

Catalytic activity of active carbons impregnated before activation of pinewood sawdust and nutshells to be used on the control of atmospheric emissions

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Abstract

This work analyses the catalytic activity of metal oxides impregnated on activated carbons to be used for the complete oxidation of benzene present in atmospheric emissions. When the impregnation step is performed before CO₂ activation, the knowledge about catalytic activity is as yet quite scarce, being the main objective of the study here reported. Pinewood sawdust and nutshells were recycled to produce the activated carbons. Non-expensive metal oxides (CoO, Co₃O₄ and CrO₃) were impregnated. When the impregnation was performed before CO₂ activation instead of after activation, at 523 K the kinetic constants were 3.6–4.3 times higher for sawdust carbons, and 2.1–2.7 times higher for nutshell carbons, due to a better metal oxide dispersion on higher mesopore areas and on wider micropores. With Co₃O₄ as catalyst, a benzene conversion of 90% was reached at a lower temperature than with CrO₃ (472 and 558 K, respectively). The carbons impregnated before CO₂ activation allowed very good conversions at temperatures that guarantee carbon stability (lower than 575 K). The results obtained led to the conclusion that activated carbon is a suitable support for metal oxide catalyst aiming the complete oxidation of benzene, mainly if an adequately porous texture is induced, proceeding to the impregnation before CO₂ activation.

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1. Introduction

Air quality is strongly affected by the emission of pollutants associated with industrial processes and transport activities. The emissions of volatile organic compounds (VOC) have an important role on air quality degradation, either through direct impacts, or as precursors of photochemical pollutants. Benzene is one of the VOC of major concern due to the dangerous impacts on human health; its carcinogenic effects have required very restrictive legislation worldwide to reduce concentrations, both in the atmosphere and in emissions. Many different methods have been developed to reduce or even destroy the VOC present on atmospheric emissions,

the most common being thermal incineration and catalytic oxidation [1,2]. Thermal incineration is an expensive process because it needs a high temperature process, usually only maintained with the help of supplementary fuel [3]. Catalytic oxidation is processed at much lower temperatures, allowing a reduction of fuel consumption, especially when large volumes of gaseous emissions containing low VOC concentrations have to be treated. In addition, the range of operation temperatures, utilized for catalytic oxidation, avoids the emission of some pollutants such as dioxins and nitrogen oxides which are usually present as unwanted products of chemical reactions associated with thermal incineration [4]. Therefore, catalytic oxidation is a promising process to reduce VOC emission, aiming to obey the increasingly restrictive environmental legislation [3,5]. The combination of adsorption with catalytic complete oxidation is showing good

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Nomenclature

A_R	reactant peak area in chromatogram with chemical reaction
A_R^0	reactant peak area in chromatogram without chemical reaction
d	crystal size
E	activation energy
ΔH	differential molar heat of adsorption
k_{ap}	apparent rate constant
k_g	velocity constant in gaseous phase
k_s	velocity constant in solid phases (s^{-1})
K	adsorption equilibrium constant
m	weight of solid phase
S_{BET}	total specific surface area of the carbons (BET method)
S'_t	non-microporous specific surface area associated with mesopores (t-method)
t_g	residence time in gaseous phase
t_s	residence time in solid phase
U	carrier gas flow rate
V_{me}	mesopore volume
V_{mi}	micropore volume
VOC	volatile organic compounds
XCAI	carbon series obtained with the following step sequence: carbonization, activation and impregnation
XCIA	carbon series obtained with the following step sequence: carbonization, impregnation and activation
X_R	reactant conversion
W_{in}	weight of reactant entering the column
W_{out}	weight of reactant leaving the column
τ	space time

results, and the identification of the best support/catalyst pair is at present the objective of many studies.

Wasfi et al. studied the efficiency of platinum, palladium and copper oxide catalysts supported on γ - Al_2O_3 for the oxidation of VOC, concluding that platinum catalysts were the most efficient, allowing good conversions at satisfactorily low temperatures [6]. Irwin et al. investigated the efficiencies of supported platinum catalysts for the destructive oxidation of malodorous organic compounds and showed that the efficiency cannot be improved significantly without excessive temperature increase, because mass transfer was the rate-controlling step [7]. Burgos et al. analysed the deep oxidation of VOC mixtures with platinum supported on Al_2O_3/Al monoliths, showing that acetone was found as an intermediate in the oxidation of 2-propanol [8]. Cordi and Falconer concluded that palladium and palladium oxide supported on Al_2O_3 allowed good conversions for the complete oxidation of VOC above 550 K [9]. Andreeva et al. studied the

benzene complete oxidation using $Au-V_2O_5/TiO_2$ and $Au-V_2O_5/ZrO_2$ as catalysts, showing that the oxidation efficiency strongly depends on the oxidizing agent [10]. Less expensive catalysts have also been tested. Kim investigated the complete oxidation of benzene, toluene, and xylene, using metal catalysts (Cu, Mn, Fe, V, Mo, Co, Ni and Zn) supported on different materials (γ - Al_2O_3 , TiO_2 and SiO_2), concluding that copper supported on γ - Al_2O_3 had the best catalytic activity, due to better dispersion of active sites on the support [5]. Vass and Georgescu also studied the complete oxidation of benzene using mixtures of metal oxides (Cu–Cr and Co–Cr) as catalysts, supported on γ - Al_2O_3 and on γ - $Al_2O_3 + SiO_2$, concluding that copper–chromium had higher activity than cobalt–chromium, the catalysts supported on γ - Al_2O_3 being more active than the ones supported on γ - $Al_2O_3 + SiO_2$ [11].

