Our present dependence on fossil fuels means that, as our demand for energy inevitably increases, so do emissions of greenhouse gases, most notably carbon dioxide (CO₂). To avoid the obvious consequences on climate change, the concentration of such greenhouse gases in the atmosphere must be stabilized. But, as populations grow and economies develop, future demands now ensure that energy will be one of the defining issues of this century. This unique set of (coupled) challenges also means that science and engineering have a unique opportunity—and a burgeoning challenge—to apply their understanding to provide sustainable energy solutions. Integrated carbon capture and subsequent sequestration is generally advanced as the most promising option to tackle greenhouse gases in the short to medium term. Here, we provide a brief overview of an alternative mid- to long-term option, namely, the capture and conversion of CO₂, to produce sustainable, synthetic hydrocarbon or carbonaceous fuels, most notably for transportation purposes.

Basically, the approach centres on the concept of the large-scale re-use of CO₂ released by human activity to produce synthetic fuels, and how this challenging approach could assume an important role in tackling the issue of global CO₂ emissions. We highlight three possible strategies involving CO₂ conversion by physico-chemical approaches: sustainable (or renewable) synthetic methanol, syngas production derived from flue gases from coal-, gas- or oil-fired electric power stations, and photochemical production of synthetic fuels. The use of CO₂ to synthesize commodity chemicals is covered elsewhere (Arakawa et al. 2001 Chem. Rev. 101, 953–996); this review is focused on the possibilities for the conversion of CO₂ to fuels. Although these three prototypical areas differ in their ultimate applications, the underpinning thermodynamic considerations centre on the conversion—and hence the utilization—of CO₂. Here, we hope to illustrate that advances in the science and engineering of materials are critical for these new energy technologies, and specific examples are given for all three examples.

With sufficient advances, and institutional and political support, such scientific and technological innovations could help to regulate/stabilize the CO₂ levels in the atmosphere and thereby extend the use of fossil-fuel-derived feedstocks.

Keywords: energy materials; CO₂ conversion; sustainable methanol; tri-reforming; solar fuel; photocatalyst

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One contribution of 13 to a Discussion Meeting Issue ‘Energy materials to combat climate change’.
1. Introduction

Fossil fuels pose a fundamental dilemma for our human society. On the one hand, their importance cannot be overstated—the combustion of coal, oil and natural gas supply close to 90 per cent of our current energy needs and makes much of what we do possible. On the other hand, their widespread use comes at a cost—the gases emitted during the burning of fossil fuels are strongly implicated as the main drivers of climate change. Burning 1 t of carbon in fossil fuels releases more than 3.5 t of carbon dioxide (CO$_2$); such cumulative concentrations of CO$_2$ now approach 1 Tt in the atmosphere (Mikkelsen et al. 2010). Nevertheless, it will remain difficult to wean our world away from fossil fuels. For all their obvious faults, they remain relatively inexpensive, widely available and readily adaptable to applications large and small, simple and complex. Figure 1 is a representation of our current global energy scenario based on fossil fuels; here, their intrinsic chemical energy is transformed into heat, electricity or movement (transportation) by combustion processes (Marbán & Valdés-Solís 2007).

There are several reasons why fossil fuels remain so popular (Fulkerson et al. 1990). First, they are accessible in one form or another in almost all regions of the world. Second, humankind has learned how to use them effectively to provide energy for a myriad of applications at every scale. Third, they are without equal as fuels for transportation: they are portable and contain a considerable amount of stored chemical energy. The overwhelming energy source for transportation derives from oil stocks (figure 1). Considering all of this, it becomes obvious that our energy supply for the foreseeable future will surely be based on fossil-derived hydrocarbon fuels, with the unavoidable production of CO$_2$.

The prediction of our future energy supply of, say, oil has typically been less accurate than predictions of demand. In figure 2, we show the so-called human development index (HDI) plotted against per capita energy consumption, with energy expressed in units of kilogram equivalents of oil. The HDI is a recognized measure of the ‘quality of life’ developed by the UN development program. It is clear that a universal curve is followed; in our current global energy economy, a higher quality of standard of living equates with increasing energy (fossil fuel) consumption (Kolasinski 2006).

Shifting the global energy balance in realistic time scales with a balanced use of oil, gas and coal while protecting our environment is now a critical universal challenge. Until new, totally renewable or sustainable energy sources supplant oil, coal and natural gas, the scientific, technical and socio-economic challenge is clear: extract maximum energy from fossil fuels while attempting to minimize harm to our environment. A recent opinion paper on emissions pathways (Rogelj et al. 2010) shows that the scale of the CO$_2$ emissions problem is not being addressed quickly enough. Indeed, current national pledges mean that there is a greater than 50 per cent chance that global warming will exceed 3°C by the year 2100.

