Second Youth of a Metal-Free Dehydrogenation Catalyst: When \( \gamma{-}\text{Al}_2\text{O}_3 \) 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” \( \gamma{-}\text{Al}_2\text{O}_3 \) composites and their catalytic performance in the ethylbenzene (EB) direct dehydrogenation (DDH) to styrene (ST) under steam- and 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 long-term trials (≥150 h) and markedly high ST selectivity (≥97%) along with process rates (λ up to 16.3 mmolST gcat 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. \( \gamma{-}\text{Al}_2\text{O}_3 \) precoking with an aliphatic C-source has shown additional beneficial effects on the ultimate \( \gamma{-}\text{Al}_2\text{O}_3@\) 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: \( \gamma{-}\text{Al}_2\text{O}_3@\) 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 multi-promoted 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 chemomechanical 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
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 °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 anticoke 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 systems.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).25 “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 conditions have resulted in a moderate number of scientific reports.6,9,26-33 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 EB35-39 and light alkane40 ODH and more recently for n-butane,41 cyclohexane,42 and EB43 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.32,34 Hence, the performance of coked catalysts is deeply influenced by the nature of coke, depending on the operating conditions used in its production (i.e., reaction temperature, C-source, and C-concentration 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 metal-oxide” have already received a great deal of attention as catalysts 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 catalysts,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 short-term EB dehydrogenation under a N2 atmosphere.46 The authors showed that alumina became active and selective faster for the process under non-oxidative conditions (N2) instead of using CO2 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 (≥97%) and the highest process rates reported so far in the literature (λ up to 16.3 mmolC·gcat−1·h−1) for related carbon-based catalysts at work in the process.

## RESULTS AND DISCUSSION

### γ-Al2O3@CEB 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 BET = 249 ± 10 m2 g−1) in the form of extruded trilobs (∼1 mm x 4 mm, Figure S1) are loaded onto a quartz fritted disk located inside a tubular quartz reactor (i.d. x length 8 x 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 $\gamma$-Al$_2$O$_3$ 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 $\gamma$-Al$_2$O$_3$ 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). Under these conditions, a dynamic dependence of formed coke (wt %) from time-on-stream (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 $\Delta^{150}$wt % increase (in the 150–300 h) of 6.5, a $\Delta^{350}$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

During the process, the sample specific surface area (SSA) varies from 249 m$^2$ g$^{-1}$ of pristine $\gamma$-Al$_2$O$_3$ to 138 m$^2$ g$^{-1}$ of the sample isolated after 10 h on stream. After 50 h, the SSA value drops down to 37 m$^2$ g$^{-1}$, and it definitively lies in the 40 ± 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 $\gamma$-Al$_2$O$_3$ 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 $\gamma$-Al$_2$O$_3@CEB$ 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 $\gamma$-Al$_2$O$_3@CEB$ samples obtained for prolonged reaction times at the target temperature$^{50}$ 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 ($\gamma$-Al$_2$O$_3@C^{300}$) 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 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 $\gamma$-Al$_2$O$_3$, $T = 600$ °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.

