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PERSPECTIVE

Photocatalytic Hydrogen Production and Oxygenate Photoreforming

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Abstract In this perspective the current state of photocatalytic hydrogen production is considered, focusing especially on photo-reforming reactions. There are fundamental thermodynamic and kinetic limitations to direct water splitting and a number of strategies have been developed to overcome them. These include the development of catalysts which have little activity for the back reaction of hydrogen oxidation, systems with spatially separated H_2 and O_2 production and the interception of the oxygen species by sacrificial water reductants. Success has been achieved in these areas over the last 20 years or so, but more needs to be done in terms of the development of high quantum efficient photo-absorbers which operate over the useable light range, and of two-photon efficient processes which can extend the useable range further. There is also an urgent need for fundamental investigations of the nature of the range of surface processes which occur during photocatalysis, and which have to occur in synchrony.

Keywords Photocatalysis · Photoreforming · Water splitting · Hydrogen production · Methanol

1 Introduction

We are in an era of necessarily rapid change in our utilisation of the earth's finite resources. It is only relatively recently in the era of mankind on this planet that we have used fossil fuels, essentially associated with the industrial revolution, and beginning in the UK in the early-mid 19th century. It is only very recently that we have finally realised that the atmosphere is not an infinite sink for CO_2 and other pollutant gases, since the planet has responded with potentially catastrophic phenomena such as the ozone hole and global warming. In light of our new knowledge we have realised that we have to live a sustainable lifestyle and that this sustainability must be achieved in the very near future; if this is not achieved then a large part of the human population will suffer extreme consequences, and the human population may finally decline. As human beings we are supposed to be the 'cleverest' creatures on the planet, but the quality of the debate in the media on this matter in recent years has often belied this fact [1], and has been a tragedy for human development and planetary health.

This paper is concerned with one part of a possible sustainable scenario—that is, the production of a potentially renewable fuel, hydrogen, made from water splitting utilising a non-polluting source of energy, namely sunlight (see Fig. 1). If we can efficiently split water into hydrogen and oxygen, then we would have a major leap forward in our global energy situation, because the combustion then represents a virtuous cycle. Here we produce hydrogen and oxygen, and then burn them again in heat engines, with useable heat released from the enthalpy of combustion, or in a fuel cell with electrical power generation, with the water reformed.

2 The Fundamental Thermodynamics and Kinetics

The difficulties associated with water splitting must not be trivialised. Most papers ignore the basic thermodynamics

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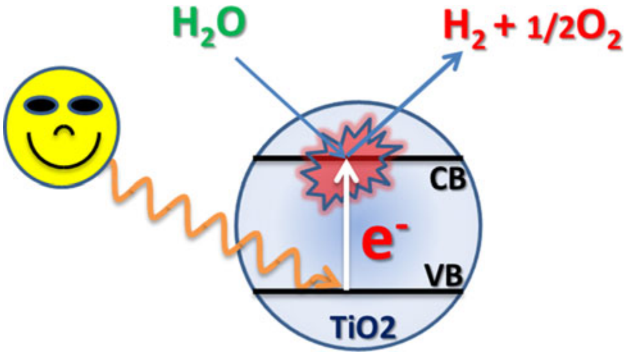

Fig. 1 Solar inputs, combined with photocatalytic technology, can drive the creation of hydrogen as a clean, sustainable fuel for the 21st century

of water splitting and this must always be the starting point for catalytic processes, as for chemistry in general. Water splitting is extremely difficult, as illustrated by the energy diagram in Fig. 2, and reactions 1 and 2 below.

$$H_2O_l \rightarrow H_2 + \tfrac{1}{2}\,O_2,\ \Delta G^0_R = 237\ \mathrm{kJ\ mol^{-1}},\ \Delta H^0_R = 286\ \mathrm{kJ\ mol^{-1}},\ \Delta S^0_R = 163\ \mathrm{J\ K^{-1}\ mol^{-1}} \quad (1)$$

$$H_2O_g \rightarrow H_2 + \tfrac{1}{2}\,O_2,\ \Delta G^0_R = 229\ \mathrm{kJ\ mol^{-1}},\ \Delta H^0_R = 242\ \mathrm{kJ\ mol^{-1}},\ \Delta S^0_R = 44\ \mathrm{J\ K^{-1} mol^{-1}}. \quad (2)$$

These energetics are expressed as kJ $\mathrm{mol^{-1}}$ of water consumed/hydrogen produced [2]. Clearly then, this is a highly endergonic reaction which is thermodynamically extremely difficult. It is only at above 1,800 K that the free energy change is zero and high equilibrium yields can be obtained by thermolysis.