Current approaches within the present fossil-fuel energy scenario (figure 1) for the reduction of CO$_2$ emissions from large-scale fossil energy facilities (e.g. power stations and cement works) are primarily focusing on carbon capture and storage (CCS), with three generic options being proposed: post-combustion capture, pre-combustion capture and oxy fuel combustion (IPCC 2005, 2007; Nguyen & Wu 2008). All three approaches are based on different physical and chemical processes involving absorption, adsorption and cryogenic capture of CO$_2$. 

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Figure 1. Current global energy scenario based on fossil fuels. Here, the distribution of current consumption of energy sources is noted. The figure shows the primary energy sources in our modern energy society, and their ultimate secondary energy outlets. (Marbán & Valdés-Solís 2007.)

Figure 2. The human development index (HDI) plotted against the per capita energy consumption of 103 of the world’s most populous nations (adapted from Kolasinski 2006).
Major reductions in emissions from the transportation sector will necessitate a change in vehicle fuels. The three leading alternatives generally advanced at present are electric (battery), hydrogen and biofuels; the first two options require fundamental large-scale changes in our energy infrastructure, while the latter will not meet the exceptionally high and ever-growing (figure 2) demand for transportation fuels. Indeed, there are forecasts that there exists a global biomass limit, which dictates any truly sustainable supply of biofuels to between 20 and 30 per cent of the projected requirement for transport fuels. A recent review by Inderwildi & King (2009) provides an excellent overview of the potential, and the challenges facing biofuels (see §2).

In order to take full advantage of the high ‘tank-to-wheel’ efficiency of electric vehicles, critical steps will also be needed to decarbonize the upstream energy (electricity) supply. In addition, batteries are fundamentally limited by their very low net gravimetric and volumetric energy densities, as shown in figure 3 by a recent comprehensive ‘net systems analysis’ of various on-board energy carriers (Pearson et al. 2009). This figure also clearly illustrates that, while the net on-board density of liquid hydrogen comfortably exceeds that of batteries, it is still extremely low when compared with carbonaceous liquid fuels such as diesel, gasoline, ethanol and methanol. In addition, the provision of hydrogen production, distribution and refuelling facilities will necessitate enormous investments for this completely new infrastructure base. This same analysis (Pearson et al. 2009) concludes:

The fundamentals of physics and electrochemistry dictate that the energy density of batteries and molecular hydrogen is unlikely ever to be competitive with liquid fuels for transport applications.

A fourth option, the focus of this review, has emerged, namely, the idea of using captured, anthropogenically produced CO₂ to synthesize liquid renewable or sustainable hydrocarbon and carbonaceous fuels (Arakawa et al. 2001; Olah 2005; Centi & Perathoner 2009). This approach offers the intriguing possibility of using primary energy from renewable, carbon-free sources (such as electricity derived

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Figure 3. Fuel energy densities: net systems volumetric and gravimetric energy densities for various on-board energy carriers (adapted from Pearson et al. 2009).
from solar, wind, wave or nuclear) to convert CO₂, in association with hydrogen (or indeed methane), into high-density vehicle fuels compatible with our current transportation infrastructure. Its real attraction is that this approach offers the prospect of decarbonizing transport without the paradigm shift in infrastructure required by electrification of the vehicle fleet or by conversion to a hydrogen economy (Pearson et al. 2009).

This increasing interest is focused on the concept of recovered CO₂ being used to synthesize fuels (through, for example, Fischer–Tropsch chemistry), and such an approach could substantially reduce carbon emissions (Arakawa et al. 2001; Sakakura et al. 2007; Centi & Perathoner 2009; Olah et al. 2009; Mikkelsen et al. 2010). This approach, which also encompasses the synthesis of commodity chemicals from CO₂, we term carbon capture and conversion (CCC). It also has merit in that in the medium term it is expected that fossil-fuel power plants fitted with CCS technologies may provide a source of high concentrations of CO₂. It is therefore critically important that the CCC technologies outlined here are developed alongside work on CCS technologies. Research and development in materials for this energy technology are of critical importance to support the new energy technologies to convert CO₂ into fuels, and indeed chemicals. There are an increasing number of excellent reviews on the important aspects of CCC (Song & Pan 2004; Song 2006; Sakakura et al. 2007; York et al. 2007; Centi & Perathoner 2009; Indrakanti et al. 2009; Olah et al. 2009; Mikkelsen et al. 2010). Our objective here is to produce a brief overview of progress in the area and its potential, and to identify barriers to future progress. We identify three cases to illustrate these aspects; this commentary interfaces with that of Züttel et al. (2010) in relation to the future development of hydrogen energy as a critical component of the new energy technology.

