

# A Review of Aerogel Applications in Adsorption and Catalysis

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## ABSTRACT

Aerogels are a special class of porous material, which have excellent physicochemical properties such as low density, high porosity, high surface area and adjustable surface chemistry. Aerogels were first prepared several decades ago, but never truly commercialized due to their high cost. Technological advancements in the production and quality of different types of aerogel cut costs down and market factors increase demand. Therefore, the viability of this porous material on the several applications has been widely studied. Among the various high-performance applications, aerogel has attracted significant attention as a chemical sorbent and catalyst for CO<sub>2</sub> capture and conversion as well as methane conversion to value-added products. Although aerogel performance for zero CO<sub>2</sub> emission to the environment is promising, some drawbacks of aerogels such as complicated drying process, mechanically weak structure and processing cost should also be considered in material development. Ultimately this review article will cover an overview regarding the aerogels synthesis, processing and their recent applications in CO<sub>2</sub> capture and conversion.

**Keywords:** Aerogel, Supercritical Drying, Catalyst, Sorbent, Carbon Capture

## INTRODUCTION

Aerogel is generally referred to any material derived from organic, inorganic or hybrid precursors that are prepared by a sol-gel process and a proper drying technology rapidly to extract the liquid in an alcogel and replace the liquid to make a three-dimensional and the highly porous network. Aerogels were firstly introduced by S. Kistler at 1930's when he extracted the pore-filling liquid of wet gels using a supercritical drying method [1-2] to obtain an air-filled solid material with nearly same dimensions as their original wet gel. The

difficult multistage processing steps developed by Kistler made aerogels obscure material for about 30 years. However, during the last decades, noticeable advancement in aerogel synthesis and their drying technologies, different types of aerogels are produced including inorganic (such as SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, etc.), organic (i.e. resorcinol-formaldehyde (RF), polyurethane, polyimide, polystyrene, etc.) [3] and carbon (i.e. carbon, carbon nanotubes, graphene) [4-5], and more recently SiC-based aerogels [6-7]. Furthermore, the combination of aerogels (aerogel composites)

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has often given an additional functionality such as mechanical strength, hydrophobicity and catalytic features to original materials and has extended some high-performance applications of aerogels [8]. Figure 1 shows the development of the aerogel after Kistler's initial work along with increasing the number of publications about aerogels during the last decades. In fact, following the significant advances in the synthesis process, aerogel has attracted significant interests by the researchers due to the promising technological functions of these materials applied for the advanced performances. The unusual aerogel properties such as low density ( $0.003\text{--}0.05\text{ g/cm}^3$ ), noticeably high surface area ( $500\text{--}2000\text{ m}^2/\text{g}$ ), high porosity ( $90\text{--}99\%$ ), with special surface chemistry that can be fabricated into a various morphologies and sizes make them suitable for many applications [9]. The aerogels are mostly used in thermal insulations in aerospace and building sectors [10], however, they are also promising materials for chemical sorption and catalysis applications that require high surface area and high porosity [11]. Some applications of aerogels includes adsorption and environmental cleanup [12], chemical sensors [13], acoustic transducers [14], energy storage devices [15], metal casting molds [16], water repellent coatings and biomedical and pharmaceutical applications [17]. Due to the above-mentioned properties, the catalytic feature of aerogels is rapidly developing for high-temperature performances in the materials and energy-related fields. The carbon capture application of aerogels is relatively a novel field and aims at cleaning flue gases from  $\text{CO}_2$  and establishing clean energy technologies with zero  $\text{CO}_2$  emissions. The  $\text{CO}_2$  release to the atmosphere is of major pollutants that cause the serious

environmental problems such as global warming and hazards for human health.  $\text{CO}_2$  conversion to fuels and chemicals is another fascinating process by which aerogel can be utilized as a catalytic material. The combination of both  $\text{CO}_2$  capture process and  $\text{CO}_2$  conversion process can contribute to ideal  $\text{CO}_2$  recycling concept. There are only a few review articles and book chapters that focus on the aerogels for the outlook of catalytic, energy and environmental-related applications [18-19]. This review paper will provide a comprehensive overview of the recent the development in aerogel materials that covers the synthesis and processing and the applications of almost all aerogels and their composites from different environmental and catalytic aspects.

