Chapter 2

Making Coke a more Efficient Catalyst in the Oxidative Dehydrogenation of Ethylbenzene using wide-pore Transitional Aluminas

The thermal activation of a silica-stabilized γ-alumina impacts positively on the oxidative dehydrogenation of ethylbenzene (EB) to styrene (ST). A systematic thermal study reveals that the transition from γ-alumina into transitional phases at 1050 °C leads to an optimal enhancement of both conversion and selectivity under pseudo-steady state conditions; where active and selective coke has been deposited. The effect is observed in the reaction temperature range of 450-475 °C at given operation conditions resulting in the highest ST yield, while at 425 °C this effect is lost due to incomplete O₂ conversion. The conversion increase is ascribed to the ST selectivity improvement that makes more O₂ available for the main ODH reaction. The fresh aluminas and catalytically active carbon deposits on the spent catalysts were characterized by gas adsorption (N₂ and Argon), acidity evaluation by NH₃-TPD and pyridine adsorption monitored by FTIR, thermal and elemental analyses, solubility in CH₂Cl₂ and MALDI-TOF to correlate the properties of both phases with the ST selectivity enhancement. Such an increase in selectivity was interpreted by the lower reactivity of the carbon deposits that diminished the COₓ formation. The site requirements of the optimal catalyst to create the more selective coke is related to the higher density of Lewis sites per surface area, no mixed Si-Al Brønsted sites are formed, while the acid strength of the formed Lewis sites is relatively weaker than those of the bare alumina.
2.1 Introduction

Styrene (ST) is industrially produced by direct dehydrogenation of ethylbenzene (EB) using steam at 580-630 °C [1]. The process suffers from high energy consumption due to low conversion per pass because of equilibrium limitations, and the high temperatures required for the endothermic reaction. The operation cost mainly depends on oil prices and utilities; decreasing the reaction temperature can have a remarkable market impact. Oxidative dehydrogenation (ODH) can address these drawbacks [2], but it is not commercialized among others mainly due to the limited catalyst stability and the lower selectivity to styrene.

A distinctive catalyst support for this reaction is γ-alumina due to its mild acidity as compared to e.g. zeolites. The coke deposits generated on the alumina under these oxidative reaction conditions do not produce deactivation, but promote the activity and selectivity [3-6]. There is a general consensus that these carbon deposits species are partially oxygenated and act as active and selective catalytic sites [3-17]. This has been confirmed by employing pre-coked catalysts [18] and by measuring the intrinsic activity of the carbon deposits separated from the alumina. Those carbon deposits were superior in respect to the alumina [6,15]. Nederlof et al. [17] demonstrated that this also holds for CO₂-assisted EB ODH; during the first 15 h time on stream the alumina shows an increase in ethylbenzene conversion from 15 to 60% and styrene selectivity from 60 to 92%. Characterizations of the Al₂O₃ samples after different times on stream show a clear correlation between the formed coke and the activity and selectivity. This is also shown in this work for the O₂-based EB ODH, where the activation period can be observed at reaction temperatures lower than 475 °C; at temperatures > 475 °C the coke build-up is fast.

The alumina by itself is not an inactive support but it provides Lewis centres and those generate 'good coke' [7,14,15]; the Brønsted acidity does not play a key role in forming selective coke for this reaction. These findings on active coke established a trend setting by using synthetic carbons that mimic the in-situ produced deposits during EB ODH [18-41]. Typically, their conversion levels are acceptable, 50-70%, while the styrene selectivity is relatively low for commercialization, up to 70%, compared to the commercial process of steam dehydrogenation (ST selectivity > 95%).

In the framework of the EB ODH catalyst development, less attention has been given on the use of inorganic supports, in particular about strategies to improve either conversion, selectivity or stability of their carbonaceous sites or combinations thereof. Few examples indicate that the acidity enhancement of γ-Al₂O₃ by H₃PO₄ [11] or HBO₃ [42,43] has a positive impact on the styrene yield. The effect of the texture of the alumina phases at high temperature, to the best of our knowledge, has not been investigated systematically. In this study, we use thermally treated SiO₂ promoted γ-Al₂O₃ at high temperature; the pore size is expanded by coarsening the nanoparticles to investigate the effect of pore size on the reaction performance. We have observed that this treatment also modifies the nature of the carbon deposit formed; making it less reactive and consequently more selective to ST. The relationships between EB ODH performance and the alumina and coke properties are discussed in this paper and rationalize previous observations [44] where the EB conversion and ST selectivity were optimal for a specific phase composition at high temperature.
2.2 Experimental

2.2.1 Materials

In this study a low SiO$_2$ stabilized γ-Al$_2$O$_3$ extrudates (Albemarle Catalysts BV) were employed. The extrudates were crushed and sieved into a 212-425 μm fraction used for the catalytic tests and characterization. The material was thermally activated at temperatures ranging from 500 to 1200 °C in ceramic crucibles using a box furnace in static air at a rate of 4 °C/min and held for 8 h. The samples were labeled as AluX00, where X00 corresponds to the treatment temperature in degree Celsius. Other inorganic commercial supports and catalysts were tested as reference: TiO$_2$ (Degussa, P25), SiO$_2$ (Fuji Silysia, G-6 5 microns), CeO$_2$ nanopowder (Sigma-Aldrich, 700290), mesoporous Al-MSU-F type (Sigma Aldrich, 643629) and Merck ultrapure alumina (1.01095.1000).