2. Substitution of fossil fuels for transport by synthetic renewable fuels

The only way to stabilize the Earth’s climate is to stabilize the concentration of greenhouse gases in the atmosphere. However, projected energy demands (figure 2) will make this much more difficult than has been previously thought (Friedlingstein 2008). Short-term strategies for the stabilization of CO₂ emissions centre on energy savings and efficient utilization (Boden et al. 2009; OECD/IEA 2009). But, a successful long-term local and global strategy must surely be able to stabilize the atmospheric CO₂ levels by substitution of fossil fuels by renewable energy sources. It is often written that the potential of renewable energy sources is higher—by several orders of magnitude—than any estimated world energy demand. Unfortunately, the vast majority of large renewable energy sources are almost always located far away from the main consumption areas. One possibility is the production of electricity to join an electric grid. If this is not a realistic possibility, the renewable energy must be harvested in the form of energy carriers. As well as conventional energy storage for sustainable electricity, the generation of chemical energy carriers is another attractive alternative, with hydrogen and liquid carbonaceous carriers as the primary candidates.

The issues relating to hydrogen have been identified in the previous section. The great value of liquid carbonaceous fuels (e.g. petrol, diesel and others) lies both in their intrinsic (high) chemical energy content (figure 3) and in the ease with
which they are stored and transported using existing infrastructure. It is of course possible to reduce CO₂ directly with hydrogen (hydrogenation), or potentially electricity, to synthesize carbonaceous fuels. However, such an approach would not impact positively on the global carbon balance since hydrogen and electricity as produced today are largely derived from fossil fuels, which, themselves, produce large amounts of CO₂.

If, however, renewable sources could be used as the energy vector to transform CO₂ into fuels, one has a most attractive route to providing carbonaceous fuels that would not contribute to net CO₂ emissions.

In figure 4, we show a generic, idealized energy cycle where one transforms CO₂ to ‘carbon-neutral’ liquid fuels in which sustainable or renewable electricity is used to produce hydrogen and the resulting Fischer–Tropsch process yields liquid hydrocarbon fuels. As noted earlier, the intrinsically high energy density of these fuels and their transportability make them highly desirable.

Importantly, such synthetic fuels do not contain any sulphur. In addition, methanol (arguably the ‘simplest’ synthetic carbonaceous fuel) is a candidate both as a hydrogen source for a fuel cell vehicle and indeed as a transport fuel, and dimethyl ether is viewed as a ‘superclean’ diesel fuel (Pan et al. 2007; Centi & Perathoner 2009; Minutillo & Perna 2009).

The energy requirement for the production of such renewable liquid fuels depends critically on the method used for the capture of CO₂ (invariably from large-scale emitters) and the method used for the production of hydrogen. As long as power generation for our present energy economy using fossil-fuel sources remain (figure 1), sources of CO₂ will be available for use in such proposed recycling systems. These would capture CO₂ from the atmosphere by physical, chemical or biological methods, and any successful cycle would rely on cheap and
abundant non-fossil primary energy sources—incidentally, the same requirements for any hydrogen economy—to ensure that the proposed synthesis cycle is CO₂-neutral (figure 4). In the biological world, fuels derived directly from photosynthesis (biofuels) could form the underpinning new technologies based on the successful principles of photosynthesis. As Barber (2009) has noted in an overview of the subject, there are significant possibilities in exploiting solar energy to generate fuels, such as hydrogen, alcohols and methane, by sustainable routes. The reader is referred to this excellent review for the potential of new photochemical energy technologies that mimic our natural system (Barber 2009). Similarly, Inderwildi & King (2009) have outlined an innovative carbon cycle for the production of synthetic fuels from biomass (figure 5). Here, biomass is converted to biogas, mainly methane, using anaerobic digestion. The biogas can then be converted into biogas, mainly methane, using anaerobic digestion. The biogas can then be converted into a mixture of CO and H₂, the so-called synthesis gas (syngas), using catalytic processes. This syngas is then converted to liquid synthetic fuel and gaseous hydrocarbons using catalysts such as Co, Ru or Fe.

3. CO₂ conversion to carbonaceous fuels

(a) Thermodynamic considerations

In figure 6, we illustrate a key aspect of the thermodynamics of any possible CO₂ conversion, where the Gibbs free energy of formation of CO₂ and related substances are shown. CO₂ is clearly a highly stable molecule and consequently a substantial input of energy, optimized reaction conditions and (almost invariably) active catalysts are necessary for any chemical conversion of CO₂ to a carbonaceous fuel.

However, it is important to note that any chemical reactions (conversions) are driven by differences in the Gibbs free energy between the reactants and products of a chemical reaction (under certain conditions), as shown by the Gibbs–Helmholtz relationship:

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0. \]
Any attempt to use CO₂ as a ‘chemical feedstock’ therefore must take close account of the relative stability of the ultimate reaction products, as compared to the reactants.

Both terms (\(\Delta H^0\) and \(T\Delta S^0\)) of the Gibbs free energy are not favourable in converting CO₂ to other molecules (Freund & Roberts 1996). The carbon–oxygen bonds are relatively strong and substantial energy must be input for their cleavage in terms of carbon reduction. Similarly, the entropy term (\(T\Delta S^0\)) makes little or no contribution to the thermodynamic driving force for any reaction involving CO₂. Importantly, one can then take the enthalpy term \(\Delta H^0\) as a good initial guide for assessing thermodynamic stability and feasibility of any CO₂ conversions.