The utilization of activated carbons as catalyst supports, for the treatment of gaseous effluents contaminated with VOC, enables advantage to be taken of both the enhanced retention of pollutants adsorbed in the well-developed porous texture of activated carbons, and the possibility of complete oxidation at lower temperatures due to the presence of the catalyst. Wu et al. prepared platinum catalysts supported on activated carbon to be used for the complete oxidation of benzene, toluene, and xylene, showing that very good conversions can be reached at temperatures lower than 473 K [3].

The knowledge concerning the performance of less expensive catalysts supported on activated carbons is as yet scarce. Aiming to guarantee the conversion of pollutant at temperatures low enough to avoid significant loss of the carbon by gasification, very high catalytic activities at low temperatures are required. For that, a good dispersion of active sites on the porous texture of the carbons is absolutely necessary because it controls the conversion efficiency. This work analyses the catalytic activity of non-expensive metal oxides supported on activated carbons for the complete oxidation of benzene present in atmospheric emissions. The catalysts were impregnated on the support using two different methodologies. For one of the carbon series prepared, the impregnation step was made after CO_2 activation. For the other carbon series, and in order to improve the dispersion of active sites on the porous texture of the carbons, a new impregnation methodology was developed, proceeding to the impregnation before CO_2 activation (between carbonization and activation). When the impregnation step is performed after CO_2 activation, the influence of carbon texture on the dispersion of active sites is already well studied [12,13]. The authors recently published studies about the influence of carbon texture on the dispersion of active sites when the impregnation step is performed before CO_2 activation [14,15]. The activated carbons contain heteroatoms that come from the raw material or are introduced into the carbonaceous matrix during the preparation procedure or in subsequent treatments. Oxygen is the most important heteroatom, that is present as a component of various surface complexes such as carboxyl, phenol, lactone, carbonyl, quinone, hydroquinone, anhydride, and ether;

these complexes significantly influence the surface functionalities [16–18]. As the surface chemistry of activated carbons has a major influence on their capacity of adsorption, studies were performed in order to analyse whether the impregnation methodology influenced the surface chemistry. To extend the studies previously carried out, the present paper analyses the catalytic activity of the impregnated active carbons when the impregnation step is performed before CO₂ activation, since this knowledge was as yet very scarce.

2. Experimental procedure and methodology

The activated carbons were prepared by first selecting the raw materials according to their carbon content, cheapness and availability. Pinewood sawdust and crushed nutshells, by-products of the wood and food industries that constitute a significant waste disposal problem, were used as the carbon precursors for the preparation of the impregnated active carbons reported herein. The fraction with an average size of 0.063 cm was washed with an acid solution, in order to reduce the sulphur and ash contents of the carbons. The acid was totally removed with distilled water and the sample was then dried. The carbonization was conducted in a silica reactor placed in a tubular furnace under flowing nitrogen. A heating rate of 10 K min⁻¹ was employed until the temperature attained 1123 K, which was maintained for 60 min. The weight loss was determined by weighing the sample before and after carbonization. The activation was carried out by partial gasification of the carbon with CO₂ at 1098 K, followed by a controlled cooling step with a rate of 20 K min⁻¹ down to ambient temperature. The activation weight loss was also determined. The time to achieve a weight loss of 30% during the activation step was determined for all the carbons, with the aim of evaluating the influence of the different catalyst present during the activation step [15].

Two series of impregnated active carbons were prepared. One used the following sequence of steps on the treatment of pinewood sawdust and nutshells: carbonization, activation and impregnation, being designated by XCAI (depending on the raw material, X will be S for sawdust and N for nutshells). To optimize the dispersion of active sites on the porous texture of the carbons, a new impregnation methodology was developed proceeding to the impregnation step between carbonization and activation according to the following sequence: carbonization, impregnation and activation, being designated by XCIA [15].

Non-expensive metal oxides (CoO, Co₃O₄ and CrO₃) were impregnated into the carbons, to be used as catalysts for the complete oxidation of benzene. The impregnation was carried out using the incipient wetness method to ensure that all the solution was retained in the texture of the impregnated material. The volume of impregnating solution was determined according to the porous volume to be filled; the contact time was chosen such that the impregnated material had a dry appearance (after ca. 10 min). The impregnation temperature

was 294 K. The resultant metal content was determined by flame atomic absorption spectrometry, after treatment of the samples with nitric acid [15].