We therefore need other ways of providing the thermodynamic energy required and one of these is by using light energy. Figure 3 shows the solar spectrum and gives two thresholds associated with its use in the context of water splitting. Here, the light energy threshold is shown, corresponding with sufficient energy to make the reaction above free energy neutral (assuming 100 % light conversion efficiency) and this is equivalent to a wavelength of ~500 nm. Thus, we can utilise light of energy greater than this, at wavelengths shorter than this. If we can use a two photon process, and combine the light energy efficiently, then of course, longer wavelengths could be useful too. However, there are a number of problems with the efficient use of solar energy for water splitting, particularly regarding the kinetics of the process, and the materials which may be utilised. Water, fortunately for us, is perfectly stable at the earth's surface, despite the fact that there is plenty of light of these wavelengths (<500 nm) arriving here. So why is this so? Well, it is because the kinetic requirement to split water is even more stringent than the thermodynamic one, that is, breaking the first O–H bond alone requires ~500 kJ $\mathrm{mol^{-1}}$ and that corresponds with a wavelength input to break the bond of <250 nm or so, as also shown on Figs. 2 and 3. Fortunately, light of this wavelength does not reach the earth's surface in any significant quantities.

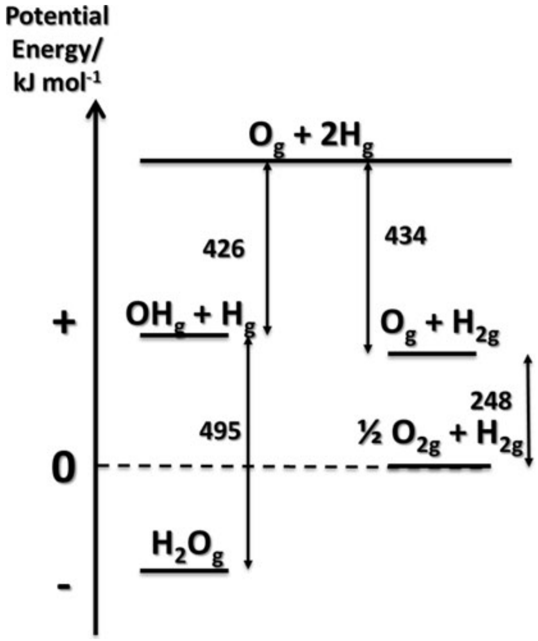

Fig. 2 Energy diagram for gas phase water splitting. It is a highly endergonic reaction, but light of the required energy (~500 nm) does reach ground level from the sun. Fortunately for life on earth this is inadequate to overcome the kinetic barrier to break the first O–H bond in water. Light of the wavelength required for that process (~250 nm) is mopped up in the stratosphere and does not reach ground level, see Fig. 3

To solve such a kinetic problem we usually use catalysis. So the ideal situation is to combine light of wavelengths shorter than the threshold to provide the thermodynamic energy requirement, with catalysis to drop the kinetic barrier to a low value. Further, the catalytic function and the photo-absorption function will, ideally, all be provided in one material. Such a material, then, should include a photon absorber which can convert the light energy by absorption and electron excitation. This, then, limits the types of material which can be applied to this problem: they must have a bandgap (E_g) in the visible range, that is, a semiconductor with E_g ~250 kJ $\mathrm{mol^{-1}}$ (~2.6 eV), as the minimum which is thermodynamically useable in a one photon process. If the semiconductor has a catalytic function too, enabling the breaking of the O–H bond, all the better, though another material, such as a transition metal (often used for bond-breaking and making reactions), could be added to the catalyst to aid in this function.

