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# Global challenges and strategies for control, conversion and utilization of $CO_2$ for sustainable development involving energy, catalysis, adsorption and chemical processing[☆]

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## Abstract

Utilization of carbon dioxide ($CO_2$) has become an important global issue due to the significant and continuous rise in atmospheric $CO_2$ concentrations, accelerated growth in the consumption of carbon-based energy worldwide, depletion of carbon-based energy resources, and low efficiency in current energy systems. The barriers for $CO_2$ utilization include: (1) costs of $CO_2$ capture, separation, purification, and transportation to user site; (2) energy requirements of $CO_2$ chemical conversion (plus source and cost of co-reactants); (3) market size limitations, little investment-incentives and lack of industrial commitments for enhancing $CO_2$-based chemicals; and (4) the lack of socio-economical driving forces. The strategic objectives may include: (1) use $CO_2$ for environmentally-benign physical and chemical processing that adds value to the process; (2) use $CO_2$ to produce industrially useful chemicals and materials that adds value to the products; (3) use $CO_2$ as a beneficial fluid for processing or as a medium for energy recovery and emission reduction; and (4) use $CO_2$ recycling involving renewable sources of energy to conserve carbon resources for sustainable development. The approaches for enhancing $CO_2$ utilization may include one or more of the following: (1) for applications that do not require pure $CO_2$, develop effective processes for using the $CO_2$-concentrated flue gas from industrial plants or $CO_2$-rich resources without $CO_2$ separation; (2) for applications that need pure $CO_2$, develop more efficient and less-energy intensive processes for separation of $CO_2$ selectively without the negative impacts of co-existing gases such as $H_2O$, $O_2$, and $N_2$; (3) replace a hazardous or less-effective substance in existing processes with $CO_2$ as an alternate medium or solvent or co-reactant or a combination of them; (4) make use of $CO_2$ based on the unique physical properties as supercritical fluid or as either solvent or anti-solvent; (5) use $CO_2$ based on the unique chemical properties for $CO_2$ to be incorporated with high 'atom efficiency' such as carboxylation and carbonate synthesis; (6) produce useful chemicals and materials using $CO_2$ as a reactant or feedstock; (7) use $CO_2$ for energy recovery while reducing its emissions to the atmosphere by sequestration; (8) recycle $CO_2$ as C-source for chemicals and fuels using renewable sources of energy; and (9) convert $CO_2$ under either bio-chemical or geologic-formation conditions into ''new fossil'' energies. Several cases are discussed in more detail. The first example is tri-reforming of methane versus the well-known $CO_2$ reforming over transition metal catalysts such as supported Ni catalysts. Using $CO_2$ along with $H_2O$ and $O_2$ in flue gases of power plants without separation, tri-reforming is a synergetic combination of $CO_2$ reforming, steam reforming and partial oxidation and it can eliminate carbon deposition problem and produces syngas with desired $H_2$/CO ratios for industrial applications. The second example is a $CO_2$ ''molecular basket'' as $CO_2$-selective high-capacity adsorbent which was developed using mesoporous molecular sieve MCM-41 and polyethylenimine (PEI). The MCM41-PEI adsorbent has higher adsorption capacity than either PEI or MCM-41 alone and can be used as highly $CO_2$-selective adsorbent for gas mixtures without the pre-removal of moisture because it even enhances $CO_2$ adsorption capacity. The third example is synthesis of dimethyl carbonate using $CO_2$ and methanol, which demonstrates the environmental benefit of avoiding toxic phosgene and a processing advantage. The fourth example is the application of supercritical $CO_2$ for extraction and for chemical processing where $CO_2$ is either a solvent or a co-reactant, or both. The $CO_2$ utilization contributes to enhancing sustainability, since various chemicals, materials, and fuels can be synthesized using $CO_2$, which should be a sustainable way in the long term when renewable sources of energy are used as energy input.

*Keywords:* Carbon dioxide; Strategy; Sustainable development; Atom efficiency; Utilization; energy; Tri-reforming; $CO_2$ reforming; Emissions; Catalysis; Conversion; Capture; Separation; Reforming; Dimethylcarbonate; Supercritical $CO_2$; Fuels

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## 1. Introduction

In the history of civilizations, the 20th century can be characterized as a century of explosive growth in energy consumption and rapid increase in population worldwide, as shown in Table 1, along with unprecedented pace of inventions of new technologies and ever-increasing expansion of man-made materials. One of the greatest revolutions in the 20th century is that of transport. Inventions of cars, trucks, and airplanes along with engine-powered trains and ships have created a new world that has become increasingly dependent on combustion of hydrocarbon fuels such as gasoline, diesel fuel, and jet fuel. Inventions of electrical power plants, electric home appliances, personal computers, and mobile cell phones have electrified the world, which is increasingly dependent on electricity generated largely from carbon-based resources such as coal and natural gas. Invention of high-pressure ammonia synthesis and development of the chemical fertilizers with nitrogen, phosphorus, and potassium and the engine-based machinery for crop production fueled the rapid growth in global population.

Environmental problems due to emissions of pollutants from combustion of solid, liquid and gaseous fuels in various stationary and mobile energy systems as well as the emissions from manufacturing plants have also become major global problems involving not only the pollutants such as $NO_x$, $SO_x$, and particulate matter, but also the greenhouse gases (GHG) such as carbon dioxide ($CO_2$) and methane ($CH_4$). There are increasing concerns for global climate change [1–3] and thus heightened interest worldwide for reducing the emissions of GHG, particularly $CO_2$ [4–7].

$CO_2$ is a colorless and odorless gas. The molecule is linear with a double bond between the carbon and oxygen atoms (O=C=O). $CO_2$ occurs in nature and serves as source of carbon for photosynthesis of plants and crops. It is present in atmosphere with a volumetric concentration of 0.038 % (377 parts per million by volume, ppmv) as of December 2004 [8]. Combustion of most carbon-containing substances produces $CO_2$. Energy utilization in modern societies today is based on combustion of carbonaceous fuels, which are dominated by the three fossil fuels: coal, petroleum, and natural gas. Complete oxidation or combustion of any carbon-based organic matter produces $CO_2$, but until recently, $CO_2$ gas was generally thought to be harmless. In fact, $CO_2$ plays an important role in the earth's carbon cycle, and is a necessary ingredient in the life cycle of animals and plants [9,10].

This article is an overview on the global issues of $CO_2$ utilization and the strategic directions that were initially introduced in an earlier report [11,12]. The purposes of this overview are to discuss the global challenges and strategic considerations for the control, conversion and utilization of $CO_2$ and the research directions of $CO_2$ utilization. It is written to facilitate the advances in this research area worldwide. It focuses on directions and approaches and is meant to be complimentary to the topical reviews on synthesis of organic chemicals [13–19], on chemical conversion of $CO_2$ over heterogeneous catalysts [20–25], on synthesis gas production from $CO_2$ reforming of $CH_4$ [25–29], on reactions in supercritical $CO_2$ as a reactant or medium [1,30–33], on polymer synthesis and processing using supercritical $CO_2$ [34,35], on thermodynamics of chemical reactions [36]; and on various chemical processes involving $CO_2$ [4,5,11,12,16,37–43].

Table 1
Worldwide energy use, population and per capita consumption in 20th century

| Energy | 1900 Use | 1900 Distn | 2001 Use | 2001 Distn |
|---|---|---|---|---|
| Source | Million tons of oil quivalent[a,b] | Percentage (%) or Unit | Million tons of oil equivalent[b,c] | Percentage (%) or Unit |
| Coal | 501 | 55 | 2395 | 24 |
| Petroleum | 18 | 2 | 3913 | 39 |
| Natural gas | 9 | 1 | 2328 | 23 |
| Nuclear | 0 | 0 | 662 | 6 |
| Renewables[d] | 383 | 42 | 750 | 8 |
| Total | 911 | 100% | 10048 | 100% |
| Population[a,b] | 1,762 | Million | 6153 | Million |
| Per Capita E Use | 0.517 | TOE[e] | 1.633 | TOE |
| Global $CO_2$ emission[b,c] | 534 | MMTCE[e] | 6607 | MMTCE |
| Per capita $CO_2$ emission | 0.30 | MTCE[e] | 1.07 | MTCE |
| Atmospheric $CO_2$[f] | 295 | ppmv[e] | 371 | ppmv |
| Life expectancy[g] | 47.3 | Years | 77.2 | Years |

[a] Source for energy in 1900: C. Flavin and S. Dunn of Worldwatch Institute (State of the World, 1999).

[b] Sources: 2001 data from Statistical Abstract of the United States 2003 (The National data Book, US Department of Commerce, 2004); 1900 population and $CO_2$ data from US Census Bureau-Historical Estimates of World Population from different sources for years up to 1950 (US Bureau of Censors, 1999).

[c] Sources for 2001 $CO_2$ data: International Energy Annual 2002 (Energy Information Administration, 2004).

[d] Including hydroelectric power, biomass, geothermal, solar and wind energy.

[e] Units: ton of oil equivalent (TOE); million metric tons of carbon equivalent (MMTCE); metric ton of carbon equivalent (MTCE); parts per million by volume (ppmv).

[f] Carbon Dioxide Information Analysis Centre (Keeling and Whorf, 2005).

[g] Data for the US from National Center for Health Statistics (U.S. Department of Health and Human Services, 2003).

Table 2
Sources of carbon dioxide ($CO_2$) emissions

| Stationary sources | Mobile sources | Natural sources |
|---|---|---|
| Fossil fuel-based electric power plants | Cars, and sports utility vehicles | Humans |
| Independent power producers | Trucks and buses | Animals |
| Manufacturing plants in industry[a] | Aircrafts | Plants and animal decay |
| Commercial and residential buildings | Trains and ships | Land emission/leakage |
| Flares of gas at fields | Construction vehicles | Volcano |
| Military and government facilities | Military vehicles & devices | Earthquake |

[a] Major concentrated $CO_2$ sources include plants for manufacturing hydrogen, ammonia, cement, limestone, and soda ash as well as fermentation processes and chemical oxidation processes.

## 2. Global energy and $CO_2$ problems

Table 1 shows the changes in worldwide consumption of various forms of primary energy sources along with global and per capita $CO_2$ emissions from 1900 to 2001, which reflects the tremendous global economic developments in the 20th century.

### 2.1. Rise in atmospheric $CO_2$ concentrations

The sources of $CO_2$ emissions include stationary, mobile, and natural sources, as listed in Table 2. The anthropogenic emissions include those from energy utilization in stationary and mobile sources, but exclude natural sources. Fig. 1 shows the changes in the global atmospheric $CO_2$ concentration for over one millennium during 1000–2004 based on recent studies [8]. Atmospheric $CO_2$ concentration changed only slightly over the period of a thousand years till 20th century, from 280 ppmv in 1000 to 295 ppmv in 1900 based on Antarctica ice core data [44], but increased to 315 ppmv in 1958 and further to 377 ppmv in 2004 based on actual analysis in Hawaii [8]. It should be mentioned that the atmospheric $CO_2$ has important and positive roles in the ecological system, since photosynthesis and food production depends on it as a carbon source. The fossil fuels that we use today originated from atmospheric $CO_2$ millions of years ago. However, through the studies in the past five decades and most notably in the last 15 years, the emissions

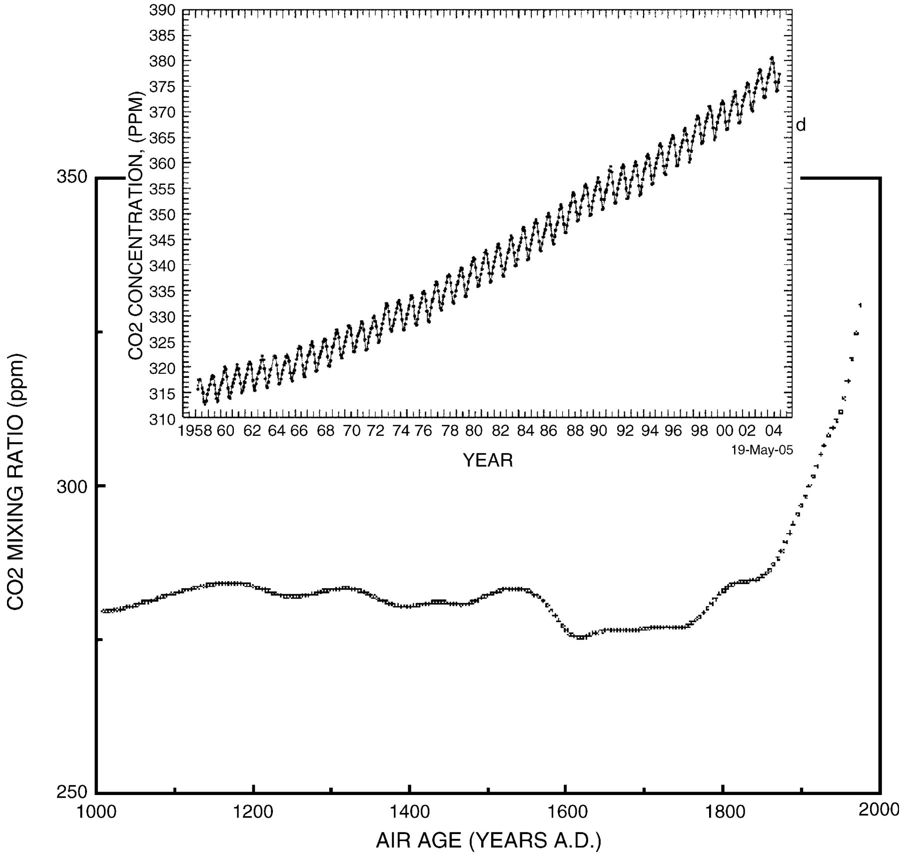


Fig. 1. Atmospheric $CO_2$ concentrations during 1000–2004 based on the analysis of ice cores for 1000–1997 [44] and actual atmospheric $CO_2$ analysis during 1958–2004 [8].

of $CO_2$ have become an important concern for global climate change because the atmospheric $CO_2$ concentrations increased significantly in the last century and continuously rising at a faster rate.

Fig. 2 shows the US energy consumption by source during 1635–2000 in quadrillion ($10^{15}$) Btu including a future projection to 2020, along with the world $CO_2$ emissions during 1750–2002 (in million metric tons of carbon) and US $CO_2$ emissions during 1800–2000 (in thousand metric tons of carbon). The growth in energy consumption and the rise in GHG emissions in the US parallel each other, as can be seen from Fig. 2. The same trend is true also for the world [45,46]. The growth rates of most regions in the world are becoming more rapid. The energy crises in 1973 and 1978 caused some slow down but the overall trends of growth continued. Since early 1980s, globalization of manufacturing led by the industrialized nations and economical developments in the developing countries have greatly accelerated the growth in energy consumption and also worldwide $CO_2$ emissions per capita. According to a recent study, about 290 billion tons of carbon have been released to the atmosphere from the consumption of fossil fuels and cement production since 1751, but half of these emissions have occurred since the mid 1970s [45].

### 2.2. Fast depletion of energy resources

A major challenge in the world is that the fossil hydrocarbon resources are being consumed so rapidly worldwide. The resources of petroleum and natural gas that took tens of millions of years to form and accumulate have been consumed so fast in the last 80 years that they have shrunk to one to two human life spans [171]. Coal resources are more abundant and projected to last longer, for two to three hundred years based on current rate of consumption, but they are also limited [172,173]. Through a comprehensive analysis in a recent review, Weisz has pointed out that the energy demand and the population growth are exhausting the world's supplies of oil, gas and coal (Weisz, 2004). Other non-conventional fossil fuels such as tar sands, oil shale, and natural gas hydrates are also being considered and tar sands are being used commercially in Canada. All of these conventional and non-conventional hydrocarbon resources are non-renewable, and thus can be exhausted.

### 2.3. Waste of energy in current systems

The existing energy systems such as stationary power plants and mobile engine systems as in cars and trucks have been improved significantly in the last eight decades since the

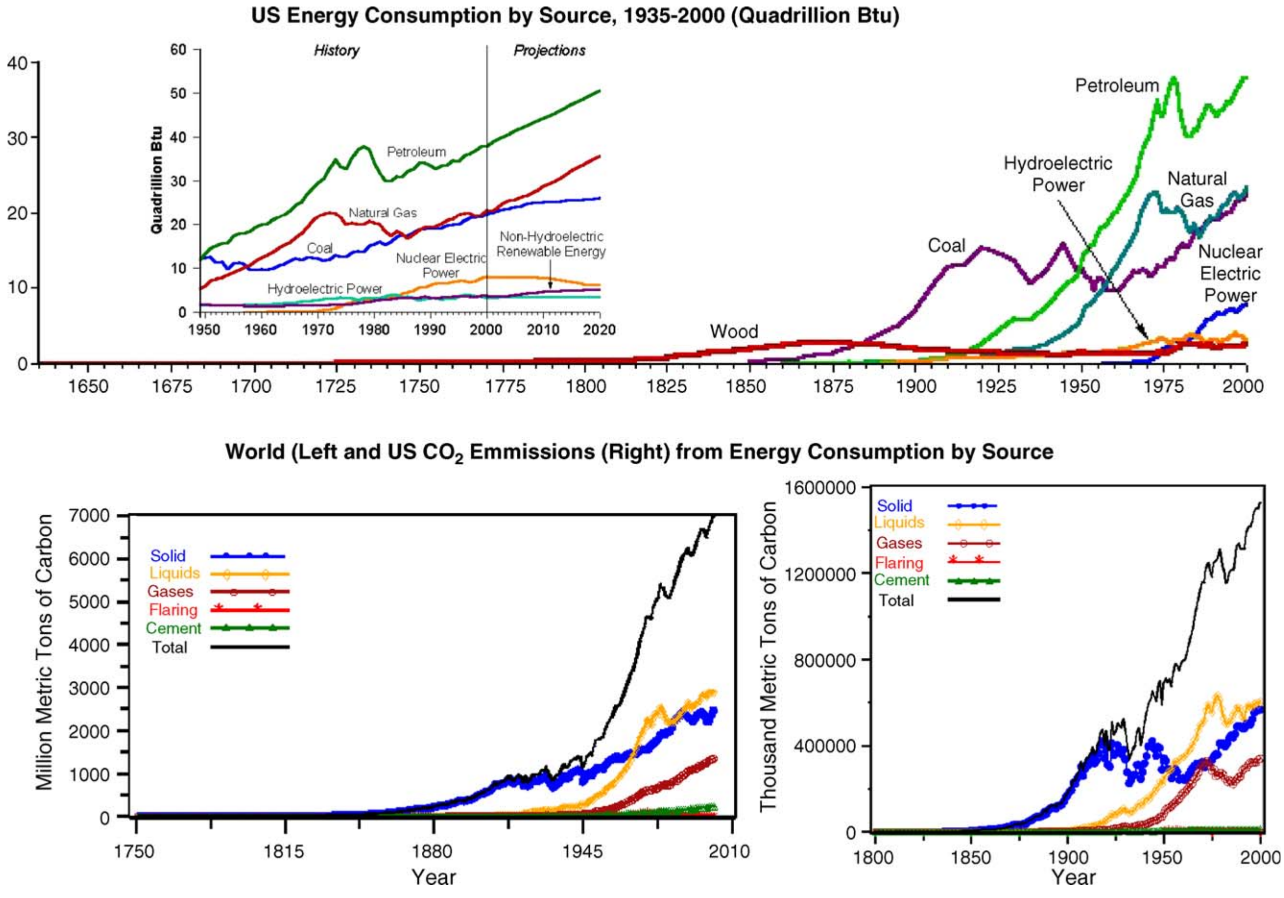


Fig. 2. Energy consumption and $CO_2$ emissions, including US consumption of different energy sources during 1650–2000 (top); projected energy consumption to 2020 (top, insert) (Source: various sections in [46]); and World $CO_2$ emissions in million metric tons of carbon (bottom left) and US $CO_2$ emissions in thousand metric tons of carbon by fuel type (bottom, right) (Source: [45]).

1920s. However, there is a fundamental limit in the energy conversion efficiency that is commonly known as the Carnot cycle efficiency. Fig. 3 shows the overall energy flow in the electric power plants in the US in 2003 [46]. It is important to note that as much as 65% of the energy input (39.62 quadrillion BTU, Quads) into the electric power plants, is wasted. In other words, a huge amount of primary energy input, as much as 25.80 Quads, is wasted as conversion loss. The useful energy output, 13.82 Quads as electricity, represents only 35% of the energy input as electricity. This is the efficiency that can be achieved in large centralized energy conversion systems today in the US. The overall system energy efficiencies for cars and trucks as well as trains and airplanes are lower than the large-scale central power plants. It is worth noting that as much as 65–80% of energy input is wasted as conversion loss in the mobile energy systems such as passenger cars.

Therefore, a fundamentally critical problem is that we consume more resources than needed because we throw away more energy as waste than we make use of the energy as work. These apply to the utilization systems for all the hydrocarbon fuels since the waste is more than the useful output of energy such as electricity or distance traveled with a gasoline engine. As a consequence, we are emitting more greenhouse gases along with the pollutants into the environment per unit of useful energy output.

## 3. Global energy challenges in the 21st century

GHG problems are largely the results of consuming the carbon-based energy using the combustion-based energy systems, as can be seen from Table 1 and Fig. 2. Based on the above discussion, the major challenges in the 21st century can be highlighted below.

- Supply clean fuels and electricity to meet the growing demand worldwide safely.
- Eliminate environmental pollution problems and stabilize GHG emissions due to energy utilization.
- Increase energy efficiency by developing new energy systems for overcoming the thermodynamic limits of existing wasteful energy systems.
- Sustainable and safe development of energy sources including renewable energy sources.
- Sustainable organic material development involving carbon-based feedstock.

As a developed civilization that is accustomed to the electrified and motorized living in the wired and wireless network, we need to develop a way to decouple the seemingly natural link between the energy utilization and the environmental problems such as emissions of $NO_x$, $SO_x$ and particulate matters as well as volatile organic compounds. One approach is to design and develop cleaner and more efficient energy systems that do not generate such pollutants, rather than by post-utilization clean up from existing systems such as trucks and stationary power plants.

There is a real need to increase the energy efficiency in a major jump, e.g., from 15–35 to 60–80%, by developing new, more efficient and cleaner energy systems, rather than incremental improvement based on the existing systems. This would minimize any $CO_2$ emissions that are associated with the wasteful energy uses and thus contributes to gradual stabilization of atmospheric $CO_2$ concentrations. Recent advances in new power system designs such as integrated gasification-combined cycle (IGCC), gas turbine combined cycle (GTCC), hydrogen energy, and fuel cell developments offer some promises and clues to the future development [46].

