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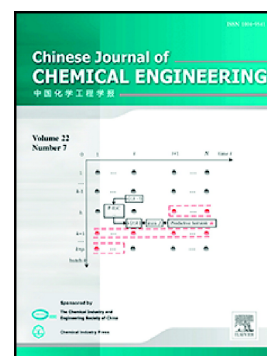
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Special Issue on Sustainable Chemical Product

Recent advances on first-principles modeling for the design of materials in CO$_2$ capture technologies

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Abstract: Novel technologies in consideration of industrial sustainability (IS) are in urgent need to satisfy the increasing demands from the society. IS realizes the production of materials and while maintaining environmental and resource sustainability. The chemical materials used in CO$_2$ capture and storage (CCS) technologies play a significant role in the disposal of greenhouse gas emissions coming from large stationary fossil-fired power plants, which breaks the principle of IS and brings severe environmental problems. This study aims at providing a detailed review of first-principles modeling (density functional theory, DFT) of materials in CO$_2$ capture technologies. DFT analysis provides insight into the atomic properties of the studied systems and builds an efficient guidance of the future design of the materials used in CO$_2$ capture technologies. Major materials including oxygen carriers, metal organic frameworks, membranes, zeolites, ionic liquids and some other promising candidates are considered. The computational studies bring the outcomes of the adsorption behaviors, structural characteristics and accurate force fields of the studied materials in short turn-around times at low cost. This review can stimulate the design of novel materials with specific target of CO$_2$ capture and promote the industrial sustainability of fossil fuel combustion technologies.

Key words: Industrial sustainability; CO$_2$ capture; Density Functional Theory; Fossil fuels

1. Introduction

With the continuous growth in human population, the demand for food, energy and fundamental living resources such as water has significantly increased. According to Godfray *et al.*[1], more than 14% of people in the world is still in hunger in this century; also, it is expected that by 2050 a growth in food supply from 70% to 100% will be needed to meet the population's demands. Industrial activities have also been increased to comply with the global demands. The increase in the industrial production of valuable goods has brought severe environmental problems and the inevitable drop in non-renewable resources such as fossil fuels. Therefore, the sustainability of the environment and resources is becoming a major global concern. In terms of industrial development, the production of valuable materials and products need to satisfy the increasing population demands; however, they need to do it in a sustainable way such that there is a balance between available resources and manufacture of valuable products. From an engineering perspective, the development of new green technologies can promote engineering sustainability, especially in consideration of industrial sustainability (IS). IS[2] refers to the transformation process including the industry that the overall production scheme contributes to a socially, environmentally and economically sustainable growth. Thus, IS requires industrial and academic practitioners to realize the industrial transformation process by taking into consideration economic, environmental and social aspects that enable the development and deployment of sustainable solutions. New materials and technologies are in urgent need to realize IS. The development and utilization of clean energies have become popular, e.g. wind, nuclear and solar energies [3],[4],[5]. In addition, the effect and treatment of industrial discharges are major considerations in terms of maintaining IS[6]. One aspect critical for the deployment of new (clean) technology in consideration of IS is the development, testing and implementation of advanced mathematical frameworks, which play a fundamental role to optimize chemical process sustainability and reduce their footprint on the environment [7],[8]. Among all the studies in the area of IS, the continuous growth in CO_2 emissions from fossil fuel combustion have attracted the most attention due to their environmental impact and global sustainability[9],[10].

According to the International Energy Agency (IEA) report in 2017[11], fossil fuel accounts for almost 80% of the overall energy supply in 2016, as shown in **Fig.1**.

Due to the current energy demands, fossil fuels are still not replaceable by renewables due to their relatively low costs and continuous development of efficient combustion technologies with near-zero emissions[12],[13],[14]. However, the environmental impact incurred when using fossil fuels during the combustion process has become a global issue that cannot be overlooked. Greenhouse gas effects are one of the most serious problems caused from the combustion of fossil fuels. Accordingly, environmental issues caused by greenhouse emissions do not comply with IS principles in modern manufacturing processes. Among all the greenhouse gas emissions, CO_2 represents almost 75% of greenhouse gases. One detrimental effect is that this gas has relatively long residence times, i.e., it remains in the atmosphere for long periods of time[15]. Thus, technologies aimed at reducing greenhouse emissions (mainly CO_2) are key to curb global warming effects while still using fossil fuels for the large-scale production of power. One approach that can be considered to reduce CO_2 emissions to the atmosphere is through the deployment of technologies that can capture, store, manage and eventually utilize the CO_2 produced from large stationary sources such as fossil-fired power plants. The development of efficient CO_2 capture systems engaged with the continuous production of power from fossil fuels is attractive since it may drive the sustainable development of fossil-fired energy technologies with near-zero emissions. CO_2 disposal technologies are usually classified as pre-combustion, which reduces carbon capacity of fuels before combustion occurs; post-combustion (flue gases generated after combustion are cleaned); and oxy-fuel combustion, which makes use of pure O_2 as oxidizer. The process schemes of these CO_2 capture technologies are described in **Fig 2**.

Post-combustion is a relatively commercially mature technology which favors low pressure processes. However, the energy penalty of CO_2 separation while adopting post-combustion technologies (using e.g. amine-based solvents) is from 25 ％ to 40％[16]. The post-combustion process normally operates at ambient pressure, low CO_2 concentrations (usually under 15％) and can often handle large flue gas flowrates. CO_2 partial pressure is usually less than 0.15 atm [17]. Pre-combustion technologies significantly reduces the energy consumptions associated with CO_2 capture, particularly in systems that operate at high pressures. Low temperatures such

as 40 ℃ are preferred to maintain the high efficiency in pre-combustion processes. According to a previous study[18], the energy penalty of the net plant efficiency in IGCC (Integrated Gasification Combined Cycle) plant with pre-combustion technology is from 7% to 9.5%. Compared to the pre and post combustion technologies, oxy-combustion usually adopts a recirculation process and lower the energy penalty through the separation of O_2 from air before combustion. A low mass flux and high CO_2 concentration of exhaust gas is expected to be separated in oxy-combustion. Despite its benefits, e.g. use of simple separation units to produce a highly pure CO_2 stream, this technology is still intensive and requires significant energy demands, mostly to separate O_2 from air. Despite the advances in carbon capture and storage (CCS) technologies, they usually sacrifice part of the overall system energy utilization efficiency to realize the CO_2 capture[19],[20],[21]. One key factor that affects the performance of CCS technologies is related to the type materials used to capture the CO_2. Therefore, a large and diverse variety of potential materials need to be tested to evaluate its impact on both the efficiency to capture CO_2 and its corresponding energy costs for recovery. **Table 1** summarizes the most frequently used materials in pre-combustion, post-combustion and oxy-combustion processes. The applications of these materials to different CCS applications will be described in the subsequent sections in this study.