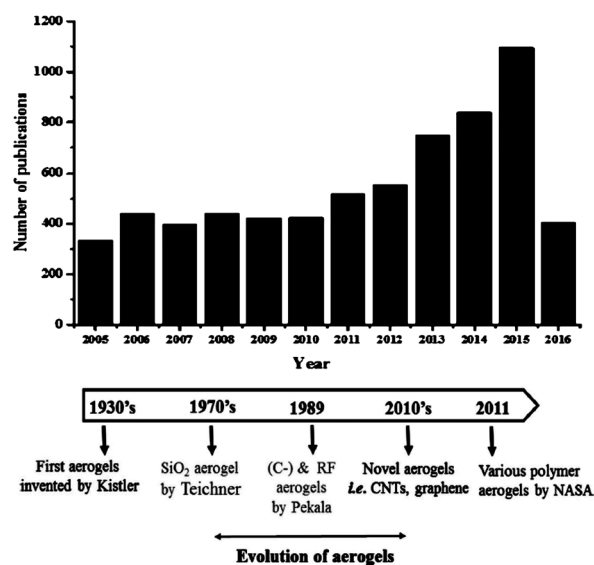


Figure 1: Number of publications (ScienceDirect record) during the last ten years containing aerogel in the content along with the evolution pattern of aerogels after invention. (Date of search: 13 Feb.2016).

## EXPERIMENTAL PROCEDURES

### Aerogel General Preparation

Preparation of aerogels is general between almost all types of aerogels. Preparation method of aerogels involves four significant steps: 1) sol-gel process, 2) aging, 3) drying and 4) thermal

treatment. Regarding aerogel activation for catalytic reactions and the use of aerogel as a support, additional thermal treatment such as calcination and reduction steps are conducted after drying [20]. The possible applications of aerogels extremely depend on the network structure and surface groups of aerogels that may be controlled by the sol-gel process parameters [21]. Therefore, it is essential to determine a precise synthesis and processing conditions for aerogels to obtain the required properties for a specific application.

### Sol-gel Process

Nearly all aerogels are prepared by the sol-gel approach but via different starting precursors and conditions. Sol is prepared from a mixture of main compounds, water, solvents, co-solvents and catalysts due to hydrolysis and condensation reactions. Usually by altering the reaction conditions (e. g. pH, temperature), the colloidal particles of sol link to form a three-dimensional and interconnected porous network, which is the most important feature of aerogel fabrication. Depending on its pore-filling solvent, gel mixture can be named alcogel and acetogel using alcohol and acetone as a pore solvent, respectively. While the hydrogel is usually prepared in the aqueous solution. During the sol-gel process, depending on the hydrolysis growth process and the rate of condensation, network particles sizes in either the polymeric or the colloidal state are formed in the range of 1–10 nm [22]. For instance, the sol-gel reaction pathway to prepare a silica aerogel network using tetraalkoxysilanes involves the hydrolysis reaction replacing the OR alkoxides with OH hydroxyl groups and, then, during condensation reactions, the silanol groups produce siloxane

bonds along with alcohol and water by-products. In most cases, condensation starts simultaneously with hydrolysis reactions and continues during the whole sol-gel process. The sol-gel process allows modifying the gel nanostructure by adjusting the reaction crucial parameters. There are many parameters that influence the sol-gel reactions and significantly control the nanostructure of the network and final material properties specifically 1) the concentrations of precursors to the solvent, 2) solvent and co-solvent types and ratios, 3) ratio of water to precursors, 4) temperature and 5) pH [23]. In addition, there is a possibility for incorporation of extra phase or a molecular compound in sol-gel reaction to provide a special feature on gel network either chemically by using suitable organofunctional alkoxide components, or physically by introducing additives/dopants in the porous network [24-25].

### Aging

The chemical reactions continue to proceed even after the gel formation [26]. It is due to the existence of an additional possibility of gel network to further grow in the solvent. This process is called aging period. In fact, the solvent inside the pores contains a reactive species (such as -OH) or unreacted monomers which can equally condense in the network. Usually, the whole process of aging takes from hours to days by immersing the gel in the initial sol or suitable solvent and under the controlled conditions [27]. The major function of the aging is to improve the mechanical strength of the fragile network of aerogels. In the aging process, the network particles undergo several phenomena such as Ostwald ripening or coarsening. Several parameters namely pH, time and temperature are

the most significant factors which can change the kinetics of aging process [28]. In addition, most of the textural properties, such as pore size, porosity, and surface area of synthesized gels are changed during aging. Aging is considered as an easy and strong technique for network strengthening of the as-prepared gels [29].

