



Article

Zirconium Containing Periodic Mesoporous Organosilica: The Effect of Zr on CO₂ Sorption at Ambient Conditions

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Abstract: Two series of zirconium-incorporated-periodic-mesoporous-organosilica (Zr-PMO) materials were successfully prepared, via a co-condensation strategy, in the presence of Pluronic P123 triblock copolymer. The first series of Zr-PMO was prepared using tris[3-(trimethoxysilyl)propyl]isocyanurate (ICS), tetraethylorthosilicate (TEOS), and zirconyl chloride octahydrate (ZrCO), and denoted as Zr-I-PMO, where I refers to ICS. The second series was synthesized using bis(triethoxysilyl)benzene (BTEE), TEOS, and ZrCO as precursors, named as Zr-B-PMO, where B refers to BTEE. Zr-PMO samples exhibit type (IV) adsorption isotherms, with a distinct H₂-hysteresis loop and well-developed structural parameters, such as pore volume, pore width, high surface area, and narrow pore-size distribution. Structural properties were studied by varying the Zr:Si ratio, adding TEOS at different time intervals, and changing the amount of block copolymer-Pluronic P123 used as well as the calcination temperature. Surface characteristics were tailored by precisely controlling the Zr:Si ratio, upon varying the amount of TEOS present in the mesostructures. The addition of TEOS at different synthesis stages, notably, enhanced the pore size and surface area of the resulting Zr-I-PMO samples more than the Zr-B-PMO samples. Changing the amount of block copolymer, also, played a significant role in altering the textural and morphological properties of the Zr-I-PMO and Zr-B-PMO samples. Optimizing the amount of Pluronic P123 added is crucial for tailoring the surface properties of Zr-PMOs. The prepared Zr-PMO samples were examined for use in CO₂ sorption, at ambient temperature and pressure (25 °C, 1.2 bar pressure). Zr-PMO samples displayed a maximum CO₂ uptake of 2.08 mmol/g, at 25 °C and 1.2 bar pressure. However, analogous zirconium samples, without any bridging groups, exhibited a significantly lower CO₂ uptake, of 0.72 mmol/g, under the same conditions. The presence of isocyanurate- and benzene-bridging groups in Zr-I-PMO and Zr-B-PMO samples enhances the CO₂ sorption. Interestingly, results illustrate that Zr-PMO materials show potential in capturing CO₂, at ambient conditions.

Keywords: CO₂ uptake; physisorption; periodic mesoporous organosilica; zirconia; one pot synthesis



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1. Introduction

Ordered mesoporous silicas with organic bridging groups, also known as periodic mesoporous organosilica (PMO), are, generally, developed with high organic content and homogeneously dispersed organic groups in the inorganic framework. PMO can be prepared by evaporation-induced self-assembly (EISA), involving the co-condensation of bridged organosilanes (AO)₃Si-R-Si-(AO)₃ (A and R denote alkyl and bridging groups, respectively) along with structure-directing agents. These structure-directing agents include

ionic surfactants [1,2] and nonionic-block copolymers [3–5]. Various aliphatic and aromatic bridging groups, such as methane, ethane, ethylene, benzene, phenylene, pyridine, and isocyanurate [6,7], have been explored to synthesize PMO. PMO exhibits high specific-surface area, large pores, thick pore walls, large pore volumes, and narrow pore-size distribution, in addition to high organic loading. Interestingly, the incorporation of organic groups into the framework does not cause pore blockage. Therefore, PMOs have become promising candidates for various applications, including wastewater treatment, CO₂ sorption, sensing, chromatography, catalysis, and drug delivery [8–19]. For instance, Zebardasti and co-workers synthesized chemostable and thermostable periodic mesoporous organosilica (PMO-THEIC) and tested for CO₂ sorption [19]. Zr-containing periodic mesoporous organosilica (Zr-PMO), with varying organic content, was synthesized by Melero et al. and applied as a hydrophobic-acid catalyst for biodiesel production. The Zr-containing active-catalytic sites are beneficial in biodiesel production, by esterification/transesterification of free fatty-acid-containing feedstocks [16]. PMO with alumino-silica (Al/Si-PMO) materials were synthesized by Assadi et al. and investigated as catalysts for ‘green’ oxidation. The authors used thiourea-based organosiloxane precursor to produce materials with catalytically active sites, along with aluminosilica structure, which featured higher mesoporosity and specific-surface area, due to the presence of Al³⁺ [17]. Cho and co-workers synthesized Benzene-Silica, with hexagonal- and cubic-ordered mesostructures, in the presence of block copolymers and weak acid catalysts. The authors used 1,4-bis(triethoxysilyl) and iron (III) chloride hexahydrate, as a bridging precursor and acid catalyst, respectively [18]. However, among the many applications of PMOs, sorption of CO₂ has, recently, received considerable attention.

Carbon dioxide (CO₂) is a major greenhouse gas. Before the Industrial Revolution, the CO₂ level in the atmosphere was well-balanced by the natural-carbon cycle. CO₂ was released mainly by wildfires, volcanic eruptions, and ocean, plant, and animal decomposition. This CO₂ in the atmosphere was absorbed by oceans and plants (via photosynthesis). Nowadays, many fossil fuels are burned daily to produce energy, including electricity, and, hence, the atmospheric CO₂ level is exponentially increasing, as never before. The current CO₂ concentration is 418.76 ppm (2022), exceeding the optimum CO₂ level (350 ppm) in the atmosphere. In 2030, the CO₂ level is estimated to be around 460 ppm.

With increased CO₂ concentration in the atmosphere, the average global temperature has risen by 1–2 °C. However, such a small temperature change can bring adverse effects in the forthcoming years, such as melting glaciers at the north and south poles, resulting in rising sea levels. Thus, there is an urgent need to control the atmospheric CO₂ level, which can be achieved by developing efficient and economical CO₂ capture and conversion methods.

Modifying nanoporous materials with basic functional groups, such as amines, and incorporating basic sites, by introducing Ca, Mg, Al, and Zr oxides, are useful ways for enhancing CO₂ adsorption. Typically, higher nitrogen- and metal-oxides loadings into porous materials result in improved CO₂ uptake. The hydrogen carbonate adducts can be formed, upon adsorption of CO₂ on the basic hydroxyl groups. Metal (M) oxides exhibit surface basicity, due to terminal hydroxyl groups, O^{2−} centers, and Mⁿ⁺-O^{2−} pairs. Therefore, sorption of CO₂ on metal oxides can yield hydrogen carbonates, monodentate, bidentate, and polydentate carbonates. The main factors involved in the synthesis of amine-modified-porous-silica adsorbents are silica support with appropriate porosity, high surface area, and high amine-loading ability. In addition to those amine-containing solid sorbents, metal-incorporated-composite materials have, also, been widely studied for CO₂ sorption. For instance, adsorption of CO₂ on basic alumina at high temperatures [20,21], mesoporous alumina modified with amines [22], and MgO/Al₂O₃ sorbents [23] have been reported, in recent years.

