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Production and testing of technical catalyst based on MnO_2 for the abatement of aromatic volatile compounds at the laboratory and pilot plant scale

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ABSTRACT

Shaping is a crucial step to produce technical catalysts that remains as some sort of dark art for catalytic researchers in academia. This contribution discusses aspects concerning the fabrication of technical catalysts based on MnO₂ powders aimed for the combustion of hazardous aromatic compounds; namely, benzene and styrene. Both laboratory and pilot plant scale catalytic tests were conducted over tablets and extrudates of the technical catalyst. Key physicochemical properties of these materials; namely, surface area, porosity, crystallinity, and mechanical resistance, were assessed and correlated to the catalytic behaviour. On the one hand, the paper describes the hurdles to be overcome when formulating and testing a technical catalyst whose characteristics must be a good compromise between its physicochemical properties and catalytic behaviour at the pilot plant scale. Furthermore, the importance of adopting adequate security and waste management protocols for testing technical catalysts is highlighted. On the other hand, the following conclusions were drawn from the analysis of results: (i) Between tableting and extrusion, only the latter was found to produce shaped bodies with suitable mechanical resistance for pilot plant scale tests. (ii) Calcination of the fabricated extrudates at temperatures from 500 °C leads to a crystallographic transformation of the MnO_2 that had a positive impact on the intrinsic activity of the technical catalyst while favouring its mechanical resistance owing to densification at the expense of a decrease in surface area and enlargement of pore size distribution. (iii) Thanks to pilot plant testing of the catalysts, it was possible to identify a detailed reaction scheme for styrene combustion in which besides the occurrence of oxidation, reactions of hydrogenation, dehydrogenation, ring opening, and isomerization take place by a combination of both surface and free radical mechanisms.

1. Introduction

This paper is a new contribution from a research project that aims for the establishment of scientific bases for understanding the effects of shaping on the physicochemical properties and functionalities of catalytic materials [1–4]. To academic researchers, shaping is nothing short of an alien operation that is left to industrial partners. In turn, the latter prefer keeping their knowledge and expertise on the subject as a secret. However, if a catalytic researcher ever aspires to take its work to industrial or at least pilot scale fruition she or he (or they) will inevitably be confronted to find a suitable formulation; i.e. a technical catalyst, for obtaining mechanically resistant bodies conserving the catalytic properties determined in laboratory scale tests and adapted to the reactor in which the concerned process is to be conducted [5]. In the case of fixed-bed reactors, a technical catalyst must normally withstand harsh temperatures and sudden changes in feed composition without physically and chemically degrading while keeping a reasonable pressure drop during operation. Tablets and extrudates are preferred for fixed bed reactors [6–8]. The addition of binders, lubricants

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Fig. 1. Pictures of: a) Mini Press Rimek II for the tableting operation as located at the former *Kilolab* in UCLouvain, Belgium. b) Lateral view of the Mn-3G-25Al tablets. c) Top view of a Mn-3G-25Al tablet after a manual shear stress test.



Fig. 2. Pictures illustrating the process for producing MnO₂ extrudates at the former Kilolab, UCLouvain, Belgium: a) Kneading of MnO₂ powder with kaolin -Base Powder, B.P.-. b) Milling of B.P. with colloidal silica. c) Dough of the extrusion mixture. d) Production of MnO₂ extrudates with a screw extruder fed manually. e) Batch of MnO₂ extrudates.



Fig. 3. Pictures of the pilot plant unit for testing catalysts at the kilogram scale: a) General view of the pilot plant. *Fan for saturating the gas flow feed to the reactor. **Plastic drum containing liquid styrene. *PID control panel for temperature. **Preheating section before reactor inlet. *Thermally insulated reactor section. b) Top view of the interior of the plastic drum containing liquid styrene stored in an open recipient. c) Lateral view of the fixed-bed reactor without thermal insulation. d) Top view of the interior of the reactor showing, from bottom to top, a pricking for collecting gases from the inlet stream, a thermowell, and the bottom sieve for holding the catalyst. e) Top view of the reactor after showing the upper sieve for adjusting the catalytic bed height with the corresponding positioning rods and the top gas pricking and thermowell for the reactor outlet gas stream.



Fig. 4. Axial (σ_2) and lateral (σ_3) compression strengths of samples of a batch of Mn-3G-10Al tablets as a function of their height (H).

Table 1

Averages (Aver.) and standard deviations (s) for the axial (σ_z) and lateral (σ_x) compression strengths for samples taken from manufactured batches of MnO₂ tablets. NC = Not calcined. Std = Standard calcination; Fsh = *flash* calcination; N.D. = Not Determined. G = Graphite; Al = Aluminum hydroxide; Nomenclature key: Mn-3G-10Al-Fsh-435 = tablets prepared with a mixture of 3.0 wt.% G, 10 wt.% Al, and calcined with the *flash* procedure at 435 °C.

| Material | Aver. σ_z (MPa) | s (MPa) | Aver. σ_x (kPa) | s (kPa) |
|--------------------|------------------------|---------|------------------------|---------|
| Mn-3G-25Al-NC | 11.8 | 3.9 | N.D. | N.D. |
| Mn-3G-25Al-Fsh-500 | 11.8 | 3.4 | N.D. | N.D. |
| Mn-3G-10Al-NC | 6.9 | 3.1 | 211.1 | 117.2 |
| Mn-3G-10Al-Std-150 | 8.4 | 4.9 | N.D. | N.D. |
| Mn-3G-10Al-Std-250 | 8.6 | 4.9 | N.D. | N.D. |
| Mn-3G-10Al-Std-320 | 8.8 | 5.1 | N.D. | N.D. |
| Mn-3G-10Al-Std-435 | N.D. | N.D. | N.D. | N.D. |
| Mn-3G-10Al-Fsh-150 | 9.3 | 3.9 | 206.6 | 98.6 |
| Mn-3G-10Al-Fsh-250 | 10.0 | 4.2 | 251.4 | 109.8 |
| Mn-3G-10Al-Fsh-320 | 9.1 | 5.3 | 201.3 | 89.4 |
| Mn-3G-10Al-Fsh-435 | N.D. | N.D. | 324.9 | 148.4 |
| Mn-3G-10Al-Fsh-500 | N.D. | N.D. | 225.2 | 133.9 |



Fig. 5. X-ray diffraction patterns of samples taken from a batch of tablets branded as Mn-3G-10Al; 3 wt.% graphite, 10 wt.% aluminum hydroxide, after calcination at different temperatures. Crystalline facets were assigned according to Xie et al. [36] for materials calcined at T < 500 °C and to Wei-Chieh et al. [39] for the material calcined at 500 °C.

and other additives to the catalytic powder during shaping is common practice. The presence of these additives can modify the catalytic properties exhibited by the original powder to a significant extent [6–10].