For both series of samples, i.e. XCAI and XCIA, the deposition of CoO was performed by impregnation with cobalt nitrate solutions prepared with Co(NO₃)₂·6H₂O. For both series carbons with two metal loads were prepared (1.5 and 3%), being designated below as XCAI/CoO-1.5, XCAI/CoO-3.0, XCIA/CoO-1.5, and XCIA/CoO-3.0. The deposition of Co₃O₄ was conducted using cobaltous acetate and sodium carbonate solutions. The precipitate of cobaltous carbonate was decomposed to Co₃O₄ in air at 528 K. The deposition of Co₃O₄ was only performed for the XCIA series, the carbon obtained being designated below as XIA/Co₃O₄-3.0. The deposition of CrO₃ was carried out by impregnating the carbonized material with an ammonical solution containing (NH₄)₂CO₃ and CrO₃. The deposition of CrO₃ was also performed only for the XCIA series, the carbon obtained being designated below as XCIA/CrO₃-3.0 [15]. The impregnated activated carbons were dried for 45 min at 383 K and packed under vacuum until use.

Carbon samples containing 6% metal were also prepared only to determine the final chemical states of the impregnated species using the X-ray diffraction (XRD) method, the crystal sizes being estimated through Sherrer formula. Transmission electron microscopy (TEM) was used to compare the external and internal deposition of impregnant on the support through observation of the surface and sections of the materials [15]. Simultaneous thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out to evaluate the stability of impregnated active carbons in air with increasing temperature.

Nitrogen adsorption isotherms at 77 K were used to evaluate the textural parameters of the carbons. Measurements were conducted in a Micromeritics 2700 flow sorptometer. The samples were first outgassed at 473 K to a vacuum of 0.1 Pa (a maximum of about 15 h for the carbons with well-developed microporous texture) and then weighed. The results were expressed in relation to the unit mass of outgassed carbon. The true adsorption equilibrium was guaranteed by checking the adsorption at regular intervals and following it over long periods of time. All isotherms were repeated at least once to obtain reproducible results. BET theory was used as a reference method for calculating the total specific surface areas (S_{BET}) of the carbons. The t-method was used for calculation of the non-microporous specific surface areas associated with the mesopores (S'_t). The micropore volume (V_{mi}) was calculated using the Dubinin–Astakhov equation applied to the micropore adsorption whenever the Dubinin–Radushkevich equation could not be applied. The mesopore volume (V_{me}) was obtained by deducting the micropore volume from the volume adsorbed at a relative pressure of 0.95 [15].

The determination of surface functional groups was made to characterize surface chemistry. Acid and basic functional groups were determined using the Boehm method that involves a selective neutralization analysis [18]. Solutions of

NaHCO_3 , Na_2CO_3 , NaOH , and HCl were prepared using deionized water. Samples of 200 mg of activated carbon and 20 mL of each solution were shaken (blanks were prepared without carbon). After reaching equilibrium the carbon was separated from the solutions by decanting. The excess of base or acid was determined by back-titration with hydrochloric acid and two solutions of sodium hydroxide with different concentrations. Temperature programmed desorption (TPD) was carried out heating the samples (rate of 50 K min^{-1}) in a He flow to the temperature of 1273 K, to monitor the amounts of CO and CO_2 with a mass spectrometer.

A quick method was needed to evaluate the catalytic activities of the twelve impregnated active carbons at different temperatures and flow rates. A microcatalytic-chromatographic technique was developed using a chromatographic reactor equipped with flame ionization and thermal conductivity detectors; it proved to be a rapid and efficient methodology [19–22]. Twelve chromatographic columns of stainless steel (internal diameter of 0.48 cm and lengths between 20 and 26 cm) were filled with about 2.2 g of each impregnated active carbon. Benzene was injected (as pulses of $0.2 \mu\text{L}$ using Hamilton syringes of $1 \mu\text{L}$) in the chromatographic column at different temperatures and flow rates of carrier gas (0.925, 0.999, 1.08, 1.11 and $1.16 \text{ cm}^3 \text{ s}^{-1}$ at STP), being distributed between stationary and mobile phases. All the experiments were repeated at least three times, until the relative standard deviation was lower than 5%. The oxidation was promoted with the oxygen present in the pure air utilized as carrier gas. The possibility of temperature control of the chromatographic column allowed the consideration of an isothermal oxidation of benzene in the chromatographic reactor. The significant excess of oxygen relative to the small amount of benzene injected in the column, allows considering a pseudo-first-order reaction [21].