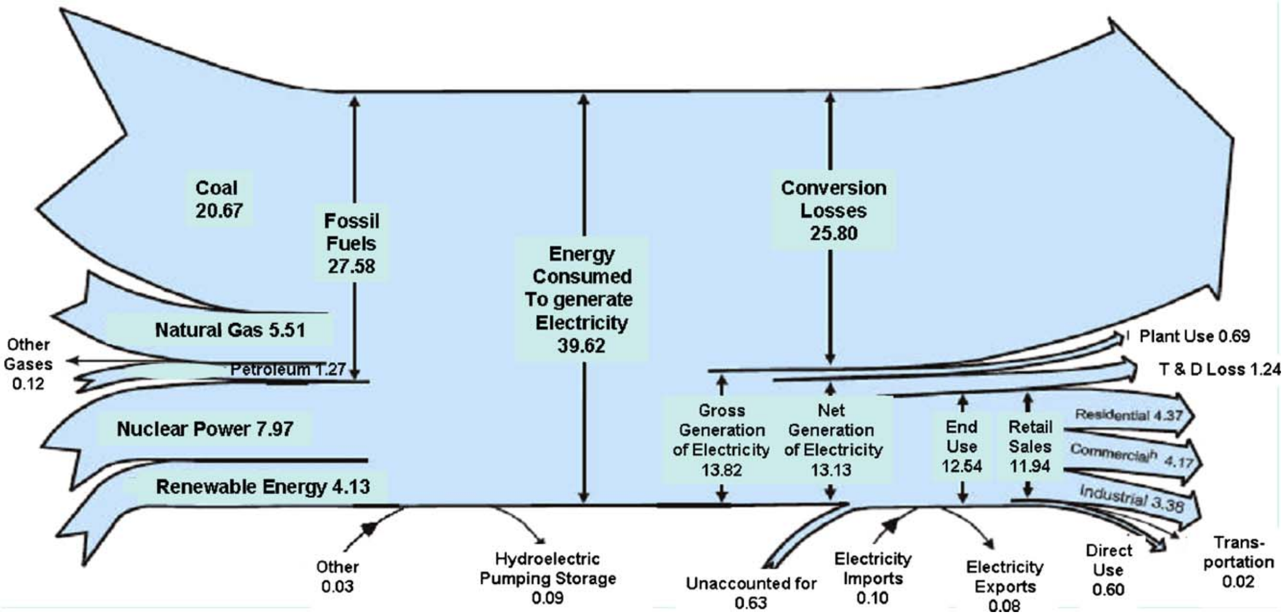


Fig. 3. The overall energy flow in the electric power plants in the US in 2003 in quadrillion BTU [46].

There is a long-term need to make more active use of renewable sources of energy (e.g., solar energy, biomass, wind, geothermal, wave) and design better conversion systems without negative impacts on the environment. For the foreseeable future (the next two decades), fossil fuels will continue to be the dominant and the most cost-effective energy resource. However, the use of more renewable resources must be emphasized even if it costs more in the near term. This is important for sustainable energy development, and government incentives are necessary to nurture the growth of renewable sources such as solar and biomass along with recycled energy sources such as organic wastes.

Biomass provides a path for renewable sources of carbon-based energy, chemicals, and materials. Solar energy conversion via photovoltaic cells is a path that has most energy and environmental benefits and also potential to grow, provided that more efficient conversion devices can be made affordable. It should be noted that renewable energy utilization systems can have some negative impacts to the human and ecological environments (effects of solar energy facilities on land use; biomass growth on land area; wind power on birds; hydropower on aqua life, etc.). Nonetheless, there are also great benefits. It is a major challenge because the use of so-called renewable energy sources encounters regional distribution and seasonable availability issues as well as energy density issues.

Hydrogen energy has the potential to decouple the link between energy utilization and environmental problems, and can make the energy conversion systems more efficient through use of fuel cells. Centralized $H_2$ production and distributed $H_2$ gen eration on-site and on-board are both viable options for the path forward. Hydrogen energy development can significantly reduce the greenhouse gas emissions, and eliminate the pollutants emissions from mobile as well as stationary sources. It should be noted that unlike petroleum or natural gas, $H_2$ molecule does not exist as a resource in nature in the earth system, $H_2$ must be produced by using sources of hydrogen atom with energy input. Therefore, $H_2$ is an energy carrier like electricity. $H_2$ production, storage, and utilization via fuel cell systems are active research subjects, but $H_2$ energy could be made sustainable if renewable sources of energy is used as energy input [47,48]. The US Department of Energy is supporting research for hydrogen energy development through major government-funded programs such as Freedom CAR and Freedom Fuel for mobile systems such as cars and trucks [49] and Future Gen for stationary systems [50] such as coal-based electric power plants.

Nuclear energy has a huge potential for growth in terms of meeting the energy needs without GHG emissions, but it also involves major challenges that have resulted in the NIMBY (not in my back yard) syndrome worldwide. This is largely related to the accidents of nuclear power plants at Three Mile Island on 28th March 1979 in the US and in Chernobyl in Ukraine on 26th April 1986. The security and safety of nuclear power plants and also the spent nuclear fuels is a more serious concern in the current global political-economical environments that have been impacted significantly by the terrorists' attacks on the US on 11th September 2001, on Spain in Madrid on 11th March 2004, and on UK in London on 7th July 2005. The security of even the non-nuclear, chemical manufacturing plants have also become major concerns. As an example, New Jersey state government in the US announced an order on 29th November 2005 making New Jersey the first state to have mandatory standards for the chemical plant security.

We still need carbon-based feedstock for manufacturing chemicals and organic materials, even if the energy problem is solved. The world today depends on carbon-based chemicals and organic materials which characterize the current civilizations and shape our life style in a wide range of applications, from clothes to shoes, from kitchen to bedroom, from homes to offices, from cosmetics to automobiles, from plastic beverage bottles to gasoline tanks, from commercial buildings to manufacturing plants, from heat-resistant polymers to aerospace materials, and from computers to mobile cell phones. As the resources of fossil fuels are being consumed rapidly, we should be concerned equally for the future supplies of feedstock for carbon-based chemicals and organic materials.

## 4. Challenges of $CO_2$ control and utilization

### 4.1. Challenges for control of $CO_2$ emissions

Fig. 4 outlines the key issues related to greenhouse gas control and utilization. The basic issues of GHG control involve energy economics, policy regulations, environmental protection and global climate change. The anthropogenic emissions of GHGs are due mainly to the fossil energy utilization. Control of $CO_2$ emissions is among most important areas of GHG control. The economic development in the US has benefited greatly from relatively cheap energy sources. The idea for regulation of $CO_2$ emissions by ratifying Kyoto

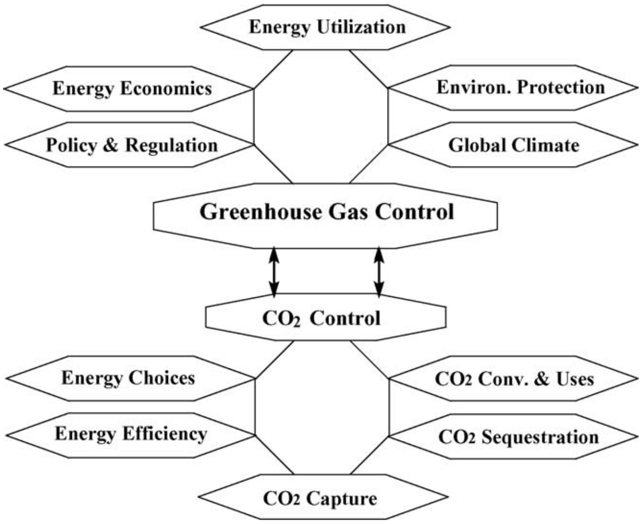


Fig. 4. Key issues related to control and utilization of greenhouse gas including $CO_2$ (modified after [47]).

Protocol has not been popular in the US, although emissions of pollutants ($SO_x$, $NO_x$, CO, HC, particulate matters, etc.) are being regulated strictly in the US However, carbon tax has already been implemented for $CO_2$ emissions in some countries in Western Europe.

The global strategy for $CO_2$ control should involve thinking and actions outside $CO_2$, as shown in Fig. 4. There are no easy solutions without involving major changes in the energy systems, and there are various opinions regarding the issues related to energy supply, greenhouse gas, and climate change. For the global challenges on energy and GHG problems, innovative ideas and revolutionary approaches are needed towards the long-term solution. There are five broadly defined technical options for control of $CO_2$ emissions: energy choices, energy efficiency, $CO_2$ capture, $CO_2$ sequestration, and $CO_2$ utilization. These options are briefly discussed below.

Energy choice is the basic consideration for selecting the primary energy input for new installations of energy systems or for switching between different forms of energy for existing energy systems. One can reduce the $CO_2$ emission per million BTU by selecting the less $CO_2$-intensive form of energy, for example, natural gas versus coal. An empirical rule of thumb is the atomic hydrogen-to-carbon ratio; the higher the H/C ratio, the lower the amount of $CO_2$ per million BTU. The H/C ratio decreases in the order of natural gas (about 4), petroleum (about 1.8–2.0), and coal (about 0.8–1.2). Fuel decarbonization before combustion is an option that is being studied as one way to mitigate $CO_2$ emissions to atmosphere [5], which is also related to the above discussion with respect to fuel H/C ratio changes.

An alternative is to use more renewable energy. Common renewable energy forms include hydropower, solar energy, wind energy, and biomass. Biomass and animal wastes are opportunity fuels whose use is also encouraged where available. They are not completely $CO_2$-neutral, because the collection, transportation and processing of biomass consume energy and fuels. When fertilizers are used for biomass production, the processes and the energy required for fertilizer production should also be considered for counting $CO_2$ emissions. The issues of major concern for biomass include the regional and seasonal availability as well as energy density and energy demand-supply balance. Combination of biomass with fossil energy in certain ways including conversion is also being explored [51].

Solar energy could also be used in selected endothermic chemical processes to reduce the need for using heat from combustion of fossil fuels, which also produces $CO_2$. The issues of concern are availability, energy density, energy efficiency, and capital cost.

Development for improved energy efficiency is an important area that has a major impact on $CO_2$ reduction. Existing energy utilization systems in the fossil fuel-based electricity generators in the US have an average efficiency of about 35%. The efficiencies for the automobiles are even lower, less than 20% [52]. Development and implementation of new energy utilization systems such as IGCC for coal-based power plants, GTCC for natural gas-based power plants, and fuel cell-based hybrid motors for transportation, could increase the energy efficiencies significantly, by 30% or more. The same principle can be applied to chemical industry, where more efficient process or more selective catalyst can make a process such as oxidation reaction more selective such that $CO_2$ formation is minimized at the source, thus improving the process efficiency and conserving hydrocarbon resource [161].

### 4.2. Needs for $CO_2$ utilization for sustainable development

$CO_2$ is not just a greenhouse gas, but also an important source of carbon for making organic chemicals, materials and carbohydrates (e.g., foods). As will be discussed below, various chemicals, materials, and fuels can be synthesized using $CO_2$, which should be a sustainable way in the long term when renewable sources of energy such as solar energy is used as energy input for the chemical processing.

The amount of $CO_2$ that is present in the global atmosphere is very large, 788 billion tons in 2002 [53]. The 2002 global $CO_2$ emission from fossil fuels is estimated to be 6975 million metric tons of carbon, which represents an all-time record and a 2% increase from 2001 [45]. As a comparison to show the magnitude of the amount of the carbon emitted to air, the total worldwide petroleum consumption in 2001 was 3913 million metric tons (Table 1). It is important to note that the amounts of $CO_2$ emitted as the concentrated $CO_2$-rich flue gases from electric power plants and effluent gases from industrial manufacturing plants have become much higher than the amounts of carbon used for making most chemicals, organic materials and liquid transportation fuels [47].

### 4.3. Challenges for $CO_2$ utilization

The energetic issues of $CO_2$ can be understood better by comparison with industrial gas products such as ethylene and synthesis gas. Production processes of synthesis gas and ethylene often consumes energy but this not a concern since the products are important and valuable as industrial chemicals. Because $CO_2$ does not present itself as a high-value product that has wide-spread industrial applications, the energy-consuming conversion is viewed as unfavorable and against the economics.

Apart from the global challenges discussed, the challenges and the barriers for $CO_2$ conversion and utilization, as outlined below, are primarily due to the lack of value-based driving forces:

- Costs of $CO_2$ capture, separation, purification, and transportation to user site.
- Energy requirements of $CO_2$ chemical conversion (plus source and cost of $H_2$ and/or other co-reactants if involved).
- Market size limitations, little investment-incentives and lack of industrial commitments for enhancing $CO_2$-based chemicals.
- Lack of socio-economical driving forces for enhanced $CO_2$ utilization.

## 5. Strategies for $CO_2$ conversion and utilization

### 5.1. Strategic objectives

The strategic objectives of $CO_2$ conversion and utilization should be based on the unique physical and chemical properties and could include one or more of the broadly defined targets listed below, which will be further elaborated in subsequent sections.

- Use $CO_2$ for environmentally benign physical and/or chemical processing that adds value to the process.
- Use $CO_2$ to produce industrially useful chemicals and materials that adds value to the products.
- Use $CO_2$ as a beneficial fluid for processing or as a medium for energy recovery, contaminant removal, and emission reduction.
- Use $CO_2$ recycling involving renewable sources of energy such as biomass and solar energy or 'waste' energy to conserve carbon resources for sustainable development.

Table 3 provides a list of the physical and chemical properties of $CO_2$ [9,10,54,55]. $CO_2$ may be used as a gas, liquid, and solid. At atmospheric pressure, $CO_2$ is about 1.5 times as heavy as air [9]. $CO_2$ may be liquefied by compressing to 2 MPa and cooling to −18 °C, or by compressing to higher pressure of 5.78 MPa at 21 °C. If liquid $CO_2$ is cooled further to −56.6 °C, the pressure drops to 0.518 MPa, solid $CO_2$ is formed which co-exists with liquid and gaseous $CO_2$ and this is known as the triple point. The solid $CO_2$ can sublimate directly into gas (without going through the liquid phase) upon absorbing heat, and thus it is called dry ice. $CO_2$ cannot exist as liquid below the triple point. If the pressure on dry ice is reduced to atmospheric pressure, the temperature of dry ice drops to −78.5 °C. $CO_2$ cannot be liquefied above 31 °C, the critical temperature. It exists as supercritical fluid when the temperature and pressure are above 31 °C (Tc) and 7.38 MPa (Pc), respectively.

### 5.2. Technical approaches to $CO_2$ utilization

isted below are some strategic considerations for developing technologies for $CO_2$ conversion and utilization, but this list is by no means exclusive. Fig. 5 shows the scope of chemical processes for $CO_2$ conversion [47]. The research on $CO_2$ conversion and utilization is a proactive approach to the sustainable development. Out-of-the-box thinking, multi-disciplinary and integrated research should be encouraged involving chemistry, materials, catalysis, chemical engineering, physics, system engineering and other disciplines, but the ideas should not be down-selected too early just based on the current process economics.

- Select concentrated $CO_2$ sources for $CO_2$ capture and/or utilization; aim for on-site/nearby uses if possible.
- Use $CO_2$ to replace a hazardous or less-effective substance in existing chemical processes for making products with significant volumes.
- Use renewable sources of energy or 'waste' energy for $CO_2$ conversion and utilization whenever possible.
- Convert $CO_2$ along with other co-reactants into chemical products that are industrially useful at significant scale.
- Fix $CO_2$ into environmentally benign organic chemicals, polymer materials or inorganic materials.
- Electric power generation with more efficient $CO_2$ capture and conversion or utilization.
- Take value-added approaches for $CO_2$ sequestration coupled with utilization.

Table 3
Physical and chemical properties of carbon dioxide

| Property | Value and unit |
|---|---|
| Molecular weight | 44.01 g/mol |
| Sublimation point at 1 atm (101.3 kPa) | −78.5 °C |
| Triple point at 5.1 atm (518 kPa) | −56.5 °C |
| Triple point pressure | 5.185 bar |
| Critical temperature ($T_c$) | 31.04 °C |
| Critical pressure ($P_c$) | 72.85 atm (7383 kPa) |
| Critical density ($\rho_c$) | 0.468 g/cm$^3$ or 468 g/L or 468 kg/m$^3$ |
| Gas density at 0 °C and 1 atm (101.3 kPa) | 1.976 g/L |
| Liquid density at | |
| 0 °C and 1 atm (101.3 kPa) | 928 g/L |
| 25 °C and 1 atm $CO_2$ (101.3 kPa) | 0.712 vol/vol |
| Solid density | 1560 g/L |
| Specific volume at 1 atm and 21 °C | 0.546 m$^3$/kg |
| Latent heat of vaporization | |
| At the triple point (−78.5 °C) | 353.4 J/g |
| At 0 °C | 231.3 J/g |
| Viscosity at 25 °C and 1 atm $CO_2$ (101.3 kPa) | 0.015 cP (mPas) |
| Solubility in water at | |
| 0 °C and 1 atm (101.3 kPa) | 0.3346 g $CO_2$/100 g-$H_2O$ or 1.713 mL $CO_2$/mL-$H_2O$ at 0 °C |
| 25 °C and 1 atm (101.3 kPa) | 0.1449 g $CO_2$/100 g-$H_2O$ or 0.759 mL $CO_2$/mL-$H_2O$ at 25 °C |
| Heat of formation at 25 °C, ΔH°gas | −393.5 kJ/mol |
| Entropy of formation at 25 °C, S°gas | 213.6 J/K mol |
| Gibbs free energy of formation at 25 °C, ΔG°gas | −394.3 kJ/mol |
| Heat capacity under constant pressure at 25 °C | 37.1 J/mol °C |
| Heat capacity at constant volume at 25 °C | 28.1 J/mol °C |
| Thermal conductivity | 14.65 mW/(m k) |
| Viscosity at 0 °C | 0.0001372 Poise |

Examples of the concentrated sources of $CO_2$ include flue gas from coal-fired and natural gas-fired electric power plants, effluents from partial oxidation unit in petrochemical plants, effluents from gasification units and water–gas-shift units in hydrogen plants and ammonia plants.

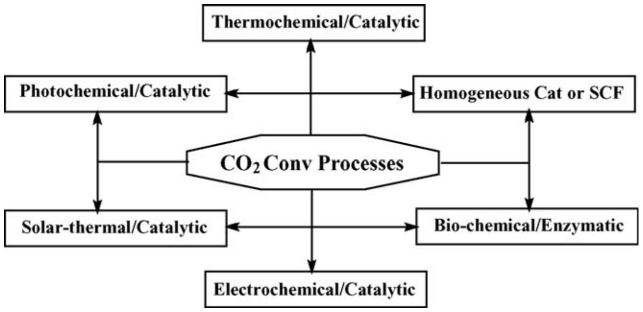


Fig. 5. Scope of chemical processes for $CO_2$ conversion (modified after [47]).

### 5.3. Thermodynamic considerations of $CO_2$ conversion

Fig. 6 illustrates the thermodynamics of $CO_2$ conversion, where Gibbs free energy of $CO_2$ and related substances are shown along with $CO_2$. The data for plotting Fig. 6 were taken mainly from comprehensive chemical handbooks [54,56]. $CO_2$ is a highly stable molecule. Consequently a substantial input of energy, effective reaction conditions, and often active catalysts, are necessary for chemical conversion of $CO_2$. In other words, many reactions for $CO_2$ conversion involve positive change in enthalpy, ΔH, and thus they are endothermic.

However, it should be pointed out that the chemical reactions are driven by the difference in Gibbs free energy between the products and reactants at certain conditions, as shown by the equation below.

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

It is true that endothermic reactions consume energy. However, endothermic reactions can be feasible and indeed useful. There appears to be some perceptions by many people that $CO_2$ conversion would be so endothermic that its conversion would not be feasible. There are many large-scale industrial manufacturing plants that are operated based on endothermic reactions in the chemical industry, and these include pyrolysis (thermal cracking) of hydrocarbons for manufacture of ethylene and propylene, dehydrogenation reaction for manufacture of petrochemicals such as styrene from ethylbenzene, and steam reforming of hydrocarbons for producing synthesis gas and hydrogen.

A simple comparison between steam reforming (Eq. (2)) and $CO_2$ reforming of $CH_4$ (Eq. (3)) can illustrate this point. Steam reforming is already used in large scale in the gas industries and fertilizer industries worldwide. Both reactions are endothermic that require over 200 kJ of energy input per mole of $CH_4$, but $CO_2$ reforming requires about 20% more energy input compared to steam reforming. The two reactions give synthesis gas products with different $H_2$/CO molar ratios; both are useful for certain applications.

$$CH_4 + H_2O = CO\,(g) + 3H_2\,(g);\quad \Delta H^\circ = +206.3\,\mathrm{kJ/mol\,CO_2} \quad (2)$$

$$CH_4 + CO_2 = 2\,CO\,(g) + 2H_2O\,(g);\quad \Delta H^\circ = +247.3\,\mathrm{kJ/mol\,CO_2} \quad (3)$$

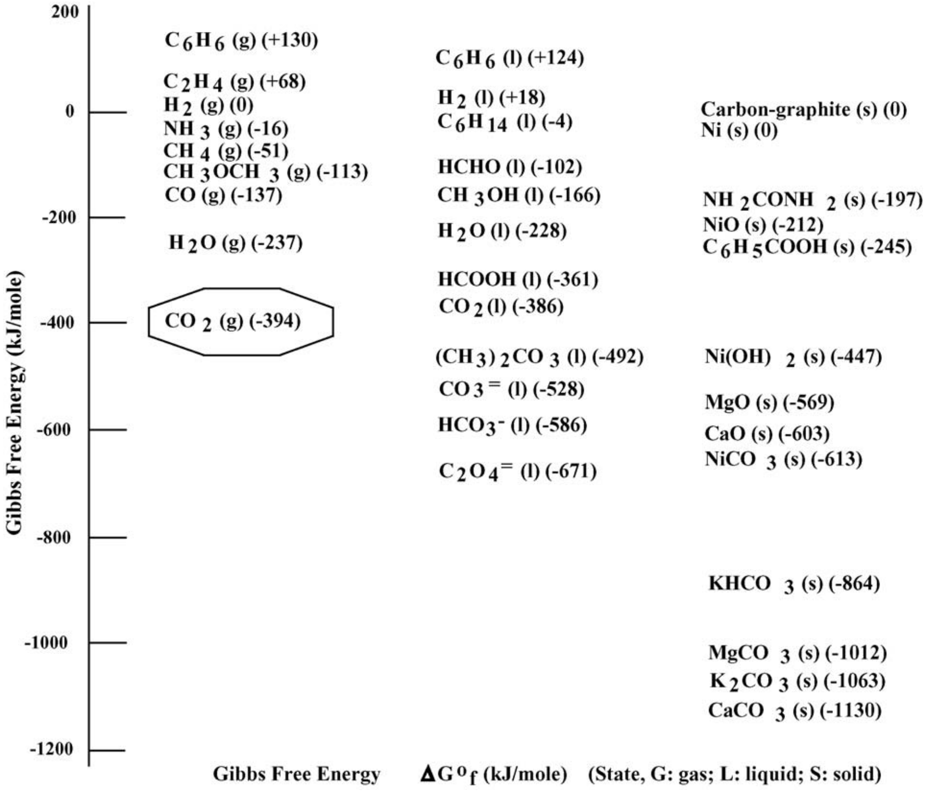


Fig. 6. Thermodynamic considerations for $CO_2$ conversion and utilization involving co-reactants (modified after [47]).