It was pointed out by Freund & Roberts (1996) in an important contribution on the surface chemistry of CO₂ that any progress in the use of CO₂ as a useful reactant (here towards fuel synthesis) will only emerge through judicious use of novel catalytic chemistry. As we will attempt to illustrate, it is in this area that materials chemistry, physics and engineering can have the greatest potential impact. Again, as these authors point out, a positive change in free energy should not by itself be taken as a sufficient reason for not pursuing potentially useful reactions involving CO₂. Thus, \(\Delta G^0\) only provides information as to the yield of products at equilibrium through the relationship \(\Delta G^0 = -RT\ln K\) and the kinetics of such a process might indeed be favourable. Thus, provided that the kinetics is favourable, CO₂ reduction to CO (a key step in all conversion reactions) may also be possible at metal surfaces, or some other catalytic material, e.g. nanoscale metal particles encapsulated in nano- and mesoporous hosts (Pan et al. 2007; Centi & Perathoner 2009). As noted by Song & Pan (2004) and Song (2006):

There appears to be some perceptions ... that CO₂ conversion would be so endothermic that its conversion would not be feasible.

Of course, a large number of industrial-scale chemical manufacturing processes are currently operated worldwide on the basis of strongly endothermic chemical
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Figure 7. The enthalpy of reaction for syngas production and Fischer–Tropsch (FT) synthesis of methanol and dimethyl ether. The various reactions labelled DRM, SRM and POM are listed in table 1 and discussed in §3c.

reactions. The steam reforming of hydrocarbons to yield syngas and hydrogen is a classic example:

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H^0 = +206.3 \text{kJ mol}^{-1}. \]

It is important to stress that the above, highly endothermic reaction is used worldwide for the high-volume production of ‘merchant hydrogen’ in the gas, food and fertilizer industries.

The corresponding CO\textsubscript{2} reforming of CH\textsubscript{4} (so-called ‘dry reforming’) illustrates the important reaction of CO\textsubscript{2} with a hydrocarbon, which will be of central importance to our considerations of converting CO\textsubscript{2} in flue gases to yield a chemical fuel:

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H^0 = +247.3 \text{kJ mol}^{-1}. \]

The energy input for CO\textsubscript{2} reforming of CH\textsubscript{4} requires approximately 20 per cent more energy input as compared with steam reforming, but this is certainly not a prohibitive extra energy cost for this chemical reaction.

Importantly, these two reactions give rise to syngas with different H\textsubscript{2}/CO molar ratios. Both are useful for the formation of syngas, for ultimate liquid fuel production.

In figure 7, we collate the relevant enthalpy contributions, which nicely illustrate the importance of chemical reactions to convert CO\textsubscript{2}. That is, it is significantly easier, thermodynamically, if CO\textsubscript{2} is used as a co-reactant typically with another substance that has a higher (i.e. less negative) Gibbs free energy, e.g. H\textsubscript{2} or CH\textsubscript{4}. These hydrogen-bearing energy carriers give up their intrinsic chemical energy to promote the conversion of CO\textsubscript{2}.

Thus, the heats of reaction (the enthalpies of reaction) for CO production from CO\textsubscript{2} as the single reactant, and with CO\textsubscript{2} energetics as a co-reactant,
are particularly important and illustrative. Compare the energetics of the thermal dissociation of CO2,

$$\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2 \quad \Delta H^0 = +293 \text{kJ mol}^{-1},$$

with that of the reaction of CO2 with H2,

$$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H^0 = +51 \text{kJ mol}^{-1}.$$

This aspect may be further illustrated by the process of ‘oxyforming’, whereby, on deliberately increasing the amount of oxygen into the dry reforming reaction, the enthalpy of reaction is significantly reduced:

$$3\text{CH}_4 + \text{O}_2 + \text{CO}_2 \rightarrow 4\text{CO} + 6\text{H}_2 \quad \Delta H^0 = +165.8 \text{kJ mol}^{-1},$$

$$5\text{CH}_4 + 2\text{O}_2 + \text{CO}_2 \rightarrow 6\text{CO} + 10\text{H}_2 \quad \Delta H^0 = +104.6 \text{kJ mol}^{-1}.$$  

(b) Renewable, synthetic methanol—a sustainable organic fuel for transport

Commercially, methanol is produced from syngas using natural gas or coal, mainly containing CO and H2 along with a small amount of CO2. The reaction is usually catalysed by Cu/ZnO-based catalysts that have high reactivity and selectivity (Centi & Perathoner 2009; Fan et al. 2009). The annual, worldwide production currently exceeds 40 Mt.

It is also possible to synthesize methanol directly from CO2 by combining it with hydrogen according to the reaction:

$$\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}.$$  

Interestingly, this can also be viewed as a mechanism for ‘liquefying’ hydrogen chemically using CO2!

