

Preparation, characterization, and testing of metal-doped carbon xerogels as catalyst for phenol CWAO

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Abstract Co-, Ce-, and Ni-doped carbon xerogels (Me-CX) synthesized by sol-gel method followed by an ion exchange process were used as catalysts for catalytic wet air oxidation (CWAO) of phenol. The prepared catalysts were characterized using TEM, SEM, BET surface area, and XRD. Me-CX catalysts were tested in mild conditions (20–60 °C, atmospheric pressure) in a semi-batch reactor in various reaction conditions (30–60 L/h, 0.05–0.2 g catalysts, 50–175 mg phenol/L). Total organic carbon (TOC) removal efficiency values obtained decrease in the following order Co-CX \cong Ce-CX > Ni-CX > K-CX for the catalysts obtained using the same procedure. TOC removal efficiencies of up to 72% were reached in case of Co-CX catalyst at 20 °C, 40 L/h, using 0.15 g catalyst and a solution of 100 mg phenol/L.

Keywords Sol-gel method · Metal-doped carbon xerogel · Catalytic wet air oxidation · Phenol · Total organic carbon

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Introduction

Phenol is one of the most common organic water pollutants, because it is produced by industries and domestic activities in large amount and it is toxic even at low concentrations. Phenol is also relevant in the field of environmental research, because it has been chosen frequently as a model pollutant and many data are available on its removal and destruction in particular with respect to wastewater treatments (Busca et al. 2008). The major sources of phenol are wastewaters from pesticide, paint, polymeric resin, petroleum, and petrochemical industries (Ahmaruzzaman 2008; Calace et al. 2002; Derbyshire et al. 2001).

Wet air oxidation (WAO) developed by (Zimmermann 1958) is one of the most economical and technologically viable oxidation processes for degradation of organic pollutants from high organic content wastewaters (Fu and Kyzas 2014). WAO has great potential for treating wastewater that contains about 10–100 g/L of chemical oxygen demand (COD) and/or toxic contaminants, and is useful where a direct biological treatment is not feasible (Fu and Kyzas 2014; Kim and Ihm 2011). However, the severe operating conditions (high pressure and temperature) and high costs limit its application in wastewater treatment. In the last two decades, catalytic wet air oxidation (CWAO) has gained some attention because it can operate at mild temperature and pressure, at lower costs (Busca et al. 2008). The addition of the solid catalyst allows operation at lower temperature and pressure values and enhances even the refractory pollutant decomposition, thereby reducing capital and operational costs (Fu and Kyzas 2014; Jing et al. 2012; Levec and Pintar 2007; Cybulski 2007). Also, the usage of solid catalysts has the advantage that the catalyst can be recovered, regenerated, and reused (Ahmaruzzaman 2008; Calace et al. 2002). Catalysts as noble metals, metal

oxides, and mixed oxides have been widely studied in CWAO process (Fu and Kyzas 2014; Kim and Ihm 2011).

A novel class of porous carbon gels that has received considerable attention over the past ten decades is the carbon xerogels that are novel micro-mesoporous carbon materials (Girgis et al. 2012). They are interesting since the accurate tailoring of the pore texture allows a significant increase in catalytic and electrocatalytic performances enabling their application in dynamic adsorption (Ribeiro et al. 2012). These materials can be obtained from the carbonization of organic xerogels that are prepared by a sol-gel method, in which a polycondensation reaction of certain organic monomers, such as resorcinol or potassium salt of 2,4-dihydroxybenzoic acid and formaldehyde in the presence of Na₂CO₃ or K₂CO₃ as catalysts, takes place, followed by evaporative drying and pyrolysis in an inert atmosphere (Pekala 1989; Cotet et al. 2012, 2014). Carbon xerogels can be obtained in the form of monoliths, beads, powders, or thin films, and their unique properties (controllable porosity, thermal stability, large pore volume, and high specific surface area) make them promising materials for application in adsorption and catalysis. They are also widely used as support matrices for various catalytic active centers, represented especially by metal species (Moreno-Castilla and Maldonado-Hodar 2005). As metal species, Pt-, Pd-, Fe-, Cu-, Ag-, Co-, Ru-, Ir-, Au-, and Ce-containing carbon xerogels were synthesized and tested as catalysts in catalytic wet peroxide oxidation, adsorption/catalysis of large molecules, for energy storage in double-layer capacitors, and catalytic support in polymer-electrolyte membrane fuel cells (Cotet et al. 2014; Antolini 2009; Girgis et al. 2011; Frackowiak and Beguin 2001; Li et al. 2003).