However, if we produce a catalyst with a lowered activation barrier to the dissociation process, so we also produce a material with an even lower activation barrier for the back-reaction, the recombination of hydrogen and

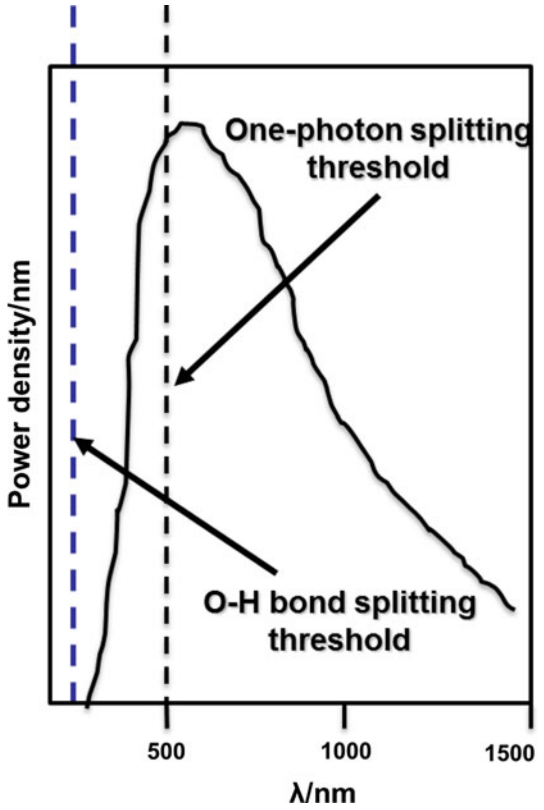

Fig. 3 Schematic diagram of the solar emission spectrum at ground level, showing maximum wavelength thresholds for the thermodynamic and kinetic splitting of water

oxygen. Thus catalysts have to be carefully fabricated in order to get over this fundamental contradiction. One way to do this is to add sacrificial agents which prevent O_2 production, as described in the following section, or to produce catalysts which are relatively inert to hydrogen or oxygen dissociation.

3 Sacrificial Water Splitting and Photocatalytic Reforming

The thermodynamic and kinetic constraints can be alleviated by utilising sacrificial water reductants which effectively remove oxygen from the system and therefore divert water splitting away from oxygen production. The simplest example of this is the photo-reforming of methanol [3–10] and this reaction is much less endergonic than pure water splitting and the problem of the back reaction with oxygen is removed.

$$\begin{aligned}&CH_3OH_l + H_2O_l \rightarrow 3H_{2g} + CO_{2g},\\ &\Delta G^0_R = 8\ \text{kJ mol}^{-1};\\ &\Delta H^0_R = 131\ \text{kJ mol}^{-1};\\ &\Delta S^0_R = 410\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned} \tag{3}$$

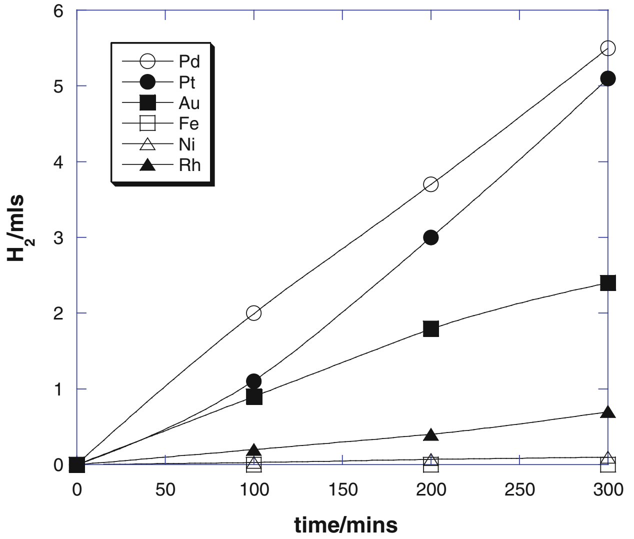

Fig. 4 Hydrogen production from the photo-reforming of methanol on a variety of metals (0.5 % weight loading) supported on P25 TiO_2

This reaction proceeds readily from the liquid phase at ambient temperature and pressure under anaerobic conditions, as shown in Fig. 4 [3–5], but only in the presence of light. Here a variety of precious metals, in combination with a semiconducting, light absorbing support, are effective for the reaction, the semiconductor in this case being P25 titania, a widely used material for photocatalysis. Other metals, such as Ni, Fe etc. are not suitable since they are not easily reducible under the conditions of the reaction [4, 5], and the presence of metal is essential for such reactions (which is not the case for photo-oxidation which is much more facile). Note that, although CO_2 is produced in the process, it is potentially part of a clean cycle if the reductant used is part of a biological cycle in which the molecule is produced from CO_2 in the atmosphere, and not from a fossil fuel source. This is discussed in the next section.