In the same way that biofuels recycle CO2 biologically, a ‘sustainable’, synthetically artificial cycle can also be envisaged where the carbon in the methanol is recycled by extracting and utilizing CO2 from the atmosphere (figure 8). Overall, such a process could be carbon-neutral. The energy input to electrolyse water to produce hydrogen and that used for the capture and release of CO2, of course, need to be carbon-neutral.

These ideas date back over 30 years, in one form or another. The obvious attraction is that carbon is effectively ‘chemically sequestered’ to yield synthetic fuels, allowing our continued exploitation of fossil fuels without causing the net accumulation of CO2 in the atmosphere.

Olah and colleagues (Olah 2005; Olah et al. 2009) have pioneered and advanced the concept, and potential widespread adoption, of the methanol economy, emphasizing the production of CH3OH (or dimethyl ether) by the chemical recycling of CO2. A real attraction of such an approach is that one could envisage the catalytic hydrogenation of CO2 focused at small, delocalized production sites as an alternative to the current large-scale, localized sites producing methanol by steam reforming of CH4.

A fundamental materials challenge in this area centres on the fact that, generally, CO2 and H2 will only react at high temperatures in multi-component heterogeneous catalysts (York et al. 2007; Centi & Perathoner 2009). A recent, important process has been developed for the homogeneous conversion of CO2 to
methanol using non-metal complexes (Ashley et al. 2009; Riduan et al. 2009). This centres on the activation of H₂ by so-called frustrated Lewis pairs in specifically designed, organometallic complexes (Mömming et al. 2009).

The critical issues for this methanol cycle (figure 8) therefore centre on the following points:

— The separation (and hence availability) of CO₂ at high (volume) concentrations, for example, in large industrial plants.
— Concentrating CO₂ directly from the atmosphere—essentially, cost-effective, energy-efficient, high-rate ‘direct air capture’ technologies.
— The development of high-performance, robust and inexpensive catalysts, operating (ideally) at low temperatures (in general, entropy considerations for such energy storage reactions are best carried out at low temperatures to reduce the free energy required).
— The availability and cost of sustainable hydrogen, particularly if the requirement is hydrogen production using renewable energy (figure 4).

A recent, detailed analysis of the ‘well-to-tank’ energetics of methanol synthesis from atmospheric CO₂ (Pearson et al. 2009) concludes that by far the greatest component of the energy requirement of the process is that to produce the hydrogen (figure 8). This aspect highlights, once again, the close links between the major research challenges in any future hydrogen economy—in this case, cheap renewable routes to the production of hydrogen—and any future economy based on renewable, carbonaceous liquid fuels.

(c) Tri-reforming: using flue gas for CO₂ conversion

Currently, around one-third of all anthropogenic CO₂ emissions originate from fossil-fuel power plants. Adding CCS (typically employing post-combustion technologies based on chemical absorption with ammines, at ca 85–90% capture...
Table 1. Main reactions for syngas production by tri-reforming of natural gas.

<table>
<thead>
<tr>
<th>reaction</th>
<th>stoichiometry</th>
<th>enthalpy, $\Delta H_{298}^0$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ reforming of methane (DRM)</td>
<td>$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$</td>
<td>+247.3 (endothermic)</td>
</tr>
<tr>
<td>steam reforming of methane (SRM)</td>
<td>$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$</td>
<td>+206.3 (endothermic)</td>
</tr>
<tr>
<td>partial oxidation of methane (POM)</td>
<td>$\text{CH}_4 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{CO} + 2\text{H}_2$</td>
<td>$-35.6$ (exothermic)</td>
</tr>
<tr>
<td>catalytic combustion of methane (CCM)</td>
<td>$\text{CH}_4 + 2\text{O}_2 \leftrightarrow \text{CO}_2 + 2\text{H}_2\text{O}$</td>
<td>$-880$ (exothermic)</td>
</tr>
</tbody>
</table>

efficiencies) leads to overall efficiency penalties of about 8–10% and increases in energy costs of some 30–60%. Therefore, it would be highly desirable if flue gas mixtures (typically 8–10% CO$_2$, 18–20% H$_2$O, 2–3% O$_2$ and 60–70% N$_2$) could be used directly for CO$_2$ conversion without costly pre-separation of CO$_2$.

Song and colleagues (Song 2000, 2001; Song & Pan 2004) have pioneered a novel process centred on the unique advantages of directly utilising flue gas, rather than pre-separated and purified CO$_2$ from flue gases, for the production of hydrogen-rich syngas from methane reforming of CO$_2$ (so-called ‘dry reforming’). The overall process, named ‘tri-reforming’, couples the processes of CH$_4$/CO$_2$ reforming, steam reforming of CH$_4$, and partial oxidation and complete oxidation of CH$_4$. The reactions involved are itemized in table 1, together with the corresponding enthalpies of reaction (298 K).

