

The novel Carbon Nanotube-assisted development of highly porous CaZrO₃-CaO xerogel with boosted sorption activity towards high- temperature cyclic CO₂ capture

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Abstracts:

Herein, for the first time, we employed three minor concentrations of Carbon Nanotubes (CNT), 2.5, 5, and 10 wt.%, as an auxiliary additive to boost the textural and structural features and CO₂ capture potential of sol-gel-derived Zr-supported CaO adsorbents. The corresponding xerogels were developed with 15/1 and 30/1 Ca/Zr molar ratios to minimize the required amount of prohibitive Zr-based precursor. For both types of Zr-decorated CaO adsorbents, 5 wt.% of CNT was recognized as the most efficient amount. In addition to 15.84 and 33.1% reduction in CaO crystallite sizes, 50.57 and 90.55% increments in pore volume values were reported for CaO adsorbents developed with 15/1 and 30/1 Ca/Zr molar ratios,

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respectively. Over 15 cycles under harsh CO₂ capture conditions, the total amount of captured CO₂ for both abovementioned types of Zr-promoted adsorbents raised from 2.01 and 1.96 to 2.92 and 3.01 g CO₂/ g adsorbent, sequentially. Zr-promoted CaO nanoadsorbents merged with 5 wt.% MWCNT showed the ultimate CO₂ capture capacity of 0.164 and 0.149 g CO₂/ g adsorbent for xerogel prepared with 15/1 and 30/1 molar ratios of Ca/Zr, respectively. Even though the xerogel containing a Ca/Zr molar ratio of 15/1 showed the best sorption durability and ultimate capture capacity, MWCNT more significantly affects the CaO xerogel developed with a Ca/Zr molar ratio of 30/1. It can be deduced that the low content of multi-walled CNT notably contributes to developing highly efficient and fluffy-like Zr-promoted xerogels containing minor concentrations of Zr-based species.

Keywords: CO₂ capture, Calcium looping, Sol-gel derived CaO sorbent, CNT additive, Bio-additive

Highlights:

- * Novel MWCNT-assisted development of highly porous and robust CaZrO₃-CaO xerogel
- * Possibility of employing low content of Zr additive in the presence of MWCNT template
- * Presenting best textural and adsorptive features for samples merged with 5 wt.% CNT
- * >50% boost in porosity and more uniform dispersion of CaZrO₃ by adding 5 wt.% CNT
- * >45% increase in the total capture capacity by adding 5 wt.% CNT over 15 cycles

1. Introduction:

The considerable pollution in our planet's environment, including water and atmosphere, endangers our society [1, 2]. The catastrophic climate breakdown rising from CO₂ emission exacerbates the atmospheric CO₂ concentration [3, 4]. According to the Paris Agreement, Negative Emission Technologies (NETs) have been considered to diminish CO₂ emissions [5]. As one of the NETs, the CO₂ capture technique has brought numerous improvements through disparate methods [6, 7]. Diminishing the CO₂ emission, mainly emitted by the flue gas released from fossil fuel combustion processes, through CO₂ capture processes has notably engrossed the attention of researchers and environmentalists in this decade as an ongoing challenge [8-10]. Comparing avenues of CO₂ capture from industrial units, including pre-combustion [11-13], oxy-combustion [14, 15], and post-combustion [16, 17], reveals the effectiveness of post-combustion methods, namely membrane [18], cryogenic [19], absorption [20], and adsorption [21]. One of the most emerging and developing techniques to separate CO₂ from post-combustion flue gases is a second-generation calcium looping (CaL) technique, derived from chemical looping combustion technology [22], based on reversible CaO carbonation/regeneration [23, 24]. In addition to CO₂ adsorption, CaL has already been exerted for the biomass and methane reforming process, H₂ production, and thermochemical energy storage [25-27]. Moreover, this process has been demonstrated as the most energy-efficient and affordable technology for industrial decarbonization, among other developing CO₂ capture processes. Practically at the CaL process, CaO particles are repeatedly circulated between inter-connected carbonator and calciner fluidized bed reactors based on specified participles as follows:

(1) CO₂ uptake at carbonator through exothermic partial carbonation reaction between CaO and CO₂, containing from post-combustion flue gas in a volume concentration of 10–15

vol.% CO₂, at temperatures between 600-700°C, optimum calculated temperature to have fastest carbonation rate [28].

(2) CaO regeneration through CaCO₃ decomposition based on Eq. 1. the CaCO₃ circulated from carbonator to calciner and fresh CaCO₃ entered through makeup flow, imported to compensate deactivated CaO particles after several cycles, are calcined a temperature beyond 800°C and under inevitably high CO₂ concentration, 70-100 vol.% CO₂, arising from either external ingination of fuel or pure-O₂ combustion to supply the required heat for calcination [29],



(3) Feeding back the regenerated CaO in the calciner to the carbonator to commence a new cycle.

The high theoretical CO₂ uptake potential, remarkable adsorption capacity at temperatures above 500°C, swift carbonation/regeneration kinetics, and the wide accessibility of CaO sources, as the practical boons of the CaL process, dramatically attract the consideration of scientific researchers [28].

After passing several multiple cycles during the CaL process, the sintering of CaO particles impresses their CO₂ capture activity. CaO sintering leads to forming of a thick layer of CaCO₃ (~100 nm) on the CaO surface, the regular breakdown of the porous configuration, and a significant reduction in the volume of active CaO surface area needed for capturing CO₂ molecules from flue gas [29]. Emanated from the sintering phenomenon, the CO₂ capture capacity of CaO particles has drastically diminished with the rising cycle number during the CaL process. The high tendency of CaO for sintering could be attributed to its lower thermal durability during calcination at a temperature above 800 °C, owing to its lower Tamman temperature (~ 500 °C) compared to the CaL process temperature [28, 29]. To

potentially increase the overall efficiency of CaO particles in the CaL process, developing high-thermal-durable CaO sorbents is required.

Motivated by tackling this predominant hurdle, numerous research in this decade focused on improving the thermal-resistance property and adsorption activity of CaO sorbents under various CaL conditions through efficient techniques. Previously proved by researchers, the incorporation of thermal-durable additives into agglomerated nanoparticles contributes to decreasing the agglomeration rate dramatically [30-32]. One of the most promising materials to mitigate agglomeration and the sintering rate of CaO particles is metal oxides, which also improve the sorption performance of CaO-based sorbents [28]. The findings on metal-promoted composites indicate that enhanced efficiency through metal incorporation for boosting the processing activity of materials [33, 34]. The addition of metal-based additives causes the formation of nano-size metal-based species that locate between CaO grains and hinder their agglomeration during the high-temperature CaO regeneration, resulting in higher free surface area and pore volume compared to unmodified counterparts. This textural modification stemming from the presence of metal-based promoters enhances the CO₂ sorption capacity at each cycle and sorption durability during the CaL process. Among diverse studied metal-based additives, such as La₂O₃, MgO, TiO₂, MnO₂, Cr₂O₃, ZrO₂, Al₂O₃, CuO, Y₂O₃, CeO₂, SiO₂, Nd₂O₃, NaCl [35], ZrO₂-promoted CaO sorbents have exhibited more promising CO₂ capture activity because of the formation of CaZrO₃ as promoter in the CaO texture. Radfarnia et al. [36] demonstrated the greater effectiveness of formed CaZrO₃ on improving the CO₂ uptake performance of CaO sorbents, two kinds of Canadian limestone, under severe CaL conditions compared to developed Ca₉Al₆O₁₈, MgO. The CO₂ separation efficiency of CaO sorbents doped with ZrO₂, La₂O₃, MgO, and Al₂O₃ through the sol-gel combustion method indicated the superior activity of ZrO₂-stabilized sample, retaining 71.5% of its primary CO₂ uptake potential after 100 consecutive

carbonation/calcination cycles under severe conditions. Antzara et al. [37] investigated the sorption performance of Zr-modified CaO sorbent, with a CaO/CaZrO₃ weight ratio of 66 wt.%/34 wt.%, in a lab-scale fluidized bed reactor under the realistic calciner condition, 920°C, and 80 vol.% CO₂ concentration. The modified sorbent held 70% of its primary uptake capacity and indicated 5 times higher ultimate sorption capacity than natural limestone after 20 repetitive cycles. In another study, it has been revealed that incorporating CaO sorbent with ZrO₂ using a sol-gel synthesis manner resulted in 88.9% higher ultimate CO₂ uptake potential and 2 times higher sorption durability during 10 consecutive multiple cycles compared to unmodified CaO [38].

As an efficient and novel method to increase the CO₂ uptake potential of CaO adsorbents, employing flammable materials to boost the sorbent porosity of CaO particles attracted significant attention due to the influence of porosity on the capture efficiency of CaO sorbents. By intermixing biomass materials, ignitable at high-temperature calcination in the furnace, they place in the inner zones of CaO texture. With the biomass-merged CaO adsorbents being calcined in the furnace, the combustion of biomass particles forms numerous macro- and meso-pores, which facilitates the diffusion of CO₂ molecules into CaO structure and expedites CO₂ sorption capacity during the carbonation stage. Accomplished investigations on pellet-size CaO sorbents have demonstrated the positive role of biomass materials on the porosity of the CaO sorbents. The removal of these templates in CaO texture during the calcination stage of preparation leads to the forming of notable pores in CaO texture associated with considerably porous CaO structure and higher accessible CaO sites. Using the template-assistance hydrothermal preparation technique and glucose and urea as carbon-based templates, the total amount of captured CO₂ by CaO over 10 multiple carbonation-calcination cycles increased by ~164% [39]. Moreover, the conducted CO₂ capture analysis under harsh CaL conditions exhibited a 142% increment in ultimate CO₂

capture capacity at the 10th cycle by hydrothermally templating MgO-promoted CaO adsorbent with xylose template [40]. In another research, hydrothermally employing the inverse opal (IO)-like carbon-nanospheres-templated preparation method on Ca₃Al₂O₆-stabilized CaO adsorbent resulted in more than 3 times higher CO₂ capture durability and capacity [41].

Among numerous carbon-based materials utilized as a carbon-based materials, Carbon Nanotube (CNT) is distinguished by its tubular structure, and considered as the most suitable additive that increase the chemical and physical process efficiency [42-46]. It can be predicted that the utilization of tubular CNT as the template creates bigger hollow zones. Even though this additive has not been recognized as cost-effective material, recently published studies reveal the capability of fabricating CNT material from biomass-derived sources, such as Stillage residue [47], Chlorella [48], Chitosan [49], Potato peels [50], and Cotton fiber [51], through utilitarian procedures, namely pyrolysis [52], microwave plasma irradiation [53], chemical vapor deposition [54], and mechanochemical treatment [55]. The novel proposed scenarios to manufacture CNT from the abovementioned biomass facilitates the implementation of CNT-including process in industrial units.

It can be concluded that doping CaO with ZrO₂ plays an efficient role in improving the CO₂ uptake activity and reducing sintering during the CaL process. It is worth noting that even though the incorporation of CaO with ZrO₂ leads to the form of CaZrO₃, which enhances the sorption durability of CaO particles, the content of free CaO to capture CO₂ molecules of flue gas gradually decreased due to the CaZrO₃ formation through the reaction of CaO with ZrO₂. Zr-based precursors have been recognized as costly materials worldwide. On the one hand, reduced ZrO₂ content added to CaO sorbents resulted in less deactivation resistance and lower sorption capacity.

Considering the thorough conducted literature review on the adsorption activity of CaO-based CO₂ sorbents, most studies corroborated the superior CO₂ capture potential and stability revealed the Zr-promoted CaO adsorbents; in addition, most research activities revealed that the utilization of high content of Zr-derived additives diminishes the accessible CaO amount and raise the sorbent cost. Moreover, to the best of our knowledge, neither has the investigation been paid to boost the CO₂ capture capacity of CaO adsorbents modified with minor ZrO₂ nor the incorporation of biomass template into Zr-supported CaO has been studied. Therefore, in this research, for the first time, MWCNT, as an auxiliary carbon-based additive, was merged with Zr-modified CaO sorbents containing minor ZrO₂ concentrations to develop novel MWCNT-templated CaZrO₃-stabilized CaO nanoadsorbents through sol-gel combustion synthesis technique, and affecting parameters, namely Ca/Zr molar ratio and MWCNT concentration, were comprehensively scrutinized. In the present paper, CNT-templated Zr-stabilized CaO sorbents with various CNT amounts, including 2.5, 5, and 10 wt.%, and high Ca/Zr molar ratios of 15/1 and 30/1 were developed by the sol-gel method. These sorbents' morphological characterizations and CO₂ uptake potential under severe CaL process conditions were comprehensively investigated. It is worth stating that incorporating MWCNT into cost-effective Zr-stabilized CaO sorbents results in a striking improvement in CO₂ capture activity.

2. Experimental

2.1. Materials:

The nitrate salts of calcium, Ca(NO₃)₂·4H₂O from *Merck*, and zirconium, ZrO(NO₃)₂·H₂O, from *Sigma Alderich*, as calcium and promoter precursors, respectively, as well as citric acid, C₆H₈O₇·H₂O from *Sigma Alderich*, as combustion agent, were employed to synthesize Zr-modified CaO powders. MWCNT, from *VCN material Company*, was also used as a nano-

scale bio-based additive. The physical properties of nano-additive MWCNT are noted in **Table 1.**

Table 1. Characterizations of MWCNT

Morphology	Diameter (nm)	Length (μm)	Purity (%)	Specific surface area (m^2/g)	Density (g/cm^3)
Tube shape	10-20	~ 30	≥ 98	200	2.1

2.2. Preparation:

Firstly, to efface the impurities on the surface of CNT particles and improve their homogeneous dispersal in a water-based solution during the sorbents' preparation, they were prewashed with 4 M HCl. f. The sol-gel combustion synthesis approach was applied to prepare all samples using citric acid as a combustion agent. Firstly, the appropriate amount of calcium nitrate and citric acids, with a Ca/citric acid molar ratio of 9/5, were dissolved into deionized water under persistent heating and stirring. As soon as the solution temperature exceeds 70 °C, the required amounts of citric acid and zirconium nitrate are specified by the corresponding Ca/Zr molar ratio (15/1 or 30/1) and a Zr/citric acid molar ratio of 9/5, were added to the mixture. The final solution was stirred under the isolated condition by inserting the vessel lid. Then, the mixture was agitated at 100 °C for 3 h. Afterward, the determined amount of MWCNT was transferred to the solution and mixed for 1 h at ambient temperature. The sol was kept at room temperature for 24 h to form a uniform soaked gel. The wet gel was desiccated in an oven at 150 °C for 3 h, creating hollow structures. To eliminate residual organic components, the arid samples were calcined at 850 °C for 1.5 h under airflow with a heating rate of 10 °C/min.

Table 2: Specifications of synthesized CaO-based samples

Sample	Ca/Zr molar ratio	CNT additive (wt.%)	Elemental composition (At. %) from ICP test		Inert material (wt.%)		Textural and structural properties of fresh samples							BET surface area of used samples (m ² /g)
							Surface area (m ² /g)		Pore volume (mm ³ /g)		Pore diameter (nm)		Average CaO crystallite size (nm)	
			Ca	Zr	CaO	CaZrO ₃	BET	Langmuir	BET _{total}	BJH	BET _{mean}	BJH		
Pure CaO	-	-	48.25	0	100	-	11.65	12.7	57.3	57.53	19.68	1.64	27	2.54
Ca/Zr molar ratio of 15/1														
CaZr15-C0	15/1	-	34.37	2.29	81.5	18.5	12.9	12.72	83.24	72.19	25.81	1.21	26.5	3.23
CaZr15-C2.5	15/1	2.5	40.05	2.66	81.5	18.5	13.6	15.73	80.37	80.37	23.64	1.21	25.6	4.64
CaZr15-C5	15/1	5	42.67	2.85	81.5	18.5	17.83	19.4	116.6	108.7	26.16	1.64	22.3	6.48
CaZr15-C10	15/1	10	47.01	3.13	81.5	18.5	13.59	15.58	88.77	91.74	26.12	1.64	25.4	5.47
Ca/Zr molar ratio of 30/1														
CaZr30-C0	30/1	-	48.62	1.62	90	10	11.23	10.86	54.17	50.4	19.3	7.99	29.6	2.64
CaZr30-C2.5	30/1	2.5	44.83	1.49	90	10	13.4	14.84	57.12	56.88	17.05	7.99	27.8	3.09
CaZr30-C5	30/1	5	51.09	1.7	90	10	20.63	22.8	93.25	96.04	18.8	9.22	19.8	5.32
CaZr30-C10	30/1	10	54.22	1.81	90	10	16.75	18.6	85.38	84.94	20.38	1.21	24.7	5.58

2.3. Characterization: 209

Using BELSORP MINI II appliance, BET (Brunauer, Emmett, Teller) specific surface 210
area and BJH (Barrett, Joyner, Halenda) pore size distribution of the synthesized samples 211
were measured by N₂ physisorption at 77 K. The sorbents were degassed at 300 °C for 3 h in 212
a vacuum before determination. 213

The X-ray diffraction (XRD) analysis patterns were acquired utilizing Siemens 5 D500 X- 214
ray diffractometer (Cu K α , λ = 0.15406 nm) to recognize the formed phases in samples. The 215
peak intensity data of samples were assembled over the 2Theta range of 10-80°. To calculate 216
the CaO crystallite size by XRD pattern, D_{avg}, Debye-Scherrer's equation [56-58] was used: 217

$$D_{avg} = \frac{0.9 \times \lambda}{\beta \times \cos \theta} \quad (2) \quad 218$$

where λ , β , and θ correspond to the radiation wavelength, the whole breadth at half of the 219
peak maximum (radians), and the peak angular position, respectively. A fitting correlation, 220
 β_0 , of 0.108° was considered for the peak broadening due to the property of the 221
diffractometer. 222

The structural morphology and textural porosity of fresh and used adsorbents before and 223
after the CO₂ uptake process was examined by scanning electron microscopy (SEM) 224
characterization on FEI Quanta 200 microscope apparatus, coupled with Oxford INCA sight 225
X energy-dispersive X-ray analysis (EDX) applying on SAMX detector to determine 226
elemental distribution. 227

To measure the quantitative content of metals, Ca and Zr, in ultimate samples, inductively 228
coupled plasma optical emission spectroscopy (ICP-OES) characterization was performed 229
through the Varian Vista-PRO CCD Simultaneous ICP-OES instrument. 230

2.4. CO₂ capture measurement:

The CO₂ uptake behavior and thermal durability of prepared samples were tested via TGA (thermogravimetric analysis), TA Instruments Discovery SDT 650 for successive 15 multiple carbonation/regeneration cycles under the severe CaL condition. The severe CaL condition for the post-combustion CO₂ capture process generally consists of the following:

- The short time resistance of CaO in carbonator owing to high inlet flue gas velocity and low content of CO₂ (10-15 wt.%).
- The calciner's high CO₂ concentration (more than 70% vol.) is caused by combusting inlet fuel to the calciner to provide a high required temperature for CaO regeneration.

To acquire valuable CO₂ capture data during the severe-condition CaL process, the CO₂ capture activity of prepared CaO-based sorbent in this work was assessed under harsh CaL conditions. 15 calcination and carbonation cycles were performed for the cyclic TGA testing, starting with a zeroth calcination step. The carbonation step was carried out at 650 °C for 10 minutes under 15% CO₂ balanced with N₂ and calcination at 950 °C for 10 minutes under 100% CO₂. The total flow rate for all the steps was 50 mL/min.

TGA results are assessed by CO₂ sorption capacity (C_n : gr of adsorbed CO₂/ gr of the whole sorbent) and CaO conversion (X_n). CO₂ sorption capacity is calculated based on a mass increase of the sample during the carbonation stage as follows [28]:

$$C_n = \frac{m_{f,n} - m_0}{m_0} \quad (3)$$

where C_n and $m_{f,n}$ are CO₂ sorption capacity and mass of carbonated sample at the n^{th} cycle, and m_0 is related to the mass of the fresh sample prior to 1st cycle.

CaO conversion is the conversion ratio of available CaO grains to formed CaCO₃ through the physical reaction with CO₂ according to the following equation [59]:

$$X_n = \frac{C_n}{0.785 \times W_{CaO}} : \left[0.785 = \frac{M_{CO_2} (=44.01)}{M_{CaO} (=56.077)} \right] \quad (4) \quad 254$$

which W_{CaO} is attributed to the weight fraction of free CaO available in the sorbent; M_{CO_2} 255
and M_{CaO} are the molar mass of CO_2 and CaO, respectively. Even though the mass of the 256
whole sorbent (CaO + inert species) is considered for C_n calculation, X_n reveals the fraction 257
of reacted CaO with CO_2 to the entire CaO [60]. Since a considerable amount of extant CaO 258
remains unreacted during CO_2 during adsorption in the carbonator due to the sorbent 259
agglomeration and sintering, the X_n value is below 100 %. 260

3. Result and discussion: 261

3.1. Characterization 262

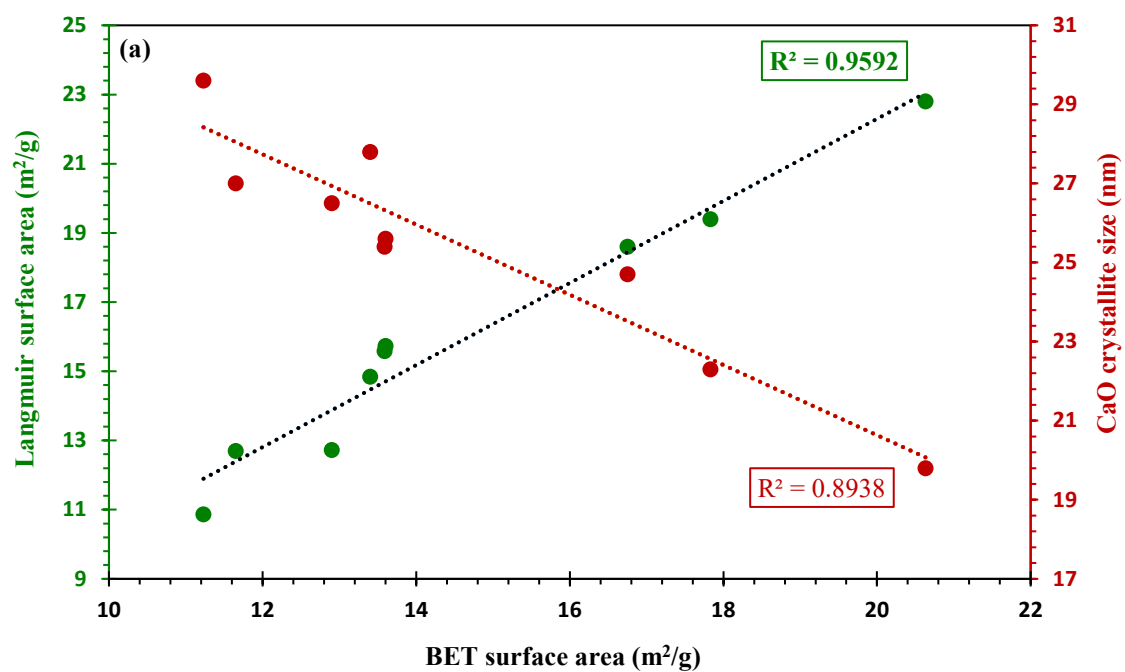
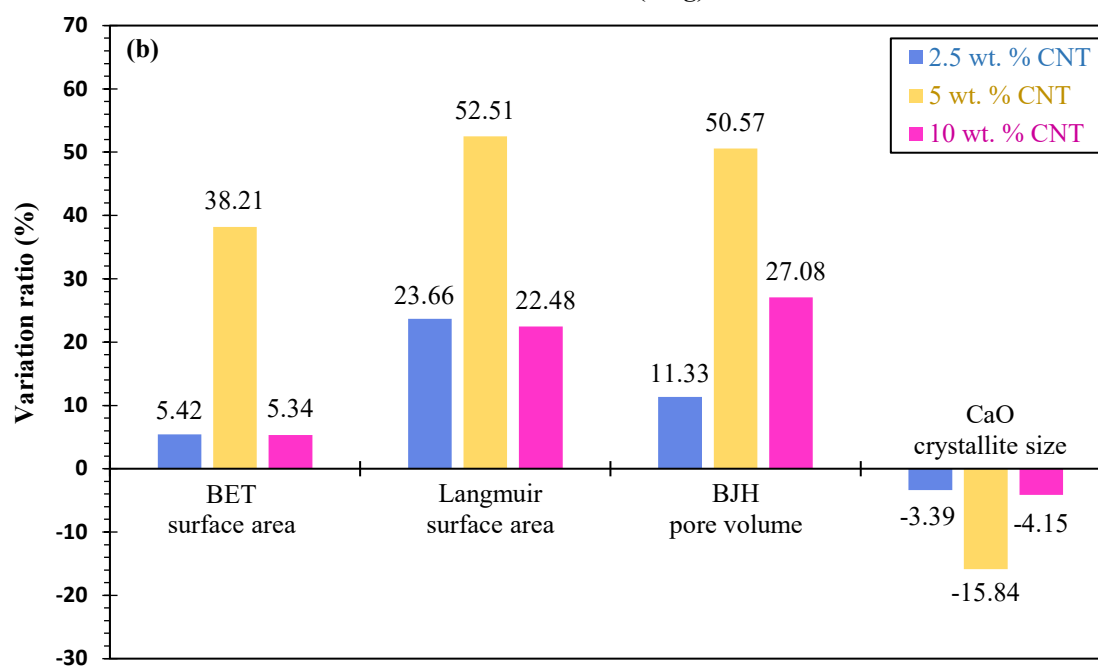
Table 2 lists the textural specifications, elemental analysis, inert materials weight 263
percentage (%), and CaO crystallite size of fresh and used adsorbents. It is worth noting that 264
the fresh and used adsorbents are referred to as adsorbents before and after passing 15 265
multiple cycles under realistic conditions in this study, respectively. There are the nominal 266
CaZrO₃ weight percentages of 81.5 and 90 wt.% for sorbents prepared with Ca/Zr molar 267
ratios of 15/1 and 30/1, respectively. To concede the preliminary considered Ca/Zr molar 268
ratios of 15/1 and 30/1 for synthesizing samples, Ca/Zr molar ratios calculated based on the 269
ICP results are presented in **Fig. S1a**, indicating the maximum error of $\leq 0.34\%$ with 270
stoichiometric outcomes. Consequently, the Ca/Zr molar ratios derived from ICP analysis 271
validate the initial molar ratios for all synthesized sorbents. Based on BET_{mean} and BJH pore 272
diameter results, it can be deduced that all prepared samples possess macro- and meso- and 273
micro-pores stemming from the combustion of embedded CNT and CaZrO₃ dispersal 274
between CaO nanoparticles. **Fig. 1a** exhibits that Langmuir surface areas and CaO crystallite 275
sizes are linearly and inversely proportional to the measured BET surface area of all 276
synthesized samples with correlation coefficients R^2 of 0.96 and 0.89, sequentially. 277