Computer aided design is key for the development and assessment of promising materials for CO_2 capture. It has been widely recognized that computer simulations at the atomistic and molecular scales can lead the development of new materials (or the optimal design of existing materials) in short turn-around times and at low cost[43][44] thereby contributing to the sustainability of the environment and industrial processes. In particular, Density Functional Theory (DFT) analysis is a powerful atomistic (first-principles) modelling method used to screen out a large number of materials that can be employed for CO_2 capture. DFT is in the range of the quantum chemical methods and is widely used to predict the properties of chemical structures. To conduct a DFT analysis of different materials such as solvent, adsorption material and oxygen carriers (OCs), different models need to be used. For solid materials, the periodic vacuum slabs of the surface model[23],[45] are used to study the surface reactions while the isolated cluster models are usually employed to study particle interactions[46]. As for liquid solvents, the continuum solvation model (SMD) developed by Marenich et al.[47] can be used to study the CO_2 absorption into aqueous solutions [48]. DFT calculations are usually conducted at 0 K and vacuum

condition. The DFT energetic results can be adjusted to specific operating conditions using the atomistic thermodynamic models such as the ab initio atomistic thermodynamics [49],[50] or through molecular dynamic simulations. DFT analysis can provide insight into elementary reaction kinetics, charge distribution or transfer and microscopic morphological properties of systems under analysis. This modelling method has been proven to be a powerful tool to study the atomic behaviour of promising materials and provide significant guidance for the design of highly efficient (low-cost) materials for CO_2 capture.

In this work, we aim to review the most recent advances that have employed first-principles modelling (i.e. DFT) to advance our knowledge on the identification and atomistic design of suitable materials for CO_2 capture. This work focuses on the most common and promising materials used for the different CO_2 capture technologies such as oxygen carriers (OCs), Metal-Organic Frameworks (MOFs), membranes, zeolites and ionic liquids. Each type of materials will be reviewed in section 2. Recent advances in other materials such as porous carbons and amine solutions will also be discussed in section 2.6. A summary of the current state-of-the-art in materials for CO_2 capture will be provided at the end. The existing reports and challenges in DFT analysis of materials used in CO_2 capture will encourage further computational reports thus promoting IS in our society.

2. Materials in CCS

This section aims to present the recent advances in the commonly used and new chemicals used in the different CO2 capture and storage technologies.

2.1 Oxygen carrers (OCs)

Chemical looping combustion (CLC) has attracted attention in the past decades due to its relatively low energy cost compared to other carbon capture and storage technologies[9],[51],[52],[53],[54],[55]. Based on the reaction properties, there are two types of chemical looping schemes that can realize the fuel conversion process. Type I CLC realizes the indirect combustion of fuels by introducing an oxygen carrier (OC), which minimizes the irreversible entropy during the combustion process. As shown in **Fig 3 (a)**, in the first reactor (the reducer), metal oxides are reduced to realize the full oxidation of either gas or solid fuels, e.g. syngas or coal. The reduced metal oxides are then transported into the second reactor (the combustor) to be

re-oxidized by air thus forming a loop. Through CLC, the combustion process is energy-effective since it simultaneously captures CO_2 and produces heat thus promoting energy, environmental and ecosystem sustainability. As shown in **Fig. 3 (b),** type II CLC also requires two reactors, i.e. a carbonator and a calciner, which includes CO_2 transport using CO_2 carriers. In the carbonator, CaO is carbonated by CO_2 into $CaCO_3$ whereas in the calciner the $CaCO_3$ undergoes calcination reaction and release CO_2 at high temperatures which increases the energy regeneration efficiency[56],[57]. Guo et al.[58] combined experimental and DFT methods to study the metal promoter (Al, Mg, Zr and Na) effect on CaO as OC. That study showed that Zr and Na benefit CO_2 adsorption while Al and Mg weaken the adsorption. To the authors' knowledge, this is the only study of Ca-based OCs using first-principles (DFT) analysis.

Oxygen Carrier (OC) development is instrumental for the succesful optimization and industrial-scale deployment of CLC technology. This material serves as an oxygen intermediate to combust fuels while energy is supplied by the redox reactions. High reaction reactivity for both the oxidation and the reduction processes is perhaps the most desired property for OC materials. In addition, large oxygen storage capacity facilitates fuel conversion. Moreover, to minimize the deactivation of OCs, high mechanical strength and long-term stability under severe operational conditions are desired (20 bar, around 1000℃[59],[60]). Furthermore, OCs should be inexpensive, easy to access and should not lead to serious environmental concerns. Numerous OC materials have been experimentally studied and tested over the past decades[61]. Compared to experimental studies, first-principles modeling studies for OCs are relatively limited. DFT, as well as other quantum chemistry methods, have been popular tools used to provide insight on elementary reaction kinetics[62],[63],[64],[65]. DFT analysis has been mostly employed in this field to study the reactivity of OCs in the redox process. In terms of OC development for CLC applications using DFT analysis, iron-based materials are the most widely studied materials[22],[66],[67] followed by Cu-based OCs[68]. Though NiO-based is one of the most popular OCs in CLC, only a limited number of DFT studies for NiO has been conducted[69],[70]. Theoretical studies focused on other metals are rather scarce in the literature.

Dong *et al.*[22] conducted a DFT analysis on Fe_2O_3 as OC using CO as a gas fuel. That study showed that Fe_2O_3 (1102) surface has higher reaction activity with CO than Fe_2O_3 (0001) surface. In another study conducted by the same group, they

reported that high index surface Fe_2O_3 (104) performs better than low index (001) surface[71]. Carbon deposition[72] and mercury adsorption[73] were also investigated by the same group to assess the impurity effects on the Fe_2O_3 surface. Methane decomposition mechanisms on Fe_2O_3 have been studied using DFT by multiple groups. Different reaction pathways have been established on Fe_2O_3 surfaces[74],[75],[76]. Due to the complexity of methane decomposition paths, this reaction mechanism is still under debate and will likely be the subject of future research studies in this area. In a different study, Fan et al.[9] considered the oxygen vacancy on α-Fe_2O_3 (001) surface, which has been shown to enhance the partial oxidation of CH_4. Other fuel molecules reacting on the Fe_2O_3 surface have been investigated such as carbon atoms or CO[77],[78]. Those DFT studies reported the reaction kinetics in a solid fuel CLC process. Supports such as Al_2O_3, ZrO_2 and MgO have also been studied as the inert support of Fe_2O_3[66],[79],[80]. ZrO_2 supported Fe_2O_3[66] and MgO supported Fe_2O_3[80] were investigated by Tan et al. Those studies showed that ZrO_2 could enhance the adsorption of CO while MgO lowered the reaction barriers of CO oxidation compared to the pure Fe_2O_3 OC.

Cu-based OCs are promising materials for the oxygen uncoupling (CLOU) process since O_2 is released in the reducer. The support effect on the sintering resistance of CuO was studied by Zhao et al. [81]; four supports (TiO_2, ZrO_2, $CuAl_2O_4$ and $MgAl_2O_4$) were studied and all the supports were shown to reduce the energy barriers of the fuel combustion process. Among them, $CuAl_2O_4$ showed the best performance in the CLOU process. A specially synthesized Cu-based OC with a core (Al_2O_3)-shell (TiO_2) support was studied by Xu and Zhao[82]. That study showed that this material could effectively prevent the impurity formation in CLOU process. Studies involving graphene[83] and ZrO_2[84] supports have also been reported and have shown that graphene improves the reaction activity of OC with CO whereas ZrO_2 contributes to the CO oxidation. Liu et al.[85] showed that Zr benefits the oxygen vacancy formation and migration on CuO surface which leads to higher reactivity of CuO as OC.

