Efficient ceria–silica catalysts for BTX oxidation: Probing the catalytic performance and oxygen storage


HIGHLIGHTS

- CeO₂ based catalysts were prepared by impregnation method and MCM-41 supports.
- The method of preparation affects the dispersion/incorporation of the CeO₂ which led to higher catalytic activities.
- CeO₂–MCM-41 material showed better BTX oxidation capacity.

ABSTRACT

This paper describes a systematic investigation on the synthesis of CeO₂ supported on SiO₂ by two different methods: (i) the in situ incorporation of CeO₂ onto MCM-41 and (ii) wet impregnation. We were interested in investigating how the CeO₂ preparation could influence their physicochemical properties and catalytic performances towards the benzene, toluene, and o-xylene (BTX) oxidation reactions. Our results showed that the catalytic performances were strongly dependent on the synthetic approach, in which the CeO₂–MCM-41 material prepared by the in situ incorporation showed better BTX oxidation activities than the CeO₂–based catalysts prepared by conventional wet impregnation. This result could be assigned to the higher specific surface area, better interaction between CeO₂ and the support, improved Ce⁴⁺/Ce³⁺ redox process, and higher concentration of oxygen vacancies as enabled by the in situ approach. The influence of CeO₂ content in the ordering of the SiO₂ mesoporous structure was also demonstrated.

1. Introduction

Ceria (CeO₂) is widely employed as heterogeneous catalysts towards a variety of reactions due to its interesting properties such as good oxidation–reduction potential, high oxygen storage capability (OSC), and controlled porosities [1–5]. These features play an important role in the context of CeO₂-catalyzed oxidation reactions, and originate from the easy formation and mobility of oxygen vacancies, mainly at the surface [6–9].

Especially, CeO₂ oxygen vacancies provide sites for oxygen activation and increase the diffusion rate of oxygen, that can be used to enhance catalytic processes [6,8–10]. In order to enhance the number of oxygen vacancies, many strategies have been employed such as the inclusion of secondary metal dopants, defects in the structure, and metal-support interactions [10–12]. One of the efficient strategies to provide higher concentration of oxygen vacancies in the CeO₂ structure is by metal-support interactions that occur by anchoring CeO₂ over a metal oxide (SiO₂, Al₂O₃, ZnO, and others) by impregnation, hydrothermal, sol–gel process, electrodeposition and metal precursor hydrolysis [8,13–20].

In this paper, we describe a simple approach for the synthesis of CeO₂ supported on SiO₂ catalysts obtained by two different methods: (i) CeO₂–MCM-41 obtained by the in situ incorporation of a cerium precursor into the mesoporous silica MCM-41 framework, and (ii) CeO₂–SiO₂ obtained by conventional wet impregnation of commercial CeO₂ over SiO₂ and Ce(NO₃)₃ over MCM-41. It is important to note that, in the CeO₂ containing MCM-41, the active site-isolation in the framework positions of solid matrices prevents metal aggregation to produce less reactive species [21]. Specifi-
cally, we were interested in studying how the preparation method of the CeO$_2$-based catalysts could influence their active site-support interaction, the concentration of oxygen vacancies, and their corresponding catalytic performances towards benzene, toluene, and o-xylene (BTX) oxidation. Although these organic compounds are harmful to the atmosphere and human health, they are still released to the environment by a variety of daily activities. Thus, the BTX oxidation was chosen as a model to probe catalytic performances as it represents one of the most important methods to their removal from the environment due to its high degradation efficiency and low energy costs [22–24].

2. Experimental

2.1. Chemicals

All reagents were purchased from commercial sources and used as received.