However, there is only scarce information on the characterization of zirconium-modified-siliceous materials and their application for CO₂ capture. For instance, Bachiller and co-workers showed CO₂ chemisorption on zirconium dioxide (ZrO₂), due to acidic and basic sites [24]. Depending on the crystallographic nature of zirconia (cubic, tetragonal,

monoclinic, or amorphous), the number of CO₂ adsorption sites on its surface, and the available terminal-hydroxyl groups, adsorption of CO₂ can be tuned [24–26]. Recently, direct synthesis of zirconium-incorporated hybrid mesoporous organosilica, with tunable zirconium content, has been reported by Zhai and co-workers [27]. They stated that a highly ordered mesostructure could be obtained, by adjusting the Zr–Si ratio, while keeping the NaCl/Si ratio constant. Nilantha and co-workers showed that, in addition to ultramicroporosity (pores < 0.7 nm), CO₂ adsorption, also, depends on the basic sites available on the surface [28]. Due to the basic nature of zirconium species and the ultramicroporosity of silica support, the zirconia–silica composite materials feature high CO₂ sorption capacities. Moreover, incorporating hydrophobic-bridging groups into these composites may further enhance CO₂ uptake. However, there is scarce information available for capturing CO₂ by zirconia–silica composites.

This study reports the synthesis, characterization, and CO₂-adsorption properties of Zr–PMO mesocomposites, with tunable-organic-bridging groups. CO₂-adsorption measurements were conducted at ambient temperature and pressure conditions (25 °C, 1.2 bar pressure). These mesostructures were prepared by varying the amount of TEOS and Pluronic P123 block copolymer, adding TEOS at different time intervals, and changing calcination temperatures. In addition, 1,4-bis(triethoxysilyl)benzene (BTEB) and tris[3-(trimethoxysilyl)propyl]isocyanurate (ICS) were used to incorporate organic-bridging groups. Commercially available block copolymer, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) or Pluronic P123 (EO₂₀PO₇₀EO₂₀), was used as the block copolymer, due to low cost, biodegradability, and its ability to create ordered mesostructures. To the best of our knowledge, this is the first attempt to utilize Zr–PMO composites with mesostructures, for CO₂ capture at ambient conditions.

2. Materials and Methods

2.1. Materials, Characterization, and Calculations

Detailed information about the chemicals, experimental procedures, and characterization techniques employed, including powder-X-ray diffraction (XRD), nitrogen (N₂) adsorption, transmission-electron microscopy (TEM), thermogravimetry (TG), ¹H-²⁹Si NMR, ¹H-¹³C NMR, and energy-dispersive X-ray spectroscopy (EDX), are included in Supporting Information. In addition, CO₂ measurements and calculations are, also, provided in Supporting Information [29].

2.2. Preparation of Zr–PMO Mesocomposites

Synthesis of Zr–PMO mesocomposites was conducted using a slightly modified method, as reported previously [26]. In a typical synthesis, 1.5 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀) and a predetermined amount of zirconyl chloride octahydrate (ZrCO) and NaCl (maintaining a NaCl to Si molar ratio of 1:4) were dissolved in 50 mL of deionized (DI) water and magnetically stirred, at 40 °C for 3.75 h. Next, a known amount of TEOS was added and pre-hydrolyzed for 15 min. Then, the calculated amount of ICS or BTEB was added to the mixture and stirred, at 40 °C for 24 h. The resulting solution was hydrothermally treated in an oven, at 80 °C for 48 h. The solid product was recovered by filtration and washed with excess DI water. Then, the polymeric template was removed by extraction, using 1.0 g of as-synthesized material, with 3 mL of 36% HCl and 100 mL of 95% ethanol, at 80 °C for 24 h, and dried overnight in an oven at 100 °C. Extracted samples were heated in a horizontal-quartz-tube furnace, at 350 °C for 2 h, under an N₂ atmosphere with a 2 °C/min heating rate. Another portion of dried samples was thermally heated in the same oven, at 600 °C for 6 h, in flowing N₂, with a 1 °C/min heating rate. The total numbers of Zr moles used in each synthesis were 0.011, and Si moles were taken as a percentage of zirconium moles. The resulting samples were labeled with starting prefix Zr, I, B, and T, referring to ZrCO, ICS, BTEB, and TEOS, and used in the initial reaction mixture. The molar percentage of silicon, originating from the silanes used in the initial synthesis mixture, is denoted as X and Y and calculated as follows: Zr-IX-TY contains X% (out of Zr moles; 0.011 mol) and

Y% (out of Zr moles; 0.011 mol) of Si moles, originating from ICS and TEOS, respectively. Zr-B-PMO samples are denoted the same way as Zr-I-PMO, and all symbols have similar meanings as above. Samples thermally treated in flowing nitrogen at 350 °C and 600 °C are marked without * and with *, respectively. For comparison purposes, samples were, also, synthesized using ZrCO only (without silane addition), using the same procedure. These samples, treated at 350 °C and 600 °C, are represented as Zr[#] and Zr*, respectively. All as-synthesized samples are denoted with superscript AS. Regarding Si content, 10% of Si moles originating from ICS or BTEB were kept constant, while the amount of Si (Y%) originating from TEOS was changed from 10, 30, 50, and 90, respectively. For instance, Zr-I10-TY refers to the samples from Zr-I10-T10 to Zr-I10-T90.

The addition of TEOS at different synthesis stages was performed as follows: the optimal molar ratio of Zr:Si was determined, based on the previous experiments for Zr-I-PMO and Zr-B-PMO samples; TEOS was added at five different time intervals (1 h, 2 h, 3 h, 3.5 h, and 3.75 h). This experiment was conducted to determine the best time to add TEOS into the reaction mixture. The resulting samples are labeled as the previous ones. For instance, Zr-I-Hh denotes the sample after adding TEOS into the initial reaction mixture, after H hours.

Moreover, a series of samples were synthesized by varying the amount of block copolymer, Pluronic P123. Different amounts of P123, ranging from 0.5 g to 4.5 g, were added to the synthesis mixtures, with the optimal molar ratio of Zr:Si determined for Zr-I-PMO and Zr-B-PMO samples. These samples are labeled as Zr-I-Pf or Zr-B-Pf, P stands for P123, and f corresponds to the amount of Pluronic P123 added.

3. Results and Discussion

3.1. Properties of Zr-PMO Samples

High-resolution thermogravimetry (HRTG) and differential thermogravimetry (DTG) profiles were employed to understand the thermal stability of composite materials synthesized with the bridging groups of isocyanurate (I) and benzene (B). Figure 1 shows the DTG and TG profiles obtained for the Zr-I10-T10^{AS}, Zr-I10-T10, and Zr-B10-T10 samples studied. The DTG profile of Zr-I10-T10^{AS} displays three weight-loss regions at the temperature ranges of 25–120 °C, 200–350 °C, and 350–450 °C, respectively. The first weight-loss region is attributed to the removal of moisture from the surface. The second and third weight-loss regions correspond to the degradation of triblock copolymer template and hydrophobic isocyanurate rings (see Figure 1). The DTG profile of the extracted sample exhibits a partial reduction in the template peak, in the temperature range of 200–350 °C, which suggests that the extraction process is not sufficient to remove the block copolymer completely (data not shown). Therefore, the samples studied were heated at 350 °C, in flowing nitrogen, to remove the template without any degradation of the benzene- and isocyanurate-bridging groups. Note that, regardless of the presence of bridging groups in Zr-PMO, all as-synthesized, extracted, and extracted and thermally treated samples showed a narrow peak, in the range of 25–120 °C, due to physically adsorbed water. As shown in Figure 1, the disappearance of the template peak, centered at about 320 °C, confirms a complete removal of P123-triblock copolymer (compare the DTG curves for Zr-I10-T10^{AS} and Zr-I10-T10). The DTG peak observed at the temperature range of 400–500 °C for Zr-I10-T10 and 450–550 °C for Zr-B10-T10 is attributed to the degradation of the isocyanurate- and benzene-bridging groups (see Figure 1). Moreover, a partial dehydroxylation of the OH groups and the transformation of hydrated-amorphous zirconium into a more crystalline-zirconium phase could, also, occur in the temperature range of 200–800 °C and contribute to both the second and third weight losses observed on the TG profile of the samples studied.