Previous reports from this project [2,4] have analyzed the effect of tableting for the formulation of technical catalysts based on vanadium aluminum mixed oxides employed in oxidation reactions. For this contribution, the emphasis is put into the analysis of key physicochemical properties and catalytic performance of MnO_2 based materials shaped by tableting and extrusion and employed in the abatement of aromatic volatile organic compounds (VOCs) at both the laboratory and pilot plant scales. The behavior of MnO_2 powders was extensively tested in VOCs abatement at UCLouvain in the past [11–14]. It was determined that this material is promising for industrial applications. Such results have been confirmed by independent researchers [15–17].

2. Experimental

This section describes the procedures employed for making tablets and extrudates based on $\gamma\text{-MnO}_2$ powder. The techniques for assessing some of the characteristics of these shaped bodies are presented next. Finally, the methods employed for the catalytic evaluation of the shaped materials are described.

2.1. Preparation of the shaped materials

2.1.1. Tablets

Tablets were prepared following procedures similar to the ones presented in our previous contributions [1,2,4]. The MnO₂ powder $(\rho_{App} = 1800 \text{ g/m}^3, \text{ particle size} < 100 \text{ }\mu\text{m})$ was gently provided by Erachem, Comilog (Faradiser M, LOT 622) and used without any treatment. MnO2 was mixed with graphite (Merck, commercial grade) and aluminum hydroxide -gibbsite- (Alcoa, commercial grade). The mixture was composed of 72 wt.% MnO2, 3 wt.% graphite, and 25 wt.% of aluminum hydroxide. The choice of graphite as a binding agent was made as in consideration to the findings presented in our previous contributions [1,2,4]. Particularly, graphite was shown to perform as both a lubricant and a binding agent for mixed oxide powders processed by tableting. On the other hand, the use of aluminum hydroxide as a secondary binding agent was done considering that preliminary results showed that, by itself, graphite did not have the same binding properties when tableting the current MnO2 powder. Its selection was based on literature reports [6,7,10,18] and taking into account that its hydroxylated surface may promote particle stickiness during compaction. The composition of this mixture was fixed after several trial and error tests in which the mechanical resistance of the obtained tablets was tested. The mixture was branded as Mn-3G-25Al, following its composition. Mixing was performed with a glass bottle that was rolled over and shaken for at least 10 min every time [1,2,4]. The Mn-3G-25Al powder was pressed in a rotatory pressing system with 10 slots (Mini Press Rimek II), Fig. 1, to produce cylindrical tablets whose diameter (ϕ) and height (h) dimensions were: 5.59 mm $\leq \phi \leq$ 5.65 mm, and 3.89 mm \leq H \leq 4.30 mm. The axial tensile strength of the produced tablets was initially tested with a dynamometer (Mecmesin) able to exert a force of 250 N. Afterwards, a rapid triage of the produced tablets was made by holding them between the operator's fingertips and checking whether they could stand under pressure. At this stage of the investigation, such a test, though flawed, was accepted as a rough quality test before submitting the shaped bodies to catalytic testing.

2.1.2. Extrudates

Extrudates of the MnO_2 powder were prepared by firstly mixing MnO_2 with 16.5 wt.% kaolin (Sigma-Aldrich, technical degree) in the industrial kneader shown in Fig. 2a. In this case, the choice of kaolin as binding agent was based on reports for the shaping of zeolites [6,7,9,19,20]. The resulting mixture was used as a base powder (BP) for the further addition of extrusion additives. The BP was then mixed with colloidal silica (Ludox, Merck), 26 wt.%, and 1.0 wt.%, polyethyl-



Fig. 6. a) Concentration of water at the outlet of the pilot plant reactor and temperature profiles at the inlet and outlet of the reactor as a function of time on stream during the drying and reaction stages of a styrene combustion test at atmospheric pressure over ca. 1 kg of Mn-3G-25Al tablets. **b)** Concentration of styrene and temperature profiles at the inlet and outlet of the reactor as a function of time on stream over ca. 1 kg of Mn-3G-25Al tablets. **b** Concentration of styrene and temperature profiles at the inlet and outlet of the reactor as a function of time on stream over ca. 1 kg of Mn-3G-25Al tablets. Insets are boxplots of the absolute values of the differences between the temperatures at the inlet and outlet of the reactor during the drying and reaction stages.



Fig. 7. a) Evolution of the concentration of styrene and temperature at the inlet and at the outlet of the pilot plant reactor, concentration of water and carbon dioxide at the outlet of the reactor as a function of time on stream during a styrene combustion test conducted at 250 °C and atmospheric pressure over ca. 1 kg of Mn-3G-25Al tablets. b) Results of a temperature programmed desorption analysis of a sample of spent Mn-3G-25Al tablets performed over a GC–MS instrument.

Table 2

List of reaction products detected and quantified by GC–MS and HPLC from a sample of the outlet gas stream of the pilot plant reactor during a catalytic test carried out over Mn-3G-25Al tablets at 250 °C. Other reaction conditions were: reaction feed: 30 Nm³/h, media of the [Styrene] \approx 343.0 – 339.6 ppmv (*t0.05*, ν = 33), GHSV = 48 000 h⁻¹, and atmospheric pressure. The test was conducted using a flow of ambient air.

| Compound | Concentration | |
|------------------------------------|-------------------|---------|
| | µg/m ³ | ppmv |
| Formaldehyde | 999 | 0.81 |
| Acetaldehyde | 305 | 0.17 |
| Acetone | 280 | 0.12 |
| 2-Propenal | 21 | ~0.01 |
| Propanal | 135 | 0.06 |
| 2-Butenal | 14 | ~0.005 |
| Butanal | 24 | ~0.01 |
| Phenylmethanal | 5316 | 1.22 |
| 3-Methylbutanal | <7.0 | |
| Pentanal | 13 | ~0.004 |
| o-Methylbenzaldehyde | 10 | ~0.004. |
| (m,p)-Methylbenzaldehyde | <7.0. | |
| Hexanal + 2,5-dimethlybenzaldehyde | 39 | ~0.01 |

ene glycol (Sigma-Aldrich) and ball milled for ca. 15 min in a planetary mill (Retsch) provided with one pot and five beads all of agate ($\varphi = 1.925$ cm), Fig. 2b. The obtained mixture, Fig. 2c, was turned into a dough with a suitable flowability for extrusion by adding different amounts of water in a trial and error manner. Batches of ca. 1 kg of extrudates were produced with a single-screw extruder, Fig. 2d, (PlasticCorder Brabender X5). Green extrudates, Fig. 2e, were dried overnight at 50 °C in a static air stove (Memmert). The effect of calcination temperature on some of the properties of the extrudates was investigated. Calcination was performed in a static oven (Carbolite) at 150, 250, 320, 430, 500, 750, and 1000 °C.