2.2.2 Characterization of bare and spent catalysts

The coke content and stability of the spent catalysts (after 60 h time on stream) were determined by thermogravimetric analysis in a Mettler-Toledo analyzer (TGA/SDTA851e) using a flow of synthetic air of 100 ml/min (STP). The temperature was increased from 30 to 900 °C at 10 °C/min. Blank curve subtraction using an empty crucible was employed.

CHN elemental analyses were carried out in a EuroVector 3000 CHNS analyzer. Approximately 2 mg of sample was accurately weighed in a 6-digit analytic balance (Mettler Toledo). The samples were burnt at 1800 °C in the presence of an oxidation catalyst and decomposed into CO$_2$, H$_2$O, and N$_2$. These gases are then separated in a Porapak QS column at 80 °C and quantified with a TCD detector. Acetonitrile (99.9%) was used as an external standard.

Textural analysis of the fresh and spent catalysts was carried out by N$_2$ and Ar physisorption at -196 °C and -186 °C, respectively, in a Micromeritics ASAP 2420 analyzer. Prior to the measurements all samples were outgassed under vacuum at 350 °C for 10 h for the fresh materials, while for the spent catalysts a mild degassing was applied, 130 °C for 24 h. The surface area was calculated by BET method [45], $S_{BET}$. The single point pore volume ($V_T$) was estimated from the amount adsorbed at a relative pressure of 0.98 in the desorption branch. The pore size distribution was derived from the BJH model [45]. For the fresh materials, the adsorption pore sizes are used. In case of spent catalysts, the desorption branch is favored to evidence the presence of closed pores.

NH$_3$-TPD experiments were carried out in a Micromeritics AutoChem II system equipped with a thermal conductivity detector (TCD). The sample (ca. 30 mg) was pre-treated by heating it up to 500 °C in He at 10 °C/min. The sample was cooled to 120 °C at a similar cooling rate, and then exposed to 1 vol% NH$_3$/He (25 ml/min) for 30 min. Subsequently, a flow of He (25 ml/min) was passed through the reactor for 60 min to remove weakly adsorbed NH$_3$ from the samples’ surface. After this baseline stabilization, the desorption of NH$_3$ was monitored in the range of 120-1000 °C using a heating rate of 10 °C/min.

The acidity was also evaluated by pyridine adsorption monitored by IR. FTIR spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a MCT-B detector and a quartz home-made IR cell having CaF$_2$ windows connected to a vacuum system that allows the controlled dosing of pyridine. Around 50 mg of sample were pressed in a 1.767 cm$^2$ self-supporting wafer and mounted into the quartz cell. Before dosing the pyridine, the sample was preheated under vacuum (5.10$^{-6}$ mm Hg) as follows: 120 °C for 2 h at 1 °C/min, then at 400 °C for 2h, 1 °C/min followed by cooling to 150 °C. Pyridine gas was dosed into the
sample wafer until full saturation at 150 °C (i.e. the pyridine bands become stable). Afterwards, the sample wafer was evacuated and cooled down to room temperature. Spectra were measured by accumulating 256 scans at a resolution 4 cm⁻¹; the spectrum of the sample after evacuation was subtracted to each spectrum. The strength of the acid sites was evaluated by recording the spectra after evacuating the sample at increasing temperatures, with 50 °C increments. The spectra were taken once the pressure remains stable. The density of acid sites was calculated according to Tamura et al. [46]:

\[ C_W = \frac{A \cdot S}{\varepsilon \cdot W} \]

where \( C_W \) is the acid site density (µmol/g); \( \varepsilon \) is the molar extinction coefficient (1.71 cm.µmol⁻¹ for Lewis sites on alumina [46]); \( S \) is the surface of the sample disc area (cm²), \( W \) the sample weight (mg), and \( A \) is the peak area (cm⁻¹).

The skeletal density was obtained by He pycnometry at room temperature after evacuating the sample chamber (1 ml) 5 times and measuring in 10 cycles; the standard deviation for each analysis is given.

XRD analysis was carried out in a Philips PW1840 using a CuKα radiation. The phase identification was done using the JCPDS database.

2.2.3 Characterization of the active coke

The coke nature and composition were analyzed after separating it from the inorganic support. The spent catalyst was treated in dichloromethane (CH₂Cl₂) under reflux for 6 h, which removes the soluble coke compounds retained on the sample [47]. The percentage of insoluble coke (IC) in total was determined by the difference in the TGA weight loss between the spent catalyst and the catalyst after refluxing in CH₂Cl₂. The carbonaceous insoluble compounds were obtained by treating the alumina matrix in a hydrofluoric acid solution (40 wt.% HF) at room temperature overnight, washing the residue by centrifugation and subsequently drying at 90 °C for 10 h. This produces brown-to-black particles that were subjected to CHN analysis to quantify the empirical CₓHᵧOᵣ formula. For the high-temperature spent samples, the alumina matrix could not be fully dissolved due to its inertness; the inorganic residue was taken into account for the calculations of the corrected C and H concentrations in the coke while O was calculated by difference. The presence of O₂, a temperature of 1800 °C and an oxidation catalyst in the CHN analysis can ensure that the formation of Al-oxycarbide is avoided.

