



Selective separation of carbon dioxide from biogas mixture using mesoporous ceria and zirconium hydroxide

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Abstract

Biogas is considered to be one of the potential and viable renewable energy resources. However, the presence of CO₂ in biogas increases the cost of its transportation. Therefore, the removal of CO₂ is of utmost essential to ensure the economic viability of the bio-gas utilisation technology. Among the various routes, pressure swing adsorption (PSA) may be considered more economically viable when adsorbent selectivity is high and heat of adsorption is low. In this work, we have synthesized mesoporous cerium oxide (CeO₂) and zirconium hydroxide (Zr(OH)₄) which possess approximately two orders of magnitude higher selectivity for the removal of CO₂ from biogas mixture compared to commercial zeolite (Na-Zeolite Y) and commercial granular activated carbon. In addition, the methane slip in CeO₂ (0.16%) was five times lower than Zr(OH)₄ (0.62%) and two orders of magnitude lower than activated carbon (18%). The high selectivity and low methane slip of ceria can be attributed to the large number of heterogeneous sites available for selective adsorption of CO₂. Based on our results on CO₂ selectivity and methane loss, we conclude that CeO₂ could be a potential adsorbent for biogas purification using PSA.

Keywords Biogas purification · CO₂ adsorption · CH₄ adsorption · Cerium oxide · Zirconium hydroxide · Pressure swing adsorption

1 Introduction

The depletion of fossil fuels for energy has forced us to look for potential alternative renewable energy resources such as biomass, solar, wind, etc. Among them, biomass-based biogas is considered as a potential option due to its

high energy density, safety, and biomass-waste availability (Kumar et al. 2015; Chaemchuen et al. 2013). The biogas produced from bio-waste primarily consists of methane CH₄ and CO₂, along with traces of hydrogen sulfide, nitrogen, and ammonia (Chaemchuen et al. 2013; Zhao et al. 2010). However, the presence of more than 40% of CO₂, significantly increases the cost of its transportation (Bae et al. 2008; Di Profio et al. 2017; Xue and Liu 2011). Therefore, the removal of carbon dioxide from biogas is paramount for making the Biogas transportation and utilization technologies commercially viable (Cebula 2009; Friess et al. 2017).

There are various methods used for selective removal of CO₂ from biogas: amine absorption, cryogenic separation, membrane separation, water-scrubbing, and adsorptive separation process (Jeon and Lee 2015; Phalakornkule et al. 2012; Yan et al. 2015; Yuan et al. 2013). Although amine-absorption, cryogenic and membrane separations are selective for the removal of CO₂, they are associated with high specific energy consumption and operating costs (Bacsik et al. 2016; D'Alessandro et al. 2010; Kamimura et al. 2014). Consequently, PSA has gained attention owing to its lower specific energy, and process simplicity, and

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particularly preferred where trace amounts of CO₂ are acceptable (Grande 2012; Oreggioni 2015).

Several adsorbents, i.e., metal-organic frameworks and zeolite imidazole frameworks (Babarao and Jiang 2011; Wu et al. 2014; Yaghi 2008), porous carbons (Coromina et al. 2016; Jalilov et al. 2015; Sangchoom and Mokaya 2015; Sha et al. 2015; Álvarez-Gutiérrez et al. 2016) and zeolites (Grande 2011; Snider and Verweij 2014; Zhang et al. 2008), have been attempted for biogas PSA process. However, most of the commercially available materials such as zeolites and carbon have shown high CO₂ adsorption capacity of the adsorbents and but less selectivity for CO₂ over methane. Considering the limitations, few researchers are now exploring the potential of metal oxides and metal hydroxides for the removal of CO₂. Although these types of adsorbents were previously investigated for CO₂ removal from flue gas, their potential, particularly for biogas purification, is being explored now (Babu et al. 2017; Mutch et al. 2018; Wang et al. 2016; Yu et al. 2018). The low cost, high tapping density, and high selectivity of these oxides and hydroxides make them a potential candidate for the PSA process (Kamimura and Endo 2016; Kim et al. 2015; Pevida et al. 2014). Until now, the oxides of aluminium, cerium, iron, zirconium, lithium, ceria, zirconia etc. have been reported for CO₂ adsorption processes (Bachiller-Baeza et al. 1998; Baltrusaitis et al. 2011; Baltrusaitis and Grassian 2005; Hornebecq et al. 2011; Li et al. 2009; Mosqueda et al. 2006). Among them, to the best of our knowledge, a study on selectivity, methane slip, the adsorption capacity of cerium oxide and zirconium hydroxide for selective removal of CO₂ from biogas mixture (Bacsik et al. 2016; Ben et al. 2012; Li et al. 2013; Kamimura et al. 2014; Yoshikawa et al. 2014) using PSA has not been explored.