Fig. 6 reveals that it is more energy-demanding if one were to use only $CO_2$ as a single reactant, but it becomes easier thermodynamically if $CO_2$ is used as a co-reactant with another substance that has higher Gibbs free energy, such as $CH_4$, carbon (graphite) and $H_2$. This trend can also be seen by the change in the reaction heat for reactions with $CO_2$ as the single reactant (Eq. (4)) and with $CO_2$ as a co-reactant (Eq. (5)).

$$CO_2 = CO + \tfrac{1}{2}O_2;\ \Delta H^\circ = +293\,\text{kJ/mol}\,CO_2 \tag{4}$$

$$CO_2 + H_2 = CO(g) + H_2O(g);\ \Delta H^\circ = +51\,\text{kJ/molCO}_2 \tag{5}$$

### 5.4. Current status of $CO_2$ conversion and utilization

Table 4 lists the existing and emerging applications of $CO_2$ in liquid, solid, and gaseous states [9,10,57–59]. The current global market for merchant $CO_2$, measured by the amount of $CO_2$ sold in the market, which excludes in-plant $CO_2$ utilized by manufacturers, is estimated to be \$3.2 billions/year in 2003 [53].

Currently, $CO_2$ is used as refrigerant for food preservation, beverage carbonation agent, supercritical solvent, inert medium (such as fire extinguisher), pressurizing agent, chemical reactant (urea, etc.), neutralizing agent, and as gas for greenhouses. Solid $CO_2$ (dry ice) has a greater refrigeration

Table 4
Current status of $CO_2$ uses in various industrial applications [9,10,57–59]

| Sectors | Industrial applications |
|---|---|
| Chemicals | # $CO_2$ is used in chemical synthesis and for controlling reactor temperatures.<br># $CO_2$ is employed to neutralize alkaline effluents.<br># $CO_2$ is used as a blowing agent for polyurethane and polystyrene foam production and for blow molding manufacturing of plastic bottles, and containers.<br># $CO_2$ is used under supercritical conditions for purifying or dying polymer, animal or vegetable fibers. |
| Pharmaceuticals | # $CO_2$ is used for making chemicals such as salicylic acid and Aspirin; for use as an inert gas, and for supercritical fluid extraction.<br># $CO_2$ is used for product transportation at low temperature (−78 °C or −108 °F) and also acidification (pH) of wastewater. |
| Foodstuffs | # Liquid $CO_2$ can be used as cryogenic fluid in chilling or freezing operations or as dry ice for temperature control during the storage and distribution of foodstuffs.<br># Packaging of foodstuffs to increase the shelf life of many food products due to its inerting properties and its growth inhibiting effect of $CO_2$ on micro-organisms.<br># Stunning of pigs and poultry in slaughterhouses instead of using electrical stunning. |
| Beverage | # Carbonation of beverages such as soft drinks, mineral water or beer;<br># supercritical $CO_2$ is used to remove caffeine from coffee beans by extraction.<br># $CO_2$ is used as shielding gas for preserving drink quality, and propellant gas for emptying tanks of drinks<br># $CO_2$ is also used in drinking water treatment in modern water works together with lime or chalk. |
| Healthcare | # $CO_2$ produces close-to-physiologic atmospheres for the operation of artificial organs.<br># $CO_2$ is used as a component in a mixture of oxygen or air as respiratory stimulant to promote deep breathing. It is also used for the surgical dilation by intra-abdominal insufflations. |
| Environment | # Small amount of liquid $CO_2$ can be used in recycling of waters from Acid Mine Drainage.<br># Waste water treatment and waste liquid treatment by injection of $CO_2$ for the pH of liquid effluents. $CO_2$ is an excellent alternative to sulfuric acid for pH balance control. |
| Pulp and paper | # $CO_2$ enables sharp tuning of the pH of recycled mechanical or chemical pulps after an alkaline bleaching.<br># $CO_2$ can be used in the Tall Oil neutralization and for increasing the performance of paper machines.<br># Precipitated calcium carbonate obtained from $CO_2$ and CaO is used as a whitener for the paper industry. |
| Electronics | # $CO_2$ is usually used as a cooling medium in environmental testing of electronic devices.<br># $CO_2$ can be used to add conductivity to ultrapure water<br># $CO_2$ can also be used as an environmentally friendly supercritical fluid for removing photoresist from wafers |
| Metals industry | # $CO_2$ is typically used as an inert gas or for environment protection.<br># $CO_2$ is used for red fume suppression during scrap and carbon charging, for nitrogen pick-up reduction during tapping and for bottom stirring.<br># $CO_2$ is used for fume suppression during ladle transfer of matte (Cu/Ni production) or bullion (Zn/Pb production) in the non ferrous metallurgy.<br># Special grades of $CO_2$ are used in $CO_2$ lasers. |
| Laboratories & analysis | # Supercritical $CO_2$ is the mobile phase in both supercritical chromatography and supercritical fluid extraction applications. |
| Safety and others | # $CO_2$ is used as carbon dioxide snow for fire extinguishers;<br># pH control and regulation of waste waters, swimming pools, etc. |

effect than water ice. Dry ice is also usually much colder than water ice, and the dry ice sublimates to a gas as it absorbs heat. It should be noted that the use of $CO_2$ for refrigeration does not directly contribute to reduction of $CO_2$ emissions.

There exist some chemical processes for $CO_2$ conversion in chemical industry, for which synthesis of urea from ammonia and $CO_2$ (Eq. (6)) and the production of salicylic acid from phenol and $CO_2$ (Eq. (7)) are representative examples. Urea is used for making various polymer materials and also for producing fertilizers. As an example of the usefulness of salicylic acid, acetyl salicylic acid is used for making Aspirin, a widely used common medicine.

### 5.4.1. Urea synthesis

$$CO_2 + 2NH_3 = H_2N\text{-}CO\text{-}NH_2 + H_2O \tag{6}$$

### 5.4.2. Salicylic acid synthesis

$$C_6H_5\text{-}OH + CO_2 = C_6H_4(OH)COOH \tag{7}$$

Urea is used in organic chemical industry. It is a preferred solid nitrogen fertilizer because of its high nitrogen content (46%). The worldwide production of urea in 2002 was about 110 million metric tons, which contains 51.8 million metric tons of nitrogen with an estimated value of $11.5 billion USD [59]. This corresponds to about 81 million metric tons of $CO_2$, and 22 million metric tons of carbon.

### 5.5. Needs for industrial and government commitments

It is important for the people and governments in the world to realize that not only the universities and research institutions but also the industries are needed for taking real actions on $CO_2$ conversion and utilization, beyond counting and trading of emissions credits, because there are potential opportunities as well as long-term benefits. The industrial investments in the $CO_2$-based new technology developments should be encouraged and facilitated by the governments. The university research in $CO_2$-based new technology should be encouraged by government grants without the requirement for cost-share or matching funds from the university. Industry-university collaboration with partial government support is one effective path forward. The real advances will not be possible without real industrial involvement. The truly successful industrial leaders in the future manufacturing industries are likely those who have invested seriously in developing more environmentally friendly and GHG-less technologies that give them the competitive edge in the increasingly environment-conscious global markets and also the public acceptance and support.

Some people may think the $CO_2$ utilization is too costly or too far away for the practical application, and that any processes using $CO_2$ are not likely to be significant or economical. Things may change if all the cost factors are considered and environmental benefits become a cost factor. As a recent example of the significance of the $CO_2$ issue, eight states in the US (CA, CT, IA, NJ, NY, RI, VT, WI) and New York City jointly filed a law suit on 21st July 2004 against five large energy companies quoted as ‘‘Global Warming Polluters’’ that collectively produce 650 million tons of $CO_2$ each year [61].

## 6. Research directions on $CO_2$ conversion & utilization

Listed below are some specific research directions and development issues, which involve new process concepts as well as expansion of known applications. Fig. 7 shows the existing and emerging application areas of $CO_2$ conversion and utilization [47].

- For applications that do not require pure $CO_2$, develop effective processes for using the $CO_2$-concentrated flue gas from industrial plants or $CO_2$-rich resources such as $CO_2$-rich natural gases without $CO_2$ separation.
- For applications that need pure $CO_2$, develop more efficient and less-energy intensive processes for separation of $CO_2$ selectively without the negative impacts of co-existing gases such as $H_2O$, $O_2$, and $N_2$.
- Replace a hazardous or less-effective substance in existing processes with $CO_2$ as an alternate medium or solvent or co-reactant or a combination of them
- Make use of $CO_2$ based on the unique physical properties as supercritical fluid or as either solvent or anti-solvent
- Make use of $CO_2$ based on the unique chemical properties for $CO_2$ to be incorporated with high ‘atom efficiency’ such as carboxylation and carbonate synthesis
- Produce useful chemicals and materials using $CO_2$ as a reactant or feedstock
- Use $CO_2$ for energy recovery while reducing its emissions to the atmosphere by sequestration
- Recycle $CO_2$ as C-source for chemicals and fuels using renewable sources of energy.
- Convert $CO_2$ under either bio-chemical or geologic-formation conditions into ‘‘new fossil’’ energies.

Some of the above strategic directions and research issues are further elaborated below by specific case studies on $CO_2$ conversion and utilization based on the recent literature. Many processes could be designed for using $CO_2$, but the chemicals and materials that have large market demands

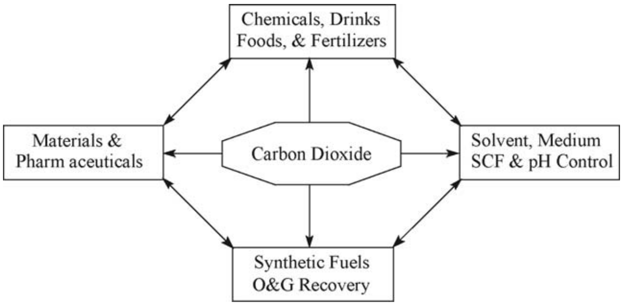


Fig. 7. The existing and emerging application areas of $CO_2$ conversion and utilization (modified after [47]).

are relatively limited [11,12]. An existing industrial process is urea synthesis, which has already found industrial application as fertilizer and as monomer for thermosetting polymers. Expanding applications of urea-based polymers can create more demand on $CO_2$ and $NH_3$ for urea synthesis.

### 6.1. *Using $CO_2$ without separation for syngas: tri-reforming versus $CO_2$ reforming*

For the development of new processes, one of preferred approaches is to explore alternate processes for using $CO_2$ from industrial effluent gases as a co-reactant in making chemicals that have relatively large market or potentially large demand in the near future. The production of synthesis gas ($CO + H_2$) is a potential area for large-scale $CO_2$ conversion and utilization. $CO_2$ reforming of $CH_4$ has been studied and reported extensively in the literature [28,29].

Tri-reforming is a recently proposed process concept as a new alternative to $CO_2$ reforming for syngas [11,12,62–65]. In this section, we discuss the two reforming processes based on experimental studies in our laboratory.

Table 5
Properties of fresh Ni/Na-Y and $Ni/Al_2O_3$ catalysts prepared by IWI method and the used catalysts after reforming

| Fresh catalysts | 8 wt.% Ni/Na-Y (IWI) | 6.6 wt.% $Ni/Al_2O_3$ (IWI) |
|---|---|---|
| BET area ($m^2\,g^{-1}$-cat.) | 476 | 185 |
| H/Ni (fresh catalyst) | 0.38 | 0.27 |
| CO/Ni (fresh catalyst) | 0.35 | 0.23 |
| Used Catalysts[a] | 8 wt.% Ni/Na-Y (IWI) | 6.6 wt.% $Ni/Al_2O_3$ (IWI) |
| H/Ni (Ni dispersion from $H_2$) | 0.32 | 0.08 |
| CO/Ni (Ni dispersion from CO) | 0.3 | 0.05 |
| Carbon deposit (wt.%) | 27.5 [66.3][a] | 82.3 [84.5][a] |

[a] Values outside brackets are after A-P reforming (1 atm) at 750 °C for 300 min, and those in brackets are after H-P reforming (27 atm) at 750 °C for 300 min.

#### 6.1.1. *$CO_2$ Reforming over Ni catalyst*

Table 5 shows the physical and chemical properties of the Ni catalysts supported on Na-Y and $\gamma$-$Al_2O_3$ prepared by incipient wet impregnation method. (IWI) [11,12]. The surface area of 8 wt.% Ni/Na-Y catalyst is much higher than that of 6.6 wt.% $Ni/Al_2O_3$ catalyst. $CO_2$ reforming of $CH_4$ was studied over Ni/

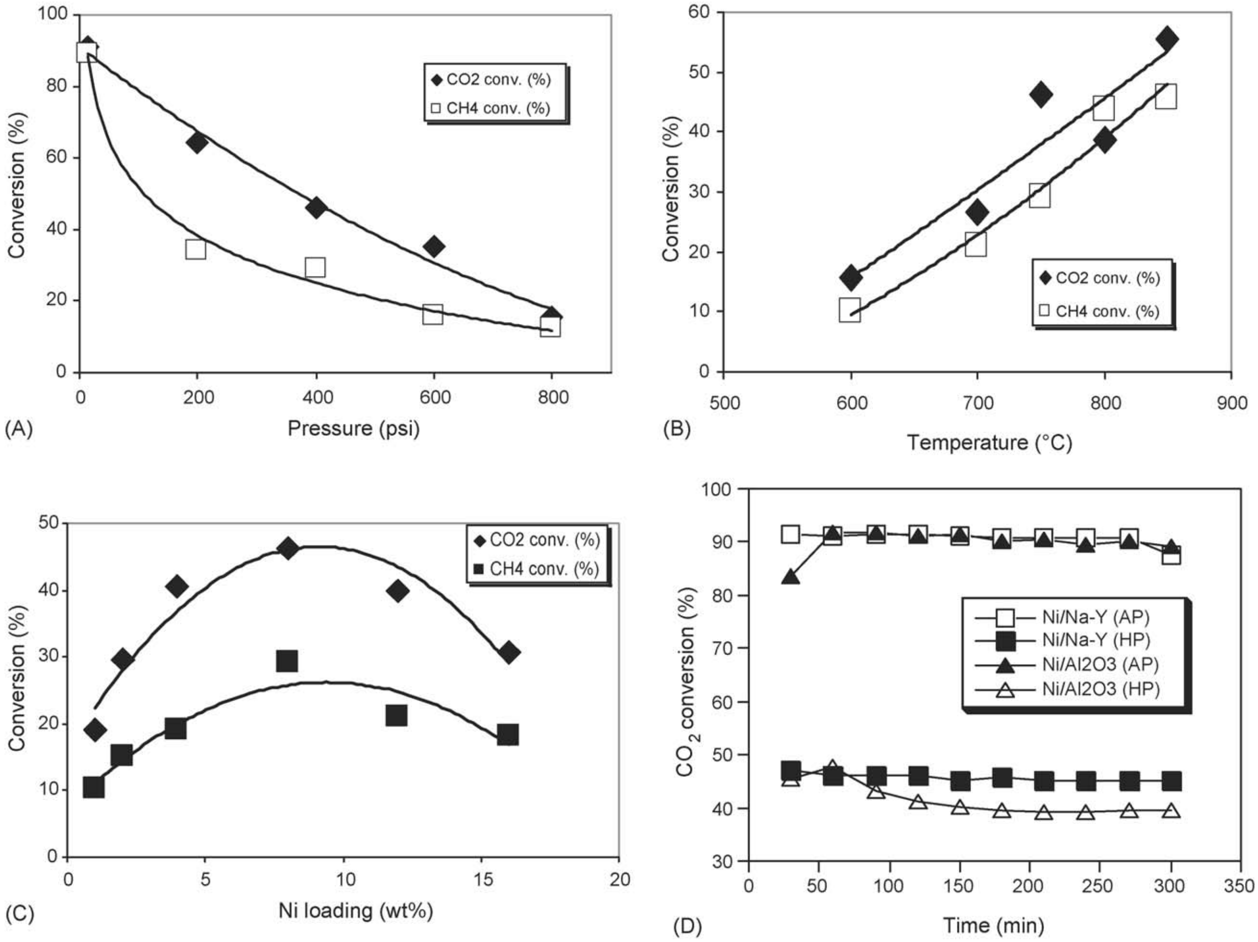


Fig. 8. $CO_2$ reforming of $CH_4$ over supported Ni catalysts. (A) Effect of reaction pressure on $CO_2$ and $CH_4$ conversion in $CO_2$ reforming of $CH_4$ on 8 wt.% Ni/Na-Y (IWI) catalyst at 750 °C; (B) Effect of reaction temperature on $CO_2$ and $CH_4$ conversion over 8 wt.% Ni/Na-Y (IWI) catalyst at 27 atm (400 psi); (C) Effect of Ni loading on $CO_2$ and $CH_4$ conversion over Ni/Na-Y (IWI) catalyst at 27 atm and 750 °C; (D) $CO_2$ conversion as a function of TOS for 8 wt.% Ni/Na-Y (IWI) and 6.6 wt.% $Ni/Al_2O_3$ (IWI) catalysts during $CO_2$ reforming of $CH_4$ at 750 °C under 1 atm (AP) and 27 atm (HP).

Table 6
Conversion and product yields for $CO_2$ reforming of $CH_4$ on 8 wt.% Ni/Na-Y and 6.6 wt.% $Ni/Al_2O_3$ catalysts prepared by IWI method

| Catalyst | 8 wt.% Ni/Na-Y | 8 wt.% Ni/Na-Y | 6.6 wt.% $Ni/Al_2O_3$ | 6.6 wt.% $Ni/Al_2O_3$ |
|---|---|---|---|---|
| Pressure-Temp | 1 atm-750 °C | 27 atm-750 °C | 1 atm-750 °C | 27 atm-750 °C |
| $CO_2$ conversion (%) | 91.1 | 46.2 | 91.8 | 43.0 |
| $CH_4$ conversion (%) | 89.1 | 29.1 | 95.3 | 33.3 |
| CO yield (%) | 85.6 | 42.6 | 81.9 | 57.9 |
| $H_2$ yield (%) | 68.9 | 40.7 | 66.3 | 29.6 |
| $H_2$/CO | 0.80 | 0.96 | 0.81 | 0.51 |

Na-Y and $Ni/Al_2O_3$ catalysts at atmospheric pressure as well as high pressure (27 atm).

Fig. 8 shows the effects of pressure (from 1 to 53 atm at 750 °C) and influence of temperature (from 200 to 800 °C at 27 atm) on $CO_2$ and $CH_4$ conversion in $CO_2$ reforming of $CH_4$ over 8 wt.% Ni/Na-Y (IWI) catalyst prepared in our laboratory [11,12]. The influences of Ni metal loading are also shown. Table 6 shows the CO and $H_2$ product yields for $CO_2$ reforming of $CH_4$ on 8 wt.% Ni/Na-Y and 6.6 wt.% $Ni/Al_2O_3$ catalysts along with the $H_2$/CO ratios of the syngas products at 1 atm and 27 atm [11,12]. Catalyst activity results show remarkable differences between atmospheric and high-pressure reaction. Both catalysts showed high conversion at atmospheric pressure whereas the conversion drastically decreased at high pressure.

Fig. 9 shows that there is a significant amount of carbon deposits formed on the Ni catalysts supported on $Al_2O_3$, particularly under elevated pressures [11,12]. The use of Y zeolite can reduce the carbon deposits significantly, but this reduction becomes insignificant at elevated pressures. The SEM photos shown in Fig. 10 reveal that filamental carbon deposits (also called carbon nano-tubes) are formed on the surfaces of Ni catalysts [11,12]. Higher carbon formation at high pressure was observed as filamental carbon compared to at atmospheric pressure.

Remarkable differences in $CO_2$ reforming of $CH_4$ at atmospheric pressure and high pressure were observed. The differences in catalyst activity at 1 atm and 27 atm are in large part due to thermodynamic limitations. The results are consistent with a vast amount of literature on $CH_4$ reforming. Both Ni/Na-Y and $Ni/Al_2O_3$ were reasonably active at atmospheric pressure with high $CO_2$ and $CH_4$ conversion (>89%). The conversions over the same catalysts show a drastic decrease at high pressure (27 atm), but the change in pressure had different impacts on $CO_2$ and $CH_4$ conversions, and varied effects on $H_2$/CO ratios of the syngas products. Carbon formation on some catalysts that display a superior performance at atmospheric pressure may be exacerbated at high pressure.

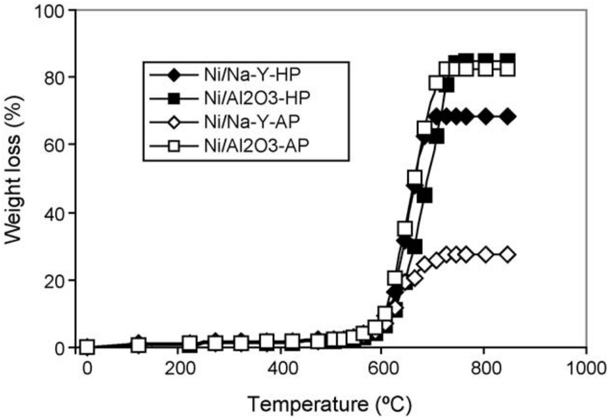


Fig. 9. Temperature programmed oxidation profiles from TGA of used 8 wt.% Ni/Na-Y, 6.6 wt.% $Ni/Al_2O_3$ catalysts after $CO_2$ reforming of $CH_4$ at 1 atm (AP) and 27 atm (HP) and 750 °C.

Low conversions of $CO_2$ and $CH_4$ and low yields of CO and $H_2$ were obtained from $CO_2$ reforming of $CH_4$ at high pressure of 27 atm with both laboratory and commercial Ni-based steam reforming catalysts, and all the catalysts suffered significant carbon formation within 300 min of TOS (time on stream) at high pressure.