The catalysts that showed better performance were tested in a conventional fixed bed flow reactor, consisted by a vertical tube of quartz having an internal diameter of 8.0 mm; about 2.2 g of each carbon was charged in the middle part of the reactor, supported by quartz wool. The catalysts were pre-treated under flowing air at 523 K for 1 h, and then cooled to room temperature before the reaction. A thermocouple was used both to control furnace temperature and to measure the reaction temperature, ranging from 423 to 523 K. The whole reactor system was heated continuously at 110°C to avoid adsorption of benzene onto the tube walls. Mass flow controllers were used for guaranteeing a stable air flow rate of $0.925 \text{ cm}^3 \text{ s}^{-1}$ at STP, containing 6.38 mg dm^{-3} of benzene. To reach this concentration, an air stream was bubbled through a saturator filled with liquid benzene under controlled temperature, after being mixed with another air stream. The entering concentration of benzene was always confirmed by gas chromatography, and this was also used to evaluate the benzene concentration leaving the reactor. The analysis was carried out with a gas chromatograph Chrompack CP9000 equipped with a flame ionization detector and a packed column. Other hydrocarbon by-products

were undetectable; thus, the conversion was calculated based on benzene consumption.

Experiments were also carried out with the fixed bed flow reactor to evaluate changes of catalytic activity/selectivity with use, through the comparison of experimental results obtained with impregnated active carbons after different times of utilization.

The activation energy (E) was determined through the values of the velocity constants at different temperatures, using the Arrhenius equation [20]. The reactant conversions, the kinetic constants and the activation energies were compared considering the influences of the carbon texture, impregnation methodology, catalyst content, catalyst species and raw material.

To evaluate the advantage of supporting catalyst in activated carbons, the catalytic activities of the impregnated active carbons prepared were compared with the catalytic activities of not noble metals supported in different matrix.

3. Results and discussion

Table 1 shows the textural parameters that were determined in order to characterize the impregnated active carbons in comparison with the non-impregnated ones: total specific surface area of the carbons determined by BET method (S_{BET}), non-microporous specific surface area associated with mesopores determined by t-method (S'_t), mesopore volume (V_{me}), micropore volume (V_{mi}), and crystal size (d).

The results obtained for textural characterization show that the two impregnation methodologies employed led to textural variation relative to the non-impregnated carbons that are completely different. For both raw materials, when the impregnation of carbons was performed after CO_2 activation (XCAI series), the impregnant species were deposited on the internal surface, blocking part of the initial porous texture. Consequently, relative to the non-impregnated carbons, both the total and mesoporous surface areas decreased, as well as the micropore and mesopore volumes [15].

On the other hand, when the impregnation was carried out before CO_2 activation (XCIA series), metal species acted as catalysts during the activation step, the texture developing being strongly dependent on the metal oxide dispersion in the carbonized material. A well-developed pore texture appeared essentially near the places where metal species acted as catalysts, remaining a micropore texture with pores of very small sizes where metal species were not present. For both raw materials, due to the presence of the catalysts during the CO_2 activation step, relative to the non-impregnated carbons the impregnation decreased the total specific surface area but increased the mesoporous surface area; the mesopore volume increased but micropore volume decreased, although the volume of the wider micropores increased [15]. Comparing CoO , Co_3O_4 and CrO_3 as catalysts of the CO_2 activation

Table 1
Textural parameters of active carbons prepared with pinewood sawdust and nutshells

Carbon	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_t ($\text{m}^2 \text{g}^{-1}$)	V_{me} ($\text{cm}^3 \text{g}^{-1}$)	V_{mi} ($\text{cm}^3 \text{g}^{-1}$)	d (nm)
SCA	1070	17.4	0.022	0.434	
SCAI/CoO-1.5	972	14.2	0.012	0.409	12.6
SCAI/CoO-3.0	873	10.6	0.005	0.383	14.1
SCIA/CoO-1.5	613	46.1	0.139	0.303	4.5
SCIA/CoO-3.0	292	92.5	0.291	0.099	2.4
SCIA/Co ₃ O ₄ -3.0	455	98.8	0.310	0.170	3.0
SCIA/CrO ₃ -3.0	544	30.5	0.102	0.270	3.5
NCAI	561	70.0	0.135	0.225	
NCAI/CoO-1.5	474	53.3	0.094	0.196	5.6
NCAI/CoO-3.0	386	35.0	0.058	0.167	8.5
NCAI/CoO-1.5	310	99.1	0.330	0.124	2.3
NCAI/CoO-3.0	272	142	0.381	0.081	1.9
NCAI/Co ₃ O ₄ -3.0	464	153	0.393	0.182	2.4
NCAI/CrO ₃ -3.0	437	84.3	0.242	0.196	2.9

step, it was concluded that the higher efficiency of Co₃O₄ was restricted by worse dispersion into the carbonized material, what is related to the larger size of its crystals. CrO₃ was the least efficient catalyst for the CO₂ activation step [15].