The insoluble carbon material was mildly analyzed by MALDI time of flight (TOF) spectrometry [48-51]. These IC particles were suspended in tetrahydrofuran (THF) by sonication and mixed with dithranol as a matrix. MALDI spectra were recorded on an Applied Biosystems, Inc. Voyager-DE PRO spectrometer by pulsed ion extraction using a solid state laser with a wavelength of 355 nm. Laser desorption-ionization (LDI)-TOF was also performed in the same instrument. Samples were suspended in THF, 1 µL was spotted directly on a stainless steel target plate. In both modes, the measurements were performed in linear mode using positive ionization. Spectra were accumulated between 100 or 300 and 3000 or 10000 Da (depending on spectrum) and calibrated externally.

2.3 Catalytic tests

The catalytic tests were carried out in a parallel flow micro reactor using a fixed volume of catalyst (0.8 ml) using down-flow 4 mm quartz reactors. The reactors are typically loaded as follows: quartz wool, 10 cm glass pearls (0.5 mm diameter), the catalyst, 10 cm glass pearls (0.5 mm diameter), and a second quartz wool plug. In this way, it is assured that the catalyst bed is located in the isothermal operational zone of the furnace. In all cases the same volume of catalyst bed was used,
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corresponding to 65 mm of bed length; so the sample mass increases with increasing packing density of the catalyst. The inertness of the glass beads was verified as they showed less than 3% EB conversion under all applied conditions. The reactor gas feed is a mixture that can consist of CO\textsubscript{2}, N\textsubscript{2}, and air that counts for a gas-flow rate of 36 ml (NTP)/min; the liquid EB-feed flow rate is 1 g/h (3.54 ml (NTP)/min vapour) that is evaporated upstream each reactor in a α-Al\textsubscript{2}O\textsubscript{3} column, resulting in a 1:9 molar ratio of ethylbenzene to gas (10 vol. % EB). This corresponds with operation at a GHSV of 3000 l/l/h. The total pressure was 1.2-1.3 \times 10^{5} Pa. The pseudo steady-state conditions refer at the reaction time where both the conversion and selectivity achieve the highest values, which are typically achieved after 2 to 6 h time on stream; the reported conversion data are given at 6-10 h time on stream or longer. The conversion and selectivity were averaged in the isothermal period after reaching pseudo steady-state conditions. We state ‘pseudo steady state conditions’ because after the conversion and selectivity achieve a maximum, they start both to decline slowly; most probably due to excessive coke build-up. The standard deviations were below 2% (see example Table S-1 in appendix) for all cases. The reactor exhaust gas was analyzed by gas chromatography using a combination of columns (0.3m Hayesep Q 80-100 mesh with back-flush, 25m × 0.53mm Porabond Q, 15 m × 0.53mm molsieve 5A and RTX-1 with 30m × 0.53mm), and TCD and FID detectors. This configuration allows the quantification of permanent gases such as CO\textsubscript{2}, H\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2}, CO as well as hydrocarbons (typically, methane, ethane, ethene, benzene, toluene, ethylbenzene, styrene, and heavy aromatics).

The catalytic tests were carried out under practical conditions of 20 % excess O\textsubscript{2} with respect to the ODH reaction, a concentrated EB feed of 10% and constant bed volume. Unless stated otherwise, for all EB conversion data the oxygen conversion is complete. The oxygen is used to generate coke, to convert ethylbenzene mainly into styrene, and to convert deposited coke into CO\textsubscript{x}. Since the selectivities to side products are small and almost constant as a function of the reaction conditions, the selectivity to styrene (ST) is in principle directly coupled to CO\textsubscript{x}. These two combined selectivities (CO\textsubscript{x} and ST) are on average responsible for 96% of the converted ethylbenzene. All physical characterizations for the spent catalysts and derived coke were done after the complete testing cycle of 60 h. Due to the O\textsubscript{2} gradient in the reactor, the coke will never be a steady-state material. Because of that, we took the complete sample, mix it and used it for characterization as an average sample of the reactions conditions applied, location in the bed, and time on stream.

2.4 Results and discussion

2.4.1 Pseudo steady-state ODH performance

Under pseudo steady-state conditions, typically after 5 h on-stream, the bare γ-Al\textsubscript{2}O\textsubscript{3} outperforms other commercial supports such as CeO\textsubscript{2}, TiO\textsubscript{2}, and SiO\textsubscript{2} (data not shown). The bare alumina (S\textsubscript{BET} = 272 m\textsuperscript{2}/g and 0.389 ml/g pore volume) is an optimized industrial catalyst support that is stabilized with SiO\textsubscript{2}; it has an extraordinarily high surface area and pore volume. The thermal activation of the bare γ-alumina was carried out to expand the pore size by coarsening the nanoparticles and investigate its effect on the reaction performance. Remarkably, both conversion of EB and selectivity to ST steadily increase with pretreatment temperature (Figure 1), showing an optimal temperature at 1050 °C (Alu1050) above which both quantities dropped significantly.
In all cases the oxygen was completely converted. The maximum ST yield of 35% was found for the Alu1050, which corresponds to ca. 22% relative increase to the Alu500 at the given GHSV of 3000 l/l/h. Figure 2-a represents the ST yield versus time on stream at various temperatures and EB:O₂ ratios for Alu500 and Alu1050. The positive effect of the calcination was observed at 450 and 475 °C reaction temperature at which full O₂ conversion was observed. At 425 °C the O₂ conversion was not complete for the Alu1050 and the catalyst performance trend was reversed (Alu500>Alu1050). It should be noted that the O₂ conversion was not always complete for some catalysts at 425 °C; this means that the O₂ concentration profiles decrease variably over the reactor bed for the Alu series (i.e. smoother or sharper). Hence, the ‘active catalyst reactor volume’ where oxygen is present is variable as a function of reactor length. This makes the comparison of the intrinsic activity complex at 425 °C. Therefore, the discussion in this paper refers to reaction temperatures ≥450 °C, where full oxygen conversion was achieved. At these temperatures, the complete catalyst bed was taken as reference for the interpretation.