2.2. Assessment of physicochemical properties

2.2.1. Porosity and surface area

The porosity (nano) and surface area were calculated from data derived from N2 adsorption-desorption isotherms at ca. -196 °C measured in a Tristar 3000 apparatus (Micromeritics) by the volumetric method following the methods discussed in previous works [1,2,4]. For the shaped bodies, the measurements were made after recovering particles crushed and sifted to an average particle size usually lower than 100 $\mu m.$ Samples of ca. 0.1500 g of these particles were weighted and outgassed overnight at 150 °C in a VacPrep (Micromeritics) unit after which a pressure of ca. 7 Pa was reached. The porosity of these samples was estimated by the BJH method [21] and the surface area by the BET method [22]. For assessing the macroporosity of some of the extrudates, mercury porosimetry measurements were conducted following the methods described in [23]. Samples were outgassed at ca. 15 Pa overnight before the analysis. A Carlo Erba 2000 porosimeter was employed for the measurements which were conducted in a pressure range between 0.01 and 200 MPa. Data interpretation was made by the use of the Kelvin equation [24] assuming a contact angle of 140° and a surface tension of 0.48 N \times m⁻¹ [25].



Scheme 1. Proposed reaction scheme for styrene combustion over MnO₂ based catalysts.



Fig. 8. Evolution of the concentration of styrene at the inlet and at the outlet of the pilot plant reactor and concentration of carbon dioxide at the outlet of the reactor as a function of time on stream during three styrene combustion tests conducted at 300 °C and atmospheric pressure over ca. 1 kg of Mn-3G-25Al tablets. **1, 2,** and **3** are results from the first, second, and third catalytic runs, respectively.

2.2.2. Crystallinity

The crystallinity of particles recovered from some of the crushed shaped materials was analyzed using X-ray diffraction (XRD). XRD patterns were recorded with a Siemens Diffraktometer D5000 instrument using Cu K α radiation. The diffractometer was operated at 40 kV and 40 mA. The measurements were performed over the 2 θ range of 10-70°. Particular attention was put to the possible transformation of the crystalline phases of manganese dioxide after calcination at different temperatures.

2.3. Catalytic properties

2.3.1. Laboratory scale tests

Particles, ca. 0.15 g, recovered after crushing and sifting the shaped bodies to a size between 500 – 350 μ m were tested in the oxidation of benzene in a "light-off" mode, i.e. in a step mode, from T_{amb} to 150, 175, 225, 259, and 280 °C. Each temperature was kept for at least 180 min. After this time, it was considered that steady state conditions were reached. Catalytic particles were mixed with about 1 cm³ of glass spheres (Dp < 200 μ m) to warranty plug flow along the reactor. The volume of the catalytic bed was maintained constant at about 1.1 cm³. The employed fixed bed reactor was made in stainless steel with $\phi = 1.4$ cm and h = 19.1 cm. The catalytic bed was placed on top of a stainless-steel porous frit previously covered by a glass wool bed to avoid that the catalyst particles were being carried out with the gas stream. The reaction set-up was provided by a PID microactivity instru-



Fig. 9. Pictures of the spent Mn-3G-25Al tablets after the catalytic tests. a) View of the top of the catalytic bed after the catalytic tests. b) Aspect of some of the tablets recovered from the top of the reactor. c) Aspect of some of the tablets recovered from the bottom of the reactor. d) Fines found on below the grid that held the fixed-bed of the reactor. e) Aspect of the broken tablets and fines found in the catalytic bed.



Fig. 10. Scheme indicating the characteristics of MnO₂ extrudates as a function of the content of added water.



Fig. 11. Specific surface area (SA_{BET}) for selected samples of MnO_2 extrudates calcined at different temperatures. Ext-NC: Not Calcined extrudates. MnO_2 powder included as reference.

Table 3

Textural properties of selected samples of $\gamma\text{-}MnO_2$ extrudates as assessed from N_2 physisorption at -196 °C. SA_{BET} apparent BET surface area; C_{BET} : C constant for the BET method [22]. Ext: Extrudate. *NC: Not Calcined. Extrudates formulation: 73.0 wt.% of a mixture with 83.5 wt.% of $\gamma\text{-}MnO_2$ and 16.5 wt.% kaolin, 26.0 wt.% colloidal silica, and 1.0 wt.% polyethylene glycol. **Calcination temperature. ^fSample taken after a benzene combustion catalytic test carried out at the laboratory scale.

| Sample | SA _{BET} (m²/g) | C _{BET} | Average pore width (nm) | Pore volume (cm ³ /g) |
|------------------------------------|-----------------------------|------------------|----------------------------|----------------------------------|
| γ-MnO ₂ -NC*, powder | 97.8 | 280 | 7.3 | 0.22. |
| Ext-NC | 99.4 | 140 | 7.4 | 0.19 |
| Ext-350** [£] | 76.0 | 112 | 9.6 | 0.18 |
| Ext-500 | 61.4 | 137 | 10.9 | 0.19 |
| Ext-1000 | 2.1 | -262 | 8.3. | 0.01 |

ment (PID ENG&Tech) operated at atmospheric pressure. Reaction conditions were controlled by the software provided by the manufacturer. For the catalytic tests, materials were dried in situ at 120 °C under a He (Praxair; 99.996%) flow of 140 mL × min⁻¹ for 1 h before running the catalytic tests. The gas stream contained a flow of 20 mL/min of mixture of 100 ppm of benzene in He (Praxair), 40 mL of O₂ (Praxair; 99.995%) and He (Praxair; 99.996%) as diluting gas to obtain a total flow of 200 mL × min⁻¹ (VVH = 37,000 h⁻¹). The reaction system used for the tests was similar to that reported in previous works [26]. Reaction products were monitored on-line by gas chromatography us-



Fig. 12. Macropores size distribution from Hg intrusion measurements for selected samples of MnO₂ extrudates calcined at different temperatures. Ext-NC: Not Calcined extrudates. MnO₂ powder included as reference.

ing a CP-3800 gas (Varian) apparatus provided with both flame-ionization (FID) and thermal conductivity (TCD) detectors. Four columns; namely, one Hayesep G, one Hayesep T, one Molsieve, and one CP-Sil 8CB columns were used for the separation of the reaction products. The quantification of the reaction products was carried out after calibration with standard gaseous mixtures.