Increasing reaction temperature increased catalyst activity whereas increasing pressure has an opposite effect. On Ni/Na-Y, significant effects of Ni loadings on catalyst activity were observed and 8 wt.% Ni loading on Na-Y gives optimum catalyst activity. TPO (temperature programmed oxidation) characterization of carbon deposits in used catalysts showed severe carbon formation at high pressure in the case of Ni/Na-Y whereas, $Ni/Al_2O_3$ results in severe carbon formation both at atmospheric as well as high pressure $CO_2$ reforming of $CH_4$. SEM investigation of used catalysts show remarkable effect of type of support (Na-Y or $Al_2O_3$) used and catalyst preparation method on the carbon structure.

### 6.1.2. $CO_2$ reforming over Rh catalysts

To see if we can eliminate carbon by using noble metal catalysts, we examined various supported Rh catalysts [67]. Laboratory-prepared Rh/Na-Y and $Rh/Al_2O_3$ catalysts (Table 7) were examined in $CO_2$ reforming of $CH_4$ at atmospheric pressure (1 atm) and high pressure (27 atm).

Fig. 11 and Table 8 show the $CO_2$ and $CH_4$ conversion for $CO_2$ reforming of $CH_4$ at 750 °C under 27 atm over rhodium catalysts. The TOS profiles in Fig. 11A illustrate that the Rh catalysts display a stable performance against deactivation at the atmospheric pressure, but begin to deactivate within the first few hours at high pressure of 27 atm. The use of higher pressure substantially decreased $CO_2$ and $CH_4$ conversion and increased catalyst deactivation during $CO_2$ reforming of $CH_4$, compared to runs at 1 atm for both Rh/Na-Y and $Rh/Al_2O_3$ catalysts.

Deactivation was related to carbon formation, and the type of support also affects both the amount and structure of the carbon deposits. The deactivation is more rapid with $Rh/Al_2O_3$ catalyst than with Rh/Na-Y catalyst during high-pressure $CO_2$ reforming. Relative to the runs at atmospheric pressure, the more

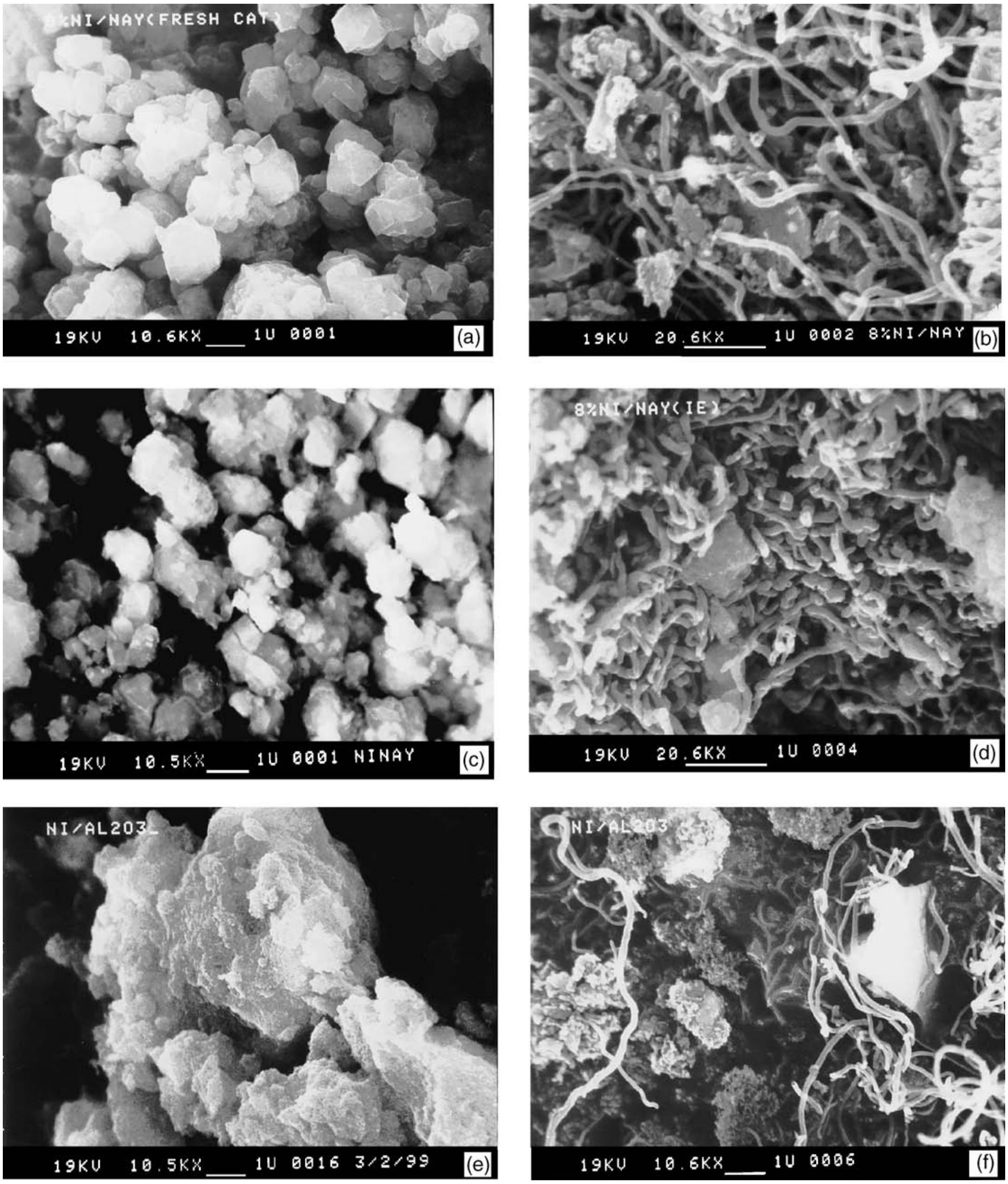


Fig. 10. SEM photographs of fresh (left) and used (right) catalysts after $CO_2$ reforming of $CH_4$ at 27 atm and 750 °C: 8 wt.% Ni/Na-Y (IWI) (a and b), 7.9 wt.% Ni/Na-Y (IE) (c and d), 6.6 wt.% Ni/$Al_2O_3$ (IWI) (e and f).

pronounced decrease in catalyst activity with time on stream at 27 atm can be attributed mainly to enhanced carbon formation. On Na-Y, Rh is dispersed on the outer surface of the zeolite as well as in its inner pores. Carbon formation that takes place on the outer surface of the catalyst can block the active sites.

The reaction system pressure significantly affects the $CO_2$ and $CH_4$ conversion over Rh catalysts and CO and $H_2$ yields as well as $H_2$/CO ratios during $CO_2$ reforming of $CH_4$. Both $CO_2$ and $CH_4$ conversion decrease significantly with increasing pressure from atmospheric pressure to 27 atm. The reaction pressure has different impacts on $H_2$ formation and CO formation, and thus increasing pressure not only decreases $CO_2$ and $CH_4$ conversion, but also can change the $H_2$/CO ratio of the products.

Catalyst stability during $CO_2$ reforming of $CH_4$ can significantly decrease upon increasing pressure from 1 atm to 27 atm for Rh/Na-Y and Rh/$Al_2O_3$. Some Rh catalysts that showed superior performance at atmospheric pressure can begin to deactivate within hours at high pressure. Significant effects of Rh loadings on catalyst activity were observed for Rh/Na-Y and Rh/$Al_2O_3$, and 2.5 wt.% seems to be optimum Rh loading to get maximum activity.

Fig. 12 shows the SEM of Rh Catalysts after $CO_2$ reforming of $CH_4$ at 27 atm and 750 °C (300 min TOS). 2.5 wt.% Rh/Na-Y (IWI) (a: fresh; b: used), 2.5 wt.% Rh/$Al_2O_3$ (IWI) (c: fresh; d: used). It is clear that carbon deposition even occurs on the Rh-based noble metal catalysts. Interesting, a completely

Table 7
Physicochemical properties of 1 wt.% Rh/Na-Y and 1 wt.% $Rh/Al_2O_3$ catalysts prepared by IWI using rhodium chloride precursor supported on Na-Y and $Al_2O_3$

| Catalyst Precursor | Rh chloride | Rh chloride |
|---|---|---|
| Fresh Catalyst | Rh/Na-Y | $Rh/Al_2O_3$ |
| Metal loading (wt.%) | 1.0 | 1.0 |
| BET area ($m^2$ $g^{-1}$-cat.) | 628 | 177 |
| H/M (fresh catalyst) | 0.66 | – |
| CO/M (fresh catalyst) | 0.55 | – |
| Used Catalyst | | |
| H/M (used catalyst) | 0.42 | – |
| CO/M (used catalyst) | 0.4 | – |
| Carbon deposit (wt.%)[a] | 5.3 [7.4][a] | 0.5 [1.4][a] |

[a] Values outside brackets are after A-P reforming (1 atm; 750 °C; TOS:300 -min); values inside brackets are after H-P reforming (27 atm; 750 °C; TOS:300 min).

different morphology of the carbon deposits was observed after $CO_2$ reforming on 2.5 wt.% Rh/Na-Y (IWI).

TPO characterization of carbon deposits in used catalysts (in Fig. 11D) showed that, Rh supported on Na-Y and $Al_2O_3$ show much smaller amounts of carbon deposition after the reaction compared with Ni catalysts. SEM investigation of used catalysts shows different effect of type of support (Na-Y or $Al_2O_3$) on the carbon structure. A very unusual form of carbon on used Rh/Na-Y catalyst was observed by SEM in Fig. 12, where the carbon deposits in the form of closely-knit coils dominate.

### 6.1.3. Tri-reforming over Ni catalysts

A novel process concept called tri-reforming of $CH_4$ has been proposed in our laboratory using $CO_2$ in the flue gases from fossil fuel-based power plants without $CO_2$ separation [62,66; Song, 2000]. The tri-reforming process is a synergetic combination of $CO_2$ reforming, steam reforming, and partial oxidation of $CH_4$ in a single reactor for effective production of industrially useful syngas. Both experimental testing and computational analysis show that tri-reforming can not only produce synthesis gas ($CO + H_2$) with desired $H_2$/CO ratios (1.5–2.0), but also could eliminate carbon formation which is usually a serious problem in the $CO_2$ reforming of $CH_4$ [63]. These two advantages have been demonstrated by tri-reforming of $CH_4$ in a fixed-bed flow reactor at 850 °C with supported nickel catalysts.

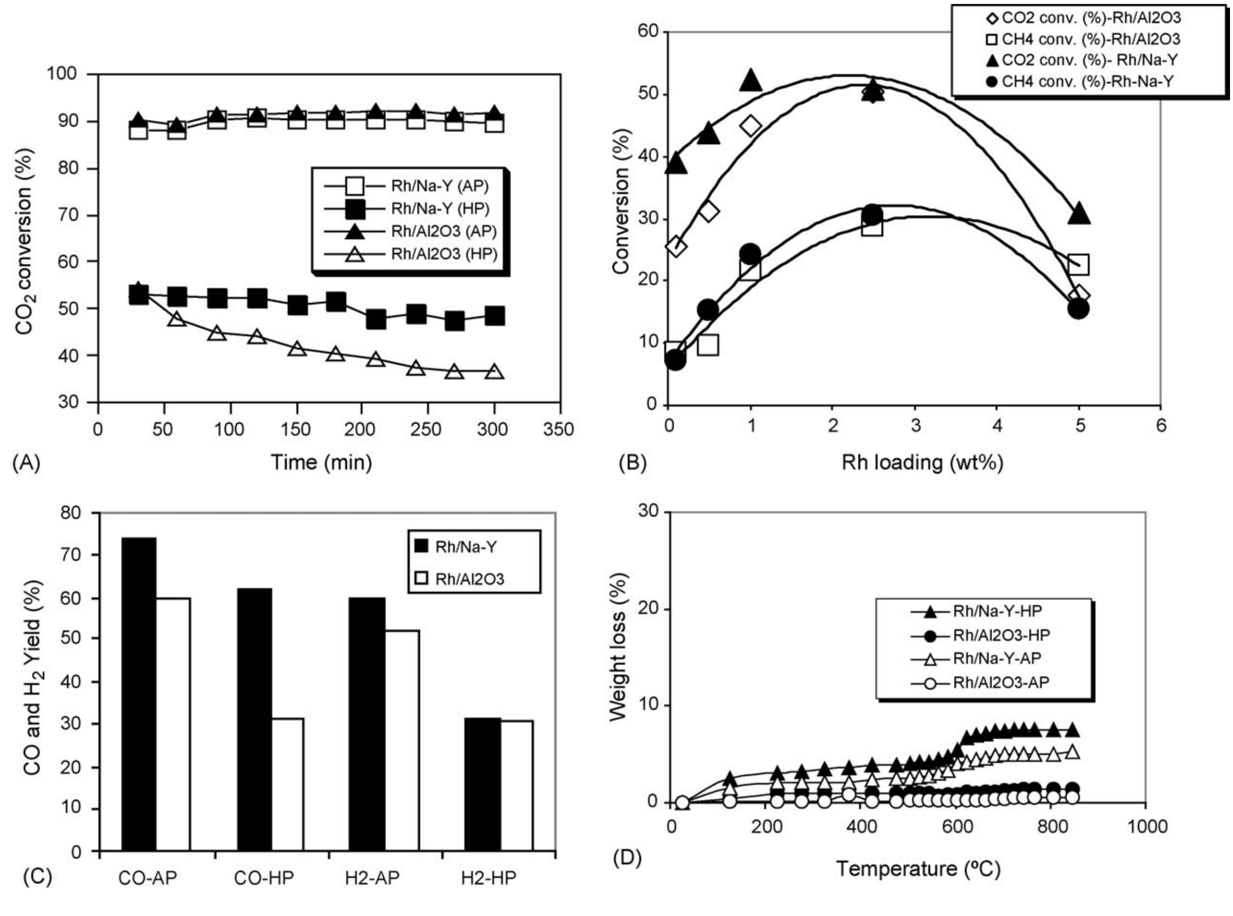


Fig. 11. $CO_2$ reforming of $CH_4$ over rhodium catalysts. (A, top left) $CO_2$ conversion for 1 wt.% Rh/Na-Y and 1 wt.% $Rh/Al_2O_3$ at 1 atm (AP) and 27 atm (HP) at 750 °C. (Rh chloride was used for IWI); (B, top right) Effect of Rh loading on $CO_2$ and $CH_4$ conversion over Rh/Na-Y (IWI) and $Rh/Al_2O_3$ (IWI) catalysts in at 27 atm and 750 °C (TOS: 90 min); (C, bottom left) CO and $H_2$ yields for 1 wt.% Rh/Na-Y and 1 wt.% $Rh/Al_2O_3$ at 1 atm (AP) and 27 atm (HP) at 750 °C. (Rh chloride was used for IWI) (TOS: 90 min); (D, bottom right) Temperature programmed oxidation profiles from TGA of used 1 wt.% Rh/Na-Y (IWI) and 1 wt.% $Rh/Al_2O_3$ (IWI) used catalysts after $CO_2$ reforming of $CH_4$ at 1 atm and 27 atm and 750 °C (after TOS of 300 min).

Table 8
Conversion and product yields for $CO_2$ reforming at 750 °C over 1 wt.% Rh/Na-Y and 1 wt.% Rh/$Al_2O_3$ catalysts prepared by IWI using rhodium chloride precursor (TOS: 90 min)

| Rh precursor | Rh chloride, IWI | Rh chloride, IWI | Rh chloride, IWI | Rh chloride, IWI |
|---|---|---|---|---|
| Catalyst | 1 wt.% Rh/Na-Y | 1 wt.% Rh/Na-Y | 1 wt.% Rh/$Al_2O_3$ | 1 wt.% Rh/$Al_2O_3$ |
| Pressure-Temp | 1 atm-750 °C | 27 atm-750 °C | 1 atm-750 °C | 27 atm-750 °C |
| $CO_2$ conv. (%) | 90.4 | 52.3 | 91.3 | 45.0 |
| $CH_4$ conv. (%) | 89.1 | 24.2 | 89.1 | 21.5 |
| CO yield (%) | 78.6 | 25.7 | 82.1 | 51.6 |
| $H_2$ yield (%) | 60.9 | 17.9 | 60.9 | 31.7 |
| $H_2$/CO ratio | 0.77 | 0.69 | 0.74 | 0.61 |

Fig. 13 shows the results of tri-reforming over various supported Ni catalysts in terms of: (A) $CO_2$ conversion; (B) $H_2$/CO ratios; and (C) $CH_4$ conversion in the tri-reforming reaction over 100 mg supported Ni catalysts at 1 atm with feed composition of $CH_4$:$CO_2$:$H_2O$:$O_2$ = 1:0.48:0.54:0.1 ($CH_4$ flow rate = 25 ml/min). The figure also includes a time-on-stream profile (D) for $CO_2$ and $CH_4$ conversions in the tri-reforming reaction over Ni/MgO/CeZrO catalyst at 850 °C under 1 atm with feed composition of $CH_4$:$CO_2$:$H_2O$:$O_2$ = 1:0.475:0.475:0.1 ($CH_4$ flow rate = 25 ml/min, in a stainless reactor).

Fig. 14 shows the features of the catalysts prepared for tri-reforming including: (A) $CO_2$-TPD over supports and supported Ni catalysts; (B) $CO_2$-TPD over supported Ni catalysts; (C) TPR over Ni catalysts supported on different supports; and (D) carbon deposits analysis on the used catalysts by TPO-IR after tri-reforming reaction.

Over 95% $CH_4$ conversion and about 80% $CO_2$ conversion can be achieved in tri-reforming over Ni catalysts supported on an oxide substrate. The type and nature of catalysts have a significant impact on $CO_2$ conversion in the presence of $H_2O$ and

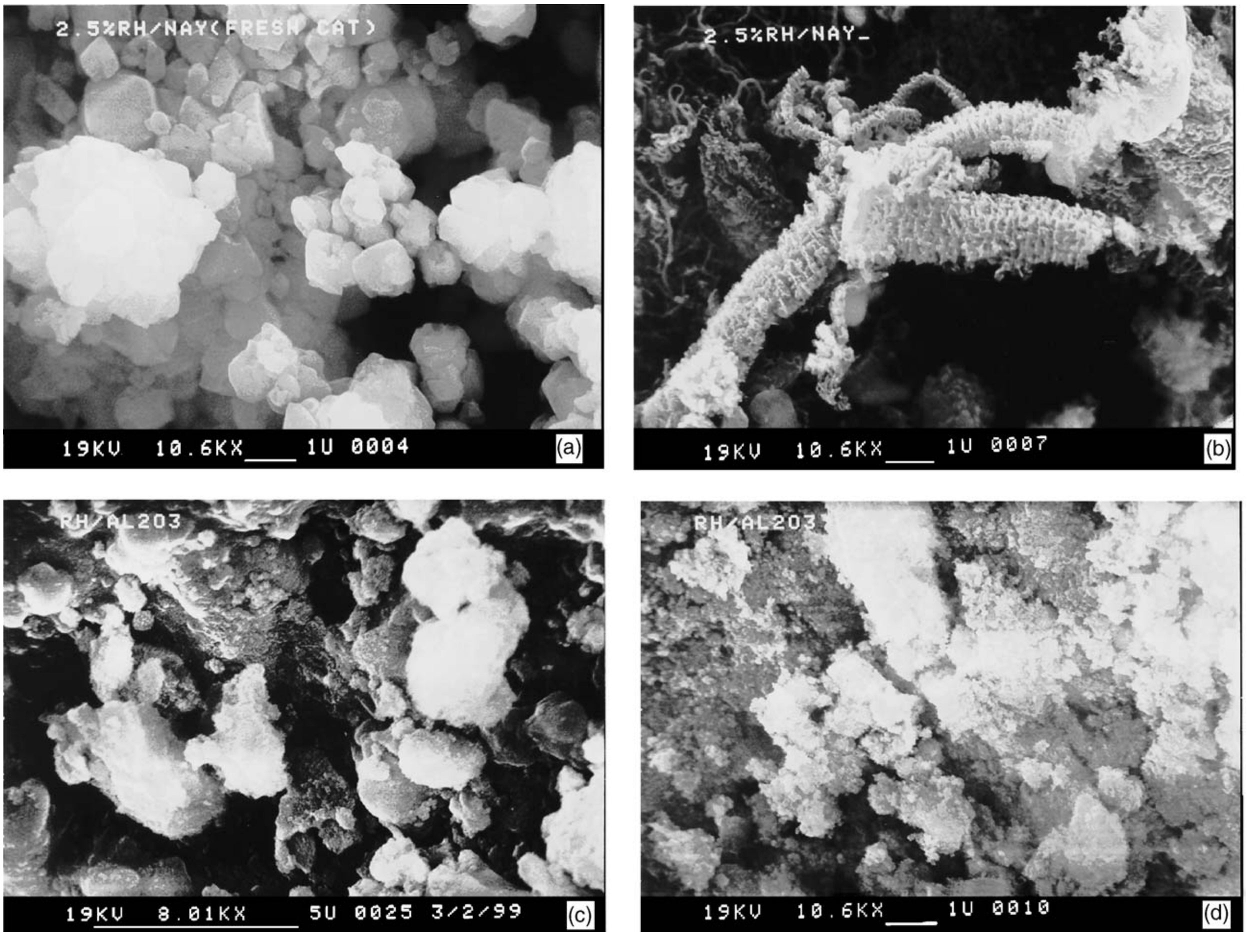


Fig. 12. SEM of Rh Catalysts after $CO_2$ reforming of $CH_4$ at 27 atm and 750 °C (300 min TOS). 2.5 wt.% Rh/Na-Y (IWI) (a: fresh; b: used), 2.5 wt.% Rh/$Al_2O_3$ (IWI) (c: fresh; d: used).