Additionally, **Fig. S1b** shows the linear proportion between BET pore volumes and BJH pore volumes for all synthesized CaO-based xerogels, validated with a correlation coefficient R^2 of 0.945. Incorporating CNT into CaO particles of CaZr15-C0 and CaZr30-C0 underlines increases in structural and textural features, including BET surface area and BJH pore volume, and reduction in CaO crystallite sizes. For samples with a 15/1 molar ratio of Ca/Zr, the highest, most BJH pore volume of 108.7 mm³/g, and the smallest CaO crystallite size of 22.3 nm are reported in the case of CaZr15-C5 followed by CaZr15-C10 (91.74 mm³/g and 25.4 nm), CaZr15-C2.5 (80.37 mm³/g and 25.6 nm), and CaZr15-C0 (72.19 mm³/g and 26.5 nm). Considering the morphological values of this cluster of sorbents, their BET and Langmuir surface area are in the order of CaZr15-C5 with 17.83 and 19.4 m²/g, CaZr15-C2.5 with 13.6 and 15.73 m²/g, CaZr15-C10 with 13.59 and 15.58 m²/g, and CaZr15-C0 with 12.9 and 12.73 m²/g, respectively. Among synthesized xerogels with a 30/1 molar ratio of Ca/Zr, CaZr30-C5 shows the highest BJH pore volume and the lowest CaO crystallite size value of 19.8 nm. The reported surface area amounts indicate that CaZr30-C5 possessed the most BET and Langmuir surface areas of 20.63 and 22.8 m²/g, respectively, followed by CaZr30-C10 with 16.75 and 18.6 m²/g, CaZr30-C2.5 with 13.4 and 14.84 m²/g, and CaZr30-C0 with 11.23 and 10.86 m²/g, respectively. As it is explicit for both clusters, the addition of MWCNT until 5 wt.% contributed to enhancing the surface area of Zr-promoted CaO, even though more than 5 wt.% MWCNT adversely affects the accessible surface-resident CaO area.

To numerically evaluate the effectiveness of CNT on textural and structural properties of CaZr15-C0 and CaZr30-C0, variation rates (%) in BET and Langmuir surface area, BJH pore volume, and CaO crystallite sizes by incorporating 2.5, 5, and 10 wt.% of CNT into CaZr15-C0 and CaZr30-C0 sorbents are illustrated in **Fig. 1b** and **c**, respectively. There are remarkable improvements in principal textural characteristics. The integration of 5 wt.% CNT into CaZr15-C0 results in 38.21, 52.51, and 50.57% increment in BET, Langmuir

surface area, and BJH pore volume quantities, respectively, and also a 15.84 % reduction in
CaO crystallite size. In addition to a 33.1% reduction in CaO crystallite size, by merging
CaZr30-C0 with 5 wt.% of CNT, BJH pore volume quantities, BET, and Langmuir surface
areas increase 90.55, 83.7, and 109.94%, respectively. Based on reported improvement rates,
it can be concluded that the combustion of embedded CNT into CaZr15-C0 and CaZr30-C0
forms higher volumes of pores and affects the distribution of durable Zr-based species, which
leads to dwindling the micro-size CaO agglomerates. However, the textural characteristics
drop by increasing the number of merged CNT contents from 5 wt.% to 10 wt.%. It can be
noted that this phenomenon probably arises from the heterogeneous dispersal of excess CNTs
into CaO texture between CaO NPs during the synthesis due to a larger volume of CNT
particles, resulting in the asymmetrical pore formation and heterogeneous scattering of
CaZrO₃ grains between CaO grains. With the MWCNT being increased from 5 wt.% to 10
wt.%, their particles formed bigger aggregates during the preparation, not completely
overcome by the stirring force, which adversely affects their embedding into CaO texture.
Accordingly, the macropore volume decreased in sorbent prepared with 10 wt.% MWCNT
compared to counterparts with 5 wt.% due to the non-uniform distribution of template
particles in the inner zone of CaO configuration. Additionally, the heterogeneous scattering
of CaZrO₃ aggravated the agglomeration of CaO particles, conducive to decreased surface
area and CaO crystallite sizes.

As a result, 5 wt.% can be considered the more suitable and optimum amount of CNT
compared to 10 wt.% to have the most porous CNT-templated Zr-modified adsorbent with
the best textural features, and increasing the MWCNT contents aggravate sorbents' porosity.



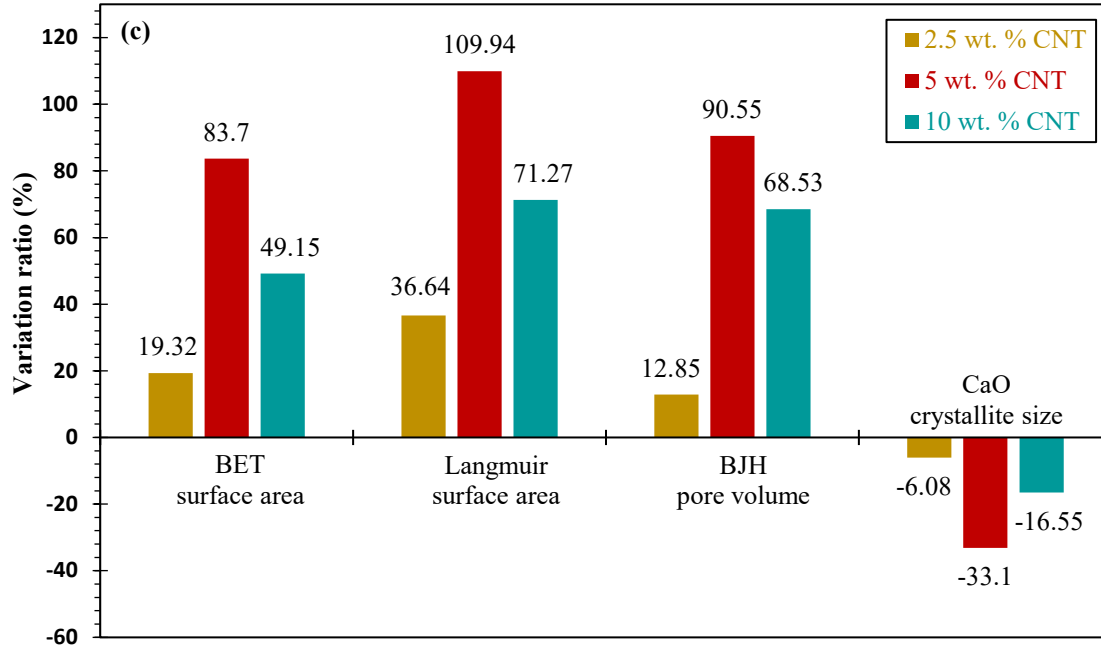


Fig. 1: (a) Langmuir surface area and CaO crystallite size of all developed Zr-decorated CaO-based xerogels versus BET surface area, and variation rate (%) of BET and Langmuir surface area, BJH pore volume, and CaO crystallite size by adding 2.5, 5, and 10 wt.% of CNT to (d) CaZr15-C0, and (e) CaZr30-C0.

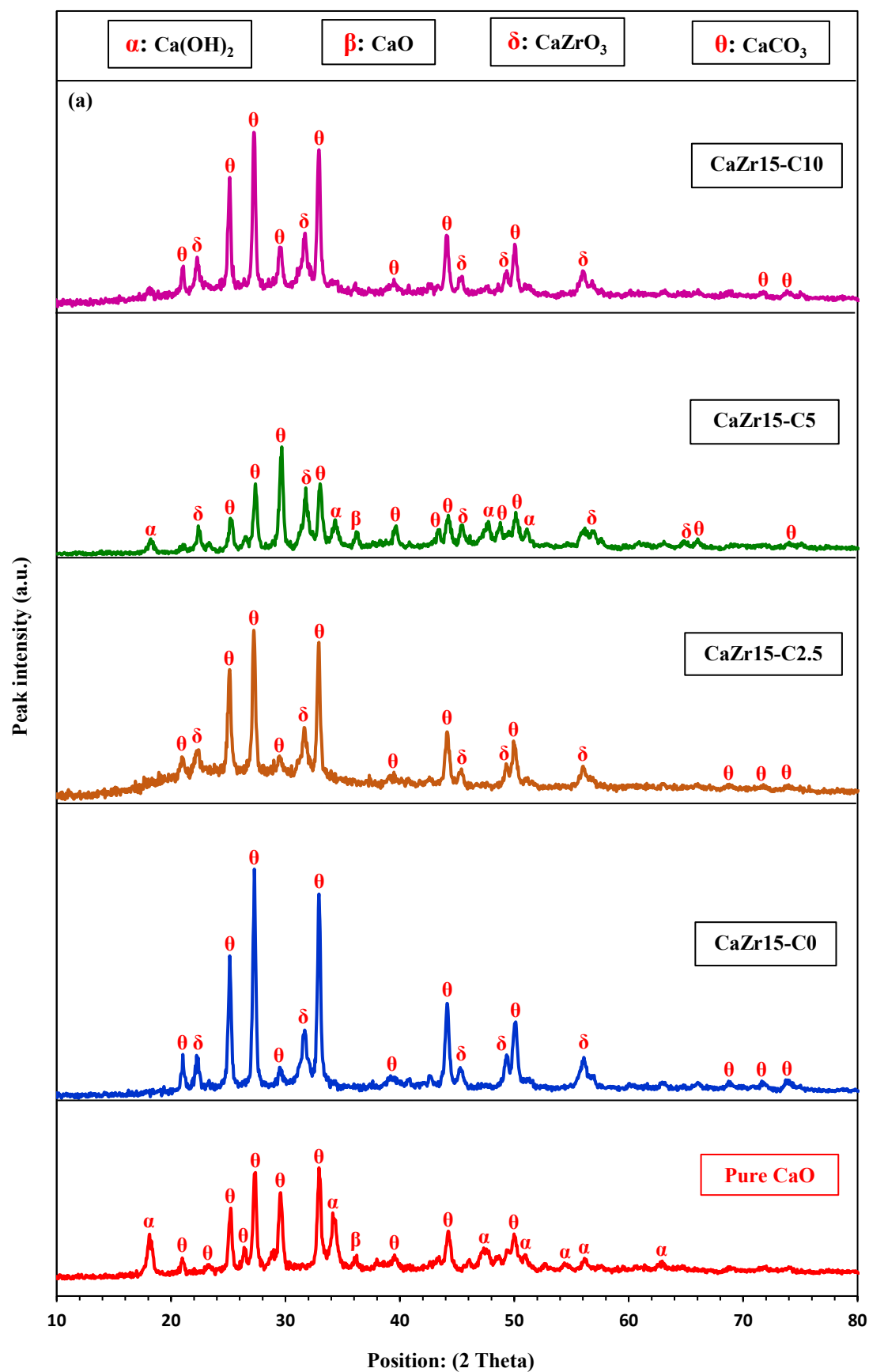
The X-ray diffraction patterns of pure CaO, CNT-templated Zr-supported CaO adsorbent with Ca/Zr molar ratios of 15/1 and 30/1 over $10^\circ \leq 2\theta \leq 80^\circ$ are depicted in Figs. 2a and b. CaCO_3 , Ca(OH)_2 , and CaZrO_3 are the identified crystalline phases with high peak intensity. Since the sol-gel-derived synthesized CaO-based samples possess hygroscopic nature, the ambient moisture and CO_2 during the cooling step of calcination are adsorbed by CaO particles, resulting in the development of Ca(OH)_2 and CaCO_3 components identified in XRD characterization, due to Eqs. 6 and 7 [29]. According to Eq. 7, CO_2 gas molecules are also adsorbed by interfaces of formed Ca(OH)_2 . CaCO_3 developed during post-calcination emerges in three diverse structures, β - CaCO_3 , calcite, μ - CaCO_3 , vaterite, and λ - CaCO_3 , aragonite. The diversity in the type of developed CaCO_3 is related to the different CO_2 adsorption temperatures and the various adsorbers, including CaO and Ca(OH)_2 . It is worth mentioning that the high-temperature pre-carbonation stage purges CaO particles from physisorbed CO_2 and/or H_2O molecules that facilitate CO_2 capture at the carbonation step.

The sol-gel combustion synthesis procedure readily develops a temperature of ≥ 1000 °C. As Eq. 8 shows, by diffusing Ca^{2+} into the ZrO_2 lattice, CaZrO_3 species are produced via a solid-state reaction between CaO and ZrO_2 , eased with the annealing phenomenon at the temperature above 1200 °C [28]. Comparing the XRD patterns reveals that CaZr15-C5 possesses CaZrO_3 peaks with lower intensity and wider broadening than CaZr15-C10 arising from the homogeneous distribution of CaZrO_3 crystallites between CaO particles.



There is considerable diversity between the XRD patterns of CaZr15-C5 and CaZr15-C10 . As it is apparent, in the case of CaZr15-C5 , the peaks related to CaO -based phases, namely CaO , Ca(OH)_2 , and CaCO_3 , possessed lower intensity and more broadening compared to CaZr15-C10 , indicating its smaller CaO grain size presented in **Table 2**. These patterns corroborate that the additional MWCNT, more than 5 wt.%, adversely influences the porosity of CaO texture, resulting in a bigger CaO crystallite size due to the heterogeneous dispersal of 10 wt.% CNT particles into CaO texture during the preparation. It can be stated that this trend for sorbents containing 5 and 10 wt.% CNT is partially observed for samples prepared with a Ca/Zr molar ratio of 30/1. On the other hand, Comparing the XRD patterns of CaZr30-C2.5 and CaZr30-C5 indicates that CaZr30-C5 presented the CaO -presenting peaks with lower intensity and more transverse width than those of CaZr15-C2.5 . This phenomenon demonstrates the higher porosity, smaller CaO crystallite size, and decreased CaO agglomerates growth in CaZr30-C5 compared to CaZr30-C2.5 , corroborating the highly efficient content of 5 wt.% CNT for both kinds of Zr-promoted CaO adsorbents.

Fig. 3 exhibits N_2 adsorption/desorption isotherms for all synthesized samples. All adsorbents illustrate similar trends classified as reversible type II isotherms, which generally demonstrate a macro-porous texture and unlimited monolayer-multilayer adsorption up to high P/P_0 [61]. With an increase in the P/P_0 , monolayer adsorption is completed, and the multilayer adsorption commences on the inner surface, an indicator of mesoporous structure [62, 63]. Derived by the capillary condensation of N_2 molecules into multilayers of mesoporous structure in the P/P_0 varied between the high pressure of 0.8-1, isotherms of CNT-templated sorbents possess the hysteresis loop type of H3, non-rigid aggregates of plate-like particles associated with slit-shaped pores. The abovementioned hysteresis type II isotherm consists of a network of meso and macropores, completely unfilled through pores' condensate. The higher amount of N_2 was adsorbed by CaZr15-C5 and CaZr30-C5 among prepared xerogels with 15/1 and 30/1 molar ratios of Ca/Zr, respectively. It can be concluded that both sorbents, CaZr15-C5 and CaZr30-C5, possess high multilayer adsorption, indicative of structures containing a higher volume of meso and macropores [64-67].



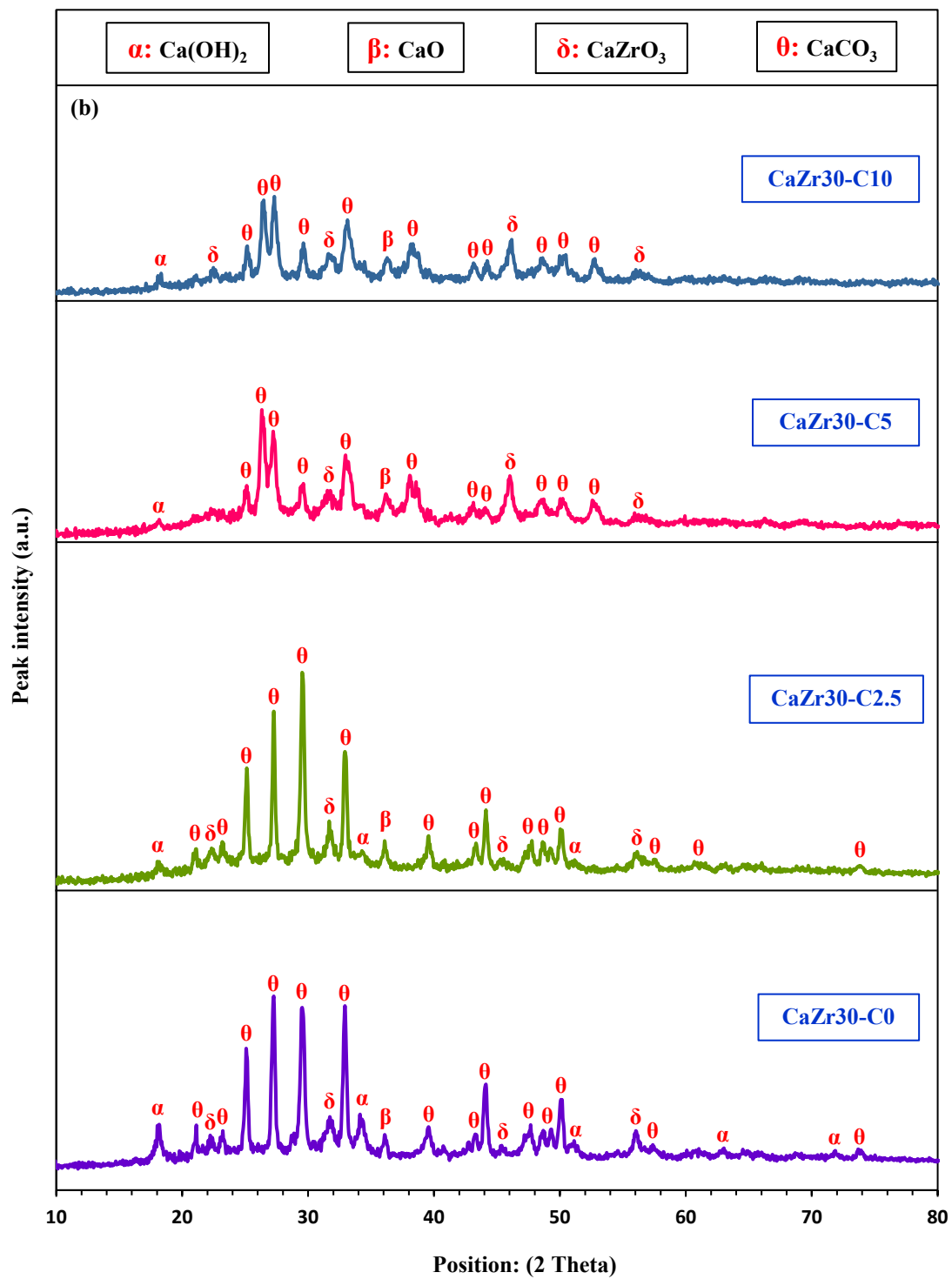


Fig. 2: XRD patterns of (a) pure CaO, CaZr15-C0, CaZr15-C2.5, CaZr15-C5, and CaZr15-C10, and (b) CaZr30-C0, CaZr30-C2.5, CaZr30-C5, and CaZr30-C10.

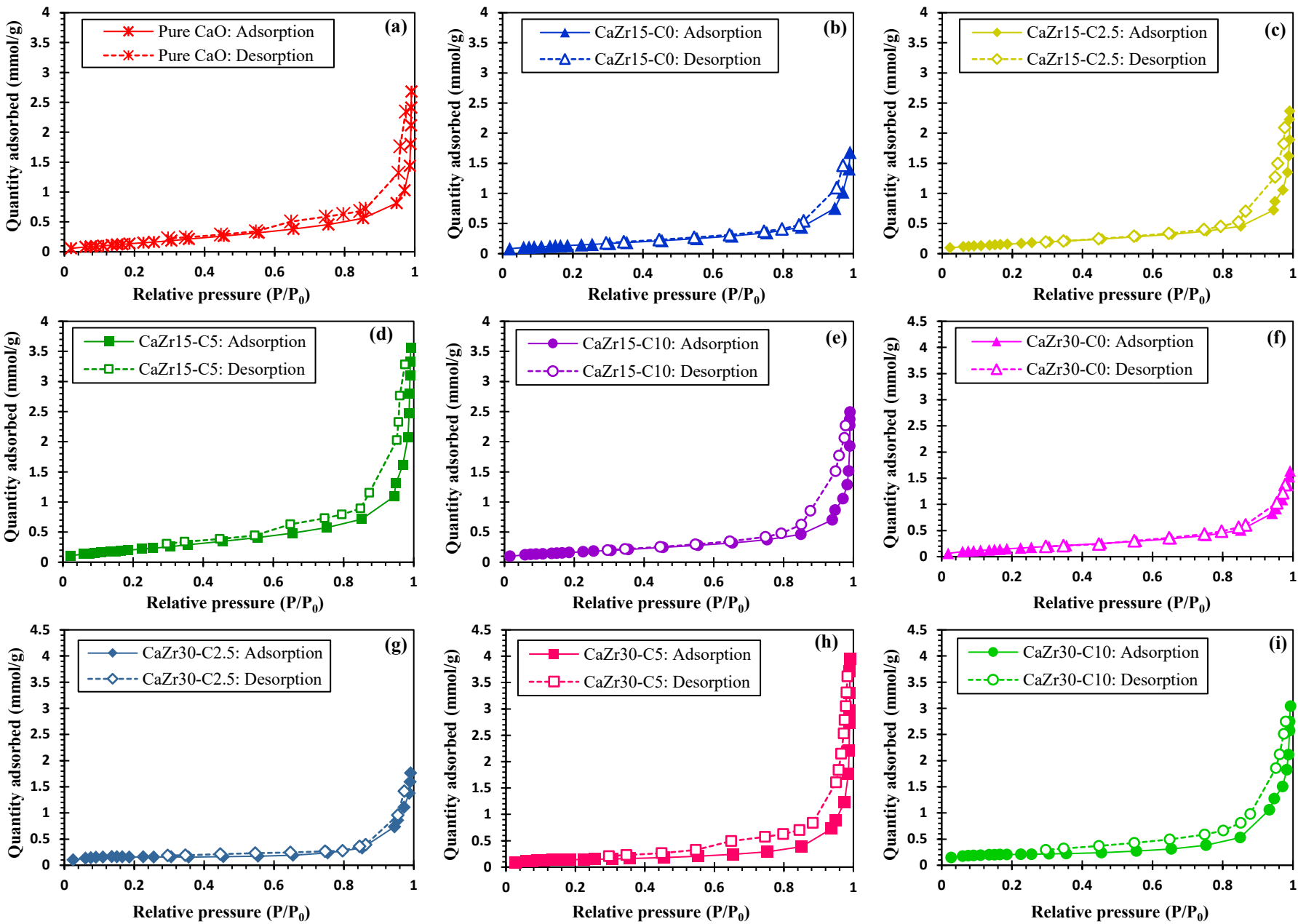


Fig. 3: N₂ adsorption/desorption isotherm of (a) pure CaO, (b) CaZr15-C0, (c) CaZr15-C2.5, (d) CaZr15-C5, (e) CaZr15-C10, (f) CaZr30-C0, (g) CaZr30-C2.5, (h) CaZr30-C5, and (i) CaZr30-C10.