Figure 2. Raman spectra of coked $\gamma$-Al$_2$O$_3$ composites prepared at variable TOS (10, 300, 650, 1020 h) under the following conditions: 300 mg of $\gamma$-Al$_2$O$_3$, $T = 600$ °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\textsubscript{EB} composites at variable reaction times present the two main and distinctive components of the carbonaceous phases at \textasciitilde{}1340 and \textasciitilde{}1605 cm\textsuperscript{-1} attributed to the so-called G and D peaks.\textsuperscript{51–57} According to literature reports on related materials, the spectra were fitted by four components (G, D1, D3, and D4) considering a Lorentzian-shaped band for G and Gaussian-shaped bands for D1, D3, and D4.\textsuperscript{44,47,54} The D1/G ratio has been conventionally used to determine the degree of structural order of carbons\textsuperscript{35,56} at least in systems featuring D1/G \textless{} 1.1.\textsuperscript{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.\textsuperscript{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 restructuring to finally give graphitized or pseudo-graphitized C-networks. XRD diffractograms of two representative γ-Al2O3@C\textsubscript{EB} samples (@C\textsubscript{150} and @C\textsubscript{650}) have been recorded for the sake of characterization completeness, and their profiles are briefly commented in the caption of Figure S5 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\textsubscript{EB} sample under steam- and oxygen-free conditions have (partially) been discussed in the literature.\textsuperscript{33,43} 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 reactions. 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.\textsuperscript{42} 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\textsuperscript{-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 surface that reaches a relative maximum value of 27% after 13 h. The progressive SSA reduction of γ-Al2O3@C\textsubscript{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 \(X_{\text{EB}}\) in the 25–50 h range. Afterward, \(X_{\text{EB}}\) 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\textsubscript{EB} under steam- and oxygen-free conditions in a relatively long-term 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\textsuperscript{-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 \textasciitilde{}10 to \textasciitilde{}20 h) until a maximum value of 5.20 mmol\textsubscript{ST} g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1} (\(X_{\text{EB}} = 68\%\)) that keeps constant up to 60 h on stream. A similar EB dehydrogenation profile for a short-term trial (20 h) using γ-Al2O3@C\textsubscript{EB} under non-oxidative conditions (N\textsubscript{2} as a diluent) has already been discussed by Makkee and co-workers.\textsuperscript{40} Their contribution has first shown the key role played by defect and edge sites of carbon deposits in γ-Al2O3@C\textsubscript{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 catalytic activity loss due to the reduction of surface area in the composite that well fits with the initial and discontinuous trend observed on our \(X_{\text{EB}}\) 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 (\(X_{\text{EB}}\) close to 80% and 90% for 5 and 10 vol % EB, respectively), which prevails, and it almost constantly maintains such a high value all throughout 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 \(X_{\text{EB}}\), at 5 and 10 vol % EB in He, \(X_{\text{EB}}\) reduces progressively as a consequence of the saturation of the available catalyst active sites (Figure 4B). Anyway, a significant increase of the \(\lambda\) value is measured throughout the whole long-term experiment (Table 1). Indeed, the DDH process rate measured for γ-Al2O3@C\textsubscript{EB} at T = 600 °C with 5 vol % EB increases by about 40% compared with the \(\lambda\) 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-Al2O3@C\textsubscript{EB} unveils a \(\lambda\) value of 13.24 mmol\textsubscript{ST} g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-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

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Figure 3. DDH of EB with γ-Al2O3@C\textsubscript{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\textsuperscript{-1}, GHSV (STP) = 3000 h\textsuperscript{-1}, atmospheric pressure.
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@CEB at 600 °C and 10 vol % EB in the stream provides at the steady state

Figure 4. DDH of EB with γ-Al₂O₃@CÈB as the catalyst under industrially relevant conditions. A: 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. B: 300 mg of γ-Al₂O₃, T = 600 °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

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"Reaction conditions: ambient pressure and (otherwise stated) 30 mL min⁻¹ as the flow rate; He as the diluent. Flow rate: 10 mL min⁻¹."
X_{EB} and S_{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 chemophysical 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-Al_{2}O_{3} in the form of beads (S_{BET} = 6 ± 2 m^{2} g^{-1}, Sasol) was employed as the starting metal oxide for EB DDH under identical conditions outlined above for its congener γ-Al_{2}O_{3} using 2.8 vol % EB in He at 550 and 600 °C. As Figure S6 shows, the catalytic performance of the α-Al_{2}O_{3}@C\textsuperscript{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-Al_{2}O_{3}@C\textsuperscript{EB} counterpart at both the target operative temperatures (550 and 600 °C, Table 1, entries S vs 1 and 6 vs 2). The amount of coke on the light-gray α-Al_{2}O_{3}@C\textsuperscript{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-Al_{2}O_{3} (SSA: 6 ± 2 m^{2} g^{-1}; TPV = 0.035 cm^{3} g^{-1}) compared with γ-Al_{2}O_{3} (SSA: 249 ± 10 m^{2} g^{-1}; TPV = 0.815 cm^{3} 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 Bronsted 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 Bronsted acid sites have been investigated by Fourier transform infrared spectroscopy (FT-IR) using pyridine as a probe molecule in the vapor phase.\textsuperscript{35,66} 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 cracking-side 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\textsuperscript{-1} range show sharp bands due to the interaction of the probe basic molecule with Lewis acid sites (LAS) on the γ-Al_{2}O_{3} sample only (1448 and 1610 cm\textsuperscript{-1}). No appreciable signals at 1540 cm\textsuperscript{-1} (Bronsted acid sites, BAS) are available on both materials. As a result, the thermally pretreated α-Al_{2}O_{3} sample reveals a negligible acid (Lewis and Bronsted) 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-Al_{2}O_{3}@C\textsuperscript{EB} composite (Figure S6).