2.2. Preparation of CeO$_2$–MCM-41 catalyst by the in situ incorporation of Ce

CeO$_2$–MCM-41 (1.0, 5.0 and 10 wt%) catalyst was prepared by the in situ incorporation of Ce into the MCM-41 framework. Tetraethyl orthosilicate (TEOS, 99%, Sigma–Aldrich), and Ce(NO$_3$)$_3$·6H$_2$O (95%, Sigma–Aldrich) were the precursors and hexadecyltrimethylammonium bromide (CTAB, Sigma–Aldrich) was the structural template. A solution of CTAB in water (4 g/25 mL) was added to a solution of TEOS (2.5 g) in aqueous tetramethylammonium hydroxide (TMAOH, 25 wt%, Sigma–Aldrich), and the mixture was stirred for 30 min. Next, (CeNO$_3$)$_3$·6H$_2$O (0.47 g, 2.4 g, and 4.7 g for 1.0, 5.0, and 10 wt% catalysts, respectively), and the remaining TEOS (21.0 g) were added. After additional stirring at 40 ºC for 24 h, the mixture was autoclaved at 100 ºC for 24 h and then cooled to room temperature. The resulting solid was separated by filtration, washed with deionized water and ethanol and dried at 40 ºC. The solid was then heated from room temperature to 550 ºC under flowing nitrogen and calcined for 3 h at 550 ºC under a flow of air to remove the residual organic compounds. The TEOS/C16-TAB/TMAOH/water molar ratio was 1.0/0.12/0.3/22.0.

2.3. Preparation of CeO$_2$–MCM-41 obtained by the impregnation of Ce (NO$_3$)$_3$·6H$_2$O over MCM-41

Briefly, 126 mg of Ce(NO$_3$)$_3$·6H$_2$O was dissolved in 30 mL of deionized H$_2$O. Then, 1.0 g of pure MCM-41 (obtained by the same protocol above mentioned without the use of Ce(NO$_3$)$_3$·6H$_2$O) was added to the resulting suspension and vigorously stirred at 80 ºC to produce a paste. After that, 50 mL of deionized water was added and the suspension was stirred until completely dry (≈5 h). The resulting solids were then treated at 550 ºC for 3 h under air.

2.4. Preparation of CeO$_2$–SiO$_2$ catalyst by wet impregnation

CeO$_2$–SiO$_2$ catalyst was prepared by wet impregnation method. 50 mg of CeO$_2$ (Riedel-de Haén) were suspended in 30 mL of water. Then, 1 g of SiO$_2$ (70–230 mesh, VETEC) was added to resulting suspension and vigorously stirred at 80 ºC until the formation of a paste. Then, 50 mL of distilled water was added and the suspension was kept under stirring to dryness (≈5 h). The resulting solid were then treated at 120 ºC for 2 h under air. The solid was then heated from room temperature to 550 ºC under a flow of air.

2.5. Catalyst characterization

The catalysts were characterized physically and chemically after calcination.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Geigerflex-3034 diffractometer with CuK$_\alpha$ radiation (40 kV, 40 mA, $\lambda = 0.15418$ nm). The Bragg angle (2θ) ranged from 15° to 70°, with a step size of 0.05°, and a step time of 4.0 s. Samples were previously dried at 110 ºC overnight and pulverized.

The reducibility of the catalytic surface was determined by Temperature-Programmed Reduction (TPR) in a Quantachrome ChemBET-300 instrument equipped with a thermal conductivity detector. Prior to analysis ca. 150 mg was packed into a quartz cell, heated for 2 h at 200 ºC under a stream of pure He and then cooled to room temperature. The experiments were performed between 30 and 900 ºC in a flow of 5% H$_2$/N$_2$, the temperature increasing linearly at a rate of 10 ºC/min. The O$_2$-chemisorption was conducted at 600 ºC using a ChemBET analyzer (Quantachrome Instruments$^\text{®}$).

Micro-Raman spectra were collected using a Renishaw RL633 laser spectrometer. Measurements were performed by using a helium–neon laser (632.8 nm and an effective power of 6 mW at the sample's surface) equipped with a CCD detector, 50× lens, and an experimental resolution of typically 1 µm for 10 accumulations of 20 s.

Textural characteristics of the matrices were determined from nitrogen adsorption isotherms, recorded at –196 ºC in an Autosorb IQ – Quantachrome Instrument. The samples (ca. 200 mg) were degassed for 2 h at 300 ºC before analysis. Specific surface areas were determined by the Brunauer–Emmett–Teller equation (BET method) from adsorption isotherm generated in a relative pressure range 0.07 < $P/P_0$ < 0.3. The total pore volume was calculated from the amount of N$_2$ adsorbed at a relative pressure close to unity. The average pore diameter was determined by the Barrett–Joyner–Halenda (BJH) method from the N$_2$ desorption isotherms.