In this paper, preparation, characterization, and preliminary results on testing of Co-, Ce-, and Ni-doped carbon xerogel catalysts in catalytic wet air oxidation of phenol were considered.

Experimental

Materials

K₂CO₃ (CristalRChim), formaldehyde solution, min. 37% (Merck), Co(CH₃COO)₂·4H₂O (Silal Trading), Ce(NO₃)₃·

6H₂O (Merck), Ni(NO₃)₂·6H₂O (Reactivul București), 2,4-dihydroxybenzoic acid (Fluka), and phenol (LAB-SCAN), all of analytical grade, were used. Double-distilled water was used throughout this work.

Catalyst preparation and characterization

Potassium salt of 2,4-dihydroxybenzoic acid obtained from 2,4-dihydroxybenzoic acid (A) and K₂CO₃ (2 molar ratio) in aqueous solution under stirring and formaldehyde (A/formaldehyde, 0.5 molar ratio) were used as precursors for the polycondensation reaction in the presence of K₂CO₃ as catalyst (A/catalyst, 100 molar ratio) (Cotet et al. 2007). The sol-gel process took place in sealed glass bottles at 70 °C for 72 h. The resulted potassium-doped wet gel was then immersed in a 0.1-M doping metal alcoholic or aqueous solution, in this case Co(CH₃COO)₂·4H₂O, Ce(NO₃)₃·6H₂O or Ni(NO₃)₂·6H₂O. This process was repeated two or three times at 24-h intervals, with fresh metal solution (Table 1). Potassium ions from the wet gel were replaced with the corresponding metal through ion exchange process, when the metal-doped gel was obtained. The metal-doped gel was then dried under ambient conditions (20 ± 2 °C) and then pyrolyzed at 750 °C for 2 h in argon atmosphere, when Me-CX (Co-CX, Ce-CX, Ni-CX) catalyst was obtained. K-CX sample (blank) was also prepared using the same stages described above without the metal-K ionic exchange stage. The labeling of the prepared catalysts is presented in Table 1 underlying that two groups of catalysts were prepared, one when the same procedure was followed (ethanol as a solvent and the ion exchange process was repeated two times) using three different metals, and the second one when the same metal was used (Ni) but the synthesis procedure was different (water and ethanol were used as solvent, and the ion exchange process was repeated two or three times).

Transmission electron microscopy (TEM) analysis was performed using a Hitachi Automatic TEM H7650 microscope (125 KeV). Metal nanoparticles diameter (D_{med, nanopart}) and particle size polydispersity were calculated using “ImageJ” software and several TEM images.

Scanning electron microscopy (SEM) analysis was carried out using Quanta 3D FEG Scanning Electron Microscope.

Table 1 Labeling of the prepared catalysts used in this study

Catalyst	Metal	Precursor	Solvent	No. of changes /fresh metal solution, mL
Ce-CX	Ce	Ce(NO ₃) ₃ ·6H ₂ O	Ethanol	2/150
Co-CX	Co	Co(CH ₃ COO) ₂ ·4H ₂ O	Ethanol	2/150
Ni1-CX	Ni	Ni(NO ₃) ₂ ·6H ₂ O	Ethanol	2/150
Ni2-CX	Ni	Ni(NO ₃) ₂ ·6H ₂ O	Ethanol	3/150
Ni3-CX	Ni	Ni(NO ₃) ₂ ·6H ₂ O	Double-distilled water	2/150