Coupling CO$_2$ and H$_2$O can give syngas with the desired H$_2$/CO ratios for methanol and dimethyl ether synthesis and higher-carbon Fischer–Tropsch synthesis of fuels. It also helps to avoid the formation of particulate (solid) carbon deposits arising from reactions such as

$$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2\text{O} \quad \text{and} \quad 2\text{CO} \rightarrow \text{C} + \text{CO}_2.$$  

Experimental studies by Song & Pan (2004) have shown that the introduction of the CO$_2$ tri-reforming reaction may also enhance the durability and lifetime of metal nanoparticle catalysts owing to the addition of oxygen (and consequent oxidation of carbon deposits).

It is possible to achieve up to 95 per cent methane conversion by this process at equilibrium temperatures in the range 1073–1123 K. To achieve effective conversion (of both CO$_2$ and CH$_4$), the flue gas is combined with natural gas and used as chemical feedstocks for the production of syngas (CO + H$_2$) with desired H$_2$/CO ratios. In addition, the process makes use of ‘waste heat’ in the power plant and heat generated in situ from partial oxidation of methane (POM) with the O$_2$ present in the flue gas (table 1). In effect, the two endothermic reactions noted in table 1 are thermally sustained by the waste heat content of the exhaust gases, and the partial combustion of the primary methane fuel.

In summary, the advantages of tri-reforming centre on the prevention of carbon deposition, controllable H$_2$/CO ratios (for effective syngas production) and a more autothermic reaction enthalpy than simple dry reforming of methane with CO$_2$. 

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The growing worldwide interest towards the tri-reforming process is connected to the attractive possibility of potential integration of this technology into gas-turbine-based electric power cycles, having very low overall CO2 emissions (Halmann 1993; Song 2006; Minutillo & Perna 2009). Detailed experimental studies, computational analysis and engineering evaluations are under way on the tri-reforming process. The great attraction is that the CO2 in power plant exhausts could now be used directly in catalytic processes to generate a syngas suitable for ultimately delivering energy fuels (and a variety of chemical products).

In terms of catalyst materials, the majority of studies have focused on the important CH4–CO2 reforming component of the tri-reforming process (Song & Pan 2004; Song 2006; Cho et al. 2009). Both nanoparticulate Ni and Co have frequently been employed as active metal components owing to their high intrinsic catalytic activities, wide availability and (relatively) low costs (Hu 2009). The critical problem for all of these (and other) catalytic materials centres on serious carbon deposition in the industrial CO2 reforming of methane. This leads to rapid catalyst deactivation and reaction inhibition as the supporting structures become blocked by carbon particulate deposits (York et al. 2007; Fan et al. 2009). Comprehensive investigations, however, have revealed that such carbon deposition was strongly influenced by the precise mode of operation of the chemical conversion process. Importantly, fluidized-bed reforming leads to significant enhancement in the CH4 conversion process and a considerably reduced carbon deposition when compared with the fixed-bed operation process (Wurzel et al. 2000; Tomishige 2004; Hao et al. 2009). Further optimization of the fluidized-bed configuration has taken the form of innovative approaches using a fluidized bed assisted by an external, axial magnetic field. Hao et al. (2008) have recently reported studies of CH4–CO2 reforming on aerogel Co/Al2O3 nanoparticulate catalysts in a magnetic fluidized bed. In their study, Co was introduced as the active catalyst component for the reforming process; here, they have taken advantage of the high Curie temperature of Co (ca 1120°C) that makes it ideally suited for the high operating temperatures of between 700 and 1000°C necessary for the reforming process. In addition, the influence of an external magnetic field on the catalytic activity and stability of these catalyst systems was investigated in detail and compared with data for a conventional fluidized bed and a static bed. These impressive studies are summarized in figure 9, which is a compilation of conversion efficiencies for both CH4 and CO2. Also shown are images of the operating catalysts that clearly demonstrate that carbon deposition is considerably reduced through improving the gas–solid efficiency by the use of the external magnetic field. For these ferromagnetic particulate catalysts, it is quite clear that magnetic-field enhancement of operating process properties may be a most important avenue for future, major studies.

One should also highlight the very great potential of ‘sustainable methane’ for the tri-reforming process, and this might alleviate some of the issues discussed by Inderwildi & King (2009) in their recent review of biofuels.

A recent, extensive investigation for the treatment of CO2 from fossil-fuel-fired power plants, using the tri-reforming process integrated with full electrical power co-generation, reveals an impressive estimated reduction in CO2 emissions close to 85 per cent (Minutillo & Perna 2009).

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Figure 9. Aerogel Co/Al₂O₃ catalysts for CH₄–CO₂ reforming. (a) (i) Conventional and (ii) magnetic fluidized bed. (b) Conversions of (i) CH₄ and (ii) CO₂. (c) Microstructure of the catalysts after 20h operation: (i) magnetic fluidized bed, (ii) fluidized bed and (iii) fixed bed. Note that in the fluidized-bed operation mode, (i), carbon deposition is mainly of particulates, while in the fixed-bed mode, (iii), we see extensive filamentous, graphitic carbon, causing deactivation of the catalyst (after Hao et al. 2008). Symbols: (b) (i) filled squares, magnetic fluidized bed; filled triangles, fluidized bed; filled inverted triangles, fixed bed; dotted line, equilibrium conversion; (ii) open squares, magnetic fluidized bed; open triangles, fluidized bed; open inverted triangles, fixed bed; dotted line, equilibrium conversion.
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Figure 10. Basic principle of photoreduction of CO$_2$ by water on an effective Pt semiconductor photocatalyst.

