₃ (CK-300 Ketjen, $S_{\text{BET}} = 249 \pm 10 \text{ m}^2 \text{ g}^{-1}$) in the form of extruded trilobs (~1 mm × ~4 mm, Figure S1) are loaded onto a quartz fritted disk located inside a tubular quartz reactor (i.d. × length 8 × 800 mm). Helium (He) was fed into the reactor (30 mL min⁻¹) using a mass flow controller (BROOKS MFC) while keeping the system at the target temperature (either 550 or 600 °C) for 2 h prior to passing the He flow

through a glass evaporator filled with liquid EB maintained at constant temperature throughout an external thermal bath. Under these conditions, the γ -Al₂O₃ sample changes its color from white to dark gray in a few hours, until it becomes deep black after 10 h on stream (Figure S1). The coke deposited on γ -Al₂O₂ was quantitatively measured by thermogravimetry/ differential thermal analysis (TG/DTA) at variable times until a maximum of 1020 h on stream (T = 600 °C, [EB] = 2.8 vol % in He, flow rate = 30 mL min⁻¹, GHSV (STP) = 3000 h⁻¹, atmospheric pressure) (Figure S2).46 Under these conditions, a dynamic dependence of formed coke (wt %) from time-onstream (TOS) is observed. Indeed, coke deposits rapidly grow in the 1 h on stream with a sample weight increase of 22.6% after 150 h. From that time, coke grows more slowly with a Δ^{150} wt % increase (in the 150–300 h) of 6.5, a Δ^{350} wt % increase (in the 300–650 h) of 6.3, and a $\Delta^{370} wt$ % increase in the 650–1020 h of 3.8 (Figure 1).46



Figure 1. Dependence of coke deposition (wt % measured by thermogravimetric analyses (TGA)) and coke formation rate (wt % h^{-1}) from TOS. Reaction conditions: 300 mg of γ -Al₂O₃, T = 600 °C, [EB] = 2.8 vol % in He, flow rate = 30 mL min⁻¹, GHSV (STP) = 3000 h^{-1} , atmospheric pressure. Curve fitting has no physical meaning but it is just proposed as a guide to the eyes.

During the process, the sample specific surface area (SSA) varies from 249 m² g⁻¹ of pristine γ -Al₂O₃ to 138 m² g⁻¹ of the sample isolated after 10 h on stream. After 50 h, the SSA value drops down to 37 m² g⁻¹, and it definitively lies in the 40 \pm 10 $m^2 g^{-1}$ range for all samples isolated at higher reaction times (650 h) (Figure S4). The amount of coke deposits is largely affected by the applied dehydrogenation conditions other than by the nature of the C-source and the inorganic support where cracking-side reactions take place (vide infra). There is no doubt that coke formation is an accumulative process. Nevertheless, prolonged dehydrogenation runs show that the incremental coke decreases almost asymptotically. The trend outlined on Figure 1 has similar precedents from the literature.⁴⁹ It is evident that the coke formation rate (wt % h^{-1}) is very fast when acidic sites of γ -Al₂O₃ are fully exposed and the surface of the inorganic support is maximum, while it rapidly drops down as acidic sites are gradually covered by coke and the material SSA decreases. The elemental analysis data recorded for γ -Al₂O₃@C^{EB} samples are used to measure the H/C ratio as a TOS function. It can be observed that the longer the reaction time, the lower the H/C ratio in the coke (Table S1). Such a trend is in line with a higher degree of graphitized carbon in those γ -Al₂O₃@C^{EB} samples obtained for prolonged reaction times at the target temperature⁵⁰ and it well fits with the observed temperature shift of differential thermogravimetry (DTG) peaks recorded for each sample (Figure S2). A TPD analysis (Figure S3) conducted on one representative sample from this series (γ -Al₂O₃@C³⁰⁰) has finally demonstrated the virtual absence of O-containing functionalities in the coke deposits formed under rigorous non-oxidative environments. This evidence supports the presumed role of C-sites (prevalently in the form of edge sites, defects, and vacancies) directly engaged in the EB activation/conversion (vide infra). The Raman spectra



Figure 2. Raman spectra of coked γ -Al₂O₃ composites prepared at variable TOS (10, 300, 650, 1020 h) under the following conditions: 300 mg of γ -Al₂O₃, T = 600 °C, [EB] = 2.8 vol % in He, flow rate = 30 mL min⁻¹, GHSV (STP) = 3000 h⁻¹, atmospheric pressure. For D1/G and D1/D3 deconvoluted peak ratios, see Table S1.

recorded on γ -Al₂O₃@C^{EB} composites at variable reaction times present the two main and distinctive components of the carbonaceous phases at ~1340 and ~1605 cm⁻¹ attributed to the so-called G and D peaks.^{51–53} According to literature reports on related materials, the spectra were fitted by four components (G, D1, D3, and D4) considering a Lorentzianshaped band for G and Gaussian-shaped bands for D1, D3, and D4.^{44,47,54} The D1/G ratio has been conventionally used to determine the degree of structural order of carbons^{55,56} at least in systems featuring D1/G ≤ 1.1 .⁵⁷ For amorphous carbons (D1/G > 1.1 as for our samples; see Table S1), D1/D3 ratios obtained from peak deconvolution are then chosen as primary indicators of the coke structural order. As shown in Figure 2A–D, the D1/D3 ratio increases appreciably while prolonging the sample exposure to the target temperature.^{44,47}

Such a trend suggests an improvement in the coke structural organization on TOS. It can be speculated that coke deposits in long-term reaction samples gradually undergo dehydrogenation and restructuration to finally give graphitized or pseudo-graphitized C-networks. XRD diffractograms of two representative γ -Al₂O₃@C^{EB} samples (@C¹⁵⁰ and @C⁶⁵⁰) have been recorded for the sake of characterization completeness, and their profiles are briefly commented in the caption of Figure SS in the Supporting Information.