Small-angle X-ray scattering (SAXS) was carried out on the D11A-SAXS beam line at the LNLS synchrotron laboratory (Campinas, Brazil), using a Huber-423 three-circle diffractometer. The SAXS setup was equipped with a Si (111) monochromator, giving a horizontally focused X-ray beam. The incident X-ray wavelength $\lambda$ was 1.488 nm and the scattering angle 2θ was varied from 0° to 10°.

Transmission electron microscope (TEM) images were taken with a Tecnai-G2-20 (FEI) electron microscope with an acceleration potential of 200 kV. The scanning electron microscopy (SEM) images were obtained using a JEOL field emission gun microscope JSM 6330F operated at 5 kV. The samples were prepared by drop-casting an aqueous suspension containing the nanostructures over a silicon wafer, followed by drying under ambient conditions.

2.6. Benzene, toluene and o-xylene oxidation

The catalytic oxidation of benzene, toluene and o-xylene was investigated. The reactions were performed in a fixed-bed tubular quartz reactor under atmospheric pressure. The following conditions were chosen: 0.11 g of catalyst, inlet benzene (>99%, Vetec) concentration 1.2 g m$^{-3}$, toluene (>99%, Vetec) concentration 0.7 g m$^{-3}$, o-xylene (>99%, Vetec) concentration 0.5 g m$^{-3}$ in air and temperature range 150–400 ºC. The reaction data were collected after at least 2 h on stream at room temperature. The reaction products were determined by gas chromatography coupled to mass spectrometry (GC–MS). The reactant and product mixtures were analyzed with two in-line gas chromatographs equipped with FID and TCD detectors and an HP-5 column. The catalytic activity was expressed as the percent conversion of benzene, toluene and...
The conversion of the compounds (benzene, toluene and o-xylene) was calculated as follows:

$$\text{CBTXs} (\%) = \frac{[\text{BTXs}]_{\text{in}} - [\text{BTXs}]_{\text{out}}}{[\text{BTXs}]_{\text{in}}} \times 100\%$$

where CBTXs (%) = percent BTX conversion; [BTXs]_{in} = input quantity and [BTXs]_{out} = output quantity.

3. Results and discussion

We started our studies by focusing on well-defined CeO₂–MCM-41 materials obtained by the in situ incorporation of the cerium precursor into the mesoporous silica MCM-41 framework. During the synthesis, SiO₂ is evenly distributed in the hexagonal structure of rod-like surfactant micelles of CTAB molecules (cetyltrimethylammonium bromide) to produce the MCM-41 structure [25,26]. In this case, Ce(NO₃)₃ (cerium precursor) was also added to the recipe in order to produce CeO₂, together with MCM-41, in the micellar solution of CTAB. It is expected that this approach would lead to catalysts with strong CeO₂–MCM-41 interactions. For the sake of comparison, we also prepared a CeO₂–SiO₂ catalyst by wet impregnation [27] of commercial CeO₂ into SiO₂ in order to investigate the influence of both methods on the structural features and catalytic properties towards the BTX oxidation.

Fig. 1 shows the XRD patterns of the CeO₂–MCM-41 and CeO₂–SiO₂. Whereas the diffractogram of CeO₂–SiO₂ indicated four lines corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes of cubic fluorite (CeO₂) [6], the CeO₂–MCM-41 did not present any well-defined peaks assigned to CeO₂ phases. This observation suggests that the CeO₂ is better dispersed on the in MCM-41 framework relative to commercial silica and may exhibit an improved interaction with the mesoporous silica. The broad peak observed in CeO₂–MCM-41 diffractogram is due to amorphous SiO₂ [28,29].

TPR experiments were performed in order to investigate the redox properties of the prepared catalysts. One broad reduction peak associated with the reduction of Ce⁴⁺ to Ce³⁺ in the bulk of the CeO₂ was registered in the TPR profiles of both catalysts (Fig. 2) [30–32]. This peak was centered at 864 and 665 °C for CeO₂–SiO₂ and CeO₂–MCM-41, respectively, indicating the higher reducibility for the CeO₂–MCM-41 catalyst. This can be assigned to the high dispersion of CeO₂ and interaction with the MCM-41 structure [7,14,33]. In addition, the shift to a lower reduction temperature can also be ascribed to the higher surface CeO₂ concentration and smaller crystallite size presented in this sample, which is consistent with XRD data [6,8,9,14].