## Drying

The process of drying of gels without any collapse of the original porous structure is an important step during aerogel preparation. Three drying procedures are used for the obtained gels such as 1) supercritical drying (using i.e. alcohol, acetone, or CO<sub>2</sub>) [30], 2) ambient pressure drying, and 3) freeze-drying [31]. Normal pressure drying induces tension in the pores liquid surface at solid-liquid-vapor interface, which forms a capillary tension in pores walls. This is the main cause of the structural collapse and dimensional shrinkage in a dried gel. For an efficient drying of gels, the gradient of the capillary stresses developed in pores walls must impartially be avoided. The most efficient way to dry the gels, is extracting the pores liquid under the supercritical condition. In supercritical drying, the gel is placed inside the batch pressure vessel, then the pressure and temperature of vessel surpass the critical point (TC, PC) of the solvent. Due to no distinct separation between liquid and vapor phases, the capillary stresses are not built up; therefore, a crack-free solid gel is finally obtained. The critical drying condition is very different depending on the type of solvent [32]. The most commonly used solvent is CO<sub>2</sub> because of its mild critical temperature (TC=31°C) in supercritical CO<sub>2</sub> (scCO<sub>2</sub>) drying. The operation of this drying technique is safer compared to the supercritical

drying of other solvents (for example, ethanol TC = 240 °C) [33]. Normal drying is a promising, simple and safe technique to dry the gels under the room temperate conditions and may be a suitable way for the mass industrial productions. However, in this method, the surface of the pore walls inside the gel must be chemically treated with some non-polar groups to prevent further condensations in surface after being compressed by capillary stresses. In addition, the pore-filling solvent must be exchanged with a hydrocarbon or a solvent with less surface tension to avoid the capillary stresses tolerable by the pore walls. Freeze drying is a simple drying method used to prepare aerogels with practical porous structures. The liquid inside the gels is first frozen and removed by a sublimation process under very low pressures. The final materials are called cryogel with maximum 80% porosity and only half of the surface area of its aerogel counterpart. A rapid freezing rate often results in the small ice crystals and therefore, products are formed with small pore sizes and high pore surface area. The cryogels have more high volume of macroporosity, a large extent of shrinkage and low specific surface area compared to their scCO<sub>2</sub> counterparts [34].

## Thermal Treatment

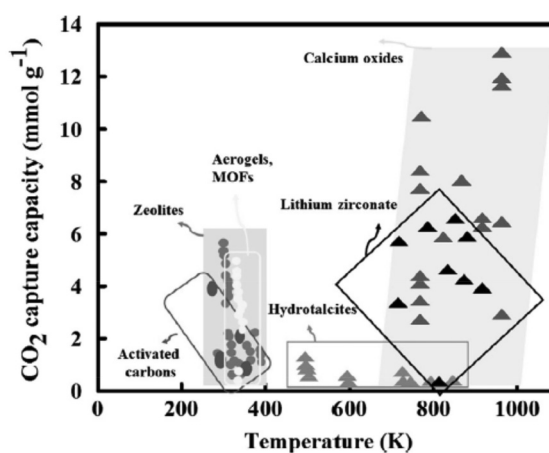
In addition to the processing steps, mixed metal oxide aerogels, which are prepared for sorption and catalysis purposes, undergo an extra processing step of calcination and activation. In the calcination process, aerogel is exposed to the high temperature (usually above 600 °C) and atmospheric pressure with/without an inert atmosphere of N<sub>2</sub> or Ar to decompose some volatile materials and enhances the network with the pure metal oxides.