Table 2 Reaction conditions used in phenol CWAO process for Co-CX catalyst

Catalyst	Parameter			
	Temperature (°C)	Air flow (L/h)	Catalyst quantity (g)	Phenol concentration (mg/L)
Co-CX	20	30	0.05	50
	30	40	0.10	100
	40	50	0.15	150
	50	60	0.20	175
	60			

Surface area and pore size distribution measurements were performed using Brunauer-Emmett-Teller (BET) method and a Sorptomatic 1990 apparatus (Thermo Electron-Corp). Prior to N₂ adsorption at −196 °C, samples of about 0.1 g were outgassed for 20 h at 105 °C.

X-ray diffraction (XRD) measurements were performed on a Shimadzu 6000 diffractometer using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), equipped with a graphite monochromator.

Catalytic wet air oxidation experiments

Phenol oxidation reaction was carried out in a thermostated stirred semi-batch reactor operated at atmospheric pressure. For a typical run, 25 mL of phenol solution (100 mg/L) was contacted with 0.1 g catalyst ($d < 250 \text{ }\mu\text{m}$) at $20 \pm 2 \text{ }^\circ\text{C}$ under a 40 L/h air flow. The catalyst and phenol solution were maintained in contact under the established reaction conditions, for 3 h. The reaction was also performed without catalyst and using a blank sample, K-CX, in the same conditions. All the experiments were realized in triplicate; the presented values are averaged values.

In order to study the influence of the reaction conditions over the CWAO efficiency for Co-CX catalyst, various air flows (30–60 L/h), catalyst quantities (0.05–0.2 g), temperatures (20–60 °C), and phenol concentrations (50–175 mg/L) were considered (Table 2).

Taking into account the fact that in this stage of the research, we were interested to see how metal-doped carbon

xerogel acts as catalyst for total oxidation of phenol, we used only total organic carbon (TOC) method in order to establish the final concentration of the organics in solution. TOC analysis was realized using Hach Lange equipment, which includes TOC-X5 stirrer, LT 200 thermostat, DR 2800 spectrophotometer, and TOC vials (LCK 385, LCK 386).

CWAO efficiency, E_{TOC} (%), was calculated using total organic carbon values for initial (TOC_i , mg/L) and final (TOC_f , mg/L) solution, with Eq. (1):

$$E_{\text{TOC}}, \% = \frac{\text{TOC}_i - \text{TOC}_f}{\text{TOC}_i} \times 100 \quad (1)$$

Results and discussion

Catalyst characterization

SEM investigations of Me-CX samples revealed the presence of metallic particle conglomerates distributed on a porous carbon matrix (Fig. 1). Conglomerates up to 20 μm in length were identified on the carbon xerogel surface.

TEM images of K-CX and Co-CX are presented in Fig. 2. In case of K-CX sample, a porous carbon matrix without metal nanoparticles was observed (Fig. 2a). In case of Me-CX catalysts, exemplified for Co-CX (Fig. 2b), well-dispersed metal nanoparticles into the porous carbon xerogel were visualized.