In the selective neutralization analysis, NaHCO₃ neutralizes carboxylic acids, Na₂CO₃ neutralizes carboxylic and lactone groups, NaOH neutralizes carboxylic, lactone, and phenol groups, and HCl neutralizes basic surface groups. Carbonyl groups are determined through the titration with two solutions of NaOH with different concentrations [18]. The experimental results showed that neither the acidic nor the basic functional groups present on the carbon surface were significantly affected by the impregnation methodology. When carbonaceous material is subjected to a programmed temperature increase, the surface oxygen complexes desorb mainly as CO₂ (coming from the decomposition of carboxyl, anhydride and lactone groups) and CO (coming from the decomposition of phenol, carbonyl, anhydride, pyrone, quinone and ether groups). The oxygen content of the samples was determined through the amounts of CO and CO₂ desorbed. TPD analysis also showed that functional groups present on the carbon surface were not significantly affected by the impregnation methodology, suggesting that it mainly influences the carbon texture.

The experiments carried out with the chromatographic reactor, to evaluate the catalytic activities of the twelve impregnated active carbons, showed that the peak areas of benzene in the chromatogram decreased with increasing temperature, thus showing the presence of a chemical reaction. As flame ionization detector is selective for organic compounds, the interference of inorganic products is eliminated from the chromatograms, making the determination of reactant peak areas easier and safer. Distortion of peak profiles did not occur and no other peak appeared, even when the flow rate of carrier gas was decreased. This means that products of partial oxidation were not formed. At each temperature, from the first injection to the last, good reproducibility of the peak areas was observed; therefore, it was possible to state that irreversible

adsorption was not present and that the disappearance of benzene was exclusively due to complete oxidation. Thus, the conversion rate could be calculated based simply on benzene consumption.

The differential detectors produce signals proportional to solute gas phase concentration, recording chromatographic peaks whose areas are proportional to the weight of solute passing the detector. Therefore, for chromatographic reactors, the total weights of reactant entering and leaving the column (W_{in} and W_{out}) are, respectively, proportional to the reactant peak areas without and with chemical reaction (A_{R}^0 and A_{R}). If these reactant peak areas are measured with the same detector sensitivity, then at each temperature the reactant conversion (X_{R}) can be determined through the following equation:

$$X_{\text{R}} = 1 - \frac{A_{\text{R}}}{A_{\text{R}}^0} \quad (1)$$

For first-order catalytic reactions associated with linear adsorption isotherms on the catalyst support, the continuous flow model for ideal chromatographic reactors relates W_{in} , W_{out} , the velocity constants in gaseous and solid phases (k_{g} and k_{s}), and the residence time in gaseous and solid phases (t_{g} and t_{s}):

$$\frac{W_{\text{in}}}{W_{\text{out}}} = \frac{A_{\text{R}}}{A_{\text{R}}^0} = \exp(k_{\text{g}}t_{\text{g}} + k_{\text{s}}t_{\text{s}}) \quad (2)$$

Eqs. (1) and (2) are transformed in Eq. (4) to define the apparent rate constant, k_{ap} :

$$k_{\text{ap}} = k_{\text{s}} + k_{\text{g}} \frac{t_{\text{g}}}{t_{\text{s}}} \quad (3)$$

$$-\ln(1 - X_{\text{R}}) = -\ln \frac{A_{\text{R}}}{A_{\text{R}}^0} = k_{\text{ap}}t_{\text{s}} \quad (4)$$

Sometimes both k_{s} and k_{g} can be independently evaluated. Nevertheless, it frequently happens that k_{s} is at least one order of magnitude greater than k_{g} , and $t_{\text{g}}/t_{\text{s}}$ is less than 0.2. In this case, it is not possible to evaluate independently k_{s} and k_{g} ,

k_{ap} being approximately equal to k_s . Then, X_R can be related to the residence time in the solid phase through the following equation:

$$-\ln(1 - X_R) = -\ln \frac{A_R}{A_R^0} = k_s t_s \quad (5)$$

At each temperature, k_s can be calculated through the experimental values of A_R , A_R^0 and t_s , determined through chromatograms obtained at different flow rates, and plotting $\ln(A_R/A_R^0)$ against t_s , where the slope is ($-k_s$).

The reactant peak areas without chemical reaction (A_R^0) were determined in parallel with a column filled with a non-impregnated carbon. In order to confirm that there is no chemical reaction with the non-impregnated carbon, the stability of A_R^0 values was evaluated by lowering the column temperature (the sensitivity of the flame ionization detector is not affected by column temperature in the range considered). As the sensitivity depends on the carrier gas flow rate, A_R^0 was determined for all the flow rates utilized. These values were also compared with those obtained with the columns filled with the impregnated carbons at temperatures at which no reaction can occur. The observed results showed good agreement.

The residence time in solid phase (t_s) was calculated by subtracting the residence time in gaseous phase (t_g) from the global chromatographic retention time measured in the chromatograms. The residence time in gaseous phase corresponds to the chromatographic retention time of a non-adsorbed gas. It was determined experimentally by injecting helium into a chromatograph fitted with a thermal conductivity detector. These values were compared with the ones calculated using porosity parameters, column volume and flow rate. Good agreement was noted, and t_g/t_s was always smaller than 0.1. Therefore, considering that k_s is much larger than k_g , Eq. (5) can be used to calculate k_s .

