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ORIGINAL ARTICLE

On choosing the most appropriate catalysts for the conversion of carbon dioxide to fuels and other commodities, and on the environmentally benign processing of renewable and nonrenewable feedstocks

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Abstract Until recently the drive to discover and utilize renewable feedstocks for the production of energy and for the manufacture of materials was exceptionally strong. Now, however, because of the realisation that nonrenewable (e.g. gas and oil) reserves are still superabundant, a different emphasis is appearing. This involves utilizing both nonrenewable and renewable feedstocks in an environmentally responsible manner. One important recent development involves the drive to utilize feedstocks, such as pyrolysis oil, microalgae and general bio-waste, like sawdust and other nonedible products from lignocellulose. Another is the aim to ensure that CO_2 can be converted to fuels or useful materials, thereby diminishing its concentration in the atmosphere. This paper focuses on these themes; but it also addresses other important specific questions. Among these, the following are of particular interest: (i) How may catalytic cracking be made more environmentally acceptable? (ii) The emergence of single atom catalysts as means of effecting important chemical reactions.

Keywords CO_2 · Catalyst · Photocatalyst · Environmentally benign · Fuel · Renewable and nonrenewable feedstocks · Bio-oil · Catalytic hydrothermal reactor · Microalgae

Introduction

For a variety of reasons, the title of this article is significantly different, and so is its content, from the lecture I (JMT) gave on *"Some of Tomorrow's Catalysts: Actual and Desired"* at the KOPRC Forum in August, 2015. In the relatively short interval that has elapsed since that Forum, many significant new developments have occurred in the fields circumscribed by the title of this article. Also, I have been the author or co-author of other related articles, which have appeared, or are shortly to appear, that address many of the questions raised by this broad field. Moreover, even before presenting my KOPRC talk at Oxford, I had reviewed in detail the many facets that arise in considering how humankind is going to cope with powering the planet in an environmentally responsible manner in the next 50 years and beyond—see, for example, Refs. [1–5]. See also the definitive review by Centi and co-workers [6] published in 2015, and references therein. Hence, the situation pertaining to all of the topics relevant to those touched upon or implied by the title of this paper is rapidly changing. For example, I did not know until late October 2015 that there is now perceived to be enough natural gas available in the world to serve the needs of the planet for an estimated 230 years! So the frequently repeated mantra [7] that it is necessary to seek more renewable sources of energy is simply not true. For example, as recently as 9 January 2016, it was announced [8] that Australia is increasing natural gas production by roughly 150 % over the next 4 years.

In addition to these macro developments, progress in the evolution of new catalysts, especially for the processing of

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CO_2, continue to be reported. Furthermore, the agreement reached in the UN meeting in Paris, December 2015, calls for further action to be taken, not only to stabilize but to decrease the amount of anthropogenically produced CO_2 in the Earth's atmosphere if the target of keeping the temperature rise of the Earth to less than 2 °C by 2030 is to be met.

In predicting and pontificating about what catalysts are likely to be needed and used to fulfil the desiderata implied by the title of this paper, it is salutary to recall that numerous, well-intentioned predictions—often made by experts of unimpeachable credentials—tend to fall short of realisation. As in my Oxford lecture, I recall here that the Commission set up by President Roosevelt to advise him on scientific and technological developments in the foreseeable future, missed many seemingly obvious developments when they reported in 1937. They made no mention of the future, expected use of antibiotics, despite the fact that Alexander Fleming had discovered penicillin in 1928. They also did not find it pertinent to mention that, in future, devices such as the fax machine (invented in the early 1840s) or the fuel cell (also first described and tested in the 1840s) would ultimately be in popular use.

Given the fact that there is still an abundance (almost a superabundance) of fossil-based feedstocks, and also that there is public clamour for the operations of a civilized life to generate less CO_2, all kinds of socio-political, as well as technological, initiatives are constantly being pursued.

What is absolutely necessary is that more efficient ways are needed of utilizing nonrenewable feedstocks. To give an interesting recent example, aircraft manufacturers are *"rethinking the airplane for climate sake"*. (This statement figured as the title of an article in the *International New York Times* in January 2016). In essence, the concept called distributed propulsion is one of several being studied by the NASA Armstrong Flight Research Center in California, to develop technologies that could lead to completely new and far less polluting aircraft designs. For example, future planes may be powered by batteries or hybrid gas-electric systems, and have lighter wings that can quickly change shape so as to handle better the stresses brought on by turbulent air.

Converting carbon dioxide to fuel and other products

It is well known that the French worker, Sabatier, over a Century ago, demonstrated how methane could be produced synthetically by passing a mixture of CO_2 and H_2 over a supported Ni catalyst:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Previously, when it was felt that natural gas could be in short supply in various parts of the world, the Sabatier reaction could be used to produce synthetic natural gas (SNG), for transport and other purposes. Nowadays, it is not the thermally activated Sabatier reaction that is attracting the attention of those chemists devoted to the diminution of anthropogenic CO_2 but its photocatalytic equivalent. At present, there is no proven, highly active and desirable photocatalyst that has been discovered to convert CO_2 to CH_4 in a sustained manner and with high efficiency. The quest for such a photocatalyst, discussed by workers such as Corma et al. [9] and Ozin et al. [10] is likely to last for a long time.

For several decades CO_2 has been used as a feedstock to produce salicylic acid (a precursor in the manufacture of aspirin), and urea, the most compact form of soil fertiliser. But these industrial processes, although they utilize CO_2 as a feedstock, are far from being carbon neutral. It is gratifying to note, however, that many of the polymeric products previously synthesized from nonrenewable sources can now be readily prepared in an entirely sustainable manner. The case of polyurethane is a good example. Langanke et al. [11] have shown how CO_2 can be used as feedstocks in copolymerizations using epoxides—see Fig. 1. In fact, the Bayer material science (BMS) organisation now produces this industrial synthesis on the scale of 10^3 ton per annum.

What is glaringly obvious is that the amount of CO_2 liberated into the atmosphere as a result of human activity (some 50 gigatonnes per annum) far exceeds the amount of CO_2 currently used as a feedstock for the production of useful materials. The latter amounts, at present, languish in the megaton range per annum.

A constructive development is the use of CO_2 (sunlight and water) as a feedstock for the growth of algae using genetically enhanced cyanobacterias to generate ethanol and O_2—see Fig. 2. This work is carried out by the Algenol Biofuels Company, which, in its facility in Florida, utilizes CO_2 gas liberated from an industrial plant. At present, this Company produces 8000 gallons of ethanol per acre per year, and they quote a solar energy conversion of 2–3 %. When their plant grows to occupy 2000 acres (at the seashore [12]), the Algenol Company will produce ca. 14×10^6 gallons of ethanol per annum. An important advantage possessed by producing ethanol from algae rather than corn is that no land is used up that could otherwise have been used to produce food. The algae bio-photoreactors all operate at the seashore.

Important as this development is, its merits need to be carefully stated:

- it converts anthropogenically produced CO_2 to generate ethanol;
- this ethanol can be readily catalytically dehydrated to yield ethylene using a number of single-site heterogeneous catalysts, such as DAF-4, SAPO-34 and others, as described elsewhere [13] by one of us (JMT);

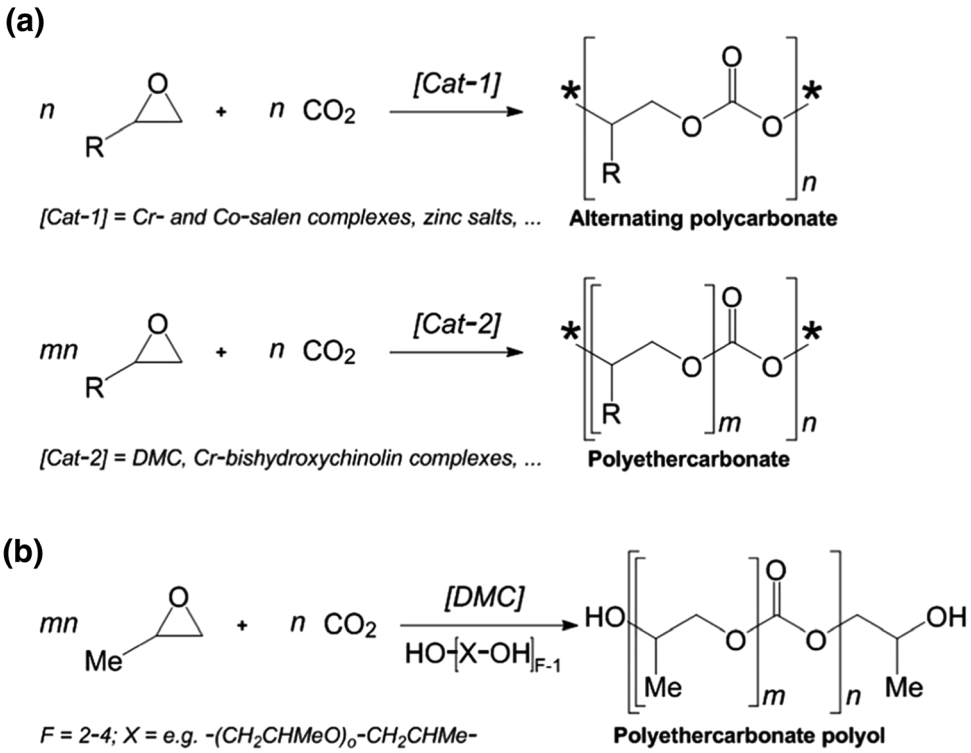

Fig. 1 **a** Copolymerization of epoxides and CO_2 to alternating poly-carbonates (*top*; * = end group) and polyethercarbonates (*bottom*). **b** Tailored polyethercarbonate polyols obtained from propylene oxide and CO_2 using zinc hexacyanocobaltate (DMC) as a catalyst and a multi- functional alcohol as a starter (After Langanke et al. [11])