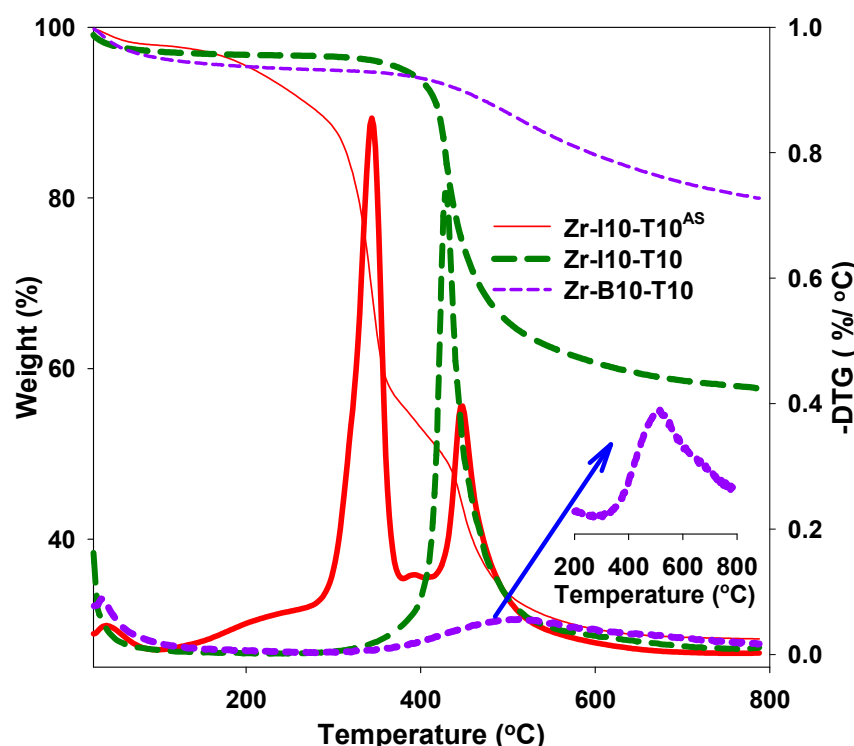


Figure 1. DTG curves for selected as-synthesized (AS), extracted, and thermally treated (350 °C) Zr-I-PMO and Zr-B-PMO samples.

The presence of high concentrations of Si in isocyanurate and benzene-bridging groups can cause a structural collapse and shrinkage upon thermal treatment, which reduces the surface properties, including surface area, microporosity, pore volume, and pore width. As a result, synthesis was performed by keeping a low concentration of Si (10%) moles, originating from bridging groups, with progressively increasing Si moles (Si %) from TEOS, in the Zr-Si composites studied. N₂-adsorption isotherms measured at −196 °C, for the series of Zr-I10-TX and Zr-B10-TX (X = 10, 30, 50, 90) samples, are shown in Figures 2 and 3, respectively. All samples, except Zr-I10-T10, feature a type-IV-adsorption isotherm with broad capillary-condensation/evaporation steps and H1/H2-type-hysteresis loops. In the H1-type-hysteresis loop, the adsorption branch and desorption branch should be parallel, vertically, whereas in the H2-hysteresis-loop the adsorption branch and desorption branch are not parallel, which is related to more complex pore structures, featuring some network effects, such as pore blocking and/or pore openings [30]. This complexity can be observed in the case of the adsorption isotherm for Zr-I10-T10, which is type IV, with a hysteresis loop resembling a somewhat distorted H2-type, due to nonuniformity of the pore openings and pore blocking. A noticeable change in the quantitative and qualitative adsorption properties is observed for the series of Zr-I10-T10 to Zr-I10-T90 and for Zr-B10-T10 to Zr-B10-T90 samples (see Figures 2 and 3, Table 1). For the Zr-I10-TX series, the shape of the hysteresis loops of N₂-adsorption isotherms changes from H1 (channel-type mesopores) to H2 (cage-like mesopores), as the molar concentration of TEOS (Si%) gradually increases from 10% to 90% (see Figure 2, left panel). All Zr-B10-TX samples display H2-hysteresis loops; however, those loops are not prominent for Zr-B10-T10 and Zr-B10-T30 samples with a low concentration of TEOS (Si%) (see Figure 3, left panel). The H2-hysteresis loop is characteristic of the cage-like or constricted mesopores.

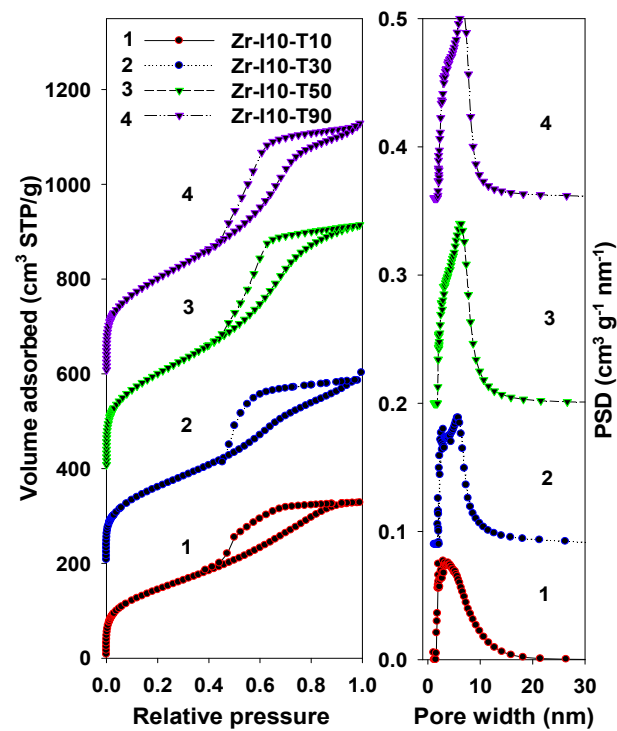


Figure 2. N₂-adsorption isotherms (left panel) and corresponding PSD curves (right panel), for Zr-I10-TX samples; isotherms are shifted by a multiple of 200 cm³ STP/g. PSD curves 2, 3, and 4 are shifted by 0.1 cm³ g⁻¹ nm⁻¹, 0.2 cm³ g⁻¹ nm⁻¹, and 0.35 cm³ g⁻¹ nm⁻¹ in relation to curve 1, respectively.