2.3.2. Pilot plant scale tests

A homemade pilot plan unit; whose configuration is displayed in Fig. 3, was employed for testing the shaped catalysts in the oxidation of styrene. The unit was provided with a plastic drum containing the styrene feed, Fig. 3b, of the fixed-bed reactor. Styrene was fed to the reactor by saturating a gas flow stream of air with the styrene in vapor phase from the drum. Saturation was done by leaving a recipient of $\phi = 24.5$ cm with styrene open inside the drum and fanning out the vapor in equilibrium with the liquid. The flow of gas fed to the reactor was preheated by a heating resistor wrapped around the inlet tube whose temperature was controlled by a conventional PID controller. The inlet tube was thermally isolated from the environment. The set-point of this controller was adjusted according to the temperature desired at the reactor inlet. For example, to achieve 250 °C at the reactor inlet, it was necessary to set an initial set-point of 350 °C for the temperature of the heating resistor afterwards lowering and holding it to 330 °C during the catalytic test. The temperature was monitored both at the inlet and exit of the reactor with thermocouples placed in their corresponding thermowells, Fig. 3d. The reactor had an internal diame-



Fig. 13. Apparent kinetic constant (k^{App}); assuming a pseudo-first reaction order kinetics, as a function of reaction temperature for the combustion of benzene over selected samples of MnO₂ extrudates calcined at different temperatures. Nomenclature: NC: Not Calcined, Ext: Extrudate, 350, 500, 750, and 1000 are calcination temperatures in °C. a) k^{App} [L/s × g], b) k^{App} [L/s × m²].



Fig. 14. Pictures of: a) the top of the reactor of the pilot plant unit and b) exit tube of the outlet of the reactor taken after the overnight explosion of MnO₂ extrudates calcined at 500 °C during a test for the catalytic combustion of styrene.



Fig. 15. Catalytic performance of MnO₂ extrudates calcined at 500 °C and tested in styrene combustion in a pilot plant. Reaction feed: 30 Nm³/h; [Styrene] \approx 340–400 ppmv; GHSV = 48 000 h⁻¹, *p*_{am}.

ter of 20 cm and an adjustable height from 2.5 to 12.5 cm. The latter was set with a movable metallic grid placed at the top of the reactor. During the tests, the reactor was thermally isolated from the surroundings hence its operation was adiabatic. For the catalytic tests, 1 kg of the shaped catalyst were placed inside the reactor, Fig. 3e. Therefore, the catalytic bed had a height of 2 cm corresponding to a volume of

0.62 L. An inlet gas flow of 30 $\text{Nm}^3 \times \text{h}^{-1}$, i.e. VHSV = 48,000 h⁻¹, with a mean styrene concentration within a 95% confidence interval -C.I.-(t-Student, degrees of freedom = 73) between 338.3-341.0 ppmv and ambient air was fed to the reactor. The fresh catalyst was dried at 250 °C under ambient air flow. The evolution of the water concentration at the reactor inlet and exit was monitored during drying to determine the duration of the drying procedure. A first set of reaction tests was carried out using the tablets branded as Mn-3G-25Al (See Section 2.1). The first test of this set was performed by cooling down the reactor to 100 °C after drying the catalyst and then allowing the flow of ambient air and styrene to enter the reactor. Afterwards, the temperature of the inlet flow of gas was ramped up to 150 and 200 °C. The mean inlet concentration of styrene, μ_{Sty} , for this test was within a 95% confidence interval ($t_{0.05,\nu = 15}$; i.e. t-Student distribution, $\nu =$ degrees of freedom) between 309.6 - 303.9 ppmv. The second test of the set was carried out at 250 °C. In this case, the reactor was heated to the reaction temperature ramping up the temperature of the stream of ambient air from 100 °C to 250 °C. The mixture containing styrene was only allowed into the reactor after the concentration of water reached a steady state at the exit of the reactor. For this test, μ_{Sty} was between 343.0 – 339.6 ppmv, $t_{0.05,\nu = 33}$). The repeatability of this test was checked by running it thrice. Two more tests with the catalyst's tablets were conducted at 300 °C using the same procedure described above for the tests at 250 °C. Extrudates of the catalyst were tested in a second set of reactions following similar procedures to the one described above. The choice of the featured reaction conditions was made according to the goals of the DEPOLAIR project. Namely, the project aimed at implementing a portable catalytic unit based on MnO_2 and operated at temperatures between 150 and 250 °C for the combustion of residual styrene from Belgian polystyrene factories up to levels below 25 ppmv.

Reaction products were analyzed on-line by a micro-gas chromatograph. The detection limit for styrene in this instrument was ca. 1.0 ppmv. Other characteristics of the instrument as well as its set up are described elsewhere [27,28]. CO production was monitored by a photoacoustic analyzer (Innova). For the analysis of partially oxidized products, some of the catalytic tests at 250 °C were conducted with air bag samples taken from the effluent coming out of the catalytic bed. These samples were taken using a lung chamber that allows, through an electric pump, to fill a bag of fluorinated material, Tedlar (Aldrich) located inside a drum receiving the reactor effluent. The bag was filled with the effluent to be removed without having been in contact with other elements than the sampling line (Teflon), the bag valve (Teflon) and the fluorinated material of the walls of the bag. These three materials are known for their low adsorption of gaseous molecules and are among the materials recommended by the EN13725 norm [29]. In addition, DNPH capturing aldehydes and Tenax cartridges; both supplied by Supelco, were used for sampling the gas at the outlet of the reactor. DNPH cartridges were analyzed by HPLC, while the TENAX ones were analyzed by making thermal desorption coupled to a GC-MS (TD-GC-MS) following the procedures described in previous works [27,28]. A TPD analysis of a sample of spent catalysts was conducted to identify adsorbed reaction intermediates.

In general, the confidence intervals and other statistical descriptors presented herein were calculated according to conventional procedures presented in statistics textbooks [30,31]. For building confidence intervals, Eq. (1) below was employed:

$$\overline{y} - \left| t_{\frac{\alpha}{2}, n-1} \right| s_{\frac{y}{\sqrt{n}}} \le \mu \le \overline{y} + \left| t_{\frac{\alpha}{2}, n-1} \right| s_{\frac{y}{\sqrt{n}}}$$
(1)

Where: \bar{y} is the average of the performed measurements; $\left| t_{\frac{\alpha}{2},n-1} \right|$ is the absolute value of the two-tail t-Student statistic with an α type-I error, herein, $\alpha = 0.05$ as for 95% confidence, and *n* experimental points; and, $s_{\bar{y}}$ = the standard deviation referred to the average of the performed measurements.