Most importantly, the C-source used for the initial coke growth is found to affect the ultimate catalyst performance.\textsuperscript{44} In a further DDH trial, pristine γ-Al_{2}O_{3} was precoked with an aliphatic C-feedstock (C\textsubscript{4}H\textsubscript{8}, 5 vol % in He) at 600 °C for 2 h at 30 mL min\textsuperscript{-1} as the flow rate before purging the reactor with He for additional 2 h. The as-obtained γ-Al_{2}O_{3}@C\textsuperscript{C\textsubscript{4}H\textsubscript{8}} 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-Al_{2}O_{3} 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 m\textsuperscript{2} g\textsuperscript{-1}; hence, 0.19 g of coke (16 wt %) per g of γ-Al_{2}O_{3} are required to cover its surface area (249 m\textsuperscript{2} g\textsuperscript{-1}) with a single layer. Moreover, the N\textsubscript{2}-physisorption measurement carried out on the precoked γ-Al_{2}O_{3}@C\textsuperscript{C\textsubscript{4}H\textsubscript{8}} 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_{2}O_{3}@C\textsuperscript{C\textsubscript{4}H\textsubscript{8}} (267 ± 10 m\textsuperscript{2} g\textsuperscript{-1}) falls in the same range of values given for pristine γ-Al_{2}O_{3} and BJH curves recorded for the two samples show almost superimposable profiles (Figure S8). It can be inferred that γ-Al_{2}O_{3} 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.\textsuperscript{3,26,27,66,68} 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\textsuperscript{-1} range on the two samples γ-Al_{2}O_{3} and γ-Al_{2}O_{3}@C\textsuperscript{C\textsubscript{4}H\textsubscript{8}} has revealed a nearly 20% reduction of acid sites in the latter (Figure S9 and Table S2). Once the ethane precoked γ-Al_{2}O_{3}@C\textsuperscript{C\textsubscript{4}H\textsubscript{8}} 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\textsuperscript{-1}, it shows a discontinuous activity trend in the first hours on stream before stabilizing on 73% as X_{EB} and 97% as S_{ST} (Figure S9A). Worthy of note, γ-Al_{2}O_{3}@C\textsuperscript{C\textsubscript{4}H\textsubscript{8}} outperforms the already excellent X_{EB} values recorded with γ-Al_{2}O_{3}@C\textsuperscript{EB} under identical conditions (Table 1, entry 7 vs 2). The improved performance of γ-Al_{2}O_{3}@C\textsuperscript{C\textsubscript{4}H\textsubscript{8}}, is confirmed at higher EB concentrations (5 and 10 vol %), Figure S9A-II,III, where it reaches λ values as high as 16.26 mmol\textsubscript{ST} g\textsuperscript{-1} h\textsuperscript{-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_{EB} and S_{ST} almost completely (Figure S9A-IV). It should be pointed out that the amount of coke measured on γ-Al_{2}O_{3}@C\textsuperscript{C\textsubscript{4}H\textsubscript{8}} after 150
h on stream is about 21.6 wt %, and it is rather close to that recorded for $\gamma$-Al$_2$O$_3@$C(EH) after the same time (see Figure S10 vs Figure S2). However, C-deposits grown on precoked $\gamma$-Al$_2$O$_3@$C(EH) have markedly different morphological properties. This is unambiguously demonstrated by the higher SSA and total pore volume recorded on $\gamma$-Al$_2$O$_3@$C(EH) and $\gamma$-Al$_2$O$_3@$C(EH) after comparable EB DDH runs. While SSA of $\gamma$-Al$_2$O$_3@$C(EH) rapidly drops down to $40 \pm 10$ m$^2$ g$^{-1}$ after 50 h on stream and the material total pore volume is almost completely suppressed ($0.074$ cm$^3$ g$^{-1}$), $\gamma$-Al$_2$O$_3@$C(EH) holds a relatively high SSA ($184$ m$^2$ g$^{-1}$) and total pore volume ($0.440$ cm$^3$ g$^{-1}$) even after 150 h on stream (Figure S11A,A). In spite of the accumulative nature of coke deposits under non-oxidative conditions (see § 3.1), the performance of the precoked $\gamma$-Al$_2$O$_3@$C(EH) neither changes nor converges to those of $\gamma$-Al$_2$O$_3@$C(EH) once those new carbonaceous deposits from EB cracking are formed and layer over the C(EH) phase. On the contrary, $\gamma$-Al$_2$O$_3@$C(EH) shows a markedly high stability on TOS along with higher $X_{EB}$ of its $\gamma$-Al$_2$O$_3@$C(EH) counterpart, regardless of the EB concentration used in the stream (Figure 5A-I). Hence, it is reasonable to assume a different growth mechanism of coke deposits on plain $\gamma$-Al$_2$O$_3$ and precoked $\gamma$-Al$_2$O$_3@$C(EH) once they are employed as EB DDH catalysts.