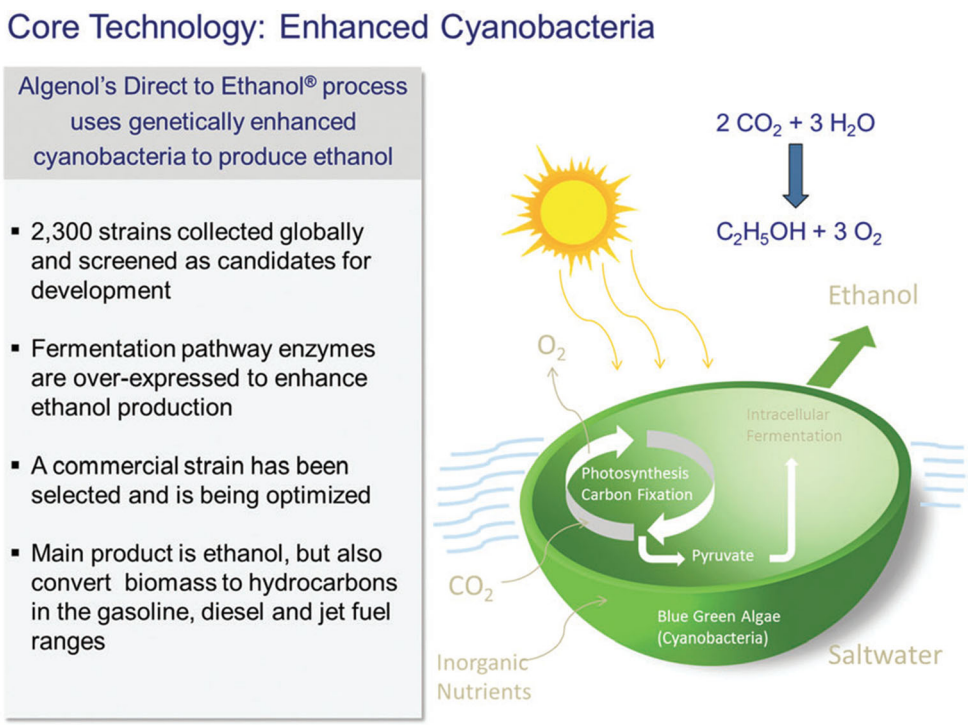

Fig. 2 Representation of the use of enhanced cyanobacteria (algae) by the Algenol Biofuels Company to convert CO_2 and H_2O in sunlight to ethanol (By kind permission of R.R. Chance)

- if the final use of the ethanol is as a fuel (blended into gasoline) or as a source of polyethylene, its ultimate fate is to generate more CO_2, which, however, can then be used as feedstock in subsequent algal-based solar-driven production of more ethanol.

We shall return below to the important part microalgae are likely to play in future production of "green" hydrocarbons (i.e. sulphur-free) and diesel fuels. Other biochemically oriented methods of consuming CO_2 as a feedstock are being explored by the German investigator,

Erb [14]. Such work involves the creation of customized, CO_2-fixing biochemical pathways to produce biomass and fine chemicals from atmospheric CO_2.

In Erb's work, Rubisco chemistry figures eminently: Rubisco is D-ribulose-1, 5-bisphosphate carboxylase/oxyglucose. This is a member of the carboxylase family of enzymes—see Thomas and Harris [5] for more details. Rubisco chemistry has also influenced the recent, ingenious work of Kanan et al. [15, 16]. These workers set out to emulate nature's strategy for C–C bond formation, which is to deprotonate C–H bonds to form carbanions and then to trap these intermediates with CO_2 to form C–CO_2 moieties. They use a purely inorganic approach, which has the advantage of circumventing the need to select the appropriate, robust enzyme co-factor, and some other complications associated with the approach of the synthetic biologist.

What is commendable about what Kanan et al. [15] accomplish is their ability to synthesize ethylene glycol and ethanol using only CO_2 and H_2. Their work leads to the ready synthesis of polyethylene furandicarboxylate—also designated polyethylene furanoate, PEF—which is a viable substitute for polyethylene terephthalate (PET) [17], and is used extensively as a container material for portable water and mineral drinks.

The H_2 required for the preparation of ethylene glycol—a powerful chemical building block for other materials—may be produced by either wind-powered or solar-powered water-splitting, using either wind or photovoltaic power for electrolysis. Kanan [15] estimates that by replacing the entire 15 M tonne year^{-1} PET market with PEF, 20–35 M tonne year^{-1} of CO_2 would be saved from liberation to the environment.

It is relevant at this junction to note that Freund [18] and colleagues in Berlin have constructed a method of attaching a neutral CO_2 molecule to a radical ion of CO_2, thus forming a $(CO_2)_2^-$ species, which may then be transformed into an oxalate species, whereby a C–C bond is formed. These oxalate species may then be further catalytically transformed with water or ammonia into useful fuels and other products.

Some other relevant aspects of converting CO_2 to fuel

It has been estimated (by environmentalists and city planners) that about 40 % of all fossil fuels are utilized in heating homes and other buildings. As a consequence, revolutionary methods are now being invoked to seek alternative methods of achieving the minimum amount of nonrenewable feedstock for this purpose. It is, therefore, relevant to note that an apartment block in Hamburg (Germany) has been built that uses microalgae placed within the façade to generate heat and biomass. This has been done by engineers [19] who are engaged in the establishment of zero—or even surplus—energy buildings as part of the goal to achieve sustainable architecture.

The solar fuel network is an international community of scientists dedicated to the idea of establishing a situation in which solar energy is harnessed for the production of fuels that can ultimately replace those derived from nonrenewable sources. Bearing in mind the scale of the operations involved when all the fuels and other products of the catalytic cracking of petroleum are considered—see Figs. 3 and 4 for some relevant quantitative facts—this is indeed a tall order, as has been pointed out previously [20]. Faced with the magnitude of this task, some scientists declare that there is a long road still to be travelled before we see the onset of widespread use of solar fuels.

On the other hand, as pointed out by Jacobson et al. [21, 22], civil engineers in Stanford University and the Nobel prizewinning Paul Krugman, in a recent (February 2016) article in the *International New York Times*, "wind, sun and tide", are already making a significant contribution to civilized life. In the main, these three sources of power are used to convert sunlight to an abundant generation of H_2. It is also relevant to mention that numerous concentrated solar power plants of 200 and 300 MW are also capable of providing the electricity to electrolyze water for the generation of H_2. Krugman's article quoted a recent report by the investment firm Lazard that the cost of electricity generation using wind power fell 61 % from 2009 to 2013, while the cost of solar power fell 82 % in the same period. This trend is continuing.

But whilst there are increasingly more viable methods of generating relatively cheap H_2—which can sustain the hydrogen economy, and bolster the use of fuel cells (burning H_2) for transport, hospitals, shopping malls and the like—the next goal is to achieve highly efficient photocatalytic conversion of CO_2 to CH_4. In other words, it is the photochemical Sabatier reaction that needs to be conquered. (It must not be forgotten that as much energy from the sun reaches the Earth's surface in a few hours as the world currently consumes (largely as fossil fuel) in 1 year.)

To date, some significant progress has been made. For example, Sastre et al. [9] have made a worthwhile attempt

A 75,000 barrel-a-day fluidized catalytic cracker cycles (between the reactor itself and a regenerator, that turns off the accumulated coke) some 5000 tonnes of La-Y Zeolite (faujasite) catalyst per 24 h for a sustained period of 2 to 3 years.

In the Paraguana Refinery Centre, Venezuela, there is a fluidized catalytic cracker that processes some 940, 000 barrels a day of petroleum.