(d) Photochemical production of synthetic fuels

As noted in §3a, the CO$_2$ reduction process is highly endothermic. Therefore, sustainable CO$_2$ utilization is possible only if renewable energy, such as solar, wind, wave or nuclear, is used as the energy source. Solar photocatalytic reduction of CO$_2$ has the potential to be a means both of CO$_2$ recycling and of storing intermittent solar energy in synthetic carbon-neutral fuels suitable for storage and use in the residential, industrial and transportation sectors. However, the efficient photoreduction of CO$_2$ using solar radiation is one of the most challenging tasks of environmental catalysis. In a recent report, the US Department of Energy (Bell et al. 2007) has identified the development of advanced catalysts for the photo-driven conversion of CO$_2$ and water as one of the three priority research directions for advanced catalysis science for energy applications.

Inoue et al. (1979) were the first to report the photocatalytic reduction of CO$_2$ in aqueous solutions to produce a mixture of formaldehyde, formic acid, methanol and methane using various wide-band-gap semiconductors. Since then, intensive efforts have been focused on the photochemical production of fuels by CO$_2$ reduction using a variety of photocatalysts (Halmann 1993; Hwang et al. 2005; Indrakanti et al. 2009; Olah et al. 2009).

The primary steps of photocatalytic reduction of CO$_2$ are absorption of light photons in a photocatalyst material, and subsequent conversion of these photons into electron–hole pairs, which then have to be spatially separated to drive chemical oxidation and reduction half-reactions at the semiconductor–electrolyte interface (figure 10).

The overall conversion efficiency of photocatalytic production of solar fuels is currently significantly lower than that of photovoltaic solar systems. Unlike photovoltaic electricity generation, where absorption of a photon results directly in the formation of an electron–hole pair, all methods of producing solar fuels must involve the coupling of an absorption process with multi-electron...
redox reactions. In the case of CO₂ photoreduction using water as a reductant, both multi-electron transfer reactions of CO₂ reduction and water oxidation have to occur simultaneously. As a result, current CO₂ photoreduction catalysts are less effective than current solar water-splitting catalysts (Indrakanti et al. 2009). Several other important factors limit the solar-to-fuel energy conversion efficiency of photocatalytic systems, including inefficient absorption of solar energy, fast recombination processes of the photo-excited electron–hole pairs and facile backward redox reactions.

The properties of potential photocatalysts are determined by the redox potentials of the rate-limiting steps of water oxidation and CO₂ reduction:

\[
\begin{align*}
2\text{H}_2\text{O}(l) & \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- & E_{\text{ox}}^0 = -1.23 \text{V}, \\
\text{CO}_2(aq) + \text{e}^- & \rightarrow \text{CO}_2^-(aq) & E_{\text{red}}^0 = -1.65 \text{V}.
\end{align*}
\]

These values impose a minimum threshold for the energy of photo-excited electrons required to reduce CO₂ and also the energy levels of the conduction and valence bands of a photocatalyst. Wide-band-gap semiconductors are the most suitable photocatalysts for CO₂ reduction because photo-generated electrons in the bottom of the conduction band can have sufficient negative redox potential to drive CO₂ reduction, while the photo-generated holes in the valence band can be sufficiently energetic (positive holes) to act as acceptors and oxidize water to O₂. A significant disadvantage of using wide-band-gap semiconductors is the inability to use visible light efficiently. Quite simply, light with energy smaller than the semiconductor electronic band gap cannot generate electron–hole pairs and is therefore wasted as heat. As a result, only the UV and near-UV parts of the solar spectrum can be used with the present photocatalysts such as TiO₂ (with an electronic band gap of around 3.2 eV), yielding a low absorption coefficient and, consequently, low conversion efficiency in the visible region.

Although many semiconductors have smaller band gaps and absorb in the visible range (e.g. CdS and Fe₂O₃ with band-gap values of 2.4 and 2.3 eV, respectively), just a few of them are catalytically active because the energy levels of either the conduction or valence bands are unsuitable for CO₂ reduction and/or water oxidation. This limitation, together with poor photo-corrosion stability of many semiconductors, limits significantly the number of potential photocatalyst materials.