BJH pore size distributions of pure CaO and both clusters of xerogels, prepared with 15/1 and 30/1 molar ratios of Ca/Zr, are presented in **Fig. 4a** and **b**. Even though pure CaO and prepared sorbents with Ca/Zr molar ratios of 15/1 mainly possess broad distribution of micropores, which have pores' diameters of 1-2 nm, the heterogeneous dispersal of pores is apparent for sorbents with a 30/1 molar ratio of Ca/Zr. As shown in **Fig. 4a**, **Fig. 1a**, and **Table 2**, the larger volume of micropores in the texture of CNT-templated samples indicates the effect of CNTs on increasing the pore volume into CaO configuration. Among exhibited BJH curves in **Fig. 4a**, CaZr15-C5 possesses a more significant amount of micropores, mesopores, and macropores. In addition to the effect of CNT removal on the formation of pores, the presence of an adequate amount of CNT during the sorbents' synthesis modify the dispersal of CaZrO₃; however, extra content of CNTs can underline the non-uniform scattering of CNTs and CaZrO₃ species into CaO structure, leading to a drastic reduction in pore volume and the formation of meso- and macro-pores. On the other hand, **Fig. 5b** demonstrates that incorporating 5 and 10 wt.% of CNT into CaZr30-C0 increases the volume of mesopores and micropores, respectively. A larger volume of macropores with a pore diameter of ≥ 80 nm is developed than CaZr30-C0. The significant differences in the type of formed pores in the cases of CaZr30-C5 and CaZr30-C10 can be attributed to the dispersal of CNTs into CaO structure during synthesis, which influences the distribution of formed CaZrO₃. It can be deduced that with the addition of the optimum amount of CNT, 5 wt.%, the formation of micro-, meso- and macro-pores enhanced, which shows its more porosity compared to CaZr15-C0 and CaZr30-C0. Among prepared xerogels with Ca/Zr molar ratios of 15/1 and 30/1, CaZr15-C5 and CaZr30-C5 possess the highest pore volume quantities.

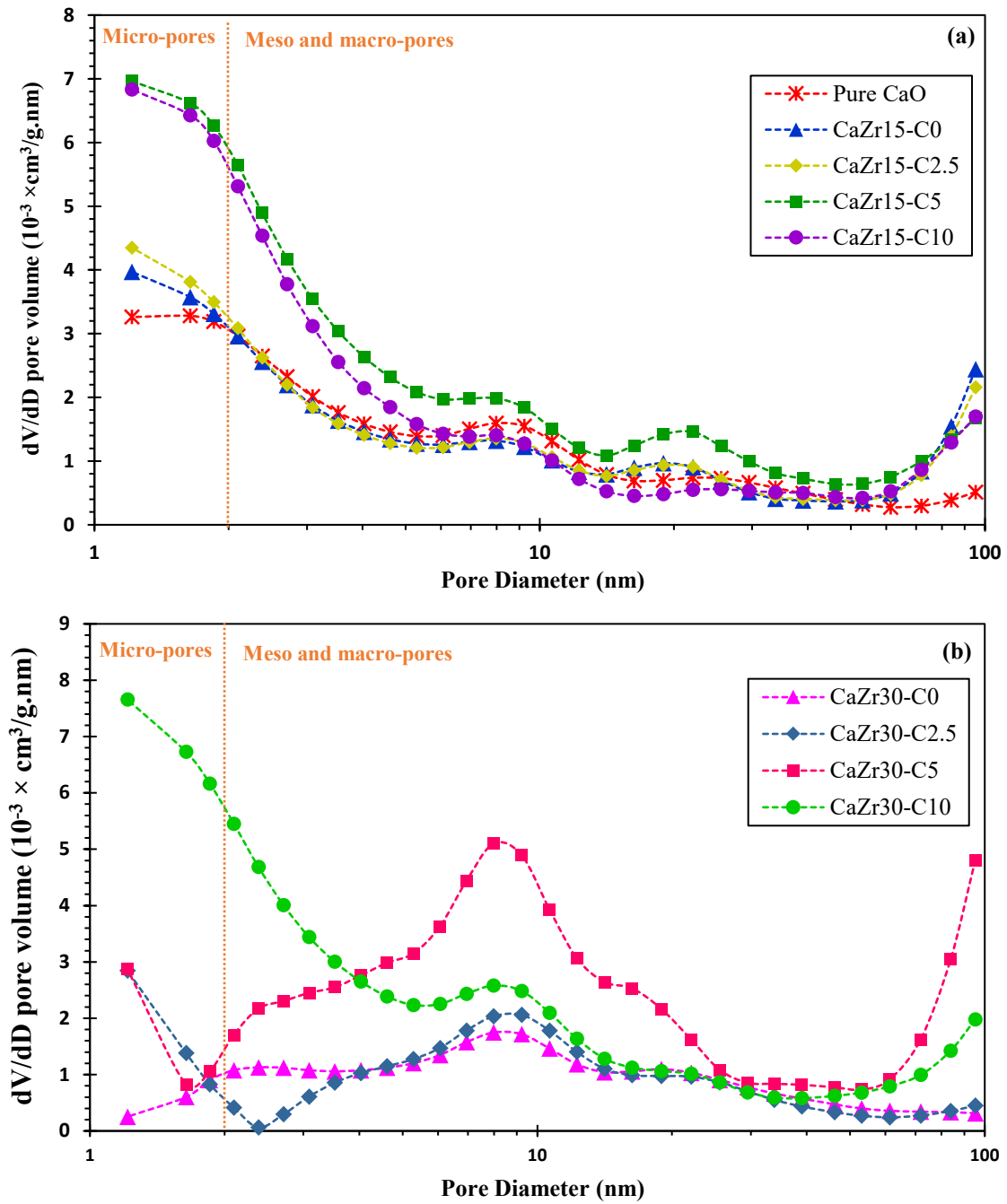
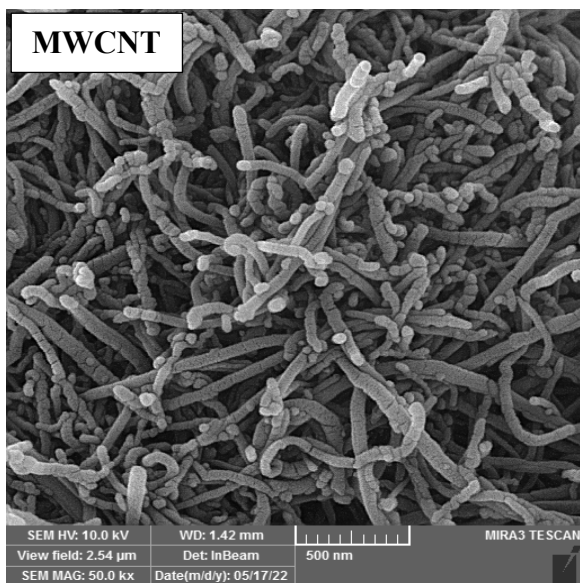
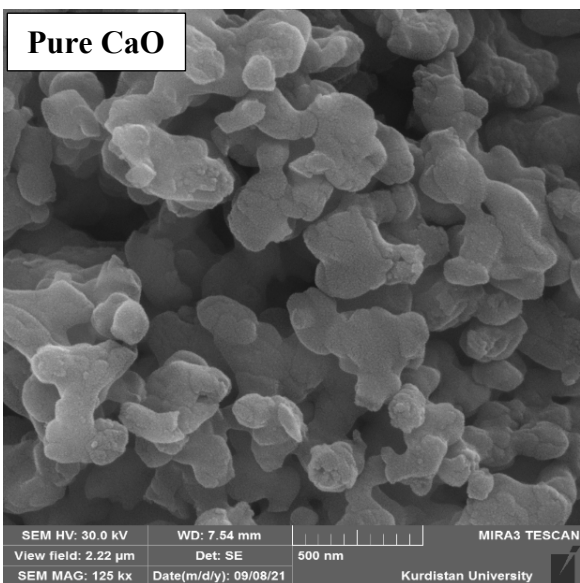
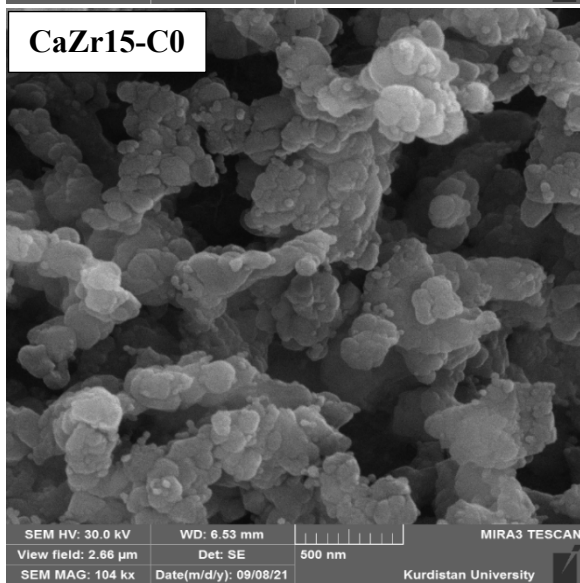
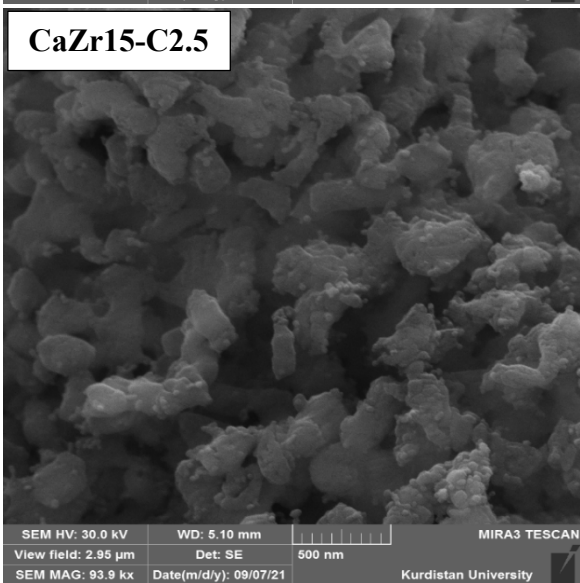
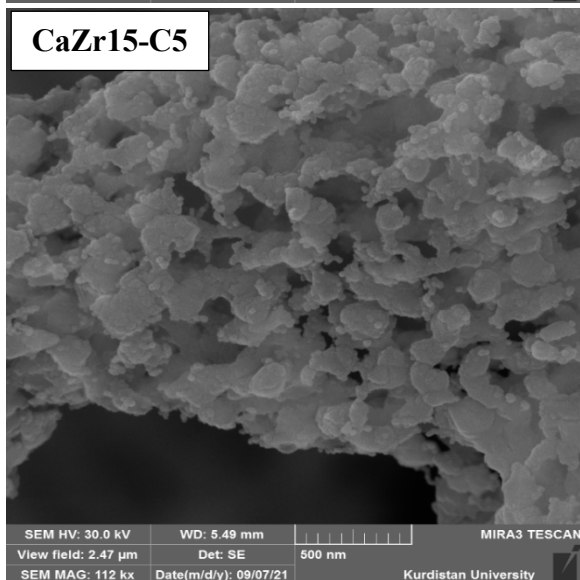
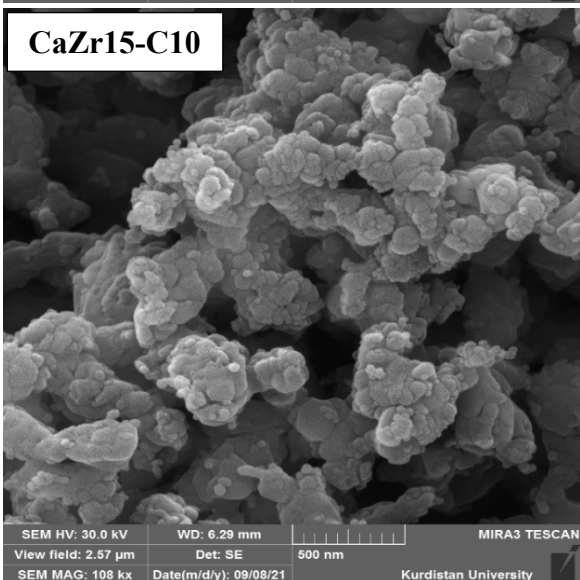


Fig. 4: Pore size distribution curves for (a) pure CaO, CaZr15-C0, CaZr15-C2.5, CaZr15-C5, and CaZr15-C10, and (b) CaZr30-C0, CaZr30-C2.5, CaZr30-C5, and CaZr30-C10.

FESEM images and EDX spectra of MWCNT and all developed samples with Ca-Zr molar ratios of 15/1 and 30/1 are illustrated in **Fig. 5** and **Fig. S2**. The EDX diagrams of Zr-promoted adsorbents in **Fig. S2** reveal the appearance of Zr, Ca, O, and C. The representative SEM pictures of MWCNT corroborate the tubular structure and its size and length nanometer scale. Pure CaO shows the clumpy structure and compact surface associated with the

residence of Ca, O, and C elements on the sorbent's surface. According to optical observation 422
on SEM images of CaZr15-C0 and CaZr30-C0, the formation of CaZrO₃ moderately 423
decreases CaO surface-present particle size and CaO micro-agglomerates. Comparing four 424
prepared sorbents with a Ca/Zr molar ratio of 15/1, the porosity and the formation of fluffy 425
zones are significantly improved by merging with CNT. The development of Zr-stabilized 426
CaO adsorbents modified with 5 wt.% CNTs form the hollowest structure, associated with 427
the smallest CaO surface-particles size. The most uniform scattering of CaZrO₃ among CaO 428
particles in CaZr15-C5 is the main reason for its superior textural and morphological 429
properties confirmed with BET-BJH and SEM illustrations. In the cases of prepared xerogels 430
with a Ca/Zr molar ratio of 30/1, the efficient role of embedded CNT is manifest in presented 431
SEM images. Identical to CaZr15-C0, with the addition of CNT, the CaO surface-resident 432
grain size and agglomerates decrease, which underlies the emergence of fluffy areas. Among 433
this cluster of sorbents, CaZr30-C5 presents more porosity. High conformity between 434
reported textural and morphological characterizations in **Table 2** and depicted FESEM 435
pictures can be observed. In addition to textural properties, namely BET surface area and 436
BJH pore volume distribution, the morphology of CaZr15-C5 and CaZr30-C5 consist of more 437
porous zones and smaller CaO surface-occupant sizes. Similarly, the representative FESEM 438
pictures infer the efficient role of CNT in morphological properties of CaO particles and 439
reducing the surface-resident CaO agglomerates. 440

Based on reported Ca/Zr mol.% of ~ 15 in **Fig. 1a**, the appearance of CaZrO₃ in the XRD 441
patterns depicted in **Fig. 2**, and the elemental identification of Zr element via EDS spectra for 442
developed Zr-modified adsorbents, it can be acclaimed that the employed synthesise method 443
was suitable to develop the required adsorbents. 444



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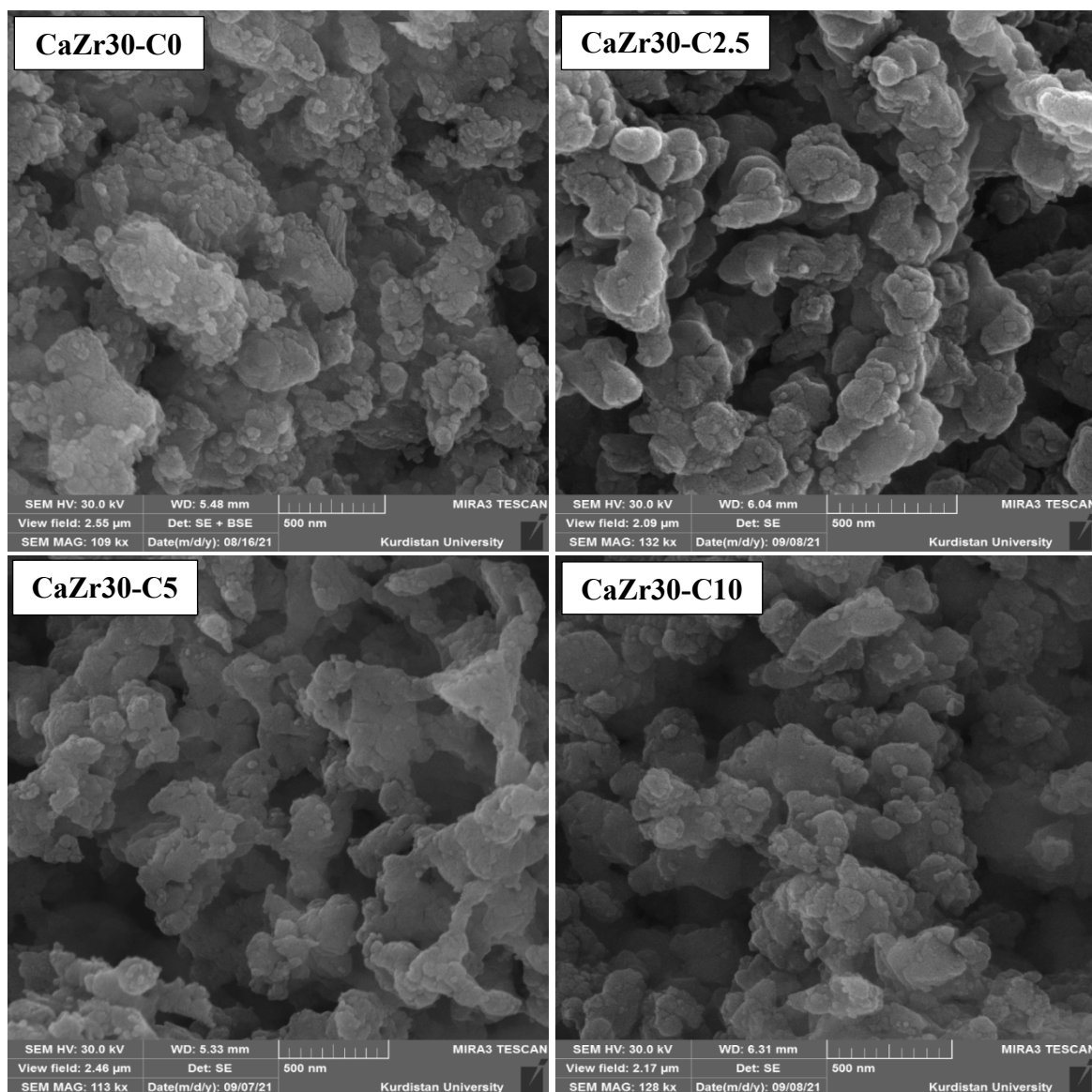


Fig. 5: SEM images of pure CaO, CaZr15-C0, CaZr15-C2.5, CaZr15-C5, CaZr15-C10, CaZr30-C0, CaZr30-C2.5, CaZr30-C5, and CaZr30-C10.

3.2. CO₂ capture activity

CO₂ capture activity of all synthesized sorbents to assess the influence of CNTs was analyzed under severe CaL conditions. CO₂ capture activity is evaluated by CO₂ capture capacity and CaO conversion curves versus the number of cycles.

The CO₂ uptake capacity and rate over carbonation time at 1st and 15 cycles for samples developed with Ca/Zr molar ratios of 15/1 and 30/1 are depicted in **Fig. S3** and **Fig. S4**, respectively, and discussions are included in **the supporting information file**. CO₂ adsorption capacity and CaO conversion values of untreated CaO and nano-scale xerogels

synthesized with Ca/Zr molar ratio of 15/1 over 15 multiple carbonation/calcination cycles
 under severe CaL conditions are depicted in **Fig. 6a** and **b**, respectively. Although the higher
 initial CO₂ capture capacity belongs to pure CaO, Zr-supported samples demonstrate superior
 CO₂ uptake capacity and CaO conversion. Improved with the homogeneous dispersion of
 CaZrO₃ and more formation of fluffy zones stemming from the combustion of embedded
 CNT, the CO₂ capture activity of CaZr15-C0 is enhanced in the presence of CNT.
 Furthermore, incorporating diverse contents of CNT into CaZr15-C0 significantly diminished
 the deactivation. Conformed with superior morphological and textural characteristics,
 CaZr15-C5 exhibits the highest CO₂ capture capacity and CaO conversion among CNT-
 templated samples. The CO₂ capture activity of all synthesized samples is listed in **Table 3**.
 The highest ultimate CO₂ capture capacity of 0.16 g CO₂/ g sorbent, most CaO conversion of
 25.64 %, and the lowest uptake deactivation of 39.48 % belong to CaZr15-C5. Increasing the
 content of CNT from 5 to 10 wt.% aggregates cyclic activity due to the heterogeneous
 scattering of CNTs in the case of CaZr15-C10. Total amount of captured CO₂ during 15
 multiple carbonation/calcination cycles is in order of CaZr15-C5 (2.92 g CO₂/ g sorbent) >
 CaZr15-C2.5 (2.62 g CO₂/ g sorbent) > CaZr15-C10 (2.56 g CO₂/ g sorbent) > CaZr15-C0
 (2.01 g CO₂/ g sorbent). CaO conversion diagrams indicate the effectiveness of CNT on
 raising accessible CaO sites subjected to CO₂ molecules, in accordance with better
 morphological and textural properties of CNT-incorporated adsorbents. It is worth
 concluding that the 5 wt.% of CNT additive is the optimal amount for Zr-modified CaO
 sorbents.