In this work, we intend to compare the PSA performance of ceria and zirconium hydroxide for biogas mixture separation. Particularly, we have studied the adsorption capacity, selectivity, and methane slip of ceria and zirconium hydroxide using CO₂ and CH₄ gas system in a high-pressure volumetric analyzer (HPVA-100) up to 11 bar. The results clearly suggested that CeO₂ and Zr(OH)₄ were far superior compared to commercial zeolite (Na-Zeolite Y) and activated carbon (GAC) for biogas purification applications.

2 Experimental

2.1 Raw materials

Cerium nitrate hexahydrate (Ce(NO₃)₂·6H₂O), zirconium nitrate, and sodium zeolite-Y powder used for synthesis were procured from Sigma Aldrich. Sodium hydroxide pellets and Granular activated carbon were obtained from Merck. Ultra-pure deionized water was used through

the synthesis of ceria and zirconium hydroxide. Similarly, high-purity CO₂ (99.998%), CH₄ (99.998%) and He (99.998%) were used for high-pressure adsorption experiments.

2.2 Synthesis of mesoporous CeO₂ and Zr(OH)₄

The mesoporous cerium oxide, i.e. hereafter referred to as ceria, was synthesized using an easy-to-handle template-free method that permits precipitation of mesoporous ceria nanoparticles from sodium hydroxide solution (Kamimura et al. 2014). Initially, a solution of NaOH in H₂O was mixed in a glass beaker with a molar ratio of 0.0045 mol NaOH/mol H₂O and cerium(III) nitrate 6-hydrate was added to NaOH aqueous solution at a molar ratio of 0.15 mol CeO₂/mol NaOH. The solution was then stirred for 2 h at room temperature in bubbling air and subsequently filtered, washed with deionized water until pH reached 7. The yellow precipitate recovered was then dried at 100 °C for 12 h to obtain mesoporous ceria.

The mesoporous zirconium hydroxide was also made using the solution synthesis method (Kamimura and Endo 2016). Initially, NaOH in water solution was prepared at a molar ratio 0.009 mol NaOH/mol H₂O and mixed with a solution of Zr(NO₃)₂·2H₂O in water prepared at 0.01 mol Zr(OH)₄/mol NaOH molar ratio. The mixture was stirred for 24 h and filtered. The white precipitate obtained was washed with deionized water and dried at 100 °C for 12 h to obtain zirconium hydroxide.

2.3 Material characterization

The powder XRD data of cerium oxide and zirconium hydroxide was recorded using a powder X-ray diffractometer (Rigaku Miniflex) using Cu K α radiation ($\lambda = 0.15406$ nm, 40 kV, 40 mA) at 2θ values of 10–90° and a scanning speed of 3° min⁻¹. The samples were pulverized before the sample was analyzed in XRD.

In addition to the crystal structure, the pore size distribution was determined from Density Functional Theory (DFT) by analysis of N₂ adsorption–desorption measurements at 77 K using a Quantachrome Autosorb (& the associated software) and the pore size distribution was modelled in DFT using both the adsorption and desorption branches. The CeO₂ and Zr(OH)₄ were degassed at 120 °C for 12 h, whereas the GAC, zeolite-Y were degassed at 300 °C for 12 h. The specific surface area of samples was estimated using the Brunauer–Emmett–Teller (BET) method within the relative pressure range from 0.02 to 0.99. The total pore volume was calculated based on the nitrogen adsorbed at a relative pressure of 0.99.

2.4 CO₂ and CH₄ high-pressure adsorption

The CO₂ and CH₄ pure component adsorption and desorption were measured using High-Pressure Volumetric Analyser II (HPVA-100) from Micromeritics Instruments Ltd. at 298 K up to 11 bar. Before the adsorption experiments, the sample was degassed at 0.020 mbar (HPVA II Series 2013) for 12 h while maintaining the temperature at 120 °C for CeO₂ and Zr(OH)₄ and 300 °C for zeolite-Y and GAC.

3 Results and discussions

3.1 XRD analysis

The XRD pattern of cerium oxide is shown in Fig. 1. The distinct peaks observed at 28.5°, 33°, 47.5°, 56.4°, 69.7°, and 78° clearly corroborated with the crystal structure of ceria (Kamimura et al. 2014). Similarly, Fig. 2 shows two broad peaks at about 31° and 52° in the XRD pattern of zirconium hydroxide, which is consistent with earlier reported results (Kamimura and Endo 2016). Overall, the XRD analysis confirmed the targeted synthesis of the ceria and zirconium hydroxide.