Catalytic Activity Measurements. As discussed in the introduction section, earlier evidence of an effective EB DDH activity of a γ -Al₂O₃@C^{EB} sample under steam- and oxygen-free conditions have (partially) been discussed in the literature.^{43,45} The absence of any oxidizing atmosphere for the process rules out the redox action of ketonic/quinonic carbonyl oxygen as functionalities directly engaged in long-term dehydrogenation runs. On the other hand, the observed catalytic activity under oxidant-free environments offers a useful hint regarding the comprehension of the role played by defects/vacancies in coke deposits as active sites for the EB C– H bond activation.³² In a first catalytic trial (Figure 3), 0.3 g of γ -Al₂O₃ was tested at atmospheric pressure and 550 °C with 2.8 vol % EB in He and 3000 h⁻¹ as GHSV.

Under the applied conditions, EB dehydrogenation and ST selectivity show distinct phases of activity. As for the former, the initial increase of EB conversion in the 1 h on stream is ascribed to a rapid coke generation at the pristine γ -Al₂O₃



Figure 3. DDH of EB with γ -Al₂O₃@C^{EB} as the catalyst. Catalytic conditions: 300 mg of γ -Al₂O₃, T = 550 °C, [EB] = 2.8 vol % in He, flow rate = 30 mL min⁻¹, GHSV (STP) = 3000 h⁻¹, atmospheric pressure.

surface that reaches a relative maximum value of 27% after 13 h. The progressive SSA reduction of $\gamma\text{-Al}_2O_3 @C^{EB}$ together with the decrease of incremental wt % of coke on TOS (Figure 1) mirrors the successive EB conversion decrease and its stabilization on a pseudo-plateau comprising 18-20% as $X_{\rm EB}$ in the 25-50 h range. Afterward, $X_{\rm EB}$ slightly increases and stabilizes close to 25%. Noteworthy, the catalyst shows a pretty good stability on stream even after a long-term run (200 h). ST selectivity starts at 92% and increases rapidly to 97% after the first 10 h on stream (where cracking side-products-benzene (BZ) and toluene (TOL)-prevail), and it almost constantly maintains such a high value all throughout the process. The evidence of a renewed catalytic performance of γ -Al₂O₃@C^{EB} under steam- and oxygen-free conditions in a relatively longterm trial has prompted us to explore the same metal-free composite under industrially relevant conditions in terms of both operative temperature and EB concentrations.

To this aim, a fresh sample of γ -Al₂O₃ was tested at atmospheric pressure and 600 °C with 2.8–10 vol % EB in He and 3000 h⁻¹ as GHSV. Results are shown in Figure 4A,B, and specific reaction rate values are outlined on Table 1, entries 2–4.

Similar to the previous run at 550 °C, EB conversion meets with a discontinuous activity trend in the first hours on stream followed by a steady increase of the process rate (from ~ 10 to ~20 h) until a maximum value of 5.20 mmol_{ST} g_{cat}^{-1} h⁻¹ (X_{EB} = 68%) that keeps constant up to 60 h on stream. A similar EB dehydrogenation profile for a short-term trial (20 h) using γ - $Al_2O_3 @C^{EB}$ under non-oxidative conditions (N₂ as a diluent) has already been discussed by Makkee and co-workers.⁴³ Their contribution has first shown the key role played by defect and edge sites of carbon deposits in γ -Al₂O₃ $\hat{\emptyset}C^{EB}$ composites for the non-oxidative EB DDH. However, their short-term catalytic investigation accounts only partially for the inherent potentiality of this catalytic system. They claimed a progressive catalyst activity loss due to the reduction of surface area in the composite that well fits with the initial and discontinuous trend observed on our X_{EB} curve after 6–8 h on stream (Figure 4). Nevertheless, a "second catalyst youth" is possible once the system is kept for prolonged times under non-oxidative conditions at the target reaction temperature. After 20 h on stream, the catalyst stabilizes on relatively high EB conversion values $(X_{EB} = 68\%; 5.20 \text{ mmol}_{ST} \text{ g}_{cat}^{-1} \text{ h}^{-1})$, showing an excellent stability up to over 60 h on stream and a markedly high ST selectivity (\geq 99%) all over the catalytic run. The latter is slightly reduced when higher EB concentrations are used in the stream and stabilizes at 97% for 10 vol % EB (Figure 4B). As for $X_{\rm EB}$, at 5 and 10 vol % EB in He, $X_{\rm EB}$ reduces progressively as a consequence of the saturation of the available catalyst active sites (Figure 4B). Anyway, a significant increase of the λ value is measured throughout the whole longterm experiment (Table 1). Indeed, the DDH process rate measured for γ -Al₂O₃@C^{EB} at T = 600 °C with 5 vol % EB increases by about 40% compared with the λ value calculated for the same system at 2.8 vol % EB in the stream (Table 1, entry 3 vs 2). Noteworthy, the catalyst productivity is nearly tripled when EB concentration passes from 2.8 to 10 vol % (Table 1, entry 2 vs 4). Under these severe conditions, γ - Al_2O_3 @C^{EB} unveils a λ value of 13.24 mmol_{ST} g_{cat.}⁻¹ h⁻¹, which is markedly higher than those reported so far for C-based systems under non-oxidative and industrially relevant conditions (Table 1). Table 1 compares the most relevant C-based networks from the literature as metal-free catalysts applied to