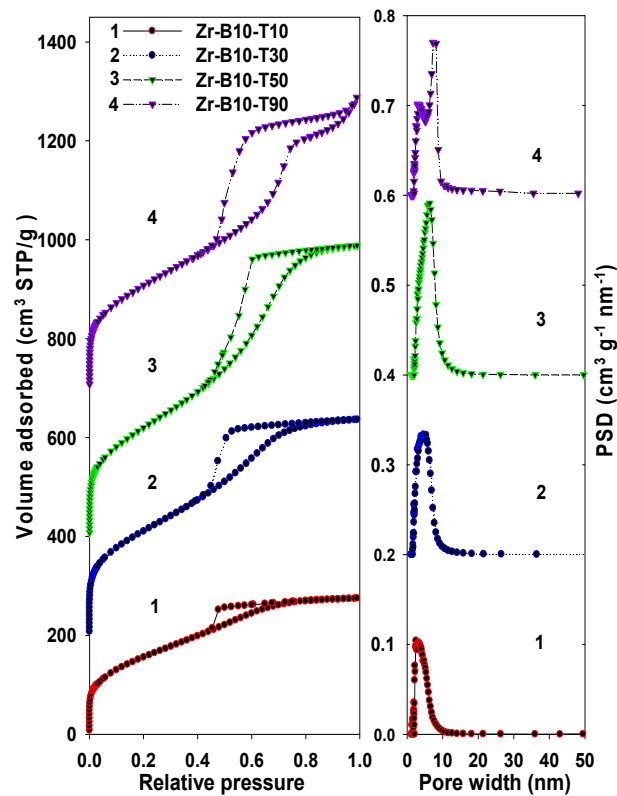


Figure 3. N₂-adsorption isotherms (left panel) and corresponding PSD curves (right panel), for Zr-B10-TX samples; isotherms 2, 3, and 4 are shifted by 200 cm³ STP/g, 400 cm³ STP/g, and 700 cm³ STP/g, in relation to isotherm 1, respectively. PSD curves are shifted by a multiple of 0.2 cm³ g⁻¹ nm⁻¹.

Table 1. Adsorption parameters for Zr-I-PMO and Zr-B-PMO samples studied.

Sample	V _{sp} (cc/g)	V _{mic} (cc/g)	S _{BET} (m ² /g)	W _{max} (nm)	Initial Molar Ratio Zr/Si
Zr [#]	0.19	0.01	96	6.9	-
Zr-I10-T10	0.51	0.08	528	3.9	5:1
Zr-I10-T30	0.60	0.07	593	5.8	5:2
Zr-I10-T50	0.79	0.07	739	6.1	5:3
Zr-I10-T90	0.81	0.07	743	6.6	5:5
Zr-B10-T10	0.42	0.09	571	3.3	5:1
Zr-B10-T30	0.67	0.09	767	4.7	5:2
Zr-B10-T50	0.91	0.05	809	6.3	5:3
Zr-B10-T90	0.90	0.07	761	7.7	5:5
Zr [*]	0.10	0.01	46	4.4	-
Zr-I10-T10*	0.29	0.04	350	3.9	5:1
Zr-I10-T30*	0.51	0.07	556	5.0	5:2
Zr-I10-T50*	0.64	0.06	657	5.4	5:3
Zr-I10-T90*	0.68	0.05	649	6.1	5:5
Zr-B10-T10*	0.35	0.05	456	4.2	5:1
Zr-B10-T30*	0.43	0.07	556	4.4	5:2
Zr-B10-T50*	0.61	0.04	604	5.8	5:3
Zr-B10-T90*	0.67	0.06	601	6.9	5:5

V_{sp}—single-point-pore volume determined at the relative pressure of 0.98; V_{mic}—volume of fine pores (micropores and mesopores <3 nm) calculated by integration of PSD curve up to 3 nm; S_{BET}—specific-surface area calculated from adsorption data, in relative-pressure range 0.05–0.20; W_{max}—pore width calculated at the maximum of PSD, using an improved KJS method.

For Zr-B10-T50/Zr-I10-T50 and Zr-B10-T90/Zr-I10-T90 samples, desorption steps start at the relative pressure of ~0.64 and finish, suddenly, at a relative pressure of about 0.42, as compared to the other samples studied. N₂-adsorption isotherms shown in Figures 2 and 3 (left panel) were used to evaluate the surface properties, including the specific-surface area, pore volume (fine pores < 3 nm) and single-point-pore volume, primary-mesopore volume, and diameter (see Table 1). Note that the gradual increase in the amount of TEOS in the initial-reaction mixture enhances the cross-linking between siloxane bonds. It, also, reduces the structural collapse and, subsequently, enlarges the specific-surface area, pore volume, and pore diameter. For instance, the Zr-I10-T10 sample exhibits surface area, single-point-pore volume, and pore width of 528 m²/g, 0.51 cm³/g, and 3.9 nm, respectively, and these values increase to 743 m²/g, 0.81 cm³/g, and 6.6 nm for Zr-I10-T90. Samples thermally treated at 600 °C (Zr-I10-TX* and Zr-B10-TX* (X = 10, 30, 50, and 90)) did not show a significant change in the shape of isotherms and their PSD curves, compared to the respective samples thermally treated at 350 °C (compare the plots shown in Figures 2–5). Nevertheless, the samples thermally treated at 600 °C show a slight decrease in the structural parameters, as compared to the similar samples thermally treated at 350 °C (see Table 1). For instance, the Zr-I10-T50 sample exhibits surface area and pore width of 739 m²/g and 6.1 nm at 350 °C, respectively, and these values decrease to 657 m²/g and 5.4 nm, respectively, upon thermal treatment at 600 °C. Similarly, surface area and pore width of the Zr-B10-T50 sample decrease from 809 m²/g to 604 m²/g and 6.3 nm to 5.8 nm, respectively, as the temperature increases from 350 °C to 600 °C (see Table 1).

For comparison purposes, we, also, studied the surface properties, shape of the N₂-adsorption isotherms, and PSD curves for the Zr[#] and Zr^{*} samples as well as Zr–Si composites. Zr[#] and Zr^{*} samples show H3 and H2 types of hysteresis loops (Figure 6), with relatively reduced structural parameters to those of Zr–Si mesostructures (see Table 1). Among all samples studied, Zr-I10-T50/Zr-I10-T90 and Zr-B10-T50/Zr-B10-T90 exhibit the highest surface parameters, including high surface area, pore width, and pore volume. As shown in Table 1, the surface properties of the samples did not change significantly, beyond

50% of Si concentration. Thus, other preparations were conducted, by keeping 50% of Si (TEOS) as the optimum Si concentration.