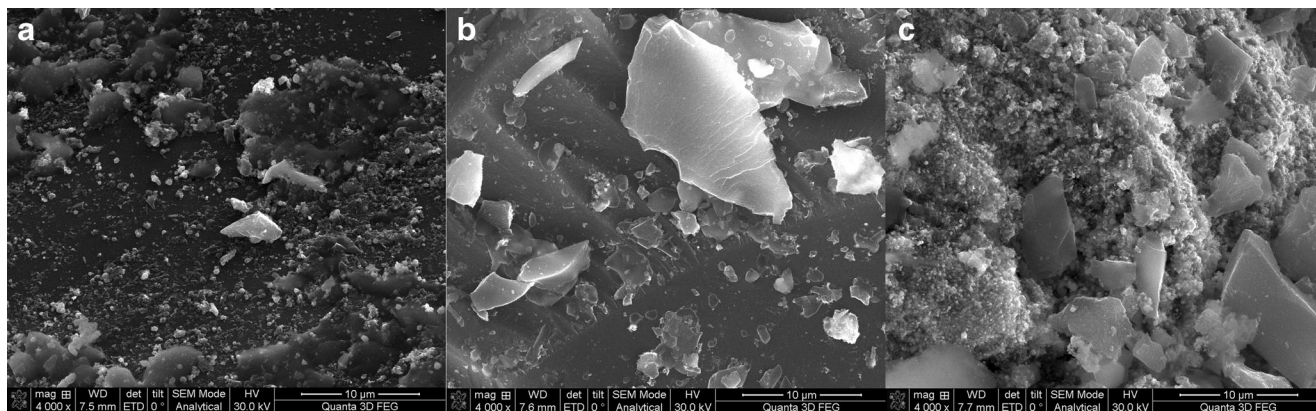


Fig. 1 SEM images of **a** Co-CX, **b** Ce-CX, and **c** Ni1-CX catalyst ($\times 4000$)

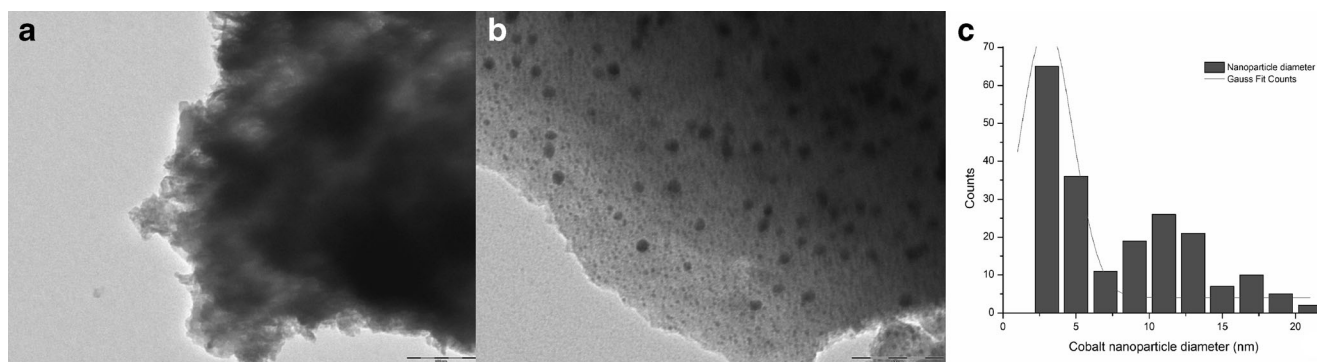


Fig. 2 TEM images of **a** K-CX, **b** Co-CX, and **c** Co nanoparticle diameter distribution

The metal nanoparticle diameter and particle size polydispersity were determined using “ImageJ” software and several TEM images, and the results are presented in Table 3. Metal nanoparticles in 3 to 14 nm range were identified. In case of Co-CX, a bimodal distribution was evidenced (Table 3, Fig. 2c).

All catalysts showed a type IV hysteresis, corresponding to a micro-mesoporous structure, while pore size distribution showed a Gaussian type with a maximum at about 5 nm. Median pore diameter ($d_{med, pore}$) is presented in Table 3. The nitrogen adsorption-desorption isotherm and pore size distribution of Co-CX catalyst is presented as an example in Fig. 3. The measured BET surface area (S_{BET}) and pore-specific volume (V) derived from the N_2 adsorption isotherms are presented in Table 3. The S_{BET} measured for blank sample (K-CX) was about 6 m^2/g , while for metal-doped carbon xerogel samples, S_{BET} values were ranging in 210–275 m^2/g interval. S_{BET} values of Me-CX are higher than K-CX sample due to the strengthening of the porous structure produced by the metal ions (Cotet et al. 2006).

The pore-specific volume, 0.005–0.167 cm^3/g , provides a complementing proof that carbon xerogels are mixed-porosity carbons, with general even distribution within micro-mesopores (Girgis et al. 2012).