Fig. 3 Statistics of catalytic cracking

Tents	Heart Valves	Perfumes	Cassettes	Dresses
Crayons	Candles	TV Cabinets	Dishwasher parts	Tires
Parachutes	Trash Bags	Shag Rugs	Tool Boxes	Golf Bags
Telephones	House Paint	Electrician's Tape	Shoe Polish	Percolators
Enamel	Water Pipes	Tool Racks	Motorcycle Helmet	Life Jackets
Pillows	Hand Lotion	Car Battery Cases	Caulking	Rubbing Alcohol
Dishes	Roller Skates	Epoxy	Petroleum Jelly	Tennis Rackets
Cameras	Surf Boards	Paint	Transparent Tape	Rubber Cement
Anesthetics	Shampoo	Mops	CD Player	Fishing Boots
Artificial Turf	Wheels		Faucet Washers	Vaporizers
Artificial limbs	Paint Rollers		Antiseptics	Balloons
Bandages	Shower Curtains		Clothesline	Sun Glasses
Dentures	Guitar Strings		Curtains	Solvents
Model Cars	Luggage		Food Preservatives	Diesel fuel
Folding Doors	Aspirin		Basketballs	Motor Oil
Hair Curlers	Safety Glasses		Soap	Bearing Grease
Cold cream	Antifreeze		Vitamin Capsules	Ink
Movie film	Football Helmets		Antihistamines	Floor Wax
Soft Contact lenses	Awnings	Fishing Rods	Purses	Ballpoint Pens
Drinking Cups	Eyeglasses	Lipstick	Shoes	Football Cleats
Fan Belts	Clothes	Denture Adhesive	Dashboards	Upholstery
Car Enamel	Toothbrushes	Linoleum	Cortisone	Sweaters
Shaving Cream	Ice Chests	Ice Cube Trays	Deodorant	Boats
Ammonia	Footballs	Synthetic Rubber	Footballs	Insecticides
Refrigerators	Combs	Speakers	Putty	Bicycle Tires
Golf Balls	CD's & DVD's	Plastic Wood	Dyes	Sports Car Bodies
Toothpaste	Paint Brushes	Electric Blankets	Panty Hose	Nail Polish
Gasoline	Detergents	Glycerin	Refrigerant	Fishing lures

Fig. 4 A selection of products from petroleum—emphasizing their ubiquity (This list was compiled by J.D. Keasling)

Complete Photocatalytic Reduction of CO_2 to Methane by H_2 under Solar Light Irradiation

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ABSTRACT: Nickel supported on silica–alumina is an efficient and reusable photocatalyst for the reduction of CO_2 to methane by H_2, reaching selectivity above 95% at CO_2 conversion over 90%. Although NiO behaves similarly, it undergoes a gradual deactivation upon reuse. About 26% of the photocatalytic activity of Ni/silica–alumina under solar light derives from the visible light photoresponse.

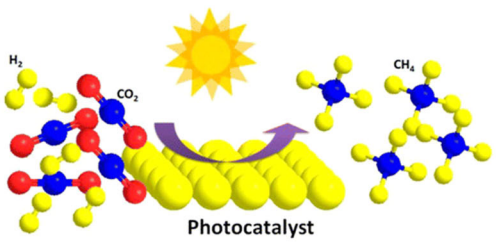

Fig. 5 A recent report in the Journal of the American Chemical Society towards complete photocatalytic reduction of CO_2 to methane by H_2 under solar light irradiation (After Sastre et al. [9])

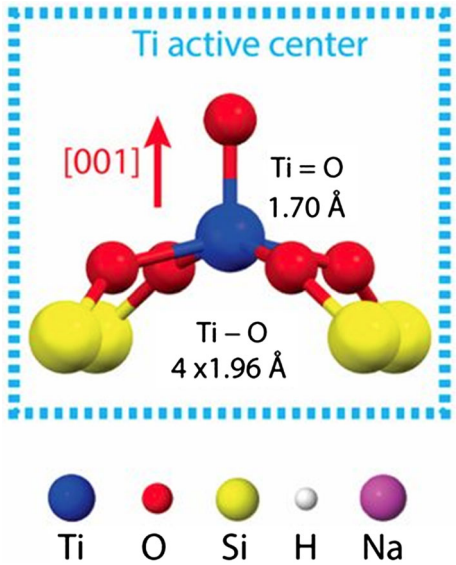

Fig. 6 5-coordinated titanium at the catalytic active centre of the photocatalytic titanosilicate JDF-L1 (After Yoo et al. [27])

to achieve complete photocatalytic reduction of CO_2 to methane by H_2 under solar light irradiation (Fig. 5). Ozin and co-workers [23, 24] have also made a promising start, but their catalyst ($In_2O_{3-x}(OH)_y$) goes only as far as photocatalytically converting CO_2 to CO (which is still a worthwhile goal). In a thorough review of the entire question of photocatalytically converting CO_2 to CH_4, Dhakshinamoorthy et al. [7], focusing on TiO_2 as the photocatalyst, concluded that the average productivity of the less-TiO_2-based photocatalyst is about 100 μ mol g^{-1} h^{-1} of catalyst with sunlight. They emphasized the need to increase this productivity by orders of magnitude. In the main, the solar fuels community has concentrated most of its efforts on improving the efficiency of the hydrogen evolution reaction (HER), by employing solar light to drive a photochemical cell typified by the set up: $TiO_2-Ti-pn+Si$ as photocathode. At a symposium organised by J. A. Barber for the Solar Fuels Network (London, July 2015), a protagonist in the field, Professor Harry Gray of Caltech, urged those working on the generation of solar fuels to concentrate more on using CO_2 rather than H_2O as the material for the production of useful fuels.

An attractive feature of the photocatalytic conversion of CO_2 to CH_4 is that if successful on a large scale, the practice of blending H_2 with natural gas—which involves careful control of the relative amounts of H_2 and natural gas—can be replaced by the much safer and utilitarian blending of sunlight-derived CH_4 with the natural gas grid. This strategy, if and when successful, would ultimately stabilize the amount of CO_2 in the Earth's atmosphere ($CO_2 \rightarrow CH_4 \rightarrow CO_2 \rightarrow CH_4$, etc.).

A few further remarks on TiO_2 are appropriate here. The high oxidation potential of photogenerated holes makes bulk TiO_2 a powerful oxidant for water and organic molecules, a fact that has given rise to many practical applications of solid state photocatalytic activity, such as

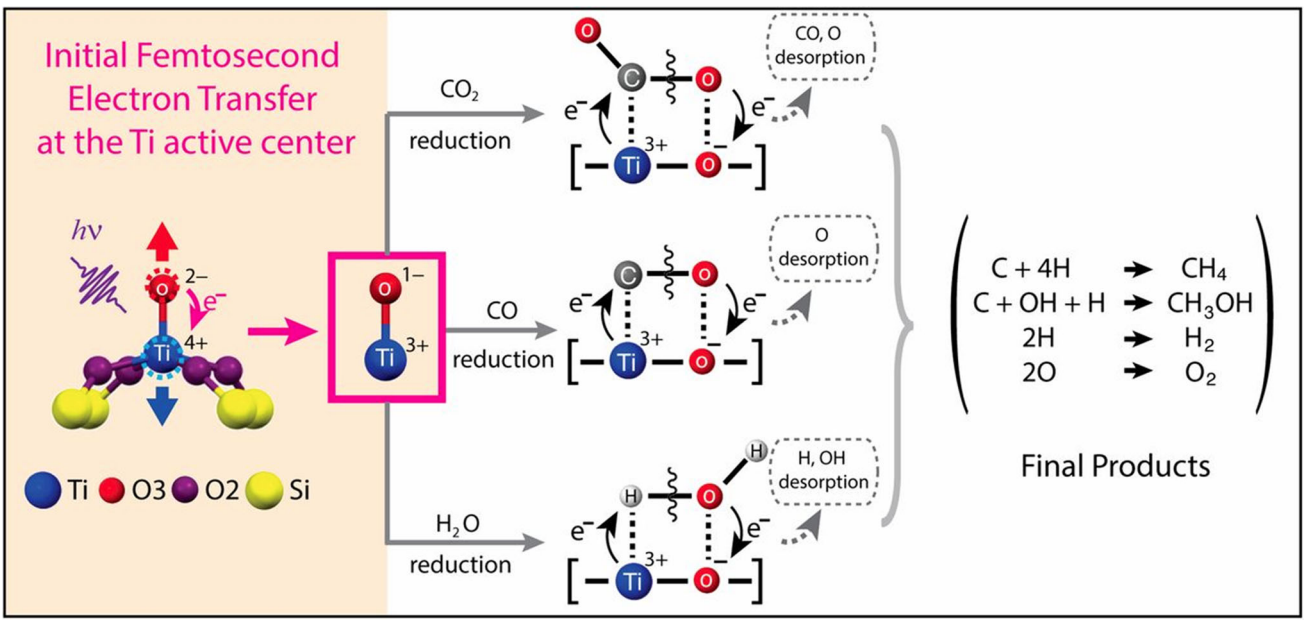

Fig. 7 Schematic illustration from a 4D ultrafast electron microscopy study of the titanium active centre of JDF-L1, showing photocatalytic reduction of CO_2 and H_2O and emphasizing the femtosecond laser induced electron transfer and subsequent Ti=O bond dilation (After Yoo et al. [27])