Figure 11 displays the quantum efficiency of photocatalytic water splitting plotted against wavelength of a wide range of inorganic materials (Osterloh 2008). Note that this interesting summary represents only the water-splitting component of the photocatalytic process, but it nevertheless highlights a range of potential materials for the combined H₂O/CO₂ photochemical process. For any prospective photocatalyst to be considered economically viable, it has to display a quantum efficiency of greater than 10 per cent in the visible region of the solar spectrum. To date, no materials have been discovered that satisfy this criterion, as seen in the shaded area in figure 11. Worldwide, active research is now focused on the search for new photocatalysts efficient in the visible spectrum of sunlight. Several groups of novel efficient photocatalysts have recently been discovered, including oxynitrides (e.g. Ga₁₋ₓZnₓO₁₋ᵧNₓ; Maeda et al. 2006; Jiang et al. 2008;
Luo et al. 2009; Varghese et al. 2009), tantalates (e.g. NaTaO₃ and others; Kudo & Miseki 2008), bismuth-based photocatalysts (e.g. BiVO₄; Long et al. 2006; Shang et al. 2009; Jiang et al. 2010) and some others (Kudo & Miseki 2008).

For a combination of cost, stability and performance, TiO₂ still remains one of the most effective photocatalysts among other semiconductors, and it has been used to convert CO₂ to useful compounds, in both gas- and aqueous-phase
photoreactions (Ni et al. 2007; Nguyen & Wu 2008; Indrakanti et al. 2009). Several approaches have been employed to enhance the efficiency of photocatalysts. Promising methods to expand the light absorption of TiO₂ into the visible region are band-structure modification by suitable cation or anion doping and the use of co-catalysts loaded on the surface as nanoparticles (Jiang et al. 2008; Kudo & Miseki 2008; Luo et al. 2009). Using photocatalyst and co-catalyst materials in the nanocrystalline form also offers the attractive opportunity to minimize the distances (and thus the times) over which photo-induced electron–hole pairs have to survive and be transported to reactant molecules after photo-excitation. The formation of heterojunction structures between two nanostructured semiconductors with different band gaps and matching band potentials can also extend light absorption, improve charge separation, increase the lifetime of charge carriers, and enhance the interfacial charge-transfer efficiency (Long et al. 2006; Tada et al. 2006; Yang et al. 2009). Deposition of noble metal nanoscale clusters on the photocatalyst surface has also been shown to enhance the photocatalytic activity owing to increased transfer rates of photo-generated electrons to the absorbed metal/semiconductor clusters, thus decreasing markedly the possibility of electron–hole recombination (Baba et al. 1985; Zhang et al. 2009).

An alternative approach using the photoelectrocatalytic reduction of CO₂ has been proposed recently (Centi et al. 2007; Centi & Perathoner 2009). In this concept, water dissociation occurs at a photoanode and CO₂ reduction at a photocathode, which are attached to both sides of a proton-conducting membrane. Such a photoelectrocatalytic device shows a strong similarity to proton-exchange membrane fuel cells and can take advantage of significant technological developments of that energy technology.

Developments of cheap, reliable and efficient methods for the production of solar fuels represent a major challenge in solar energy utilization. The key issue in optimizing photocatalyst materials is to achieve the same conversion efficiency for visible-light-induced CO₂ reduction as already demonstrated for near-UV irradiation and, at the same time, to significantly increase the chemical stability against damage from incident light and also attack from highly reactive species formed during the photoelectrochemical redox reactions (figure 10).

4. Concluding remarks

In a recent masterly survey of their work over the past 15 years, Olah et al. (2009) expound a vision that reflects the basis of our present review:

Carbon dioxide … can be chemically transformed from a detrimental greenhouse gas causing global warming into a valuable, renewable and inexhaustible carbon source of the future allowing environmentally neutral use of carbon fuels and derived hydrocarbon products.

With carbon capture and sequestration (storage) becoming a key element in worldwide efforts to control/minimize emissions, it can be anticipated that large amounts of CO₂ will become available as feedstock for innovative conversions to synthetic fuels. Of course, ‘whole process’ energy balances and economics remain
a critical issue—as indeed is the case for any overall vision of energy futures. It is an obvious, but nevertheless a most potent, fact that any new fossil fuels can only be formed naturally over geological time scales.

The challenge, therefore, is to achieve such transformations from natural and industrial sources, as well as human activities, via CO₂ capture and subsequent conversion to synthetic fuels over, what one might term, less demanding time scales! The cycle in figure 12 reflects particularly the tri-reforming route to a sustainable fuel (§3c).

In this work, we have attempted a brief overview of the current scientific challenges in the area, with an emphasis on the important, underlying thermodynamic considerations and the urgent agenda for materials research and development (figure 12). This vision in many ways constitutes humankind’s artificial version of the natural recycling of CO₂ to energy fuels by photosynthesis using sunlight as the primary energy source (Barber 2009).

To bring any, or all, of these innovative approaches into real life, technologies will require major advances in research and development, as well as significant socio-political commitments to CO₂ capture and utilization. International collaborative research between developed, and developing countries (figure 2) is also absolutely critical in such a venture. Our hope is that this present summary helps to catalyse such a worthwhile development.

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