4 Sustainability and Bio-derived Reactants

Although methanol is a bio-molecule (traditionally called ‘wood alcohol’ due to its production, since antiquity, by the pyrolysis of wood residues), it is produced in much smaller volumes in this way than are bio-ethanol and bio-diesel, being produced mainly by steam reforming of fossil fuels and the catalytic conversion of the synthesis gas so-produced. So instead of reforming methanol, can we reform these more widely-produced, and more sustainable sources of a sacrificial reductant? As Fig. 5 shows we can indeed reform a variety of molecules in this way, including a range of alcohols. Most interestingly perhaps, we can utilise a by-product of bio-diesel production, namely glycerol.

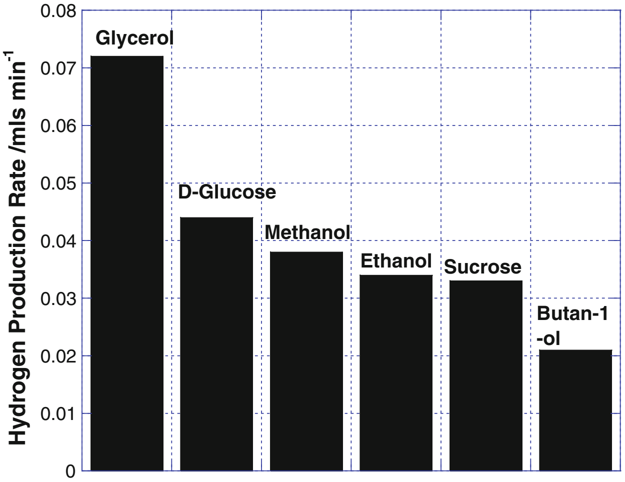

Fig. 5 Hydrogen production rates for the photoreforming of a variety of bio-derivable feedstocks

As can be seen in Fig. 5 there is a variation in rate of hydrogen production between the different molecules and also many of them give other products. So, for instance, ethanol produces methane, as well as CO_2 and H_2, while butan-1-ol gives propane [11, 12]. On the other hand some polyols produce only CO_2 and hydrogen with glycerol being very effective [12–14], showing the highest production rate combined with 100 % atom efficiency to H_2, the reaction being –

$$C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2 \qquad (4)$$

Note also that although ethanol can be used, much ethanol is produced, at some cost, from sugars, whereas hydrogen can also be produced directly from these sources using ambient temperature photocatalytic reforming, as shown in Fig. 5 [11, 12, 15].

This kind of reactivity pattern is largely dictated by the metal function and the reaction occurs by initial decarbonylation on the Pd component of the photocatalyst. Pd is a good decarbonylator of such molecules. Thus the catalytic cycle occurs as shown in Fig. 6 and consists of decarbonylation on the metal, oxidation of the adsorbed CO on the metal by an activated oxygen species produced by light-induced splitting of water. Without the introduction of light, the reaction is poisoned by adsorbed CO, in a similar way to the poisoning of car exhaust catalysts at ambient temperature. From this pattern of activity we can establish some 'rules' for photocatalytic reforming [12]. Some important ones are that, firstly, the molecule must have an αC-H bond adjacent to a functional group, where here we define α as being the C atom adjacent to the oxygen function. Thus acetic acid and acetone do not show any significant activity for photo-reforming to produce H_2 [12]. Secondly, alkyl groups attached to alcohols generally yield the corresponding alkanes. Thirdly, as described above, the photo-absorbing function must be accompanied by a metal function that is reducible under the conditions of reaction.