3.2 Surface and pore characteristics of adsorbents

Since the surface characteristics play an indispensable role in determining the selectivity, the N₂ adsorption–desorption isotherm experiments were studied to inspect surface characteristics of CeO₂, zirconium hydroxide, GAC, and zeolite-Y. Figure 3a, b show the nitrogen adsorption–desorption isotherms for CeO₂, Zr(OH)₄, and GAC, zeolite-Y respectively. Similarly, Fig. 4a, b show the pore-size distribution for ceria, zirconium hydroxide, and GAC, zeolite-Y respectively. Additionally, the surface area, total pore volume, micropore

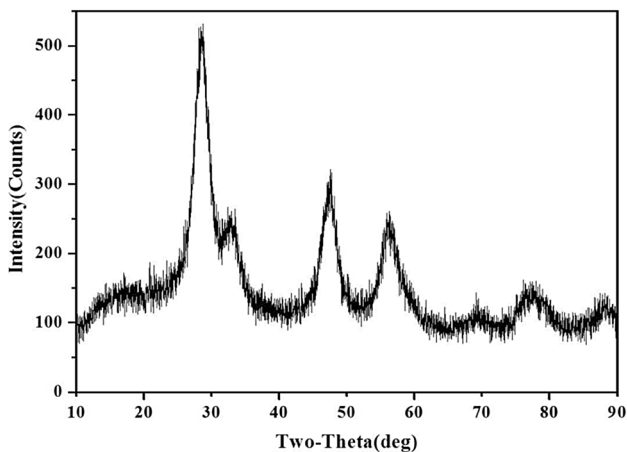


Fig. 1 X-ray diffraction pattern of mesoporous CeO₂

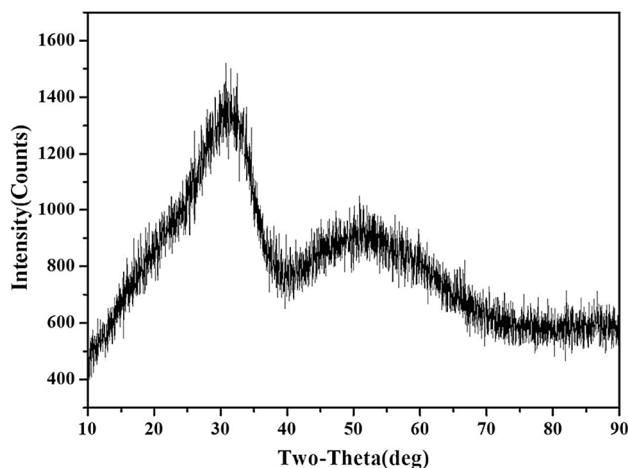


Fig. 2 X-ray diffraction pattern of mesoporous Zr(OH)₄

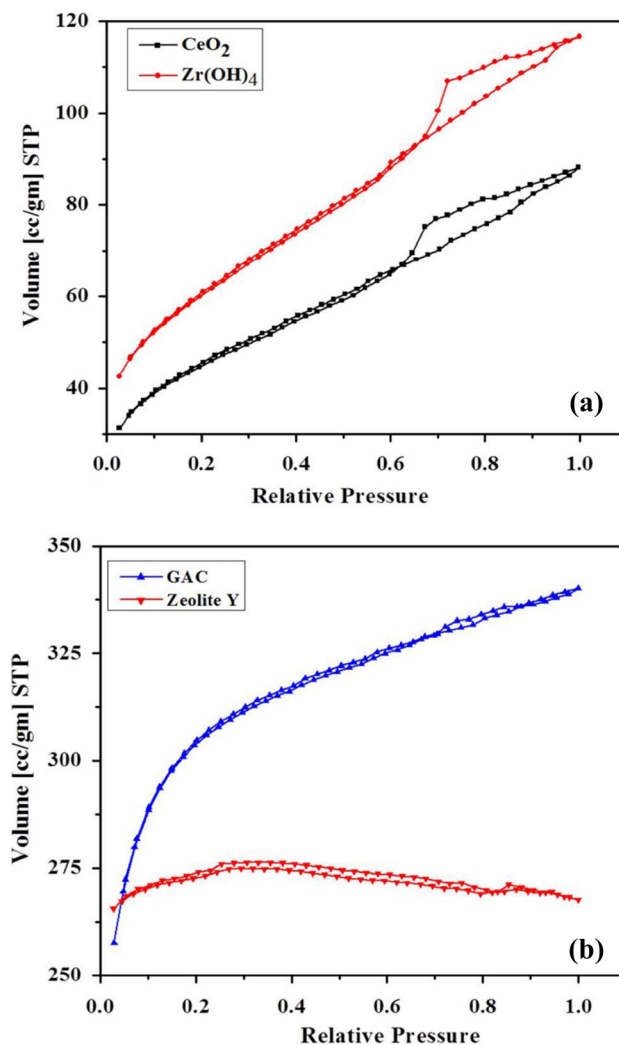


Fig. 3 N₂ adsorption–desorption isotherms at 77 K a CeO₂, Zr(OH)₄, b GAC and Zeolite-Y