NiO (001) perfect and defective surfaces have been considered in DFT studies for CLC applications. A report by Cai et al.[23] has shown that the oxygen vacancy on NiO enhanced the O_2 dissociation in the reduction process. The impurity of CLC (H_2S) on NiO (001) perfect and defect surfaces was studied by Guo et al.[86]. The results from that DFT study showed that impurity may notably reduce the CO adsorption on the surface. The oxidation process of Ni in CLC was also studied using

DFT[87]. Other OCs like Mn_3O_4 (001) [88] and $CaSO_4$ [89] have also been investigated in CO and CH_4 conversions, respectively. Those works have provided the elementary reaction kinetics of the studied systems. Theoretical studies on supports of NiO are limited even for the most common Al_2O_3 supported NiO.

Mixed OCs which contain more than one metal elements have attracted much attention as OCs. Studies focusing on perovskites such as $BaMnO_3$ and $SrMnO_3$ have been reported. Results from those studies have shown that different compositions of those materials have resulted in different reaction activity performances[90],[91]. Note that Fan *et al* [24] reported a DFT analysis combined with experimental data that studied the role of metal oxide support. In that work, the structure of ilmenite ($FeTiO_3$) has been chosen to represent the TiO_2-supported iron oxide. That study presents a comprehensive understanding of the TiO_2 support effect on iron-based OC and provides a representative demonstration of DFT study in this area. Since $FeTiO_3$ is the active component of ilmenite while it also contains MgO and Al_2O_3[92], that study can be used as a basis to develop a new study of trace metal elements in ilmenite as mixed OCs.

In summary, CLC is an energetically favorable process with inherent CO_2 separation characteristics that can significantly contribute to curb greenhouse gas emissions. To enhance CLC performance, DFT analysis of OCs will provide the fundamental atomistic understanding of the studied systems. However, DFT simulation reports of Ni-based OCs[23] as well as the other materials, natural ores for instance, are limited in the literature. Furthermore, some significant topics such as lattice transfer performance for OCs using DFT analysis have not been reported in the literature. To screen and design promising OCs without too much cost, further DFT-based studies are needed.

2.2 MOFs

Metal-organic frameworks (MOFs) are one of the most promising adsorbents of CO_2 capture and have become the main focus of research for many experimental and theoretical studies. MOFs are highly ordered crystals containing both metal nodes (metal ions or metal clusters) and organic linkers, which enable MOFs to have a wide variety of properties for multiple applications[93]. The diversity of MOFs, different metal sites and different linkers, leads to the need for a large scale screening of these materials using atomistic (DFT) methods. As adsorbents, MOFs are known for their high pore volume, high surface area and internal surface (higher than 7,000 m^2/g) [94]. Also, physical and chemical properties of MOFs such as pore size or functional

groups can be tailored by choosing different building blocks and synthesis strategies[95]. The methods to synthesize MOFs have been the focus of multiple studies in this area since they can potentially tune desirable characteristics for MOFs[93]. As for the materials' strength, structures of MOFs have high robustness, which means that the adsorbed species can be removed to realize the activation of adsorbents while maintaining the crystal structure of MOFs. All the characteristics described above make MOFs promising candidates for CO_2 capture adsorbents for post-combustion technologies, which have been tested through multiple experimental and simulational studies[96],[97],[98].

One area of research in MOF is focused on coordinatively unsaturated sites (CUM), which tend to form reversible bonds with CO_2[94]. The most popular potentials used to simulate the interactions between CO_2 and MOFs, i.e., a combination of Lennard-Jones (LJ) potential and Coulombic potentials[99], cannot accurately predict the adsorption properties since those potentials have been mostly developed for physical adsorption processes. Therefore, first-principles based force field studies are popular to analyze and evaluate the capabilities of MOFs to adsorb CO_2 [100],[101]. DFT analysis on MOFs can also provide lattice constants and atomic geometries as well as particle properties during the gas adsorption process, e.g. mechanics of adsorption, particularly for CO_2 capture[102]. Computer-aided design allows efficient and fast screening of MOFs for CO_2 capture. The aim of this section is to review those recent modelling studies that have considered the adsorption properties of MOFs for CO_2 such as adsorption, selectivity and impurity effects. Also, a summary of the optimization strategies to improve CO_2 separation process by MOFs is described. DFT-based force fields, which are constructed to simulate the expected behavior of MOFs in the CO_2 capture process, will be described at the end of this section.

In the selection of adsorbents to capture CO_2, the adsorption properties such as adsorption capacities and CO_2 selectivity are usually key for the identification of a promising solvent. Ramsahye *et al.*[103] calculated the charge distribution of the MIL-53 by DFT analysis. Periodic models as well as cluster models of MIL-53 were employed and have shown to achieve good agreement with structures observed from experiments. The charge distribution predicted from DFT simulations was used to simulate a grand canonical Monte Carlo (GCMC) model, which is the most commonly used simulation method in this area. Then the adsorption capacity, as well as selectivity of CO_2, were estimated. That work showed that the Mulliken charges

from periodic models are more transferable between the two changing structures of MIL-53 due to its flexibility, which would provide a better prediction for the entire adsorption process. Hu *et al.*[104] showed that Zr-BFDC (O-heterocyclic ligand contained) performed the best among three studied UiO-type of MOFs. MOFs have been simulated in numerous studies and shown to be promising CO_2 adsorbents with high adsorption capacity and easy to regenerate. Borges *et al.*[105] reported a study focused on selectivity of CO_2 capture among H_2, N_2, CH_4 and CO. That study indicated that MIL-160 was a promising adsorbent of selective CO_2 adsorption. The adsorption mechanism (i.e. the binding energies of CO_2) was obtained from DFT analysis. The results from that work showed that CO_2 tends to be adsorbed on the Zr-metal cluster. Liu *et al.* reported[106] that the side position where the CO_2 is closer to the hydrogen side of the organic linker is the most favored site among multiple configurations. DFT has been shown to be an effective tool for the prediction of adsorption mechanism in MOF-contained systems. Impurity effects on the CO_2 adsorption process can also be obtained from DFT simulations. Yu *et al.*[107] simulated the CO_2 adsorption using Mg-MOF-74 in a system that contained water. The water-coordinated MOF has lower binding energy with CO_2, which leads to a decrease in the adsorption capacity of CO_2. Regarding the functional group effects, Torrisi *et al.*[97] reported four functionalized MIL-53 containing different groups (OH-, COOH-, NH_2- and CH_3-). The results reported that each functional group have different favored adsorption sites and bonding energies. Functional groups (especially OH- and COOH-) have enhanced the adsorption of CO_2 by MIL-53 in consideration of capacity of CO_2 and the selectivity of CO_2 over CH_4.

The computational studies mentioned above provide guidelines for the optimization of MOFs or even the design of new MOFs for CO_2 capture. Unsaturated sites, polar functional groups, alkylamine incorporation and pore size can contribute to CO_2 capture with MOFs[94]. Nazarian *et al.*[108] analyzed 879 MOFs which structures were optimized using DFT analysis. In some cases, the computationally optimized structures make the CO_2 adsorption significantly different from the experimental results; the major source of discrepancy was due to the use of force fields that were not able capture the key characterisits of the system; therefore, the development of accurate force fields for those systems is indeed needed to further advance the design of new MOFs materials. In terms of force field development for MOFs, DFT calculations can optimize the structures of the studied materials such as the surface model or the isolated cluster configurations. Also, the interactions and

distances between the particles can be obtained by DFT analysis as well as the energetic and electronic properties of the configurations. These results are then used in the specific force field models such the 12-6 Lennard-Jones potential. Grand Canonical Monte Carlo (GCMC) simulations can be used to validate the force field models by comparing the GCMC predictions with experimental observations [109]. Especially for the MOFs with open metal sites, general force fields such as UFF (Universal force field)[110] cannot accurately simulate the adsorption behavior since they cannot predict the strong interactions present between CO_2 and the adsorbent containing open sites. As mentioned above, CUM contained MOFs has been widely studied using DFT analysis given that the open metal site has the potential to form a chemical bond with CO_2. Haldoupis *et al.*[111] reported that the favorable adsorption sites of CO_2 are the existing open metal sites of the studied M-MOF-74 (M stands for Mn, Co, Ni, Cu). Also, they parametrized the interactions between CO_2 and the unsaturated sites using the DFT-derived interaction energy. The developed force fields were able to predict consistent adsorption isotherms that agree well with previous experimental results. Poloni *et al.* [112] studied MOF-74 (Ca and Mg) as well as BTT-type MOFs containing unsaturated sites (BTT stands for 1,3,5-benzenetristetrazolate). That study showed that binding energies are highly sensitive to the existing divalent cations in BTT; similarly, the open V and Ti sites favored the CO_2 adsorption in M-MOF-74.