The crystalline structure of the samples was analyzed by X-ray diffraction (XRD). The powder XRD pattern of the carbon xerogel samples are shown in Fig. 4. All

patterns show the presence of an important background with broad peaks at $2\theta = 25^\circ$ and 45° for amorphous carbon (Gich et al. 2013; Fort et al. 2015). The three Ni containing xerogels present a well-defined signature of metallic Ni nanoparticles at $2\theta = 44.5, 51.8,$ and 76.3 corresponding to (111), (200), and (220) Bragg reflections, respectively. All the identified peaks match well with of the standard face-centered cubic (fcc) structure (ICDD file no. 04-0850) (Kang et al. 2013).

A weak reflection at 44.18 can be observed in the diffractogram of Co-CX that can be assigned to (111) reflection line of face-centered cubic beta-cobalt (JCPDS 15-0806) indicating the formation of Co nanoparticles (Jaumann et al. 2013).

Regarding Ce-CX sample, the XRD pattern suggests that cerium is incorporated as face-centered cubic fluorite-type CeO_2 (JCPDS 78-0694), with the specific Bragg reflections (111), (200), (220), (311), and (222) (Hu et al. 2006).

Phenol total oxidation results

The catalysts, Co-CX, Ce-CX, Ni1-CX, Ni2-CX, and Ni3-CX, prepared as described above were used for catalytic wet air oxidation of phenol. Figure 5 shows the TOC efficiency for all tested catalysts, by comparison with experiments conducted without catalyst and using the blank sample (K-CX). Also, the prepared catalysts in Fig. 5 are

Table 3 Morphological and structural characteristics of the prepared catalysts

Catalyst	$D_{med, nanopart}$, nm	Polydispersity, %	S_{BET} , m^2/g	V , cm^3/g	$d_{med, pore}$, nm
K-CX	n.a.	n.a.	6	0.005	— ^a
Ce-CX	12 ± 3	25.97	231	0.167	3.83
Co-CX	3 ± 1 11 ± 1	48.56 6.83	225	0.136	3.84
Ni1-CX	9 ± 1	14.30	210	0.190	4.57
Ni2-CX	8 ± 2	30.89	275	0.161	3.62
Ni3-CX	5 ± 1	20.97	218	0.119	3.10

n.a. not applicable
^a Macroporous—out of range of the apparatus

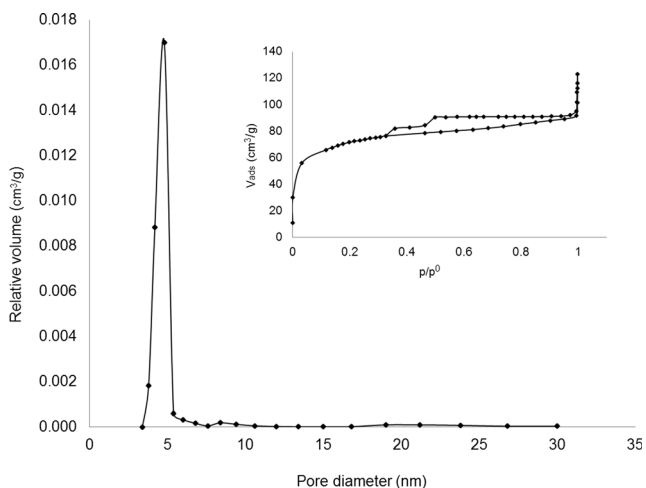


Fig. 3 Co-CX pore size distribution and adsorption-desorption isotherm (*inset*)

grouped according to the procedure used to prepare them (Table 1). The following series were depicted based on these results: Co-CX \cong Ce-CX > Ni1-CX > K-CX (ethanol as a solvent and the ion exchange process was repeated 2 times) and Ni2 > Ni3 > Ni1 (water for Ni3 and ethanol for Ni1 and Ni2 were used as solvent, while the ion exchange process was repeated two times for Ni1 and Ni3, and three times for Ni2 (Table 1)). When the solvent was changed, double-distilled water instead of ethanol, Ni3-CX catalyst (Table 1), TOC efficiency was slightly smaller but in the same range (34%), indicating that the ionic exchange process takes place in similar conditions for both solvents. When the number of ion exchange stages was increased, Ni2-CX catalyst (Table 1), a small increase of TOC efficiency was recorded (up to 40%), suggesting that the ion exchange equilibrium was not