CO₂ capture capacity values and calculated the CaO conversion amounts of untreated
 CaO, CaZr30-C0, CaZr30-C2.5, CaZr30-C5, and CaZr30-C10 over 15 CaL cycles under
 harsh conditions are plotted in **Fig. 6c** and **d**, sequentially. The CNT-merged samples
 demonstrate higher CO₂ uptake capacity and CaO conversion compared to CaZr30-C0, and

the superior performance belongs to CaZr30-C5, so a higher amount of CO₂ is captured by 485
CaZr30-C5 in most cycles. Even though the analogous activity is presented by CaZr30-C5 486
and CaZr30-C10, due to less amount of employed CNT in CaZr30-C5, 5 wt.% CNT can be 487
considered the optimum content to improve the cyclic activity of CaZr30-C0. The precise 488
total amounts of captured CO₂ are in the order of CaZr30-C5 (3.01 g CO₂/g sorbent) > 489
CaZr30-C10 (2.99 g CO₂/g sorbent) > CaZr30-C2.5 (2.13 g CO₂/g sorbent) > CaZr30-C0 490
(1.96 g CO₂/g sorbent). 491

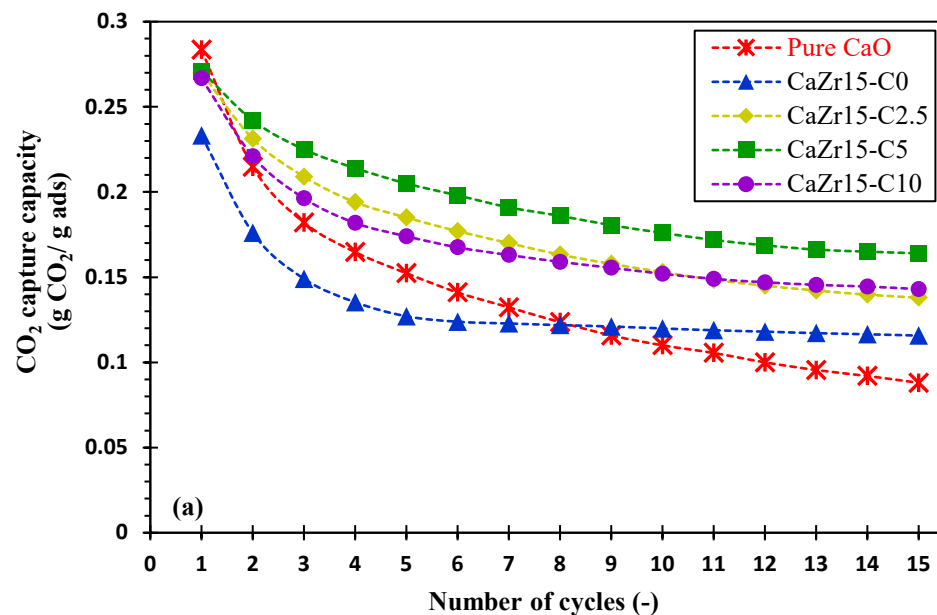
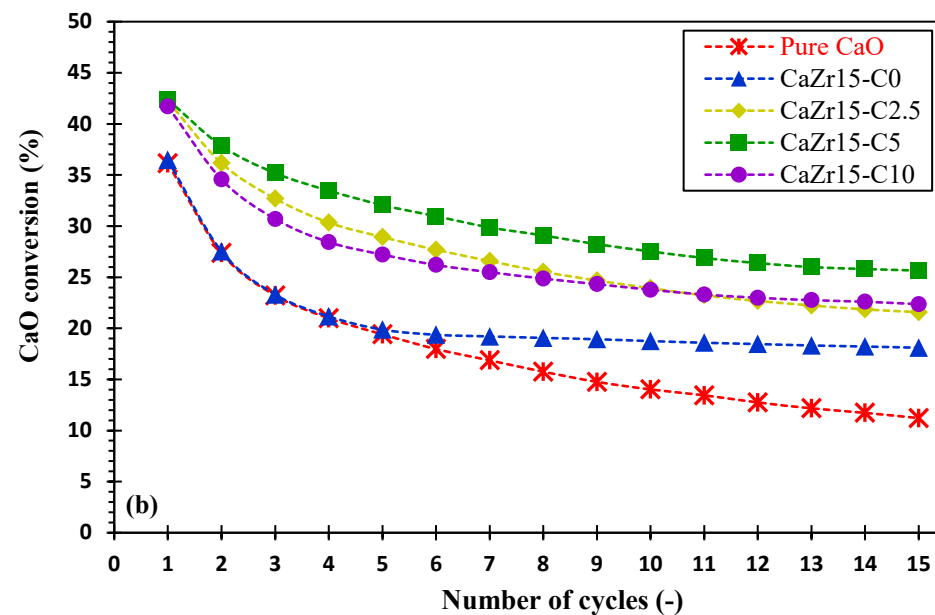
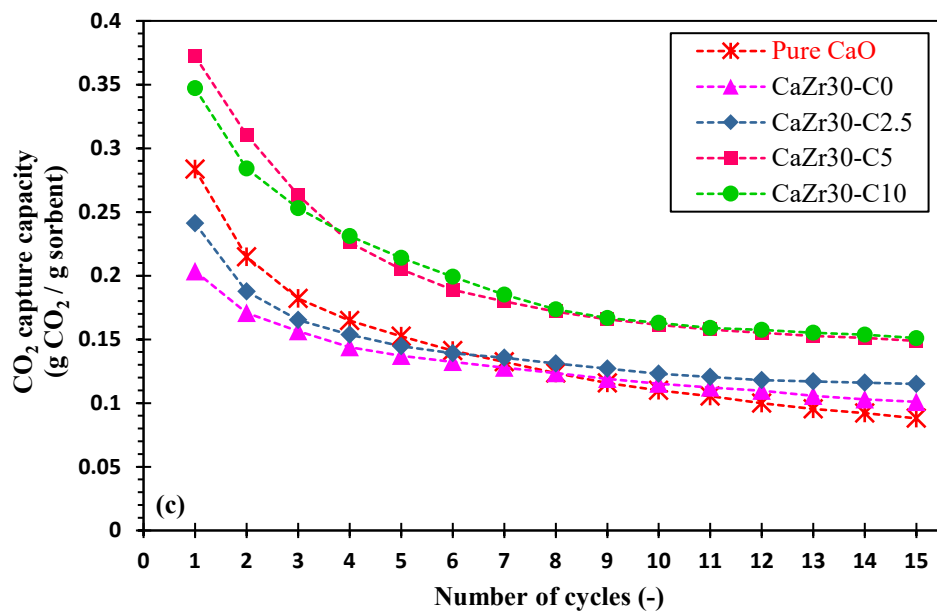
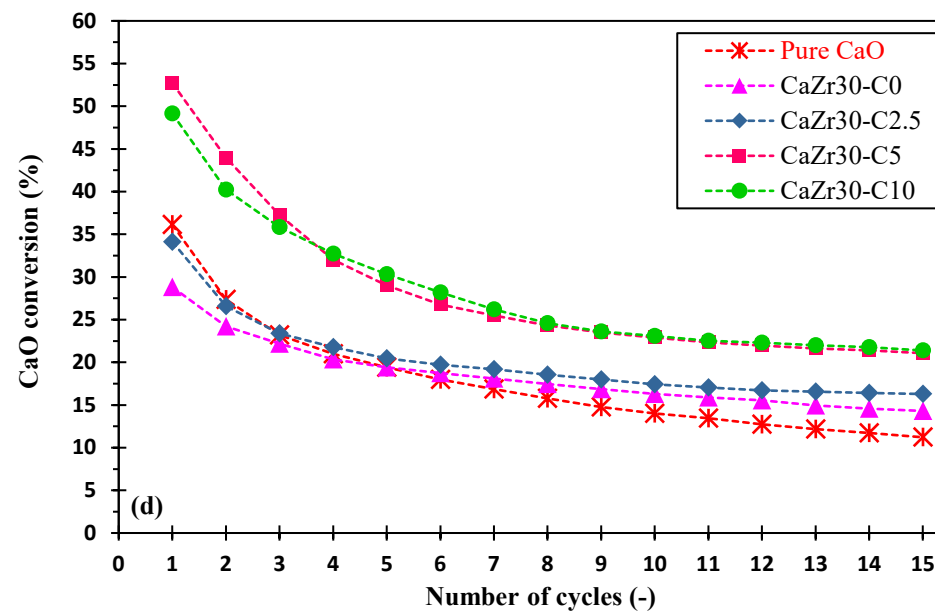


Fig. 6: CO₂ capture capacity and CaO conversion of samples developed with Ca/Zr molar ratios of (a and b, respectively) 15/1, and (c and d, respectively) 30/1, under severe CaL conditions

Table 3: Comparison of the CO₂ uptake activity of all developed sorbents

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Sorbent	CO ₂ capture capacity (g CO ₂ / g sorbent)		CaO conversion (%)		The total amount of captured CO ₂ (g CO ₂ /g sorbent) over 15 multiple cycles	Deactivation (%)
	1 st cycle	15 th cycle	1 st cycle	15 th cycle		
Pure CaO	0.2835	0.088	36.13	11.21	2.1	31.04
Ca/Zr molar ratio of 15/1						
CaZr15-C0	0.2332	0.1157	36.46	18.1	2.01	50.37
CaZr15-C2.5	0.27	0.138	42.22	21.58	2.62	48.88
CaZr15-C5	0.271	0.164	42.37	25.64	2.92	39.48
CaZr15-C10	0.2667	0.143	41.7	22.36	2.56	46.38
Ca/Zr molar ratio of 30/1						
CaZr30-C0	0.2035	0.101	28.81	14.3	1.96	50.38
CaZr30-C2.5	0.241	0.115	34.12	16.28	2.13	52.28
CaZr30-C5	0.372	0.149	52.71	21.07	3.01	60.02
CaZr30-C10	0.347	0.151	49.14	21.38	2.99	56.48

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EDX dot-mappings of Ca and Zr elements occupied on the surface of CaZr15-C5 and CaZr15-C10 are illustrated in **Fig. 7**, which corroborates the more homogeneous dispersal of CaZrO₃ between CaO particles for CaZr15-C5. However, CaZr5-C10 possesses the clumpy scattering of Zr in some zones during the sorbent preparation. Despite the efficient role of CNT in increasing the fluffy areas and porosity, excessive addition of CNT, more than 5 wt.%, underlies the substantial decrease in CO₂ capture capacity and deterioration of the textural and structural characteristics, namely pore volume distribution and value, surface area, and CaO crystallite size. There is a highly remarkable correlation between EDX dot-mapping analyses and XRD patterns of CaZr15-C5 and CaZr15-C10. The CaZr15-C5 that

shows the CaZrO_3 peaks with slightly lower intensity and wider broadening has a more homogeneous CaZrO_3 dispersal than CaZr15-C10.

In order to investigate the morphological changes in CaZr15-C5 and CaZr15-C10 occurring during 15 multiple carbonation/calcination cycles under severe conditions, SEM pictures of used abovementioned samples are presented in **Fig. 8**, apparently revealing the sintering phenomenon in several areas. By comparing the SEM micrographs of fresh and used CaZr15-C5 and CaZr15-C10, larger CaO grains and CaO micro-agglomerates emanate after 15 multiple cycles leading to the significant reduction in free and accessible CaO particles for CO_2 adsorption and the limitation for the CO_2 diffusion into inner areas. The aforementioned mishaps are the central grounds for the sorption deactivation over the CaL process. There is a striking conformity between SEM micrographs and the ultimate CO_2 capture capacity of CaZr15-C5 and CaZr15-C10, in which used CaZr15-C5 captured a higher amount of CO_2 at the 15th cycle possesses the lower sintered areas and more porous structure compared to used CaZr15-C10.

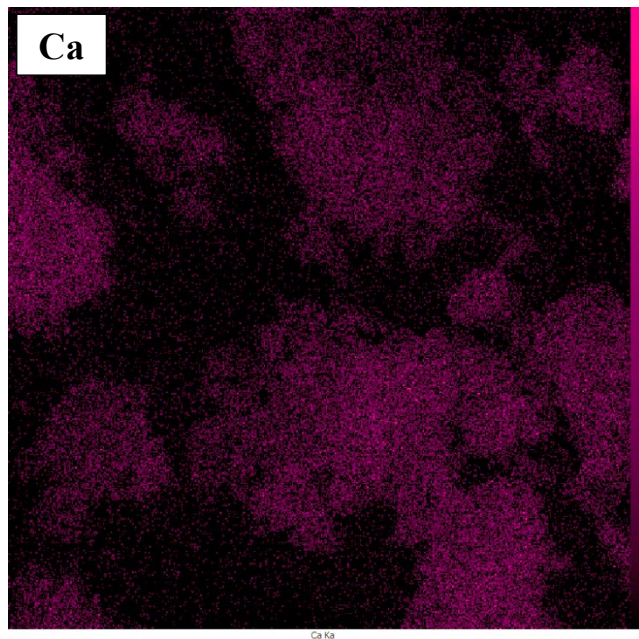
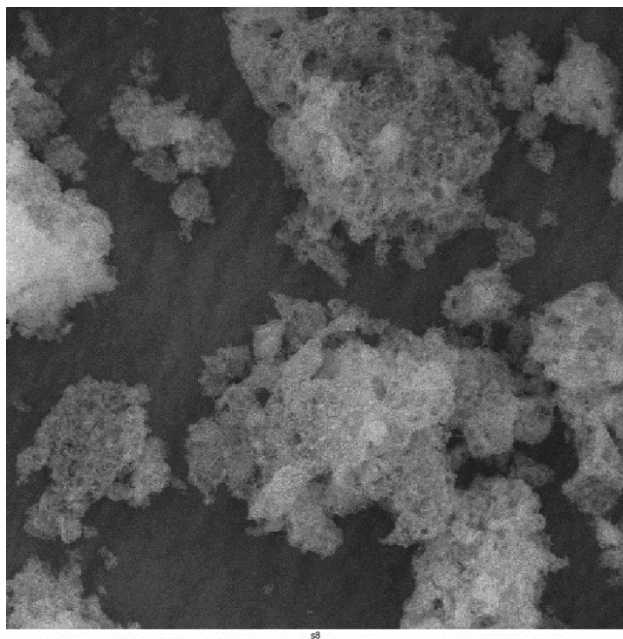
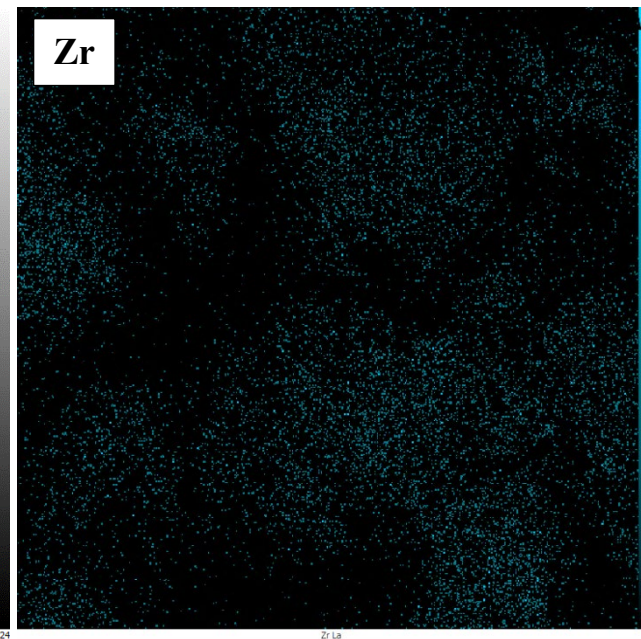
BET surface area of the used CaZr15-C0, CaZr15-C2.5, CaZr15-C5, and CaZr15-C10 are reported in **Table 2**. This enhancement in ultimate surface area value is acquired with the addition of MWCNT. The surface area values of 12.9, 13.6, 17.83, and 13.59 m^2/g , recorded for fresh CaZr15-C0, CaZr15-C2.5, CaZr15-C5, and CaZr15-C10, reduced to 3.23, 4.64, 6.48, and 5.47 m^2/g , stemming from the CaO agglomeration during the CaL process. Following the SEM images and ultimate sorption capacity (at the 15th cycle), used CaZr15-C5 that presented better porosity and higher ultimate sorption capacity has more BET surface area of 6.48 m^2/g among developed samples with a Ca/Zr molar ratio of 15/1. As a result, the SEM images and BET surface area values corroborate the superior sorption performance of CaZr15-C5 compared to CaZr15-C0, CaZr15-C2.5, and CaZr15-C10.

Fig. 7 also shows the EDX dot. mapping of Ca and Zr for fresh CaZr30-C5 and CaZr30-C10. The widely distributed Zr element, related to the scattering of CaZrO₃ species between Ca, is visible. It should be noted that the dispersion of inert phases considerably affects the materials' porosity, thermal durability and agglomeration [68-70]. These diagrams confirm the more uniform dispersal of CaO and CaZrO₃ for CaZr30-C5 and CaZr30-C10, apparently indicative of morphological improvement using CNTs. There are no significant differences in Zr scattering between CaZr30-C5 and CaZr30-C10. Based on visual morphological observations, 5 wt.% of CNT is sufficient to homogenize the CaZrO₃ dispersion among CaO grains.

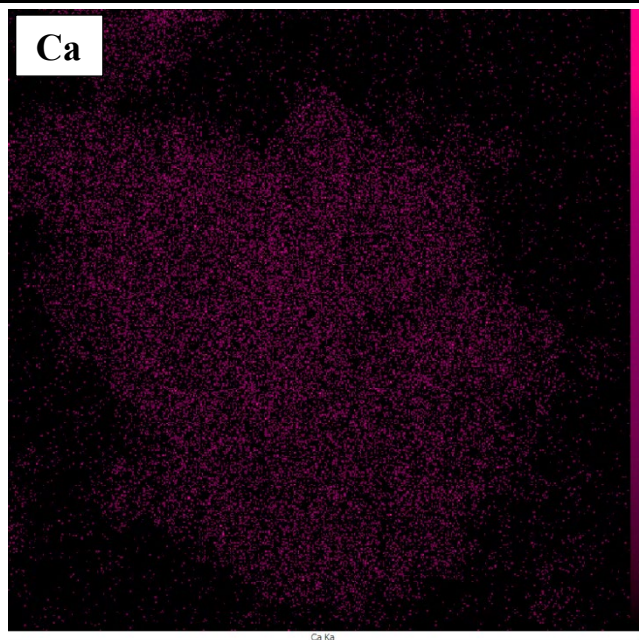
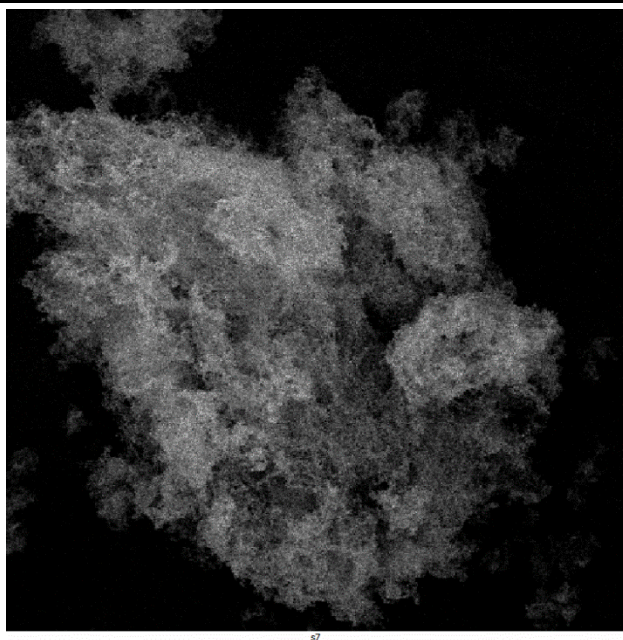
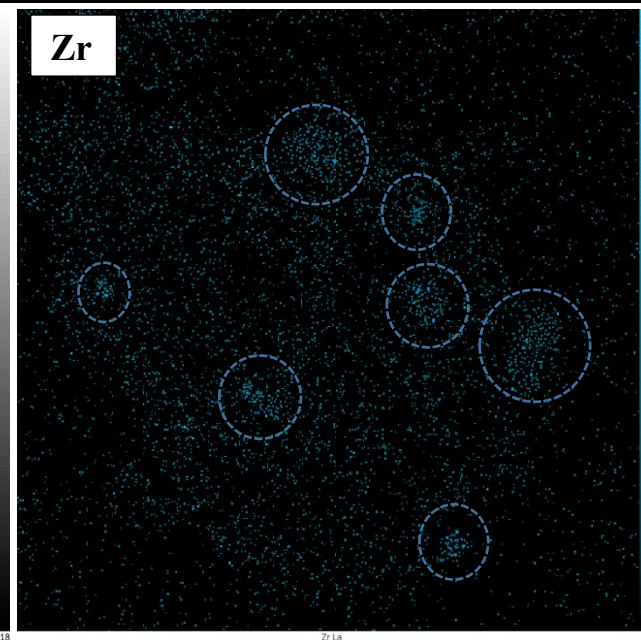
FESEM pictures of used CaZr30-C5 and CaZr30-C10 over 15 multiple CaL cycles under severe conditions are presented in **Fig. 8**. The formation of sintered CaO sites, enlarging CaO grain size. The aggregation of surface-located CaO particles is evident in the sorption deactivation of CaZr30-C5 and CaZr30-C10 over multiple CaL cycles because of developing sintering-favored CaCO₃ layers during the process. Comparing the depicted SEM images of fresh CaZr30-C5 and CaZr30-C10 with used counterparts demonstrates that fluffy-like zones, the volume of pores, and accessible CaO particles gradually decline over the multicycle process.

Reported BET surface area values for used MWCNT-incorporated sorbents with the Ca/Zr molar ratio of 30/1 in **Table 2** indicates the significant decrement in surface area values after passing 15 multiple CaL cycles under harsh condition. These surface area values verified the calculated ultimate sorption capacity for CaZr30-C0, CaZr30-C2.5, CaZr30-C5, and CaZr30-C10; CaZr30-C10 with the highest capture capacity at 15th cycles, 0.151 g CO₂/ g sorbent, possess the most surface area of 5.58 m²/g.

Fresh CaZr15-C5



Fresh CaZr15-C10



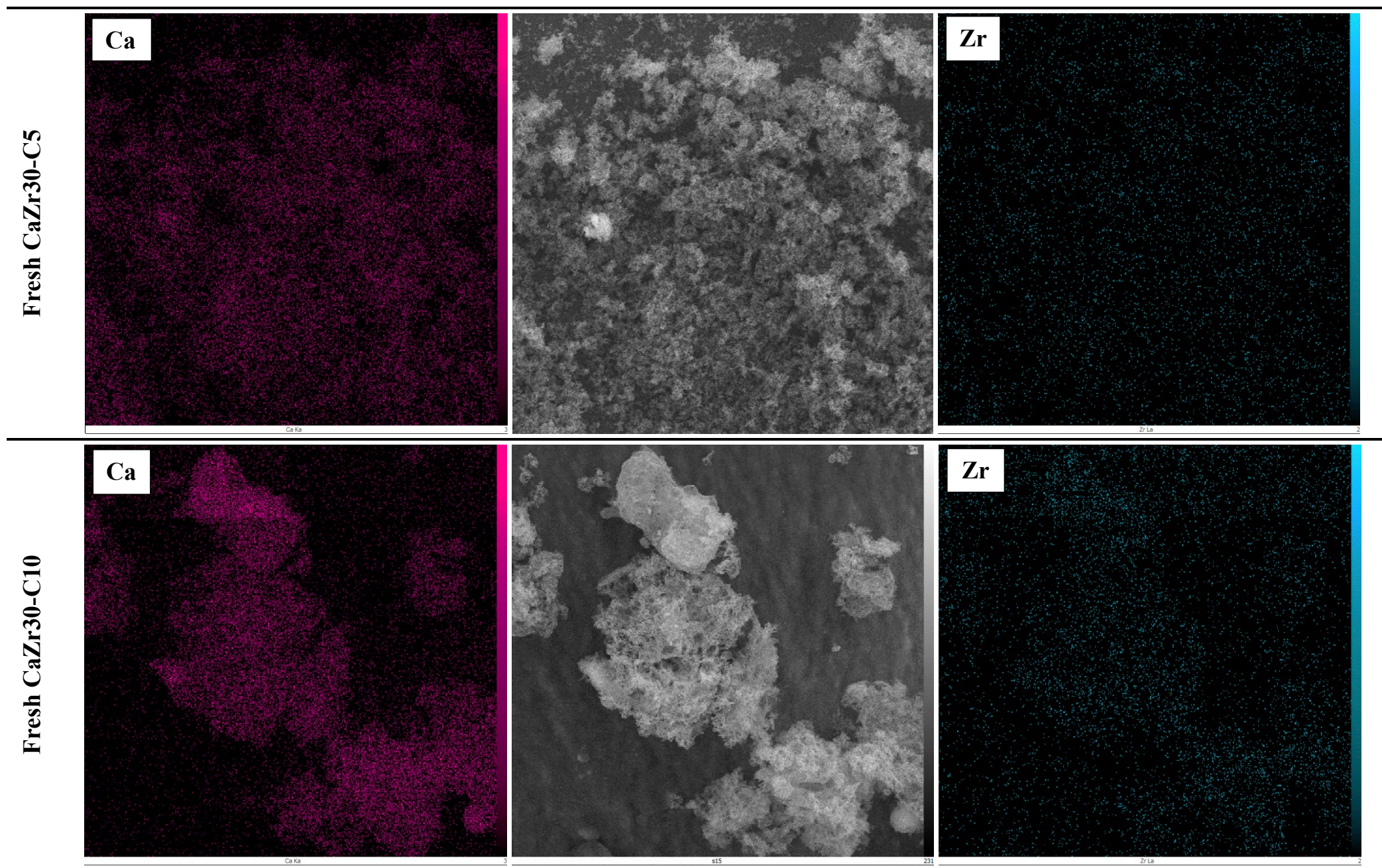


Fig. 7: EDX dot-mapping analysis of the distributed Ca and Zr elements into the textures of fresh CaZr15-C5, CaZr15-C10, CaZr30-C5, and CaZr30-C10

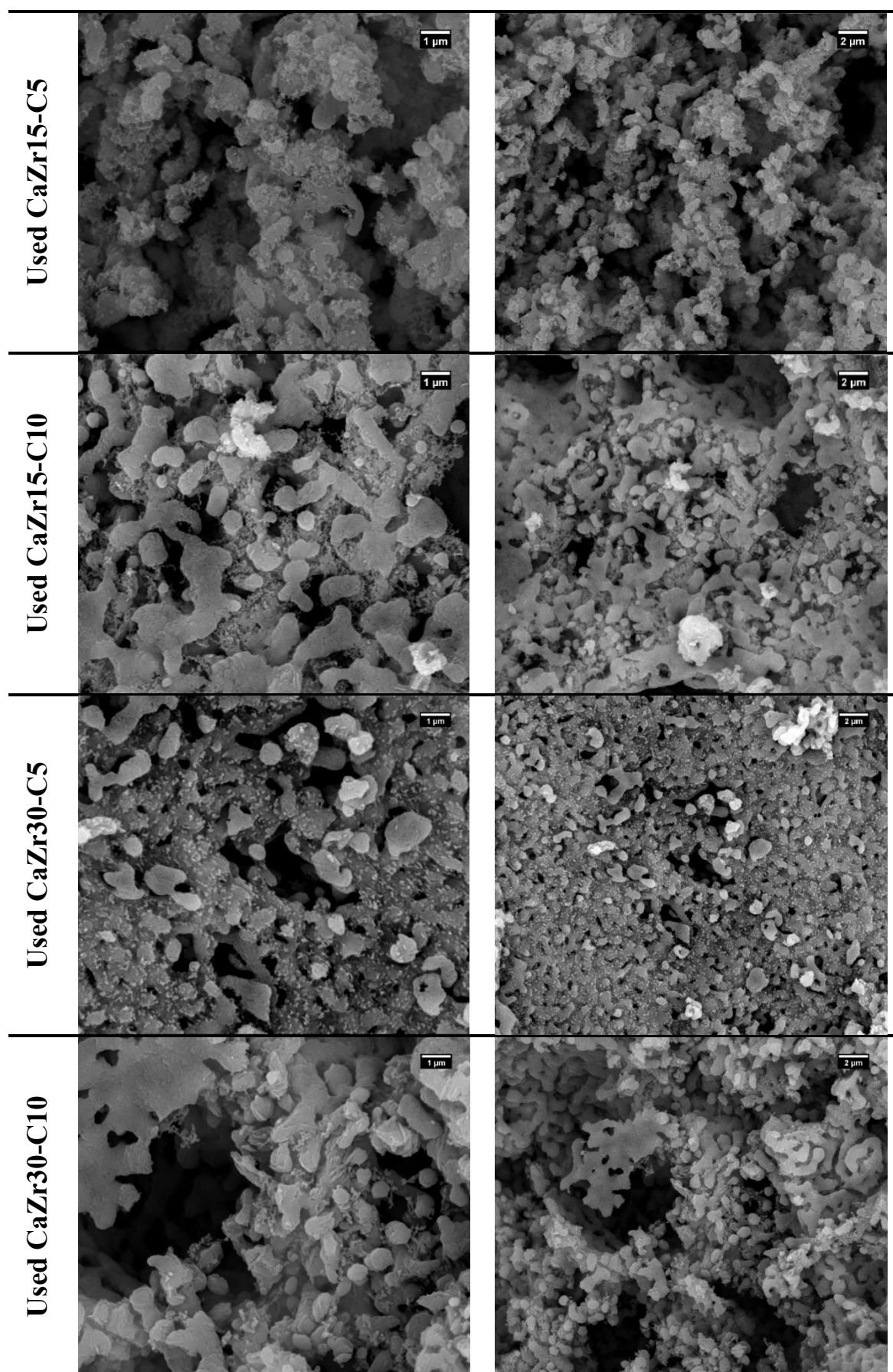


Fig. 8: SEM images of used CaZr15-C5, CaZr15-C10, CaZr30-C5, and CaZr30-C10, after processing during 15 cycles.