Another research avenue in MOFs is the simulation of breathing MOFs, i.e. MOFs with flexible strucutres like MOF-5. Adequate force fields that can predict flexible MOFs are currently under investigation [113]. Zhao *et al.*[25] performed a DFT analysis to obtain the angle bending parameters around Cu of Cu-BTC ($Cu_3(BTC)_2$ with BTC (benzene-1,3,5-tricarboxylate), which is a breathing MOF. The new force field, which was developed to describe the breathing MOF, Cu-BTC, combined parameters estimated from DFT and slightly modified existing parameters, i.e. the intramolecular force constants from a widely used CVFF (Consistent Valence Force-Field) [114],[115]. The new force field is evaluated by its prediction of Cu-BTC crystal structures, adsorption behavior, etc. According to the comparison of the experimental outcomes and simulated results, the newly developed force field can give an accurate prediction of the properties of Cu-BTC such as the crystal structure, vibrational properties and the adsorption behavior.

DFT analysis can provide the characteristics of MOFs such as lattice parameters of MOFs, which can lay a solid foundation for future structure-relation studies of CO_2

capture using MOFs. Also, the development of new force fields improve the accuracy of the simulational outcomes and extend the systems that can be explored using DFT analysis.

2.3 Membranes

The application of membranes in CO_2 capture mainly includes H_2/CO_2 separation for pre-combustion, CO_2/N_2 separation for post-combustion and O_2/N_2 separation for oxy-fuel combustion. Membranes act as filters in the separation process since they only allow targeted components in the gas mixtures to permeate through, while leaving the rest of the species behind, which produces a pure stream of the desired gas component. Membrane-based technology has shown great potential in CCS since it does not require significant investment in large-scale power plant facilities. Also, this technology is not energy intensive like the traditional solvent-based technologies, which require large amounts of heat to regenerate the solvent. Moreover, membranes only need to be replaced when they reached their life span. Depending on their specific configuration, membranes can also be designed to suit the different needs for the separation processes.

The design of a membrane for CO_2 capture is mostly driven by the permeability and selectivity of the membrane. Permeability represents the gas permeation flux per unit pressure, whereas selectivity denotes the ratio of the permeabilities among different gas species. Membranes used for CO_2 capture are typically classified as: inorganic frameworks (*e.g.* metallic, carbon, silica, zeolite and metal-organic frameworks[116]; and organic frameworks, which mainly includes cellulose acetate and polymers[117].

Considering the number of different frameworks and possible configurations that can be employed to build a membrane, measuring the performance of the different membrane candidates under a wide range of operating conditions in a laboratory is not only time-consuming, but also expensive. On the other hand, computational simulations can be used for screening and identification of the most promising structures for different applications. In what follows, we will discuss the first-principles calculation studies on membranes that are H_2 selective, CO_2 selective, and N_2 selective respectively.

H_2 selective membranes are mainly used in pre-combustion CO_2 capture process to separate a mixture of H_2 and CO_2 at high pressures and temperatures. Metal membranes are to a certain extent ideal for this type of processes because of their

potential infinite H_2 selectivity[118]. Hydrogen purification membranes made of Palladium (Pd) and its alloys have been heavily studied over the past 50 years[28]. The main drawback of pure Pd-based membranes is that they are prone to surface contamination and H_2-induced embrittlement at temperatures below 300 °C. On the other hand, Pd-alloy membranes have the potential to resist surface poisoning while maintaining desirable properties of pure Pd membrane. Kamakoti *et al.*[119] used plane wave DFT calculations to examine the binding energy and diffusion activation energies for dilute interstitial H in pure Pd, bcc and fcc CuPd alloys with ~ 50 at.% Pd. The dilute interstitial hydrogen loading was approximated by placing a single H atom on each of the compound's computational supercells. The diffusion activation energy was calculated using harmonic transition state theory (TST) with zero-point corrections. Results from this study have shown that H atom has the strongest binding energy with pure Pd, which also has the smallest net activation energy for H diffusion. As an indicator of the calculation accuracy, the predicted H diffusion activation energy in pure Pd (0.24 eV) was found to be in excellent agreement with experimental results (0.23 eV). Ling *et al.*[120] applied DFT-based calculation to evaluate the interactions between H_2 and a wide range of compositions of PdCuAg alloy membranes. DFT calculation was employed to obtain the hydrogen solubility, diffusivity, and permeability of each composition examined. A contour map was generated as a function of the alloy composition based on a large collection of DFT results. That study concluded that the solubility of hydrogen increases with Ag concentration while this variation can also cause a decrease in the diffusivity. Specific compositions that have a higher permeability than pure Pd have also been identified. Chandrasekhar *et al.*[121] calculated hydrogen solubility for 78 Pd-based binary intermetallics and used this information as a screening parameter to generate a shorter list of candidates to study hydrogen permeability. The study revealed that no material has higher hydrogen permeability than pure Pd. However, their work significantly increases the set of materials for which hydrogen permeability is known.

Carbon-based membranes separate H_2 from gas mixtures by molecular sieving. Zhang *et al.*[122] calculated the H_2 permeability and selectivity of sp-sp^2 hybridized carbon allotrope membranes with different natural pores, *i.e.*, graphyne, graphdiyne, and rhombic-graphyne. Their calculations showed that these properties are highly dependent on the pore sizes and membrane shapes. Among all the structures, rhombic-graphyne showed the largest discrepancy in penetration energy barrier for different gas molecules (0.54, 1.55, 1.73, and 3.00 eV for H_2, CO, N_2, and CH_4

respectively); this promotes high H_2 selectivity ($>10^{16}$) while maintaining a reasonable H_2 permeability. Wang *et al.* proposed four differently modified graphene membranes with H-deactivated pores (HP6, HP10, HP13, and HP16) and investigated their abilities to separate H_2 from gas mixtures (See **Fig. 4**)[29]. In that study, DFT-based calculations were performed to obtain the permeation energy barriers of each gas species (H_2, CO, N_2, and CH_4). It was found that H_2 has the lowest permeation energy barriers on all four pore structures studied. Among all membranes examined, HP6 membrane exhibited the highest H_2 selectivity followed by HP10. However, large permeation energy barriers of H_2 have also been observed on HP6 and HP10 membranes (13.64 kcal/mol for HP6 and 7.05 kcal/mol for HP10); these results suggest low gas permeabilities. As for HP13 and HP16, the H_2 permeation energy barriers are very small and can result in high permeabilites (0.52 kcal/mol on HP13 and 0.03 kcal/mol on HP16). However, the calculated energy barriers of CO on HP13 (1.06 kcal/mol) and HP16 (0.94 kcal/mol) are not significantly higher than those obtained for H_2, which can lead to poor selectivity of H_2 over CO. On the other hand, HP13 and HP16 can be used to separate H_2 from CO_2 and CH_4 with the selectivity of 4.6×10^3 (HP13) and 4.3×10^2 (HP16) for H_2/CO_2 mixture; and the selectivity of 5.4×10^8 (HP13) and 1.1×10^4 (HP16) for H_2/CH_4 mixture. These results indicate that H-deactivated graphene could be a promising material for H_2 selective membranes.