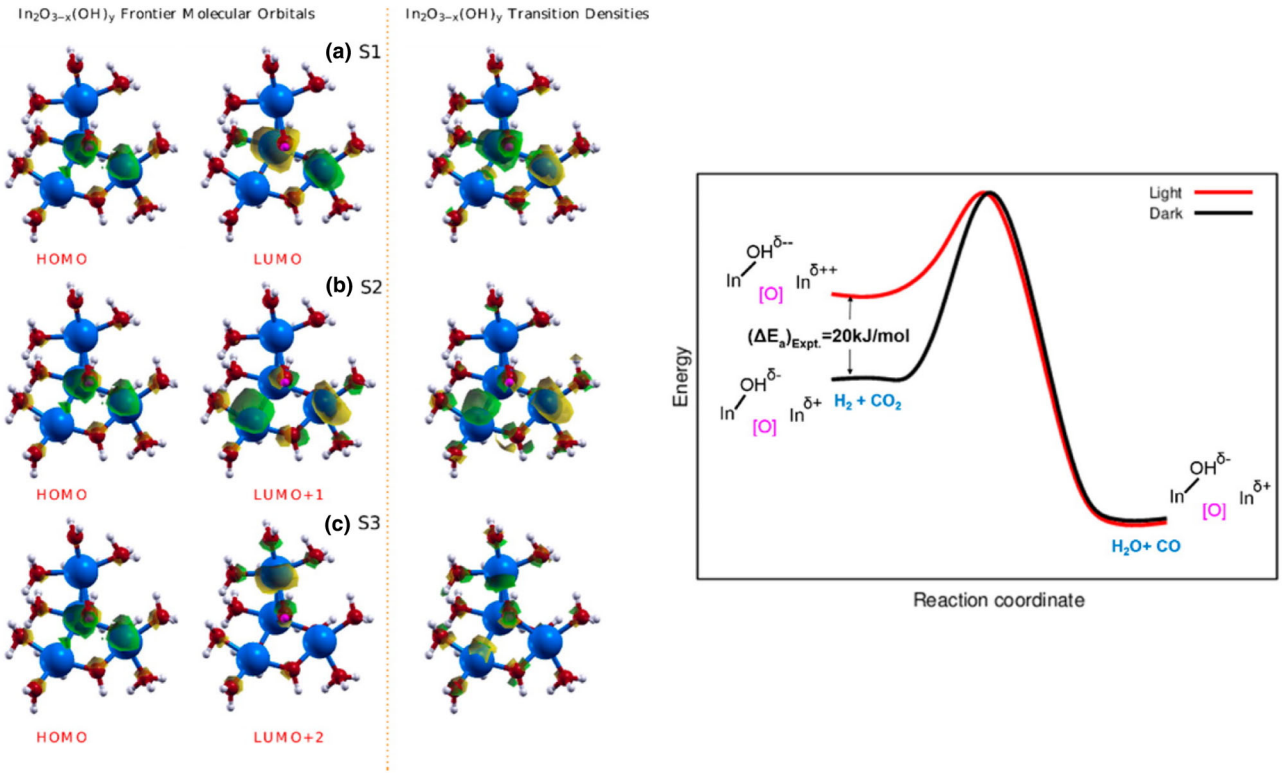

Fig. 8 (*Left*) Visualization of the main contributing molecular orbitals and transition densities for **a** S1 (HOMO → LUMO), **b** S2 (HOMO → LUMO + 1) and **c** S3 (HOMO → LUMO + 2) excited states of a defected $In_2O_{3-x}(OH)_y$ surface. (*Right*) Schematic illustration of the origin of the difference in the experimental activation energy $(\Delta E_a)_{Expt.}$ for the reverse water gas shift reaction $CO_2 + H_2 \rightarrow CO + H_2O$ involving the ground state surface frustrated Lewis pair in the dark and excited state surface frustrated Lewis pair in the light. The computational analyses of the ground state and excited state of the $In_2O_{3-x}(OH)_y$ cluster model showed that the electrons and holes trapped at the Lewis base and Lewis acid sites of the excited state surface frustrated Lewis pair enhance their Lewis basicity and Lewis acidity compared to the ground state frustrated Lewis pair. This increased 'frustration of charges' at the surface Lewis pair consequently decreases the activation barrier for the overall CO_2 reduction reaction, which is supported by the experimental measurements (After Ghuman et al. [24])

self-cleaning windows, tiles and cements (by Anpo et al. [25, 26]), anti-bacterial paints, and the purification of water by the solar breakdown of dyestuffs and other organic pollutants.

Recently, one of the present authors (JMT) has been associated with a fundamental study [27] of a single-site $Ti^{(IV)}$-based photocatalyst, a titanosilicate, known as JDF-L1 [28], with the formula: $Na_4Ti_2Si_8O_{22}4H_2O$. The essential features of the active centre in this open-structure solid, a TiO_5 arrangement, square pyramid, are shown in Fig. 6, in which there is one Ti=O apical bond and four Ti–O bonds. 4D ultrafast electron microscopy showed [27] that upon photoexcitation, the $Ti^{(IV)}$=O bond is transformed to a single bond $Ti^{(III)}$–O^- with a consequential dilation of the length of the double bond from 1.7 Å–2.5 Å. This occurs on the femtosecond time scale, and a schematic illustration of this process as well as the ensuing photochemical possibilities are shown in Fig. 7. This illustration depicts the kind of pathways that are followed in the photoreduction of CO_2 or H_2O by the JDF-L1 catalyst.

Very recently, Ozin and co-workers investigated the unique photoactive behaviour of pristine and defected indium oxide surfaces [24]. Their combined theoretical and experimental study provided fundamental insights into excited state properties, as well as an explanation for the experimentally observed enhanced activity of defected indium oxide surfaces for the gas-phase reverse water gas shift reaction, $CO_2 + H_2 + h\nu \rightarrow CO + H_2O$, in the light compared to the dark (Fig. 8). A thorough excited state study of pristine and defected forms of indium oxide (In_2O_3, In_2O_{3-x}, $In_2O_3(OH)_y$ and $In_2O_{3-x}(OH)_y$) surfaces was carried out using time dependent density functional theory calculations. The results were supported experimentally by transient absorption spectroscopy and photoconductivity measurements. They found that the surface frustrated Lewis pairs created by a Lewis acidic coordinately unsaturated surface indium site proximal to an oxygen vacancy and a Lewis basic surface hydroxide site in $In_2O_{3-x}(OH)_y$ become more acidic and basic, and hence more active in the excited

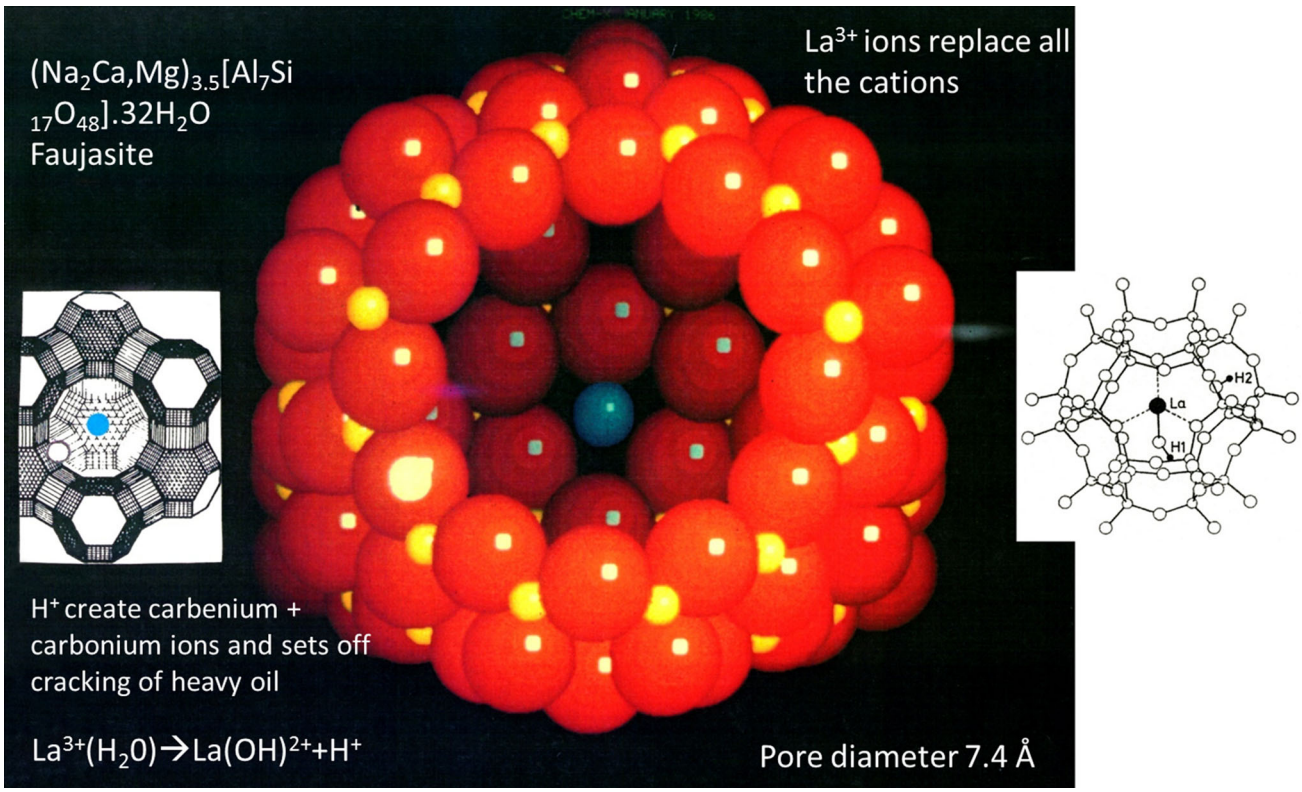

Fig. 9 La^{3+}-ion-exchanged zeolite Y has $La(OH)^{2+}$ ions and H^+ ions attached loosely to framework oxygens. The latter trigger catalytic cracking reactions via carbenium and carbonium ions