The pressure drop was negligible along the column and no radial concentration or velocity gradients were observed inside the column. The flow rates used (0.925, 0.999, 1.08, 1.11 and $1.16 \text{ cm}^3 \text{ s}^{-1}$) belong to the range of $0.08\text{--}2.5 \text{ cm}^3 \text{ s}^{-1}$ which guarantee (for the size and type of columns used) that mass transfer is not rate limiting and diffusion is not important [21]. Therefore, the continuous flow model for ideal chromatographic reactors can be applied.

Concluding, the experimental conditions allowed considering a pseudo-first-order reaction that is associated with linear adsorption isotherms, carried out in ideal chromatographic reactors. This supports the utilization of Eq. (5) to calculate the kinetic constants.

Based on the results obtained using the chromatographic reactor, the activated carbons that showed the best performance for the benzene complete oxidation (the ones impregnated with Co_3O_4 before CO_2 activation) were selected, to be tested in the fixed bed flow reactor. The conversion determined had differences relative to those obtained with the chromatographic reactor never higher than 6%, meaning that

Table 2
Kinetic parameters of active carbons prepared with pinewood sawdust and nutshells (k_s at 523 K)

Carbon	k_s ($\times 10^2 \text{ s}^{-1}$)	E (kJ mol^{-1})
SCAI/CoO-1.5	0.317	97.1
SCAI/CoO-3.0	0.447	97.0
SCIA/CoO-1.5	1.37	95.9
SCIA/CoO-3.0	1.62	93.1
SCIA/Co ₃ O ₄ -3.0	2.76	86.0
SCIA/CrO ₃ -3.0	1.39	93.2
NCAI/CoO-1.5	0.524	96.4
NCAI/CoO-3.0	0.549	94.3
NCIA/CoO-1.5	1.10	96.5
NCIA/CoO-3.0	1.48	92.3
NCIA/Co ₃ O ₄ -3.0	3.11	84.6
NCIA/CrO ₃ -3.0	1.05	92.7

the microcatalytic-chromatographic technique proved to be a rapid and efficient methodology for comparing the carbon catalytic activities.

The kinetic constants (k_s) and the activation energies (E) determined using the chromatographic reactor are expressed in Table 2.

To evaluate how the impregnation methodology influenced the kinetic parameters, the carbons compared must be impregnated with the same metal loading and catalyst species, differing only in the impregnation methodology. This was the case for the following pairs: (i) SCAI/CoO-1.5 and SCIA/CoO-1.5; (ii) SCAI/CoO-3.0 and SCIA/CoO-3.0; (iii) NCAI/CoO-1.5 and NCIA/CoO-1.5; (iv) NCAI/CoO-3.0 and NCIA/CoO-3.0. The results expressed in Table 2 show that when impregnation was performed before CO_2 activation, the kinetic constants were 3.6–4.3 times higher for sawdust carbons, and 2.1–2.7 times higher for nut-shell carbons. As it was already referred, when impregnation was performed before CO_2 activation, the volume of the wider micropores increased, as well as the volume and area of the mesopores [15]. Wider micropores favoured an easier access to the catalyst, offering a significant deposition surface. In addition, the higher mesopore areas allowed a better metal oxide dispersion, and this improved the efficiency of the catalyst. This was confirmed through the comparison of the average crystal sizes of CoO for SCAI/CoO-1.5 and SCIA/CoO-1.5 (12.6 and 4.5 nm, respectively), for SCAI/CoO-3.0 and SCIA/CoO-3.0 (14.1 and 2.4 nm, respectively), for NCAI/CoO-1.5 and NCIA/CoO-1.5 (5.6 and 2.3 nm, respectively), and for NCAI/CoO-3.0 and NCIA/CoO-3.0 (8.5 and 1.9 nm, respectively). The images obtained using TEM only allowed a qualitative comparison between external and internal deposition of impregnant on the support; nevertheless, they confirmed a better internal deposition for the carbons impregnated before CO_2 activation. According to the reactant conversions shown in Fig. 1, calculated using Eq. (1), it could be concluded that for both raw materials, the catalytic activity increased when the catalysts were supported on activated carbons with a better

development of mesopore area and volume, which could be induced, proceeding to the impregnation before CO₂ activation.

To analyse the influence of the catalyst content on the kinetic parameters, the carbons must be impregnated using the same methodology, with the same catalyst species, and differing only in the metal loading. This was the case of the following pairs: (i) SCAI/CoO-1.5 and SCAI/CoO-3.0; (ii) NCAI/CoO-1.5 and NCAI/CoO-3.0; (iii) SCIA/CoO-1.5 and SCIA/CoO-3.0; (iv) NCAI/CoO-1.5 and NCAI/CoO-3.0. Table 1 shows that SCAI/CoO-3.0 and NCAI/CoO-3.0 had lower values for S_{BET} , S_{t} , V_{mi} and V_{me} , than, respectively, SCAI/CoO-1.5 and NCAI/CoO-1.5, leading to a decrease in the metal oxide dispersion (crystal sizes increased). Nevertheless, due to its higher metal content, SCAI/CoO-3.0 and NCAI/CoO-3.0 had kinetic constants, respectively, 1.41 and 1.05 times higher than SCAI/CoO-1.5 and NCAI/CoO-1.5 (see Table 2). SCIA/CoO-3.0 and NCAI/CoO-3.0 had lower S_{BET} and V_{mi} than, respectively, SCIA/CoO-1.5 and NCAI/CoO-1.5, but higher S_{t} and V_{me} , leading to a better metal oxide dispersion (crystal sizes decreased) and to kinetic constants, respectively, 1.18 and 1.35 times higher. According to the reactant conversions shown in Fig. 1, it was concluded that the catalytic activity increased with increasing catalyst content, even for worse metal oxide dispersions.