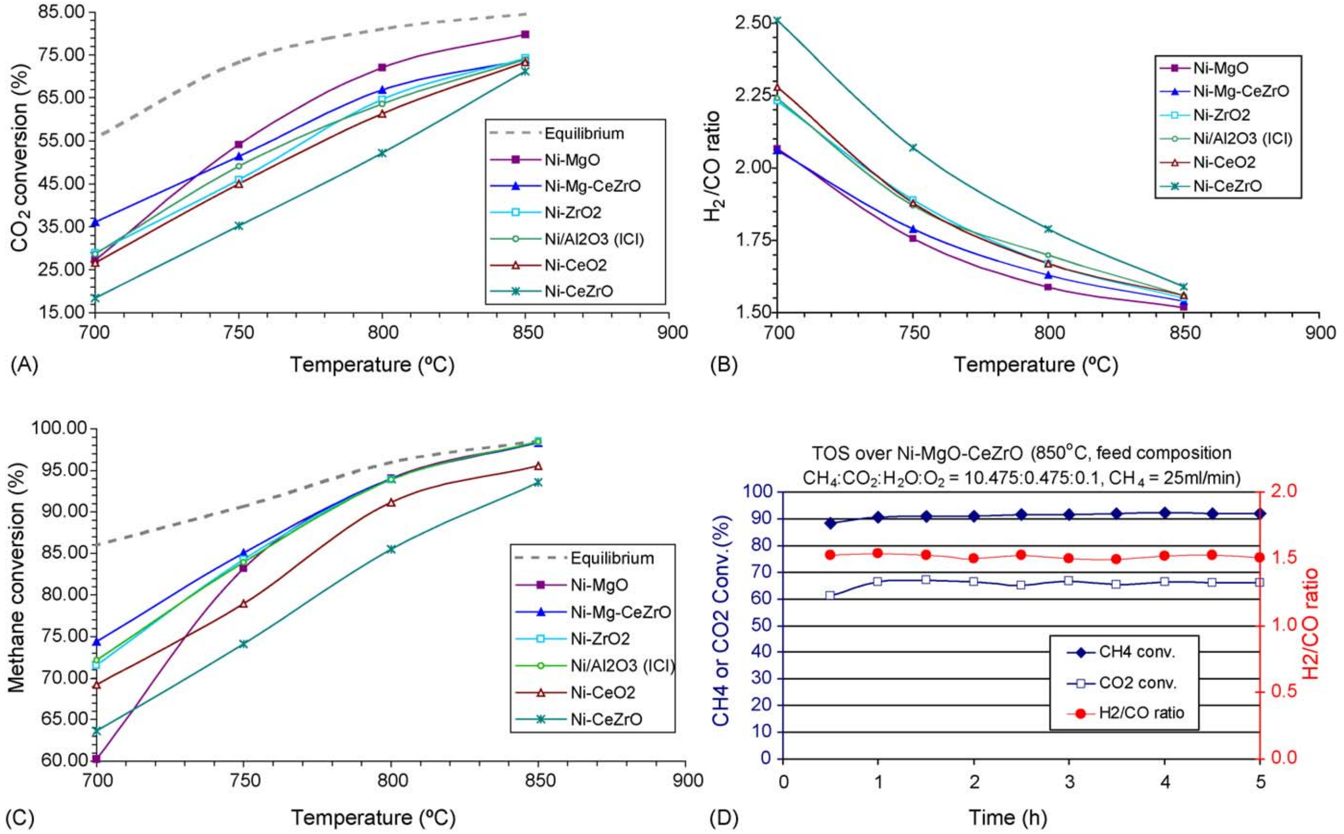


Fig. 13. $CO_2$ conversion (A, top left), $H_2/CO$ ratios (B, top right) and $CH_4$ conversion (C, bottom left) in the tri-reforming reaction over 100 mg supported Ni catalysts at 1 atm and feed composition of $CH_4$: $CO_2$: $H_2O$: $O_2$ = 1: 0.48: 0.54: 0.1 ($CH_4$ flow rate = 25 ml/min). Time-on-stream profile (D, bottom right) for $CO_2$ and $CH_4$ conversions in the tri-reforming reaction over Ni-MgO-CeZrO catalyst at 850 °C under 1 atm with feed composition of $CH_4$: $CO_2$: $H_2O$: $O_2$ = 1: 0.475: 0.475: 0.1 ($CH_4$ flow rate = 25 ml/min, in a stainless reactor).

$O_2$ in tri-reforming in the temperature range of 700–850 °C. Among the catalysts tested for tri-reforming, their ability to enhance the conversion of $CO_2$ follows the order of Ni/MgO > Ni/MgO/CeZrO > Ni/$CeO_2$ ≈ Ni/$ZrO_2$ ≈ Ni/$Al_2O_3$ > Ni/CeZrO. The higher $CO_2$ conversion over Ni/MgO and Ni/MgO/CeZrO in tri-reforming may be related to the interaction of $CO_2$ with MgO and more interface between Ni and MgO resulting from the formation of NiO-MgO solid solution. Results of catalytic performance tests over Ni/MgO/CeZrO catalysts at 850 °C and 1 atm with different feed compositions confirm the predicted equilibrium conversions based on the thermodynamic analysis for tri-reforming of $CH_4$. Kinetics of tri-reforming were also examined [63]. The reaction orders with respect to partial pressures of $CO_2$ and $H_2O$ are different over Ni/MgO, Ni/MgO/CeZrO, and Ni/$Al_2O_3$ catalysts for tri-reforming. The lowest apparent activation energy for $CO_2$ conversion over Ni/MgO during the tri-reforming process indicates that $CO_2$ is relatively easier to activate over Ni/MgO than over Ni/$Al_2O_3$ catalyst [65].

Fig. 15 illustrates the proposed process concept for tri-reforming of natural gas using flue gas from fossil fuel-based power plants, where HT represents heat transfer or heat exchange including reactor heat up and waste heat utilization. The tri-reforming process could be applied, in principle, to the production of industrially useful syngas (for synthesis of methanol and dimethyl ether, for Fischer–Tropsch synthesis, and for high-temperature fuel cells) by reforming of natural gas using gas mixtures (containing $CO_2$, $H_2O$, and $O_2$) as co-feeds. Such mixtures include, but not limited to, the flue gas from either natural gas-based electric power plant or coal-based electric power plants or the flue gas from partial oxidation units in chemical manufacturing facilities.

Although the tri-reforming concept was recently proposed and discussed at conferences [64,66,68] and in journals [63,65] and books [6,11,62], the tri-reforming process concept has already been applied by several research organizations; the term tri-reforming has been adopted in several recent reports by research groups in several countries [62,69–73] and also appeared in recent reviews [23,74]). The feasibility of tri-reforming reactions has been experimentally demonstrated in independent studies in other industrial and academic laboratories. It was proposed that tri-reforming could also be applied for converting low-quality $CO_2$-rich natural gas into industrially useful syngas [47]. Recently, tri-reforming has been demonstrated at pilot plant scale in Korea [69,70]. Most recently, the proposed tri-reforming concept has been demonstrated for solid oxide fuel cells in laboratory scale [73].

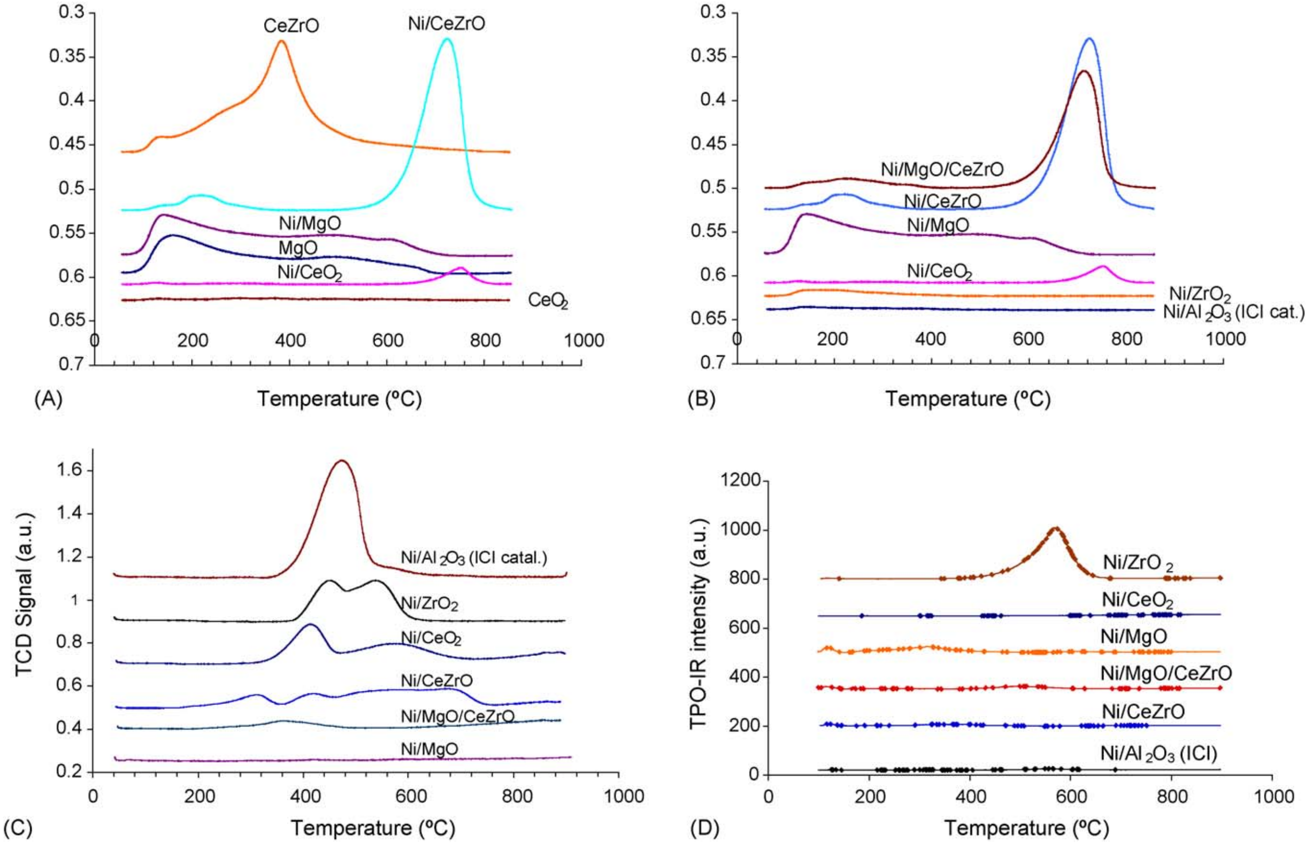


Fig. 14. Features of the catalysts prepared for tri-reforming and the conceptual flow of tri-reforming process. (A, top left) $CO_2$-TPD over supports and supported Ni catalysts; (B, top right) $CO_2$-TPD over supported Ni catalysts; (C, bottom left) TPR over Ni catalysts supported on different supports; (D, bottom right) Carbon deposits analysis on the used catalysts by TPO-IR after tri-reforming reaction.

### 6.2. Using "Molecular Basket" adsorbent for $CO_2$ separation

$CO_2$ separation is often viewed as the first step for chemical utilization. Many reports have been published on $CO_2$ separation [139,143,152,158,159,162,164,165,166,167,169,170].

As an attempt to explore new $CO_2$ adsorbent, novel $CO_2$ "molecular basket" adsorbents have been proposed and prepared in our laboratory by synthesizing and modifying the mesoporous molecular sieve of MCM-41 type with polyethylenimine (PEI) [75]. The MCM-41-PEI adsorbents were characterized by X-ray powder diffraction (XRD), $N_2$

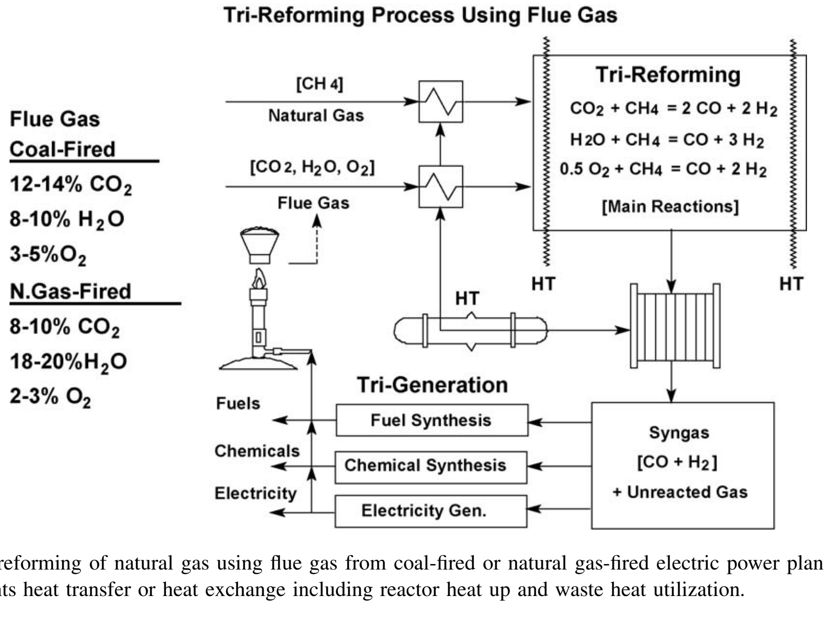
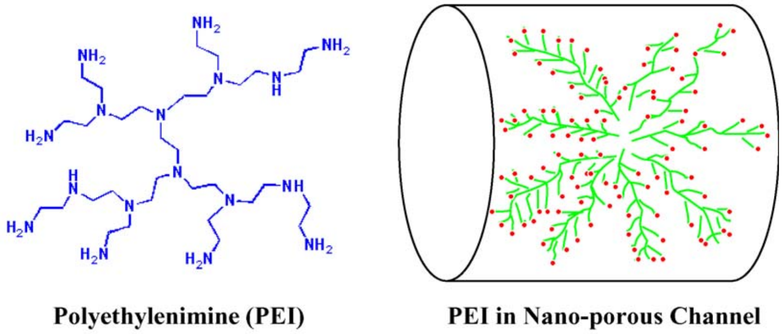


Fig. 15. Process concept for tri-reforming of natural gas using flue gas from coal-fired or natural gas-fired electric power plants and effluent gases from other industrial processes. HT represents heat transfer or heat exchange including reactor heat up and waste heat utilization.



- Large pore volume nanoporous support can store large amount of $CO_2$
- Branched $CO_2$-affinity polymers provide adsorption sites
- Branched amine facilitate the desorption
- Synergic effect on the $CO_2$ adsorption capacity and adsorption kinetic between nanoporous support and polyethylenimine

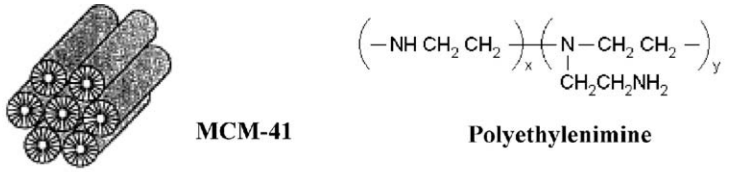
Fig. 16. $CO_2$ 'molecular basket' concept for highly-selective high-capacity adsorbent (Based on [75,76]).

adsorption/desorption, thermal gravimetric analysis (TGA) as well as the $CO_2$ adsorption/desorption performance.

Fig. 16 shows the $CO_2$ 'molecular basket' concept for highly-selective high-capacity adsorbent; Fig. 17 illustrates the formulation of MCM41-PEI as $CO_2$ 'molecular basket' adsorbent; and Fig. 18 shows the properties and performance of MCM41-PEI for $CO_2$ [73–76].

The experimental work included the effects of preparation conditions (PEI loadings, preparation methods, PEI loading procedures, types of solvents, solvent/MCM-41 ratios, addition of additive, and Si/Al ratios of MCM-41) on the $CO_2$ adsorption/desorption performance of MCM-41-PEI. With the increase in PEI loading, the surface area, pore size and pore volume of the PEI-loaded MCM-41 adsorbent decreased. When the PEI loading was higher than 30 wt.%, the mesoporous pores began to be filled with PEI and the mesoporous molecular sieve MCM-41 showed a synergetic effect on the adsorption of $CO_2$ by PEI. At PEI loading of 50 wt.% in MCM-41-PEI, the highest $CO_2$ adsorption capacity of 246 mg/g-PEI was obtained, which is 30 times higher than that of the MCM-41 and is about 2.3 times that of the pure PEI. Impregnation was found to be a better method for the preparation of MCM-41-PEI adsorbents than mechanical mixing method. The adsorbent prepared by a one-step impregnation method had a higher $CO_2$ adsorption capacity than that of prepared by a two-step impregnation method. The higher the Si/Al ratio of MCM-41 or the solvent/MCM-41 ratio, the higher the $CO_2$ adsorption capacity. Using polyethylene glycol as additive into the MCM-41-PEI adsorbent increased not only the $CO_2$ adsorption capacity, but also the rates of $CO_2$ adsorption/desorption. A simple model was proposed to account for the synergetic effect of MCM-41 on the adsorption of $CO_2$ by PEI.

More recently, it has been experimentally shown that the ''molecular basket'' adsorbent can selectively capture $CO_2$ for the separation of $CO_2$ from simulated flue gas [77,78]. Based on the laboratory studies, pilot plant tests of the MCM41-PEI adsorbent were conducted at a demonstration boiler facility under the support of US Department of Energy. The $CO_2$ ''molecular basket'' adsorbent was successfully applied to the


$$\left(-NH\,CH_2\,CH_2-\right)_x\left(\underset{\underset{CH_2CH_2NH_2}{|}}{N}-CH_2\,CH_2-\right)_y$$

- ❖ Uniform, "tailorable" 15-100 Å mesopores
- ❖ Narrow pore size distribution
- ❖ High surface area
- ❖ Large pore volume
- ❖ High thermal stability

- ❖ High amine group density, large amount of $CO_2$ adsorption sites
- ❖ Secondary and tertiary amine facilitate desorption
- ❖ Viscous liquid
- ❖ Slow $CO_2$ adsorption/desorption kinetics

Fig. 17. Formulation of MCM41-PEI as $CO_2$ 'molecular basket' adsorbent.

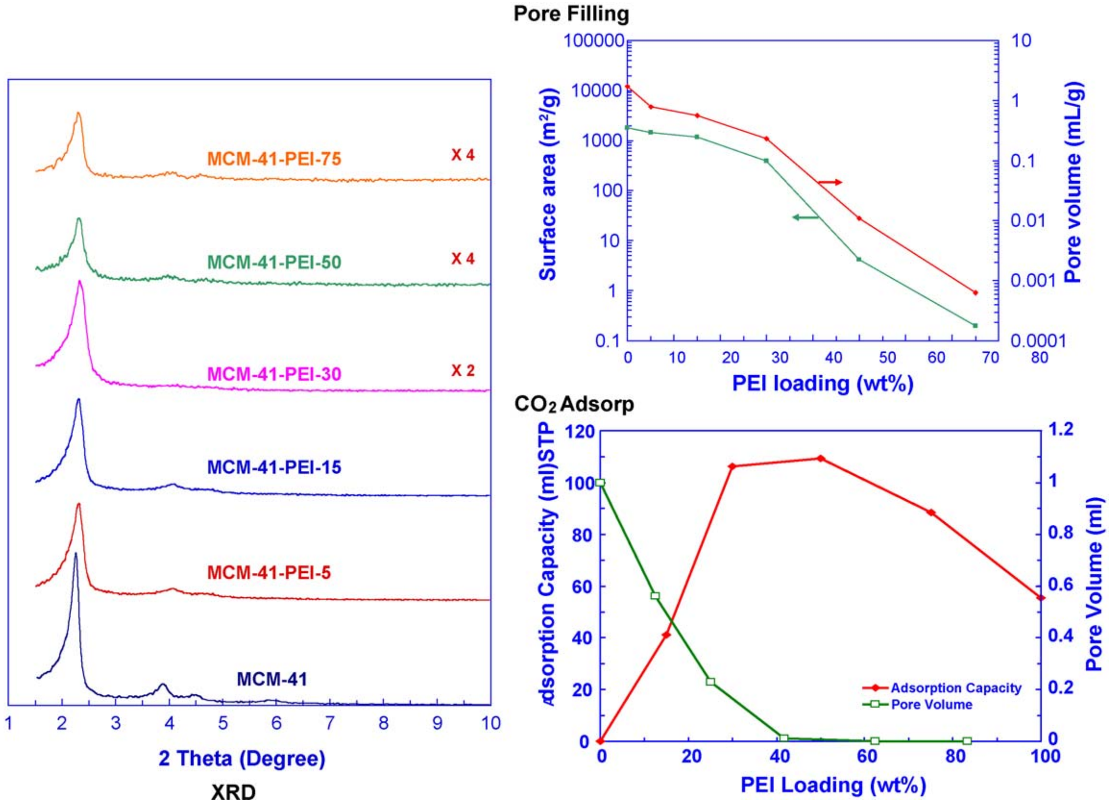


Fig. 18. Properties and performance of MCM41-PEI for $CO_2$. Left: XRD of MCM41-PEI with different PEI loading; Top right: pore volume and surface area of MCM41-PEI at liquid nitrogen temperature as a function of PEI loading; Bottom right: $CO_2$ adsorption at 75 °C versus PEI loading [75,76].

separation of $CO_2$ from natural gas-fired and coal-fired boiler flue gas [75,76]. Some recent studies have shown that lithium-containing oxides such as lithium zirconate and lithium silicate can be effective $CO_2$ absorbents [79,80].

### *6.3. Using $CO_2$ to replace phosgene: dimethyl carbonate synthesis*

Traditional route of dimethylcarbonate (DMC) synthesis uses phosgene. The use of $CO_2$ in synthesis of DMC presents an environmentally friendly and also attractive approach, since $CO_2$ can replace phosgene and chlorine (toxic chemicals), which has been discussed by Aresta and Quaranta for DMC and other chemical processes [13]. Shown below is a comparison of different chemical processes for making dimethyl carbonate (DMC), an industrially useful chemical. US phosgene use was estimated to be about 1.2 million tonnes per year [13].

In terms of environmental benefits, the new $CO_2$-based route is superior to the existing industrial processes that are based on either phosgene (Fig. 19) or CO, as both chemicals are toxic. Some recent studies by Aresta and co-workers have shown that direct oxidative carboxylation can be achieved using an olefin and $CO_2$ under an oxidative condition [81], which can produce the cyclic carbonate chemicals that are currently synthesized in industry by using phosgene.

Conventional route (SNPE, 1970s):

$$CO + Cl_2 = COCl_2\ (\text{Phosgene}) \tag{8}$$

$$COCl_2 + 2CH_3OH = CH_3OCOOCH_3 + 2HCl \tag{9}$$

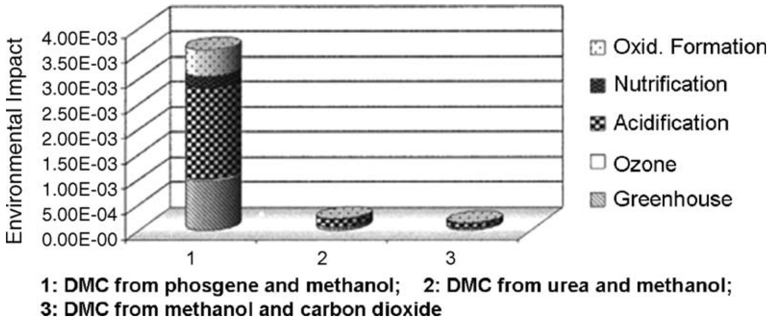


Fig. 19. Environmental benefits of dimethyl carbonate synthesis using $CO_2$ and methanol [12].