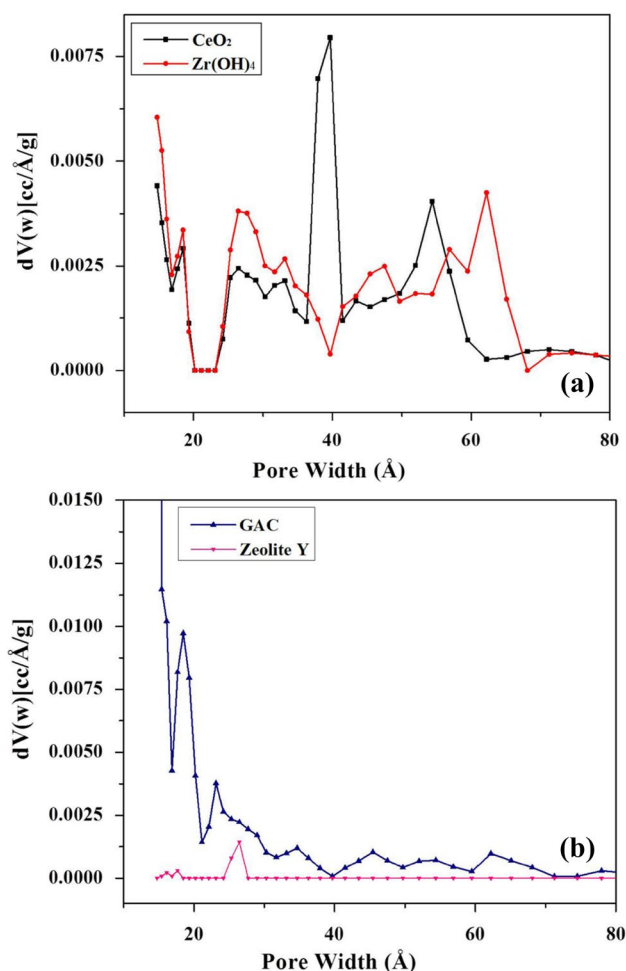


Fig. 4 Pore size distribution of **a** CeO_2 , $\text{Zr}(\text{OH})_4$ and **b** GAC, Zeolite-Y evaluated by density functional theory (DFT)

volume and micropore area estimated from the isotherms are shown in Table 1.

The presence of hysteresis in the adsorption–desorption loop clearly indicates the characteristics of type IV isotherm and the presence of significant mesopores for ceria, zirconium hydroxide. This has been further confirmed from Table 1 which shows that these adsorbents possess more than 60% (by volume) of the mesopores. Figure 3b shows the N_2 adsorption isotherms for GAC and NaY are similar

to IUPAC Type I isotherms, for which the majority of the adsorbent pore volume is microporous. This is confirmed in Table 1, where the micropore volume of these adsorbents is at least 85%. Table 1 also shows that both CeO_2 and $\text{Zr}(\text{OH})_4$ possess far lower surface area than either GAC or NaY. The latter has more numerous micropores with smaller average pore sizes below 2.5 nm.

Considering the surface area, the CeO_2 ($154 \text{ m}^2/\text{g}$) and $\text{Zr}(\text{OH})_4$ ($208 \text{ m}^2/\text{g}$) possess far lesser surface area compared to GAC ($916 \text{ m}^2/\text{g}$) and zeolite-Y ($795 \text{ m}^2/\text{g}$) due to the presence of micropores in the latter. The presence of more than 85% (by volume) micropores and pore diameter less than 2.5 nm, gives the high surface area for GAC and zeolite-Y.

3.3 CO_2 and CH_4 adsorption capacities

In order to find the actual gas storage capacities of CeO_2 , $\text{Zr}(\text{OH})_4$, GAC and zeolite-Y, the pure component adsorption isotherms were measured at 298 K at up to 11 bar for both CO_2 and CH_4 on all four previously characterized adsorbents and results are shown in Fig. 5a–d.

The isotherm parameters and the coefficient of regression estimated after curve-fitting are given in Table 2. In this work, the sips equation (supplementary material equation no. 9) was fitted to the isotherm data using the MATLAB non-linear curve fitting toolbox.

It is clear from Fig. 5 and Table 2 that the GAC possesses the highest CO_2 adsorption capacity and the order of adsorption capacity follows as shown: $\text{GAC} > \text{zeolite-Y} > \text{CeO}_2 > \text{Zr}(\text{OH})_4$. The maximum adsorption capacity (mmol/g) values from the Sips equation (supplementary material Eqs. 1–9) clearly show that GAC has almost twice the capacity of zeolite-Y, 2.5 times that of CeO_2 and 5 times of that of $\text{Zr}(\text{OH})_4$. Likewise, GAC also has high CH_4 adsorption capacities and the order of capacities follows as shown: $\text{GAC} > \text{zeolite-Y} > \text{Zr}(\text{OH})_4 > \text{CeO}_2$. This undoubtedly indicates that the GAC doesn't possess much selectivity for CO_2 over CH_4 compared to other adsorbents.