3. Results and discussion

3.1. Preparation and physicochemical properties of MnO₂ tablets

Finding a suitable formulation for making MnO₂ tablets was not an easy task. Several trial and error tests had to be done to finally determine adequate percentages of the MnO2 powder, graphite, and aluminum hydroxide. The produced tablets exhibited a thin shiny layer at their rim, Fig. 1b, from graphite acting as a lubricant [6,7,27], which is a typical feature of tablets prepared using this material [1,2,4]. Besides the formulation already mentioned in the Experimental section (Section 2.1), a series of tablets were prepared using 10 wt.% aluminum hydroxide (Merck, commercial degree) and the relationship between their height and mechanical resistance was analyzed systematically using the same instrumentation and procedures of a previous work [1,2]. Particularly, the axial (σ_z) and lateral (σ_x) compression strengths of the tablets were analyzed as a function of their height. The latter was manually adjusted in the rotary press, Fig. 1. Fig. 4 shows the results of these tests. The axial compression resistance of the tablets was systematically higher than the lateral compression resistance. Indeed, a difference of three orders of magnitude between both kinds of resistances was found. In general, an apparent lineal correlation was found be-

tween the studied variables. Where, the mechanical resistance increased with the height of the produced tablets. Considering these tests, tablets with heights larger than 3.89 mm were produced for further catalytic testing and analysis (Section 2.1). However, the integrity of the manufactured tablets was compromised by their low friction wearing resistance, Fig. 1c. Therein, tablets are shown to scratch a paper towel as if they were rods from pencils. One of the characteristics of MnO₂ powders is their fine granulometry [33]; according to measurements performed by laser diffraction, for the MnO_2 powder employed herein: $d_{10} = 18$ $\mu m,\,d_{50}=31~\mu m,$ and $d_{90}=91~\mu m,$ which makes the particles from this powder to fly easily. In addition, the structure of MnO₂ oxides forms layers and channels [33-35] making this material feel as possessing a texture similar to graphite. Such characteristics may be behind the fact that the MnO₂ employed herein was a powder with poor compactness. Furthermore, as a general remark, handling of this kind of powders must be made under defined security protocols such as always wearing fine dust protective masks and gloves.

From the produced batches of Mn-3G-10Al and Mn-3G-25Al tablets, samples were selected and submitted to two calcination procedures. The first procedure, named as Standard (Std), consisted on entering the tablets in a static oven (Carbolite) at ambient temperature and then ramping-up to the temperature of calcination at a rate of 10 °C/min. The second procedure, named as Flash (Fsh), was performed in a horizontal oven preheated to the temperature of calcination and in which the tablets were directly introduced. Both the Std and Fsh procedures were conducted for 4 h. The purpose of these experiments was to find out whether the mechanical resistance of the tablets could be improved by densification. Table 1 shows the corresponding results from the mechanical resistance tests. In general, neither of the calcination strategies led to a significant improvement of the mechanical resistance regardless of the composition of the tablets. On the other hand, the crystallography of MnO₂ was altered only after calcination at 500 °C. Fig. 5 displays the XRD patterns of samples taken from a batch of Mn-3G-10Al tablets calcined at different temperatures by the standard procedure. Similar results were found after applying the *flash* procedure. Diffraction peaks at ca. 21, 26, 38, 43, 57, and 66° were recorded for all samples calcined up to 430 °C. The peaks at ~21°, ~38°, ~43°, ~57°, and ~66° have been reported for electrolytically prepared MnO₂ [33]. A previous study made with the material employed in this work reported similar XRD patterns that were associated to the nsutite polymorph of MnO₂ which is also denominated as γ -MnO₂ [12]. Considering the report by Xie et al. [36], the facets: (120), (131), (300), and (160) correspond to the peaks at 21, 38, 43, and 57°, respectively. The other recorded peaks could not be identified from the consulted literature. This can be due to the fact that rather than a single crystallographic phase, γ -MnO₂ is a mixture of intergrown pyrolusite and ramsdellite [37]. In general, it seems safe to conclude that the material did not change its crystallinity after calcination at temperatures up to 430 °C nonetheless. Clearly, calcination at 500 °C changed this trend since the XRD pattern of the sample calcined under such a condition was completely different from the ones recorded for the other samples, Fig. 5. In this case, the recorded diffraction peaks fully matched those reported for Mn₂O₃ [38]. Particularly, comparing the pattern obtained herein with the one reported by Wei-Chieh et al. [39], the following facets could be ascribed: (211), (222), (332), (431), and (440) at ca. 24, 33, 39, 46, 50, and 55°, respectively. Both the pattern reported in Fig. 5 of the present work and the one presented by these authors are attributed to α -Mn₂O₃. Considering the above results, and as far as the physicochemical characterization performed in this study concerns, the only important change detected in the properties of the produced tablets after calcining at different temperatures was the transformation of the manganese oxide from γ -MnO₂ to α -Mn₂O₃.