New Ube chemical process – 3000 tons/Yr

$$CO + 2RONO = ROC(O)OR + 2NO \quad (10)$$

New DMC process by EniChem – 12000 tons/Yr

$$CO + 1/2\,O_2 + 2\,CH_3OH = CH_3OCOOCH_3 + H_2O \quad (11)$$

New $CO_2$-based route

$$CO_2 + 2CH_3OH = CH_3OCOOCH_3 + H_2O \quad (12)$$

DMC can be synthesized using $CO_2$ and methanol over heterogeneous catalysts. For example, selective formation of DMC has been observed over some solid oxide catalysts such as $ZrO_2$ [82,83]. The dissociative adsorption of methanol occurs more slowly than the adsorption of $CO_2$ on $ZrO_2$, but the species formed from methanol are bound more strongly. The bulk of this zirconia (prepared by the calcination of zirconium hydroxide at 673 K) had a mainly tetragonal structure, which was determined by XRD. In contrast, near its surface the monoclinic phase was major and the tetragonal phase was minor, as determined by laser Raman spectroscopy. The initial work suggests that the catalytic activity of $ZrO_2$ is related to acid-base pair sites of $ZrO_2$ surface based on temperature-programmed desorption of $CO_2$ and $NH_3$ [82,83].

Based on a detailed in-situ IR spectroscopic study, Jung and Bell [84] proposed the following mechanism for the DMC synthesis from $CO_2$ and methanol over monoclinic zirconia, as shown in Fig. 20. Methanol binds to $Zr^{4+}$ Lewis acid sites and releases an H atom, which then rapidly reacts with a surface OH group to form $H_2O$. $CO_2$ is then inserted into the Zr–O bond of the $CH_3O$–Zr species to produce m-$CH_3OCOO$–Zr. This process is facilitated by interactions of C and O atoms in $CO_2$ with Lewis acid–base pairs of sites. Methyl carbonate species can also be produced via the reaction of $CH_3OH$ with $CO_2$ adsorbed in the form of bicarbonate species, but this process is slower than that involving the reaction of $CO_2$ with methoxide species. DMC is formed by transfer of a methyl group to the terminal O atom of methyl carbonate species [84].

Tomishige et al. [85] found that $CeO_2$–$ZrO_2$ solid solution catalysts are very effective and show much higher activity than $ZrO_2$ catalyst for the selective synthesis of DMC from methanol and $CO_2$, but the activity depends strongly on the calcination temperature and composition of $CeO_2$–$ZrO_2$ (preferred ratio of Ce/(Ce + Zr) = 0.2, 0.33). BET surface area of $CeO_2$–$ZrO_2$ can be twice that of $ZrO_2$. The higher the calcination temperature, the higher the activity of the catalyst for DMC formation, though the BET surface area is lower on the catalyst calcined at higher temperature [86].

The combination of an excellent $CeO_2$–$ZrO_2$ [Ce/(Ce + Zr) = 0.2] catalyst with the $H_2O$ removal system can give a novel and more efficient process of selective DMC production starting from $CO_2$ and methanol, as illustrated in Fig. 21 according to Tomishige and Kunimori [86] who reported this method for DMC synthesis. $CeO_2$–$ZrO_2$ (Ce/(Ce + Zr) = 0.2) solid solution catalyst has a good selectivity towards DMC in the synthesis from methanol and $CO_2$. However, the methanol conversion is very low because the DMC formation is limited by the reaction equilibrium. The reaction between 2,2-dimethoxy propane (DMP) and $H_2O$ can be utilized for removing the $H_2O$ product to shift the reaction equilibrium. The addition of the DMP to the reaction system of DMC synthesis from methanol and $CO_2$ is very effective for the increase of the conversion. However, the addition of larger amounts of DMP is not suitable because of the decrease of DMC formation rate and the by-product dimethyl ether (DME) formation. Dimethyl carbonate can also be synthesized using homogeneous catalysis [87].

Use of $CO_2$ to synthesize DMC also has further beneficial environmental impact beyond $CO_2$ utilization. DMC itself is a

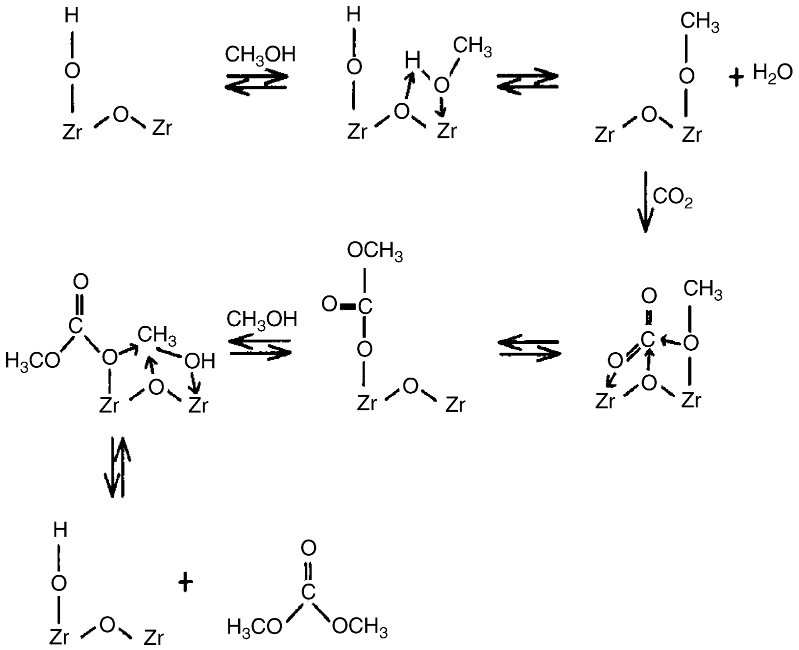


Fig. 20. Proposed mechanism for the formation of dimethylcarbonate from $CO_2$ and $CH_3OH$ over monoclinic zirconia [66].

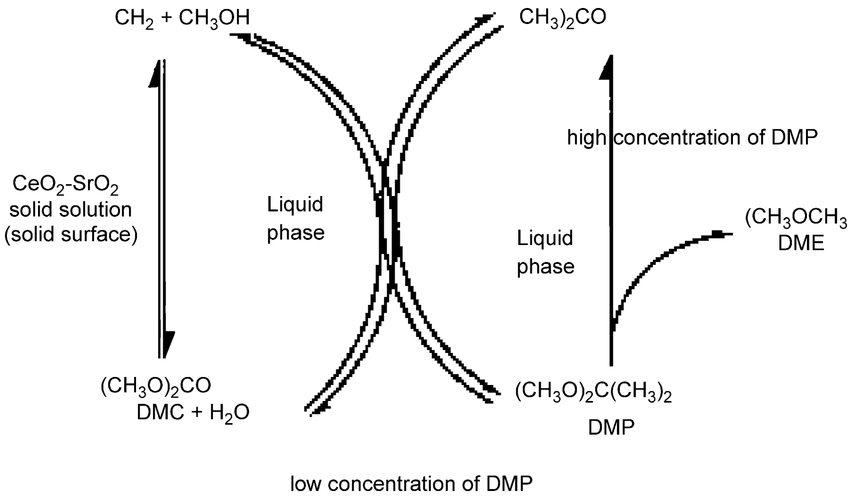


Fig. 21. Model scheme of dimethyl carbonate formation from methanol, $CO_2$ and dimethoxy propane over $CeO_2$-$ZrO_2$ catalyst [86].

unique molecule and can be used for a range of new environmentally friendly reactions to replace some of the environmentally harmful processes. For example, the transesterification of DMC with phenol gives methyl phenyl carbonate, which is converted into diphenyl carbonate (DPC) by disproportionation. $MoO_3/SiO_2$ is an active catalyst for both reactions [88]. DPC is an essential monomer in the non-phosgene route for polycarbonates. The methoxycarbonylation of aniline gives methyl *N*-phenyl carbamate in the presence of a lead compound. This reaction offers a non-phosgene route to isocyanates. As a methylating agent, DMC can be a substitute for methyl halides and dimethyl sulfate, toxic and corrosive chemicals [88]. Phenylacenitrile, aniline and phenol are selectively methylated with DMC over zeolites in the vapor-phase. The reaction of DMC with silica offers a simple and clean method for synthesizing $Si(OCH_3)_4$ [88].

### 6.4. *Use of $CO_2$ for supercritical fluid extraction*

While $CO_2$ is a greenhouse gas, it is much more environmentally benign than many of the existing solvents used in industries. Environment-friendly and energy-efficient processes can be designed by using $CO_2$ for separation and chemical reaction and materials synthesis based on the unique physical or chemical properties of $CO_2$. For example, supercritical $CO_2$ can be used as either a solvent for separation or as a medium for chemical reaction, or as both a solvent and a reactant.

The use of supercritical $CO_2$ (SC–$CO_2$) allows contaminant-free supercritical extraction of various substances ranging from beverage materials (such as caffeine from coffee bean), foods (such as excess oil from fried potato chips), and organic and inorganic functional materials, to herbs and pharmaceuticals. It is also possible to use SC–$CO_2$ to remove pollutants such as PAHs from waste sludge and contaminated soils [89] and toxics on activated carbon adsorbent [90].

Supercritical $CO_2$ extraction of essential oils and waxes has been studied and reviewed [91,92]. Chen and Lin published a review on the use of supercritical fluid extraction (SFE) in the preparation and analysis of Chinese herbal medicine (CHM), where the use of SC–$CO_2$ to replace traditional organic solvent is justified and found to be promising [93]. Consideration is given to the coupling of sub-critical $H_2O$ and SC–$CO_2$ to extract more compounds and to use the dual role of extracting useful ingredients and removing pesticide residues.

Reactive extraction of organic acids has been studied using supercritical $CO_2$ for separation of citric acid and acetic acid from their aqueous solution [94]. This is difficult, since organic acids are polar compounds, which can hardly be extracted by SC-$CO_2$. A strategy is to use reactants, which increase the solubility of the acid by a chemical reaction. Alamine 336 and Hostarex A 327 were used as reactants and oleyl alcohol was selected as an active diluent, i.e., a solvent containing functional groups that interact strongly with the acid-amine complex. The acid-amine complexes were extracted more than the amines and the acids alone under the given conditions. More recently, SC–$CO_2$ has become useful even for inorganic materials synthesis and processing. As an example, Wu et al. reported on the influence of the supercritical debinding on the properties of injection molding $ZrO_2$ ceramics. Their results indicate that with SC–$CO_2$ fluid debinding, the defects that occur in thermal debinding can be avoided and mechanical properties can be improved [95]. There are numerous reports in the recent literature on SC–$CO_2$ extraction for various applications.

### 6.5. *Using supercritical $CO_2$ as a solvent, medium or reactant*

SC–$CO_2$ can be used as a solvent or reaction medium or co-reactant for a number of organic reactions. There is a paradigm shift away from using traditional solvents in organic synthesis towards $CO_2$-mediated reactions that can lead to more environmentally friendly or greener synthetic procedures or improved outcomes (elimination of complicated product work up, higher selectivity, etc.).

Jessop et al. reported the first successful cases that demonstrate the efficient production of formic acid in a supercritical mixture of $CO_2$ and hydrogen containing a catalytic ruthenium(II) phosphine complex [96]. The use of a supercritical phase, in which hydrogen is highly miscible, leads to a very high initial rate of reaction-up to 1400 mol of formic acid per mote of catalyst per hour. The same reaction under identical conditions but in liquid organic solvents is much slower. Their results demonstrated that supercritical fluids represent a promising medium for homogeneous catalysis. Various reactions and systems have been studied. Jessop and coworkers have published reviews focusing on homogeneous hydrogenation and homogeneous catalysis in SC–$CO_2$ [31–33].

Koch and Leitner [95] reported on rhodium-catalyzed hydroformylation of olefinic substrates in SC–$CO_2$. Leitner [97] have discussed various metal-catalyzed reactions in SC-$CO_2$ in applications of compressed and particularly supercritical $CO_2$ in organic synthesis. Polymer synthesis and processing using SC–$CO_2$ has also become important and various polymerizations have been studied in SC–$CO_2$ [35,98]. A recent review has focused on the role of SC-$CO_2$ in various synthetic organic reactions such as hydrogenation, Friedel–Crafts alkylation, transition metal catalysis, palladium-mediated couplings, radical reactions, biotransformations, and polymerizations [99].

Subramaniam and Busch have studied catalytic oxidations and published a review on oxidations in $CO_2$-based reaction media, including novel $CO_2$-expanded phases [100,101]. They have discussed homogeneous catalytic oxidations in dense SC–$CO_2$ most of which involve transition metal catalysts and dioxygen or organic peroxides as oxidant. They present a new process in which the conventional solvent medium is only partially replaced by dense $CO_2$ that is called a $CO_2$-expanded solvent medium. Examples are presented that show enhanced oxidation rates compared to either neat organic solvent or SC–$CO_2$ for organic substrates (alkenes and phenols) in $CO_2$-expanded media using dioxygen and metal complexes of both Schiff base and porphyrin ligands. The authors conclude that $CO_2$-expanded media offers several advantages as follows: solvent replacement with dense $CO_2$ by up to 80 mol%, representing a substantial reduction in solvent usage; maintenance of the solubilities of the catalyst and substrate in the reaction mixture while enhancing the miscibility of dioxygen therein; lower process pressures on the order of tens of bars; and pressure-tunable dielectric constants making it possible to realize an optimum reaction medium between SC–$CO_2$ and neat solvent limits.

Recently, Jessop and co-workers reported on switchable solvent systems for catalysis and catalyst recovery using $CO_2$ as a solubility switch [102]. They invented a method for fluorous biphasic catalysis, in which the fluorous liquid is replaced by fluorinated silica, the fluorous catalyst is induced to dissolve in the organic solvent by the presence of $CO_2$, and the recovery of the catalyst after the reaction is achieved by release of the $CO_2$ pressure.

### 6.6. Using $CO_2$ as a mild oxidant

The dissociation of $CO_2$ on catalyst surface could produce active oxygen species. Some heterogeneous chemical reactions can benefit from using $CO_2$ as a mild oxidant, or as a selective source of "oxygen" atoms. For example, the use of $CO_2$ has been found to be beneficial for selective dehydrogenation of ethylbenzene to form styrene, and for dehydrogenation of lower alkanes such as ethane, propane and butane to form ethylene, propylene, and butene, respectively.

Sugino et al. [103] have made an attempt to use $CO_2$ as a diluent and oxidant in the dehydrogenation of ethlybenzene to styrene carried out over an activated carbon-supported iron catalyst. An addition of 20–30 mol% lithium nitrate to iron resulted in a significant increase in the catalytic activity. In addition to styrene, carbon monoxide and water were formed as products. This indicated that the reaction proceeds via an oxidative dehydrogenation mechanism. Yoo has found that adding $CO_2$ to the oxidation reaction of alkylaromatics with $O_2$ enhanced the rate of reaction and improved the selectivity towards the aldehyde and oxygenate products [174]. Some recent studies on heterogeneous catalytic conversion using $CO_2$ as an oxidant have been discussed in several recent reviews [11,25,161].

### 6.7. Using solar energy for $CO_2$ conversion

Using the renewable sources of energy, the reduction of $CO_2$ to form methanol or even $CH_4$ could become options when the fossil resources become scarce or more expensive. The dissociation of C–O bond in $CO_2$ is required so a catalytic approach is likely to be involved.

Anpo and Chiba studied the photocatalytic reduction of $CO_2$ with $H_2O$ and its reaction mechanism on highly dispersed titanium oxide anchored onto Vycor glass, which was prepared through a facile reaction between surface OH groups of Vycor and $TiCl_4$ [104]. They used UV irradiation of the anchored catalyst at 275 K in the presence of $CO_2$ and $H_2O$ and observed the photocatalytic formation of $CH_4$, $CH_3OH$ and CO as major products. Sayama and Arakawa [168] reported on photocatalytic decomposition of water and photocatalytic reduction of $CO_2$ to CO over $ZrO_2$ catalyst without any loaded metals under UV irradiation. The rate of $H_2$ and $O_2$ evolution increased upon addition of $Na_2CO_3$ and $NaHCO_3$. Moreover, the evolution of CO (the photocatalytic reduction product of $CO_2$) was observed from $NaHCO_3$ solutions. The work by Anpo and coworkers revealed that titanium oxide species anchored within the Y-zeolite cavities by an ion-exchange method exhibit a high and unique photocatalytic reactivity for the reduction of $CO_2$ with $H_2O$ at 328 K with a high selectivity for the formation of $CH_3OH$ in the gas phase [105]. It is interesting to note a more recent report that the photocatalytic reduction on $TiO_2$ powders produced $CH_4$ as the main product, whereas methanol and $CH_4$ were main products from the reaction on highly dispersed titanium oxide species anchored on porous glass and zeolites [106].

Frei and coworkers have used TiMCM-41 silicate sieve as a catalyst and in situ FT-IR spectroscopy to monitor the 266-nm light-induced reaction of $CO_2$ and $H_2O$ gas mixtures (including isotopic modifications ($CO_2$)-C-13, ($CO_2$)-O-18, and $D_2O$) at room temperature [107]. Carbon monoxide gas was observed as the sole product by infrared, and the growth depended linearly on the photolysis laser power. $H_2O$ was confirmed as the stoichiometric electron donor. Their work identifies CO as the single-photon, 2-electron-transfer product of $CO_2$ at framework Ti centers with $H_2O$ acting as an electron donor, which has not been established before [108].

### 6.8. Use of $CO_2$ as a recycled carbon source in fuels and chemicals

If renewable sources or waste sources of energy are used, recycling of $CO_2$ as carbon source for chemicals and fuels should be considered for applications where $CO_2$ can be used that have desired environmental benefits. $CO_2$ recycling would also make sense if such an option can indeed lead to less consumption of carbon-based fossil resources without producing more $CO_2$ from the whole system.

The amount of liquid fuel consumed in the US in 1999 was 13.60 million barrel per day, which corresponds to a very large amount of carbon estimated to be on the same order of magnitude with the $CO_2$ emitted from fossil fuel-based electric power plants. The amounts have increased significantly in 2005 but the same trend holds for 2005. The proposed approaches include hydrogenation of $CO_2$ with $H_2$ to methanol [109–111], and Fischer–Tropsch synthesis using $CO_2$-rich synthesis gas.

Hydrogenation of $CO_2$ for methanol synthesis has been the subject of a large number of studies over various catalysts [112–119], and many reports continue to appear in the current literature [120–122].

Conversion of $CO_2$ to $C_1$ to $C_{10}$ hydrocarbon fuels via methanol has also been reported by Inui et al. [123], and by Lee and co-workers [124]. There has been some reported effort on direct synthesis of aromatics from hydrogenation of $CO_2$ using hybrid catalysts composed of iron catalysts and HZSM-5 zeolite [125]. Related to the methanol synthesis and Fischer–Tropsch synthesis is the recently proposed tri-reforming process for conversion of $CO_2$ in flue gas or in $CO_2$-rich natural gas without $CO_2$ pre-separation to produce synthesis gas ($CO + H_2$) with desired $H_2/CO$ ratios of 1.5–2.0 [62,63,65].

For the $CO_2$ conversion to methanol using $H_2$, it should be noted that $H_2$ is currently produced by reforming of hydrocarbons which is an energy-intensive process and accompanied by $CO_2$ formation both from the conversion process and from the combustion of the fuels which is used to provide the process heat [40]. Therefore, methanol synthesis using $CO_2$ does not contribute to $CO_2$ reduction unless $H_2$ is produced by using renewable energy or process waste energy or nuclear energy

### 6.9. Value-Added $CO_2$ sequestration

Although storage of $CO_2$ as mineral carbonate seems preferred for the permanent sequestration, value-added $CO_2$ sequestration approaches include $CO_2$ storage into geologic formations that also enhances the recovery and production of petroleum, or natural gas, or coal-bed $CH_4$. In principle, $CO_2$ in flue gas from power plants may be used for enhanced recovery of oil and natural gas, and for enhanced coal bed methane recovery. For enhanced oil recovery, the requirement for $CO_2$ purity is a minimum, and thus the cost of gas processing (prior to use) is minimal.

The US Department of Energy/National Energy Technology Laboratory is supporting research on various $CO_2$ sequestration options [126–130,141–143,157]. The large-scale geologic sequestration projects supported by US DOE include $CO_2$ sequestration into depleting oil reservoir for enhanced oil recovery in Weyburn, Canada [127]; $CO_2$ sequestration into depleting oil well in West Pearl Queen, New Mexico; sequestration of $CO_2$-rich landfill gas into coal seems in Johnson County, Kansas, where approximately 5 million cfd (cubic feet per day) of landfill gas is treated which results in about 3 million cfd of pipeline quality natural gas [128]; $CO_2$ sequestration into coal seam in Marshal County, West Virginia and $CO_2$ sequestration into coal seam in San Juan Basin, New Mexico, which also enhances coalbed methane recovery from unminable coal seams in both locations [126]. Another approach in this direction is the so-called ocean fertilization, which make use of $CO_2$ in specific locations in the ocean and sun light to grow biomass [129].

### 6.10. Using biochemical and geochemical environments for $CO_2$ conversion

Using biochemical or geochemical environments to convert $CO_2$ is an alternative to photochemical $CO_2$ conversion (carbohydrate synthesis) under sunlight. Existing fossil fuels are believed to have originated from bio-chemical and geochemical transformations of organic substances that were initially present on the surface of the earth over the course of millions of years, which may be viewed as a detour in the carbon cycle. For example, numerous studies have shown that coal was formed from bio-chemical degradation and geochemical maturation of higher plant materials that were formed initially on the surface of the earth via photosynthesis from $CO_2$ and $H_2O$.

New ways of thinking have led to proposals for converting $CO_2$ directly in geologic formations during its long-term storage or biochemical conversion to useful C-1 chemical substances. These are still new topics for which only a few reports are available [131,132,138]. The biomimetic $CO_2$ conversion for sequestration has also been reported using the enzyme carbonic anhydrase, and good enzyme activity was observed in the presence of low levels of $SO_x$ and $NO_x$ (that might be expected from flue gases) and also in solution representative of seawater [133].