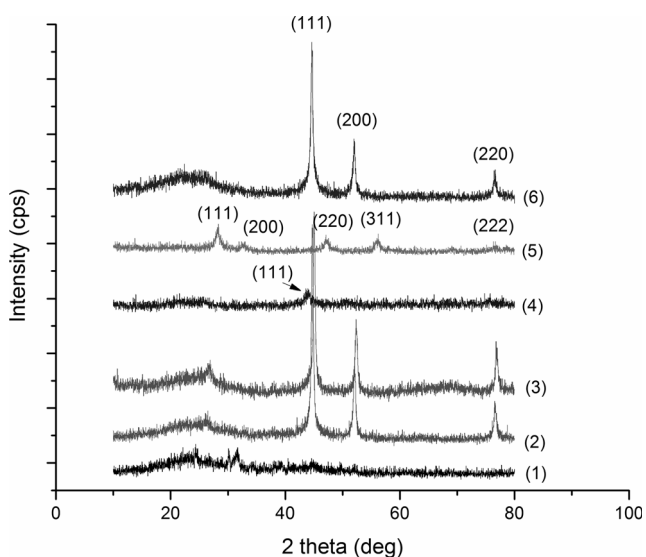


Fig. 4 XRD pattern of metal-doped carbon xerogel. Legend: (1) K-CX, (2) Ni2-CX, (3) Ni1-CX, (4) Co-CX, (5) Ce-CX, and (6) Ni3-CX

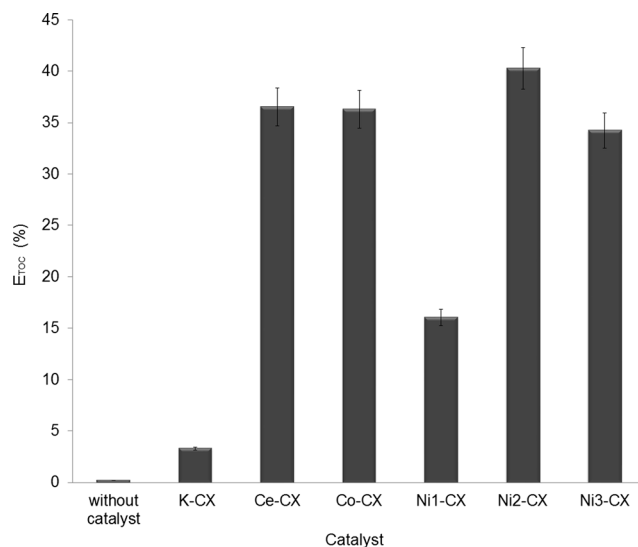


Fig. 5 Comparative TOC efficiency for phenol CWAO on the considered catalysts (20 °C, 40 L/h, 0.1 g catalyst, 100 mg/L, 3 h)

reached in the first two steps. The small decrease in the phenol concentration in case of K-CX blank sample could be attributed to the phenol adsorption on the xerogel surface. The obtained results can be correlated with the catalyst morphological and structural characteristics. Ce-CX and Co-CX have the highest surface area and pore volume between the ones obtained using the same procedure. Based on the efficiency series, which include catalysts prepared using the same methodology, the following experiments were conducted using the Co-CX catalyst, which gave best results in terms of TOC efficiency.