To quantitatively manifest the effect of CNT on the multicyclic performance of CaZr15-C0 and CaZr30-C0, the increment rates (%) in CO₂ capture capacity at the 15th cycle, CaO conversion at the 1st cycle, and the total amount of captured CO₂ by merging 2.5, 5, and 10 wt.% CNT with CaZr15-C0 and CaZr30-C0 are reported in **Fig. 9a** and **b**, respectively. There are outstanding improvements in the abovementioned characteristics when integrating with diverse CNT content. The most significant enhancements, including 41.74, 16.2, and 45.27 % in CO₂ capture capacity at the 15th cycle, CaO conversion at the 1st cycle, and the total amount of captured CO₂, are acquired by adding 5 wt.% CNT, respectively. Even though the most increase in CO₂ capture capacity of CaZr30-C0 at the 15th cycle, 49.5 %, is achieved in the case of CaZr30-C10, merging CaZr30-C0 with 5 wt.% CNT results in the highest enhancements in CaO conversion at the 1st cycle, 82.95 %, and the total amount of captured CO₂, 53.57 %.

The influence of BJH pore volume on CO₂ capture capacity at 15th cycles and the total amount of adsorbed CO₂ over 15 cycles exposed to severe CaL conditions is depicted in **Fig. 9c** and **d**. Merging CNT into Zr-stabilized CaO adsorbent raises BJH pore volume, affecting important multicyclic features. Enhancing BJH pore volume increases CO₂ capture capacity at the 15th cycle and the total amount of captured CO₂ over cycles. The highest CO₂ capture capacity at the 15th cycle of 0.164 g CO₂/g sorbent and the total amount of captured CO₂ of 2.92 g CO₂/g sorbent over 15 multiple cycles, are presented by CaZr15-C5, characterized with the highest BJH pore volume of 108.7 mm³/g.

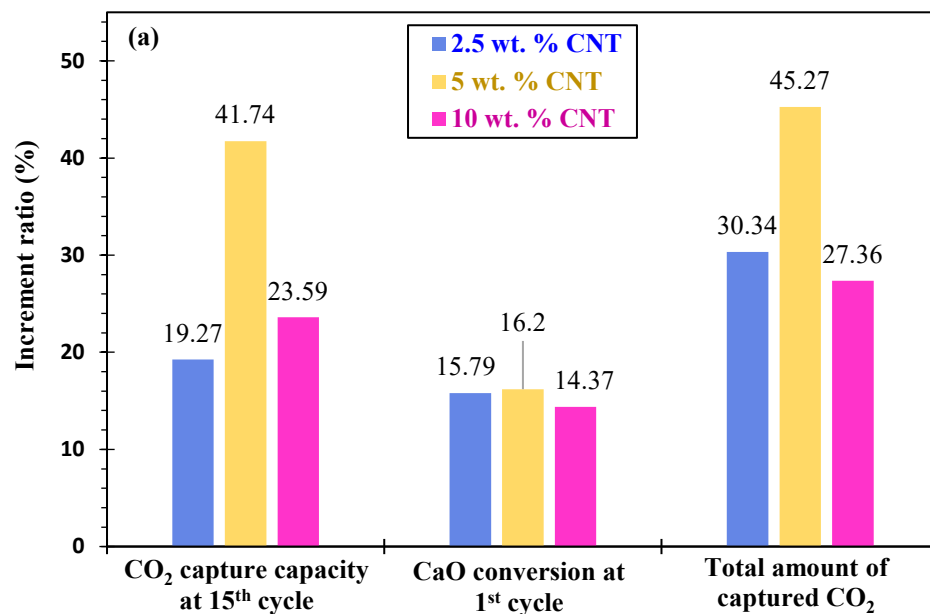
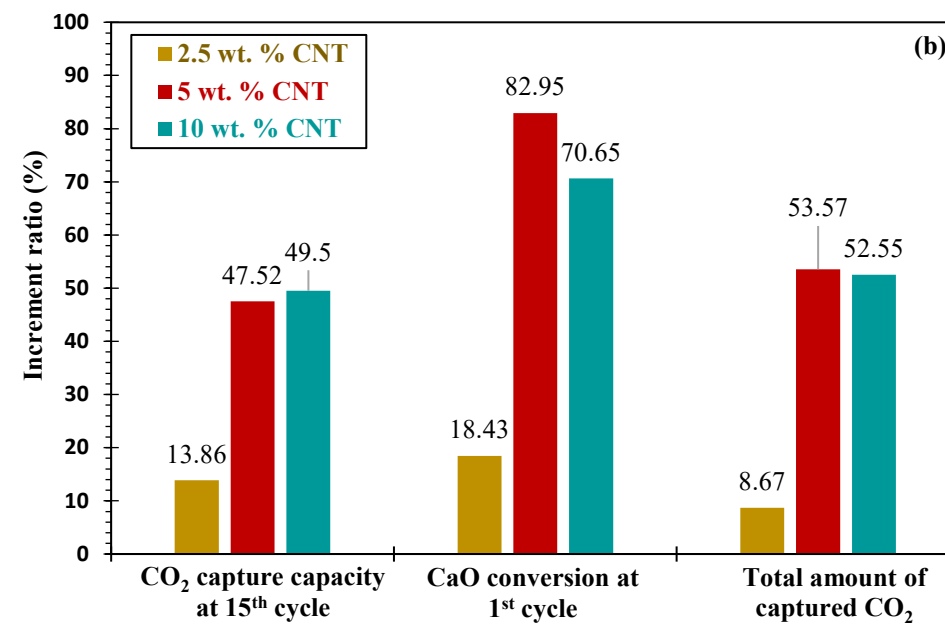
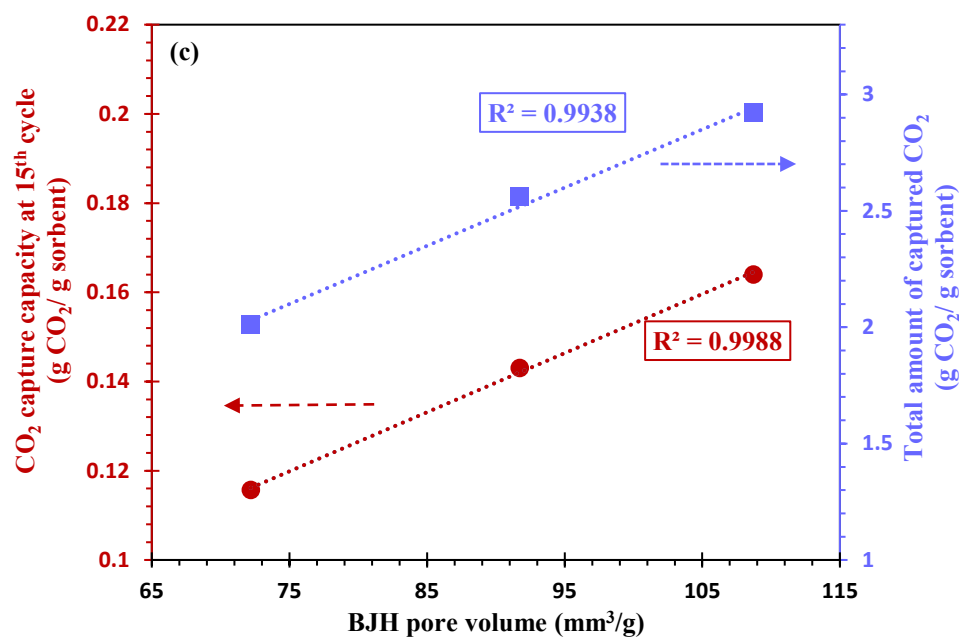
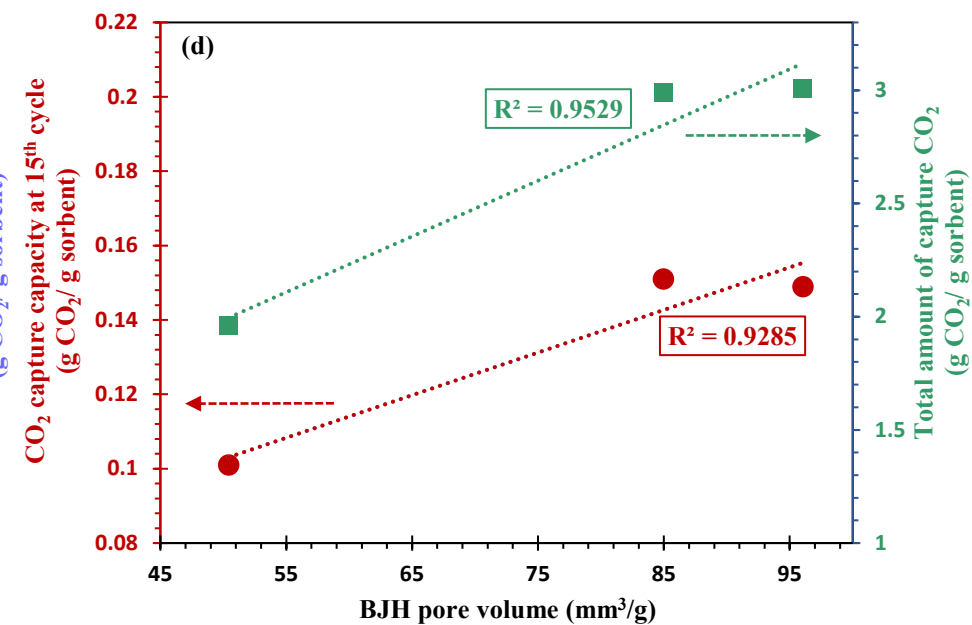
The relation between CaO crystallite size and the initial CaO conversion of all samples developed with Ca/Zr molar ratios of 15/1 and 30/1 are plotted in **Fig. 9e** and **f**, where CaO crystallite size inversely affects the initial CaO conversion. Sequentially, the highest initial

CaO conversion of 42.37% and 52.71% belongs to CaZr15-C5 and CaZr30-C5 with smaller CaO crystallite sizes of 22.3 and 19.8 nm. On the other hand, the lowest values of CaO conversion, 36.46 and 28.81 %, are reported for the CNT-free Zr-incorporated samples, CaZr15-C0 and CaZr30-C0, which possess giant CaO crystallite sizes of 26.5 and 29.6 nm, respectively. Developing CaO-adsorbents with smaller CaO grain sizes contributes to increasing the accessible CaO sites and, consequently, CaO conversion and CO₂ capture activity.

The role of BET surface area on the average sorption capacity of the 1st, 2nd, and 3rd cycles for both clusters of synthesized adsorbents are depicted in **Fig. 9g** and **h**. A direct correlation between average sorption capacity and free surface area can be seen. Sequentially, sorbents with the highest and lowest average sorption capacity have the highest and lowest BET surface area. CaZr15-C5 and CaZr30-C5, with the maximum BET surface areas of 17.43 and 20.63 m²/g, captured the higher amounts of CO₂ in their initial tricycles, 0.246 and 0.315 g CO₂/ g sorbent, respectively. Additionally, the minimum average sorption capacities of the 1st, 2nd, and 3rd cycles are obtained for CaZr15-C0 and CaZr30-C0, potentially attributed to their minimum BET surface area.

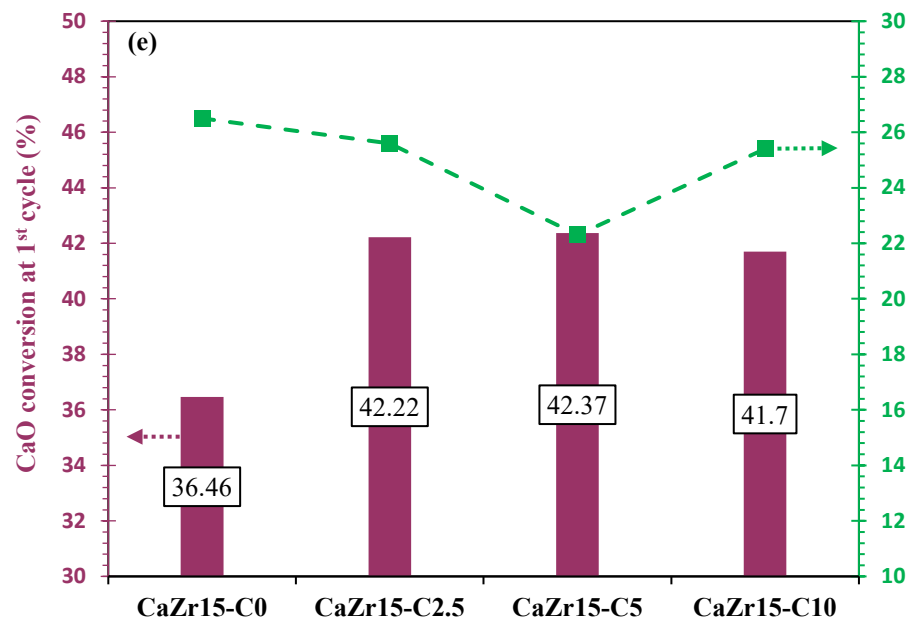
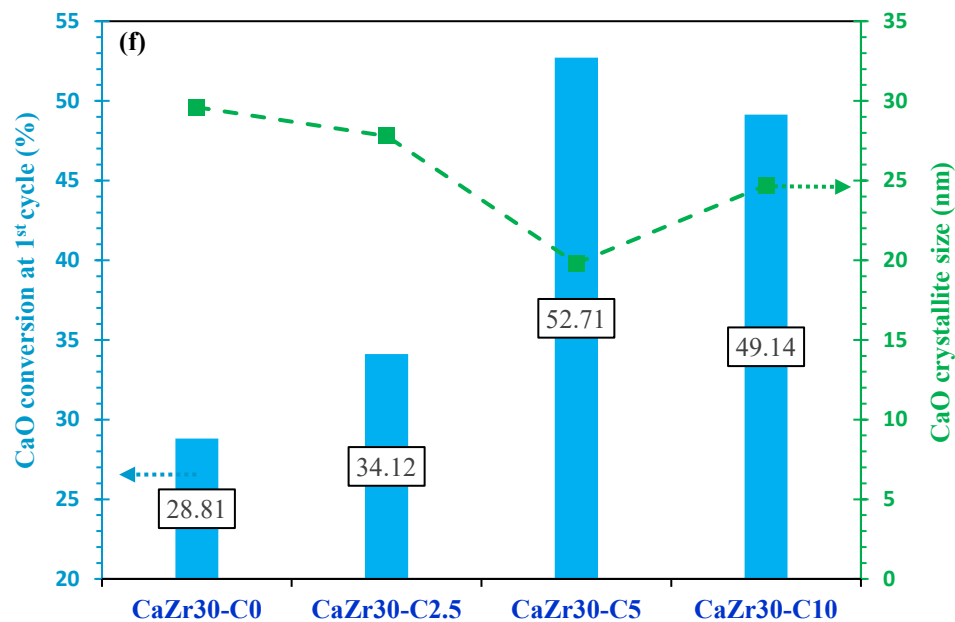
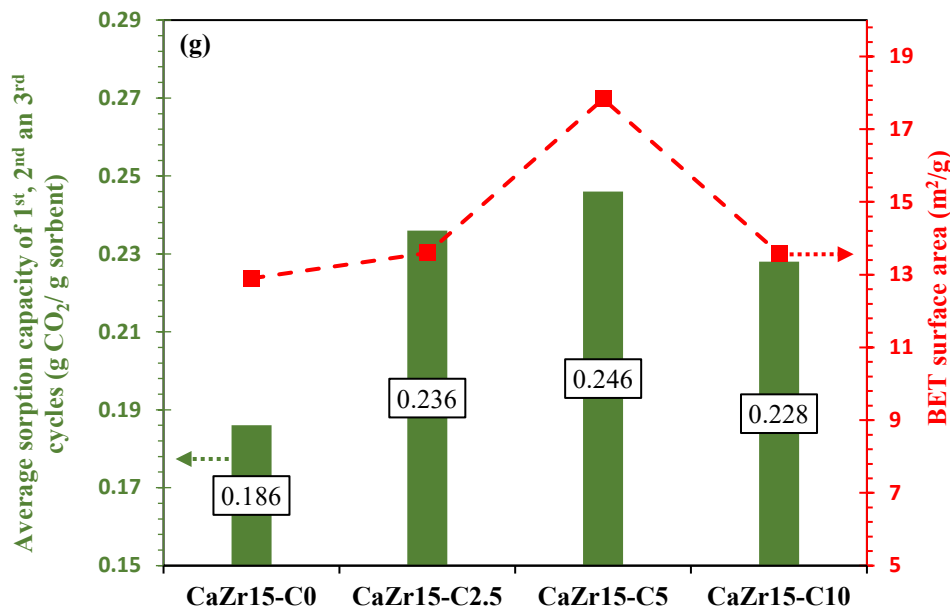
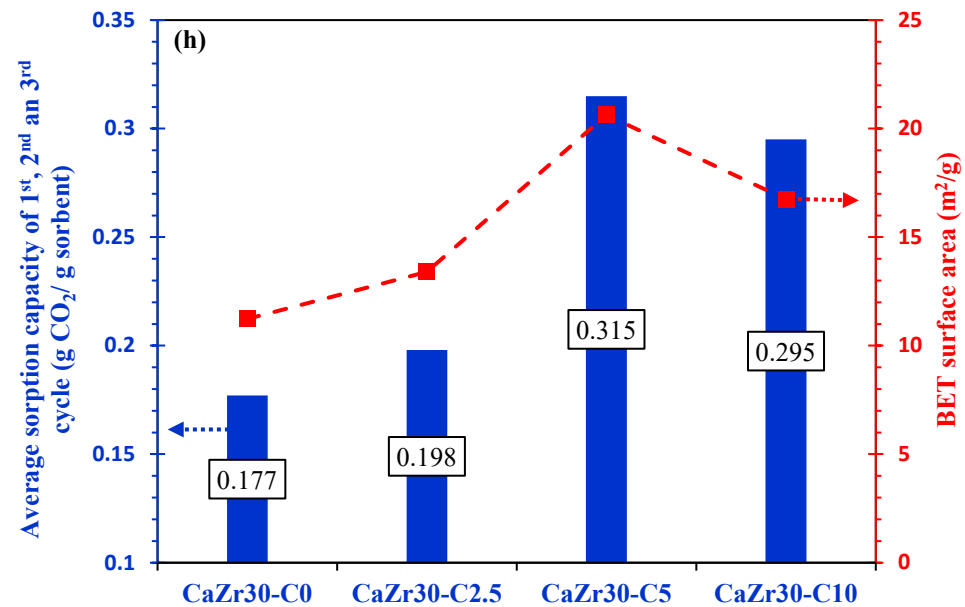
Fig. 9i indicates the direct proportion between the BET surface area of used samples and ultimate sorption capacity, at the 15th cycle, with a correlation coefficient R² of 0.953. The used adsorbent with the highest BET surface area of 6.48 m²/g is the CaZr15-C5, exhibiting the most sorption capacity of 0.164 g CO₂/ g sorbent at the final cycle. Due to the considerable sintering in inner layers of adsorbents after passing several cycles, the free surface area plays a crucial role in the sorption capacity of adsorbents. As a result, by simultaneous incorporation of 18.5 and 5 wt.% of CaZrO₃ and MWCNT into nanostructured CaO, the surface area value of used CaO increased by 155%, leading to an 86.4% increment in ultimate sorption capacity under harsh CaL condition.

Based on previous comprehensive structural and cyclic assessments, CaZr15-C5 and CaZr30-C5 are the best-developed samples. To directly compare CaZr15-C5 and CaZr30-C5, their CO₂ capture capacity and CaO conversion plots over 15 carbonation/calcination cycles under severe CaL conditions are presented in **Fig. 10a** and **b**, respectively. Due to the more CaO content, higher surface area, and pore volume, a higher amount of CO₂ is adsorbed in the case of CaZr30-C5 compared to CaZr15-C5. Nevertheless, the higher amount of thermal-resistance CaZrO₃ for CaZr15-C5 hinders the high-rate CaO sintering when CaO particles undergo several cycles under CaL conditions. More activation of CaZr15-C5, 60.52 %, arising from its higher CaZrO₃ content, is the main reason for its superior CO₂ capture capacity and CaO conversion from the 5th cycle onwards compared to CaZr15-C5. However, the higher value of the total amount of captured CO₂ in the case of CaZr30-C5, 3.01 g CO₂/ g sorbent, than that of CaZr15-C5, 2.92 g CO₂/ g sorbent, can be attributed to its higher free CaO content of CaZr30-C5, 90 wt.%, compared to CaZr15-C5, 81.5 wt.%. The Ca/Zr molar ratio of 15/1 and CNT content of 5 wt.% are the most suitable preparation parameters.