High-resolution transmission electron microscopy (HR-TEM) analyses of $\gamma$-Al$_2$O$_3@$C(EH) and $\gamma$-Al$_2$O$_3@$C(EH) 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 000x) of the $\gamma$-Al$_2$O$_3@$C(EH) (A) and $\gamma$-Al$_2$O$_3@$C(EH) (B) recovered after 150 h on stream. Reactor conditions: 300 mg of $\gamma$-Al$_2$O$_3@$C(EH), or $\gamma$-Al$_2$O$_3@$C(EH) $T = 600$ °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.](image-url)

Indeed, the two samples present large material portions featured by different morphologies of the coke deposits. Noteworthy, the recovered $\gamma$-Al$_2$O$_3@$C(EH) 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 $\gamma$-Al$_2$O$_3@$C(EH) 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. On the other hand, the recovered $\gamma$-Al$_2$O$_3@$C(EH) 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, $\gamma$-Al$_2$O$_3@$C(EH) presents a D1/D3 ratio of 3.46, whereas the recovered $\gamma$-Al$_2$O$_3@$C(EH) 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. Hence, when EB-derived coke was directly formed on pure $\gamma$-Al$_2$O$_3$, 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 $\gamma$-Al$_2$O$_3@$C(EH) after a long-term catalytic run can be explained by a prevalent homoeptaxial 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 $\gamma$-Al$_2$O$_3$ regions (featured by low Lewis acid character) not initially coated by the C$_2$H$_6$ precoking treatment.

This hypothesis is finally corroborated by the catalyst behavior after its treatment in the presence of steam (10 vol %) (Figure 5A-VI). The use of steam causes the rapid reduction of the catalyst performance with $X_{EB}$ that lies on 25% and $S_{ST}$ 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 phase 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 H$_2$O molecules (competitive H$_2$O/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), $X_{EB}$ 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 $X_{EB}$ = 67).

Catalytic DDH activity promoted by $\gamma$-Al$_2$O$_3@$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.

**CONCLUSIONS**

In summary, we have described the use of a straightforward prepared “coked” $\gamma$-Al$_2$O$_3$ 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 % steam).
EB/He, GHSV = 3000 h⁻¹). With markedly high stability on stream (even for long-term runs ≥150 h), ST selectivity as high as ≥97%, and process rates (λ) up to 16.3 mmol ST gcat⁻¹ h⁻¹, γ-Al₂O₃@C composites largely outperform all carbon-based 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 dehydrogenation catalysts) to be 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 (XEB and Sₜ) under a rigorous non-oxidative environment excludes any redox action on the incident beam and a PIXcel solid-state detector in the 10−80° 2θ region with a 0.03° step size, operating with Cu Kα radiation (λ = 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 XPert 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 °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. Determination of Lewis and Brensted 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. 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 (~1.3 cm² 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 (Brensted acid sites) and LAS (Lewis acid sites) concentrations, expressed as μequivalents of adsorbed pyridine per gram of catalyst (μeq/gcat⁻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.

Steam- and Oxygen-Free Direct Dehydrogenation (DDH) of Ethylbenzene (EB) to Styrene (ST) Using γ-Al₂O₃, α-Al₂O₃β, or γ-Al₂O₃@CᵢC₅H₆ as Catalyst Precursors.

In a typical procedure, 300 mg of a selected catalyst precursor (γ-Al₂O₃—CK-300 Ketjen (Sₜ = 249 ± 10 m² g⁻¹) in the form of extruded trilobs (~1 mm × ~4 mm), α-Al₂O₃ in the form of beads 1.6 mm (Sₜ = 6 ± 2 m² g⁻¹, Sasol), or γ-Al₂O₃@CᵢC₅H₆ (Sₜ = 267 ± 10 m² g⁻¹) in the form of extruded trilobs (~1 mm × ~4 mm)) was charged inside a tubular quartz reactor (Φ × L: 8 × 800 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-Al$_2$O$_3$@C$_{G-H}$, 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-Al$_2$O$_3$@C$_{G-H}$ was directly prepared in situ starting from a He-purged γ-Al$_2$O$_3$ sample that underwent treatment with a mixture of C$_2$H$_6$, 5 vol % in He γ 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 52CB column. EB conversion ($X_{EB}$) and ST selectivity ($S_{ST}$) were evaluated using eqs 1 and 2:

$$X_{EB} = \frac{F_{0} - F_{EB, inlet}}{F_{0} - F_{EB, outlet}} \times 100\%$$

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

where $F$ and $F_0$ are the flow rates at the reactor outlet and inlet, respectively, and $X_{EB}$, $S_{ST}$, $C_{TOL}$, 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**

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-Al$_2$O$_3$ and γ-Al$_2$O$_3$@C samples; TGA/DTG profiles of γ-Al$_2$O$_3$@C samples; nitrogen adsorption−desorption isotherm linear plots (BET) and pore volume distributions (BJH); Raman spectra; additional DDH tests with α-Al$_2$O$_3$@C; LAS determination via FT-IR spectroscopy; TEM images of coked γ-Al$_2$O$_3$@C samples (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