Table 2 also shows the heterogeneity factor (n) for CeO_2 and $\text{Zr}(\text{OH})_4$ were 2.33 and 2.12, whereas for zeolite-Y and GAC it was 1.34 and 1.18 respectively. The relatively higher value of n for CeO_2 and $\text{Zr}(\text{OH})_4$ is a clear indication that ceria and zirconium hydroxide have a more heterogeneous

Table 1 Surface and pore characteristics of adsorbents

Adsorbent	Surface area (m^2/g)	Total pore volume (cc/g)	Average diameter of pore (\AA)	Micropore volume (cc/g) and % of total	Micropore area (m^2/g) and % of total
CeO_2	154.80	0.14	35.32	0.05 (36%)	94.61 (61.1%)
$\text{Zr}(\text{OH})_4$	208.10	0.18	34.76	0.07 (39%)	127.70 (61.3%)
GAC	916.20	0.53	23.03	0.45 (85%)	856.20 (93.5%)
Zeolite-Y	795.20	0.42	20.88	0.43 (100%)	800.00 (100%)

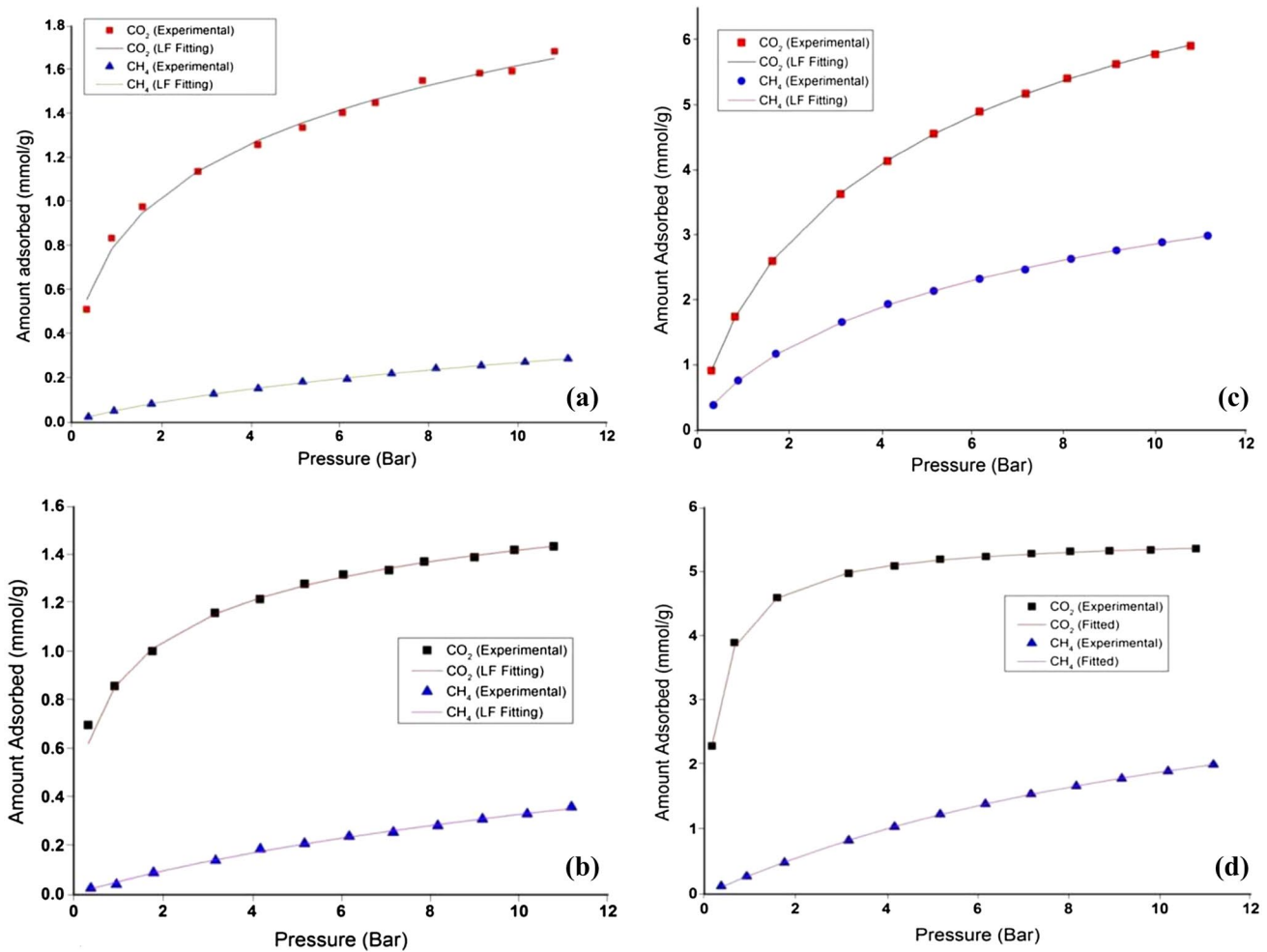


Fig. 5 CO₂ and CH₄ isotherms of a CeO₂, b Zr(OH)₄, c GAC, and d Zeolite-Y at 298 K and 10 bar

Table 2 Langmuir–Freundlich (Sips) isotherm parameters for ceria, zirconium hydroxide, GAC and zeolite-Y at 298 K

Adsorbent	Adsorbate	Isotherm parameters			R ²
		q _{m1} (mmol/g)	K ₁ (bar ⁻¹)	n ₁	
CeO ₂	CO ₂	3.9	0.2647	2.333	0.9923
	CH ₄	0.9308	0.06185	1.215	0.9994
Zr(OH) ₄	CO ₂	2.077	0.7302	2.119	0.9978
	CH ₄	1.176	0.04887	1.107	0.9961