Figure 4. DDH of EB with γ -Al₂O₃@C^{EB} as the catalyst under industrially relevant conditions. A: 300 mg of γ -Al₂O₃, $T = 600 \,^{\circ}$ C, [EB] = 2.8 vol % in He, flow rate = 30 mL min⁻¹, GHSV (STP) = 3000 h⁻¹, atmospheric pressure. B: 300 mg of γ -Al₂O₃, $T = 600 \,^{\circ}$ C, [EB] = 2.8, 5, and 10 vol % in He, flow rate = 30 mL min⁻¹, GHSV (STP) = 3000 h⁻¹, atmospheric pressure.

Table 1. EB DDH under Non-Oxidative and Steam-Free Conditions with C-Based Networks as Metal-Free Catalysts for the Process^a

entry	catalyst	$T(^{\circ}C)$	EB (vol %)	catalyst weight (mg)	$X_{\rm EB}~(\%)$	$S_{\rm ST}$ (%)	specific reaction rate (λ) (mmol _{ST} g _{cat} ⁻¹ h ⁻¹)	ref
1	γ -Al ₂ O ₃ @C ^{EB}	550	2.8	300	25	99	1.91	this work
2	γ -Al ₂ O ₃ @C ^{EB}	600	2.8	300	68	99	5.20	this work
3	γ -Al ₂ O ₃ @C ^{EB}	600	5	300	55	98	7.21	this work
4	γ -Al ₂ O ₃ @C ^{EB}	600	10	300	51	97	13.24	this work
5	α -Al ₂ O ₃ @C ^{EB}	550	2.8	300	6	92	0.42	this work
6	α -Al ₂ O ₃ @C ^{EB}	600	2.8	300	21	86	1.39	this work
7	γ -Al ₂ O ₃ @C ^{C₂H₆}	600	2.8	300	73	97	5.44	this work
8	γ -Al ₂ O ₃ @C ^{C₂H₆}	600	5	300	68	98	8.92	this work
9	γ -Al ₂ O ₃ @C ^{C₂H₆}	600	10	300	62	98	16.26	this work
10	CTF-ph	550	2.8	300	36	92	2.52	10
11	CTF-ph	600	2.8	300	69	92	4.85	10
12	CTF-ph	600	5	300	57	93	7.06	10
13	CTF-ph	600	10	300	35	92	9.01	10
14	ND@NMC/SiC	550	2.8	300	24	89	1.65	58
15	ND@NMC/SiC	600	2.8	300	56	96	4.2	58
16	ND@NMC/SiC	600	4.7	300	49	96	6.2	58
17	ND@NMC/SiC	600	10	300	38	97	9.9	58
18	N-C/CNT ^{N15,3}	550	2.8	300	30	99	2.22	9
19	N-C/CNT ^{N15,3}	600	2.8	300	55	93	3.93	9
20	N-C/CNT ^{N15,3}	600	10	300	38	96	10.1	9
21	ND/SiC(F) (33 wt %)	550	2.8	300	31	98	2.35	29
22	ND/SiC(F) (13 wt %)	600	2.8	300	53	92	3.74	29
23	ND/FLG (33 wt %)	550	2.8	150	23	97	3.41	59
24	ND/FLG (33 wt %)	600	2.8	150	41	95	5.98	59
25	ND/CNF-FLG	600	2.8	300	54	86	3.58	60
26	ND/CNF-FLG	600	4.7	300	40	93	4.8	60
27	ND/CNF-FLG	600	10	300	39	91	9.59	60
28 ^b	ND	550	2.8	50	20.5	97	2.98	6
29 ^b	5-MgO-rGO	550	2.8	50	20	98	2.95	61
30 ^b	NMCS-4-800	550	2.8	100	25	90	1.7	62
31 ^b	ND-CN	550	2.8	25	19	99	5.61	63
32	NPCB-900	550	0.02	300	9	93	0.004	64
33 ^b	ND/CNT-SiC	550	2.6	500	19	98	0.26	31
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^aReaction conditions: ambient pressure and (otherwise stated) 30 mL min⁻¹ as the flow rate; He as the diluent. ^bFlow rate: 10 mL min⁻¹.

the steam- and oxygen-free EB DDH. Although the endothermic DDH process has been much less investigated compared with oxidative protocols (ODH) for exothermic DH runs, it is striking how the coke can become the main player of the process, by ensuring unique catalytic performance and markedly high stability in relatively long-term trials and under industrially relevant conditions. Indeed, γ -Al₂O₃@C^{EB} at 600 °C and 10 vol % EB in the stream provides at the steady state

 $X_{\rm EB}$ and $S_{\rm ST}$ that are the highest reported so far in the literature for C-based systems under comparable conditions (Table 1, entry 4 vs 13, 17, 20, and 27).