CO_2-selective membranes are mainly used in post-combustion CO_2 capture process to separate a mixture of N_2 and CO_2. Cazorla *et al.*[123] calculated the CO_2 selectivity and capacity of the Calcium-decorated carbon nanostructures using DFT analysis. In their work, the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) for the exchange-correlation energy was employed. The calculated binding energy of N_2 is much smaller than CO_2 on the Ca-doped surface ($E_{bind,N2} = -0.645$ eV and $E_{bind,CO2} = -2.731$ eV on $X_{Ca} = 12.4\%$ graphene surface). Also, the formation of calcium carbonate ($CaCO_3$) promoted CO_2 selectivity. These results suggest that Ca-decorated carbon nanostructure membranes are suitable for their applications in post-combustion technologies. Ostwal *et al.*[124] used DFT calculations to investigate the means of CO_2 hopping on the 3-aminopropyl-triethoxy silane (APTS) functionalized silica membrane. The binding energy of CO_2 adsorption (15.5 kcal/mol) and the activation energy of CO_2 diffusion/hopping from one amine group to another of APTS (7.2 kcal/mol) were in good agreement with experimental results (14.33 - 21.5 kcal/mol and 8.0 kcal/mol, respectively). Therefore, CO_2

molecules are likely to follow the proposed mechanism when they interact with the APTS membrane. Wu *et al.*[125] also performed DFT-based simulations to investigate the mechanism of the fluorine-modified porous graphene membrane for CO_2/N_2 separation. Their result showed that the pore-22 graphene (with 22 carbon atoms drilled out) has small diffusion energy barriers for both CO_2 and N_2, which leads to a low selectivity. However, once the fluorine has been modified, the diffusion barrier for CO_2 decreased to 0.029 eV, while the diffusion barrier for N_2 increased to 0.116 eV. This difference suggests that CO_2 will pass through the membrane much easier than N_2, thus enhancing the selectivity of CO_2/N_2 mixture. Watanaba *et al.*[30] predicted the capability of a MOF material $Cu(hfipbb)(H_2hfibpp)_{0.5}$ ($H_2hfipbb$ = 4,4'-(hexafluoroisopropylidene)-bis-(benzoic acid) for membrane-based CO_2/CH_4 separation. In their work, DFT calculations were used to confirm the significant difference between the diffusion energy barriers of CO_2 and CH_4. The diffusion activation energies of CO_2 and CH_4 in the pore of $Cu(hfipbb)(H_2hfibpp)_{0.5}$ were calculated using TST. According to their calculations, the activation energies for CH_4 and CO_2 are 45 kJ/mol and 16 kJ/mol respectively, which justifies the high CO_2 selectivity exhibited by this material. DFT calculations has also been used to provide geometry optimized structures [126] or force constants and atomic charges that can be used to develop force fields (FFs) for molecular dynamic simulations [127] (See Section 2.2).

The concept of a N_2-selective membrane stems from the development of H_2-selective metallic membranes. Rochana *et al.*[128] studied the molecular dissociative adsorption of nitrogen and potential subsequent atomic diffusion within the Vanadium (110) surface and alloys with Ruthenium (Ru). That report showed that the binding energy of N_2 and atomic nitrogen bind on the V (110) surface is stronger than that of the Fe surface, which is traditionally used as the catalyst for ammonia synthesis. However, compared to Fe, N_2 has higher activation energy barrier for the dissociation process (0.4 eV) and the subsequent subsurface diffusion process (1.4 eV). As a result, the authors of that study concluded that nitrogen transport through a pure V membrane may be difficult to achieve. V-Ru alloys, on the other hand, may have the potential to be used as membrane materials, *i.e.*, DFT simulations perfomed in that study showed that the presence of Ru weakens the adsorption of nitrogen in the first subsurface layer, which enhances the diffusion of atomic nitrogen. Wang *et al.*[129] revealed that the graphene membrane with nanopores formed by replacing 13 C atoms with H atoms (H-pore-13) can efficiently separate N_2 from CO_2 despite the

fact that the size of the pore (4.06 Å) is larger than the size of both N_2 and CO_2 molecules. The authors further studied this phenomenon using dispersion-corrected DFT by portraying the potential energy profiles of N_2 and CO_2 molecules penetrating through the pore. The profile showed that CO_2 and N_2 molecules interact with the pore most strongly at 2.0 Å and 1.6 Å above the surface with interaction energies of 0.24 eV and 0.14 eV, respectively. Moreover, the energy barriers to pass through the pore are 0.19 eV for CO_2 molecule and 0.05 eV for N_2 molecule. Hence, it is more difficult for CO_2 to permeate the membrane compared with N_2. Similar methods were also used to examine the N_2 selectivity of the poly-(triazine imide) (PTI) membrane[130]. The computed energy barriers for CO_2, N_2 and H_2O passing through the PTI membrane are 0.262, 0.118, and 0.164 eV respectively, which suggests that PTI is also a promising material for N_2/CO_2 separating membranes.

DFT analysis has been successfully employed to theoretically investigate and predict the applicability of a wide range of materials in membrane technology. More studies are expected in this field in order to provide guidance to the experimental work and allow experimental scientists to make decisions faster thus enabling the rapid development of new and optimized membrane materials for CO_2 capture technologies.

2.4 Zeolites

Zeolites are crystallized porous aluminosilicates that contain exchangeable cations (Li^+, Na^+, Ca^{2+}, etc.). Due to the cages and channels as well as the changeable cations, zeolites have been widely used in pre-combustion and post-combustion CO_2 capture applications. The diversity of zeolites makes these materials attractive for the CO_2 adsorption process. For example, the topologies, the number of exchangeable cations in the cavities, pore sizes and Si/Al ratio are important criteria that needs to be considered in the selection of zeolites for CO_2 adsorbtion[131],[132].