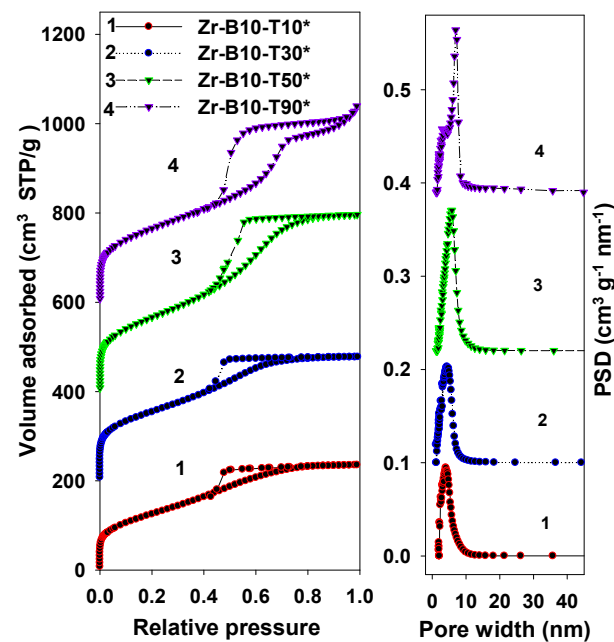


Figure 4. N_2 -adsorption isotherms (left panel) and corresponding PSD curves (right panel) for Zr-B10-TX*; isotherms are shifted by a multiple of 200 cm^3 STP/g. PSD curves 2, 3, and 4 are shifted by 0.1 cm^3 g $^{-1}$ nm $^{-1}$, 0.2 cm^3 g $^{-1}$ nm $^{-1}$, and 0.4 cm^3 g $^{-1}$ nm $^{-1}$, in relation to curve 1, respectively.

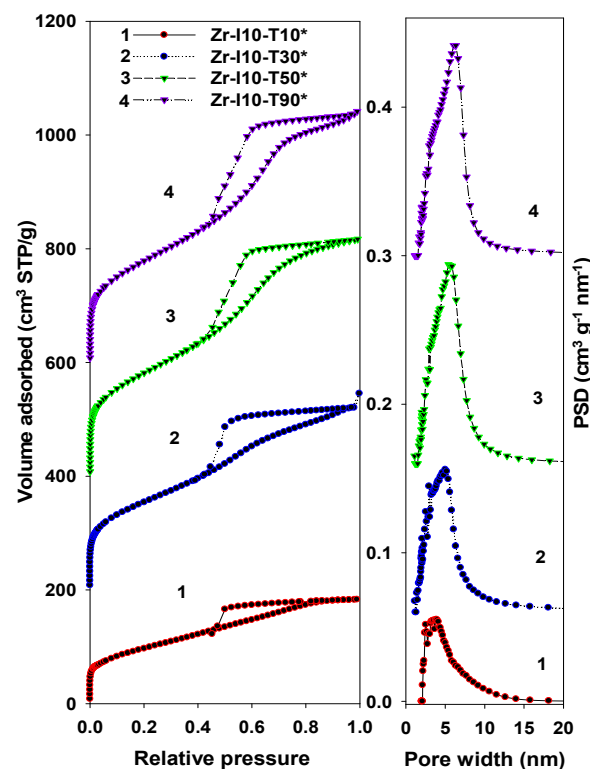


Figure 5. N_2 -adsorption isotherms (left panel) and corresponding PSD curves (right panel) for Zr-I10-TX*; isotherms 2, 3, and 4 are shifted by a multiple of 200 cm^3 STP/g. PSD curves are shifted by 0.05 cm^3 g $^{-1}$ nm $^{-1}$, 0.15 cm^3 g $^{-1}$ nm $^{-1}$, and 0.30 cm^3 g $^{-1}$ nm $^{-1}$, in relation to curve 1, respectively.

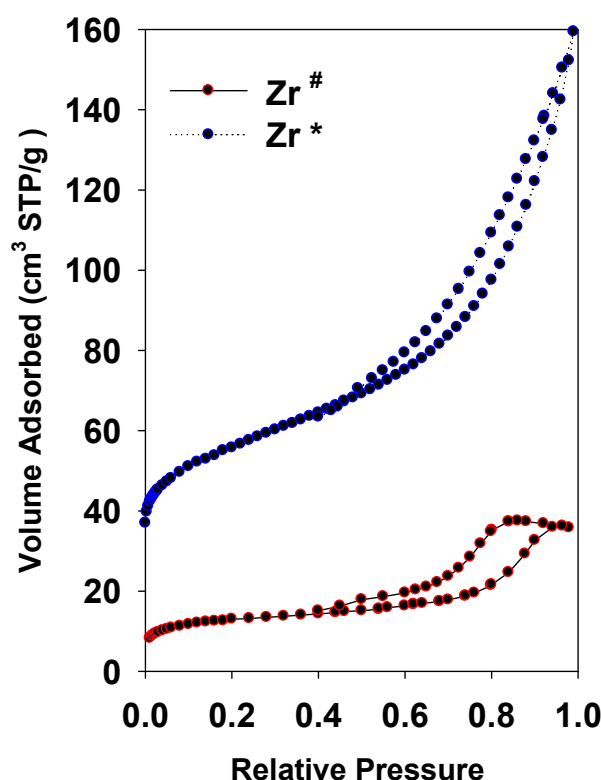


Figure 6. Nitrogen-adsorption isotherms for Zr[#] and Zr^{*} samples; top isotherm is shifted 40 cm³ STP/g from bottom one.

As illustrated above, this preparation was further extended, by adding TEOS at different synthesis stages and by keeping 10% and 50% Si-molar concentration, with respect to ICS/BTEB and TEOS. It seems that prior hydroxylation of TEOS, before adding to alkoxy silane, is essential. TEOS can undergo both hydrolysis and self-condensation, in an aqueous mixture. The addition of bridging precursors to the prehydrolyzed-TEOS mixture facilitates uniform condensation inside the framework, by avoiding structural collapse among bulky-bridging groups. Zr-B-2h exhibits the best structural parameters among the Zr-B-Hh samples studied. Thus, in the case of the Zr-B-Hh samples, the best time to add TEOS into the reaction mixture was 2 h after starting the synthesis. However, note that there is no substantial deviation in the structural parameters for Zr-B-Hh samples, upon changing the addition time of TEOS beyond 2 h (see Table S1). As can be seen from Figure S1a, Supplementary Information, all Zr-B-Hh samples (H = 1, 2, 3, 3.5, 3.75) show type-IV isotherms, with H2-hysteresis loops and narrow PSD curves.

The shape of the adsorption-hysteresis loops is unique for cage-like or constricted mesopores. Moreover, the desorption branches of Zr-B-Hh isotherms end, suddenly, at a relative pressure of about 0.45. The surface area and pore width of the Zr-B-Hh samples are in the range of 731 m²/g to 816 m²/g and 6.3 nm to 6.6 nm, respectively (see Table S1, Supplementary Information). In contrast, Zr-I-Hh samples display significant enhancement in their structural parameters, upon changing the addition time for TEOS from 1 h to 3.75 h. For instance, the Zr-I-1h sample shows the surface area and pore width of about 648 m²/g and 4.1 nm, and those values increased to 739 m²/g and 6.1 nm for the Zr-I-3.75h sample (see Table S1, Supplementary Information). Similarly, as in the case of Zr-B-Hh, all Zr-I-Hh samples, also, display type-IV isotherms (see Figure S1b, Supplementary Information), with the H2-type-hysteresis loop and narrow PSD curves.

The next attempt was made to synthesize the Zr-PMO samples, by varying the amount of block copolymer without changing the above-mentioned synthesis conditions, including 10% and 50% of Si-molar concentration of ICS/BTEB and TEOS, respectively, and the addition time of TEOS after 2 h from the start of synthesis involving BTEB, and 3.75 h in

the case of synthesis with ICS. Under the above conditions, the amount of block copolymer was changed from 0.5 g to 4.5 g. All Zr-I-PMO and Zr-B-PMO samples studied display type-IV isotherms with H2-hysteresis loops and narrow PSD curves (see Figure S2a,b, Supplementary Information). The best structural parameters obtained are for the samples prepared with 1.5 g of P123 (see Table S2, Supplementary Information). However, no substantial deviation in the shape of the N₂ isotherms and hysteresis loops of other samples is observed, compared to those obtained for the Zr-I-P1.5 and Zr-B-P1.5 samples.