Figure 2-a also evidences that the catalysts are deactivating as a function of time on stream, most probably due to ongoing coke deposition on the coked catalysts. Figure 2-b represents the time dependency at 450 °C for Alu500 (O₂:EB=0.6); it shows the activity and selectivity increase during the initial coke formation before achieving a pseudo stationary state. This is in agreement with Nederlof et al. [17] for the CO₂-assisted EB ODH, it is attributed to the formation and deposition of active coke on the alumina surface. From a practical standpoint it is beneficial starting the catalyst performance tests at the highest temperature, i.e. 475 °C, because the coke build-up is faster than that at 425-450 °C; in this way the pseudo-steady state is achieved at shorter time. This can be seen by comparing the initial performance (<5 h) for Alu500 in Figure 2-a (475 °C) and Figure 2-b (450 °C): at 450 °C the pseudo stationary conditions are achieved after 6 h, while this is reduced to 3 h at 475 °C.

From Figure 2-a, increasing the O₂:EB ratio may look favorable in terms of the overall ST yield but this will have a penalty in the selectivity to ST; a high selectivity is one of the major targets in the O₂ EB ODH to compete with the existing steam-based process. It must be emphasized that the catalytic performance in Figure 1
corresponds to pseudo-steady state conditions between 5-10 h time on stream with significant coke build up. Assuming the density of graphene (0.76 mg/m²) the number of coke layers is nearly 2.4 for Alu500 and it increases up to 3.4 for Alu1050. Therefore, we assume this increased performance corresponds to the coke deposits; no interaction between the reactants with the alumina surface or the interface alumina-coke is expected.

Figure 2. a) Time on stream performance at various temperatures of the optimal Alu1050 and Alu500 catalysts at various temperatures (475, 450, 425, and 450 °C) and O₂/EB= 0.6, 0.4 and 0.2 (vol). GHSV of 3000 l/l/h; b) time on stream dependency at 450 °C and O₂/EB= 0.6 (Alu500).

We first attempt to correlate this promoting effect to the total amount of carbon deposited, as it is considered the dominating active phase once the deposits are formed under pseudo-steady state conditions. The coke contents are displayed in Figure 3 as gravimetric quantity (i.e. g coke/g fresh alumina) as well as the volumetric coke (g coke/ml reactor bed); the latter can be more appropriately related to the product yield as it represents the actual amount of coke per reactor volume, taking into account that the performance is measured at fixed catalyst volume. From this representation, it can be unambiguously seen that the amount of volumetric coke progressively decreases with calcination temperature with a pronounced reduction above 1050 °C. Considering the increased ST product yield, this suggests that the coke becomes apparently more active (different species) or more selective for the ODH reaction. Calculation of the coke per surface area indicates that the coke on the low-temperature aluminas is more dispersed (160 μmol C/m² for Alu500) than the optimal Alu1050 (205 μmol C/m²).
Figure 3. Coke on catalyst (gravimetric and volumetric) determined by TGA as a function of the pretreatment temperature of the bare alumina after 60 hours, time on stream.

Regarding the selectivity effect, less of the available oxygen is used for the combustion-gasification of the deposited carbon; for Alu500 around 35% of the converted oxygen is used for ODH reaction, whereas this increases to 50% for the Alu1050 catalyst. The conversion increase cannot be justified by an additional pathway. Because we run at full O$_2$ conversion, part of the bed will be O$_2$ free. We did not observe changes in the heavy by-products composition indicating the stability of the by-products in the absence of O$_2$ (2% benzene/toluene and 2% oxygenated and heavy aromatics were observed in all the cases). The reaction temperatures (425-475 °C) are relatively low to justify the direct EB dehydrogenation; the conventional steam dehydrogenation is operated above 600 °C. If direct dehydrogenation would occur in the absence of O$_2$, a decrease in the EB conversion is expected due to the low equilibrium conversion at these temperatures (e.g. 20% at 450 °C, EB partial pressure of 0.1 bar [52]). The key aspect to explain the conversion increase is otherwise the improved selectivity to ST; a lower CO$_x$ formation will make more O$_2$ available for the main ODH reaction, and this is responsible for the conversion increase.