state compared to the ground state. They described how this provides a theoretical mechanism responsible for the enhanced activity and reduced activation energy of the photochemical reverse water gas shift reaction observed experimentally for $In_2O_{3-x}(OH)_y$ compared to the thermochemical reaction. To conclude, they emphasize that such fundamental insight into the role of photoexcited surface frustrated Lewis pairs for catalytic CO_2 reduction could lead to improved photocatalysts for solar fuel production.

It is relevant to note that very recently a novel approach, spearheaded by Ozin and colleagues in Canada and involving collaborators from other countries, uses visible and near infrared radiation to effect photothermal (*not* photocatalytic) conversion of CO_2 in the presence of H_2 to CO (i.e. the reverse water gas shift reaction) [29]. The solids used by the workers consist of Pd nanocrystals supported on nanorods of Nb_2O_5. Conversion rates as high as 1.8 mmol g^{-1} h^{-1} were achieved. Careful experiments disclosed that the photothermal catalysis originates from intra-band and/or inter-band optical excitation and nonradiative relaxation of Pd nanocrystals rather than being driven by UV plasmon excitation of the Pd nanocrystals or by electron-holes pair generation upon absorption of UV photons in the Nb_2O_5.

Environmentally benign processing of renewable and nonrenewable feedstocks

One of us (JMT) has recently given an account of many of the ways in which the action subsumed by this sub-heading can be fulfilled; and the reader is referred to that article, Ref [5]. There are, however, many more factors to outline in addition to those contained in Ref [5]. Three particular issues are considered here: catalytic cracking; the generation of bio-oil from renewable feedstocks; and the emergence of a new class of heterogeneous catalysts, i.e. those that are composed of supported single atoms.

Catalytic cracking

This is an extremely important applied catalytic activity in that a large majority of the materials used in civilized life are currently the products of the cracking of petroleum—see again Fig. 4. It is unlikely, in the short term, that the catalytic cracking of petroleum will cease because it is well-nigh indispensable throughout the world. What is, however, desirable is that the process can be made more efficient. The yield of desirable products must be significantly increased. Fortunately, significant progress has recently been made in this direction. Before describing it,

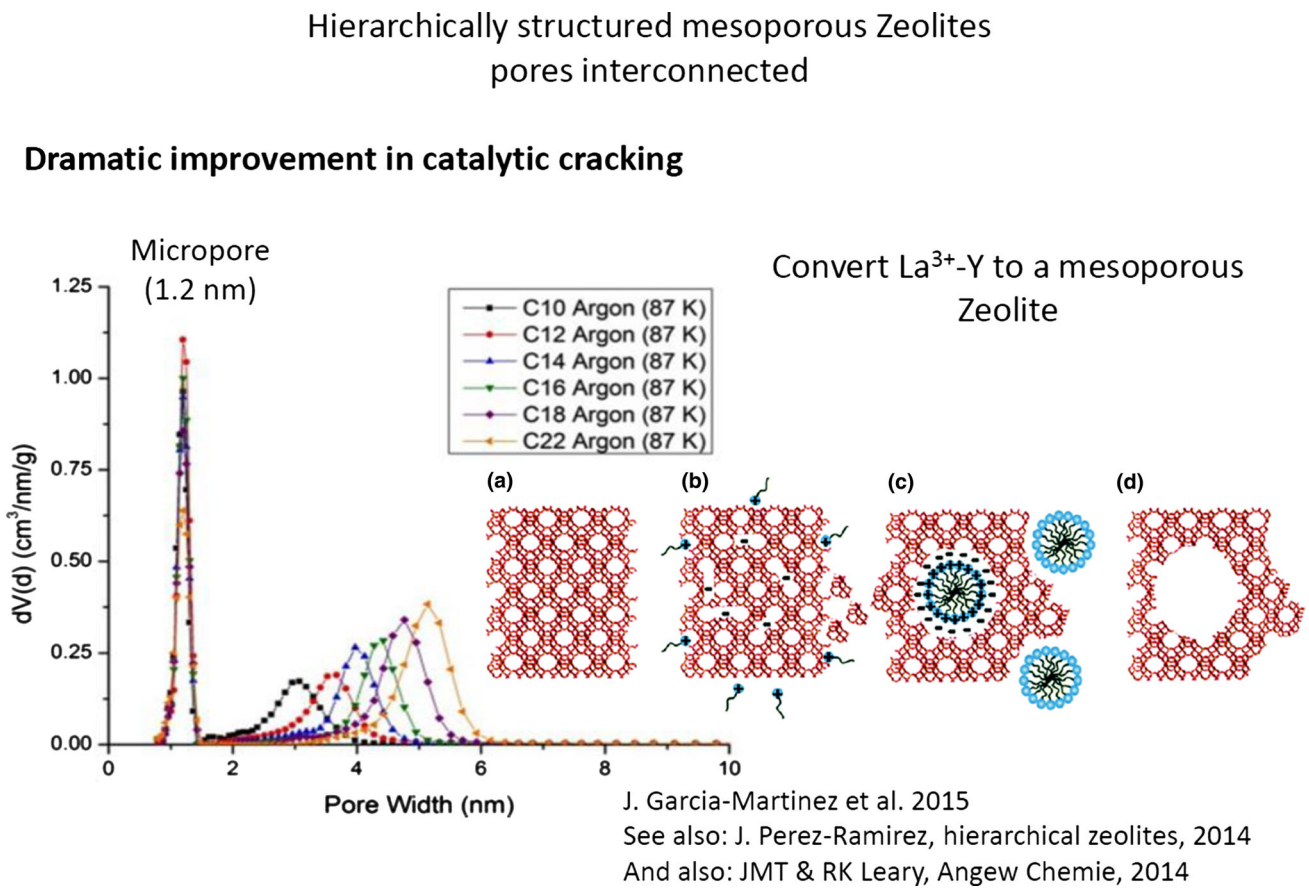

Fig. 10 Salient aspects of hierarchically structured mesoporous Zeolites

however, it is relevant to recall the scale of the operation of fluidized catalytic cracking (FCC) of petroleum.

Figure 3 reminds us of the massive scale of the cracking process by considering one single 75,000 barrel-a-day operation. And Fig. 9 illustrates the nature of the catalytically active centre (an $(LaOH)^{2+}$ entity) inside the cavities of a faujasitic zeolite. In industrial parlance, this is the La-Y ultra-stabilized Brønsted acid zeolite used on a massive scale—it is estimated that 500 K tonnes of the cracking catalyst are 'consumed' each year—to break down the hydrocarbons of petroleum into small, more useful products, such as light alkanes and alkenes, as well as octanes and other hydrocarbons of larger molecular weight suitable as the fuel for diesel engines.

That such enormous amounts of the zeolite Y (La^{3+}-exchanged) cracking catalyst are consumed every year arises because the catalyst matrix [consisting of zeolite Y, kaolin (as a filler), and typically, aluminium chlorohydrate (as a binder)] are friable and lack attrition resistance. Another important fact pertaining to faujasitic zeolite cracking catalysts is that they have quite large—but not large enough (see below)—pores (*ca.* 7.4 Å diameter). Thanks primarily to the work of the Spanish investigator, Garcia-Martinez et al. [30, 31], mesostructural zeolite Y has been prepared and is already now being utilized industrially. Mesoporous zeolites [32] and other so-called hierarchically structured zeolites are synthesized using large micelles made up of controllable diameter that consist of a long-chain surfactant template—see Fig. 10. The essential difference between a conventional zeolite (like Zeolite Y) and a mesostructured one is shown in Fig. 11, which also illustrates the improved pore characteristics of the mesoporous variety. (The Rive Company in the US manufactures the variety of mesoporous zeolites designed by Garcia-Martinez et al.). Additional indications of the improved catalytic performance of the Rive-type of mesoporous cracking catalyst are shown in Fig. 12.

The overall message derived from the introduction of mesostructured zeolites—and additional messages are continued in the collection of articles contained in Ref [32]—is that by judicious design of new solid catalysts, more efficient ways can be found for processing nonrenewable feedstocks.