GAC	CO ₂	10.08	0.2422	1.34	0.9999
	CH ₄	5.873	0.1638	1.308	0.9998
Zeolite-Y	CO ₂	5.6	3.055	1.182	0.9997
	CH ₄	3.46	0.1836	0.9279	0.9997

adsorption site energy distribution, which can facilitate increased selectivity towards either CO₂ or CH₄. Lower values of the heterogeneity factor for NaY and GAC indicate a more homogeneous adsorption site energy distribution

and associated lower selectivity towards the components of biogas.

3.4 Selectivity of CO₂ over CH₄

The selectivity of CO₂ over CH₄ is one of the important factors for selecting a biogas purification adsorbent since lower selectivity often leads to high methane loss in the PSA process (Couck et al. 2009; Mastalerz et al. 2011). The selectivity was calculated using the IAST model from the single-component isotherm from 0.3 to 10 bar for mole fractions of CO₂ from 0.3 to 0.6. These mole fractions were considered based on a typical range of CO₂ concentration in the biogas mixture.

Figure 6 shows the selectivity for a feed mixture with 50% CO₂ for a PSA pressure range of 0.3–10 bar. The selectivity values at 10 bar are as follows: cerium oxide-360 > zirconium hydroxide-180 > zeolite Y-150 > GAC-5. It is evident that the selectivity of ceria is about two