2.4.2 Textural properties of the alumina upon thermal treatment

The alumina surface has limited intrinsic activity with a low EB selectivity in the order of approximately 75% (Fig. 2-b), also observed in [15]. It is the coke deposited on the alumina surface that makes the catalyst more selective and active. However, the initial surface area and pore volume of the fresh alumina (and acidity) are important as these will determine how much and well dispersed the coke is. In addition, accessibility is highly important in heterogeneous catalysis, as diffusion limitations may completely deteriorate selectivity and reduce activity, especially for the much larger ethylbenzene with respect to oxygen. The texture and accessibility of the fresh aluminas were evaluated by textural properties as derived from N$_2$ physisorption. The textural parameters are plotted in Figure 4-a as a function of the calcination temperature. The marked reduction of surface area and pore volume is associated to the thermal coarsening of the alumina nanoparticles because the pore size increases. The BJH pore size distributions (PSD) shift towards larger pores (Figure 4-b); this is consistent with the reduction of the textural parameters. Figure 4-b additionally
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shows a broadening of the pore size distribution that is more evident for the Alu1000 upwards while full collapse occurs at 1150 °C. At 1050 °C, this corresponds to the optimal catalyst performance, the pore size distribution is broad, but still well-defined with a surface area of 101 m²/g. Analysis of an ultrapure gamma-alumina (without silica stabilization) calcined at 1050 °C shows 11 m²/g (Table S-3) and no PSD (Figure 4-c) due to structural collapse. Therefore, the preservation of the texture, or lack of pore collapse for the Alu1050 is associated to the promotion effect of silica [53]. The changes in texture were accompanied by a densification of the material with an increase of the skeletal density from 3.035 to 4.067 g/ml (Table S-2 in supplementary information).

The changes in texture of two relevant spent catalysts containing the coke were investigated as well and compared to the fresh counterparts. The isotherm of the fresh Alu500 is of the type IV with hysteresis H1 [54]; representing solids with cylindrical pore geometry with relatively high pore size uniformity and facile pore connectivity. However, the hysteresis changes into type H2 for the spent catalyst with a closure point at 0.45 relative pressure. Hysteresis H2 is believed to occur in solids where the pores have narrow necks and wide bodies, also called ink-bottle type pores, or when the porous material has interconnected pores. As the original material has no interconnectivity around 0.45 relative pressure, the spent Alu500 possesses pore neck restrictions attributed to the excessive coke build-up. This is consistent with the observed TSE effect at p/p₀ = 0.45 in the desorption branch, supposedly showing a uniform pore at 3.9 nm (inset in Figure 5-top). This is not due to a real pore but a physical phenomenon associated to the nature of the adsorbate; it is known that pore restrictions below 3.9 nm cannot be detected by N₂ because of this effect [55]. Therefore, we can only conclude that the TSE points out to pore restrictions smaller than 3.9 nm; it is uncertain whether these restrictions are relevant for this reaction in terms of mass-transfer limitations. The isotherm for the spent Alu1050 (Figure 5-bottom) maintains the H1 hysteresis (as for the fresh counterpart) with no detection of the TSE effect in the desorption PSD. This indicates that the pore expansion by high temperature calcination and limited coke build-up keep the pores accessible during the reaction.
Figure 4. a) Specific surface area and total pore volume as a function of the calcination temperature of the alumina; b) BJH pore size distribution using the adsorption branch of the isotherm; both derived from N$_2$ physisorption at -196 °C; c) Comparison of the PSD between Alu1050 and an ultrapure alumina (Merck) calcined at 1050 °C (C1050).
2.4.3 Acidic properties of the alumina upon thermal treatment

The acidity properties were evaluated by temperature programmed desorption of NH$_3$ in order to understand the reasons why the wide-pore SiO$_2$ promoted θ-alumina phase becomes a better selective coke-forming support with the calcination temperature. The TPD profiles (Figure S-1) are formed by two contributions centered at 250 and 600 °C that do not change in position in the Alu series, representing weak and stronger sites. The quantification of the total acidity per catalyst volume displays a threshold value of 385 to 420 μmol/ml-cat, which drops significantly after calcination of the alumina at 1100 °C to 245 μmol/ml-cat. A commercial ultra-pure γ-Al$_2$O$_3$ was thermally treated at 1000 °C and its acidity was quantified by NH$_3$-TPD (Figure S-1 and Table S-2). It clearly shows a less intense desorption profile with a very low acidity (90 μmol/g), while the corresponding Alu1000 has 436 μmol/g; hence the high acidity is attributed to the silica promotion.

The acidity of relevant catalysts of the series (Alu500 and Alu1050) was further assessed by pyridine adsorption, monitored by FTIR; this technique is unique in providing information about the nature and strength of the acid sites. The spectrum of the bare Alu500 (Figure 6-left and a) shows a distinctive adsorption of pyridine on Lewis Al sites at 1449 cm$^{-1}$; no Brønsted sites were detected that
typically appears at 1545 cm\(^{-1}\) [46]. This consequently implies that there are no aluminosilicate domains; silica and alumina are present as separate phases. This is in agreement with results of Daniell \textit{et al.} [56] that observed independent phases up to 5 wt.% silica in alumina. Therefore, the 1 wt. % silica present in bare alumina is a textural promoter that avoids thermal coarsening of the alumina crystallites and prevents pore collapse, as discussed in 2.4.2. At room temperature the Lewis sites density of Alu500 is 126 \(\mu\)mol/g (Table 1) that is in agreement with reported values [46,57]. It is remarkable that the density obtained from NH\(_3\) TPD is a factor 5 higher than pyridine. This is likely due to the fact that NH\(_3\) is less selective and accounts for the adsorption on crystallographic defects. The density of acid sites per surface area was further quantified using Argon physisorption (Table S-2) instead of N\(_2\). The quadrupole moment of the nitrogen molecule on highly hydroxylated surfaces causes an orientation effect of the adsorbed nitrogen molecules [58]; this can be solved using Argon physisorption at 87 K. The acid site surface density results in 0.33 sites/nm\(^2\) for the Alu500 (Table 1). The strength of the Lewis sites was evaluated after desorbing pyridine at increasingly higher temperatures up to 400 °C (Figure 6-left, spectra b-g). Quantification of the acid sites density at each evacuation temperature indicates a drop from 126 to 33.9 \(\mu\)mol/g at 400 °C (Table 1).