A selection of important manufacturing processes that can be improved by utilizing designed new solid catalysts are given in the review by Harris and Thomas [5] and also

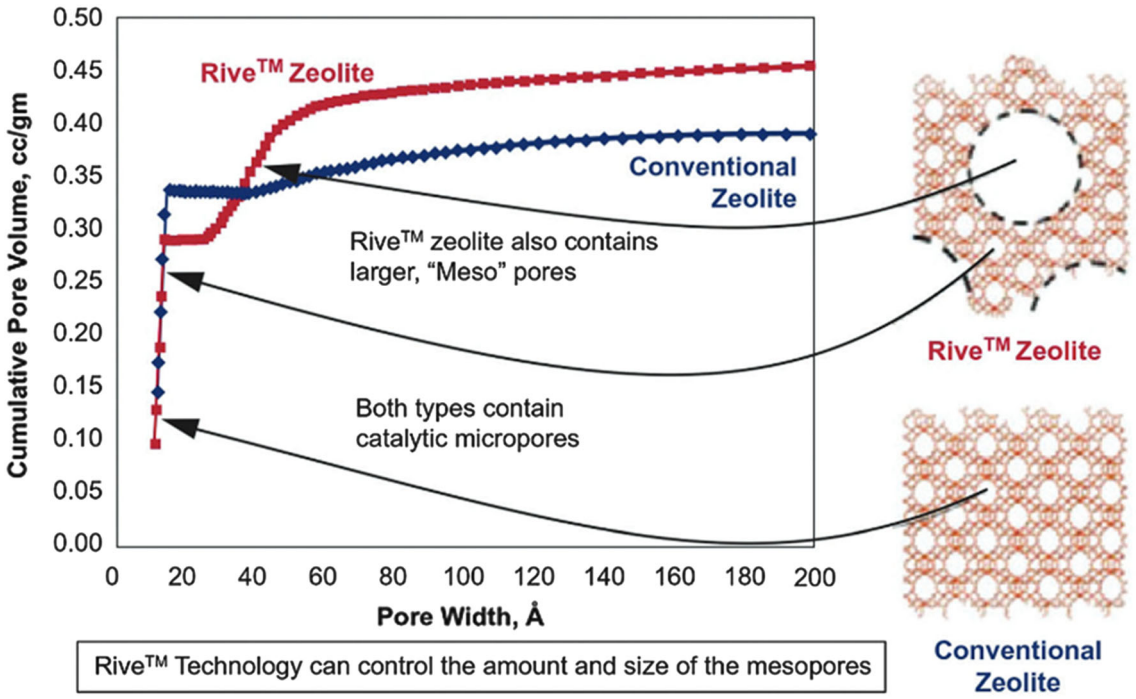

Fig. 11 The cumulative pore volumes of a conventional cracking catalyst (*blue*) and a mesostructured cracking catalyst (*red*), prepared by Rive (After Speronello et al. [31])

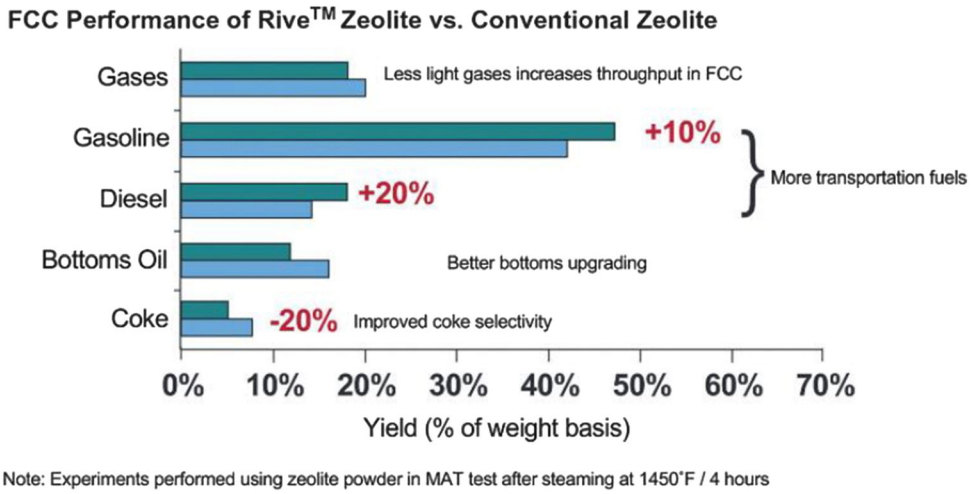

Fig. 12 The mesoporous Rive US Y zeolite catalyst shows significantly superior performance compared with the conventional cracking catalyst (After Speronello et al. [31])

in Refs. 1, 2, 13. Both catalytic dehydration reactions and a host of other processes can be facilitated by nanoporous catalysts that contain one or more types of spatially well-isolated active centres epitomized by the bifunctional catalyst shown in Fig. 13.

Sustainable chemistry by upgrading pyrolysis oil

(This section is based largely on Sect. 9.7.1 of the book by Thomas and Thomas [2]).

So-called bio-oil is produced by fast pyrolysis or liquefaction of lignocellulosic biomass. It is an aqueous highly functionalized, but essentially sulphur-free, mixture of light to medium hydrocarbons containing up to 30 % water. Because it is corrosive and possesses rather low 'heating value' (<19 M J kg^{-1}), and some other disadvantageous features, it is unattractive for use without prior treatment. If it is subjected to hydrogenation and hydrodeoxygenation (HDO) with cobalt-doped MoS_2 catalysts, high-grade transportation fuels may be extracted from it.

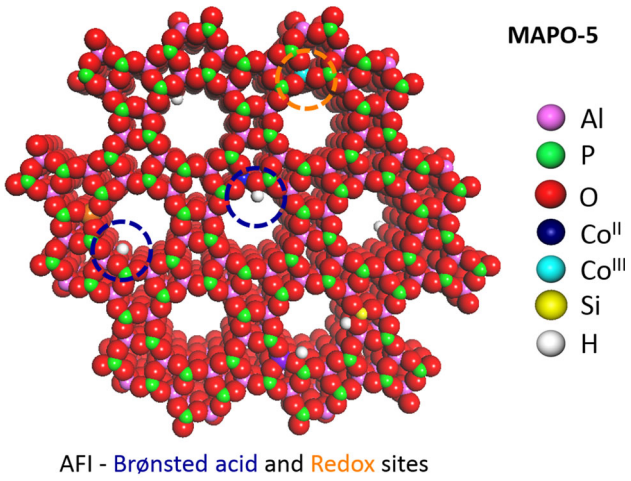

Fig. 13 Schematic of a bifunctional single-site heterogeneous catalyst derived from the microporous solid aluminophosphate ALPO-5. The Brønsted acid catalytic centres are well-separated from the redox sites

An alternative approach based on zeolites involves simultaneously catalysing several reactions, including dehydration, cracking, polymerization, deoxygenation and aromatization at temperatures between 350° and 450°. These conditions serve to convert the oxygenates into aromatic molecules and carbonaceous deposits, while the yield of alkanes does not exceed some 25 %. Very recently, Lercher [33, 34] has shown how widely applicable zeolitic catalyst HZSM-5 with a pore system containing a substantial fraction of Ni metal nanoparticles can quantitatively produce C_5–C_9 hydrocarbons from paraffins, napthenes and aromatic molecules in a cascade reaction by HDO of *n*-hexane-extracted crude bio-oil in the presence of substantial concentrations of water under mild reaction conditions (250° and 5 MPa H_2).

The components of the *n*-hexane-extracted bio-oil include mainly C_5–C_6 substituted furans, ketones and aldehydes derived from the deconstruction of cellulose and