The structural characterization of the Zr-I-PMO and Zr-B-PMO samples was performed using small-angle-X-ray diffraction (SAXRD), in the range of 2θ from 0.5° to 2° . Samples with a higher percentage of isocyanurate-bridging groups show less developed porosity, as evidenced by adsorption analysis and significant changes in the XRD patterns. This indicates that the structural order of mesoporous organosilica samples is dependent on the concentration of organic-bridging groups (data not shown). The XRD patterns of the Zr-B10-TX and Zr-I10-TX samples are displayed in Figure 7a,b and show broader reflection peaks. The XRD patterns of the Zr-B10-T10, Zr-B10-T30, Zr-B10-T50, and Zr-B10-T90 samples show peaks at a 2θ angle, equal to 0.6128° , 0.5958° , 0.6464° , and 0.8155° , with d-spacings of 144.0 Å, 148.0 Å, 136.5 Å, and 108.2 Å, respectively. In contrast, the Zr-I10-T10, Zr-I10-T30, Zr-I10-T50, and Zr-I10-T90 samples exhibit peaks at a 2θ angle, equal to 0.6432° , 0.6932° , 0.7109° , and 0.6773° , with d-spacings of 137.2 Å, 127.3 Å, 124.1 Å, and 130.3 Å, respectively. The structural order of mesoporous organosilica samples relies on the loading of organic groups and calcination temperature. Structural shrinkage and structure deterioration lead to disordered porosity at high thermal treatment (600°C). Interestingly, both Zr-B10-TX* and Zr-I10-TX* samples do not considerably alter their XRD patterns, upon thermal treatment at 600°C (see Figure S3a,b, Supplementary Information). However, the XRD patterns of thermally treated samples are much broader than the same samples without thermal treatment. The XRD patterns for Zr[#] and Zr* samples, also, display a broad peak in a similar 2θ region (see Figure S4, Supplementary Information). TEM images obtained for selected Zr-B10-T50 and Zr-I10-T50 samples (see Figure S5, left and right panels) display a worm-like structure.

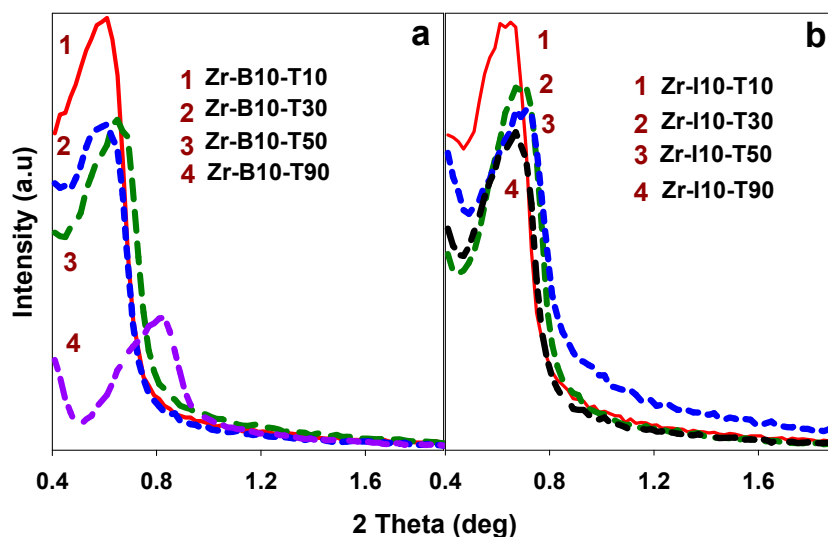


Figure 7. Small-angle XRD patterns for (a) Zr-B10-TX and (b) Zr-I10-TX samples.

Wide-angle-powder-X-ray-diffraction measurements were conducted to study the crystalline properties of the selected Zr-I10-T50, Zr-B10-T50, and Zr[#] samples (see Figure S6a). Figure S6a, Supplementary Information, shows the XRD patterns of the Zr[#] and Zr-I10-T50 samples. The pattern for the Zr[#] sample shows four XRD peaks at 2θ , equal to 31.12° , 45.69° , 56.40° , and 75.38° , with d-spacings of 2.87 Å, 1.98 Å, 1.63 Å, and 1.26 Å, respectively. All peaks correlate with NaCl-structural patterns (note that only a small amount of NaCl

was used in the synthesis). Moreover, the Zr-B10-T50 (data not shown) and Zr-I10-T50 (see Figure S6a) samples do not show long-range order. This suggests that the thermal treatment of Zr-B10-T50 and Zr-I10-T50 materials, at 350 °C, does not initiate crystallization, and the samples are amorphous. Compared to Zr[#], the Zr* sample shows additional peaks at 2 θ , equal to 30.33°, 35.45°, 50.80°, 60.02°, and 62.73° with the corresponding *d* spacings of 2.94 Å, 2.53 Å, 1.80 Å, 1.54 Å, and 1.48 Å, respectively, see Figure S6b, Supplementary Information. These peaks are characteristic of the tetragonal-long-range order of zirconium materials [31]. However, the patterns for the Zr-B10-T50* (data not shown) and Zr-I10-T50* (see Figure S6b) samples do not display any visible peaks, over the same wide-angle region. It suggests that all Zr-I-PMO and Zr-B-PMO samples thermally treated at 350 °C and 600 °C are amorphous in nature.

The ²⁹Si- and ¹H-¹³C-solid-state-NMR spectra were obtained for selected Zr-I10-T50 and Zr-B10-T50 samples. ¹H-¹³C NMR information confirms the presence of groups of isocyanurate (I) and benzene (B) in the composite samples. Moreover, ²⁹Si NMR reveals the condensation of the hybrid organosilica framework and the stability of siloxane bonds in these samples. The ¹H-¹³C CP/MAS spectrum of the Zr-I10-T50 sample shows two peaks at around 9 ppm and 20 ppm, corresponding to the carbon atom directly linked to silicon and the carbon atom in the middle of propyl linkage (see Figure S7a, Supplementary Information). An additional peak, at around 44 ppm, is responsible for the carbon atom directly attached to the nitrogen atom embedded in the isocyanurate ring. The characteristic sharp peak observed at 149.5 ppm can be attributed to the isocyanurate-bridging group [32] (see Figure S7a, Supplementary Information), whereas the peak at 128 ppm corresponds to the benzene-bridging group. The ¹H-²⁹Si-CP/MAS-NMR spectrum of Zr-B10-T50 shows two major resonance peaks, at −99.4 ppm and −72.3 ppm, referring to the Q³ [R-Si-(OSi)₃(OH)₁]/[R-Si-(OSi)₂(OZr)(OH)₁] and T³ [R-Si-(OSi)₃]/[R-Si-(OSi)₂(OZr)] units (see Figure S7b, Supplementary Information). The spectrum of Zr-I10-T50 shows peaks at −99.7 ppm and −66.1 ppm, referring to the Q³ [R-Si-(OSi)₃(OH)₁]/[R-Si-(OSi)₂(OZr)(OH)₁] and T³ [R-Si-(OSi)₃]/[R-Si-(OSi)₂(OZr)] units. Moreover, the energy-dispersive-X-ray (EDX) spectrum reveals elemental distribution throughout the silica matrix, for the samples thermally treated at 350 °C and 600 °C (see Figures S8a,b and S9a,b, Supplementary Information). These data demonstrate the incorporation of Zr species into the silica mesostructures.