Alu1050 shows Lewis sites at 1449 cm\(^{-1}\) (Figure 6-right and a) with a density of 138.9 \(\mu\)mol/g (Table 1). Brønsted sites were not detected, thus the thermal treatment at 1050 °C does not produce the mixing between silica and alumina and remain as separate phases. The acid site surface density using Ar physisorption is of 1.39 sites/nm\(^2\), that is relatively higher than that of the Alu500 (0.33 sites/nm\(^2\)). The acid strength of the Lewis sites was distinctively inferior to the Alu500. At 250 °C Alu1050 has 5 times less sites than that of Alu500, and pyridine was fully desorbed at 350 °C, while Alu500 still has 49.7 \(\mu\)mol/g at this temperature of 350 °C.

It is concluded that Alu1050 has a high acid site density per surface area, higher surface area than non-silica promoted alumina calcined at 1050 °C; both effects are ascribed to the silica promotion, while the Lewis sites are relatively weaker than that of Alu500.
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Figure 6. IR spectra of adsorbed pyridine after evacuation at various temperatures for Alu500 (left) and Alu1050 (right): a) room temperature; b) 150; c) 200; d) 250; e) 300; f) 350 and g) 400ºC.

Table 1. Lewis acid sites densities determined by FTIR pyridine adsorption.

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<th>Temperature (ºC)</th>
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<th>Alu1050</th>
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<tr>
<td></td>
<td>μmol/g</td>
<td>sites/nm²</td>
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<td>400</td>
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a. Evacuation temperature; b. Using S BET values derived from Ar physisorption at -186 ºC.

2.4.4 Coke nature and reactivity

In this section the nature of the coke will be discussed based on solubility in CH₂Cl₂, thermal analysis (TPO), chemical analysis (CHN), and MALDI information; the latter two techniques were applied on carbonaceous residues after a process of dissolution of the alumina.

The importance of the insoluble coke comes from the fact that the fraction of coke that is less active in styrene production, burns more easily under oxidative
conditions, and its nature corresponds to soluble coke; therefore insoluble coke (IC) determines the product yield (conversion times selectivity) [9,12,15]. The proportion of insoluble coke after refluxing the spent catalysts in CH₂Cl₂ was quantified (Table 2). The differences among the aluminas are undetectable, always IC > 97%, and cannot explain the differences in selectivity discussed in Figure 1. The chemical composition of the insoluble carbon deposits was further characterized after dissolving in HF the alumina from the spent catalysts. It was found that the high temperature aluminas were substantially inert and hard to dissolve completely, showing an ash residue of ca. 8-9 wt. %. Because of that, the elemental composition was tentatively corrected using the TGA residue. The chemical composition of representative samples of the low- and high-temperature treatments is given in Table 2 and plotted in a Van Krevelen-type plot (Figure 7-a) together with several reference catalysts. The C:H molar ratio stays in the typical range (1.8-2.5) reported for other untreated γ-Al₂O₃ and modified counterparts [7,15], that is typical of polycondensed/aromatic coke. The high temperature aluminas produced a priori a substantial amount of oxygen-rich coke with O:C molar ratios of 0.20 (0.19 duplo) and 0.29 (0.27 duplo). In particular, the Alu1050 has a higher concentration of oxygenates and less hydrogen, C:H=2.21; indicating less condensation apparently.

Table 2. Chemical characteristics of the coke for representative low and high temperature spent catalysts after HF treatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>IC (%)</th>
<th>Residue (%)</th>
<th>Compositional formula (at.)</th>
<th>C:H (at.)</th>
<th>O:C (at.)</th>
<th>PD (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alu500</td>
<td>99</td>
<td>1.0</td>
<td>C₅.₅₂H₂.₀₂O</td>
<td>2.73</td>
<td>0.18</td>
<td>86</td>
</tr>
<tr>
<td>Alu600</td>
<td>98</td>
<td>1.4</td>
<td>C₆.₇₂H₂.₃₉O</td>
<td>2.₈₁</td>
<td>0.₁₅</td>
<td>93</td>
</tr>
<tr>
<td>Alu1000</td>
<td>97</td>
<td>8.₆</td>
<td>C₅.₂₀H₁.₈₁O</td>
<td>2.₇₆</td>
<td>0.₂₀</td>
<td>1₄₁/₁₆₅d</td>
</tr>
<tr>
<td>Alu1050</td>
<td>&gt;99</td>
<td>8.₄</td>
<td>C₃.₄₇H₁.₅₇O</td>
<td>2.₂₁</td>
<td>0.₂₉</td>
<td>2₃₀</td>
</tr>
</tbody>
</table>