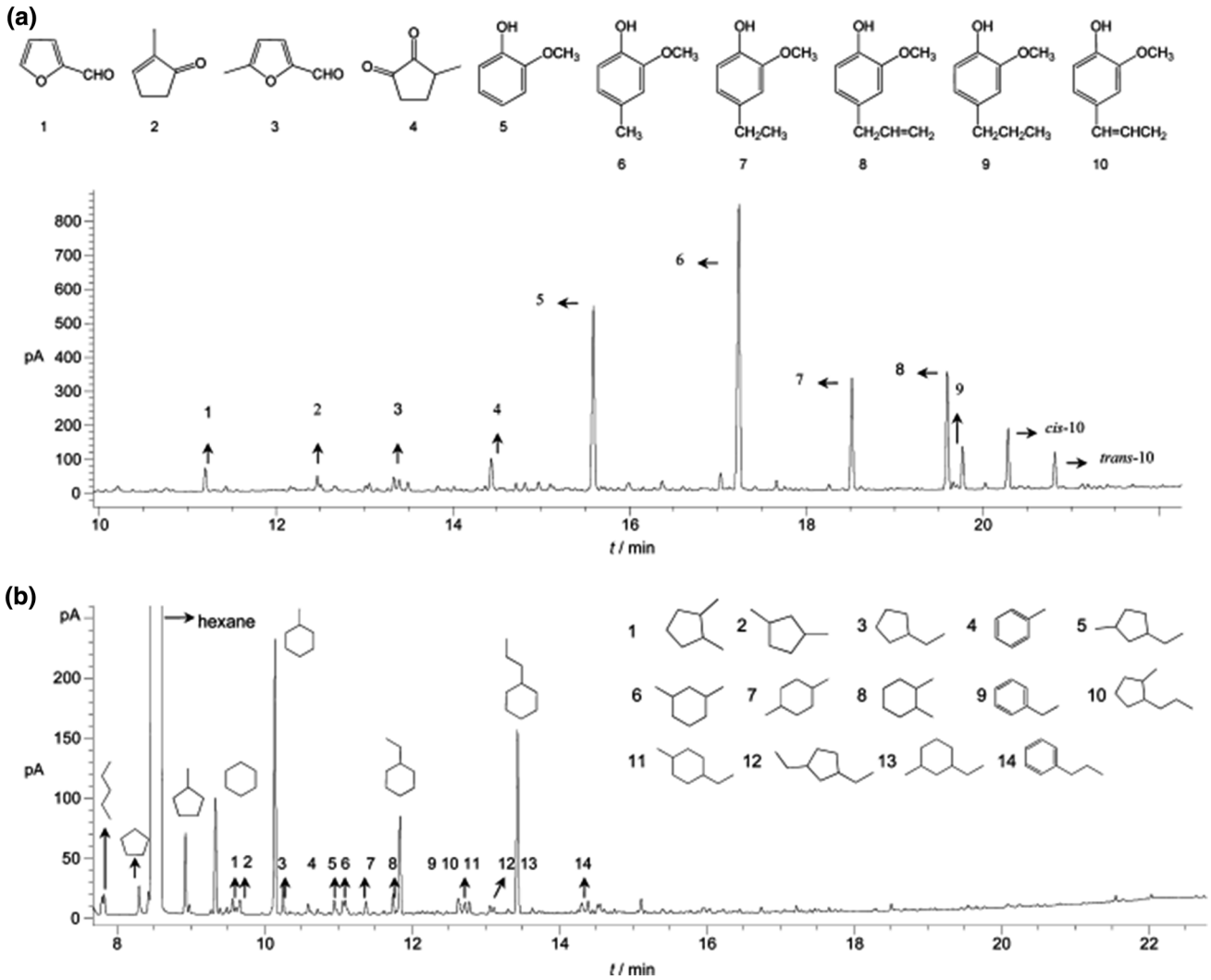

Fig. 14 Upgrading of pyrolysis oil over Ni/H5 M-5 by cascade reactions. GC (gradient correction) analysis of mixtures before and after upgrading: **a** *n*-hexane extracted crude bio-oil and **b** hydrocarbon products (After Zhao and Lercher [33])

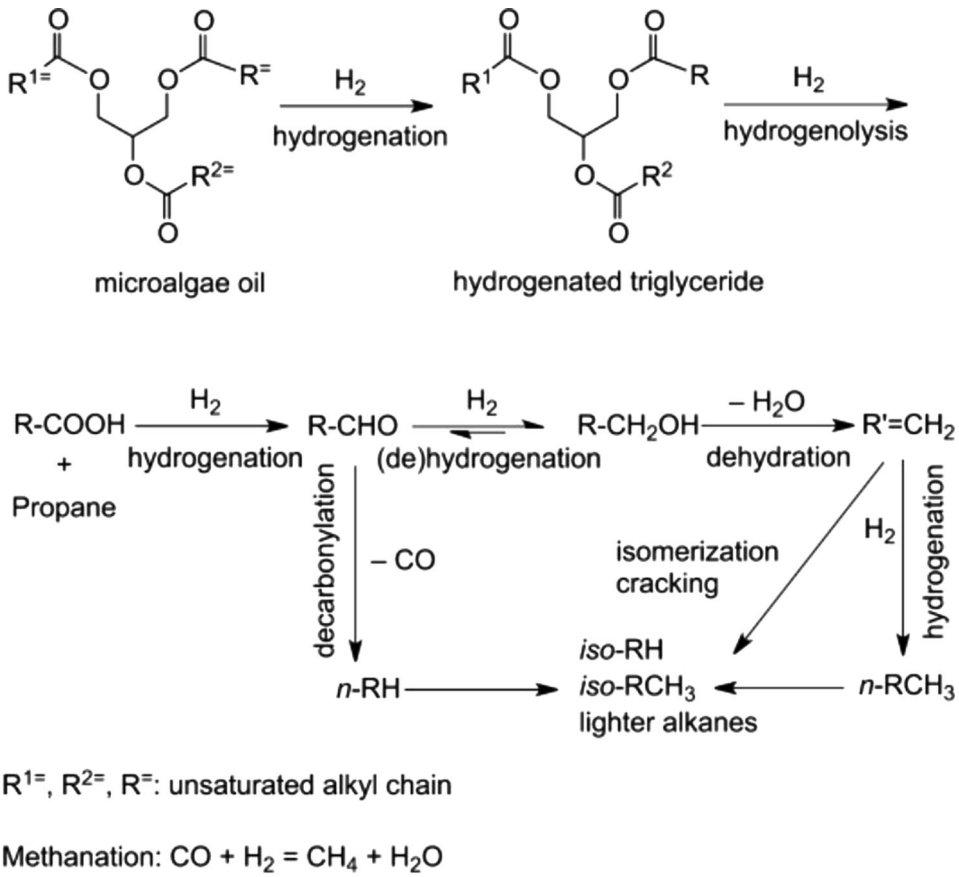

Fig. 15 Proposed reaction pathway for the transformation of microalgae oil to alkanes over bifunctional Ni/HBeta catalysts (After Peng et al. [36])

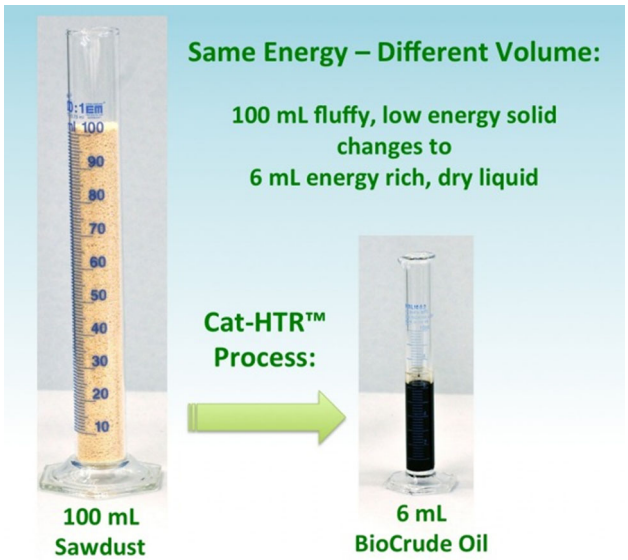

Fig. 16 Essence of the Cat-HTR process [37]

hemicellulose, as well as C_6–C_9 substituted phenols derived from the deconstruction of lignin (Fig. 14a). HDO of such a mixture on Ni/HZSM-5 in a semi-batch reaction for 4 h succeeded in quantitative conversion into the corresponding C_5–C_9 hydrocarbons, as shown in Fig. 14b.

Many other studies reporting fast (or slow) pyrolysis of biomass have recently appeared. In one, emanating from the US Department of Agriculture [35], sustainable production of bioenergy and biochar from the straw of high-biomass soybean is described in the context of 'on-farm' biorefinery, where food and bioenergy can be sustainably produced. The biochar retains mineral constituents that are beneficial to plants and is deployed for soil remediation.

Catalytic conversion of microalgae into green hydrocarbons and ethanol

As mentioned above, microalgae constitute a very viable source of 'green' hydrocarbons. This arises because of their high cellular lipid content and unusually high rate of photosynthetic growth. Algae mass captures about 3–8 % of incident solar energy, in contrast to terrestrial plants, which do so at about 0.5 %. Some microalgae have higher than 60 % oil content by weight of dry biomass, and the average oil content attains approximately 20–50 %. Microalgae grow 12 times as fast and yield 30 times as much triglycerides per unit area compared to conventional oil-producing land plants such as sunflower and rape.