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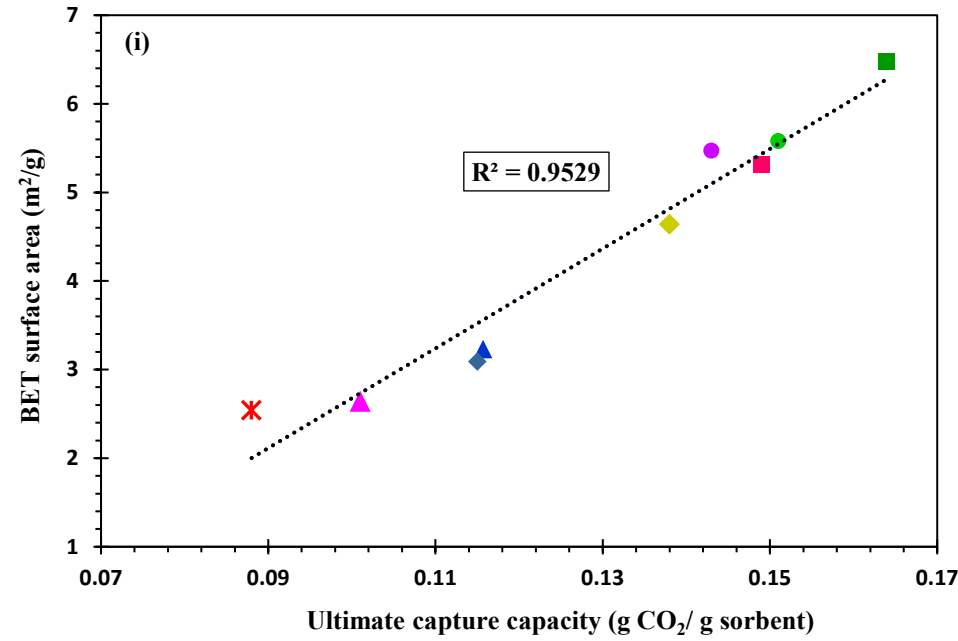


Fig. 9: Increment rate (%) of the total amount of captured CO₂, CaO conversion at 1st cycle, and CO₂ capture capacity at 15th cycle size by adding 2.5, 5, and 10 wt.% of CNT to (a) CaZr15-C0, and (b) CaZr30-C0, Total amount of captured CO₂ and CO₂ capture capacity at 15th cycle versus BJH pore volume for CNT-templated Zr-promoted CaO sorbents developed with Ca/Zr molar ratio of (c) 15/1, (d) 30/1, and CaZr30-C10, CaO conversion (%) at 1st cycle versus CaO crystallite size (nm) for CNT-templated Zr-promoted CaO sorbents developed with Ca/Zr molar ratio of (e) 15/1, (f) 30/1, mean sorption capacity at first three cycles versus BET surface area for CNT-templated Zr-promoted CaO sorbents developed with Ca/Zr molar ratio of (g) 15/1, (h) 30/1, (i) BET surface area value (m²/g) of used samples versus ultimate sorption capacity at 15th cycles (g CO₂/g sorbent)

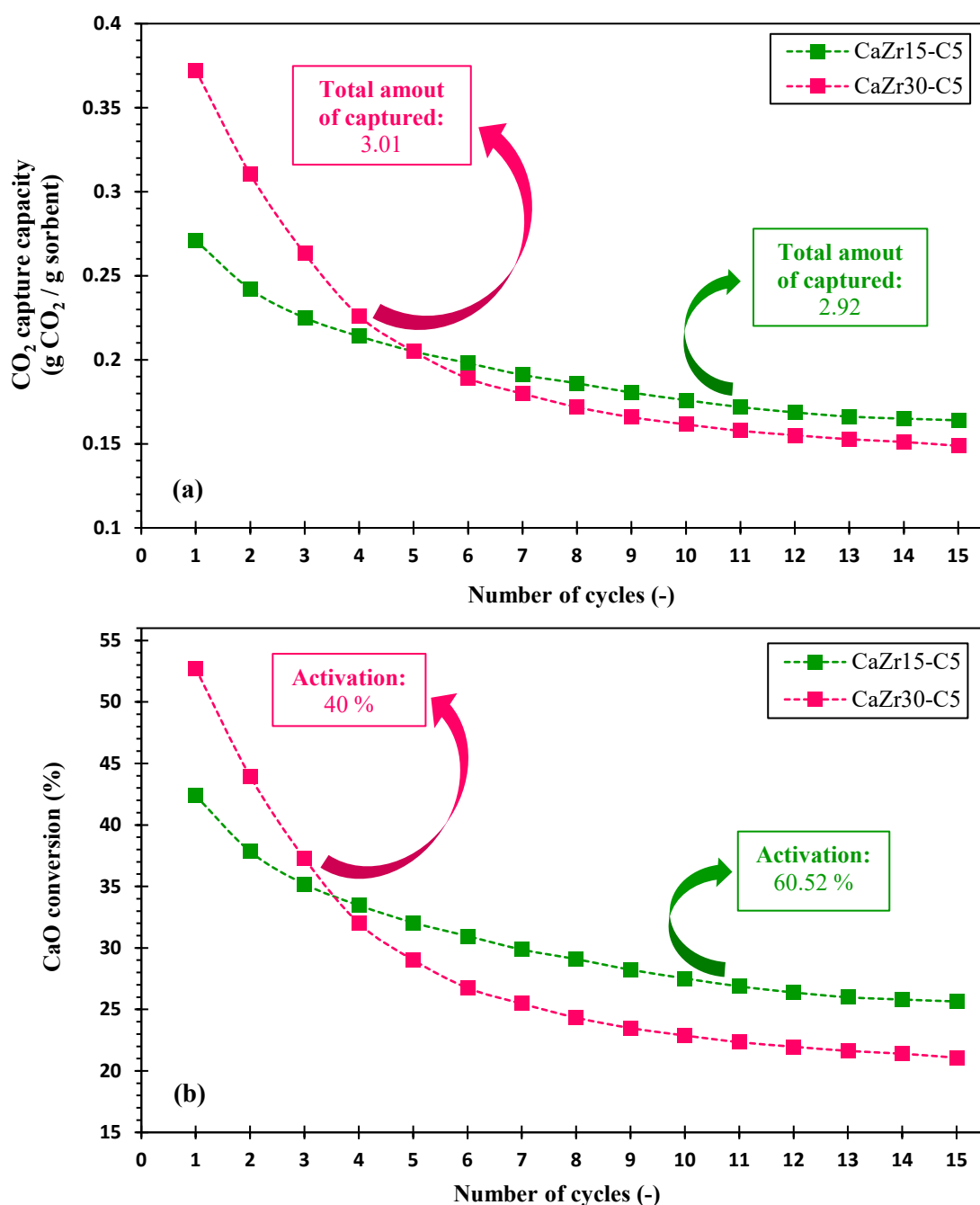


Fig. 10: Comparison of (a) CO₂ capture capacity and (b) CaO conversion of CaZr15-C5 and CaZr30-C5 during fifteen carbonation/calcination cycles under severe CaL conditions.

3.3. Outlook

Undeniable dependence of the CaL process on the applicability of CaO-based sorbents within fluidized bed reactors, including carbonator and calciner, under industrial process conditions, including short carbonation time and CO₂-rich calcination ambient, requires comprehensive assessments on scaling up cost-effective modified CaO-based sorbents in the

pilot-scale plants. Considering the economic aspects of the industrial CO₂ capture process, waste-material-derived CaO precursors, cost-effective thermal-resistance metal oxides, such as Al₂O₃ and MgO, and ubiquitous and affordable bio-based additives should be considered to develop CaO-based sorbents. Consequently, as our research's next target, we plan to conduct a thorough and detailed techno-economic investigation on the applicability of the biomaterials-incorporated durable-metal-promoted CaO sorbents derived from affordable ingredients into pilot-scale fluidized-bed reactors under industrial and realistic conditions in our forthcoming research.

4. Conclusion

The present research concentrates on improving the textural and structural properties and CO₂ adsorption performance of sol-gel-derived Zr-promoted CaO adsorbents containing minor CaZrO₃ contents by utilizing Multi-walled carbon nanotubes additive, for the first time in our knowledge. The Ca/Zr molar ratios of 15/1 and 30/1, and MWCNT concentrations of 2.5, 5, and 10 wt.% were employed to evaluate the effectiveness of MWCNT and determine the optimum parameters' values. The following worth noting outcomes can be presented:

- 1) The integration of 5 wt.% MWCNT, the best concentration based on textural and multicyclic results, into Zr-promoted CaO adsorbents, containing 10 and 18.5 wt.% CaZrO₃ resulted in the greatest improvements in textural and adsorptive features. For instance, 50.57 and 90.55% increments in pore volume, 38.1 and 83.7 increases in BET surface area, and 45.27 and 53.57% raises in the total amount of captured CO₂ over the 15 cycles CaL process reported for CaO developed with 15/1 and 30/1 molar ratios of Ca/Zr.
- 2) 5 wt.% CNT is the most efficient amount to significantly enhance the CO₂ capture activity of Zr-promoted CaO adsorbents containing a minor amount of CaZrO₃.

- 3) Combining CNT with Zr-modified CaO adsorbents homogenized the CaZrO_3 667
distribution into CaO texture. 668
- 4) Based on the multicyclic and textural data, MWCNT can be considered a remarkable 669
candidate to compensate for the decreased amount of CaZrO_3 , due to their drawbacks, 670
for preparing highly durable CaO adsorbent. 671

Author contribution:	672
Mohammad Heidari: Investigation, Project administration, Conceptualization,	673
Methodology, Formal analysis, Writing original draft. Seyed Borhan Mousavi:	674
Investigation, Methodology, Conceptualization, Formal analysis, Writing original draft.	675
Farhad Rahmani: Supervision, Project administration, Visualization, Conceptualization,	676
Review & Editing. Peter Clough: Review & Editing. Serap Ozmen: Investigation.	677

References:

1. Zhang Z X, Xu H J, Hua W S, Zhao C Y. Thermodynamics analysis of multi-stage temperature swing adsorption cycle for dilute CO₂ capture, enrichment and purification. *Energy Conversion and Management*, 2022, 265: 115794.
2. Ashrafi M, Mousavi S B, Zeinali Heris S, Heidari M, Mohammadpourfard M, Aslani H. Investigation of H₂O₂/UV advanced oxidation process on the removal rate of coliforms from the industrial effluent: A pilot-scale study. *International Journal of Hydrogen Energy*, 2022.
3. Li Y, Wang N, Guan H, Jia Z, Zhang Y, Zhao G, Gao M. Optimization study of CO₂ capture unit for subcritical coal-fired power generation unit based on Ebsilon and Aspen plus. *Energy Conversion and Management*, 2022, 269: 116111.
4. Ali Abd A, Jihad Kadhim Shabbani H, Helwani Z, Roslee Othman M. Novel design of pressure swing adsorption using compact plates for adsorption heat recuperation of CO₂ capture in biomethane upgrading process. *Energy Conversion and Management*, 2022, 268: 115999.
5. Cheng F, Small A A, Colosi L M. The levelized cost of negative CO₂ emissions from thermochemical conversion of biomass coupled with carbon capture and storage. *Energy Conversion and Management*, 2021, 237: 114115.
6. Choi S, Moon H, Bang M, Kim K, Park Y-K, Cho H H. Efficient design of heat exchange for CFB reactors in CO₂ capture system regarding geometry-induced secondary flow. *Energy Conversion and Management*, 2021, 235: 113995.
7. Sun Y, Dong B, Wang L, Li H, Thorin E. Technology selection for capturing CO₂ from wood pyrolysis. *Energy Conversion and Management*, 2022, 266: 115835.
8. Xiang D, Li P, Yuan X. Energy consumption and CO₂ emissions of petroleum coke-to-methanol with/without carbon capture using process modeling and life cycle analysis. *Energy Conversion and Management*, 2021, 248: 114823.
9. Alibrahim H A, Khalafalla S S, Ahmed U, Park S, Lee C-J, Zahid U. Conceptual design of syngas production by the integration of gasification and dry-reforming technologies with CO₂ capture and utilization. *Energy Conversion and Management*, 2021, 244: 114485.
10. del Pozo C A, Cloete S, Álvaro Á J. Carbon-negative hydrogen: Exploring the techno-economic potential of biomass co-gasification with CO₂ capture. *Energy Conversion and Management*, 2021, 247: 114712.
11. Oh H-T, Kum J, Park J, Dat Vo N, Kang J-H, Lee C-H. Pre-combustion CO₂ capture using amine-based absorption process for blue H₂ production from steam methane reformer. *Energy Conversion and Management*, 2022, 262: 115632.
12. Khallaghi N, Abbas S Z, Manzolini G, De Coninck E, Spallina V. Techno-economic assessment of blast furnace gas pre-combustion decarbonisation integrated with the power generation. *Energy Conversion and Management*, 2022, 255: 115252.
13. Szima S, Arnaiz del Pozo C, Cloete S, Chiesa P, Jiménez Alvaro Á, Cormos A-M, Amini S. Finding synergy between renewables and coal: Flexible power and hydrogen production from advanced IGCC plants with integrated CO₂ capture. *Energy Conversion and Management*, 2021, 231: 113866.
14. Serrano J R, Martín J, Gomez-Soriano J, Raggi R. Theoretical and experimental evaluation of the spark-ignition premixed oxy-fuel combustion concept for future CO₂ captive powerplants. *Energy Conversion and Management*, 2021, 244: 114498.
15. Serrano J R, Arnau F J, García-Cuevas L M, Farias V H. Oxy-fuel combustion feasibility of compression ignition engines using oxygen separation membranes for

	enabling carbon dioxide capture. <i>Energy Conversion and Management</i> , 2021, 247: 114732.	726 727
16.	Wu Y, Dai Y, Xie W, Chen H, Zhu Y. System integration for combined heat and power (CHP) plants with post-combustion CO ₂ capture. <i>Energy Conversion and Management</i> , 2022, 258: 115508.	728 729 730
17.	Mosaffa A Farshi L G. Novel post combustion CO ₂ capture in the coal-fired power plant employing a transcritical CO ₂ power generation and low temperature steam upgraded by an absorption heat transformer. <i>Energy Conversion and Management</i> , 2020, 207: 112542.	731 732 733 734
18.	Asadi J Kazempoor P. Techno-economic analysis of membrane-based processes for flexible CO ₂ capturing from power plants. <i>Energy Conversion and Management</i> , 2021, 246: 114633.	735 736 737
19.	Akrami E, Ameri M, Rocco M V. Integration of biomass-fueled power plant and MCFC-cryogenic CO ₂ separation unit for low-carbon power production: Thermodynamic and exergoeconomic comparative analysis. <i>Energy Conversion and Management</i> , 2020, 223: 113304.	738 739 740 741
20.	Kim S, Lee J W, Choi H W, Lee G J, Xu R, Yoon S H, Xu Z, Wang R, Tae Kang Y. CO ₂ capture-driven thermal battery using functionalized solvents for plus energy building application. <i>Energy Conversion and Management</i> , 2022, 260: 115606.	742 743 744
21.	Nobarzad M J, Tahmasebpour M, Heidari M, Pevida C. Theoretical and experimental study on the fluidity performance of hard-to-fluidize carbon nanotubes-based CO ₂ capture sorbents. <i>Frontiers of Chemical Science and Engineering</i> , 2022.	745 746 747
22.	Adnan M A, Pradiptya I, Haque T I, Hossain M M. Integrated diesel fueled chemical looping combustion for power generation and CO ₂ capture – Performance evaluation based on exergy analysis. <i>Energy Conversion and Management</i> , 2020, 206: 112430.	748 749 750
23.	Tregambi C, Bareschino P, Mancusi E, Pepe F, Montagnaro F, Solimene R, Salatino P. Modelling of a concentrated solar power – photovoltaics hybrid plant for carbon dioxide capture and utilization via calcium looping and methanation. <i>Energy Conversion and Management</i> , 2021, 230: 113792.	751 752 753 754
24.	Colelli G, Chacartegui R, Ortiz C, Carro A, Arena A P, Verda V. Life cycle and environmental assessment of calcium looping (CaL) in solar thermochemical energy storage. <i>Energy Conversion and Management</i> , 2022, 257: 115428.	755 756 757
25.	Liu G, Zhao Y, Heberlein S, Veksha A, Giannis A, Ping Chan W, Thye Lim T, Lisak G. Hydrogen and power co-production from autothermal biomass sorption enhanced chemical looping gasification: Thermodynamic modeling and comparative study. <i>Energy Conversion and Management</i> , 2022, 269: 116087.	758 759 760 761
26.	Xu Y, Zhang T, Lu B, Luo C, Wu F, Li X, Zhang L. Glycine tailored effective CaO-based heat carriers for thermochemical energy storage in concentrated solar power plants. <i>Energy Conversion and Management</i> , 2021, 250: 114886.	762 763 764
27.	Zhang C, Li Y, Yang L, Fan X, Chu L. Analysis on H ₂ production process integrated CaO/Ca(OH) ₂ heat storage and sorption enhanced staged gasification using calcium looping. <i>Energy Conversion and Management</i> , 2022, 253: 115169.	765 766 767
28.	Heidari M, Tahmasebpour M, Antzaras A, Lemonidou A A. CO ₂ capture and fluidity performance of CaO-based sorbents: Effect of Zr, Al and Ce additives in tri-, bi- and mono-metallic configurations. <i>Process Safety and Environmental Protection</i> , 2020, 144: 349-365.	768 769 770 771
29.	Heidari M, Tahmasebpour M, Mousavi S B, Pevida C. CO ₂ capture activity of a novel CaO adsorbent stabilized with (ZrO ₂ +Al ₂ O ₃ +CeO ₂)-based additive under mild and realistic calcium looping conditions. <i>Journal of CO₂ Utilization</i> , 2021, 53: 101747.	772 773 774

30. Mousavi S B, Zeinali Heris S, Estellé P. Viscosity, tribological and physicochemical features of ZnO and MoS₂ diesel oil-based nanofluids: An experimental study. *Fuel*, 2021, 293: 120481. 775
776
777
31. Seyedi S S, Shabgard M R, Mousavi S B, Zeinali Heris S. The impact of SiC, Al₂O₃, and B₂O₃ abrasive particles and temperature on wear characteristics of 18Ni (300) maraging steel in abrasive flow machining (AFM). *International Journal of Hydrogen Energy*, 2021, 46(68): 33991-34001. 778
779
780
781
32. Yahyavi S R, Haghighi M, Shafiei S, Abdollahifar M, Rahmani F. Ultrasound-assisted synthesis and physicochemical characterization of Ni–Co/Al₂O₃–MgO nanocatalysts enhanced by different amounts of MgO used for CH₄/CO₂ reforming. *Energy Conversion and Management*, 2015, 97: 273-281. 782
783
784
785
33. Rahmani F Haghighi M. One-pot hydrothermal synthesis of ZSM-5–CeO₂ composite as a support for Cr-based nanocatalysts: influence of ceria loading and process conditions on CO₂-enhanced dehydrogenation of ethane. *RSC Advances*, 2016, 6(92): 89551-89563. 786
787
788
789
34. Rahmani F Haghighi M. C₂H₆/CO₂ oxidative dehydrogenation (ODH) reaction on nanostructured CrAPSO-34 catalyst: One-pot hydrothermal vs. conventional hydrothermal/impregnation catalyst synthesis. *Korean Journal of Chemical Engineering*, 2016, 33(9): 2555-2566. 790
791
792
793
35. Hu Y, Lu H, Liu W, Yang Y, Li H. Incorporation of CaO into inert supports for enhanced CO₂ capture: A review. *Chemical Engineering Journal*, 2020, 396: 125253. 794
795
36. Radfarnia H R Iliuta M C. Metal oxide-stabilized calcium oxide CO₂ sorbent for multicycle operation. *Chemical Engineering Journal*, 2013, 232: 280-289. 796
797
37. Antzara A N, Arregi A, Heracleous E, Lemonidou A A. In-depth evaluation of a ZrO₂ promoted CaO-based CO₂ sorbent in fluidized bed reactor tests. *Chemical Engineering Journal*, 2018, 333: 697-711. 798
799
800
38. Yoon H J Lee K B. Introduction of chemically bonded zirconium oxide in CaO-based high-temperature CO₂ sorbents for enhanced cyclic sorption. *Chemical Engineering Journal*, 2019, 355: 850-857. 801
802
803
39. Armutlulu A, Naeem M A, Liu H J, Kim S M, Kierzkowska A, Fedorov A, Müller C R. Multishelled CaO microspheres stabilized by atomic layer deposition of Al₂O₃ for enhanced CO₂ capture performance. *Advanced Materials*, 2017, 29(41): 1702896. 804
805
806
40. Naeem M A, Armutlulu A, Imtiaz Q, Donat F, Schäublin R, Kierzkowska A, Müller C R. Optimization of the structural characteristics of CaO and its effective stabilization yield high-capacity CO₂ sorbents. *Nature communications*, 2018, 9(1): 1-11. 807
808
809
810
41. Kim S M, Armutlulu A, Kierzkowska A M, Müller C R. Inverse opal-like, Ca₃Al₂O₆-stabilized, CaO-based CO₂ sorbent: stabilization of a highly porous structure to improve its cyclic CO₂ uptake. *ACS Applied Energy Materials*, 2019, 2(9): 6461-6471. 811
812
813
814
42. Javadpour R, Zeinali Heris S, Mohammadfam Y. Optimizing the effect of concentration and flow rate of water/ MWCNTs nanofluid on the performance of a forced draft cross-flow cooling tower. *Energy*, 2021, 217: 119420. 815
816
817
43. Javadpour R, Heris S Z, Mohammadfam Y, Mousavi S B. Optimizing the heat transfer characteristics of MWCNTs and TiO₂ water-based nanofluids through a novel designed pilot-scale setup. *Scientific Reports*, 2022, 12(1): 15154. 818
819
820
44. Karimi Bakhtiyar N, Javadpour R, Zeinali Heris S, Mohammadpourfard M. Improving the thermal characteristics of a cooling tower by replacing the operating fluid with functionalized and non-functionalized aqueous MWCNT nanofluids. *Case Studies in Thermal Engineering*, 2022, 39: 102422. 821
822
823
824

45. Javadpour R, Zeinali Heris S, Meyer J P. Experimental study of the effect of filled bed type on the performance of a cross-flow cooling tower with the approach of using nanofluids. *Energy Reports*, 2022, 8: 8346-8360. 825-827
46. Aghaei Sarvari A, Zeinali Heris S, Mohammadpourfard M, Mousavi S B, Estellé P. Numerical investigation of TiO₂ and MWCNTs turbine meter oil nanofluids: Flow and hydrodynamic properties. *Fuel*, 2022, 320: 123943. 828-830
47. Yao Y, Lian C, Wu G, Hu Y, Wei F, Yu M, Wang S. Synthesis of “sea urchin”-like carbon nanotubes/porous carbon superstructures derived from waste biomass for treatment of various contaminants. *Applied Catalysis B: Environmental*, 2017, 219: 563-571. 831-834
48. Wang G, Deng Y, Yu J, Zheng L, Du L, Song H, Liao S. From chlorella to nestlike framework constructed with doped carbon nanotubes: a biomass-derived, high-performance, bifunctional oxygen reduction/evolution catalyst. *ACS applied materials & interfaces*, 2017, 9(37): 32168-32178. 835-838
49. Zhang Y, Lu L, Zhang S, Lv Z, Yang D, Liu J, Chen Y, Tian X, Jin H, Song W. Biomass chitosan derived cobalt/nitrogen doped carbon nanotubes for the electrocatalytic oxygen reduction reaction. *Journal of Materials Chemistry A*, 2018, 6(14): 5740-5745. 839-842
50. Osman A I, Blewitt J, Abu-Dahrieh J K, Farrell C, Al-Muhtaseb A a H, Harrison J, Rooney D W. Production and characterisation of activated carbon and carbon nanotubes from potato peel waste and their application in heavy metal removal. *Environmental science and pollution research*, 2019, 26(36): 37228-37241. 843-846
51. Yang M, Yuan Y, Li Y, Sun X, Wang S, Liang L, Ning Y, Li J, Yin W, Che R. Dramatically enhanced electromagnetic wave absorption of hierarchical CNT/Co/C fiber derived from cotton and metal-organic-framework. *Carbon*, 2020, 161: 517-527. 847-849
52. Zhou S, Zhang B, Liao Z, Zhou L, Yuan Y. Autochthonous N-doped carbon nanotube/activated carbon composites derived from industrial paper sludge for chromate (VI) reduction in microbial fuel cells. *Science of the Total Environment*, 2020, 712: 136513. 850-853
53. Wang Z, Ogata H, Morimoto S, Ortiz-Medina J, Fujishige M, Takeuchi K, Muramatsu H, Hayashi T, Terrones M, Hashimoto Y. Nanocarbons from rice husk by microwave plasma irradiation: From graphene and carbon nanotubes to graphenated carbon nanotube hybrids. *Carbon*, 2015, 94: 479-484. 854-857
54. Fathy N A. Carbon nanotubes synthesis using carbonization of pretreated rice straw through chemical vapor deposition of camphor. *RSC advances*, 2017, 7(45): 28535-28541. 858-860
55. Reva V, Filatenkov A, Yagofarov V, Gulevskii D, Kuryavyi V, Mansurov Y N. Analysis of the Formation of Multi-Layer Carbon Nanotubes in the Process of Mechanical Activation of the Pyrolysis Products of Vegetable Raw Materials. in *IOP Conference Series: Materials Science and Engineering*. 2016. IOP Publishing. 861-864
56. Mousavi S B, Heris S Z, Estellé P. Experimental comparison between ZnO and MoS₂ nanoparticles as additives on performance of diesel oil-based nano lubricant. *Scientific reports*, 2020, 10(1): 1-17. 865-867
57. Mousavi S B, Zeinali Heris S, Hosseini M G. Experimental investigation of MoS₂/diesel oil nanofluid thermophysical and rheological properties. *International Communications in Heat and Mass Transfer*, 2019, 108: 104298. 868-870
58. Mousavi S B Zeinali Heris S. Experimental investigation of ZnO nanoparticles effects on thermophysical and tribological properties of diesel oil. *International Journal of Hydrogen Energy*, 2020, 45(43): 23603-23614. 871-873