a) Insoluble coke after refluxing in CH₂Cl₂.
b) Alumina residue due to incomplete dissolution in 30 wt. % HF.
c) Pore diameter (PD) for the corresponding alumina at the pore size distribution maxima (Figure 4).
d) Cylindrical geometric value calculated as 4(Vₜ)/S BET as having a substantially more asymmetric pore size distribution.
Figure 7. a) Modified Van Krevelen plots representing the composition of the carbon deposits of various Alu samples (Table 2) as well as data adapted from prior work [7,15]; b) oxidation rate in air (TPO) using the TGA derivative patterns of the spent Alu catalysts (>60 h time on stream).

It is remarked that the variability in the ash content within a sample for the high temperature alumina introduces uncertainty in the representativeness of the samples used in the TGA and CHN analyses. As the oxygen content is very sensitive to the ash residue, we believe that the relatively high oxygen content for Alu1050 derived coke can be due to an overestimation. This is supported by the coke oxidation patterns (discussed later in Figure 7-b); no promotion to lower temperature was observed that would be expected for such an oxygen-rich coke.

The insoluble coke was analyzed by MALDI and LDI time-of-flight mass spectrometry. These techniques use a mild ionization and reflect directly the molecular distribution of the carbon deposits as the energy input of the laser is low. LDI is particularly selective to oxidized products and was chosen for these ODH carbon deposits, as the matrix addition made the spectra interpretation more complex. The spectrum of the Alu500 derived insoluble coke shows a wide molecular distribution of masses centered on ca. 1500 Da (Figure 8-a). The spectrum can be assigned to large platelets of polyaromatic hydrocarbons up to 4500 Da, as it shows long series with 24 Da of mass increase revealed upon high resolution magnification (insets in Figure 8). This is due to the addition of –CH=CH– entity to build a new aromatic ring, with the abstraction of two hydrogen atoms from the main aromatic-polycondensed structure. The interpretation of this spectrum, is in agreement with the Iwasawa-Ogasawara quinone-based active site model postulated for the EB ODH reaction: condensed aromatic rings with conjugated double bonds containing quinone/hydroxyquinone C=O functional groups [5,59-61]. However, the O groups must be embedded in the lighter units (<500 m/z) as no mass increase involving O was observed. The spectrum of the Alu1050 (Figure 8-c) shows also a 24 Da C2H2 increase, in agreement with the enlargement of the condensed rings. The emission intensity of a LDI spectrum gives a proof of the coke nature; the intensity is a measure of the coke reactivity (i.e. oxidation ability) as the emission is directly coupled to ionization. The comparison of the emission intensities in Figure 8 evidences the low reactivity of the Alu1000 and Alu1050 derived cokes as compared to the Alu500, in a factor of ca. 2.5 to 10.
Figure 8. LDI time-of-flight spectra of the thermally treated alumina: a) 500 °C (300 shoots, top); b) 1000 °C (400 shoots, middle) and c) 1050 °C (400 shoots, bottom).

The thermal stability of the carbon deposits is related to the mechanism of total oxidation in EB ODH and can explain the selectivity trends; CO<sub>x</sub> in EB ODH results from the combustion of the carbon deposits rather than from the direct combustion of ethylbenzene [15]. Looking at the oxidation rate patterns of the spent catalysts (Figure 7-b), a trend exists with a shift of ca. 20 K towards higher temperatures in the maxima with increasing the calcination temperature of the alumina. This enhanced oxidation stability can explain the lower formation of CO<sub>x</sub> and, consequently the increase of the ST selectivity. The TPO shift in the carbon oxidation rate is consistent with the lower ionization intensity of the MALDI pattern for the optimal Alu1050. Hence, the increased oxidation stability indicates the lower reactivity of the Alu1050-derived coke and can explain the selectivity increase to ST. The increased oxidation stability of the coke can be ultimately attributed to the acidity and textural changes upon thermal treatment. Alu1050 has higher density of Lewis acid sites per surface area, it does not collapse texturally keeping 101 m<sup>2</sup>/g (compared to a non-silica promoted alumina calcined at 1050 °C with 11 m<sup>2</sup>/g); both effects are ascribed to the silica promotion. Si-Al Brønsted acid sites are not involved, while the acid strength of the Lewis sites is relatively weaker (the “good” Lewis acidity) than the low-temperature Alu500. Other phenomenon that changes the surface chemistry of the alumina upon thermal treatment cannot be ruled out to play a role too; for instance, the surface segregation of impurities upon thermal treatment [62].

2.5 Conclusions

Modification of a SiO<sub>2</sub>-stabilized γ-alumina by thermal treatment into a transitional phase having wider pores and a high density of Lewis sites per surface area enhance the conversion and selectivity for the oxidative dehydrogenation of ethylbenzene to styrene; the effect is observed when the O<sub>2</sub> conversion is complete. The EB conversion increase comes from the ST selectivity enhancement that makes more O<sub>2</sub> available for the main ODH reaction. The ST selectivity improvement is attributed to the coke nature that is less reactive and consequently less prone to CO<sub>x</sub> formation. The site requirements of the optimal catalyst to create the more selective coke seem to be related to the higher density of Lewis sites per surface area, no mixed Si-Al
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Brønsted sites are involved, while the acid strength of the Lewis sites is relatively weaker.