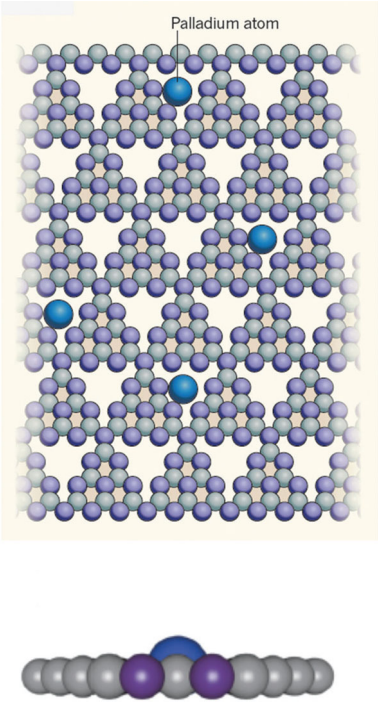

Fig. 17 (*Top*) Schematic of a single atom Pd catalyst comprising isolated Pd atoms on a solid support of carbon nitride (C_3N_4; carbon, *grey*; nitrogen, *purple*), which acts as a catalyst for hydrogenation reactions. Strong bonds to the nitrogen atoms firmly anchor the Pd atoms in roughly triangular pores in the stacked, two-dimensional layers of the support. There is approximately one roughly triangular cage per 50 $Å^2$ in each layer, and it is estimated that up to 10 % of them are occupied by a single Pd atom. (*Bottom*) View parallel to the C_3N_4 plane showing the density functional theory-optimized position of the Pd atom incorporated in the C_3N_4 support (After Vilé et al. [40])

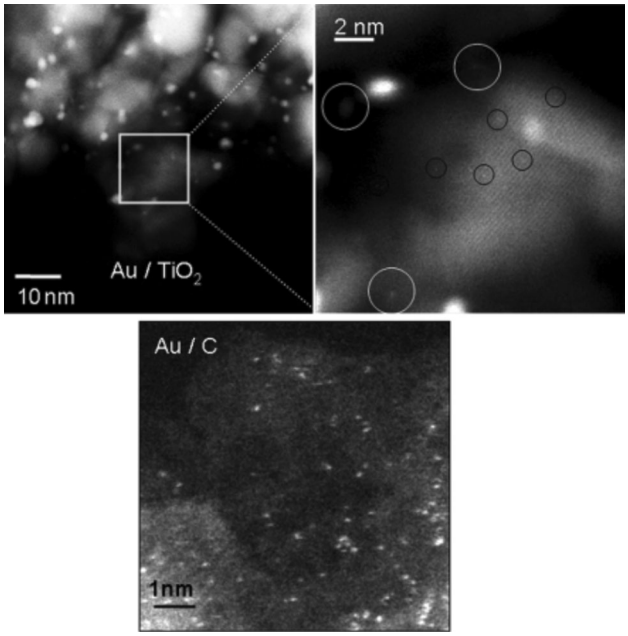

Fig. 18 Aberration-corrected scanning transmission electron microscopy images of nanoclusters of Au on a titania (*top*) or an activated carbon (*bottom*) support. Sub-nanometer clusters (*white circles*), which are approximately 0.5 nm in diameter and contain roughly 10 Au atoms, and individual Au atoms (*black circles*) are observed (After Thomas et al. [43])

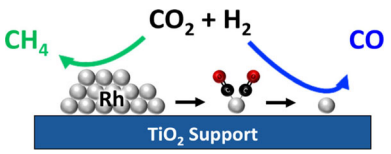

Fig. 19 Schematic depiction of different reaction pathways promoted by isolated atoms vs nanoparticles of Rh on TiO_2 (After Matsubu et al. [44])

Moreover, they do not require arable land—where they would compete with the production of food—and they can utilize waste water, sea water and industrial CO_2 (flue gases) to grow as valuable biomass.

It is estimated that there are between 60,000 and 80,000 species of algae; and the number of products that may be derived from them are many and varied (especially from those that are genetically engineered): medicines, pharmaceuticals, foodstuffs, jet fuel, bioethanol, biodiesel and ingredients for several consumer products. In this brief review, we shall focus on but two main products: diesel-range alkanes and bioethanol.

Microalgae to diesel

Currently, three approaches are used for microalgae oil refining. The first involves transesterification of triglycerides and alcohol into fatty acid alkyl esters (FAAEs) and glycerol. The second employs conventional hydrotreating catalysts, such as sulfided NiMo and CoMo for upgrading. The third, which is the one we focus on here, relies on supported noble and base metal catalysts for decarboxylation and decarbonylation of carboxylic acids to alkanes at 300–300 °C, but these catalysts exhibited low activities and selectivities for C_{15}–C_{18} alkanes when triglycerides were converted.

Recently, a more efficient method has been described by Peng et al. [36]. who used a novel Ni catalyst supported on an acidic zeolite, HBeta. This quantitatively converts crude microalgae oil under mild conditions (260 °C, 40 bar H_2) to diesel-range alkanes as high-grade second-generation transportation biofuels. From measurements of product distributions for this transformation, these authors formulated the reaction mechanism given in Fig. 15. The pathway proceeds through an initial metal-catalysed hydrogenation of double bonds in the alkyl chain, followed by hydrogenolyses of the formed saturated triglyceride

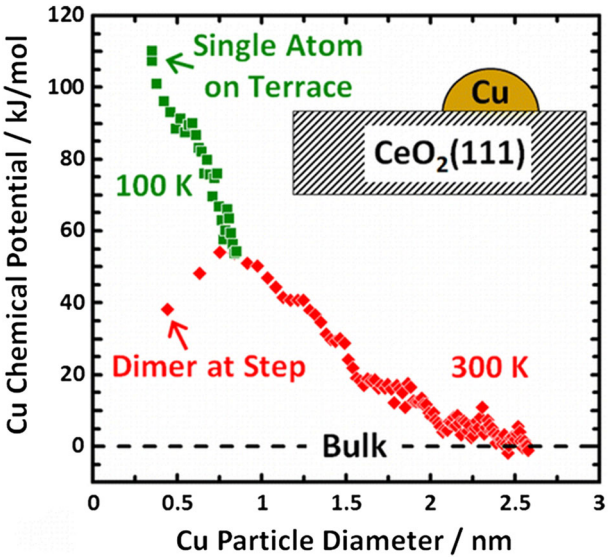

Fig. 20 Chemical potential of Cu atoms in Cu nanoparticles on $CeO_{1.95}(111)$ relative to that in bulk Cu(solid), versus the effective diameter of the Cu particle down to the single atom limit (After James et al. [45])

leading to fatty acid and propane. The subsequent hydrogenation of the carboxylic groups of fatty acid leads to the corresponding aldehyde (rate-determining step), followed by either decarbonylation or hydrogenation. Subsequent acid-catalysed dehydration and metal-catalysed hydrogenation lead to the long-chain *n*-alkane. Because of an abundance of acidic sites in the zeolite, hydroisomerization and hydrocracking of the alkanes also takes place; and CO may react with H_2 to produce methane (by the classic methanation reaction).

The Licella approach

Using catalytic hydrothermal technology, Maschmeyer and colleagues [37] have recently developed (and commercialized) a catalytic hydrothermal reactor which converts feedstocks such as sawdust into bio-crude oil of such good quality—it is essentially free of sulphur—that it can be readily blended with stocks of either diesel, kerosene or gasoline. The first commercial plant, now being completed in Canada, is intended to transform 200,000 tonnes of waste annually into the desired 'green' bio-oil. Figure 16 illustrates the overall conversion.

This development is of great significance in this environmentally conscious age, especially when one reflects on the fact that only some 18 % of a tree is used in paper production; it therefore means that converting the 'tree waste' into bio-oil is a significant step forward.

Single atom heterogeneous catalysts

Great interest is now being given to the increasing variety of this category of catalysts. Short accounts have been given elsewhere—see Thomas and Harris [5], Yang et al. [38], Flytzani-Stephanopoulos [39], Vile et al. [40] and Thomas [41]. A spectacular example of a stable single atom Pd catalyst for selective hydrogenation has recently been reported by Vile et al. [40]. Unlike many other previous workers in this field, they use a structurally adept solid as the support for atomically dispersed Pd, namely, nanoporous carbon nitride, C_3N_4. The merit of their system (see Fig. 17) is that the individual atoms of Pd are so firmly anchored to the nanoporous walls of the C_3N_4 that they exhibit minimal tendency to migrate and coalesce to form nanoclusters. This catalyst was shown to be active in a three-phase hydrogenation of alkynes in flow mode, and both its selectivity and activity surpassed those of nanoparticulate Pd. Apart from C_3N_4, there is now great interest focused on another 'indented' (holey) nitrogenous graphene-like carbon of empirical formula C_2N. Recent theoretical work done on this catalyst support for single atoms of members of the 3d transition metal series, using an augmented wave version of the density functional theory approach, indicates that Cr and Mn single atoms would catalyse the conversion (by an Eley–Rideal mechanism) of CO and O_2 to yield CO_2 [42].

In Fig. 18, we show high-resolution images of other few-atom catalytic systems, comprising Au nanoclusters or single atoms supported on TiO_2 or activated carbon [43]. Each small spot here is the image of a single metal atom. Christopher and colleagues [44] have also studied isolated metals, in their case, supported on TiO_2. They found significant differences in catalytic selectivity between individual atoms of Rh and nanoparticles of the same metal—see Fig. 19. In an elegant assessment of the energetics of single atoms and nanoparticle metal catalysts, namely of Cu on the (111) face of CeO_2, Campbell and co-workers [45] were able to arrive at quantitative values of the chemical potential of this metal from the single atom extreme to the bulk state, as shown in Fig. 20. Such work is of great value in ascertaining the long-term thermal stability of single atom catalysts, which is a subject that is now of great relevance.

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