3.2. Catalytic performance of MnO_2 tablets in the pilot plant scale combustion of styrene

Given the results presented in the previous section, it was decided to make a series of catalytic tests at the pilot plant scale, Fig. 3, with the tablets branded as Mn-3G-25Al without submitting them to calcination. Setting up the catalytic tests at the pilot reactor required a more careful analysis of its operation as compared with a conventional laboratory scale reactor. An analysis of the drying stage was carried out. Fig. 6 shows the evolution of the main operating variables; namely, the inlet and the outlet reactor temperatures, H₂O, CO₂, and styrene concentrations, during a catalytic test performed over ca. 1.0 kg of Mn-3G-25Al tablets. During the whole test there was a temperature difference, ΔT , between the inlet and outlet of the reactor; see boxplots insets. For the drying stage, see boxplot in Fig. 6b, the median of ΔT was 21 °C, the minimum and maximum were 10 and 45 °C, respectively, and there were two temperature outliers around 55 and 58 °C. These outliers, as well as the maximum in the boxplot, corresponded to the early stages of the stabilization of the temperature of the flow at the outlet of the pilot of the reactor once the inlet temperature reached the set-point of 250 °C; i.e. the temperature setpoint for the drying stage. Afterwards, the difference in temperature between the inlet and exit flow narrowed down to ca. 15 °C. Therefore, as it is the case for this kind of reactors [6,37], gradientless operation is not possible. Basically, temperature gradients in pilot plant and industrial scale reactors are due to thermal gradients inside the catalytic reactor. Such a phenomenon is normal, in this case, since the catalytic conversion is a function of the spatial coordinates of the reactor. For example, for a cylindrical shaped reactor, even if conversion does not depend on either the radial or angular coordinates, conversion will be at least be a function of the axial coordinate. Such a conversion profile will lead to a corresponding thermal profile. Such a situation is normally averted in laboratory micro-reactors where gradient-less operation is preferred to access intrinsic kinetic data [6,40,41]. Following the evolution of the concentration of water exiting the reactor, Fig. 6a, permitted setting a reasonable duration time for the drying stage; i.e. ca. 3 h. One may notice that, since ambient air was used for the tests, a media for the concentration of water between 6732–7364 mg/m³ (t0.05, ν = 7) was part of the reactor feed. During drying at 250 °C, the concentration of water increased to a maximum of ca. 8500 mg/m^3 to further decrease as a function of time until reaching $\tilde{6}395 \text{ mg/m}^3$ at the end of the drying stage. The latter value was well within the confidence interval for the media of the concentration of water in ambient air mentioned above. After the drying stage was deemed complete, the temperature of the system was lowered to ca. 100 °C; where, styrene from the plastic drum that contained it, Fig. 3, was allowed to enter the system, Fig. 6b. After stabilization of the operation of the reactor under these conditions, the temperature at the reactor inlet was raised to ca. 200 °C and allowed to stabilize once again. The concentration of styrene at the outlet of the reactor initially increased until reaching a steady state concentration that remained regardless of rising temperature to 200 °C. Therefore, the media of styrene concentration at the reactor outlet was within the confidence interval: 178.0 ppmv $\leq \mu_{Sty} \leq$ 186.6 ppmv (t0.05, $\nu = 11$). Under steady state conditions, the conversion of styrene was thus found to be within the C.I. (t0.05, v = 31) 0.38 - 0.41. Fig. 6b shows the evolution of the concentration of CO₂ during the catalytic test. CO₂ was part of the reactor feed as it was present in ambient air. During the stages prior to the introduction of styrene, its concentration displayed a media (t0.05, $\nu = 11$): 492.2 ppmv $\leq \mu_{CO2} \leq 501.1$ ppmv. During the reaction, when styrene was fed, the concentration of CO₂ raised to values whose median was ca. 798.1 ppmv. After stopping the feed of styrene to the reactor, the outlet concentration of CO2 increased until reaching a maximum at ca. 1200 ppmv thence decreasing until the initial level of ambient air. This trend indicated that a fraction of the styrene fed to reactor or of some of its partial oxidation products were retained by the catalyst during this test. Indeed, the molar based selectivity to CO_2 under these conditions was around 70%; i.e., ca. 30% of the styrene entering the reactor was not combusted.

The results from one of the catalytic tests performed at a reactor inlet temperature of 250 °C are shown in Fig. 7a. The behavior of the difference in temperature at the beginning of the reaction stage was similar to that reported above for lower temperatures. At steady state conditions, the media of the absolute value of the difference in temperature between the outlet and inlet streams was within the C.I. (t0.05, $\nu = 11$): 9.5-10.6 °C. Where, in contrast to the tests conducted at temperatures up to 200 °C, the temperature of the outlet stream was higher than the one at the inlet stream. This, of course, can be explained by the exothermicity of the oxidation reactions. At steady state conditions, the conversion of styrene reached ca. 80%. The media of the concentration of CO_2 at the outlet of the reactor was 2107.1 ppmv $\leq \mu_{CO2} \leq 2130.8$ ppmv (t0.05, ν = 71). Accordingly, at 250 °C, the selectivity to CO₂ was ca. 86%. Therefore, as in the case of the tests conducted at lower temperatures, not all the converted styrene was combusted to CO2. Fig. 7b presents the results from a TPD test made on a sample of spent Mn-3G-25Al catalyst. Strongly held styrene, acetone, benzene, and acetic acid were found to desorb from the sample. In addition, Table 2 shows further analyses of gas samples from the reactor outlet by GC-MS and HPLC that demonstrate the presence of multiple aldehydes as well as acetone and acrolein obtained as partial oxidation products. Considering these compounds, the reaction scheme presented in Scheme 1 is proposed for the combustion of styrene over the shaped MnO₂ catalysts studied herein. The scheme illustrates how styrene is sequentially oxidized to a group of aldehydes whose number of carbon atoms decreases until turning the aromatic compound into CO and CO₂. The presence of o-, m-, and p-methylbenzaldehyde, as well as of 2,5-demethylbenzaldehyde and benzene suggests that radical species play a role in the reaction in conjunction with the heterogeneous reaction occurring at the surface of the catalyst. It is also interesting to notice that hydrogenation reactions take place during the oxidation sequence. Namely, the conversion of benzene into hexanal requires not only the hydrogenation of the aromatic ring but its opening as well. As far as the literature review of this work goes, previous studies on the catalytic combustion of styrene did not shed light on the reaction mechanism since they almost exclusively focus on following the conversion of the compound without any regard for products distribution [11,12,15,42]. Therefore, insights on the oxidation mechanism of styrene were only found in studies concerning the flame combustion of aromatics and its oxidation in liquid phase. Particularly, Blanquart et al. [43] compiled and analyzed kinetic data for the homogeneous combustion of several hydrocarbons. They postulated that in the case of aromatics the formation of benzyl radicals in flames is favored due to their larger stabilization conferred by the resonance of the aromatic ring. In addition, allylic radicals are formed by reactions involving hydrogen abstraction. Following this work, the same group [44] further proposed that atomic oxygen can attack the vinylic carbon of styrene to form a benzyl radical via the cleavage of the carbon-carbon bond. This leads to the simultaneous formation of formyl radicals. In addition, hydroxyl radicals were proposed to react via addition either to the benzylic or vinylic carbons to form phenylmethanal and benzyl radicals, respectively. This kind of mechanism might well operate also in liquid phase where styrene oxidation to phenylmethanal takes place [45,46]. On the other hand, Kwon and Castaldi [47] presented evidence that suggests that the combustion of styrene-butadiene rubber involves a mechanism in which bond scission is followed by hydrogenation, gas phase addition reactions and partial oxidation. From the findings of this work, no mechanism can be proposed but it is notable that also dehydrogenation and ring opening reactions are happening during the combustion of styrene. The mechanism leading to the featured scheme is doubtlessly associated to a combination of free radical and surface reaction mechanisms. Finally, it is important to remark that the insight in the reaction mechanism cast herein was only possible due to the scale at which the catalytic tests were carried out.