This experimental evidence suggest a non-innocent role played by the starting metal oxide and C-source with respect to the chemicophysical and morphological nature of the formed coke, directly engaged in the catalytic runs. To shed light on this, we have set up two model experiments. In a first trial, α -Al₂O₃ in the form of beads ($S_{BET} = 6 \pm 2 \text{ m}^2 \text{ g}^{-1}$, Sasol) was employed as the starting metal oxide for EB DDH under identical conditions outlined above for its congener γ -Al₂O₃, using 2.8 vol % EB in He at 550 and 600 °C. As Figure S6 shows, the catalytic performance of the α -Al₂O₃@C^{EB} composite depends on rather moderate values in terms of both EB conversion and ST selectivity. Despite the pretty good catalyst stability on TOS, its performance in the steady-state conditions largely falls behind those of its γ -Al₂O₃@C^{EB} counterpart at both the target operative temperatures (550 and 600 °C, Table 1, entries 5 vs 1 and 6 vs 2). The amount of coke on the light-gray α -Al₂O₃@C^{EB} samples, measured via TG analysis after more than 90 h on stream, is below 1 wt %. The significantly lower surface area and pore volume of α -Al₂O₃ (SSA: $6 \pm 2 \text{ m}^2 \text{ g}^{-1}$; TPV = 0.035 cm³ g⁻¹) compared with γ -Al₂O₃ (SSA: 249 \pm 10 m² g⁻¹; TPV = 0.815 cm³ g⁻¹) is reasonably invoked to justify the moderate wt % increase on the former sample even after a long-term (> 90 h) catalytic run. However, the different surface chemical properties (Lewis and Brønsted acid sites (BAS)) of the two metal oxides at the target temperature at which coke is grown are key features to be taken into account while referring to the different samples' performance and coke properties. Lewis and Brønsted acid sites have been investigated by Fourier transform infrared spectroscopy (FT-IR) using pyridine as a probe molecule in the vapor phase.^{65,66} Both alumina samples have been thermally pretreated at 550 °C for 1 h to assess their chemical properties at the temperature where EB DDH and crackingside processes are supposed to take place (Experimental Section). The spectroscopic pyridine adsorption-desorption experiments on both samples are reported in Figure S7A,B and clearly account for a radically different chemical surface composition of the two samples. The FT-IR pyridine desorption spectra at 150 °C in the 1400–1700 cm⁻¹ range show sharp bands due to the interaction of the probe basic molecule with Lewis acid sites (LAS) on the γ -Al₂O₃ sample only (1448 and 1610 cm⁻¹). No appreciable signals at 1540 cm^{-1} (Brønsted acid sites, BAS) are available on both materials. As a result, the thermally pretreated α -Al₂O₃ sample reveals a negligible acid (Lewis and Brønsted) character that well matches with the low coke loading measured after employing the sample for long-term catalytic runs and consequently with the modest EB DDH performance of the α -Al₂O₃@C^{ÉB} composite (Figure S6).

Most importantly, the C-source used for the initial coke growth is found to affect the ultimate catalyst performance.⁴⁴ In a further DDH trial, pristine γ -Al₂O₃ was precoked with an aliphatic C-feedstock (C₂H₆, 5 vol % in He) at 600 °C for 2 h at 30 mL min⁻¹ as the flow rate before purging the reactor with He for additional 2 h. The as-obtained γ -Al₂O₃@C^{C₂H₆ composite shows a very moderate coke loading (roughly estimated < 1 wt % by TGA) as witnessed by the light-gray color of the recovered coke-coated γ -Al₂O₃ trilobs (Figure S8). Such a carbonaceous deposit is largely below the theoretical amount of coke required for creating a C-surface monolayer.} Calculated from unit cell dimensions, graphitic carbon has a single side surface area of about 1300 m² g⁻¹; hence, 0.19 g of coke (16 wt %) per g of γ -Al₂O₃ are required to cover its surface area $(249 \text{ m}^2 \text{ g}^{-1})$ with a single layer. Moreover, the N_2 -physisorption measurement carried out on the precoked γ - $Al_2O_3 @C^{C_2H_6}$ sample does not reveal any appreciable modification of the material SSA and pore size distribution. Indeed, the Brunauer-Emmett-Teller (BET) value of γ -Al_2O_3($C^{C_2H_6}$ (267 ± 10 m² g⁻¹) falls in the same range of values given for pristine γ -Al₂O₃₁ and BJH curves recorded for the two samples show almost superimposable profiles (Figure S8). It can be inferred that γ -Al₂O₃ pretreatment with ethane generates C-islands prevalently located in the correspondence of the surface-exposed Lewis acid sites where cracking-side reactions are more likely to occur.^{8,26,27,67,68} The ethane precoking is found to slightly alter the acidity of the pristine alumina. Indeed, a quantitative analysis of LAS based on FT-IR pyridine desorption spectra measured at 150 °C in the 1400-1700 cm⁻¹ range on the two samples γ -Al₂O₃ and γ -Al₂O₃@ C^{C₂H₆} has revealed a nearly 20% reduction of acid sites in the latter (Figure S9 and Table S2). Once the ethane precoked γ -Al₂O₃ $@C^{C_2H_6}$ sample is employed as the catalyst for EB DDH at 600 °C with 2.8 vol % EB in He at atmospheric pressure and a flow rate of 30 mL min⁻¹, it shows a discontinuous activity trend in the first hours on stream before stabilizing on 73% as $X_{\rm EB}$ and 97% as $S_{\rm ST}$ (Figure 5A-I). Worthy of note, γ -Al₂O₃@