TOC efficiency increases up to about 35% as air flows increases from 30 to 50 L/h, while with a further increase of the flow rate, the efficiency drops to about 21% (Fig. 6). This difference could be due to the fact that as

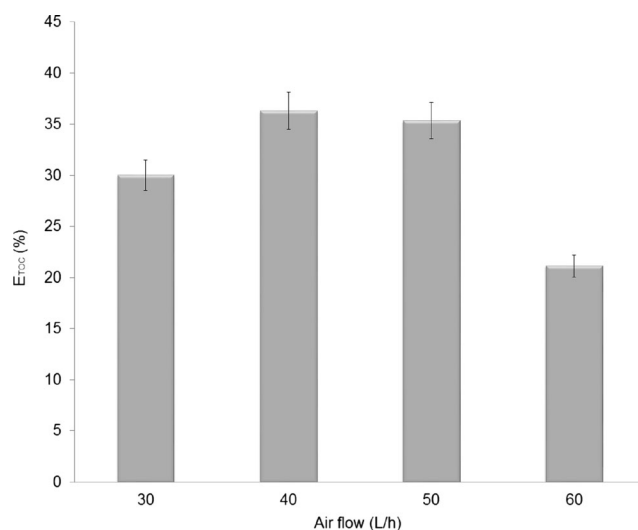


Fig. 6 Air flow influence over the maximum TOC efficiencies obtained for phenol CWAO on Co-CX (20 °C, 0.1 g catalyst, 100 mg/L, 3 h)

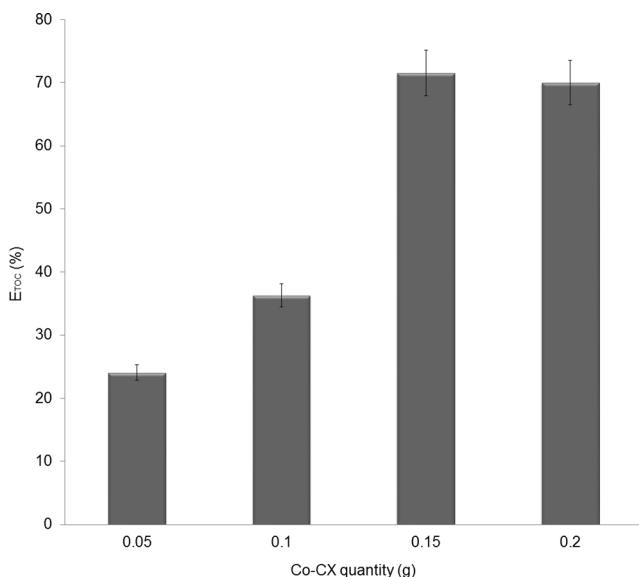


Fig. 7 Co-CX quantity influence over the maximum TOC efficiencies obtained for phenol CWAO (20 °C, 40 L/h, 100 mg/L, 3 h)

the air flow increases, the oxygen diffusion towards the catalyst surface is limited.

In the case of the catalyst quantity (Fig. 7), exemplified for Co-CX, as the quantity increases, the efficiency increases, reaching a maximum of about 72% at 0.15 g. A further increase of the catalyst quantity led to a slight decrease of the efficiency, a fact that might be due to diffusional limitation that occurs with an increase of solid mass quantity.

When various temperature values were considered (Fig. 8), TOC efficiency slightly increases with the temperature in 20–60 °C interval up to 55% for 60 °C. Further increase in the