DFT analysis of zeolites as CO_2 adsorbents can predict the adsorption behavior such as adsorption capacity, favored sites and selective adsorption among gaseous mixtures. Zukal *et al.*[31] reported the CO_2 adsorption in Na-A zeolites using a periodic slab model to provide accurate predictions of the dispersion interactions. That study showed that simulation results agree well with the experimental outcomes and CO_2 tends to be stable when it interacts with 3 Na^+ cations simultaneously. Thang *et al.*[133] studied the faujasite-type zeolites using the DFT/CC (coupled cluster)

method[134]. Compared to results reported from other simulation methods, a better prediction of the interaction energy through DFT/CC calculations was obtained in that study, which has also been shown to agree well with experimental results. Cation site effects have been studied by Nachtigall *et al.*[32]. In that study, periodic DFT calculations indicate that dual or multiple cation sites tend to adsorb gas molecules rather than single cation sites. As for CO_2 in mixtures, the selective adsorption of CO_2 over N_2 (exhaust gas composition) is studied with a NaKA zeolite (Na-A type zeolite with partial substitution of Na^+ by K^+)[46]. Both the isolated cluster and the periodic model were adopted in that study and have shown that it is the high carbonate forming at the K^+ ion positions in the 8R windows, which enhances the selectivity towards CO_2 adsorption. Another focus of selective adsorption on CO_2 is with natural gas (i.e. a mixure of CO_2 and CH_4). Fischer *et al.*[135] conducted the dispersion-corrected DFT calculations to estimate the interactions of the adsorbed molecules (CO_2, N_2 and CH_4) with different synthetic zeolites. The results from that work showed that the difference in the binding energy between zeolite-CO_2 and zeolite-CH4 in K^+ or Rb^+ containing adsorbents is significant for the selective adsorption of CO_2. Compared to other CO_2 capture materials such as MOFs, DFT studies using zeolites are limited despite the fact that atomistic computational methods have shown to be efficient to predict CO_2 adsorption phenomena.

2.5 Ionic liquids

Ionic liquids (ILs) are considered promising candidates in industrial processes for conventional volatile compounds separation and storage[136]. ILs are salts with melting points lower than 100 °C[137]. This type of materials often present excellent thermal stability, good solubility as well as the possibility of ionic and composition substitutions, which make them attractive for different industrial applications including CO_2 capture. ILs also allow the combination of different ions, which offers the flexibility to tune materials for further improvement. This makes ILs particularly attractive since they offer the potential to be designed for specific purposes. Compared with experimental reports, DFT analysis is an efficient and inexpensive approach that can be employed to screen a large number of potential ILs to build up specific structure-property relationships. ILs are popular in the area of CO_2 capture due to its experimentally reported high CO_2 capture capacities and its desirable chemical or physical properties[34],[138],[139].

DFT analysis on ILs applied for CO_2 capture is usually combined with molecular dynamic simulations (MD). DFT simulations predict the charge distribution and charge transfer, structural and energetic properties of short-range intermolecular interactions within isolated ions, ion-ion and ion-CO_2 mixtures[140]. On the other hand, MD predicts the dynamic properties of the systems such as the diffusivity of CO_2 confined at specific pressures and temperatures. Aparicio *et al.*[141] reported the microscopic structures and intermolecular forces of choline benzoate and choline salicylate ILs in the pure state and also in the CO_2 absorption process. The studied CO_2-ion pairs show strong interations with benzoate ainion. The volume increase of the studied ions, cholinium benzoate ([BE][CH]) and cholinium salicylate ([SA][CH]), is apparently larger than other ions such as lactate[142]. The mechanism of CO_2 absorption on the studied ILs as well as the CO_2 effects are provided. That study reported that there is no overlap in the system containing the studied ions and CO_2. Also, the CO_2 absorption increases the molecular mobility and ciscosity of the heterogeneous systems. Shaikh *et al.*[33] used DFT analysis and MD simulations to predict CO_2 absorption on amino acid ionic liquids (AAILs). That study showed that glycinate ([GLY]) adsorbs CO_2 better than 1,1,1-trimethylhydrazinium ([aN111]) though [GLY] increased the liquid viscosity. The balance of high CO_2 capture capacity and low viscosity should therefore be taken into account for AAILs. Steckel[137] studied the interaction of CO_2 with acetate ion. Multiple DFT functionals were evaluated and have shown that they were not able to accurately reproduce all the geometries and energetic calculations obtained from coupled-cluster singles and doubles (CCSD) optmizations; on the other hand, the range-separated hybrid meta-GGA[143] (M11) and nonlocal (VV10[144] and vdwDF10[145]) functionals lead to better results among all the studied DFT methods. That study gives guidance of DFT-based MD calculations and the parametrization of the force fields based on DFT analysis. Damas et al.[146] used DFT to evaluate the interactions of cations and anions derived from ionic liquids with CO_2, SO_2 and H_2S. The results suggest that IL-based anions are more likely to interact with CO_2 when the cation-anion interactions are weaker. That study provides a comprehensive mechanism of the studied system and more absorption species since it extends on a previous report[147] that only considered CO_2 capture adopting the 1-ethyl-3methylimidazolium (C_2mim^+) and bis(trifluorosulfonyl)imide (Tf_2N^-). Garcia *et al.*[148] screened different density functional methods to study CO_2 capture by ILs. Binding energies of gas-ILs of a set of 54 ILs were estimated. The results show that

ωB97XD[149] can simulate the long-range corrections to provide suitable charge transfer considering the dispersion corrections through DFT-D2 approach[150]. The resulting correlations between CO_2 and ILs are key to optimize the design of ILs for CO_2 capture. To mimick the interactions in consideration of both physical and chemical absorption, a new force field was developed in CO_2 absorption on ILs. Zhang *et al.*[35] developed a ReaxFF force field based on CO_2 capture by tetrabutylphosphonium glycinate, $[P(C_4)_4][Gly]$. The resulting force field is used in NPT ensemble MD simulations to predict the equilibrium density at 300K and 1 atm. Multiple sets of interactions are considered such as periodic DFT simulations of the reaction pathways between CO_2 and anion in the condensed phase, gas-phase CO_2-anion interactions. The ReaxFF-based MD simulation predicts the equilibrium density at 300 K, which is within about 1% of the experimental value. Mondal *et al.*[151] provided force field parameters for imidazolium cation based ILs combining anions of acetate, thiocyanate and dicyanamide. The DFT derived fractional charges were used to modify the CLaP force field[152],[153],[154] and build a transferable force field. The improved force field was used in MD simulations and showed that the intermolecular structure and dynamics agree well with experimental results. That work showed that the scheme used to define the non-bonded and torsional interaction parameters by the partial charges can be used to establish transferable force fields in this area.

The DFT studies of ILs discussed above show that simulations are powerful tools to screen this highly diverse and tunable material based on the specific targets pursued for CO_2 absorption. However, some aspects of greenhouse emission disposal are still under debate using ILs. Further research on absorption selectivity of CO_2 over impurities is therefore needed to further support the development of this material for CO_2 capture applications.

2.6 Additional materials

The materials discussed in the previous sections represent the most commonly used materials considered for CO_2 capture. First principles (DFT) studies on other materials that have shown potential as attractive CO_2 adsorbents. These materials are discussed next.