Figure 5. DDH of EB with γ -Al₂O₃@C^{EB} (X_{EB} , red solid squares; S_{ST} , blue empty squares) and γ -Al₂O₃@C^{C₃H₆} (X_{EB} , orange solid spheres; S_{ST} , green empty spheres) as catalysts at comparison. Reaction conditions: 300 mg of γ -Al₂O₃ or γ -Al₂O₃@C^{C₃H₆}, T = 600 °C, [EB] = 2.8 vol % in He (A-I,IV,VI), 5 vol % in He (A-II), 10 vol % in He (A-III), 2.8 vol % in He, and 10 vol % steam (A-V); Flow rate = 30 mL min⁻¹, GHSV (STP) = 3000 h⁻¹, atmospheric pressure. γ -Al₂O₃@C^{EB} (X_{EB} , red solid squares; S_{ST} , blue empty squares) are those reported in Figure 4B and shown here for the sake of comparison.

 $C^{C_2H_6}$ outperforms the already excellent X_{EB} values recorded with γ -Al₂O₃@ C^{EB} under identical conditions (Table 1, entry 7 vs 2). The improved performance of γ -Al₂O₃@ $C^{C_2H_6}$ is confirmed at higher EB concentrations (5 and 10 vol %), Figure 5A-II,III, where it reaches λ values as high as 16.26 mmol_{ST} g_{cat}⁻¹ h⁻¹ along with a markedly high stability on TOS (Table 1, entries 8 and 9 vs 3 and 4).

When EB concentration is restored to 2.8 vol %, the system recovers its original performance in terms of $X_{\rm EB}$ and $S_{\rm ST}$ almost completely (Figure 5A-IV). It should be pointed out that the amount of coke measured on γ -Al₂O₃@C^{C₂H₆} after 150

h on stream is about 21.6 wt %, and it is rather close to that recorded for γ -Al₂O₃@C^{EB} after the same time (see Figure S10 vs Figure S2). However, C-deposits grown on precoked γ -Al₂O₃@C^{C2H6} have markedly different morphological properties. This is unambiguously demonstrated by the higher SSA and total pore volume recorded on $\gamma\text{-Al}_2O_3 @C^{C_2\breve{H}_6}$ and $\gamma\text{-}$ Al₂O₃@C^{EB} after comparable EB DDH runs. While SSA of γ - $Al_2O_3 @C^{EB}$ rapidly drops down to $40 \pm 10 \text{ m}^2 \text{ g}^{-1}$ after 50 h on stream and the material total pore volume is almost completely suppressed (0.074 cm³ g⁻¹), γ -Al₂O₃@C^{C₂H₆ holds a relatively high SSA (184 m² g⁻¹) and total pore volume (0.440 cm³ g⁻¹) even after 150 h on stream (Figure S11A,A').} In spite of the accumulative nature of coke deposits under nonoxidative conditions (see § 3.1), the performance of the precoked γ -Al₂O₃@C^{C₂H₆} neither changes nor converges to those of γ -Al₂O₃@C^{EB} once those new carbonaceous deposits from EB cracking are formed and layer over the $C^{C_2H_6}$ phase. On the contrary, γ -Al₂O₃@C^{C_{2H₆} shows a markedly high</sup>} stability on TOS along with higher X_{EB} of its γ -Al₂O₃@C^{EB} counterpart, regardless of the EB concentration used in the stream (Figure 5A-I-IV). Hence, it is reasonable to assume a different growth mechanism of coke deposits on plain γ -Al₂O₃ and precoked γ -Al₂O₃@C^{C₂H₆} once they are employed as EB DDH catalysts.

High-resolution transmission electron microscopy (HR-TEM) analyses of γ -Al₂O₃@C^{C₂H₆} and γ -Al₂O₃@C^{EB} after 150 h on stream have unambiguously pointed out the existence of alternative mechanisms to coke growth (Figures 6 and S12).