## Adsorption Applications

A promising way to reduce greenhouse gases release in the atmosphere is to abate the emission of CO<sub>2</sub> [35]. The CO<sub>2</sub> capture technology must be able to be implemented both economically and on a very large scale [36]. The current technologies depend on the selective capture of CO<sub>2</sub> from flue gas and air by liquid amines and by membrane separation [37]. However, these developed technologies suffer from some problems such as energy-intensive capture and regeneration process, high corrosion of process equipment, oxidative degradation of the aqueous amines and highly possible production of toxic compounds during the CO<sub>2</sub> capture [38]. Porous solid materials such as zeolites, metal-organic frameworks (MOFs), activated carbon, and calcium oxides, etc. are considered as the emerging technologies for post-combustion and atmospheric CO<sub>2</sub> capture replacing the above-mentioned technologies [39]. Although the selectivity was low, high extent of porosities in these sorbents give a high adsorption capacity around 10 mmol/g at temperatures of about 500 °C and a moderate adsorption capacity of 6 mmol/g at room temperatures. Figure 2 shows CO<sub>2</sub> capacity and adsorption/desorption temperatures of well-known solid sorbents. To increase the CO<sub>2</sub> capacity of these porous sorbents at low temperatures, the active materials such as potassium carbonate, amines [40] and ionic liquid-amino acid moieties [41-42] impregnate on the surface of porous adsorbents such as conventional mesoporous silica (such as SBA-15, MCM-41). Sometimes the amine dispersion on the surface via the impregnation method is not homogenous; therefore, it significantly affects the sorption capacity results [43]. Besides above-mentioned

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porous sorbents, aerogels application for capturing CO<sub>2</sub> is quite promising due to their numerous advantages such as low density, high porosity, and high surface area. In addition, the flexibility of the sol-gel process, the microstructural form, as well as the composition and surface chemistry of aerogel can be modified intentionally for CO<sub>2</sub> capture [44]. For this purpose, recent investigations have focused on using aerogels as new CO<sub>2</sub> capture materials by changing the physicochemical properties of different aerogels.

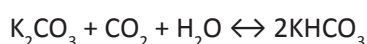


**Figure 2:** CO<sub>2</sub> capturing properties versus sorption temperature for various solid porous sorbents.

In this regard, various amines modified SiO<sub>2</sub> aerogels [45] have been studied with the CO<sub>2</sub> capacity of 6.97 mmol/g and 7.9 mmol/g under simulated flue gas conditions (in pre-humidified 10% CO<sub>2</sub>), respectively [46]. Furthermore, the other parameters that vastly impact on the rate of CO<sub>2</sub> uptake are the temperature and partial pressure of CO<sub>2</sub>, sorbent particle size, the density of the sorbent, gas/solids contacting, equipment responsiveness, etc. The partial pressure of CO<sub>2</sub> and temperature of sorption are important parameters regarding the kinetics of sorption, as at the optimal pressure, the kinetics of the sorption is usually slow at low temperature [47]. Generally, the newly

developed sorbents must exhibit excellent capture properties such as CO<sub>2</sub> capacity, H<sub>2</sub>O capacity, kinetics (rate of CO<sub>2</sub> uptake) and cyclic stability (over thousands of cycles) [48]. The co-adsorption of the low concentration water present in the flue gas may lead to an increase in the sorbent stability. However, adsorption of water at a large quantity could severely affect sorbent capacity and require the excess energy to vaporize the adsorbed water during the regeneration process. Amine-grafted sorbent using commercially available 10-micron size aerogel (Cabot Corp. Nanogel@) was developed with a sorption capacity of around 6.1 mmol/g [49]. Also, this sorbent had a fast kinetic by achieving 90% of its equilibrium capacity within 10 min and can maintain its capacity up to 10 adsorption/desorption cycles.

Besides supported amines, supported potassium carbonate, K<sub>2</sub>CO<sub>3</sub>, was proposed as a promising sorbent for low-temperature CO<sub>2</sub> capture. This sorbent adsorbs CO<sub>2</sub> in the presence of H<sub>2</sub>O at 60-100 °C by the following reaction:



Regeneration of K<sub>2</sub>CO<sub>3</sub> occurs at 120-300° C with the release of CO<sub>2</sub> and H<sub>2</sub>O. Based on the above reaction, the theoretical amount of CO<sub>2</sub> adsorbed per gram of potassium carbonate is calculated at 7.2 mmol/g. Our patented θ-alumina aerogel with a surface area around 420 m<sup>2</sup>/g used as a support for 50% K<sub>2</sub>CO<sub>3</sub> shows the highest CO<sub>2</sub> capture efficiency at the above-mentioned condition (50). Using conventional alumina as support, sorbent efficiency is lower than our aerogel sorbent due to excess water adsorption by hydrophilic γ-alumina and low potassium carbonate dispersion on the low surface area of θ-alumina (51).