Porous carbons stand out in the area of CO_2 adsorption due to their relatively low prices compared to the other materials such as MOFs[16]. In addition, a variety of

allotropes of carbon such as nanotubes or graphenes allow the specific applications of porous carbons. Mo *et al.*[37] conducted a functionalized carbon study to analyze CO_2 adsorption. The N-containing molecular segment models of coal (2-methylpyridine, $C_{13}H_9N$, $C_{23}H_{12}N$, and N-doped graphenes) was evaluated by CO_2 uptakes. That study found that the DFT method of BLYP-D3 combined with a 6-311++G (d, p) basis set can accurately simulate the interactions in the studied particles such as 2-methylpyridine, $C_{13}H_9N$ and $C_{23}H_{12}N$, which improves the accuracy of the calculations of CO_2 adsorption in the system containing similar compositions. Jiao *et al.*[36] showed that the addition of pyridinic-nitrogen in nanotubes enhances CO_2 adsorption strength with varying charge states. That study showed that reversible CO_2 adsorption (i.e. desorption) can be controlled through the injection of electrons into the nanotubes. Then, the idea of switching the charge-carrying states of the nanotubes becomes a new scheme for CO_2 uptakes. As for fullerene (C_{60}), Gao *et al.*[155] used DFT analysis to evaluate the potential application of fullerene of CO_2 adsorption. Their results showed that calcium decorated fullerene have the potential to adsorb 16 CO_2 molecules in a unit cluster with 4 decorated Ca atoms. Graphene has also been studied for CO_2 adsorption using DFT calculations. Rad *et al.*[38] provided microscopic information of the CO_2 uptakes by Al-doped graphene such as the adsorption energy and electronic states. The outcomes of that study showed the potential of functionalized graphene materials as CO_2 adsorbents. Another porous carbon materials that have been studied are mesoporous silica nanoparticles such as SBA-15[39] or MCM-41[40]. Zhuo *et al.*[156] simulated the CO_2 and N_2 adsorption on mimetic MCM-41. DFT analysis of this system showed that CO_2 has preferable adsorption sites over N_2 on the materials' surface. MCM-41 also has higher adsorption selectivity of CO_2 over N_2. As for SBA-15, Zukal *et al.*[157] evaluated the functionalized SBA-15 with 3-aminopropyl-trimethoxysilane using the CO_2 adsorption energy distribution obtained from non-local DFT calculations. That study revealed that amine ligands on the surface seem to enhance CO_2 capture on the studied material. The CO_2 adsorption capacity of the studied material is highly related to the amount of amine groups. Especially, the tethered amine ligands react strongly with CO_2 to forma carbamate. The high isosteric heats of adsorption indicate that strong interactions between CO_2 and amine groups exist. Amine-based solvents, e.g. monoethanolamine (MEA), appears to be the most promising and widely used materials in amine scrubbing post-combustion technology to capture CO_2[42],[43],[158],[159],[160],[161],[162]. Yamada *et al*[48] developed a continuum

solvation model (SMD)[47] in DFT analysis to study the CO_2 absorption in an aqueous solution of 2-amino-2methyl-1-propanol (AMP). SMD is popular to predict solvation free energies of neutral and ionic in the solutions. The established pathway of CO_2 absorption is a two step mechanism via a zwitterion intermediate. The carbamate forms fast and decomposes reversibly. Except for the materials mentioned in this section, an increasing number of innovative materials are considered in the area of CO_2 capture, such as new polymers[163], zinc orthogermanate[164], perovskite[165],metal oxides[166],[167] and hydrotalcite[168]. Polymers have attracted much attention recently due to their structural tunability[163]. In particular, Zinc orthogermanate (Zn_2GeO_4) is a polymer ternary oxide material that has shown to be promising to capture CO_2 in photoreduction. This material plays a vital role to improve the reduction of CO_2 into renewable hydrocarbon fuel as a photo catalyst[164]. In addition, perovskites can be regarded as composite OCs that have high activities and also favour ionic and electronic migration during the redox reactions [169]. Unlike other OC materials, perovskites allow relatively low energy for oxygen anions and electron transport from the bulk to the active surface. The urgent need for high efficient CO_2 disposal technologies encourages practitioners to explore new and novel materials with suitable properties for CO_2 capture.

3. Summary

This review has presented the recent contributions and advances on first-principles (DFT) modelling applied to the design of materials suitable for CO_2 capture tehcnologies. Testing and validation of computer aided design materials using experiments will shed light into the development of new materials that can eventually promote the sustainable production of power using fossil-fired systems. The oxygen carrier (OC) used in CLC has attracted much attention due to its energy effciency since it makes use of oxy-combustion process through a 2-reactor scheme. The application of OCs in different systems still requires more research in DFT analysis to provide microscopic structure-property relations, which will guide the design of materials depending on the specific CO_2 capture targets. MOFs and ILs are both favored by their tunable properties since in principle they can be designed to satisfy a specific separation target requirement. The focus of MOFs in the application of CO_2 capture is on its unsaturated sites as well as the breathing property of some of the specific MOFs. On the other hand, zeolites, porous carbons, amine-based solutions are relatively mature candidates in the area of CO_2 disposal, which are currently

applied in industry. However, insights on the mechanisms and microscopic structures of the systems using these relatively traditional materials are still lacking in the literature. DFT methods can significantly enhance the application of these materials since they can reveal properties that can be exploited for CO_2 capture. Computational modelling allows efficient screening of a large set of materials and can accelerate the development of novel materials that can support fossil-fired power production under near zero emissions. Therefore, modelling studies in this area can drive the design and optimization of new materials with properties ideally suited for CO_2 capture thus promoting the sustainability of new and efficient CO_2 capture technologies.

Acknowledgements

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Table 1 Materials commonly used in CCS technologies

Type	Technology	Commonly used materials	Features
Oxygen carrier	Oxy-combustion (chemical looping combustion)	Fe_2O_3[22], NiO[23], ilmenite[24]	Low-cost, energy efficient, inactivation by impurity production