Figure 6. Representative high-resolution TEM micrographs (500 000×) of the γ -Al₂O₃@C^{C₂H₆} (A) and γ -Al₂O₃@C^{EB} (B) recovered after 150 h on stream. Reaction conditions: 300 mg of γ -Al₂O₃@C^{C₂H₆ or γ -Al₂O₃, *T* = 600 °C, [EB] = 2.8 vol % in He; flow rate = 30 mL min⁻¹, GHSV (STP) = 3000 h⁻¹, atmospheric pressure. Yellow arrows highlight the graphitized C-layers on the two samples.}

Indeed, the two samples present large material portions featured by different morphologies of the coke deposits. Noteworthy, the recovered γ -Al₂O₃@C^{C₂H₆} catalyst shows the presence of well-ordered and highly graphitized carbon areas formed by layer-by-layer growth of EB cracking-derived carbons over the precoked γ -Al₂O₃@C^{C₂H₆} sample surface (Figure 6A). The thickness of the carbon shell appears rather homogeneously distributed all over the alumina crystallites and limited to 1–2 nm. Fast Fourier transformation patterns of local areas in the sample (Figure 6A) show spots in the 3.5–3.6 Å range. These interplanar distances, greater than the (0 0 2) spacing between graphite planes (3.38 Å), fall in the range classically reported for graphitic nanostructures.^{69,70} On the other hand, the recovered γ -Al₂O₃@C^{EB} sample shows alumina grains totally embedded in carbon coke deposits (carbon thickness > 5 nm) containing both graphitized and disordered

amorphous carbon phases. Such morphological differences have been additionally supported by the Raman spectra of the C-shells on the two samples. As Figure S13 shows, the D1/D3 ratios obtained from peak deconvolution on the two amorphous C-deposits (D1/G > 1.1) are consistent with samples featuring different coke structural orders. Indeed, after 150 h on stream, γ -Al₂O₃@C^{C₂H₆} (D1/G = 1.39) presents a D1/D3 ratio of 3.46, whereas the recovered γ -Al₂O₃@C^{EB} sample (D1/G = 1.94) lies on a markedly lower D1/D3 ratio (2.91).

This evidence led us to postulate an epitaxial growth of the newly generated C-deposits, where their "layer-by-layer growth" retains memory of the morphology of the underlining C-layers.^{71,72}

Hence, when EB-derived coke was directly formed on pure γ -Al₂O₃, the lattice mismatch between the inorganic substrate and the formed C-film translates into heteroepitaxially grown carbonaceous deposits featured by various morphologies mixing crystalline and amorphous phases. The high SSA and total pore volume of the recovered γ -Al₂O₃@C^{C₂H₆ after a long-term catalytic run can be explained by a prevalent homoepitaxial growth of EB-derived coke deposits on the ethane-preformed coke islands. Such a layer-by-layer growth mode at zero or low lattice misfit between the support and C-films is supposed to leave behind pores arising from those γ -Al₂O₃ regions (featured by low Lewis acid character) not initially coated by the C₂H₆ precoking treatment.}

This hypothesis is finally corroborated by the catalyst behavior after its treatment in the presence of steam (10 vol %) (Figure 5A-V,VI). The use of steam causes the rapid reduction of the catalyst performance with $X_{\rm EB}$ that lies on 25% and $S_{\rm ST}$ close to 97% all over the treatment (50 h) (Figure 5A-V). This trend is largely ascribed to a partial gasification of the catalyst active phase⁷³ as well as by an evident "quenching" of the coke active sites. The latter is supposed to be caused by either a partial oxidation of the high-energy C-sites directly engaged in the EB activation (edge sites, defects, and vacancies) or their saturation by H₂O molecules (competitive H₂O/EB interaction with C-active sites). Hence, the use of steam detrimentally alters the catalyst performance, leaving behind permanently modified coke layers. As a result, when steam-free DDH conditions are restored (Figure 5A-V), $X_{\rm EB}$ is not entirely recovered but it has (at the steady state a slightly lower catalytic performance (Figure 5A-V vs A-I); from $X_{EB} = 73$ to $X_{\rm EB} = 67$).

Catalytic DDH activity promoted by γ -Al₂O₃@C composites then appears to be related to the ultimate structure of the coke deposits formed under non-oxidative conditions. Our experimental evidence confirm the existence of a coherent trend between the increased graphitic order of carbon deposits and the increased catalytic performance of the composites. This trend is perfectly in line with previous (and related) outcomes from the literature.^{34,41,42}

CONCLUSIONS

In summary, we have described the use of a straightforward prepared "coked" γ -Al₂O₃ composite as a highly efficient, durable, and selective metal-free catalyst for direct EB dehydrogenation (DDH) to ST under steam- and oxygen-free conditions. We have unveiled the unique potential of a catalytic system already known to the scientific community but never exploited for EB DDH under severe conditions close to those commonly used in industrial plants (600 °C, 10 vol %