O₂-chemisorption measurements also support the XRD and TPR analysis and allowed us to estimate the total amount of oxygen storage capacity (OSC) available in each catalyst, which is related to the number of oxygen vacancies in the samples. The CeO₂–MCM-41 catalyst exhibited a higher density of oxygen sites than CeO₂–SiO₂ catalyst (5.15 × 10¹ and 3.22 × 10¹ mmol/m² for CeO₂–MCM-41 and CeO₂–SiO₂, respectively), indicating an interaction between CeO₂ and the support as well as the higher oxygen vacancies concentration at the CeO₂–MCM-41 surface [34].

We also investigated the presence of oxygen vacancies in the CeO₂–SiO₂ and CeO₂–MCM-41 by Raman spectroscopy as shown in Fig. 3A and B. The Raman spectrum (Fig. 3A) of CeO₂–SiO₂ indicated a band centered at 466.4 cm⁻¹, which is assigned to the F₂g mode of the fluorite structure (symmetric stretching vibration of the oxygen atoms around Ce⁴⁺ ions) [6,35]. Interestingly, the F₂g mode for the CeO₂–MCM-41 was broadened and shifted to 461.3 cm⁻¹, which suggests the presence of defects on the CeO₂ structure [6,36,37]. We also observed in the Raman spectra of CeO₂–MCM-41 two weak bands in the 540–620 cm⁻¹ region corresponding to the non-degenerate LO modes of CeO₂, assigned to the oxygen vacancies introduced into the ceria structure [6,36]. Therefore, our data indicate that CeO₂–MCM-41 presents increased the content of oxygen vacancies relative to the CeO₂–SiO₂ catalyst, which is in agreement with XRD and TPR results.

Surface areas and average pore sizes obtained by BET showed that specific surface area for the CeO₂–MCM-41 catalyst was much higher (727 m²/g) than CeO₂–SiO₂ (153 m²/g). The CeO₂–MCM-41 catalysts also displayed a much smaller average BJH pore diameter.
(1.9 nm) relative to CeO₂–SiO₂ (9 nm). These results are depicted in Table 1. The isotherm for CeO₂–SiO₂ catalyst (Fig. 4) corresponds to type IV (IUPAC classification), which is typical of mesoporous materials. The shape of the hysteresis loop type H1 appeared at relative pressures $P/P^0 \approx 0.9–1.0$ and could be related to the formation of textural mesoporosity [38]. The CeO₂–MCM-41 exhibited a type IV isotherm (Fig. 4) (IUPAC classification), with well-defined H3 loops that did not level off at relative pressures close to the saturation vapor pressure, as reported for aggregates of plate-like particles giving rise to slit-shaped pores. Thus, the high BET surface areas, type IV nitrogen adsorption–desorption isotherm, and narrow pore size distribution confirm the uniform mesoporosity and ordered structure of the CeO₂–MCM-41 material.

The ordered hexagonal structure of CeO₂–MCM-41 was further confirmed by HRTEM image (Fig. 5A), showing the hexagonal arrangement of uniform pores (inset of Fig. 5A). The HRTEM results also reveal the absence of individual, small CeO₂ aggregates, which agrees with XRD results and indicate that cerium could be successfully incorporated into the MCM-41 structure. On the other hand, the TEM image of CeO₂–SiO₂ catalyst (Fig. 5B) showed the presence of elongated and irregular particles of CeO₂ and SiO₂. Also, the mass-thickness contrast detected from the TEM image indicates that SiO₂ and CeO₂ particles were directly connected (Fig. 5B).

The structure of CeO₂–MCM-41 was also studied by SAXS. The synchrotron radiation small-angle pattern for the CeO₂–MCM-41 (Fig. 6) showed (1 0 0), (1 1 0) and (2 0 0) reflections at $2\theta = 1.67^\circ$, $2.91^\circ$, and $3.33^\circ$, respectively. These reflections can be attributed to the 2-D hexagonal symmetry that is typical of the MCM-41 ordered hexagonal structure [25]. Therefore, these results indicated that in situ CeO₂ generation during the synthesis of MCM-41 did not prevent the formation of ordered mesoporous silica, which agree with HRTEM data.