### 6.11. Evaluating the potential of growth in $CO_2$ utilization markets

This author did an analysis of potential of market growth for $CO_2$ conversion and utilization by calculating the hypothetical $CO_2$ demand for making all the carbon-based organic chemicals and materials [47]. Table 9 shows the US annual production of $CO_2$, $CO_2$-based and $CO_2$-related chemicals, as well as synthetic organic chemicals and materials based on the

Table 9
US Production of Synthetic Plastics and Related Chemicals and Estimated Potential Upper Limit of $CO_2$ Demand for Chemicals and Materials

| Chemicals and materials | Production in common units[a] | Metric tons (tonnes) |
|---|---|---|
| Synthetic plastics | 80727 millions of lb | 36,650,058 |
| Synthetic fibers | 10219 millions lb | 4,639,426 |
| Synthetic rubbers | 2414 thousands of metric tons | 2,414,000 |
| | 1. Polymers subtotal (1999) = | 37,584,996 as C, 43,703,484 as Comp |
| Ammonia (reference for urea) | 14972 thousands of tons | 13,579,604 |
| Urea for fertilizer (1999)[a,b] | 5453 thousands of tons | 4,945,871 |
| Urea for chemicals (1999)[a,b] | 18,660 millions of lb[b] | 8,471,640 |
| Urea for chemicals (1994)[c] | 15.90 billions of lb (7,952 thousands of tons) | 7,218,600 |
| | 2. Urea-equivalent $CO_2$ (1999)= | 2,686,185 as C, 9,839,508 as $CO_2$ |
| Methanol for chemicals (1994)[c] | 12.18 billions of lb | 5,529,720 |
| | 3. MeOH-Equivalent $CO_2$ (1999)[d] | 2,428,590 as C, 8,895,937 as $CO_2$ |
| $CO_2$ – Liquid + Solid (1994)[c,e] | 11.80 billions of lb (5,899 thousands of tons) | 5,357,200 |
| | 4. Liquid + Solid $CO_2$ (1999)[f] | 1,711,143 as C, 6,267,924 as $CO_2$ |
| Ultimate US $CO_2$ demand for chemicals and materials | Total US Potential (1 + 2 + 3 + 4) = | 44.4 MMT as C, 162.8 MMT as $CO_2$ |
| Ultimate world $CO_2$ demand for chemicals and materials | Estimated for World Potential | 177.6 MMT as C, 651.3 MMT as $CO_2$ |

[a] Source: ACS. Facts & Figures for the Chemical Industry. C&EN, June 26, 2000, 48–89.

[b] A significant fraction of the urea is used for making thermosetting plastics that are included in synthetic plastics (2,691 millions of lb urea-based thermosetting resins were produced in 1999).

[c] Source: ACS. Facts & Figures for the Chemical Industry. C&EN, June 24, 1996, 38–79.

[d] 1999 production of methanol was estimated (as 1.17 times 1994 production).

[e] Liquid and solid $CO_2$ only.

[f] 1999 production of liquid + solid $CO_2$ was estimated (as 1.17 times 1994 production).

data published [134,135]. The methodology of estimation used here is similar to that used by Halmann and Steinberg [5], except for the modification by considering carbon equivalence in this work. Steinberg used the production data for the plastics in the US in 1980. The present estimation for the carbon-based synthetic materials is based on the US production of plastics, fibers, and rubbers in the 1999 [135].

The US production of liquid and solid $CO_2$ amounts to 5.36 million tonnes per year (Table 9), which is mainly consumed in the food and beverage industries (refrigerant, coolant, and carbonated drinks). In addition, there are about 10 million tones of $CO_2$ consumed in making 4.95 million tons of urea fertilizers and 8.47 million tones of urea for chemicals synthesis.

Table 9 also shows the potential upper limit of $CO_2$ demand estimated by this author for chemicals and materials. If we assume that the potential chemical market demand is that for making all the carbon-based synthetic materials plus several $CO_2$-related major chemicals and materials using $CO_2$, then the upper limit of potential $CO_2$ demand for synthetic organic chemicals and polymer materials could increase to 44.41 million metric tons of carbon equivalent (Table 9). This calculated number corresponds to a stoichiometric reaction system where all the carbon in $CO_2$ is converted to the chemicals (urea, methanol, etc.) and synthetic polymer materials (plastics, fibers, rubbers). This is, of course, a hypothetical scenario since there are thermodynamic and kinetic issues with chemical reactions involving $CO_2$, but it does provide an useful measure in terms of order of magnitude.

By this estimation, the upper limit of potential market demand worldwide for $CO_2$ in making organic chemicals and materials is estimated to be 178 million metric tons of carbon equivalent. The detailed statistical data of chemicals production are not available for all the countries in the world, but the author did a simplified estimation based on the US chemical production. US chemical industry is the largest in the world, and the plants in the US provide 24% of the world's total chemical production [136]. Consequently, the upper limit of potential market demand for $CO_2$ in the world is estimated by the author to be four times that for the US For some chemicals such as urea, this estimate is lower than the real value. The 2002 world production of urea is 110 million metric tons, which is equivalent to 80.7 million metric tons of $CO_2$ and 22 million metric tons of carbon.

Table 10 shows the US production of liquid fuels in 1999 [137]. The amount of liquid fuels consumed in the US reached 13.60 million barrels per day, in which 12.75 million barrels per day liquid fuels were used for transportation fuels in 1999. By simple calculation of carbon equivalence, it becomes apparent that the liquid fuels correspond to a very large amount of carbon that is on the same order of magnitude with the $CO_2$ emitted from fossil fuel-based electric power plants in the US, as can be seen from Table 10. The total production of liquid fuels in the world is estimated to be about four times of the US annual production, based on the fact that US petroleum consumption is about 25% of the world total consumption [137]. Detailed statistical data of chemicals production and fuels consumption are not yet available for 2005 but the same overall trends hold for 2005.

Table 10
Us production of liquid fuels and their carbon equivalence

| US fuels | 1999 Daily production[a] | 1999 Annual production | Total annual production[b] | C-equivalent of annual prod[c] |
|---|---|---|---|---|
| | Million barrels per day | Million barrels per year | Million metric Tons (tonnes) | Million metric tons (tonnes) |
| Gasoline | 8.38 | 3058.7 | 354.8 | 301.6 |
| Distillate Fuels (Diesel, etc) | 3.55 | 1295.8 | 171.0 | 145.4 |
| Jet Fuel | 1.67 | 609.6 | 77.4 | 65.8 |
| | Total = 13.60 (12.75 in transportation) | | US total = | 512.8 |
| | | | World liquid fuel[d] = | 2051.2 |
| | | | 1997 US Electric Utilities Annual $CO_2$ Emissions | 523.4 as C |

[a] Source: Annual Energy Review 1999, EIA, US DOE, 2000.

[b] 1 barrel of oil (US) = 42 US gallons = 0.15899 cubic meters ($m^3$) = 158.99 liters. Assume average density values of the fuels at ambient temperatures as follows: 0.73 g/mL for gasoline; 0.80 g/mL for jet fuel; 0.83 g/mL for distillate fuels (diesel fuel and heating oils).

[c] Assume the average carbon content in the liquid fuels is 85 wt.%.

[d] Estimated based on the fact that US petroleum consumption is about 25% of the world's total consumption.

Table 11
Order of Magnitude Estimates for the Worldwide Capacity of $CO_2$ Utilization

| Option of $CO_2$ utilization | Worldwide capacity (order of magnitude in giga ton carbon) |
|---|---|
| Non-chemical utilization | 0.01–0.1 GtC per year |
| Chemicals and materials | 0.1–1 GtC per year |
| Synthetic liquid fuels | 1–10 GtC per year |

[a]Estimated based on the US and the world production of chemicals and materials as well as liquid fuels in 1999.

Table 11 shows the order of magnitude estimates by the author for $CO_2$ utilization, based on the data shown in Tables 9 and 10. For comparison, Table 12 shows the order of magnitude estimates published in a recent reviews by Herzog for the worldwide capacity of various options for $CO_2$ sequestration [153–156]. The worldwide capacity for utilization of $CO_2$ for making chemicals and materials is less than 1 Giga tons of carbon per year, which is relatively small compared to several other options such as ocean sequestration.

However, it should be noted that the amount of $CO_2$ that can be utilized for making chemicals and materials can be potentially large enough for expanding commercial-scale applications worldwide. For example, the consumption of merchant liquid $CO_2$ in the US, Western Europe and Japan amounted 10.6 million metric tons in 2002 [140]. Global merchant $CO_2$ demand as an industrial gas will increase at an average annual growth rate of 2.4% from $3.2 billion in 2003 to $3.6 billion in 2008 [53]. The global urea market, which uses $CO_2$ and ammonia for the synthesis, is estimated to be $16.5 billion USD for over 110 million metric tons of urea [60]. These and other application areas can be large enough for considering further significant growth by developing new applications and expanding existing applications using $CO_2$.

Table 12
Order of magnitude estimates for the worldwide capacity of various sinks[a]

| Sequestration option | Worldwide capacity (order of magnitude in giga ton carbon) |
|---|---|
| Ocean | 1000s GtC |
| Deep saline formations | 100s–1000s GtC |
| Depleted oil and gas reservoirs | 100s GtC |
| Coal seams | 10s–100s GtC |
| Terrestrial | 10s GtC |
| Utilization (chemical conversion) | <1 GtC per year |

[a] Source. H. J. Herzog. Using Carbon Capture and Sequestration Technologies to Address Climate Change Concerns. Am. Chem. Soc. Div. Fuel Chem. Prepr., 2001, 46(1), 53–55.

## 7. Summary and conclusions

The mitigation of emissions of greenhouse gases, particularly $CO_2$, and their effective utilization present to the world both a difficult challenge and a major opportunity for sustainable development in energy and environment.

Global strategy for control of $CO_2$ should begin with energy issues since the problem originates from the way the energy sources are selected and used.

The amounts of carbon in $CO_2$ emitted as greenhouse gas from combustion of fossil fuels worldwide have become higher than the amounts of petroleum and petroleum products consumed as chemical feedstock in the world, namely the amount of carbon used for making most chemicals, organic materials and liquid transportation fuels.

$CO_2$ conversion and utilization research is important and should be an integral part of research and development for carbon management and sustainable development.

When applicable, using $CO_2$ in concentrated sources without $CO_2$ separation is desired (e.g., tri-reforming versus $CO_2$ reforming).

For applications where pure $CO_2$ is needed, more efficient $CO_2$ separation method is desired (e.g., $CO_2$ 'molecular basket' versus conventional zeolite or carbon adsorbents).

$CO_2$ can be used effectively in chemical processing to reduce environmental impact, although the amount of $CO_2$ used is small compared to that from fossil fuel combustion.

More work is needed for more effective uses of $CO_2$ to replace toxic chemicals such as phosgene (e.g., $CO_2$ versus phosgene for DMC synthesis).

Value-added strategies and novel approaches are needed for more effective and energy-efficient $CO_2$ conversion and utilization.

Various strategic considerations, technical approaches, and specific research directions have been presented. Selected case studies have been discussed. More research is necessary towards effective $CO_2$ conversion into useful substances using renewable sources of energy.

$CO_2$ issue is truly global and thus people and governments worldwide should seriously consider supporting research and industrial commitments on $CO_2$ conversion and utilization, as well as international collaborative research involving developing countries.

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## References

[1] S.A. Levin, The problem of pattern and scale in ecology, Ecology 73 (6) (1992) 1943–1967.

[2] J.M. Melillo, A.D. Mcguire, D.W. Kicklighter, B. Moore, C.J. Vorosmarty, A.L. Schloss, Global climate-change and terrestrial net primary production, Nature 363 (6426) (1993) 234–240.

[3] D.S. Schimel, Terrestrial ecosystems and the carbon-cycle, Global Change Biol. 1 (1) (1995) 77–91.

[4] J. Paul, C.-M. Pradier (Eds.), Carbon Dioxide Chemistry: Environmental Issues, Royal Society of Chemistry, Cambridge, UK, 1994, p. 405.

[5] M.M. Halmann, M. Steinberg, Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology, Lewis Publishers, Boca Raton, FL, 1999, p. 568.

[6] M.M. Maroto-Valer, C.S. Song, Y. Soong, Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century, Kluwer Academic/Plenum Publishers, New York, 2002, p. 447.

[7] DOE/NETL, Carbon Sequestration. Technology Roadmap and Program Plan 2005. US Department of Energy, National Energy Technology Laboratory, May 2005.

[8] C.D. Keeling, T.P. Whorf, Atmospheric $CO_2$ records from sites in the SiO air sampling network, in: Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U. S. Department of Energy, Oak Ridge, TN, USA, 2005.

[9] J.S. Lindsey, Carbon Dioxide. McGraw-Hill Encyclopedia of Chemistry, second ed., McGraw-Hill, New York, 1993, pp. 157–159.

[10] R. Pierantozzi, fourth ed., Carbon Dioxide. Kirk-Othmer Encyclopedia of Chemical Technology, vol. 5, John Wiley and Sons, New York, 1993, pp. 35–53.

[11] C.S. Song, A.M. Gaffney, K. Fujimoto (Eds.) $CO_2$ Conversion and Utilization. American Chemical Society, Washington, DC, ACS Symposium Series, vol. 809, 2002, 420 pp.

[12] C.S. Song, S.T. Srimat, S. Murata, W. Pan, L. Sun, A.W. Scaroni, J.N. Armor, Effects of pressure on $CO_2$ reforming of $CH_4$ over Ni/Na-Y and Ni/$Al_2O_3$ catalysts, in: C.S. Song, A. M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington DC, ACS Symposium Series, vol. 809, 2002, pp. 258–274 (Chapter 17).

[13] M. Aresta, E. Quaranta, Carbon dioxide: a substitute for phosgene, Chemtech. 27 (3) (1997) 32–40.

[14] M. Aresta, Perspectives of carbon dioxide utilisation in the synthesis of chemicals. Coupling chemistry with biotechnology, Stud. Surf. Sci. Catal. 114 (1998) 65–76.

[15] M. Aresta, Key issues in carbon dioxide utilization as a building block for molecular organic compounds in the chemical industry, Am. Chem. Soc. Div. Petrol. Chem. Prepr. 45 (1) (2000) 92–93.

[16] M. Aresta (Ed.), Carbon Dioxide Recovery and Utilization, Springer, 2003, p. 384.

[17] M. Aresta, Carbon dioxide utilization. Greening both the energy and chemical industry: an overview, Am. Chem. Soc. Symp Ser. 852 (2003) 2–39.

[18] M. Aresta, A. Dibenedetto, I. Tommasi, Developing innovative synthetic technologies of industrial relevance based on carbon dioxide as raw material, Energy Fuels 15 (2001) 269–273.

[19] M. Aresta, A. Dibenedetto, Key issues in carbon dioxide utilisation as a building block for molecular organic compounds in the chemical industry, in: C.S. Song, A.M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington, DC, ACS Symposium Series, vol. 809, 2002, pp. 54–70 (Chapter 4).

[20] M. Aresta, A. Dibenedetto, The contribution of the utilization option to reducing the $CO_2$ atmospheric loading: research needed to overcome existing barriers for a full exploitation of the potential of the $CO_2$ use, Catal. Today 98 (4) (2004) 455–462.

[21] T. Inui, M. Anpo, K. Izui, S. Yanagida, T. Yamaguchi (Eds.), Advances in Chemical Conversions for Mitigating Carbon Dioxide (Studies in Surface Science and Catalysis), vol. 114, Elsevier, Amsterdam, 1998, p. 691.

[22] T. Inui, Effective conversion of $CO_2$ to valuable compounds by using multifunctional catalysts, in: C.S. Song, A. M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington, DC, ACS Symposium Series, vol. 809, 2002, pp. 130–152 (Chapter 9).

[23] T. Inui, Reforming of $CH_4$ by $CO_2$, $O_2$ and/or $H_2O$, Catal. R. Soc. Chem. 16 (2002) 133–154.

[24] H. Arakawa, Research and development on new synthetic routes for basic chemicals by catalytic hydrogenation of $CO_2$, Stud. Surf. Sci. Catal. 114 (1998) 19–30.

[25] S.-E. Park, J.S. Yoo, J.-S. Chang, K.Y. Lee, M.S. Park, Heterogeneous catalytic activation of carbon dioxide as an oxidant, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46 (1) (2001) 115–118.

[26] J.R. Rostrup-Nielsen, Aspects of $CO_2$-reforming of methane, Stud. Surf. Sci. Catal. 81 (1994) 25–41.

[27] J.R. Rostrup-Nielsen, B.J.H. Hansen, L.M. Aparicio, Reforming of hydrocarbons into synthesis gas on supported metal catalysts, Sekiyu Gakkaishi 40 (5) (1997) 366–377.

[28] S.B. Wang, G.Q.M. Lu, G.J. Millar, Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: state of the art, Energy Fuels 10 (4) (1996) 896–904.

[29] M.C.J. Bradford, M.A. Vannice, $CO_2$ reforming of $CH_4$, Catal. Rev. -Sci. Eng. 41 (1) (1999) 1–42.

[30] Y.H. Hu, E. Ruckenstein, Catalytic conversion of methane to synthesis gas by partial oxidation and $CO_2$ reforming, Advances in Catalysis 48 (2004) 297–345.

[31] P.G. Jessop, T. Ikariya, R. Noyori, Homogeneous catalysis in supercritical fluids, Science 269 (5227) (1995) 1065–1069.

[32] P.G. Jessop, T. Ikariya, R. Noyori, Homogeneous hydrogenation of carbon-dioxide, Chem. Rev. 95 (2) (1995) 259–272.

[33] P.G. Jessop, F. Joo, C.C. Tai, Recent advances in the homogeneous hydrogenation of carbon dioxide, Coord. Chem. Rev. 248 (21–24) (2004) 2425–2442.

[34] W. Leitner, Reactions in supercritical carbon dioxide ($scCO_2$), Topics Curr. Chem. 206 (1999) 107–132.

[35] A.I. Cooper, Polymer synthesis and processing using supercritical carbon dioxide, J. Mater. Chem. 10 (2) (2000) 207–234.

[36] D.L. Tomasko, H.B. Li, D.H. Liu, X.M. Han, M.J. Wingert, L.J. Lee, K.W. Koelling, A review of $CO_2$ applications in the processing of polymers, Ind. Eng. Chem. Res. 42 (25) (2003) 6431–6456.

[37] X.D. Xu, J.A. Moulijn, Mitigation of $CO_2$ by chemical conversion: plausible chemical reactions and promising products, Energy Fuels 10 (2) (1996) 305–325.

[38] H. Audus, H. Oonk, An assessment procedure for chemical utilisation schemes intended to reduce $CO_2$ emissions to atmosphere, Energy Conv. Manag. 38 (1997) S409–S414.

[39] P.W.F. Riemer, W.G. Ormerod, International perspectives and the results of carbon-dioxide capture. disposal and utilization studies, Energy Conv. Manag. 36 (6–9) (1995) 813–818.

[40] J.N. Armor, Catalytic fixation of $CO_2$, $CO_2$ purity, energy, and the environment, Am. Chem. Soc. Div. Petrol. Chem. Prepr. 45 (1) (2000) 141–142.

[41] H. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. DuBois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielson, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, Catalysis research of relevance to carbon management: progress, challenges, and opportunities, Chem. Rev. 101 (4) (2001) 953–996.

[42] C.-J. Liu, R.G Mallinson, M. Aresta (Eds.) Utilization of Greenhouse Gases. American Chemical Society, Washington, DC, ACS Symposium Series, vol. 852, 2003, 412 pp.

[43] J.J. Spivey, Catalysis in the development of clean energy technologies, Catal. Today 100 (1–2) (2005) 171–180.

[44] D.M. Etheridge, L.P. Steele, R.L. Langenfelds, R.J. Francey, J.-M. Barnola, V.I. Morgan, Historical $CO_2$ record from the Law Dome DE08, DE08-2, and DSS ice cores (atmospheric $CO_2$ concentrations, Antarctic ice cores). in: Trends: A Compendium of Data on Global Change, on line at the Carbon Dioxide Information Analysis Center, http://cdiac.esd.ornl.gov/, June 1998.

[45] G. Marland, T.A. Boden, R.J. Andres, Global, Regional, and National $CO_2$ Emissions, in: Trends: A Compendium of Data on Global Change, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A, 2005

[46] EIA/AER, Annual Energy Review 2003, Energy Information Administration, U.S. Department of Energy, Report No. DOE/EIA-0384(97), 2004.

[47] C.S. Song, $CO_2$ Conversion and utilization: an overview, in: C.S. Song, A. M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington DC, ACS Symposium Series, vol. 809, 2002, pp. 2–30 (Chapter 1).

[48] C.S. Song, Fuel processing for low-temperature and high-temperature fuel cells, challenges, and opportunities for sustainable development in the 21st Century, Catal. Today 77 (2002) 17–50.

[49] DOE/EERE. Partnership Plan. Freedom CAR and Fuel Partnership. November 2004. http://www.eere.energy.gov/vehiclesandfuels/pdfs/program/fc_fuel_partnership_plan.pdf, viewed June 30, 2005.

[50] DOE/FE. FutureGen - Tomorrow's Pollution-Free Power Plant. Office of Fossil Energy, http://fossil.energy.gov/programs/powersystems/futuregen/index.html#top, US Department of Energy, viewed July 20, 2005.

[51] K.-W. Lee, Clean fuels from biomass, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46 (1) (2001) 61–64.

[52] DOE/EPA. Fuel Economy. Internet Resource Developed by U.S. Department of Energy and U.S. Environmental Protection Agency, http://www.fueleconomy.gov/feg/atv.shtml. Viewed May 20, 2001.

[53] E. Gobina, Carbon dioxide utilization and recovery. BCC Report E-131, Business Communications Company, Norwalk, CT, December 2004.

[54] Lange's HDBK. Lange's Handbook of Chemistry, 13th Edition, McGraw-Hill, New York, 1985, p. 9–4 and p. 9–70.

[55] J.E. Ferguson, Carbon Dioxide. MacMillan Encyclopedia of Chemistry, vol. 1, MacMillan References, New York, 1997, pp. 302–308.

[56] CRC Handbook of Chemistry and Physics. 75th Edition, CRC Press, Boca Raton, FL, 1994, p. 5–4.

[57] W. Ormerod, P. Riemer, A. Smith, Carbon dioxide utilisation. iea greenhouse gas R&D programme, ISBN 1 898373 17 5, IEA, London, U.K., January 1995.

[58] Air Liquid. $CO_2$: Main Applications. http://www.airliquide.com/, Viewed June 2005.

[59] ACP, Liquid $CO_2$: Main Applications. http://www.acpco2.com/, Viewed June 2005.

[60] D.H. Lauriente, CEH Report: Urea. Chemical Economics Handbook Program, SRI Consulting, Menlo Park, CA, July 2004.

[61] NYS, Eight States and NYC Sue Top Five US Global Warming Polluters. Press Release, Office of New York State Attorney General, July 21, 2004.