EB/He, GHSV = 3000 h^{-1}). With markedly high stability on stream (even for long-term runs \geq 150 h), ST selectivity as high as \geq 97%, and process rates (λ) up to 16.3 mmol_{ST} g_{cat} h⁻¹, γ -Al₂O₃@C composites largely outperform all carbonbased systems reported so far in the literature as metal-free DDH catalysts operating under non-oxidative environments. This finding also contributes to an in-depth rewriting of the role of coke in a challenging heterogeneous process. It forces us to change our way of thinking of "coke in catalysis"-from a classical drawback to be overcome for keeping alive the catalyst activity and stability (for the majority of metal and metal-free dehvdrogenation catalysts) to being considered as a highly active and selective phase for the dehydrogenation process to occur. Moreover, it adds an additional (but fundamental) tile to the complex puzzle on the nature of the active sites in carbon-based catalysts for DDH. The high catalyst stability on TOS along with its unique performance $(X_{EB} \text{ and } S_{ST})$ under a rigorous non-oxidative environment excludes any redox action of ketonic/quinonic carbonyl functionalities in the EB activation and dehydrogenation path. On the other hand, the formation of high-energy C-sites in the form of surface defects/ vacancies in coke deposits is supposed to be the unique active phase potentially engaged in the EB C-H bonds activation/ dehydrogenation steps. Hence, the manner in which coke is formed affects its ultimate performance in catalysis. Indeed, when highly ordered and graphitized C-deposits are grown over a precoked γ -Al₂O₃@C^{$\hat{C}_{2}H_{6}$} composite, their catalytic performances are markedly superior to those resulting from layer-by-layer growth EB cracking-derived carbons on the plain γ-Al₂O₃ support. We have demonstrated that when EB-derived coke is formed on pure γ -Al₂O₃, the lattice mismatch between the inorganic oxide and the formed C-layers translates into heteroepitaxially grown carbonaceous deposits featured by various morphologies mixing crystalline and amorphous phases. On the other hand, the reduced acid surface character of the precoked γ -Al₂O₃@C^{C₂H₆ sample along with the} existence of preformed coke islands fosters the generation of well-ordered and highly graphitized carbon deposits throughout the whole catalytic run. All these findings taken together pave the way for the development of cheap and durable dehydrogenation catalysts while offering new hints to the comprehension of the dehydrogenation mechanism at work in the presence of plain C-sites.

EXPERIMENTAL SECTION

Material Characterization Methods. Thermogravimetric analyses (TGA/DTG) were performed under air (100 mL min⁻¹) on a SETARAM Analyzer (TGA/DTG) using a thermo-program between 30 and 900 °C at the heating rate of 10 °C min⁻¹. Raman spectra with 1.5 cm⁻¹ spectral resolution were acquired using the 659.43 nm wavelength of a diode laser, after excluding any photochemical effect on the sample. The laser power was 1 mW, and the duration of the acquisition was 100 s. The beam profile was cleaned by one Notch filter in reflection, and the scattered radiation, after being cleaned by one spatial and two Notch filters, was dispersed using a single grating monochromator (Acton Trivista) and detected by a liquid N₂-cooled CCD detector (Princeton Instruments). Three different points were probed on each sample. A description of the Raman setup has been reported in a previous study.⁷⁴ Samples were analyzed by registering the spectra for each sample randomly on 3 different positions. All recorded curves were baselined and fitted using a Lorentzian-

shaped band for G and Gaussian-shaped bands for D1, D3, and D4, and the D- and G-peaks intensities were used for the calculation of the I(D1)/I(G) - I(D1)/I(D3) ratios. Transmission electron microscopy (TEM) measurements were performed using a ZEISS LIBRA200FE microscope equipped with a 200 kV FEG source. Before each analysis, samples were finely crushed in an agate mortar, suspended in isopropanol, and sonicated for a few minutes. Then, each suspension was drop-cast onto a holey carbon-coated copper grid (300 mesh), and the solvent was evaporated at ambient pressure. The Brunauer-Emmett-Teller (BET) specific surface area (SSA) and porosity (based on BJH methods) were measured on an ASAP 2020 Micromeritics instrument, using N₂ as the absorbent at the liquid N2 temperature. All samples were completely degassed/activated at 250 °C for 14-18 h. X-ray powder diffraction qualitative measurements were carried out with a Panalytical X'PERT PRO powder diffractometer in a reflection-transmission mode equipped with a parabolic mirror on the incident beam and a PIXcel solid-state detector in the $10-80^{\circ} 2\theta$ region with a 0.03° step size, operating with Cu K α radiation ($\lambda = 1.5418$ Å). Antiscatter slits were used both on the incident (0.25 and 0.5° divergence) and on the diffracted (7.5 mm height) beam. Background correction, peak finding, peak fitting, and the final phase assignments were carried out with instrument software X'Pert High Score Plus, version 2.2.5 (2009). Temperature-programmed decomposition-under He flow (TPD-He) was performed in a homemade reaction rig, placing 50 mg of the sample in a Pyrex U-shaped tubular reactor housed into a furnace. The sample was pretreated at room temperature (rt) under a constant stream of pure He (20 mL min⁻¹) for 3 h before being heated at a rate of 10 $^{\circ}$ C min⁻¹ to the target temperature (520 °C). Decomposition products were detected by a quadrupole mass spectrometer (HPR-20 QIC gas analysis mass spectrometer system, Hiden Analytical Ltd., U.K.) connected downstream.⁷⁵ Determination of Lewis and Brønsted acid sites of pure alumina and C-composite samples was carried out by Fourier transform infrared spectroscopy (FT-IR) (Biorad FTS-60A) using pyridine as the probe molecule in the vapor phase.⁶⁶ All alumina samples were finely crushed in a mortar and thermally pretreated at 550 °C, under vacuum for 1 h. Afterward, 10-15 mg of each material was pressed in the form of self-supporting pellets $(\sim 1.3 \text{ cm}^2 \text{ geometrical area})$, and before each analysis they were outgassed overnight at 150 °C under high vacuum. After that, samples were contacted with pyridine vapors at room temperature for 15 min and finally outgassed for 30 min in high vacuum at different temperatures (i.e., rt, 50, 100, 150 °C). BAS (Brønsted acid sites) and LAS (Lewis acid sites) concentrations, expressed as μ equivalents of adsorbed pyridine per gram of catalyst ($\mu_{eq}^{Py} g_{cat}^{-1}$), were determined by integrating the peaks at 1540 and 1449 cm⁻¹, respectively, of the spectra collected after outgassing at 150 °C, according to the procedure outlined in the literature.⁷⁶