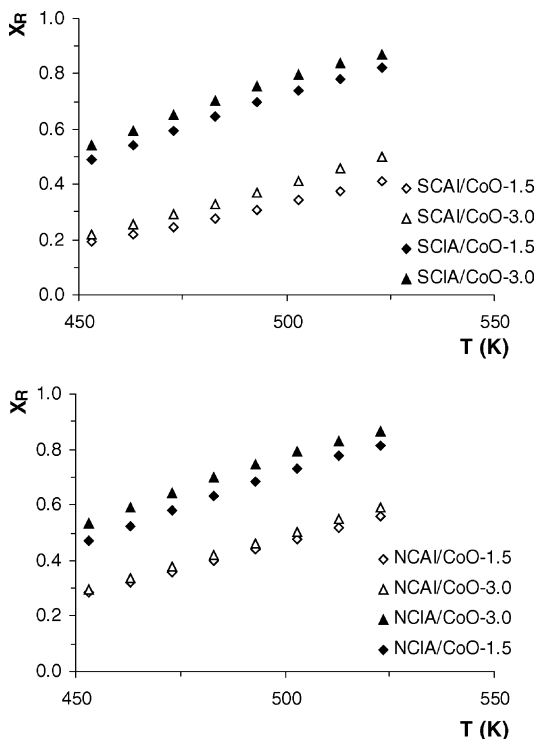


Fig. 1. Influence of the impregnation methodology on the conversion of benzene through complete oxidation (reaction conditions: weight of impregnated active carbons, 2.2 g; flow rate of carrier gas, $0.925 \text{ cm}^3 \text{ s}^{-1}$ at STP).

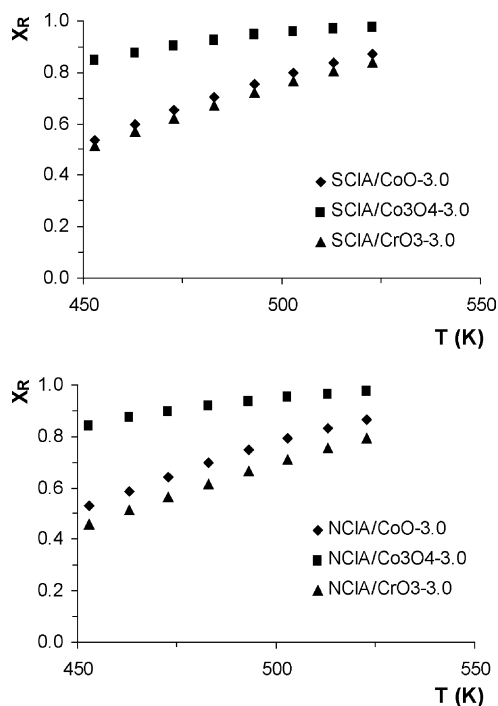


Fig. 2. Influence of the catalyst species on the conversion of benzene through complete oxidation (reaction conditions: weight of impregnated active carbons, 2.2 g; flow rate of carrier gas, $0.925 \text{ cm}^3 \text{ s}^{-1}$ at STP).

To analyse the influence of the catalyst species on the kinetic parameters, the carbons must be impregnated using the same methodology, with the same metal loading, and differing only in the catalyst species impregnated. This was the case for the following carbons: (i) SCIA/CoO-3.0, SCIA/Co₃O₄-3.0 and SCIA/CrO₃-3.0; (ii) NCAI/CoO-3.0, NCAI/Co₃O₄-3.0 and NCAI/CrO₃-3.0. The crystal sizes of CoO, Co₃O₄ and CrO₃ were, respectively, 2.4, 3.0 and 3.5 nm for sawdust carbons, and 1.9, 2.4 and 2.9 for nutshell carbons. TEM images confirmed better internal deposition in the carbons impregnated with CoO. Nevertheless, Fig. 2 shows that Co₃O₄ was the best catalyst for the complete oxidation of benzene (as it was for the CO₂ activation step), despite having a worse dispersion than CoO. Analysing Table 2, it can be seen that the kinetic constants of SCIA/Co₃O₄-3.0 and NCAI/Co₃O₄-3.0 were, respectively, 2.0 and 3.0 times higher than the ones of SCIA/CrO₃-3.0 and NCAI/CrO₃-3.0, certainly related to the lowest catalyst efficiency of CrO₃ (also the worst catalyst for the CO₂ activation step), in addition to the lowest mesoporous area and mesopore volume development that implied the worst CrO₃ dispersion, confirmed through its bigger crystal sizes. It could be observed that with Co₃O₄ as catalyst, a benzene conversion of 90% was reached at lower temperatures than with CrO₃ (respectively, 470 and 544 for sawdust carbons, and 472 and 558 for nutshell carbons). Concluding, for the complete oxidation of benzene, the catalytic activity of cobalt was better than that of chromium, the oxidation state of cobalt in Co₃O₄ being better than in CoO.