The catalytic activity of the CeO₂–MCM-41 and CeO₂–SiO₂ samples was examined towards the oxidation of BTX compounds. We were interested in investigating how the catalytic performances of the CeO₂–MCM-41 and CeO₂–SiO₂ towards BTX oxidation were dependent upon their physicochemical properties. Fig. 7A–C depicts the conversion percentages for the oxidation of benzene (Fig. 7A), toluene (Fig. 7B), and o-xylene (Fig. 7C) as a function of reaction temperature employing CeO₂–MCM-41 and CeO₂–SiO₂ as catalysts. The inset in Fig. 6A–C shows the TOFₘₐₓ at maximum conversion of BTX. From Fig. 7A–C, it can be observed a significant difference regarding the activities of CeO₂–MCM-41 and CeO₂–SiO₂. While no appreciable conversion was detected for the

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Density of oxygen sites (μmol/m²)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (Å)</th>
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<tr>
<td>1 wt% CeO₂–MCM-41</td>
<td>$2.99 \times 10^3$</td>
<td>832</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>5 wt% CeO₂–MCM-41</td>
<td>$5.15 \times 10^3$</td>
<td>727</td>
<td>0.5</td>
<td>1.9</td>
</tr>
<tr>
<td>10 wt% CeO₂–MCM-41</td>
<td>$3.89 \times 10^3$</td>
<td>169</td>
<td>0.8</td>
<td>2.5</td>
</tr>
<tr>
<td>5 wt% CeO₂–SiO₂</td>
<td>$3.22 \times 10^3$</td>
<td>153</td>
<td>0.7</td>
<td>9.0</td>
</tr>
</tbody>
</table>

![Fig. 4. N₂-adsorption–desorption isotherms of CeO₂–MCM-41 and CeO₂–SiO₂ catalysts and pore size distribution curves (inset) generated by the BJH method from the N₂ desorption isotherms.](image)

![Fig. 5. HRTEM (A) and TEM (B) images of CeO₂–MCM-41 and CeO₂–SiO₂ catalysts, respectively. The scale bar the inset corresponds to 2 nm.](image)

![Fig. 6. SAXS pattern of CeO₂–MCM-41 catalyst.](image)
pure SiO$_2$ support and CeO$_2$ (<3%, not shown in the Fig. 7), both CeO$_2$–MCM-41 and CeO$_2$–SiO$_2$ displayed high catalytic activities at relatively low temperatures, showing that the appropriate combination of oxides can provide higher activities relative to their individual counterparts. The oxidation of benzene, toluene and o-xylene began to take place at above 60 °C. Only H$_2$O and CO$_2$ were detected as the oxidation products, and the BTX conversion increased with temperature for both catalysts. CeO$_2$–MCM-41 was notably more active than the CeO$_2$–SiO$_2$ at the higher temperatures. Specifically, 74% and 33% conversion for benzene, 53% and 19% conversion for toluene, and 37% and 15% conversion for o-xylene were observed at 350 °C when CeO$_2$–MCM-41 and CeO$_2$–SiO$_2$ were employed as catalysts, respectively. The TOF values followed the same trend corresponding to 157 and 48 h$^{-1}$ for benzene, 96 and 29 h$^{-1}$ for toluene and 72 and 23 h$^{-1}$ for o-xylene using CeO$_2$–MCM-41 and CeO$_2$–SiO$_2$ as catalysts, respectively.

Assuming the same CeO$_2$ content for both catalysts (5 wt%), the higher activities for CeO$_2$–MCM-41 can be explained due to its higher specific surface area, stronger ceria-support interactions, and higher oxygen vacancy concentrations. In this case, the greater reducibility of CeO$_2$–MCM-41 was translated into higher oxidation activities [6,8,14]. The high amount of oxygen vacancies can result in an enhancement in the surface oxygen mobility [39]. In oxidation reactions, the catalyst is subjected to cycles of oxidation and reduction, in which both processes are affected by the oxygen mobility of the catalyst. It is a consensus that, when CeO$_2$ based catalysts are involved, the oxidation of hydrocarbons occurs via the Mars-van Krevelen mechanism in which the solid oxidizes the substrate molecule, and the re-oxidation of the reduced solid by the oxygen-containing gaseous phase, which is the rate-determining step of the reaction [2,9,40,41]. Therefore, the results reported herein indicate that the methodology used to prepare CeO$_2$–MCM-41 led to the highest active catalyst for BTX oxidation.