2.6 References

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Figure S-1. NH₃ temperature programmed desorption (TPD) profiles: a) Alu series and b) comparison with a commercial γ-Alumina (Merck 1.01095.1000) calcined at 1000 °C.

Figure S-2. Nitrogen sorption isotherms at -196 °C K for the fresh Alu series.
Table S-1. Example of the accuracy of the conversion and selectivity quantities

<table>
<thead>
<tr>
<th>Data points</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35.71</td>
<td>81.36</td>
</tr>
<tr>
<td>2</td>
<td>36.18</td>
<td>82.71</td>
</tr>
<tr>
<td>3</td>
<td>35.62</td>
<td>84.13</td>
</tr>
<tr>
<td>4</td>
<td>36.08</td>
<td>82.64</td>
</tr>
<tr>
<td>5</td>
<td>34.99</td>
<td>82.94</td>
</tr>
<tr>
<td>6</td>
<td>34.98</td>
<td>82.26</td>
</tr>
<tr>
<td>7</td>
<td>34.54</td>
<td>82.79</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>35.44</strong></td>
<td><strong>82.69</strong></td>
</tr>
<tr>
<td>σ (%)</td>
<td>1.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>
### Table S-2. Structural, textural and acidic properties of the fresh thermally treated aluminas.\(^a\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>(V_T) (cm(^3)/g)</th>
<th>(V_T') (cm(^3)/ml bed)(^b)</th>
<th>(S_{BET}) (m(^2)/g)</th>
<th>(S_{BET}') (m(^2)/ml bed)</th>
<th>(D_{BJH\ ads}) (Å)</th>
<th>Density (g/cm(^3))</th>
<th>Acidity ((\mu)mol/g)</th>
<th>Acidity ((\mu)mol/ml bed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>(\gamma)</td>
<td>0.639 (0.628)</td>
<td>0.389 (0.382)</td>
<td>272</td>
<td>165 (138)</td>
<td>84</td>
<td>3.035</td>
<td>637</td>
<td>388</td>
</tr>
<tr>
<td>Alu500</td>
<td>(\gamma)</td>
<td>0.649 (0.661)</td>
<td>0.431 (0.439)</td>
<td>271</td>
<td>180 (152)</td>
<td>86</td>
<td>3.108</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Alu600</td>
<td>(\gamma)</td>
<td>0.644</td>
<td>0.446</td>
<td>255</td>
<td>177</td>
<td>93</td>
<td>3.084</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Alu700</td>
<td>(\gamma)</td>
<td>0.635</td>
<td>0.402</td>
<td>239</td>
<td>151</td>
<td>101</td>
<td>3.003</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Alu800</td>
<td>(\gamma)</td>
<td>0.636</td>
<td>0.436</td>
<td>214</td>
<td>147</td>
<td>118</td>
<td>3.099</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Alu900</td>
<td>(\delta)</td>
<td>0.608 (0.593)</td>
<td>0.473 (0.461)</td>
<td>179</td>
<td>139 (108)</td>
<td>138</td>
<td>3.295</td>
<td>540</td>
<td>420</td>
</tr>
<tr>
<td>Alu1000</td>
<td>(\theta)</td>
<td>0.492</td>
<td>0.435</td>
<td>119</td>
<td>105</td>
<td>141</td>
<td>3.316</td>
<td>436</td>
<td>385</td>
</tr>
<tr>
<td>Alu1050</td>
<td>(\theta)</td>
<td>0.458 (0.382)</td>
<td>0.327 (0.273)</td>
<td>101 (60)</td>
<td>72 (43)</td>
<td>230</td>
<td>3.376</td>
<td>398</td>
<td>284</td>
</tr>
<tr>
<td>Alu1100</td>
<td>(\theta)</td>
<td>0.354</td>
<td>0.356</td>
<td>54</td>
<td>54</td>
<td>294</td>
<td>3.658</td>
<td>244</td>
<td>245</td>
</tr>
<tr>
<td>Alu1150</td>
<td>(\theta,\alpha)</td>
<td>0.165</td>
<td>0.157</td>
<td>20</td>
<td>19</td>
<td>330(^d)</td>
<td>4.009</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Alu1200</td>
<td>(\theta,\alpha)</td>
<td>0.117</td>
<td>0.143</td>
<td>16</td>
<td>20</td>
<td>293(^d)</td>
<td>4.067</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>C1050(^f)</td>
<td>(\theta,\alpha)</td>
<td>0.051</td>
<td>–</td>
<td>11</td>
<td>–</td>
<td>185(^d)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^{a}\) \(\text{\(N_2\) (-196 °C) isotherms are given in Figure S-2 and NH}_3\)-TPD in Fig. S-1.  
\(^{b}\) Quantity per reactor volume.  
\(^{c}\) Skeletal density.  
\(^{d}\) Geometrical pore size as there is no maximum in the BJH pore size distribution.  
\(^{e}\) Values between brackets are derived from Argon physisorption at -186 °C.  
\(^{f}\) Ultrapure alumina (commercial: Merck 1.01095.1000) thermally treated at 1050 °C.