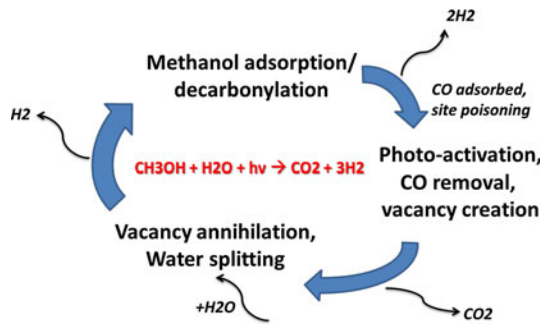

Fig. 6 The cycle for the photo-reforming of methanol on Pd/TiO_2 catalysts

5 Direct Water Splitting

Of course a 'Holy Grail' in this field is pure water splitting, but as described above, this is intrinsically much more difficult than the reactions described above. However, a number of approaches have been developed to tackle this problem, and progress is being made.

5.1 One-Pot Systems

To co-produce hydrogen and oxygen from water in one environment, we need to stop the back reaction of hydrogen oxidation, which intrinsically has a very low activation barrier. So catalysts which are essentially inactive for this process must be produced. An early report of such a system goes back to Domen et al. [16, 17] in the early 1980s where Ni on $SrTiO_3$ was used to enable the reaction. The trick here, then, is to passivate the surface of the Ni (as surface NiO) while maintaining a core of metal. This implies that there is no role for the metal in the catalysis itself, being there only as an electron trap to extend the lifetime of the light driven electron–hole pair creation, as is claimed by many to be the role of the metal. Since that time more complex materials have evolved which are (a) more active and (b) absorb a wider wavelength range. So Domen et al. [18] have gone on to produce a range of multi-interfacial materials, mixes of oxides and oxynitrides, which are more efficient than this early material-for instance, a mixed Rh/Cr oxide supported on zinc doped Ga_2O_3, which operates in the visible region. In a similar vein, the Can Li group have made Pt–RuO_2 with Zn_2GeO_4 photocatalysts to co-produce H_2 and O_2 from water, though the wavelength threshold is only ~390 nm and so does not cover the solar range [19].

5.2 Separated H_2 and O_2 Production

This type of system is described by Anpo et al. [20] for instance; here a membrane is used to allow H^+ diffusion to a chamber adjacent to the photo-active electrode where they are produced, and in that chamber the protons are recombined on a Pt electrode. However, a driving potential, and an acidic electrolyte solution are utilised in such systems and yields are generally very low.

5.3 Grätzel-Type Cells

Again, this is a kind of photo-electro-catalytic system where a driving potential is applied between two electrodes. However, in this case this enables a two-photon process to be used and so enables lower energy light (and thus smaller bandgap materials than titania) to be used [21]. Questions remain about the efficiency of such a system in terms of rates of hydrogen production, quantum yield and the energy balance.

6 International Validation of Literature Claims

Because photocatalytic water splitting has become such a hot topic, and because huge amounts of support money are available in some places in the world, there is a temptation to over-egg results, to grab headlines (‘impact’ as our politically over-conscious funders would have us call it), and there is much discussion about the reproducibility of some of the claims in the literature. Also sometimes claims are made for pure water splitting, while not using pure water, but having sacrificial additives present.

A solution to this problem, which has become essential, is to generate a round-robin of photocatalyst synthesis and rate measurement. It is now a NECESSITY that claims for high H_2 yields are verified in labs outside of the claim. This can be achieved in a number of ways, including the exchange of materials between labs for testing and exchange of recipes between labs for catalyst synthesis. Such a development is essential to the progress of the field, and to the development of sustainable hydrogen production in particular. Various agencies are beginning to formulate ways of standardising measurement procedures for comparison purposes.

7 Summary and Outlook

The splitting of water to provide hydrogen in a sustainable manner using sunlight energy as input represents an exciting technological opportunity to relieve some of the problems associated with fossil fuel consumption. Although the technology is difficult, a range of approaches are being developed which have delivered improvements in the performance of photocatalysts.

However much more needs to be done to develop useable materials and the main obstacles to be overcome continue to be the following –

7.1 Solar Absorbers and Materials Synthesis

Most photocatalytic work is still carried out on titania, but it has an extremely limited wavelength of absorption. We need to develop materials which have efficient absorption over the appropriate wavelength range which is useable (i.e. high quantum yield). Although much work is reported in the literature on doped titania, the materials so-produced are often not better, and often worse in performance than titania itself. It almost seems as if the attitude here is sometimes “if it’s coloured it must be good”. Often doping does not narrow the intrinsic bandgap, but rather induces useless trap sites, which immobilise the excited electron. Ease of electron transfer is a *sine qua non* in catalysis. However, progress is being made in this area (the examples in Sect. 5.1 above for instance), and much more is needed.