At higher temperatures (over 600 °C), the capture capacity of calcium oxide has been applied for CO<sub>2</sub> removal through carbonate formation. The calcium oxide weak structure is likely to sinter. Therefore, capacity decreases significantly during an extended cyclic performance. Many approaches have been proposed to maintain this capacity for a long period of time but the problem remains unsolved due to the higher efficiency and excellent stability cannot be attained. While capturing techniques appear promising and have favorable thermodynamics, the cost has been substantial, due to the capture sorbents must be very finely divided for the maximum surface area. Moreover, these reactions are non-catalytic and depend entirely on molecular reactions at the surface of the sorbents. This is a real and unsatisfied need for improved capture capability of sorbents which have enhanced capture efficiencies. The novel calcium-oxide-based refractory sorbents synthesized by flame spray pyrolysis (FSP) for CO<sub>2</sub> capture was developed [52]. FSP was used for converting precursor droplets into solid nanoparticles in flames. FSP allows for the controlled synthesis of nanoparticles with high specific surface areas. The most stable sorbent (40 wt% ZrO<sub>2</sub>-60 wt% CaO) gives a CO<sub>2</sub> capacity of 10.76 mmol/g in an extended cyclic operation of 50 without any activity loss. Carbonation was conducted at 700 °C in 30% CO<sub>2</sub> for 30 min. Despite many preceding efforts to produce a high CO<sub>2</sub> capacity sorbent, a practical amount of 10.78 mmol/g has never been exceeded during extended cyclic operation. In accordance with our invention, a CaO aerogel sorbent comprised of a uniform dispersion of individual nanoparticles of calcium oxide was synthesized as substantially fluffy clusters of particles. Our patented sorbents had a

BET surface area in the range of about 70 to about 150 m<sup>2</sup>/g, a pore volume in the range of about 1 to about 6 cm<sup>3</sup>/g and a bulk density in the range of about 0.02 to about 0.05 g/cm<sup>3</sup>. The CaO aerogels were mixed with metal oxide stabilizer (specially zirconia) by three methods of 1) Mixing stabilizer during alcogel preparation, 2) Impregnation of aerogel with stabilizer precursor solution, and 3) Shelling aerogel or calcined aerogel surface by core-shell method. Our capturing results show the CaO-ZrO<sub>2</sub> aerogel sorbent had a CO<sub>2</sub> capacity of 15.6 mmol/g with activity loss of 10% during 30 extended cyclic operations [53]. The other proposed process for combustion with a direct CO<sub>2</sub> collection is chemical-looping combustion (CLC) which produce streams of relatively pure carbon dioxide and condensable steam [54]. Preparation of suitable oxygen carriers is crucial for the long-term operation of a CLC process. Nickel and iron oxides (NiO and Fe<sub>2</sub>O<sub>3</sub>) are promising materials for CLC. However, they exhibit a slow solid-state reaction between active metal oxides and support material at high temperature. Our highly effective alumina aerogel support calcined at over 800°C was used to fabricate NiO- and Fe<sub>2</sub>O<sub>3</sub>-supported compositions via the incipient wetness impregnation (IWI) method. These oxygen carriers exhibit the promising activities towards CLC process [50].

### Catalysis Applications

A comprehensive review on aerogels in catalysis up to the year 1990, covered preparation, physicochemical properties, and catalytic applications of mainly high-temperature aerogels such as partial oxidation, hydrogenation and oxidative coupling [55]. Binary mixed oxide aerogels that are mostly NiO, CuO, Li<sub>2</sub>O, and Fe<sub>2</sub>O<sub>3</sub> oxides