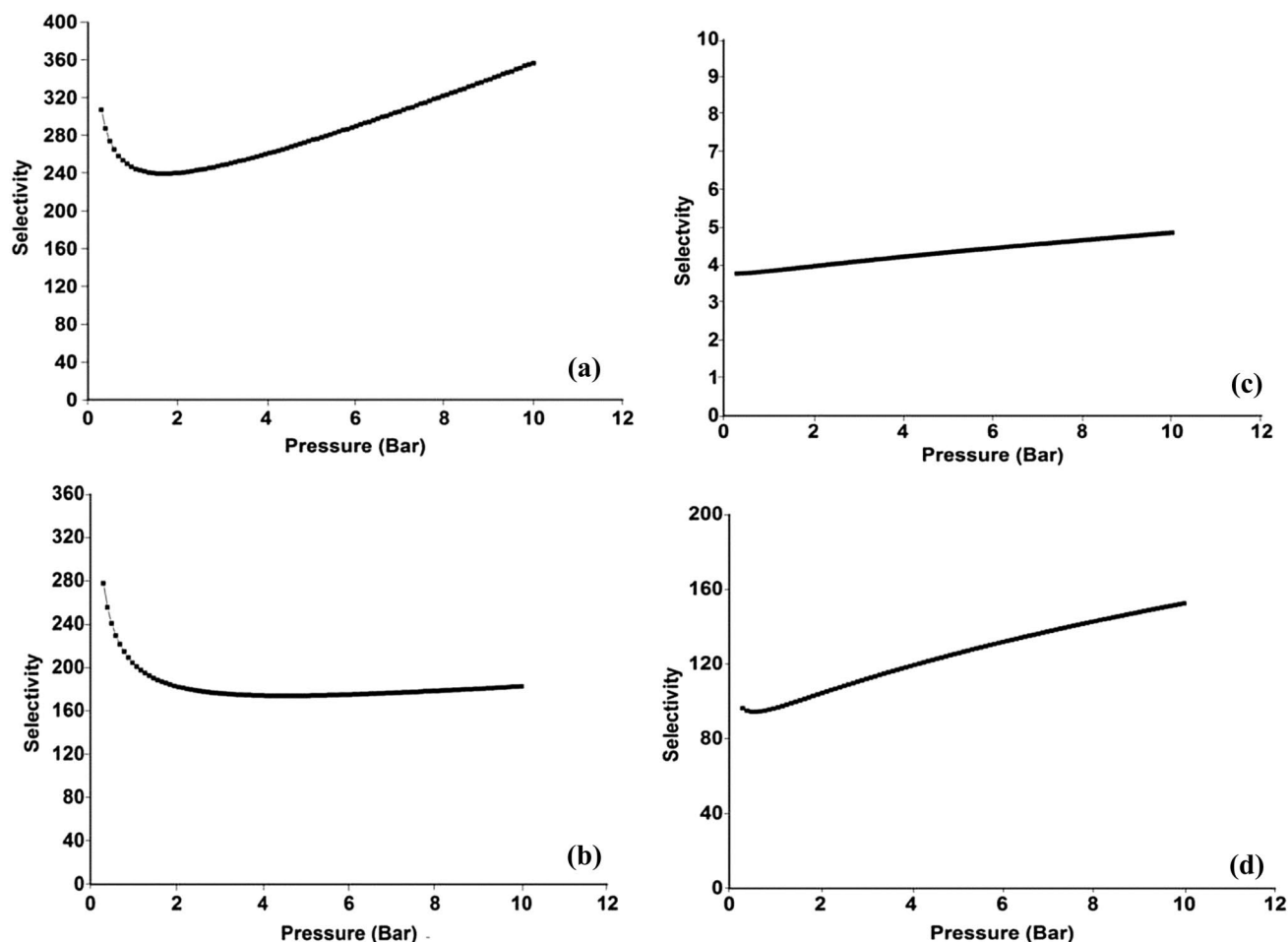


Fig. 6 CO₂/CH₄ selectivity of **a** CeO₂, **b** Zr(OH)₄, **c** GAC, and **d** Zeolite-Y

Table 3 Amount of CO₂, CH₄ adsorbed (mmol/g) for various adsorbents at 298 K and 10 bar pressure and its pseudo selectivity

Adsorbent	Adsorbate		Pseudo selectivity
	CO ₂ (mmol/g)	CH ₄ (mmol/g)	
CeO ₂	1.7	0.3	5.7
Zr(OH) ₄	1.4	0.4	3.5
GAC	5.9	2.9	2.0
Zeolite-Y	5.4	2	2.7

times larger than zirconium hydroxide, zeolite-Y and an order of magnitude larger than GAC. The high selectivity of ceria could be attributed to the presence of a large number of heterogeneous adsorption sites, as evident from the high heterogeneity factor n in the sips isotherm. The pattern of predicted selectivity of adsorbents also correlated well with the pseudo selectivity values that are given in Table 3. Here, the term pseudo selectivity is

defined based on the experimental values observed from the single-component adsorption and it is the ratio of CO₂ adsorbed to the CH₄ adsorbed at 10 bar.

It is also noted from Figs. 6 and 7 that the selectivity of ceria increases with increasing pressure and mole fraction of CO₂. This can be attributed to increasing vertical interactions between the strongly adsorbed species and the surface adsorption sites in the pressure range investigated. The heterogeneous surface of ceria may potentially generate strong electrostatic field gradients which strongly interact with quadrupolar and linear CO₂. When the pressure of the gas increases, the intermolecular force between adsorbate and the adsorbents increases significantly. In this case, the CO₂ is quadrupolar, whereas CH₄ is polarizable. Hence, the intermolecular interaction between the CO₂ and ceria is much higher than the CH₄ and ceria. Therefore, the selectivity towards CO₂ is higher than for CH₄ in ceria. (Hamon et al. 2010; Yang and Zhong 2006).

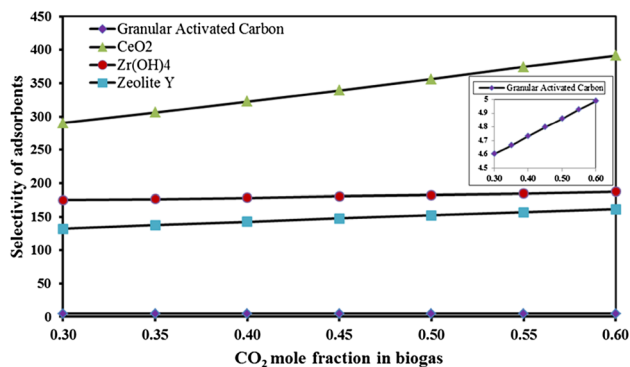


Fig. 7 Variation of CO₂/CH₄ selectivity with a mole fraction of CO₂ in biogas at 10 bar