59.	Antzara A, Heracleous E, Lemonidou A A. Improving the stability of synthetic CaO-based CO ₂ sorbents by structural promoters. <i>Applied energy</i> , 2015, 156: 331-343.	874 875
60.	Jing J-y, Li T-y, Zhang X-w, Wang S-d, Feng J, Turmel W A, Li W-y. Enhanced CO ₂ sorption performance of CaO/Ca ₃ Al ₂ O ₆ sorbents and its sintering-resistance mechanism. <i>Applied Energy</i> , 2017, 199: 225-233.	876 877 878
61.	Lazaro A, Brouwers H, Quercia G, Geus J. The properties of amorphous nano-silica synthesized by the dissolution of olivine. <i>Chemical Engineering Journal</i> , 2012, 211: 112-121.	879 880 881
62.	Naghash-Hamed S, Arsalani N, Mousavi S B. Facile copper ferrite/carbon quantum dots magnetic nanocomposite as an effective nitro group reduction reaction nano catalyst for reduction of Para-nitroaniline and Ortho-nitroaniline. <i>Nano Futures</i> , 2022.	882 883 884
63.	Naghash-Hamed S, Arsalani N, Mousavi S B. The catalytic reduction of nitroanilines using synthesized CuFe ₂ O ₄ nanoparticles in an aqueous medium. <i>ChemistryOpen</i> , 2022.	885 886 887
64.	Thommes M, Kaneko K, Neimark A V, Olivier J P, Rodriguez-Reinoso F, Rouquerol J, Sing K S. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). <i>Pure and applied chemistry</i> , 2015, 87(9-10): 1051-1069.	888 889 890 891
65.	Yan F, Jiang J, Chen X, Tian S, Li K. Synthesis and characterization of silica nanoparticles preparing by low-temperature vapor-phase hydrolysis of SiCl ₄ . <i>Industrial & Engineering Chemistry Research</i> , 2014, 53(30): 11884-11890.	892 893 894
66.	Yan F, Jiang J, Li K, Liu N, Chen X, Gao Y, Tian S. Green synthesis of nanosilica from coal fly ash and its stabilizing effect on CaO sorbents for CO ₂ capture. <i>Environmental science & technology</i> , 2017, 51(13): 7606-7615.	895 896 897
67.	Sing K S. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). <i>Pure and applied chemistry</i> , 1985, 57(4): 603-619.	898 899 900
68.	Delir Kheyrollahi Nezhad P, Haghighi M, Rahmani F. CO ₂ /O ₂ -enhanced ethane dehydrogenation over a sol-gel synthesized Ni/ZrO ₂ -MgO nanocatalyst: Effects of MgO, ZrO ₂ , and NiO on the catalytic performance. <i>Particulate Science and Technology</i> , 2018, 36(8): 1017-1028.	901 902 903 904
69.	Delir Kheyrollahi Nezhad P, Haghighi M, Jodeiri N, Rahmani F. Sol-gel preparation of NiO/ZrO ₂ (x)-MgO(100-x) nanocatalyst used in CO ₂ /O ₂ oxidative dehydrogenation of ethane to ethylene: influence of Mg/Zr ratio on catalytic performance. <i>Journal of Sol-Gel Science and Technology</i> , 2016, 80(2): 436-450.	905 906 907 908
70.	Rahmani F, Haghighi M, Mohammadkhani B. Enhanced dispersion of Cr nanoparticles over nanostructured ZrO ₂ -doped ZSM-5 used in CO ₂ -oxydehydrogenation of ethane. <i>Microporous and Mesoporous Materials</i> , 2017, 242: 34-49.	909 910 911 912
		913

**The novel Carbon Nanotube-assisted development of highly porous
CaZrO₃-CaO xerogel with boosted sorption activity towards high-
temperature cyclic CO₂ capture**

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Result and discussion:

Characterization

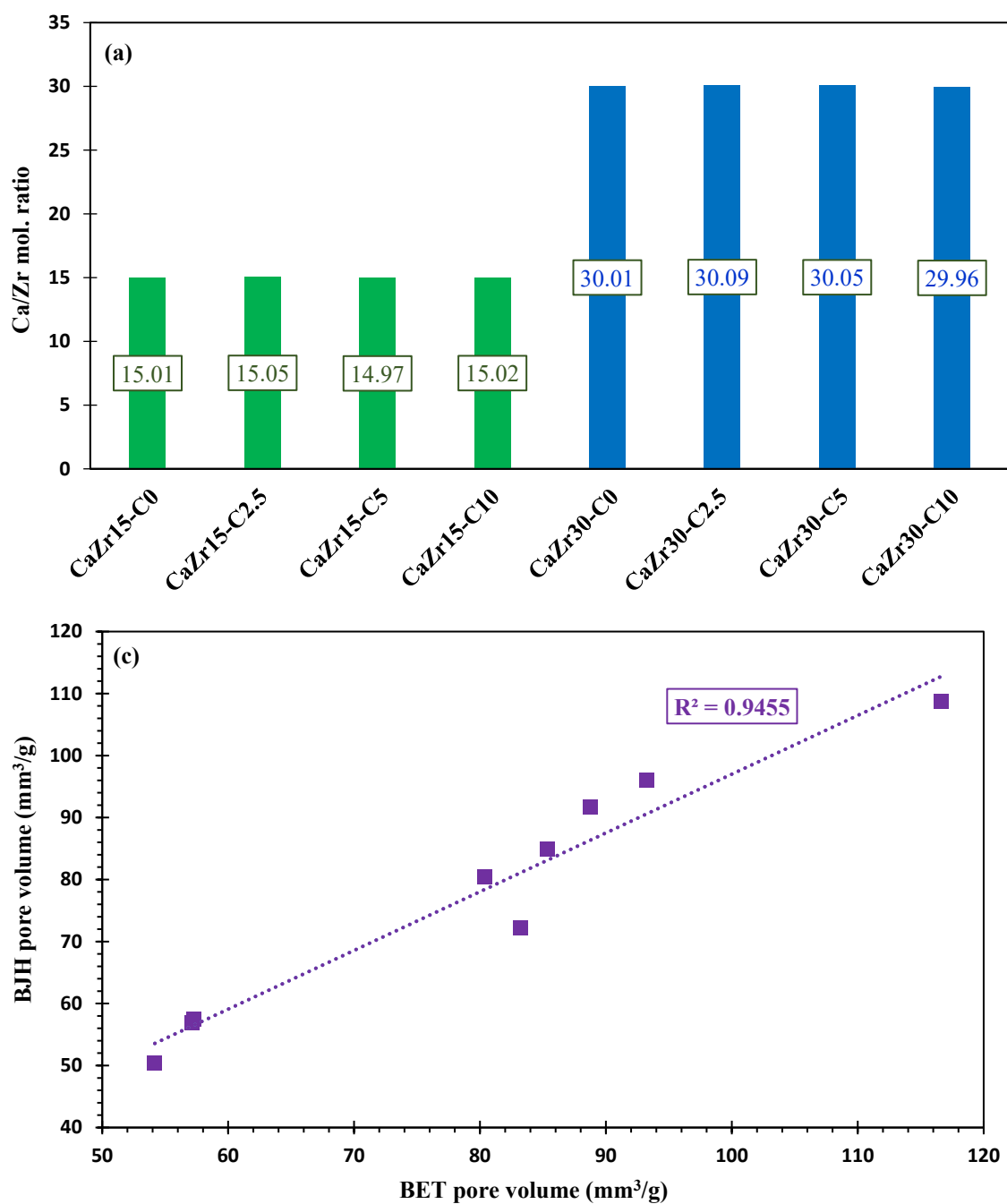
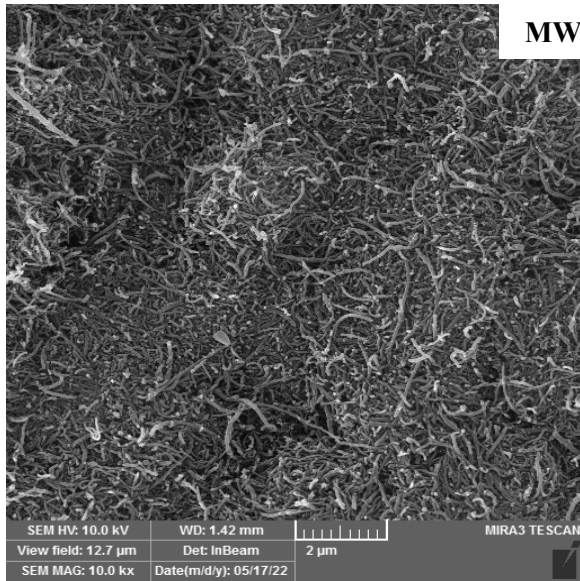
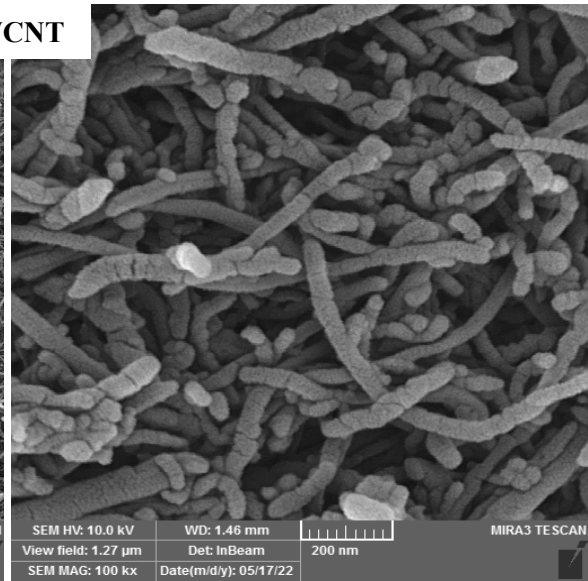
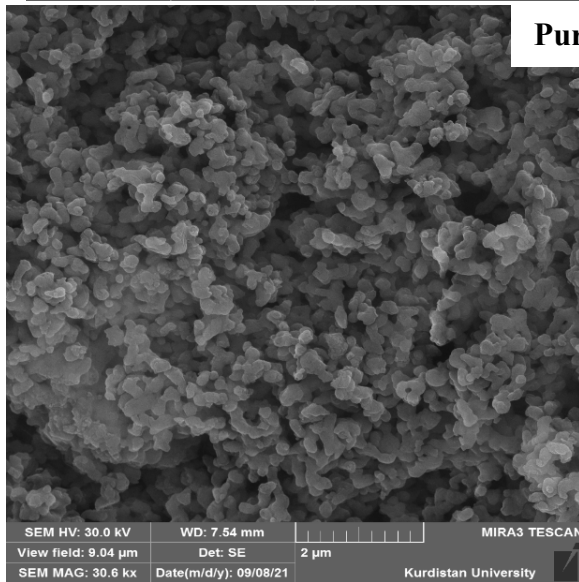
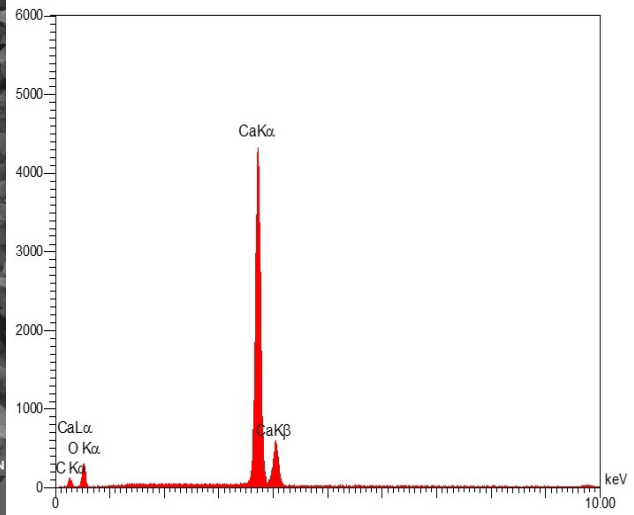


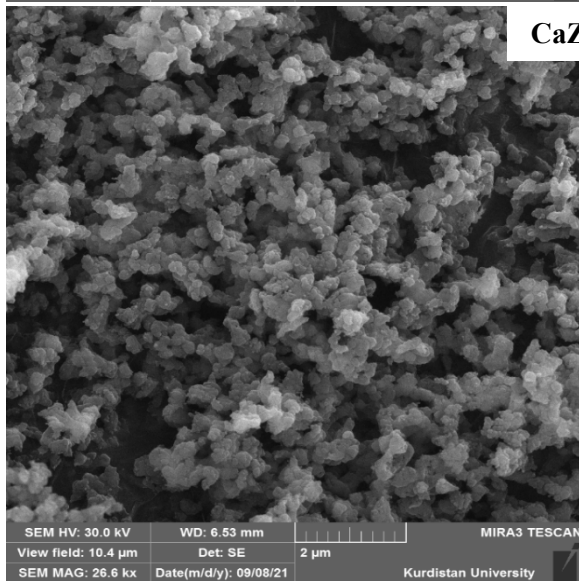
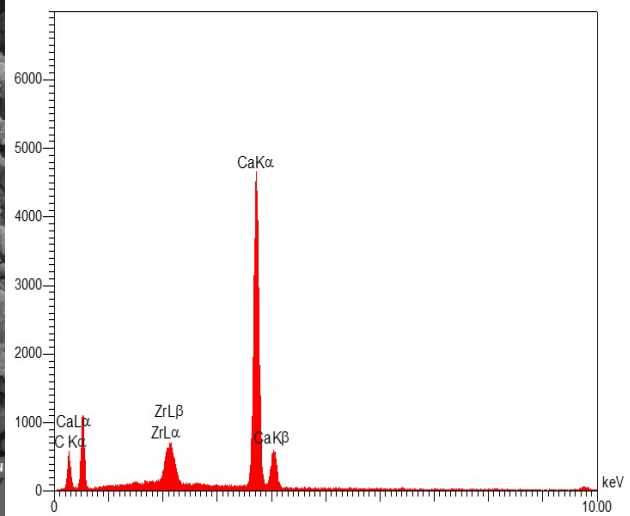
Fig. S1: (a) Ca/Zr molar ratio derived from ICP analysis of all developed Zr-decorated CaO-based xerogels, and (c) BJH pore volume versus BET pore volume for all synthesized CaO-based sorbents.



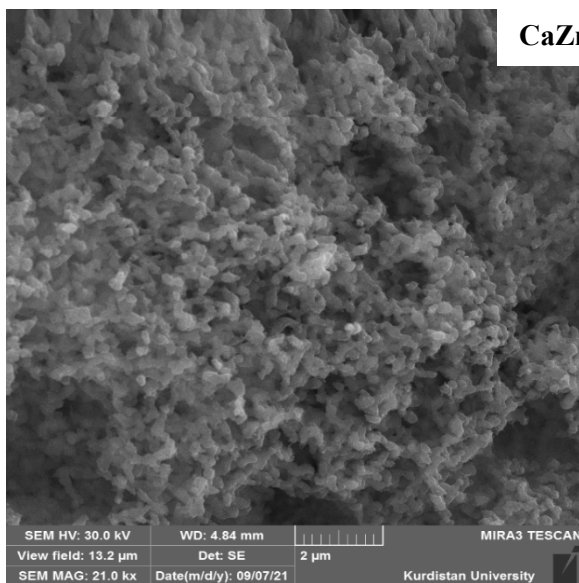
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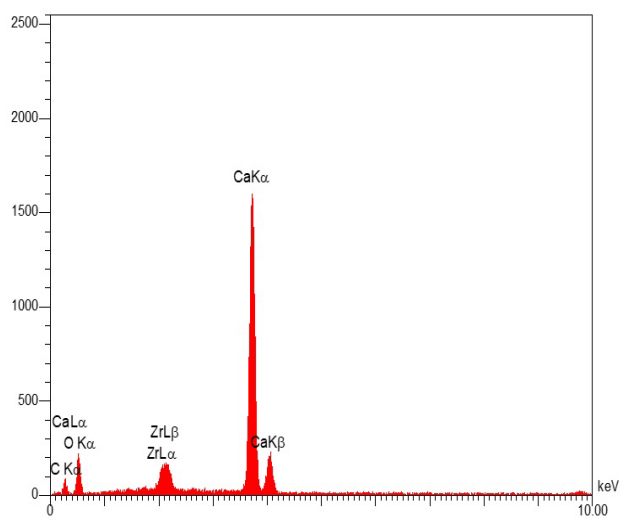
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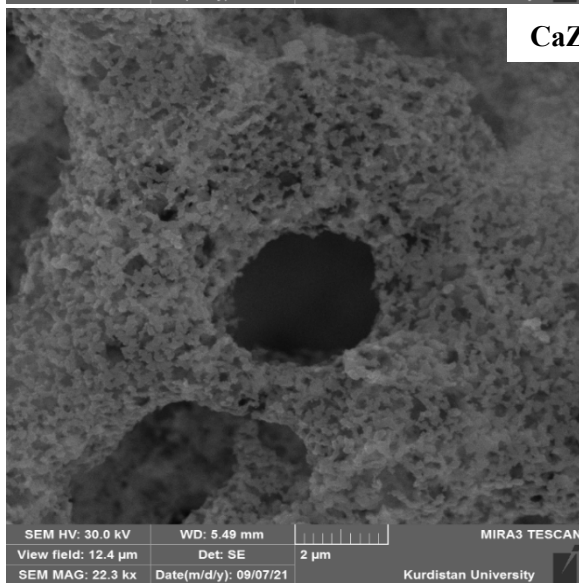
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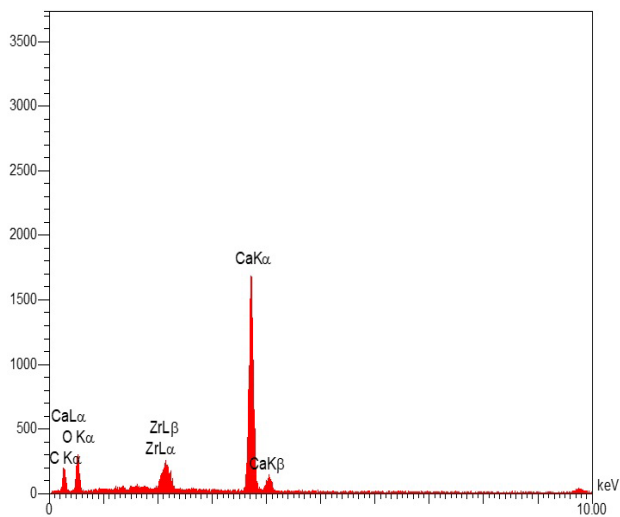
CaZr15-C2.5



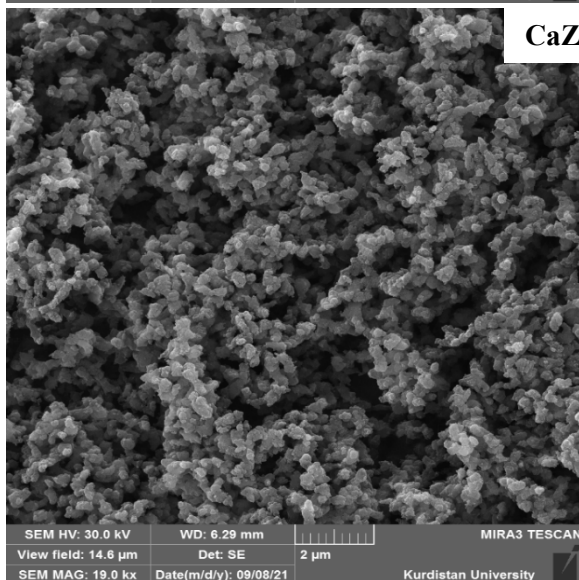
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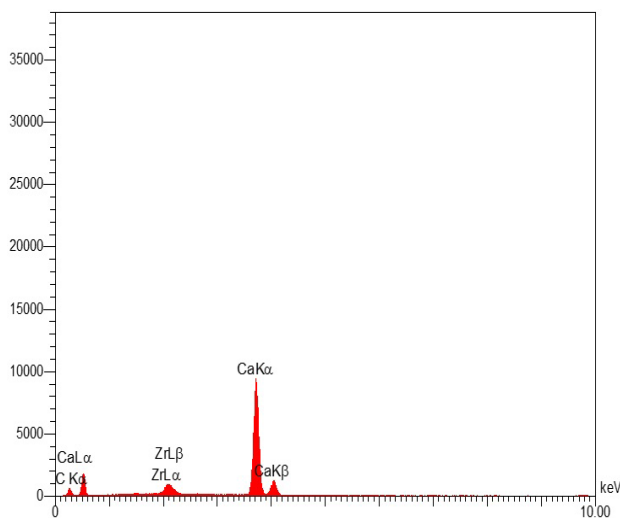
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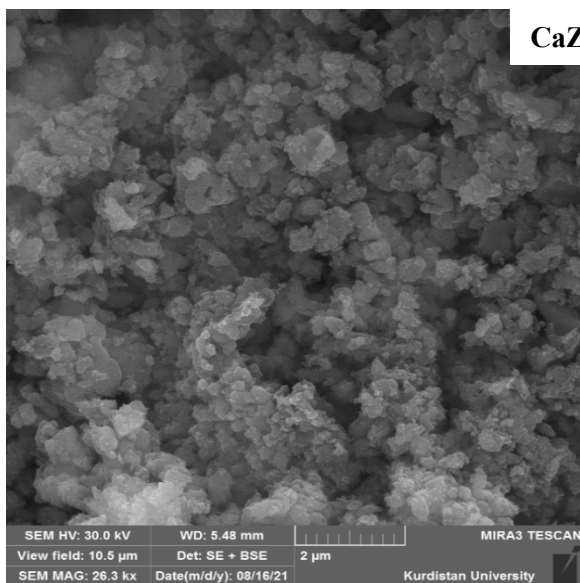
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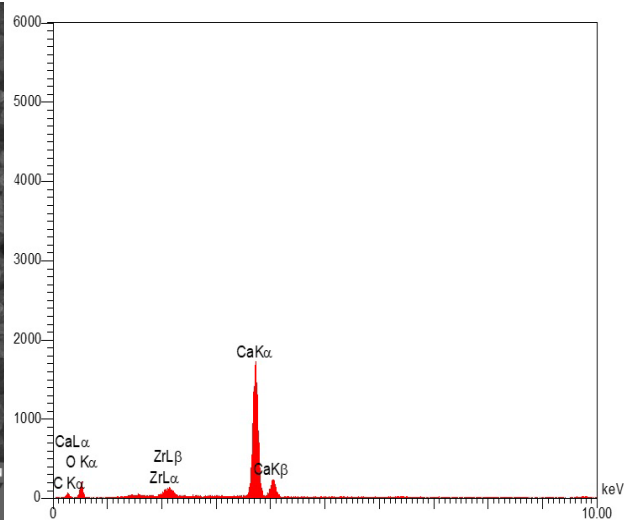
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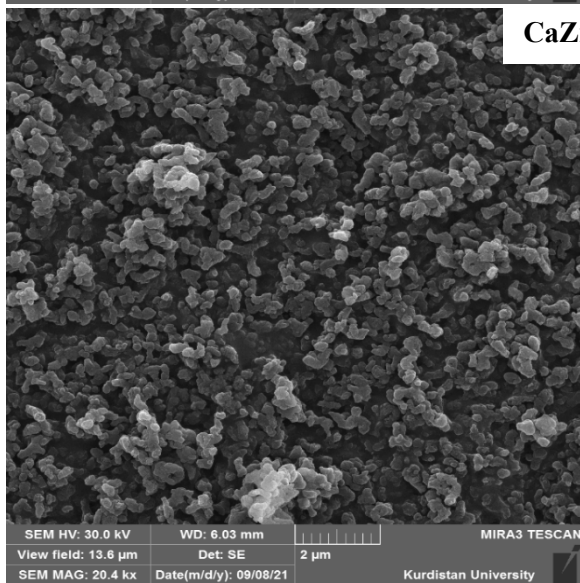
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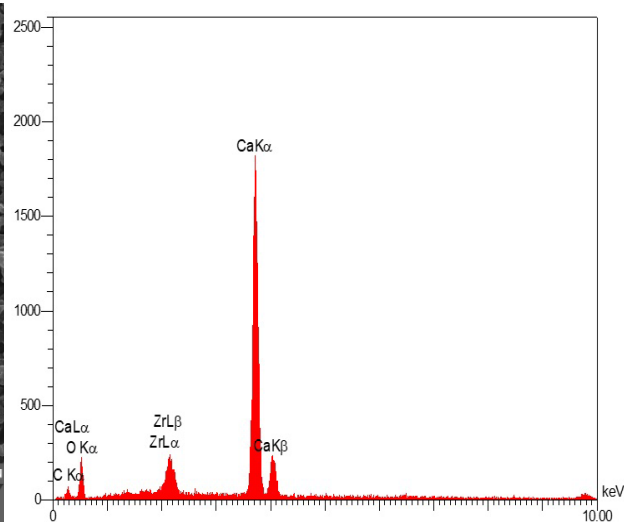
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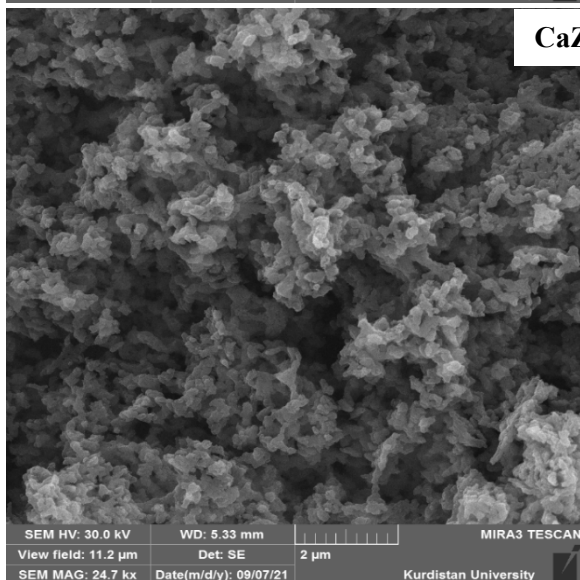
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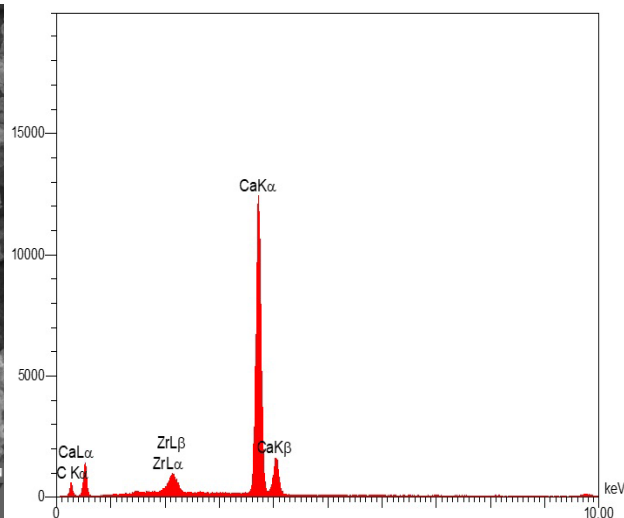
CaZr30-C2.5