We also investigated the influence of CeO$_2$ content in the ordering of mesoporous structure and its catalytic performance. Fig. 8A and B shows HRTEM images of 1 and 10 wt% CeO$_2$–MCM-41. As expected, the increase of cerium content on the in situ CeO$_2$ generation during the MCM-41 synthesis promoted partial disordering of mesoporous silica but it does not prevent the overall formation of the mesoporous structure (Fig. 8B). Both 1 and 5 wt% CeO$_2$–MCM-41 (Figs. 8A and 5A, respectively) displayed high uniformity, while the sample containing 10 wt% CeO$_2$ were less uniform. Indeed, this behavior was similar to other reported catalysts [25,26], in which transition metals have been incorporated.
into the MCM-41 structure by mixing the dissolved metal precursor into the initial solution of TEOS, water, and CTAB. It is plausible that the increase of CeO₂ content did not contribute to the formation of ordered surfactant aggregates, which are uniformly distributed in the hexagonal phase of rod-like surfactant micelles of alkyltrimethylammonium bromide surfactant.

BET and O₂-chemisorption analyses are in agreement with the HRTEM results as depicted in Table 1. A slight decrease of surface area (832–727 m²/g) and an increase in the density of oxygen sites (2.99–5.15 µmol/g) were detected when the CeO₂ content was increased from 1 to 5 wt%. Interestingly, the partial disordering of mesoporous structure observed for the 10 wt% CeO₂–MCM-41 was also accompanied by significant changes in its textural properties, leading to surface areas and density of oxygen sites corresponding to 169 m²/g and 3.89 × 10⁵ µmol/m², respectively.

Fig. 9A–C depicts the conversion % for the oxidation of benzene (Fig. 9A), toluene (Fig. 9B), and o-xylene (Fig. 9C) as a function of reaction temperature employing 1, 5, and 10 wt% CeO₂–MCM-41 as catalysts, respectively. As expected, BTX conversion % increased with the increase of CeO₂ content, since CeO₂ is the active phase of the catalysts. Although a significant increase of BTX conversion was observed when the CeO₂ content varied from 1 to 5 wt%, this behavior was not obtained for the 10 wt% CeO₂–MCM-41 catalyst. The sample containing 10 wt% CeO₂ was only slightly better than 5 wt% CeO₂–MCM-41 catalyst. Here, it is plausible that the disordering of mesoporous structure observed for the 10 wt% CeO₂–MCM-41 catalyst led to a lower specific surface area, poorer interaction of ceria with the support, and lower concentration of oxygen vacancies in the CeO₂ structure, thus leading to detrimental effects over their catalytic performances.

The catalytic stability towards the benzene oxidation was investigated as a function of time for the 5 wt% Ce/MCM-41 catalyst as shown in Fig. 10. This material was chosen as it corresponds to the sample having the best uniformity, higher concentration of oxygen vacancies, and best textural properties. It can be observed that no significant loss of catalytic activity was detected even after 24 h when the reaction was performed both at 50 and 350 °C. This observation indicates that these materials may represent
promising candidates for gas-phase catalytic applications. It is important to note that the observed conversion at low temperature (50 °C) could not be assigned to an adsorption effect, as the chromatograms collected during the reaction at different temperatures clearly shows the substrate conversion and the concomitant appearing of CO2 as the reaction product (Fig. S1). In order to demonstrate that our reported approach for the synthesis of CeO2–MCM-41 prepared by the in-situ incorporation of cerium precursor during the MCM-41 formation was effective for the production of optimized catalysts, their performance was also compared with those from a CeO2/MCM-41 obtained by impregnation of cerium nitrate precursor over MCM-41 support as depicted in Fig. S2 under the same metal loading (5 wt%). It can be observed that BTX conversion % employing the 5 wt% CeO2/MCM-41 catalyst (Fig. S3) obtained by wet impregnation were significantly lower than the 5 wt% CeO2/MCM-41 catalyst prepared by in-situ incorporation of cerium precursor during the MCM-41 formation. Its performance was also compared with other catalysts reported in the literature as depicted in Table 2 [42–48]. It is important to note that some catalytic results regarding the BTX oxidation are dependent on the employed operating conditions, including nature of the organic compound, reaction mixture composition, overall gas flow rate, and type of the reactor [22–24]. Moreover, most of reported ceria-based catalysts are employed combining other highly active phases such as noble metals or metal oxides (Pd, Pt, Co, Mn, CeO2, among others, Table 2). In this paper, silica (an inert phase) was used as the support in order to focus on the contribution of CeO2. Regarding the CeO2–MCM-41 catalysts, which presented the highest activity, the T50% (temperature for the 50% organic compound conversion) was higher relative to other reported catalysts. It is interesting to note that the T50% of 10 wt% CeO2–MCM-41 was higher than Pt-based catalysts and comparable to the value of the V2O5/4.37%Au/TiO2 catalysts, prepared by in-situ incorporation of a cerium precursor during the MCM-41 formation. Its performance can be put to work to yield improved catalytic performances.