Complete conversion of styrene was achieved during the test at 300 °C. Fig. 8 shows the results of three pilot plant scale catalytic tests carried out over Mn-3G-25Al tablets. For the third test, the steady state concentration of the styrene fed to the reactor was increased to 309.0 ppmv $\leq \mu_{Sty} \leq 312.1$ ppmv (t0.05, $\nu = 43$) as compared to the first two tests in which the media of the concentration of styrene was between 224.7 ppmv $\leq \mu_{Sty} \leq 226.7$ ppmv (t0.05, $\nu = 43$). The conversion of styrene remained at the same level nonetheless with a consequent increase in the production of CO₂ when styrene concentration increased. Besides CO₂, CO in a concentration within the C.I.: 15.4 ppmv $\leq \mu_{CO} \leq 15.5$ ppmv (t0.05, $\nu = 104$) was measured. The presence of additional reaction products was not found under the detection limits of the employed analytical techniques.

Despite these promising results, the integrity of the catalyst tablets was found to be severely affected during the catalytic tests. Fig. 9 displays pictures taken for the spent catalyst after performing the third catalytic run at 300 °C. Severe attrition was found with a total loss in catalyst fines of ca. 30% from the original fresh catalyst loaded to the reactor. Consequently, the first part of the study led to discard tableting as a suitable method for shaping the γ -MnO₂ powder. Extrusion was thence tested as shaping method.

3.3. Preparation and physicochemical properties of MnO_2 extrudates

One of the first tasks that was made for manufacturing γ -MnO₂ extrudates was finding a suitable viscosity for the dough to be extruded. As mentioned in the Experimental section, kaolin was selected for preparing a base powder of the extrudates. The role of the selected clay was to provide plasticity to the extrusion dough [6-8,48]. The inclusion of polyethylene glycol to the formulation was intended to provide additional plasticity whereas colloidal silica was intended to act as a binder. The viscosity of the resulting formulation was adjusted by adding water to it and then kneading the dough by hand in a ceramic mortar. This was a totally empiric process in which the apparent flowability of the dough inside the extruder was adjusted by sequential trial and error. In general, it was found that dough with water contents below 15 wt.% were extrudable in batches of a couple of hundred grams, whereas doughs with water loadings higher than 15 wt.% had lower viscosity hence allowing to make extrudates in a rather continuous operation. Fig. 10 summarizes these findings schematically. In the end, it was decided to prepare doughs with water contents near 15 wt.% in order to make green extrudates with a relatively higher mechanical strength that allowed an easier manipulation during further operations.

A word of caution about the handling of residues must be stated concerning the whole shaping operation. Indeed, even though the yield for the production of shaped bodies is fair either by tableting or extrusion, when working at the kilogram scale significant material is lost. Therefore, residues disposal can be problematic for both the health and the environment. In addition, shaping might become quite a costly operation requiring a considerable know-how.

Aiming an improvement on the mechanical resistance of the extrudates, calcination at different temperatures was performed. As it could be expected from what is known in ceramics production [49], this property improved with an increase in the temperature of calcination due to densification. Particularly, extrudates calcined at 750 and 1000 °C were very hard to break. Concurrently, the effect of the calcination temperature on the surface area and porosity of the shaped bodies was investigated. Fig. 11 plots the values of the BET surface area (SA_{BET}) for samples of extrudates calcined at different temperatures. As a reference, the values of SA_{BET} for both a sample of the $\gamma\text{-}MnO_2$ powder (SA_{BET} = 98.0 m²/g, C_{BET} = 280) and a sample of green; non-calcined, extrudates (SA_{BET} = 99.4 m^2/g , C_{BET} = 140) are plotted. In general, calcination reduced the surface area. The higher the calcination temperature, the higher was the loss in surface area. At 1000 °C, the densification process was so severe that SA_{BET} reduced to ca. 2.1 m²/g (C_{BET} = -262). The negative value of this last C_{BET} constant implies that the BET model became highly inaccurate for the calculation of the surface area hence the reported value can only be considered for qualitative comparison purposes. Table 3 summarizes calculated BJH average pore widths and volumes for the studied samples. The fact that the average pore width of the materials increased along with the strong reduction of the pore volume agrees with the sintering process leading to densification. On the other hand, Fig. 12 shows the macropore size distribution; assessed by Hg intrusion, for selected samples of the fabricated extrudates and for a sample of the γ -MnO₂ powder. The results coincide with the trends described for surface area and mesoporosity discussed before as a strong increase in the average macropore size of the extrudates calcined at 1000 °C was recorded. Once again, the shift from a mesoporous to a macroporous material is a consequence of densification [49].

Considering the facts discussed above, one may conclude that extrusion of the $\gamma\text{-MnO}_2$ powder employed herein is a more suitable shaping method for the fabrication of mechanically strong catalyst bodies. The rheological properties of the formulated extrusion dough must be considered during the process. Stronger green bodies were found when the content of water in the dough was around 15.0 wt% without the risk of stopping production too often. Further calcination of the made extrudates enhanced their mechanical resistance due to densification.

3.4. Catalytic performance of MnO₂ extrudates

Samples from the produced extrudates were tested at both the laboratory and pilot plant scale.

3.4.1. Catalytic tests at the laboratory scale

Tests at the laboratory scale were carried out using benzene as model molecule and served to determine an appropriate temperature for the calcination of the extrudates to be tested at the pilot plant scale. The selection of benzene for these tests was due to safety concerns for its handling in the microreactor setup. In addition, no supplier for gaseous mixtures of styrene were found at the time of execution of the research project.

Fig. 13a shows the apparent pseudo-first order reaction rate constant (k^{App}) for benzene combustion as a function of reaction temperature for the γ -MnO₂ extrudates calcined at different temperatures. k^{App} was defined according to the expression:

$$k^{App} = \frac{F_0}{wC_0} \left(\ln \left(1 - x \right) \right)$$
(2)