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CaZr30-C5



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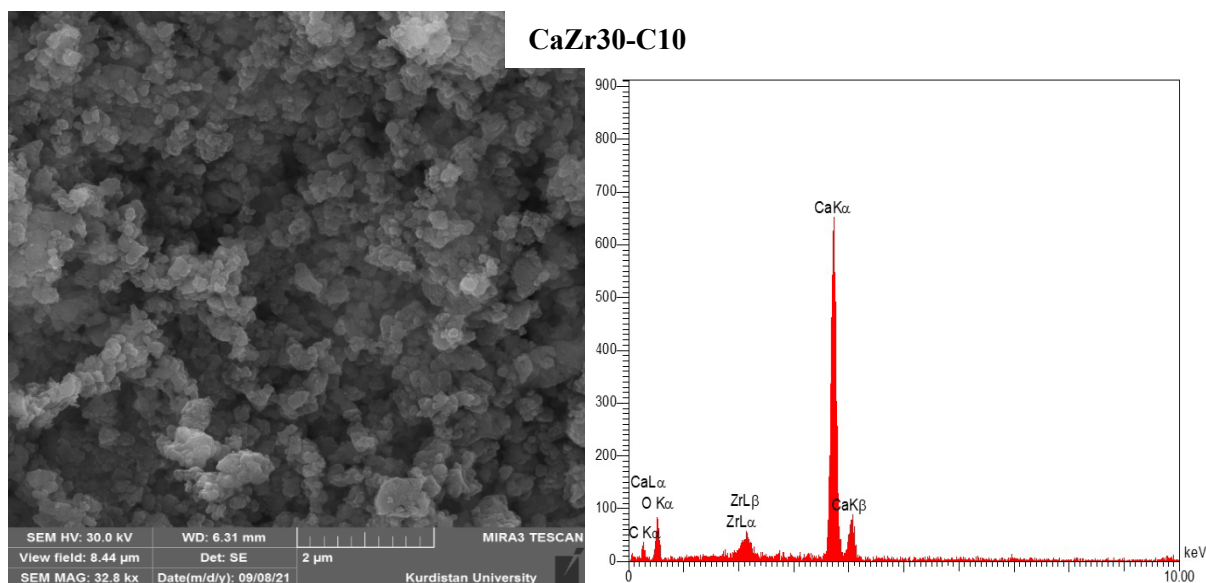


Fig. S2: SEM images and elemental EDS of pure CaO, CaZr15-C0, CaZr15-C2.5, CaZr15-C5, CaZr15-C10, CaZr30-C0, CaZr30-C2.5, CaZr30-C5, and CaZr30-C0.

CO₂ capture activity

To assess the role of CNT on the CO₂ uptake activity of CaZr15-C0 and CaZr, the CO₂ capture capacity of pure CaO, CaZr15-C0, CaZr15-C2.5, CaZr15-C5, and CaZr15-C10 during 1st and 15th cycles versus carbonation time is plotted in **Fig. S3a** and **b**, respectively. The highest initial capture capacity belongs to pure CaO due to its higher content of free CaO compared to Zr-promoted CaO sorbents containing 18.5 wt.% CaZrO₃. Since pure CaO suffers more from sintering and deactivation due to its lower thermal-durability feature and less porosity, the synthesized Zr-promoted sorbents present better CO₂ capture profiles than pure CaO at 15th cycles. The higher amount of CO₂ is adsorbed by CNT-templated samples compared to CaZr15-C0 at the 15th cycle. Even though CaZr15-C5 shows lower CO₂ capture capacity than CaZr15-C10 for an initial 5 min at the 15th cycle, ultimately, CaZr15-C5 adsorbs the more amount of CO₂ at the 15th carbonation step. However, over time, CaZr15-C5 presents a larger capture capacity than CaZr15-C10 at the ultimate cycle, indicating the more CO₂ capture capacity of CaZr15-C5 related to the capture process by CaO sites located in the interior zones. The larger volume of pore and porous zones in CaZr15-C5 than in

CaZr15-C10 results in a significantly more content of adsorbed CO₂ at the end of the carbonation stage.

It has been previously mentioned that merging CaO with costly ZrO₂ promoters decreases the available CaO for CO₂ capture during the formation of thermal-durable CaZrO₃. In this regard, the influence of CNT, in diverse contents of 2.5, 5, and 10 wt.%, on CaZr30-C0, containing the less CaZrO₃ content of 10 wt.% compared to CaZr15-C0 (18.5 wt.%), is assessed. **Fig. S3c** and **d** plot the CO₂ capture profiles of CaZr30-C0, CaZr30-C2.5, CaZr30-C5, and CaZr30-C10 during the carbonation time at the 1st and 15th cycles, respectively. The CNT-templated samples captured more CO₂ during the initial and final carbonation cycles compared to CNT-free counterparts, which similarly corroborates the effectiveness of CNT. Despite the identical CO₂ adsorption capacity at the swift carbonation step, the more porosity of CaZr30-C5 compared to CaZr30-C10 contributes to its better sorption activity in the slow carbonation stages, accompanied by the higher capture capacity of (0.372 g CO₂/g sorbent) than that of CaZr30-C10 (0.347 g CO₂/g sorbent) at 1st cycles. Nonetheless, to a large extent, CaZr30-C5 and CaZr30-C10 exhibit equal capacity at the 15th cycle (0.149 and 0.151 g CO₂/g sorbent).

Fig. S4a and **b** illustrate the CO₂ capture rate of pure CaO and prepared samples with a Ca/Zr molar ratio of 15/1 versus carbonation time at the 1st and 15th cycles. There are two distinct carbonation stages based on the CO₂ capture rate profile: a kinetically swift carbonation stage and a diffusion-controlled slow carbonation stage. The fast carbonation, which relates to the reaction of easy-accessible CaO surface with CO₂, consists of the uptrend CO₂ capture rate. Additionally, the slow carbonation stage corresponds to the reaction between CO₂ molecules and interior CaO sites in pores of sorbent texture. After reaching the maximum CO₂ capture rate, the fast carbonation stage terminates, and the slow carbonation stage starts with the diffusion of CO₂ into inner zones. Although prepared samples with a

Ca/Zr molar ratio of 15/1 demonstrate identical capture capacity at the fast carbonation stage, the more porous regions and pores' volume of CaZr15-C2.5, CaZr15-C5, and CaZr15-C10 cause the higher capture capacity at the diffusion carbonation stage. Due to the lower easy-accessible CaO surface, CaZr15-C0 reaches a higher maximum CO₂ capture rate at less time in 1st cycle, indicative of its less fast carbonation than CNT-templated counterparts. The main reason for the higher maximum CO₂ capture rate of CaZr15-C0 compared to CNT-templated samples is its higher free CaO content that utterly saturates at ~ 0.2 min. According to **Fig. S3b**, the higher uptake capacity of CaZr15-C10 rather than CaZr15-C5 for an initial 5 min of carbonation is associated with a significantly higher uptake rate at the termination of the quick carbonation stage, which can be attributed to its higher easy-accessible CaO sites. Comparing the CO₂ capture rate curves for 1st and 15 cycles demonstrates the effect of sintering on decreasing the fast carbonation time by ~ 50% owing to the sintering phenomenon and diminishing the easy-accessible CaO surface.

The CO₂ capture rate diagrams of samples developed with a Ca/Zr molar ratio of 30/1 at the 1st and 15th cycles, derived from **Fig. S3c** and **d**, are plotted in **Fig. S4c** and **d**. These figures indicate that the sintering rate of easy-accessible CaO sites over cycles reduces the fast carbonation span at the 15th cycle compared to the initial cycles. A higher CO₂ capture rate for CaZr30-C5 after ~1 and ~0.5 min at the 1st and 15th carbonation steps, respectively, can be ascribed to its more suitable textural and structural characteristics. Among developed samples with a Ca/Zr molar ratio of 30/1, the highest maximum CO₂ capture rates at the end of the 1st and 15th fast carbonation stages are reported in the case of CaZr30-C10.

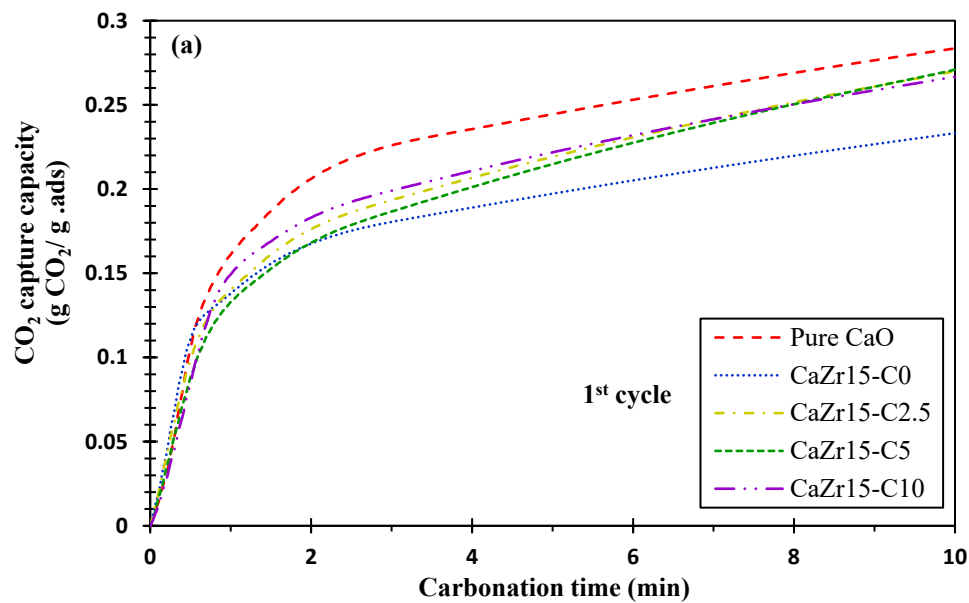
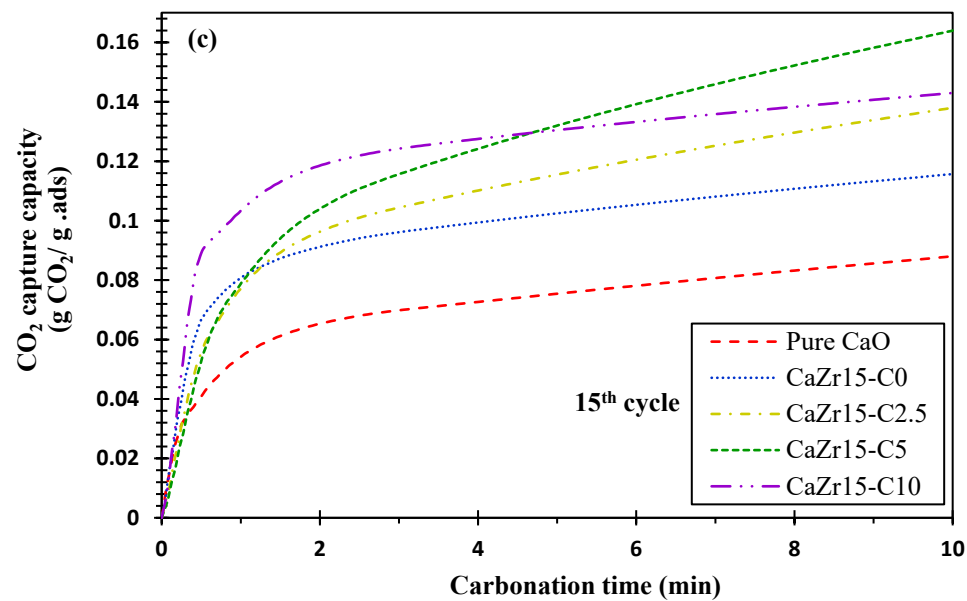
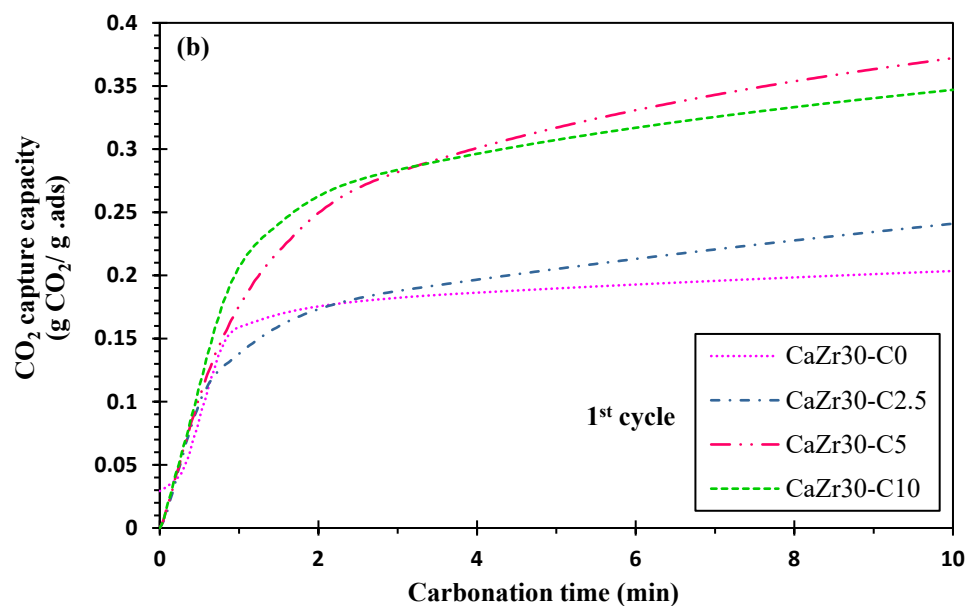
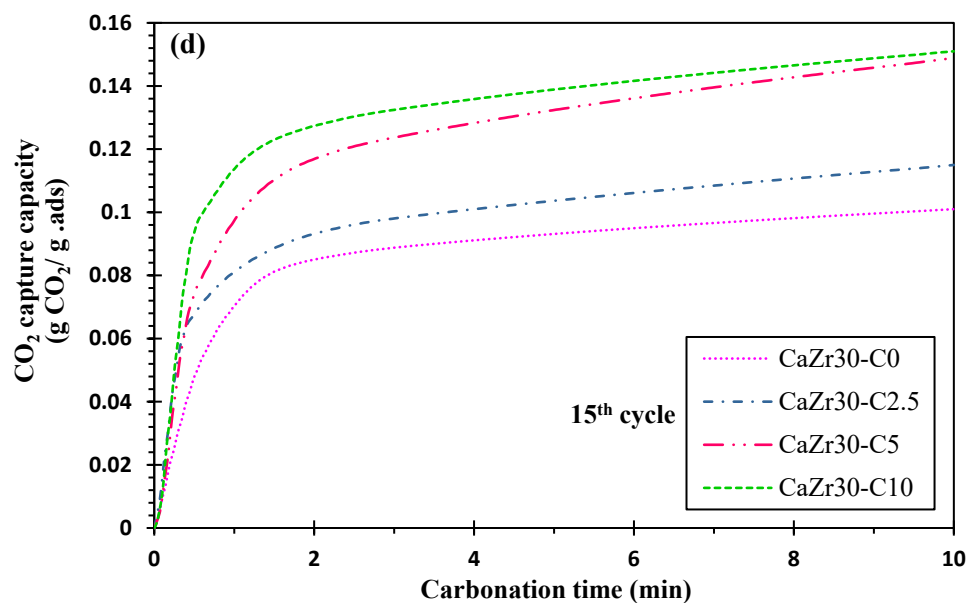


Fig. S3: Evaluation CO₂ capture capacity during carbonation time at 1st and 15th cycles for samples developed with Ca/Zr molar ratios of (a and b, respectively) 15/1 and (c and d, respectively) 30/1, under severe CaL conditions.

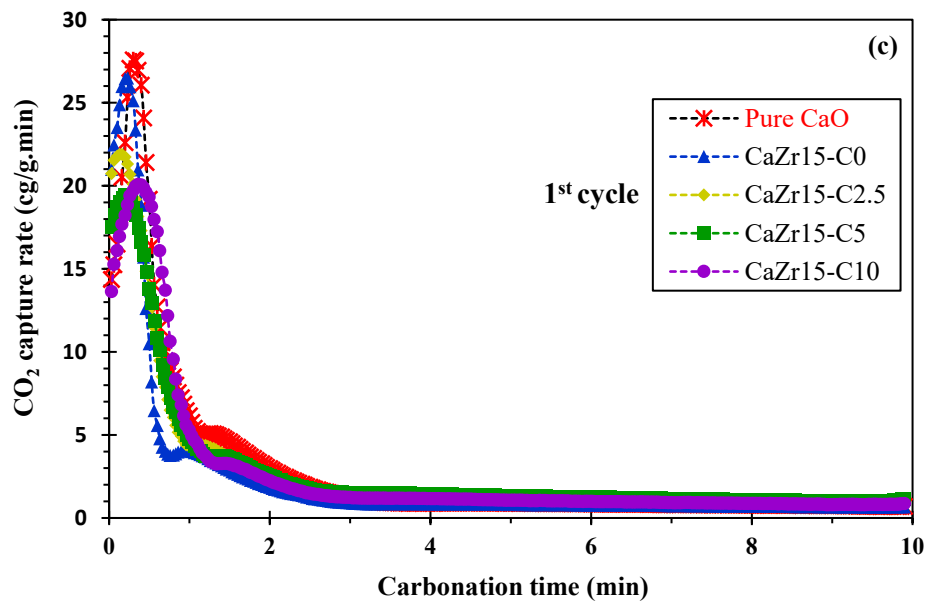
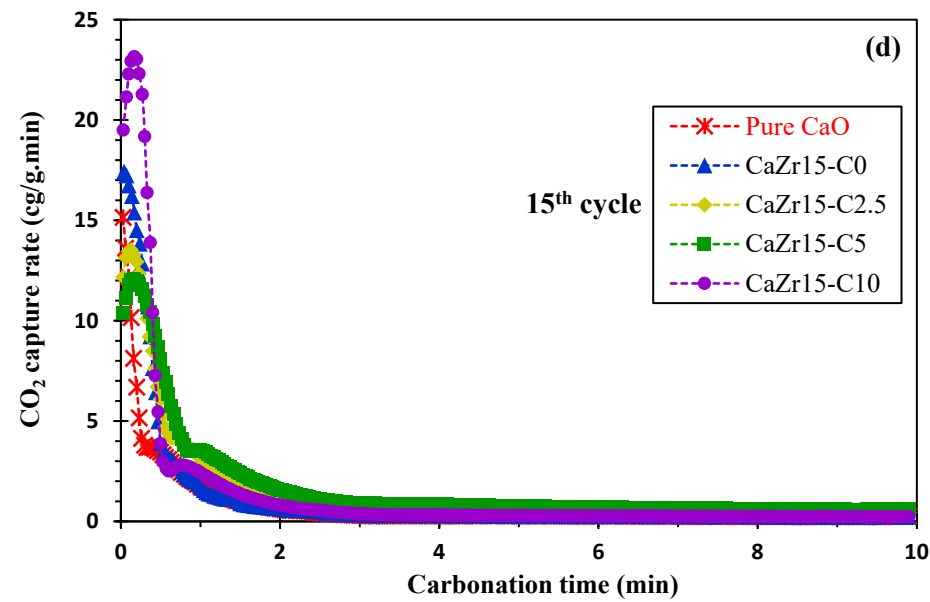
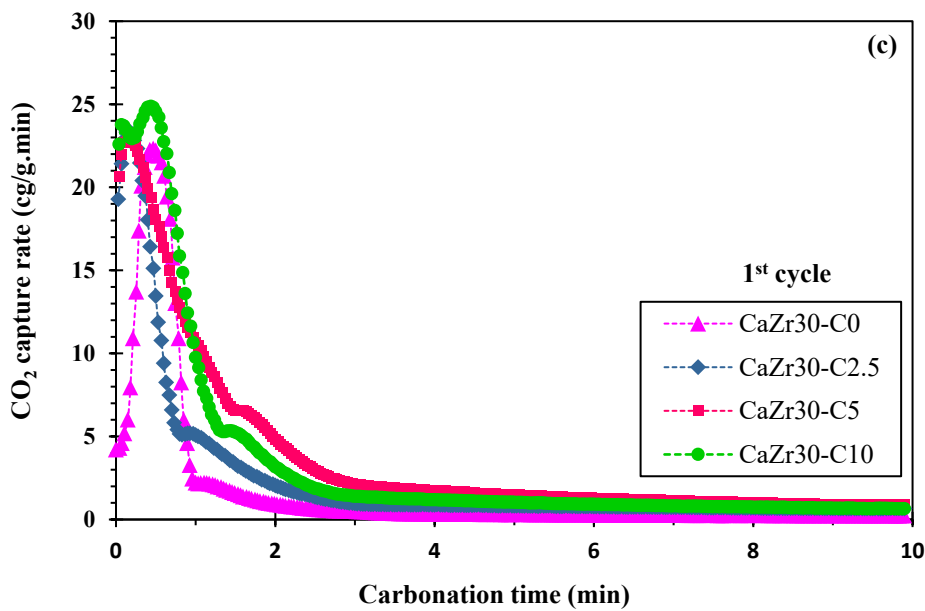
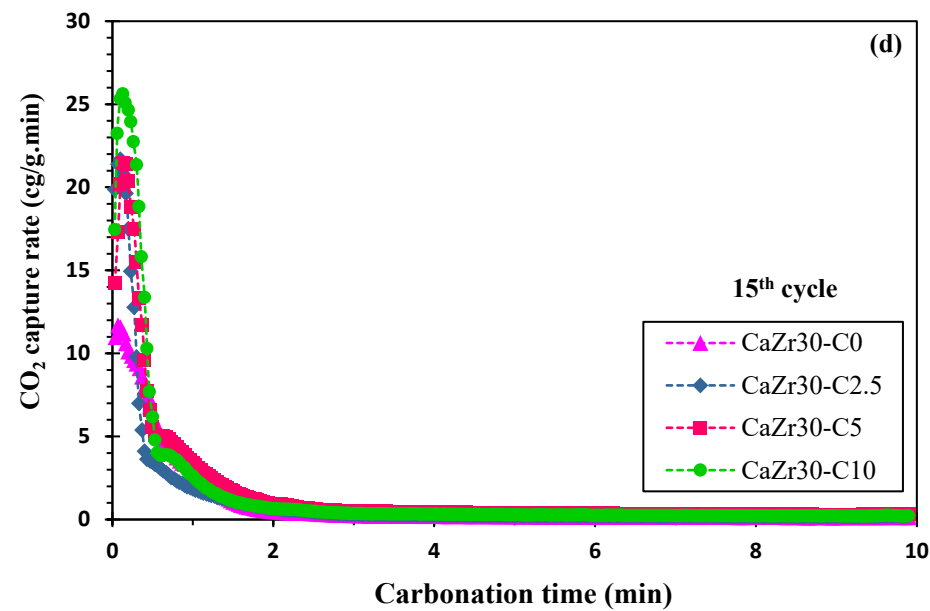


Fig. S4: Evaluation CO₂ capture capacity during carbonation time at 1st and 15th cycles for samples developed with Ca/Zr molar ratios of (a and b, respectively) 15/1 and (c and d, respectively) 30/1, under severe CaL conditions



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