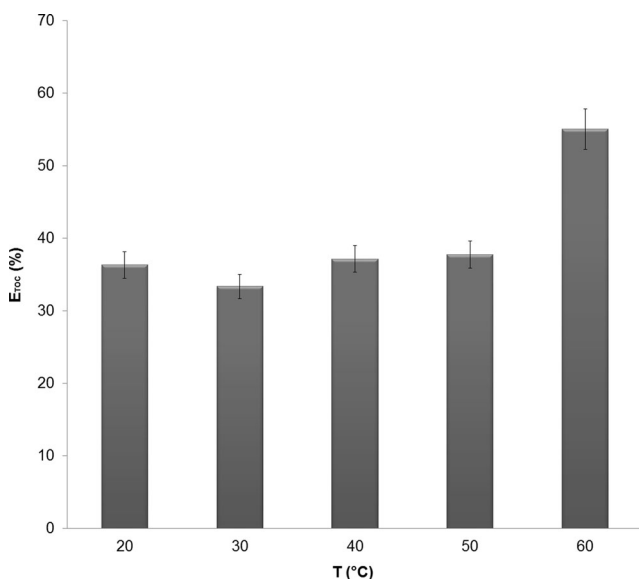


Fig. 8 Reaction temperature influence over the maximum TOC efficiencies obtained for phenol CWAO on Co-CX (0.1 g catalyst, 40 L/h, 100 mg/L, 3 h)

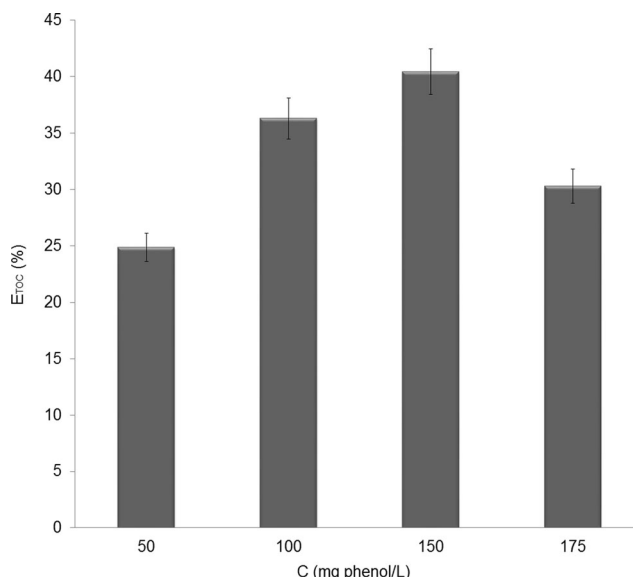


Fig. 9 Phenol initial concentration influence over the maximum TOC efficiencies obtained for phenol CWAO on Co-CX (20 °C, 40 L/h, 0.1 g catalyst, 3 h)

temperature had as effect an intense evaporation of the solution even when a reflux operation was considered.

The influence of phenol concentration in solution over the maximum TOC efficiency for Co-CX catalyst is presented in Fig. 9. As concentration increased, TOC efficiency increased up to about 40% in case of 150 mg/L, while at 175 mg/L, efficiency drops to about 30% (higher number of phenol molecules on the same surface/number of active centers).

Preliminary experiment on the catalyst reuse (Co-CX) showed that after regeneration (pyrolysis at 750 °C for 2 h), TOC efficiency decreases from 72 to about 32% (20 °C, 40 L/h, 0.15 g catalyst, 100 mg/L, 3 h). This decrease might be attributed to metal leaching from the catalyst or modification of the catalyst structure. A detailed analysis of these processes is under study for the various metals considered and for several preparation procedures.

Conclusions

Ce-, Ni-, and Co-doped carbon xerogel monolithic materials with high surface area and metal nanoparticle dispersed in the xerogel structure were synthesized and characterized. Morphological and structural analysis of the studied catalysts showed the presence of metallic nanoparticles in case of cobalt and nickel and presence of CeO₂ particles in case of Ce-CX. Studied catalysts showed a type IV hysteresis corresponding to a mesoporous structure, while pore size distribution showed a Gaussian type distribution with a maximum at about 5 nm and specific surface areas in 200 m²/g range.

Me-CX catalysts showed high efficiency for the CWAO of phenol with efficiencies up to about 37% in case of Co-CX

and Ce-CX catalyst, for the typical run (25 mL of phenol solution 100 mg/L, 0.1 g catalyst, 20 ± 2 °C, 40 L/h). The maximum value for TOC efficiency, 72%, was reached for Co-CX catalysts when 0.15 g catalyst was used in the same reaction conditions.

Further studies are under work in order to establish the optimum preparation conditions, working condition for CWAO of various organic compounds, catalyst reproducibility, metal leaching, and lifetime.

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