### 4. Conclusion

The CeO2–MCM-41 catalyst prepared by the in situ impregnation of a cerium precursor during the MCM-41 synthesis presented improved catalytic performance relative the CeO2–SiO2 catalyst prepared by the conventional wet impregnation. The higher catalytic activity was a result of its higher specific surface area, improved interaction between ceria and the support, facilitated Ce4+/Ce3+ redox process, and higher concentration of oxygen vacancies at the CeO2 surface, which benefits the migration of oxygen species across its structure and thus oxidation activity. Indeed, our results demonstrate that the method of preparation strongly affects the dispersion/incorporation of the CeO2 into SiO2, which can be put to work to yield improved catalytic performances.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2015.10.097.

### References


Table 2

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<th>Catalyst</th>
<th>T50% (°C)</th>
<th>Compound</th>
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<tr>
<td>CeO2–SiO2</td>
<td>&gt;350</td>
<td>BTX</td>
<td>This work</td>
</tr>
<tr>
<td>5% CeO2–MCM-41</td>
<td>252</td>
<td>Benzene</td>
<td>This work</td>
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<tr>
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<td>290</td>
<td>Toluene</td>
<td>This work</td>
</tr>
<tr>
<td>10% CeO2–MCM-41</td>
<td>&gt;350</td>
<td>o-Xylene</td>
<td>This work</td>
</tr>
<tr>
<td>CeO2</td>
<td>&gt;500</td>
<td>Toluene</td>
<td>[42]</td>
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<tr>
<td>Au/Co</td>
<td>&gt;400</td>
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<td>[42]</td>
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<td>[45]</td>
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<tr>
<td>Pt/CeO2 (3DL)</td>
<td>232</td>
<td>o-Xylene</td>
<td>[46]</td>
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<tr>
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<td>131</td>
<td>Benzene</td>
<td>[47]</td>
</tr>
<tr>
<td>Pt/Al2O3</td>
<td>170</td>
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<td>[47]</td>
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<tr>
<td>V2O5/4.37%Au/TiO2</td>
<td>200</td>
<td>Benzene</td>
<td>[48]</td>
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</table>

a Gas mixture: 341, 199 and 142 ppm benzene, toluene and o-xylene in air respectively; GHSV: 12,000 h⁻¹.

b Gas mixture: 0.7% v/v toluene, 10 vol.% O2 in helium; GHSV: 7.6 × 10⁻³ mol (h gcat⁻¹).

c Gas mixture: 600 ppm toluene, 20 vol. % O2 in helium, flow rate of 50 ml min⁻¹.

d Gas mixture: 200 ppm benzene, 20 vol.% O2 in helium; GHSV: 30 ml (h gcat⁻¹).

e Gas mixture: 1000 vppm in air; flow rate: 50 ml min⁻¹.

f Gas mixture: 150 ppm in air; flow rate: 100 mL min⁻¹.

g Gas mixture: 1000 vppm in air; VHSV: 21,500 h⁻¹.

h Gas mixture: 1200 vppm in air; VHSV: 21,500 h⁻¹.