To evaluate the stability of impregnated active carbons in air with increasing temperature, DTA experiments were carried out. For all the impregnated carbons, the results showed that at about 575 K an exothermic reaction begins to be observed with an enthalpy of $-404.5 \text{ kJ mol}^{-1}$, related to the reaction between carbon and oxygen. This means that temperatures lower than 575 K must be used for guaranteeing carbon stability. Figs. 1 and 2 show that the carbons impregnated before CO_2 activation allowed very good conversions at temperatures that guarantee carbon stability.

The comparison of experimental results obtained with the fixed bed flow reactor, for impregnated active carbons having different times of utilization, showed that catalytic activity/selectivity is enough stable if the reaction temperature is maintained below 575 K.

The catalytic activities, of the impregnated active carbons prepared, were compared with those of other catalysts: 5% Cu supported in $\gamma\text{-Al}_2\text{O}_3$ [5] and 8.5% Cu–Cr supported in $\gamma\text{-Al}_2\text{O}_3$ [11]. For that, the kinetic constants determined with the chromatographic reactor were used to estimate the conversions that would be obtained with the prepared active carbons in a fixed bed flow reactor at the experimental conditions referred on the publications ($m/U = 0.50 \text{ g s cm}^{-3}$ [5], and space time $\tau = 0.90 \text{ s}$ [11]). The results are presented in Table 3 for a temperature of 523 K. The analysis of these results allowed to conclude that the catalysts prepared by impregnating metal oxides in activated carbons (mainly those impregnated before CO_2 activation), can be significantly better than 5 wt.% Cu/ $\gamma\text{-Al}_2\text{O}_3$ and 8.5% Cu–Cr/ $\gamma\text{-Al}_2\text{O}_3$. Therefore, it seems to be possible to conclude that activated carbon is a suitable support for metal oxide catalysts, to be used for the complete catalytic oxidation of benzene, especially if an adequate porous texture is induced proceeding to the impregnation before CO_2 activation.

Table 3

Comparison of benzene conversions through complete oxidation at 523 K using different catalysts

Catalyst	Conversion (%)	
	$m/U = 0.50 \text{ g s cm}^{-3}$	$\tau = 0.90 \text{ s}$
SCAI/CoO-1.5	9.4	14
SCAI/CoO-3.0	13	20
SCIA/CoO-1.5	30	40
SCIA/CoO-3.0	35	43
SCIA/Co ₃ O ₄ -3.0	56	68
SCIA/CrO ₃ -3.0	32	44
NCAI/CoO-1.5	14	22
NCAI/CoO-3.0	36	56
NCAI/CoO-1.5	18	23
NCAI/CoO-3.0	34	41
NCAI/Co ₃ O ₄ -3.0	57	61
NCAI/CrO ₃ -3.0	28	36
5 wt.% Cu/ $\gamma\text{-Al}_2\text{O}_3$ [5]	7	
Cu–Cr/ $\gamma\text{-Al}_2\text{O}_3$ [11]		22

4. Conclusion

For both raw materials, the impregnation before CO_2 activation decreased the total specific surface area but increased the volume of the wider micropores, the mesopore volume, and the mesoporous surface area; at 523 K the kinetic constants were 3.6–4.3 times higher for sawdust carbons, and 2.1–2.7 times higher for nutshell carbons, due to a better metal oxide dispersion on higher mesopore areas and on wider micropores, which also favoured an easier access to the catalyst; CrO_3 was the worse catalyst for the complete oxidation of benzene, and Co_3O_4 was the best, despite having a worse dispersion than CoO . A benzene conversion of 90% was reached with Co_3O_4 as catalyst at a lower temperature than with CrO_3 (472 and 558 K, respectively). The carbons impregnated before CO_2 activation allowed very good conversions at temperatures that guarantee the carbon stability (lower than 575 K). The impregnation of metal oxides in activated carbons (mainly before activation) led to catalysts with a better performance than 5 wt.% Cu/ $\gamma\text{-Al}_2\text{O}_3$ and 8.5% Cu–Cr/ $\gamma\text{-Al}_2\text{O}_3$. The results obtained led to the conclusion that activated carbon is a suitable support for metal oxide catalyst, to be used for the complete oxidation of benzene, especially if an adequate porous texture is induced proceeding to the impregnation before CO_2 activation.

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