Steam- and Oxygen-Free Direct Dehydrogenation (DDH) of Ethylbenzene (EB) to Styrene (ST) Using γ -Al₂O₃, α -Al₂O₃, or γ -Al₂O₃@C^{C₂H₆ as Catalyst Precursors. In a typical procedure, 300 mg of a selected catalyst precursor (γ -Al₂O₃—CK-300 Ketjen ($S_{BET} = 249 \pm 10 \text{ m}^2 \text{ g}^{-1}$) in the form of extruded trilobs ($\sim 1 \text{ mm} \times \sim 4 \text{ mm}$), α -Al₂O₃ in the form of beads 1.6 mm ($S_{BET} = 6 \pm 2 \text{ m}^2 \text{ g}^{-1}$, Sasol), or γ -Al₂O₃@C^{C₂H₆</sub> ($S_{BET} = 267 \pm 10 \text{ m}^2 \text{ g}^{-1}$) in the form of extruded trilobs ($\sim 1 \text{ mm} \times \sim 4 \text{ mm}$)) was charged inside a tubular quartz reactor ($\emptyset \times \text{L}$: $8 \times 800 \text{ mm}$) equipped with a}}

quartz fritted disk as the catalyst holder and used as a fixed-bed continuous flow reactor operating under atmospheric pressure. The reactor was then purged with pure He at a flow rate of 30 mL min⁻¹ (using a BROOKS mass flow controller (MFC)) for 2 h during which the temperature was raised and stabilized at the desired operative value (550 or 600 °C). To eliminate undesired reagent/product condensations throughout the whole reactor line, all pipes (before and after the reactor) were wrapped with a heating tape and maintained at the constant temperature of 110 °C. Except for the case of γ -Al₂O₃ $@C^{C_2H_6}$, after the line purging, the reactor was fed with 2.8, 5, or 10 vol % EB in He at the total flow rate of 30 mL min⁻¹ by flowing He through a glass evaporator filled with liquid EB and maintained at constant temperature with a thermally regulated bath. γ -Al₂O₃@C^{C₂H₆ was directly prepared} in situ starting from a He-purged γ -Al₂O₃ sample that underwent treatment with a mixture of C_2H_6 , 5 vol % in He at 600 °C for 2 h at a flow rate of 30 mL min⁻¹. Afterward, the as-precoked $Al_2O_3@C^{C_2H_6}$ composite was purged for an additional 2 h with pure He at the target temperature before being fed with 2.8, 5, or 10 vol % EB in He at the total flow rate of 30 mL min⁻¹.

Whatever the catalyst used, EB and reaction products (styrene (ST), benzene (BZ), and toluene (TOL)) were analyzed in real time at the reactor outlet using a PERICHROM (PR 2100) gas chromatograph equipped with a flame detector and a calibrated CP WAX S2CB column.

EB conversion (X_{EB}) and ST selectivity (S_{ST}) were evaluated using eqs 1 and 2

$$X_{\rm EB} = \frac{F_0 C_{\rm EB,inlet} - F C_{\rm EB,outlet}}{F_0 C_{\rm EB,inlet}} \times 100\%$$
(1)

$$S_{\rm ST} = \frac{C_{\rm ST,outlet}}{C_{\rm ST,outlet} + C_{\rm TOL,outlet} + C_{\rm BZ,outlet}} \times 100\%$$
(2)

where *F* and *F*₀ are the flow rates at the reactor outlet and inlet, respectively, and *C*_{EB}, *C*_{ST}, *C*_{TOL}, and *C*_{BZ} represent the concentrations of ethylbenzene, styrene, toluene, and benzene, respectively. The overall C-balance amounts to nearly 100% for all catalytic runs.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b02555.

Additional figures; digital images of γ -Al₂O₃ and γ -Al₂O₃@C samples; TGA/DTG profiles of γ -Al₂O₃@C samples; nitrogen adsorption-desorption isotherm linear plots (BET) and pore volume distributions (BJH); Raman spectra; additional DDH tests with α -Al₂O₃@C; LAS determination via FT-IR spectroscopy; TEM images of coked γ -Al₂O₃@C samples (PDF)

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Notes

The authors declare no competing financial interest.

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