|			
Metal organic framework	Pre-combustion; post-combustion; oxy-combustion	Cu-BTC[25], ZIFs[26], MIL-102[27]	Chemical diversity, high modulability, large surface area, expensive
Membrane	Pre-combustion; post-combustion; oxy-combustion	Pd-alloys[28], Modified-graphenes[29], MOFs[30]	Flexible, energy efficient, tradeoff between CO_2 permeability and selectivity
Zeolite	Pre-combustion; post-combustion;	Na-A zeolite[31], alkaline zeolite[32]	Molecular sieving property, high capacity under moderate conditions , high regeneration temperatures
Ionic liquid	Pre-combustion; post-combustion	amino acid ionic liquids[33], 1-ethyl-3-methylimidazolium cation based liquid[34], tetrabutylphosphonium glycinate[35]	High thermal stability, high modulability, low rate of adsorption
Porous carbon	Pre-combustion	nanotube[36], functionalized carbon[37], graphene[38]	Cheap, large adsorption capacity under high pressures, low selectivity,
Mesoporous silica nanoparticle	Pre-combustion	SBA-15[39], MCM-41[40]	Tunable surface, cheap
Amine-based solvent	Post-combustion;	mono-ethanolamine(MEA), piperazine[41], 2-amino-2methyl-1-propanol[42]	Commercially mature, high energy penalty to regenerate
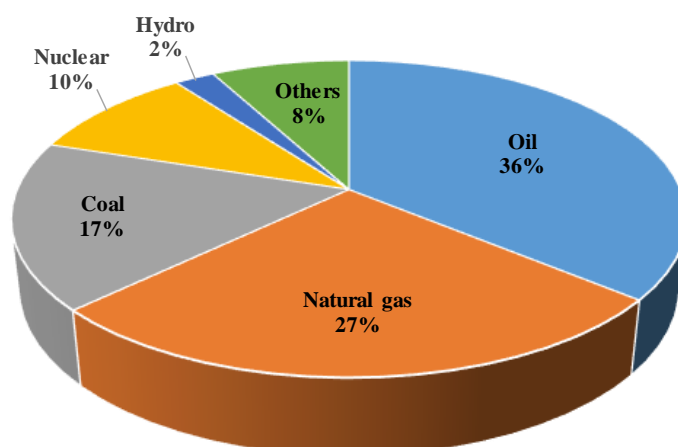
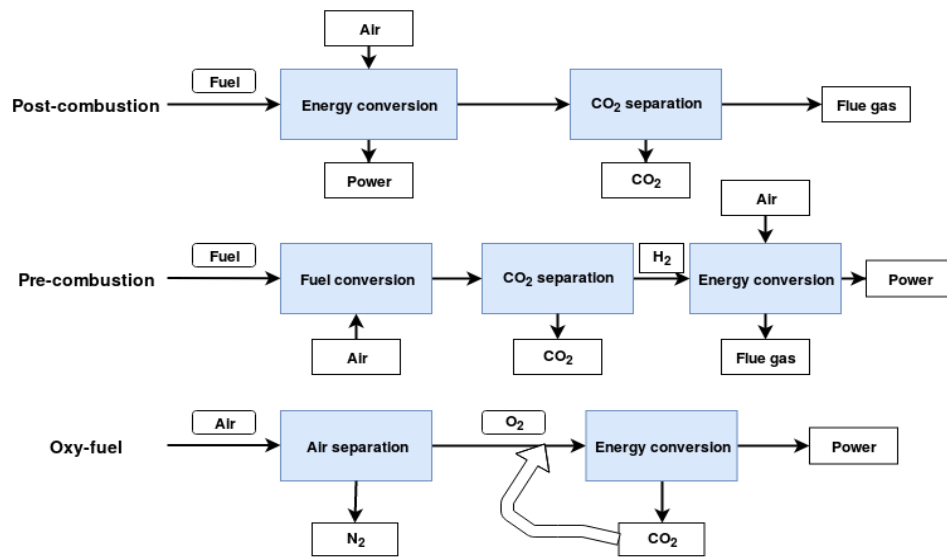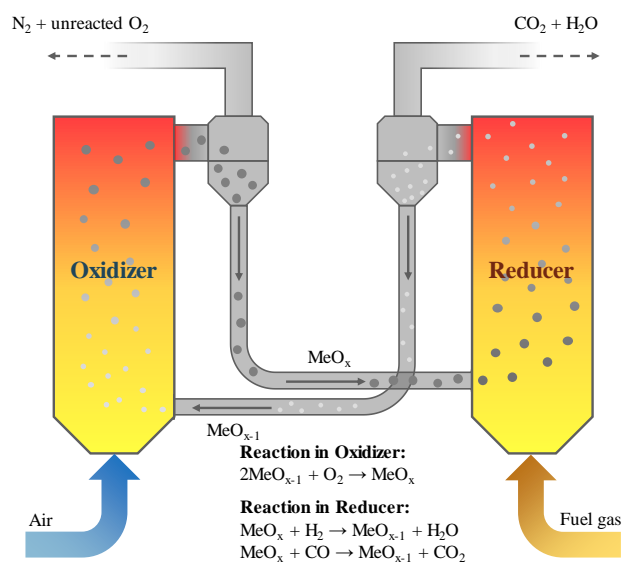**Fig.1** Contribution of fossil fuels to the overall energy supply in 2016

Fig.2 Process scheme of CO_2 capture technologies

N$_2$ + unreacted O$_2$ CO$_2$ + H$_2$O

Oxidizer   **Reducer**

MeO$_x$

MeO$_{x-1}$

Reaction in Oxidizer:
2MeO$_{x-1}$ + O$_2$ → MeO$_x$

Reaction in Reducer:
MeO$_x$ + H$_2$ → MeO$_{x-1}$ + H$_2$O
MeO$_x$ + CO → MeO$_{x-1}$ + CO$_2$

Air   Fuel gas

(a) Reaction scheme of a type I CLC process

Low concentration CO$_2$ stream   CO$_2$

Carbonation   **Calcination**

MeCO$_3$

MeO

High
concentration
CO$_2$ stream

Carbonation:
MeO + CO$_2$ → MeCO$_3$

Calcination:
MeCO$_3$ → MeO + CO$_2$

Heat
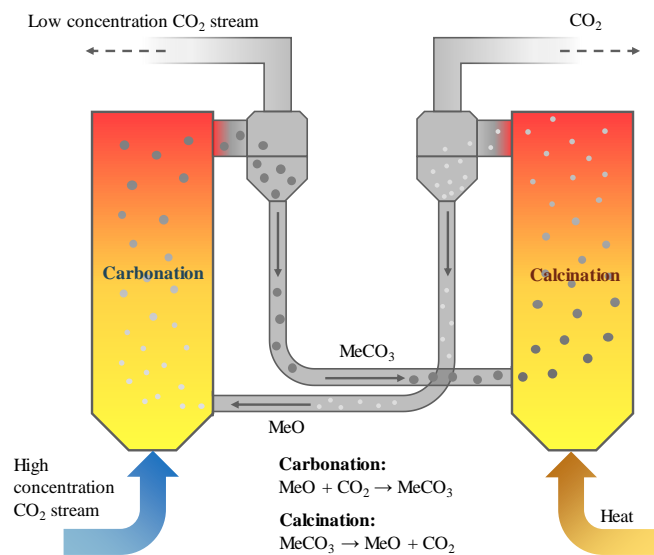
(b) Reaction scheme of type II CLC process

Fig. 3 Reaction schemes of CLC processes
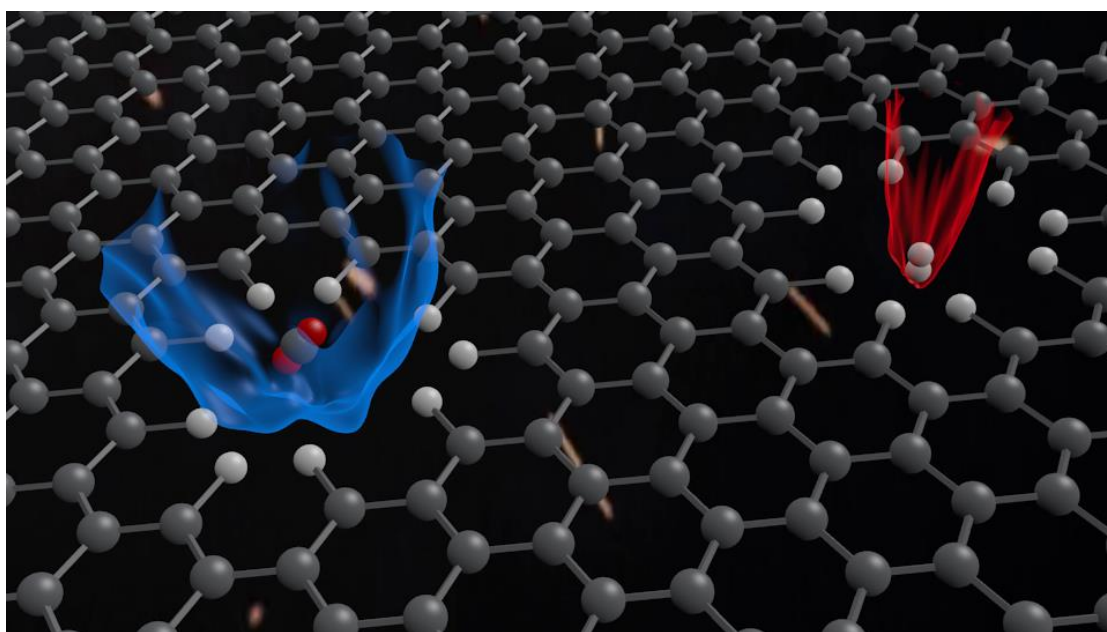
Fig.4 CO_2 and H_2 penetrate through HP13 membrane