7.2 Low Rate

This also relates to item 7.1 above—materials need to be able to absorb the maximum amount of useable light, to be able to convert it into product hydrogen with high atom efficiency. Academic studies usually have hours on the time axis because yields are slow in the small area systems they use. Essential to the achievement of higher rates is high quantum efficiency, that is, using the maximum amount of light feasible, and implicit in this is to produce material in which e–h pair recombination is minimised, that is, their lifetime is longer than that of the rate limiting step in the process.

7.3 Longevity and Photo-hydro-stability

In relation to item 7.1, it is often the case that new types of photocatalysts that are produced with a smaller bandgap than TiO_2, appropriate to absorb a useful amount of visible light, are not stable over long periods of time under reaction conditions, that is, in the presence of water and light. For instance, sulphides generally oxidise in the process.

7.4 Engineering

Photoreactors are rather different from the reactors that we are used to in heterogeneous catalysis, and large-scale application is a surface problem—reactors must be essentially 2-D as opposed to the normal volume reactors. The volume of catalyst is still important, but a reactant (light) is thinly distributed and so must intercept the maximum area possible for useable, large scale production. This means the creation of huge area arrays of solar-catalytic panels, on which are coated thin layers of catalyst (probably <0.1 mm thick). It is essential therefore to reduce the per metre cost of materials and to make solar reactors as efficient as possible by appropriate design—for instance double parabolic reflectors, in which light is focused onto a catalyst coated in a tubular reactor, have been shown to give good efficiency in terms of the full day solar absorption.

7.5 Fundamental Understanding

There is rather a paucity in understanding the surface chemistry involved in photocatalysis; after all, it is at the surface where the essential reaction steps take place. Much more needs to be done in the surface science community to address the basic problem of the effect of light on the surface chemistry of model catalysts (e.g. titania, and metal nanoparticles on titania), especially focusing on in situ studies of the reacting system. Work is beginning in this field, both from the experimental and theoretical point of view, but these generally do not involve studying the reacting system. Important questions are, among others: what is the fate of the photoexcited e–h pair; what is nature of the metal-support interaction during adsorption and light exposure; do the metal, the photo-support or both participate in the surface chemistry; what is the optimum coverage, particle size and morphology for photocatalysis? By obtaining the fundamental understanding of these things we will make great advances in the field generally.

8 Future Applications

8.1 Large Scale Production and the Hydrogen Economy

It is possible that large scale production of hydrogen will be applied in the future and here large arrays of efficient solar convertors will be needed. Although it might be nice to apply this in remote, non-agricultural areas, this may not be easy, since a ready supply of water (and biofuel if using sacrificial hydrogen production) will be required with as low a transport cost as possible. As in all things technological the economics of application will dominate, and the economics of hydrogen production will be increasingly favourable as the century proceeds. Further, security of energy supply may become even more important than it is now.

Whether such technologies can produce sufficient power to supply the market for a major user of fossil fuels, namely vehicles, at the current Western level of consumption is doubtful. However, future scenarios of energy usage, in a world of declining fossil fuel supplies, and where there is an urgent need to stop using such fuels, are extremely unclear and unpredictable. However, we should have a range of technologies available for the crisis situations which will occur during this century when the use of fossil fuels may cease, for one reason or another. One such reason could be the development of an enforced legal framework to reduce CO_2 emissions, in a similar way that automotive emission legislation has developed over the last 40 years. Such legislation would advance the field of photocatalytic fuel production enormously.

8.2 Domestic Application and the Photocatalytic Window

It may be that photocatalytic hydrogen production is an area for local generation of useable hydrogen gas for domestic use and for use in fuel cells, rather than for large scale production, particularly in areas with high solar power density. It could be applied in the form of a solar panel or, if the materials used can be made efficient while transmitting a significant fraction of the light, they may be able to replace windows. Such application in the modern domestic arena will need careful engineering, and may first appear on the small scale in more remote, poorer locations where natural supplies of combustible material for cooking have been exhausted.

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