[62] C.S. Song, W. Pan, S.T. Srimat, J. Zheng, Y. Li, Y.H. Wang, B.Q. Xu, Q.M. Zhu, Tri-reforming of methane over Ni catalysts for $CO_2$ conversion to syngas with desired $H_2/CO$ ratios using flue gas of power plants without $CO_2$ separation, Stud. Surf. Sci. Catal. 153 (2004) 315.

[63] C.S. Song, Tri-reforming: a new process for reducing $CO_2$ emissions, Chem. Innovat. (formerly Chemtech, ACS) 31 (1) (2001) 21–26.

[64] C.S. Song, Tri-reforming: a new process concept for effective conversion and utilization of $CO_2$ in fuel gas from electric power plants, Am. Chem. Soc. Div. Fuel Chem. Prep. 45 (2002) 772–776.

[65] C.S. Song, W. Pan, Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired H-2/CO ratios, Catal. Today 98 (4) (2004) 463–484.

[66] C.S. Song, Proceedings of 2nd Topical Conference on Natural Gas Conversion and Utilization. Held in conjunction with AIChE 2002 Spring National Meeting, New Orleans, March 11–14, 2002, p. 402.

[67] S.T. Srimat, C.S. Song, Effects of pressure on $CO_2$ reforming of $CH_4$ over Rh/Na-Y and $Rh/Al_2O_3$ catalysts, in: C.S. Song, A. M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington, DC, ACS Symposium Series, vol. 809, 2002, pp. 289–302 (Chapter 19).

[68] C.S. Song, Chemicals, fuels and electricity Co-generated from coal. A proposed concept for utilization of $CO_2$ from power plants, in: Proceedings of 16th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, October 11–15, Paper No. 16-5, 1999.

[69] S.-H. Lee, W. Cho, W.-S. Ju, B.-H. Cho, Y.-C. Lee, Y.-S. Baek, Tri-reforming of $CH_4$ using $CO_2$ for production of synthesis gas to dimethyl ether, Catal. Today 87 (2003) 133.

[70] S.-H. Lee, W. Cho, W.-S. Ju, J.-S. Chang, S.-E. Park, Y.-S. Baek, Proceedings of the 7th International Conference on Carbon Dioxide Utilization. Seoul, Korea, October 12–16, 2003, p. 203.

[71] M. Halmann, A. Steinfeld, Proceedings of the 17th International Conference on Efficiency, Costs, Optimization, Simulation and Environmental Impacts of Energy and Process Systsems, Guanajuato, México, July 7–9, 2004. Paper No. 185.

[72] M. Halmann, A. Steinfeld, Paper presented at the 8th International Conference on carbon Dioxide Utilization, Oslo, Norway, June 22–26, 2005.

[73] D.J. Moon, Development of tri-reforming catalyst for utilization of $CO_2$ in SOFC and MCFC fuel reforming applications, in Proceedings of the 8th International Conference on carbon Dioxide Utilization, Oslo, Norway, June 22–26, 2005.

[74] G. Centi, S. Perathoner, Heterogeneous catalytic reactions with $CO_2$: status and perspectives, Stud. Surf. Sci. Catal. 153 (2004) 1–8.

[75] X. Xu, C.S. Song, J.M. Andresen, B.G. Miller, A.W. Scaroni, Novel polyethyleneimine-modified mesoporous molecular sieve of MCM-41 type as adsorbent for $CO_2$ capture, Energy Fuels 16 (2002) 1463–1469.

[76] X. Xu, C.S. Song, J.M. Andresen, B.G. Miller, A.W. Scaroni, Preparation and characterization of novel $CO_2$ ‘‘Molecular Basket’’ adsorbents based on polymer-modified mesoporous molecular sieve MCM-41, Microporous Mesoporous Mater 62 (2003) 29–45.

[77] X. Xu, C.S. Song, B.G. Miller, A.W. Scaroni, Adsorption separation of carbon dioxide from flue gas of gas-fired boiler by a novel nanoporous ‘‘Molecular Basket’’ adsorbent, Fuel Process. Technol. 86 (14–15) (2005) 1457–1472.

[78] X. Xu, C.S. Song, B.G. Miller, A.W. Scaroni, Influence of moisture on $CO_2$ separation from gas mixture by a nanoporous adsorbent based on polyethylenimine-modified molecular sieve MCM-41, Ind. Eng. Chem. Res. 44 (2005) 8113–8119.

[79] K. Essaki, K. Nakagawa, M. Kato, $CO_2$ absorption by lithium silicate at room temperature, J. Chem. Eng. Jpn. 37 (6) (2004) 772–777.

[80] M. Kato, K. Essaki, S. Yoshikawa, K. Nakagawa, H. uemoto, Reproducibility of $CO_2$ absorption and emission for cyclical pellet type lithium orthosilicate, J. Ceram. Soc. Jpn. 112 (5) (2004) S1338–S1340.

[81] A. Dibenedetto, M. Aresta, $Nb_2O_5$ as catalyst in the oxidative carboxylation of olefins, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46 (1) (2001) 119–121.

[82] K. Tomishige, T. Sakaihori, Y. Ikeda, K. Fujimoto, A novel method of direct synthesis of dimethyl carbonate from methanol and carbon dioxide catalyzed by zirconia, Catal. Lett. 58 (1999) 225–229.

[83] K. Tomishige, Y. Ikeda, T. Sakaihori, K. Fujimoto, Catalytic properties and structure of zirconia catalysts for direct synthesis of dimethyl carbonate from methanol and carbon dioxide, J. Catal. 192 (2) (2000) 355–362.

[84] K.T. Jung, A.T. Bell, An in situ infrared study of dimethyl carbonate synthesis from carbon dioxide and methanol over zirconia, J. Catal. 204 (2) (2001) 339–347.

[85] K. Tomishige, Y. Furusawa, Y. Ikeda, M. Asadullah, K. Fujimoto, $CeO_2$–$ZrO_2$ solid solution catalyst for selective synthesis of dimethyl carbonate from methanol and carbon dioxide, Catal. Lett. 76 (1–2) (2001) 71–74.

[86] K. Tomishige, K. Kunimori, Catalytic and direct synthesis of dimethyl carbonate starting from carbon dioxide using $CeO_2$-$ZrO_2$ solid solution heterogeneous catalyst: effect of $H_2O$ removal from the reaction system, Appl. Catal. A: Gen. 237 (1–2) (2002) 103–109.

[87] D. Ballivet-Tkatchenko, O. Douteau, S. Stutzmann, Reactivity of carbon dioxide with *n*-butyl(phenoxy)-,(alkoxy)-, and (oxo)stannanes: insight into dimethyl carbonate synthesis, Organometallics 19 (2000) 4563–4567.

[88] Y. Ono, Dimethyl carbonate for environmentally benign reactions, Catal. Today 35 (1–2) (1997) 15–25.

[89] A. Akgerman, C. Erkey, S.M. Ghoreishi, Supercritical extraction of hexachlorobenzene from soil, Ind. Eng. Chem. Res. 31 (1) (1992) 333–339.

[90] S.J. Macnaughton, N.R. Foster, Supercritical adsorption and desorption behavior of DDT on activated carbon using carbon-dioxide, Ind. Eng. Chem. Res. 34 (1) (1995) 275–282.

[91] E. Reverchon, G. Dellaporte, F. Senatore, Supercritical $CO_2$ extraction and fractionation of lavender essential oil and waxes, J. Agric. Food Chem. 43 (6) (1995) 1654–1658.

[92] E. Reverchon, Supercritical fluid extraction and fractionation of essential oils and related products, J. Supercrit. Fluids 10 (1) (1997) 1–37.

[93] Y.T. Chen, Y.C. Ling, An overview of supercritical fluid extraction in Chinese herbal medicine: from preparation to analysis, J. Food Drug Anal. 8 (4) (2000) 235–247.

[94] N. Kapucu, A. Guvenc, U. Mehmetoglu, A. Calimli, Reactive extraction of organic acids by supercritical $CO_2$, Rev. Chem. Eng. 15 (4) (1999) 233–243.

[95] Y. Wu, W.J. Si, Y.S. Jing, H.Z. Miao, Influence of the supercritical debinding on the properties of injection molding $ZrO_2$ ceramics, Rare Met. Mater. Eng. 32 (2003) 296–298.

[96] P.G. Jessop, T. Ikariya, R. Noyori, Homogeneous catalytic-hydrogenation of supercritical carbon-dioxide, Nature 368 (6468) (1994) 231–233.

[97] D. Koch, W. Leitner, Rhodium-catalyzed hydroformylation in supercritical carbon dioxide, J. Am. Chem. Soc. 120 (51) (1998) 13398–13404.

[98] D.A. Canelas, J.M. DeSimone, Polymerizations in liquid and supercritical carbon dioxide, Adv. Polym. Sci. 133 (1997) 103–140.

[99] R.S. Oakes, A.A. Clifford, C.M. Rayner, The use of supercritical fluids in synthetic organic chemistry, J. Chem. Soc. Perkin Trans. 1 (2001) 917–941.

[100] G. Musie, M. Wei, B. Subramaniam, D.H. Busch, Catalytic oxidations in carbon dioxide-based reaction media, including novel $CO_2$-expanded phases, Coord. Chem. Rev. 219 (2001) 789–820.

[101] B. Subramaniam, D.H. Busch, Use of dense-phase carbon dioxide in catalysis, in: C.S. Song, A. M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington DC, ACS Symposium Series, vol. 809, 2002, pp. 364–386 (Chapter 24).

[102] C.D. Ablan, J.P. Hallett, K.N. West, R.S. Jones, C.A. Eckert, C.L. Liotta, P.G. Jessop, Use and recovery of a homogeneous catalyst with carbon dioxide as a solubility switch, Chem. Commun. (24) (2003) 2972–2973.

[103] M.O. Sugino, H. Shimada, T. Turuda, H. Miura, N. Ikenaga, T. Suzuki, Oxidative dehydrogenation of ethlybenzene with carbon dioxide, Appl. Catal. A: Gen. 121 (1) (1995) 125–137.

[104] M. Anpo, K. Chiba, Photocatalytic reduction of $CO_2$ on anchored titanium-oxide catalysts, J. Mol. Catal. 74 (1–3) (1992) 207–212.

[105] M. Anpo, H. Yamashita, Y. Ichihashi, Y. Fujii, M. Honda, Photocatalytic reduction of $CO_2$ with $H_2O$ on titanium oxides anchored within micropores of zeolites: Effects of the structure of the active sites and the addition of Pt, J. Phys. Chem. B 101 (14) (1997) 2632–2636.

[106] H. Yamashita, K. Ikeue, M. Anpo, Photocatalytic reduction of $CO_2$ with $H_2O$ on various titanium oxide catalysts, in: C.S. Song, A. M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington, DC, ACS Symposium Series, vol. 809, 2002, pp. 330–343 (Chapter 22).

[107] W.Y. Lin, H.X. Han, H. Frei, $CO_2$ splitting by $H_2O$ to CO and $O_2$ under UV light in TiMCM-41 silicate sieve, J. Phys. Chem. B 108 (47) (2004) 18269–18273.

[108] N. Ulagappan, H. Frei, Mechanistic study of $CO_2$ photoreduction in Ti silicalite molecular sieve by FT-IR spectroscopy, J. Phys. Chem. A 104 (33) (2000) 7834–7839.

[109] M. Steinberg, $CO_2$ mitigation and fuel production, Am. Chem. Soc. Div. Petrol. Chem. Prepr. 45 (1) (2000) 74–76.

[110] M. Steinberg, $CO_2$ Mitigation and fuel production, in: C.S Song, A.M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington, DC, 2001.

[111] M. Steinberg, $CO_2$ Mitigation and fuel production, in: C.S. Song, A. M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington, DC, ACS Symposium Series, vol. 809, 2002. pp. 31–37 (Chapter 2).

[112] C. Schild, A. Wokaun, A. Baiker, On the mechanism of CO and $CO_2$ hydrogenation reactions on zirconia-supported catalysts—a diffuse reflectance FTIR Study. 2. Surface species on copper zirconia catalysts—implications for methanol synthesis selectivity, J. Mol. Catal. 63 (2) (1990) 243–254.

[113] Y. Nitta, O. Suwata, Y. Ikeda, Y. Okamoto, T. Imanaka, Opper-zirconia catalysts for methanol synthesis from carbon-dioxide - effect of ZNO addition to CU-ZRO2 catalysts, Catal. Lett. 26 (3–4) (1994) 345–354.

[114] D.B. Clarke, A.T. Bell, An Infrared study of methanol synthesis from $CO_2$ on clean and potassium-promoted Cu/$SiO_2$, J. Catal. 154 (2) (1995) 314–328.

[115] M. Sahibzada, D. Chadwick, I.S. Metcalfe, Hydrogenation of carbon dioxide to methanol over palladium-promoted Cu/ZnO/$Al_2O_3$ catalysts, Catal. Today 29 (1–4) (1996) 367–372.

[116] H. Sakurai, M. Haruta, Synergism in methanol synthesis from carbon dioxide over gold catalysts supported on metal oxides, Catal. Today 29 (1–4) (1996) 361–365.

[117] T. Fujitani, I. Nakamura, T. Uchijima, J. Nakamura, The kinetics and mechanism of methanol synthesis by hydrogenation of $CO_2$ over a Zn-deposited Cu(1 1 1) surface, Surf. Sci. 383 (2–3) (1997) 285–298.

[118] Y. Borodko, G.A. Somorjai, Catalytic hydrogenation of carbon oxides—a 10-year perspective, Appl. Catal. A: Gen. 186 (1–2) (1999) 355–362.

[119] A. Baiker, Utilization of carbon dioxide in heterogeneous catalytic synthesis, Appl. Organomet. Chem. 14 (12) (2000) 751–762.

[120] Y.K. Park, J.K. Jeon, S.K. Ihm, Design of copper based hybrid catalysts for $CO_2$ hydrogenation, Stud. Surf. Sci. Catal. 153 (2004) 25–32.

[121] K. Omata, M. Hashimoto, Y. Watanabe, T. Umegaki, S. Wagatsuma, G. Ishiguro, M. Yamada, Optimization of Cu oxide catalyst for methanol synthesis under high $CO_2$ partial pressure using combinatorial tools, Appl. Catal. A: Gen. 262 (2) (2004) 207–214.

[122] H. Tominaga, M. Nagai, Density functional study of carbon dioxide hydrogenation on molybdenum carbide and metal, Appl. Catal. A: Gen. 282 (1–2) (2005) 5–13.

[123] T. Inui, K. Kitagawa, T. Takeguchi, T. Hagiwara, Y. Makino, Hydrogenation of carbon-dioxide to C1-C7 hydrocarbons via methanol on composite catalysts, Appl. Catal. A: Gen. 94 (1) (1993) 31–44.

[124] S.S. Nam, H. Kim, G. Kishan, M.J. Choi, K.W. Lee, Catalytic conversion of carbon dioxide into hydrocarbons over iron supported on alkali ion-exchanged Y-zeolite catalysts, Appl. Catal. A: Gen. 179 (1–2) (1999) 155–163.

[125] C.K. Kuei, M.D. Lee, Hydrogenation of carbon-dioxide by hybrid catalysts, direct synthesis of aromatics from carbon-dioxide and hydrogen, Can. J. Chem. Eng. 69 (1) (1991) 347–354.

[126] C.M. White, B.R. Strazisar, E.J. Granite, J.S. Hoffman, H.W. Pennline, Separation and capture of $CO_2$ from large stationary sources and sequestration in geological formations—Coalbeds and deep saline aquifers, J. Air Waste Manag. Assoc. 53 (6) (2003) 645–715.

[127] DOE/NETL Weyburn. Projects Facts. WEYBURN CARBON DIOXIDE SEQUESTRATION PROJECT. US Department of Energy, National Energy Technology Laboratory, March 2005.

[128] DOE/NETL Kansas. Projects Facts. Landfill Gas Sequestration in Kansas. US Department of Energy, National Energy Technology Laboratory, February 2005.

[129] M. Markels, R.T. Barber, Sequestration of carbon dioxide by ocean fertilization, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46 (1) (2001) 45–48.

[130] D. Beecy, The role of carbon sequestration in a national carbon management strategy, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46 (1) (2001) 38–44.

[131] D. Mahajan, C. Song, A.W. Scaroni, Micro-reactor study on catalytic reduction of $CO_2$ into liquid fuels: simulating reactions under geologic formation conditions, Am. Chem. Soc. Div. Petrol. Chem. Prepr. 45 (1) (2000) 113–117.

[132] D. Mahajan, C.S. Song, A.W. Scaroni, Catalytic reduction of $CO_2$ into liquid fuels: simulating reactions under geological formation conditions, in: C.S. Song, A. M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington, DC, ACS Symposium Series, vol. 809, 2002, pp. 166–180 (Chapter 11).

[133] G.M. Bond, J. Stringer, D.K. Brandvold, F.A. Simsek, M.G. Medina, G. Egeland, Development of integrated system for biomimetic $CO_2$ sequestration using the enzyme carbonic anhydrase, Energy Fuels 15 (2) (2001) 309–316.

[134] ACS. Facts & figures for the chemical industry. Chem. Eng. News, June 24, 1996, pp. 38–79.

[135] ACS. Facts & figures for the chemical industry. Chem. Eng. News, June 26, 2000, pp. 48–89.

[136] OTP (Office of Technology Policy, U.S. Department of Commerce.). Meeting the Challenge: U.S. Industry Faces the 21st Century. Chemtech, 1996, vol. 26, pp. 46–54.

[137] B. Suresh, Y. Ishikawa, CEH Report: Carbon Dioxide. Chemical Economics Handbook Program, SRI Consulting, Menlo Park, CA, August 2003.

[138] D. Beecy, F.M. Ferrell, J.K. Carey, Advanced concepts for $CO_2$ conversion, storage, and reuse, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46 (1) (2001) 99–100.

[139] A. Chakma, $CO_2$ capture processes—opportunities for improved energy efficiencies, Energy Conv. Manag. 38 (1997) S51–S56.

[140] V.R. Choudhary, A.S. Mamman, B.S. Uphade, R.E. Babcock, $CO_2$ Reforming and simultaneous $CO_2$ and steam reforming of methane to syngas over $Co_xNi_{1-x}O$ supported on macroporous silica-alumina precoated with MgO, in: C. Song, A.M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington, DC, pp. 224–240.

[141] DOE/FE. Capturing Carbon Dioxide. Office of Fossil Energy, U.S. Department of Energy, 1999a.

[142] DOE/FE, 1999b. Project Facts-Advanced Power and Fuel Technologies. The Vision 21 EnergyPlex Concept. DOE/FE-0364, Office of Fossil Energy, U.S. Department of Energy, 1999b.

[143] DOE/OS-FE. Carbon Sequestration. State of the Science. Office of Science and Office of Fossil Energy, U.S. Department of Energy, February 1999.

[152] G. Gottlicher, R. Pruschek, Comparison of $CO_2$ removal systems for fossil-fueled power plant processes, Energy Conv. Manag. 38 (1997) S173–S178.

[153] H.J. Herzog, Using carbon capture and sequestration technologies to address climate change concerns, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46 (1) (2001) 53–55.

[154] H.J. Herzog, What future for carbon capture and sequestration? Environ. Sci. Technol. 35 (7) (2001) 148A–153A.

[155] H. Herzog, E. Drake, E. Adam, $CO_2$ capture, reuse, and storage technologies for mitigating global climate change. Report to U.S. Department of Energy, DE-AF22-96PC01257, January 1997, pp. 66.

[156] H.J. Herzog, E.M. Drake, Carbon dioxide recovery and disposal from large energy systems, Ann. Rev. Energ. Env. 21 (1996) 145–166.

[157] R. Kane, D.E. Klein, Opportunities for advancements in chemical processes in carbon sequestration and climate change mitigation, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46 (1) (2001) 275–277.

[158] E.S. Kikkinides, R.T. Yang, S.H. Cho, Concentration and recovery of $CO_2$ from flue-gas by pressure swing adsorption, Ind. Eng. Chem. Res. 32 (11) (1993) 2714–2720.

[159] W.J. Koros, R. Mahajan, Pushing the limits on possibilities for large scale gas separation: which strategies? J. Memb. Sci. 175 (2) (2000) 181–196.

[161] L.E. Manzer, $CO_2$ Emission reductions: an opportunity for new catalytic technology, in: C.S. Song, A. M. Gaffney, K. Fujimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington, DC, ACS Symposium Series, vol. 809, 2002, pp. 39–52 (Chapter 3).

[162] C.L. Mariz, Carbon dioxide recovery: large scale design trends, J. Can. Petrol. Technol. 37 (7) (1998) 42–47.

[164] A. Meisen, X.S. Shuai, Research, Development issues in $CO_2$ capture, Energy Conv. Manag. 38 (1997) S37–S42.

[165] T. Mimura, S. Shimojyo, T. Suda, M. Iijima, S. Mitsuoka, Development of energy-saving absorbents for the recovery of carbon-dioxide from boiler flue-gas, Kagaku Kogaku Ronbun 21 (3) (1995) 478–485.

[166] M.T. Sander, C.L. Mariz, The fluor daniel ECONAMINE FG Proces - past experience and present-day focus, Energy Conv. Manag. 33 (5–8) (1992) 341–348.

[167] S. Satyapal, T. Filburn, J. Trela, J. Strange, Performance and properties of a solid amine sorbent for carbon dioxide removal in space life support applications, Energy Fuels 15 (2) (2001) 250–255.

[168] K. Sayama, H. Arakawa, Photocatalytic decomposition of water and photocatalytic reduction of carbon dioxide over $ZrO_2$ catalyst, J. Phys. Chem. 97 (3) (1993) 531–533.
[169] I.M. Smith, $CO_2$ reduction – prospects for Coal. IEA Report No. CCC/26, IEA Coal Research, London, U.K., 1999, 84 pp.
[170] A.M. Wolsky, E.J. Daniels, B.J. Jody, $CO_2$ capture from the flue-gas of conventional fossil-fuel-fired power-plants, Environ. Prog. 13 (3) (1994) 214–219.
[171] P.B. Weisz, Basic choices and constraints on long-term energy supplies, Phys. Today 57 (2004) 47–52.
[172] C.S. Song, H.H. Schobert, Opportunities for developing specialty chemicals and advanced materials from coals, Fuel Process. Technol. 34 (1993) 157–196.
[173] H.H. Schobert, C.S. Song, Chemicals and materials from coal in the 21st century, Fuel 81 (2002) 15–32.
[174] J.S. Yoo, The role of $CO_2$ for the gas-phase $O_2$ oxidation of alkylaromatics to aldehydes, in: C.S. Song, A.M. Gaffney, K. Fijimoto (Eds.), $CO_2$ Conversion and Utilization, American Chemical Society, Washington, DC, ACS Symposium Series, vol. 809, 2002, pp. 112–129 (Chapter 8).