3.2. CO₂ Physisorption

CO₂ sorption was, also, investigated for selected samples (Zr[#]/Zr-I10-TX/Zr-B10-TX) at room temperature (25 °C) up to 1.2 bar pressure. Zr[#] shows a relatively low CO₂ uptake of about 0.72 mmol/g at 25 °C (see Table S3, Supplementary Information). Small CO₂ uptake by Zr[#] can be due to the inadequate microporosity of this sample. Figure 8a,b show a comparison of CO₂-adsorption isotherms, measured at 25 °C, for the selected Zr-I-PMO and Zr-B-PMO samples. As can be seen from Table S3 and Figure 8a,b, all samples thermally treated at 350 °C (Zr-I10-TX/Zr-B10-TX) (X = 10, 30, 50, and 90) exhibit relatively high CO₂ uptake, in the range from 1.71 mmol/g to 2.08 mmol/g, at 25 °C. However, the CO₂ uptake for Zr-B10-TX and Zr-I10-TX increases slightly, with an increasing amount of Si (X%), from 10 to 90. For instance, the CO₂ uptake of 1.73 mmol/g for Zr-B10-T10 increases to 2.08 mmol/g for Zr-B10-T50. This confirms that increasing the TEOS percentage in the initial-reaction mixture has no significant effect on the CO₂ uptake. Therefore, the enhancement of CO₂ uptake from 0.72 mmol/g for the Zr[#] sample to 1.84 mmol/g for the Zr-I10-T50 sample and 2.08 mmol/g for the Zr-B10-T50 sample can be due to two main contributions: (1) different types of hydroxyl groups available on the zirconium surface after introducing TEOS in the reaction mixture, and (2) the hydrophobicity of the isocyanurate- and benzene-bridging groups. Note that three types of OH groups are available on the zirconia-silica surface, which significantly affect CO₂ uptake and the structure formation between those groups and CO₂ [33,34]. These are called terminal, bi-bridged, and tri-bridged OH groups and can be identified by infrared (IR) spectroscopy [20,21]. It is

well-established that these different types of OH groups are available on the zirconia–silica surface, at higher temperatures up to 600 °C. The terminal-OH groups directly attached to zirconium cations react with CO₂ and form hydrogen-carbonate (HCO₃) species (see Scheme S1a, Supplementary Information). As illustrated in Scheme S1b, surface-bidentate-carbonate complexes can, also, be possible through acid–base-pair sites (Zr⁴⁺-O²⁻) present on the zirconia surface. Through the acid–base-pair mechanism, the electron-donor ability of the oxygen atom of the CO₂ molecule toward the Zr atom (Scheme S1b) increases the Lewis basicity of Zr⁴⁺. It, thus, enhances the affinity of acidic CO₂ toward basic sites. We, previously, showed that CO₂ uptake could be improved with increasing hydrophobicity of the pore walls, by introducing benzene-bridging groups [35]. Moreover, Farhang and co-workers studied two different types of hydrophobic-fumed-silica particles, by changing the strength of hydrophobicity [36]. They reported that most hydrophobic silica showed higher CO₂ sorption. Liu and co-workers studied the hydrophobic effect of CO₂ on two Cu-containing (HKUST-1) and Ni-containing (Ni/DOBDC) metal-organic frameworks (MOFs) as well as two zeolite (5A, NaX) materials. They demonstrated that two MOFs adsorb more CO₂ than hydrophobic-zeolite materials [37–42]. Although hydroxyl groups available on the zirconia surface show strong interaction with water, isocyanurate- and benzene-bridging groups increase hydrophobicity and reduce the hydrophilic effect, consequently enhancing CO₂ uptake. Note that the nitrogen content in isocyanurate groups did not significantly affect CO₂ adsorption because of less accessibility, hindering the reaction between hindered-nitrogen atoms (embedded) in isocyanurate rings and CO₂.

Table 2 shows a comparison of the CO₂-uptake values reported for PMOs at ambient conditions. For instance, a periodic mesoporous organosilica, with a basic urea-derived framework (PMO-UDF), was prepared and characterized by Sun and co-workers as well as tested for CO₂ sorption [43]. They reported a CO₂ uptake of 0.62 mmol/g for PMO-UDF-15. Sim et al. investigated the CO₂ adsorption on amine- and phenylene-functionalized organosilica with benzene-bridging groups (BPMO). The authors reported CO₂ uptake of 0.57 mmol/g and 3.30 mmol/g for BPMO and *N*-[3-(trimethoxysilyl)propyl]-ethylenediamine-modified BPMO (A2-BPMO), respectively, at ambient conditions [37]. Zebardasti and coworkers synthesized periodic mesoporous organosilica (PMO-THEIC), by reacting 3-isocyanatopropyltriethoxysilane (IPTES) with 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (THEIC), and tested for CO₂ capture [19]. They reported that PMO-THEIC has approximately three-fold higher CO₂-capture capacity (1.10 mmol/g), as compared to pure inorganic SBA-15 (0.40 mmol/g) [19]. Van Der Voort and co-workers prepared amine-functionalized PMOs and investigated for CO₂ adsorption [44]. They used several nucleophiles, such as diaminobutane (DAB), diaminohexane (DAH), diaminododecane (DADD), diethylenetriamine (DETA), and tetraethylenepentamine (TEPA), to obtain dangling functionalities with different properties. The authors observed an increase in CO₂ uptake, as the nitrogen content decreases, with the order of PMO-DADD > PMO-DAH > PMO-DAB. A similar trend was, also, observed for their polyamines-functionalized PMOs [44]. Gunathilake et al. studied mesoporous alumina–zirconia–organosilica composites, for CO₂ capture at ambient conditions [34]. They used tris[3-(trimethoxysilyl)propyl]isocyanurate (ICS) as bridging groups. The CO₂-adsorption capacities of alumina–organosilica mesostructures and zirconia–organosilica mesostructures were 1 mmol g^{−1} and 1.93 mmol g^{−1}, respectively, at 25 °C [34].