Where, F_0 = inlet molar flow of benzene [mol × s⁻¹]; w = catalyst weight [g]; C_0 = molar concentration of benzene [mol × L⁻¹]; and, x = benzene molar conversion. Taking the behavior of the extrudates that were not calcined (Ext-NC) as a reference, one may see: (i) Calcination at 750 and 1000 °C had a detrimental effect in the catalytic activity. Such an effect can be associated to the strong loss in surface area of MnO₂ discussed before (Table 3 and Fig. 11). (ii) Calcination at 350 °C, Ext-350, had a positive effect on the catalytic activity. At each one of the tested temperatures, k^{App} for Ext-350 was higher than k^{App} for Ext-NC. (iii) Calcination at 500 °C, Ext-350, led to a catalyst with a better catalytic performance than Ext-NC for reaction temperatures from 250 °C. This latter result suggests that under certain temperatures the catalytic activity of γ -MnO₂ is similar to that of α -Mn₂O₃ (see XRD results, Section 3.1). According to Lahousse et al. [11], there are differences in catalytic performance between the different crystalline phases of MnO_2 . Particularly, these authors tested β -MnO₂, ramsdellite MnO₂, γ-MnO2 and in the catalytic combustion of ethylacetate and n-hexane and found that γ -MnO₂ performed better as compared to β -MnO₂, and ramsdellite. The authors attributed the observed differences to changes in the coordination of the structural oxygen atoms and to the relative distribution of anionic vacancies on the surface of the materials. Kim and Shim [16] compared the catalytic performance of $\rm Mn_3O_4,\,Mn_2O_3$ and MnO₂ in the combustion of benzene and toluene (1000 ppm, total flow rate 100 cm³/min, 0.4 g of catalyst, T = 200-280 °C) and found that Mn₃O₄ performed better than Mn₂O₃ and that latter was better than MnO₂ under the tested reaction conditions. The differences in catalytic performance among these materials were ascribed to changes in oxygen mobility; deduced from temperature programmed reaction analyses and surface area. When expressing k^{App} in terms of the surface area of the catalysts for some selected extrudates, Fig. 13b, the results obtained herein coincide with the findings of Kim and Shim [16]; which implies that Mn₂O₃ obtained after calcining the extrudates at 500 °C is intrinsically more active than $\gamma\text{-}MnO_2\text{-}$ In addition, and as discussed before, the mechanical resistance of the catalyst extrudates increased with the reaction temperature due to densification. Calcination of the γ-MnO₂ extrudates at 350 and 500 °C was thus found to be a good compromise between catalytic activity and mechanical resistance. In consequence, batches of 1 kg of Ext-350 and Ext-500 was submitted for testing at the pilot plant scale. Interestingly, the particles recovered from the Ext-1000 °C catalyst were more active for temperatures from and above 250 °C, Fig. 13b, in the reaction when the catalytic performance was expressed in terms of the BET surface area of the materials. However, this calcination under such a harsh temperature was discarded due to costly safety and energy demands. In addition, despite the higher intrinsic activity of Ext-1000 °C from the practical point of view, a higher amount of this material would be required for large scale operations since its apparent activity was well below the rest of the tested materials.

3.4.2. Catalytic tests at the pilot plant scale

The catalytic tests at the pilot plant scale for Ext-350 were initially carried out by adapting the protocol used for MnO2 tablets (see Experimental section). Briefly, after conducting the drying stage, the reactor was allowed to cool down to 100 °C and styrene was introduced in the reactor feed. Afterwards, the temperature was raised to 250 °C. However, the use of this testing protocol led to an incident during the first test with Ext-350. Specifically, a sudden production of CO2 was recorded accompanied by a strong increase in temperature to ca. 350 °C which was followed by an explosion in which the upper part of the reactor cover was ejected and its exit tube severely damaged by fines jetted during the explosion, Fig. 14. Fortunately, the adopted security protocols protected the physical integrity of both the pilot plant operator and the facilities. An analysis of the causes of the accident led to the conclusion that the explosion occurred because of the accumulation of adsorbed styrene in the extrudates at low temperature and its further sudden combustion at 250 °C. Alternative reaction protocols were then tested for avoiding new accidents. Finally, a protocol consisting on pre-heating the catalytic bed by flowing air at 300 °C for 2 h and then cooling it down to 250 °C for the introduction of styrene to the reactor feed was deemed safe and adopted for further catalytic runs. In addition, it was decided to implement a recorder/controller system with a security control on the temperature which will shut down the heating in case the temperature difference between the outlet an inlet of the reactor would be higher than the fixed set point. Under such conditions, the extrudates calcined at 350 °C presented a good catalytic performance (results not shown) but had a strong tendency to physical degradation as it was previously found for MnO₂ tablets. This problem did not present itself for Ext-500 whose mechanical properties were

better. Fig. 15 presents the results of a catalytic test conducted over Ext-500 using the protocol discussed above. A total conversion of styrene was obtained from 250 °C, whereas the selectivity to CO_2 was not closer to completion only after operating the reactor at 300 °C. Overall, the performance of the catalyst was stable during the time of operation of the reactor without observing a significant degradation of the integrity of the catalytic bodies. The ensemble of these results allows to conclude that calcination of the extrudates at 500 °C leads to catalysts with appropriate physicochemical properties for eliminating styrene emissions under the conditions tested herein.

4. Conclusions

Even though the implementation of catalytic materials at the industrial level requires knowledge of scaling up, shaping protocols, and testing at pilot plant scales, very scarce studies analyze these aspects related to technical catalysts production. In this work, a study of the shaping and testing of MnO₂ based powders as combustion catalysts for the elimination of aromatic volatile compounds; namely, styrene and benzene, was conducted. Tablets and extrudates of MnO₂ were manufactured and key physicochemical properties were assessed and correlated to their performance in the aforementioned reactions at both laboratory and pilot plant scales. The results obtained under the conditions of the present study lead to conclude the following: (i) Tableting of MnO₂ powders was not a suitable protocol for their shaping because the mechanical resistance of the formed bodies was insufficient to warrant stable operation at the pilot plant scale. The trends in mechanical resistance could not be modified to a significant extent after increasing the calcination temperature of the MnO₂ tablets. (ii) Extrusion of MnO₂ powders and further calcination at 500 °C was adequate for shaping and producing a stable technical catalyst suitable for styrene abatement at the pilot plant scale. For the latter, an accident occurred during the testing of a batch of extrudates illustrating the high importance of adopting well defined security protocols during runs at this scale. In addition, the potential issue of waste management during shaping operations was evidenced. On the other hand, the characterization of the surface area and crystallinity of the materials after the adopted calcination temperatures allowed establishing that the intrinsic activity of the materials based on γ -MnO₂ can be enhanced after transforming it into Mn₂O₃. Such a transformation can be achieved by calcination at 500 °C. Finally, the pilot plant testing of the catalysts allowed drawing a unique insight into the reaction pathways involved in styrene combustion. Particularly, results suggested the occurrence of oxidation, hydrogenation, dehydrogenation, ring opening, and isomerization reactions taking place by a combination of both surface and free radical mechanisms. Such an insight can be hardly attained after laboratory scale tests due to the very low concentration of reaction intermediates at the reactor effluents. Detection and quantification under such conditions is only feasible after applying very special analytical procedures normally unavailable in academic research laboratories.

Uncited references

[32].

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