associated mainly with Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, and MgO were developed for the above reactions. Commercially available metal alkoxides, acetates or acetylacetonates are used as primary sol-gel precursors. The method of the preparation is the co-gelling of both metal derivatives in suitable organic solvents (or dispersing agents) by reaction with water in stoichiometric amounts. The supercritical drying is performed with respect to the solvent (dispersant) which have the highest critical temperature when two different solvents or dispersants have been selected. The first Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> aerogels were prepared from the mixing of two butanolic solutions of iron (III) acetylacetonate and of aluminum *s*-butylate in *s*-butanol [56]. Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> aerogel catalyst showed much higher productivities (300 times more) than the unsupported Fe<sub>2</sub>O<sub>3</sub> or the conventional xerogels [57]. Moreover, the mixed aerogel did not deactivate by carburization or through the formation of inactive carbon species, due to the oxidized form which was the best way to obtain such high activities in hydrocarbons, and that only the aerogel was able to maintain an adequate state of oxidation with time on stream. The same trend was also reported when alumina used as support [58]. Binary and ternary aerogels containing copper catalysts were tested in the synthesis of methanol with carbon dioxide and hydrogen feeds [59]. As with Fischer-Tropsch reactions, pre-oxidized aerogels were considered more efficient in the synthesis than the pre-reduced aerogels. Pure ZrO<sub>2</sub> aerogel is also a good catalyst for the methanol synthesis. The presence of zirconia is positive for the formation of methanol due to an electronic interaction between copper and zirconia. Recently a series of mixed silica aerogels containing lanthanum

and niobium oxides was prepared with BET surface areas of 700 to 800 m<sup>2</sup>/g before reaction [60]. These catalysts were used for the oxidative coupling of methane with a methane-to-oxygen ratio of 3:1 at atmospheric pressure at 800 °C. For La-SiO<sub>2</sub> aerogels, a methane conversion of 20% was achieved and the selectivity to C<sub>2</sub> was 30%. Nb-SiO<sub>2</sub> were as active as the La-SiO<sub>2</sub> catalysts but less selective in C<sub>2</sub> in the range of 8%. Ternary aerogels La-Nb-SiO<sub>2</sub> yielded to the same result (selectivity in C<sub>2</sub> 40% and methane conversion 13%). Since the aerogel method seems to be unique for producing solid with large textural properties stable at the temperatures that are generally selected for catalytic reactions. Aerogels are suggested to be evaluated in hydrotreatment processes such as hydrodenitrogenation (HDN) and hydrodesulphurization (HDS) because of their very large pore volumes and good stabilities [61]. Aerogels can find applications as components in solid superacid catalysts [62] using large surface area aerogel supports. Aerogels provide a way to make very advanced catalysts for problematic reactions. Metal-on aerogel support catalysts are very attractive since the sol-gel step allows to disperse the metal as a thin film or in any desired shape [63]. Aerogels can show a monodisperse distribution of particle which is easily fluidized. Therefore, they can be used in real conditions and are not restricted to the laboratory scale. The mixed aerogels or their parent gels yield to very homogeneous mixtures originating from chemical interactions at the molecular level in the liquid phase (or dispersed in a liquid phase). Aerogels are a sort of a three-dimensional dry structure of the sol-gel product with all their catalytic capabilities intact and available for discovery. Because aerogels exhibit high solid-state

chemical reactivities, they can also be applied to synthesize new catalysts with large surface areas and pores at moderately lower temperatures than the sintering temperatures which deteriorated the mixtures of powders. Aerogels show great promise in catalytic applications. Compared to conventional catalysts, their activity and selectivity in several catalytic reactions appear to be much higher. Besides, in some catalytic reactions, common catalysts become deactivated with time on stream. Currently, aerogel applications in CO<sub>2</sub> conversion to the value-added products have been attracted many interests, because CO<sub>2</sub> is a cheap, non-toxic and abundant C<sub>1</sub> feedstock. CO<sub>2</sub> chemical utilization is a challenge and an important topic [64]. Thus, any efficient reaction using CO<sub>2</sub> as a raw material has positive consequences on efforts towards carbon management. However, CO<sub>2</sub> is a thermodynamically stable compound, and then its reduction requires high energy. It is probably the reason why currently the toxic carbon monoxide is used mostly in industry. CH<sub>4</sub> and CO<sub>2</sub> are relatively inexpensive due to their natural abundance. The reaction between CO<sub>2</sub> and CH<sub>4</sub> to produce synthesis gas (CO + H<sub>2</sub>) can be used in chemical energy transmission systems or utilized in the Fischer-Tropsch reaction to produce liquids. Many researches have been conducted on the catalytic performance of noble metals such as Rh, Ru, Pd, Pt and Ir for CO<sub>2</sub> reforming of CH<sub>4</sub> [65]. Rh and Ru are generally accepted to show both high activity and stability in CH<sub>4</sub> dry reforming. Typically, the catalyst activity was in the order of Rh ≈ Ru > Ir, Pt, and Pd. The nature of support may have some effects on the activity of noble metals. Ni-based catalysts have been broadly investigated [66-67] due to their similar activity and relatively low price when compared with noble