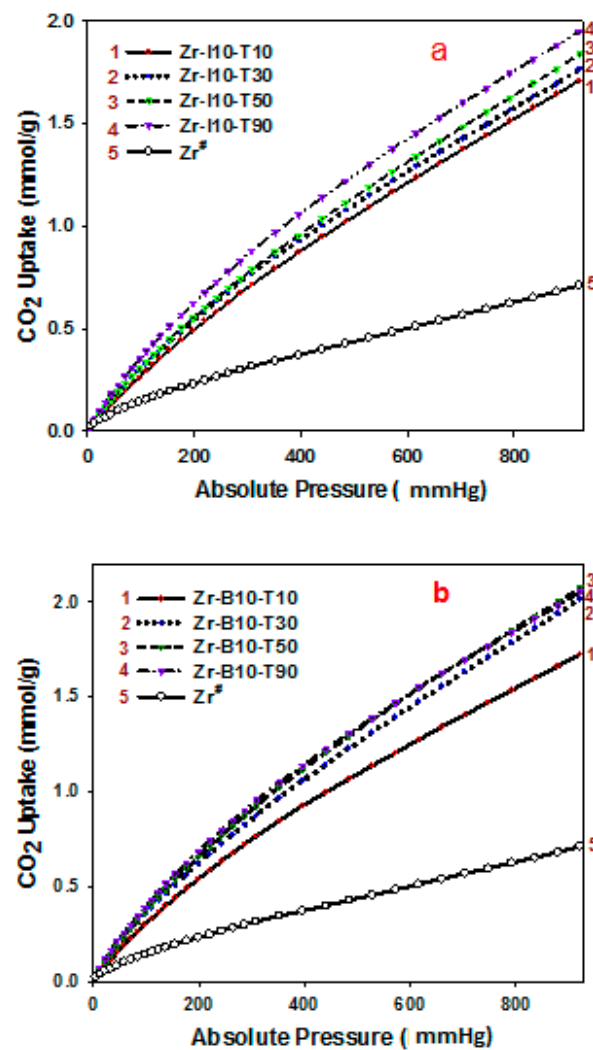


Figure 8. CO₂-sorption isotherms at 25 °C, measured on (a) Zr-I10-TX and Zr[#] (as synthesized) and (b) Zr-B10-TX and Zr[#] (as synthesized) samples.

Table 2. Comparison of CO₂-uptake values reported previously for various PMO sorbents at ambient conditions.

Adsorbent	BET SSA (m ² /g)	CO ₂ Uptake (mmol/g)	Reference
PMO-UDF-15	979	0.62	[43]
BPMO	645	0.57	[37]
A2-BPMO	180	3.03	[37]
PMO-DADD	450	0.88	[44]
SBA-15	650	0.40	[19]
PMO-THEIC	697	1.10	[19]
Al-I-PMO	326	1.00	[34]
Al-Zr-PMO	381	1.33	[34]
Zr-B-PMO	809	2.08	Current study
Zr-I-PMO	743	1.95	Current study

4. Conclusions

Two series of zirconium-incorporated-mesoporous-silica materials with isocyanurate- and benzene-bridging groups (Zr-I-PMO and Zr-B-PMO) were synthesized, by a co-condensation strategy, using triblock-copolymer Pluronic P123 as a structure-directing agent. Zirconia exhibited excellent chemical and physical properties, including mechanical and thermal stability. The incorporation of zirconium into the framework was confirmed by energy-dispersive-X-ray spectra (EDX). ^1H - ^{13}C NMR confirmed the presence of benzene- and isocyanurate-bridging groups present in Zr-I-PMO and Zr-B-PMO samples, respectively. The extraction process, followed by thermal treatment at 350 °C, in flowing N_2 assured the complete removal of the polymeric template, without degradation of the isocyanurate- and benzene-bridging groups. Zr-I-PMO and Zr-B-PMO materials displayed type-IV- N_2 -adsorption isotherms and H2-hysteresis loops, with well-developed structural parameters, including high surface area, pore volume, pore width, and narrow pore-size distribution. Structural parameters are tailorable by varying the Zr:Si ratio, by varying the amount of TEOS in the mesostructures. The structural properties were significantly affected by changing the TEOS-addition time, amount of block copolymer P123 added, and calcination temperature. Zirconium-incorporated mesostructures with isocyanurate- and benzene-bridging groups showed a CO_2 -sorption capacity of 1.71–2.08 mmol/g at 25 °C and 1.2 bar pressure. Due to the thermal stability, hydrophobicity of the bridging groups, and relatively high CO_2 uptake for a metal-organic framework (MOF) at 25 °C, Zr-PMO mesocomposites show potential as effective sorbents for CO_2 capture at ambient conditions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jcs6060168/s1>. Scheme S1: Systematic illustration of (a) formation of hydrogen carbonate structures on terminal OH groups. (b) Formation of bidentate carbonate complex via acid base pair [6,7]. Figure S1: (a) N_2 adsorption isotherms (left panel) and the corresponding PSD curves (right panel) for Zr-B-Xh samples; isotherms 2, 3, 4, and 5 are shifted by 200 cm^3 STP/g, 500 cm^3 STP/g, 700 cm^3 STP/g, and 900 cm^3 STP/g, in relation to isotherm 1. The Ten PSD curves are shifted by a multiple of 0.2 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$. (b) N_2 adsorption isotherms (left panel) and the corresponding PSD curves (right panel) for Zr-I-Xh samples; isotherms are shifted by a multiple of 200 cm^3 STP/g; PSD curves 2, 3, 4, and 5 are shifted by 0.12 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, 0.25 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, 0.37 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, and 0.51 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, in relation to curve 1, respectively. Figure S2: (a) N_2 adsorption isotherms (left panel) and the corresponding PSD curves (right panel) for Zr-B-Pf samples; isotherms 2, 3, 4, and 5 are shifted by 200 cm^3 STP/g, 600 cm^3 STP/g, 900 cm^3 STP/g, and 1200 cm^3 STP/g, in relation to isotherm 1, respectively. The PSD curves are shifted by 0.12 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, 0.31 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, 0.48 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, and 0.62 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, in relation to curve 1, respectively. Figure S2: (b) N_2 adsorption isotherms (left panel) and the corresponding PSD curves (right panel) for Zr-I-Pf samples; isotherms 2, 3, 4, and 5 are shifted by 200 cm^3 STP/g, 500 cm^3 STP/g, 700 cm^3 STP/g, and 1000 cm^3 STP/g, in relation to isotherm 1, respectively. PSD curves 2, 3, 4, and 5 are shifted by 0.12 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, 0.27 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, 0.39 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, and 0.53 $\text{cm}^3 \text{ g}^{-1} \text{ nm}^{-1}$, in relation to curve 1, respectively. Figure S3: Small-angle XRD patterns of (a) Zr-B10-TX* and (b) Zr-I10-TX* samples. Figure S4: Small-angle XRD patterns of Zr[#] and Zr* samples. Figure S5: TEM images of (a) Zr-B10-T50 and (b) Zr-I10-T50 samples. Figure S6: Wide-angle XRD patterns of (a) Zr[#] & Zr-I10-T50 and (b) Zr* & Zr-I10-T50* samples. Figure S7: (a) ^1H - ^{13}C CP/MAS NMR and (b) ^1H - ^{29}Si CP/MAS NMR spectra of Zr-B10-T50 and Zr-I10-T50 samples. Figure S8: EDX spectra of the (a) Zr-B10-T50 and (b) Zr-I10-T50 samples. Figure S9: EDX spectra of (a) Zr-I10-T50* and (b) Zr-B10-T50* samples. Table S1: Adsorption parameters for Zr-I-PMO and Zr-B-PMO samples, synthesized by varying time for TEOS addition. Table S2: Adsorption parameters for Zr-I-PMO and Zr-B-PMO samples, synthesized by varying the amount of block copolymer. Table S3: CO_2 sorption data at 25 °C, for selected Zr-I-PMO and Zr-B-PMO samples [45–47].

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