Table 4 Amount of CO₂ uptake at P₁ and P₂ at 298 K

Adsorbent	CO ₂ adsorbed		Working capacity (P1–P2) mmol/g
	P1 (1 bar)	P2 (10 bar)	
GAC	1.2182	3.882	2.6638
CeO ₂	0.6564	1.3425	0.6861
Zr(OH) ₄	0.7308	1.2594	0.5286
Zeolite Y	3.5514	5.1097	1.5583

3.5 CH₄-slip

Methane slip is the proportion of CH₄ that escapes with the CO₂ during the PSA process and a larger CH₄ slip could significantly affect the process economics. Besides, CH₄ in the CO₂ stream would need to be burnt off by an additional catalytic process to obtain a pure CO₂ stream (Bacsik et al. 2016) in order to reduce the overall GHG footprint. Therefore, lower CH₄ slip is one of the important prerequisites for a potential material in the biogas upgrading process (Stenersen and Thonstad 2017; Storvik 2016).

The CH₄ slip for a PSA process operating between adsorption pressure (P₁) and desorption pressure (P₂) is estimated using Eq. (1). The P₁ and P₂ values have been specified in Tables 4, 5.

$$CH_4\text{slip}(\%) = \frac{CH_4\text{uptake at } P_1 - CH_4\text{uptake at } P_2}{CO_2\text{uptake at } P_1 - CO_2\text{uptake at } P_2} \times 100 \tag{1}$$

The methane slip for GAC, CeO₂, Zr(OH)₄ and zeolite-Y is shown in Fig. 8. It is evident that GAC has the highest CH₄ slip of 18%, whereas zeolite-Y and CeO₂ have almost negligible CH₄ slip. The 18% methane slip can be interpreted as “for every 100 molecules of CO₂ adsorbed on the adsorbent, 18 molecules of CH₄ is also adsorbed on the surface along

Table 5 Amount of CH₄ uptake at P₁ and P₂ at 298 K

Adsorbent	CH ₄ adsorbed		Working capacity (P1–P2) mmol/g
	P1 (1 bar)	P2 (10 bar)	
GAC	0.3168	0.7989	0.4821
CeO ₂	0.0027	0.0038	0.0011
Zr(OH) ₄	0.0036	0.0069	0.0033
Zeolite Y	0.037	0.0336	0.0034

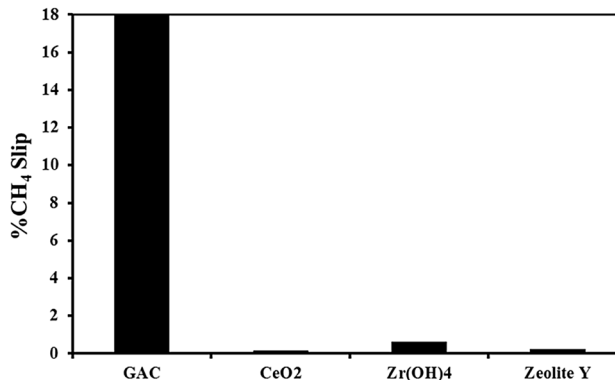


Fig. 8 Methane slip (%) in adsorbents

with CO₂”. The high methane slip of GAC is due to the unreasonably high adsorption capacity for methane in addition to CO₂, which is unfavorable for the separation process. Moreover, the highly homogenous surface of GAC is one of the reasons for large methane adsorption.

In the case of CeO₂ and zeolite-Y, the low methane slip can be attributed to the highly selective adsorption site and low adsorption capacity at high pressure. Moreover, since the selectivity of cerium oxide is almost double that of zeolite-Y at say 10 bar, the amount of methane lost in the PSA process using ceria is expected to be far lesser than that of PSA process using zeolite-Y.

4 Conclusions

The removal of CO₂ from biogas using mesoporous cerium oxide and zirconium hydroxide has been evaluated along with commercial granulated activated carbon and zeolite-Y using High-Pressure Volumetric Analyser (HPVA-100). The high selectivity for CO₂ and low methane-slips of adsorbents are paramount for an economic PSA process. Our experiments and models suggest that CeO₂ exhibits twice the selectivity for preferentially adsorbing CO₂ compared to commercial zeolite-Y and twofolds higher selectivity compared to commercial carbon. This is attributed to the

presence of a highly heterogeneous surface of cerium oxide compared to the other adsorbents. The high selectivity and low methane slip at high pressures indicate that CeO₂ could be a potential adsorbent for biogas purification in the PSA process.

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Compliance with ethical standards

Conflict of interests The authors declare that they have no conflicts of interest.

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