metals. However, Ni-based catalysts were readily deactivated by carbon deposition and sintering. Thus, more efforts were made for the development of a stable Ni-based catalyst with high activity.  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$  were used as a support to prepare Ni-based catalysts for  $\text{CH}_4$  reforming reaction. The pre-oxidized support with Lewis basic site is observed to enhance the carbon-resistant ability of the catalyst for the strong adsorption capacity of  $\text{CO}_2$ . Moreover, strong interaction might promote the dispersion of Ni on the support, while much stronger interaction may decrease the reducibility of Ni on the catalyst surface. Besides, the formation of fibrous carbon is significantly influenced by the metal particle size which indicates that the support can affect the catalytic stability of the catalyst. The other potential use of  $\text{CO}_2$ , as an alternative feedstock replacing CO in the methanol synthesis has received attention as a second effective way of  $\text{CO}_2$  utilization in the past decades. Under proper conditions, methanol made from atmospheric  $\text{CO}_2$  by its reaction with hydrogen is considered the most economical way to reduce the greenhouse effect [68]. Most of the catalysts for  $\text{CO}_2$  hydrogenation contained Cu and Zn as the main components together with different modifiers (Zr, Ga, Si, Al, B, Cr, Ce, V, Ti, etc.) [69]. The Cu–ZnO/ $\text{ZrO}_2$  prepared by reverse co-precipitation under ultrasound irradiation was found to show a significant improvement in the total surface area of the metal phase, and then the enhanced  $\text{CO}_2$  conversion and methanol yield [70]. In the noble metal-based catalysts, the supported Pd catalysts are the most commonly used catalyst, which exhibits considerable activity and selectivity for hydrogenation of  $\text{CO}_2$  to methanol, and the supports has a significant effect on the performance

of the catalyst. Transitional metal carbides are a type of metal-derived compounds with the incorporation of carbon in the metal lattice. They have an excellent catalytic performance for hydrogenation, which is like those of Pt, Rh, and other noble metals [71]. Thus, the metal carbides can be used as potential alternatives for noble metal catalysts. Due to superior hydrogen adsorption, activation and transfer capabilities of metal carbides, they have potential application in  $\text{CO}_2$  hydrogenation reactions. Different carbides were tested for  $\text{CO}_2$  hydrogenation, the results indicated that  $\text{Mo}_2\text{C}$  and  $\text{Fe}_3\text{C}$  showed high  $\text{CO}_2$  conversion and good methanol selectivity [72]. Practically, a highly active, selective and poisoning-resistant catalyst for methanol synthesis is desirable.

## CONCLUSIONS

Technological advancements in the production and quality of basic materials are fundamental foundations for more innovation and growth. New advanced materials arising from developments in the material sciences offer new growth prospects through the support of new existing industrial and commercial products and processes. Two cutting-edge processes of 1)  $\text{CO}_2$  (dry) reforming of methane and 2) oxidative coupling of methane using  $\text{CO}_2$  and  $\text{O}_2$  as an oxidant have been developed for  $\text{CO}_2$  utilization and value-added products production. In these promising reactions, high surface area  $\theta$ -alumina (over  $400 \text{ m}^2/\text{g}$ ),  $\alpha$ -alumina (over  $200 \text{ m}^2/\text{g}$ ) aerogels, mixed alumina-magnesia and alumina-zirconia and silica aerogels support will be used to prepare very active catalysts. Ni-Rh (or Ru) supported  $\alpha$ -alumina or magnesia aerogel will be the potential candidates for  $\text{CO}_2$  reforming reaction.

In the search for excellent catalysts, hundreds of materials have been tested for oxidative coupling of methane. Among them, Li-magnesia aerogel,  $\text{Re}_2\text{O}_3$  (Re: La, Sm, Gd)-silica aerogel and  $\text{Mn-Na}_2\text{WO}_4$ -silica aerogel which showed higher performance than most other materials will be applied for oxidative coupling reactions in future.

## NOMENCLATURES

CLC:	Chemical-Looping Combustion
FSP:	Flame Spray Pyrolysis
HDN:	Hydrodenitrogenation
HDS:	Hydrodesulphurization

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