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Recent Advances in Catalytic/Biocatalytic Conversion of Greenhouse Methane and Carbon Dioxide to Methanol and Other Oxygenates
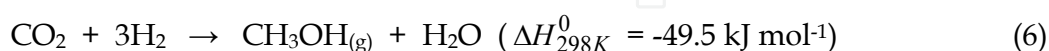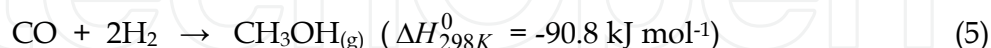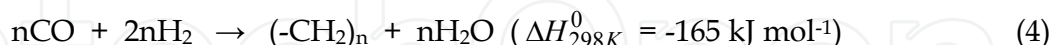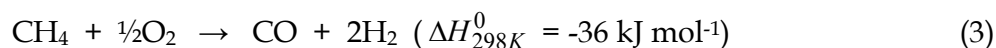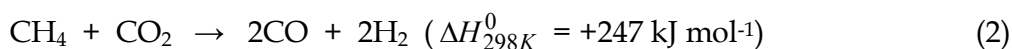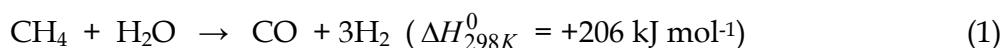
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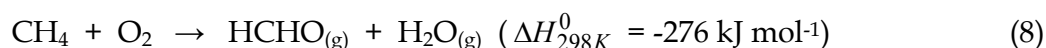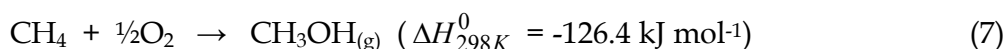*Queensland University of Technology, Brisbane*
Australia

1. Introduction

Methane gas has been identified as the most destructive greenhouse gas (Liu *et al.*, 2004). It was reported that the global warming potential of methane per molecule relative to CO_2 is approximately 23 on a 100-year timescale or 62 over a 20-year period (IPCC, 2001). Methane has high C-H bond energy of about 439 kJ/mol and other higher alkanes (or saturated hydrocarbons) also have a very strong C-C and C-H bonds, thus making their molecules to have no empty orbitals of low energy or filled orbitals of high energy that could readily participate in chemical reactions as is the case with unsaturated hydrocarbons such as olefins and alkynes (Crabtree, 1994; Labinger & Bercaw, 2002). Consequently, only about half of the hydrocarbons containing these ubiquitous C-H bonds are reactive enough to take part in traditional chemical reactions (Bergman, 2007). This is a great challenge that needs to be addressed because several of these un-reactive hydrocarbons are found in petroleum from which several organic products including petrochemicals, fine chemicals, plastics, paints, important intermediates and pharmaceuticals are produced. Methane, besides being a greenhouse gas, is also the major constituent of large, underutilized resources of natural gas (located in remote areas of Asia, Siberia, Western Canada and offshore reservoirs of Australia, and therefore expensive to transport) and coal bed methane (CBM). It is therefore a promising feedstock for producing other value-added products if the problem of C-H activation can be solved. The selective transformation of these ubiquitous but stable C-H bonds to other functional groups could therefore revolutionize the chemicals industry. A clear understanding of the reactions involving C-H activation is therefore an important and interesting challenge.

Generally, there are two routes for converting methane to transportable liquid fuels and chemicals, namely indirect and direct routes. At the moment, commercial catalytic technologies are based on the indirect route that involves a two-step process in which methane is first converted to synthesis gas by steam reforming (Eqn.1), CO_2 reforming (Eqn. 2) or partial oxidation (Eqn. 3) followed by either Fischer-Tropsch synthesis of hydrocarbons (Eqn. 4) or methanol synthesis (Eqns. 5 and 6) and subsequent conversion to hydrocarbons.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \ (\Delta H^0_{298K} = +206 \text{ kJ mol}^{-1}) \tag{1}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \ (\Delta H^0_{298K} = +247 \text{ kJ mol}^{-1}) \tag{2}$$

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \ (\Delta H^0_{298K} = -36 \text{ kJ mol}^{-1}) \tag{3}$$

$$nCO + 2nH_2 \rightarrow (-CH_2)_n + nH_2O \ (\Delta H^0_{298K} = -165 \text{ kJ mol}^{-1}) \tag{4}$$

$$CO + 2H_2 \rightarrow CH_3OH_{(g)} \ (\Delta H^0_{298K} = -90.8 \text{ kJ mol}^{-1}) \tag{5}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH_{(g)} + H_2O \ (\Delta H^0_{298K} = -49.5 \text{ kJ mol}^{-1}) \tag{6}$$

The direct route is a one-step process in which methane or natural gas is reacted with oxygen or another oxidizing species to give the desired product, e.g. methanol or formaldehyde (Eqns. 7 and 8). The direct route is regarded to be more energy efficient than the indirect route since it bypasses the energy intensive endothermic steam reforming step of syngas formation.

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CH_3OH_{(g)} \ (\Delta H^0_{298K} = -126.4 \text{ kJ mol}^{-1}) \tag{7}$$

$$CH_4 + O_2 \rightarrow HCHO_{(g)} + H_2O_{(g)} \ (\Delta H^0_{298K} = -276 \text{ kJ mol}^{-1}) \tag{8}$$

The selective catalytic conversion of methane via partial oxidation into transportable liquids such as methanol, formaldehyde and other oxygenates is one direct route for activating and converting natural gas- or CBM-derived methane to value-added chemicals. This partial oxidation reaction is one of the greatest challenges in heterogeneous catalysis because of the high driving force to full oxidative conversion to CO or CO_2 (Eqns. 9 and 10).

$$CH_4 + {}^3\!/_2O_2 \rightarrow CO + 2H_2O_{(g)} \ (\Delta H^0_{298K} = -519.6 \text{ kJ mol}^{-1}) \tag{9}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(g)} \ (\Delta H^0_{298K} = -802.6 \text{ kJ mol}^{-1}) \tag{10}$$
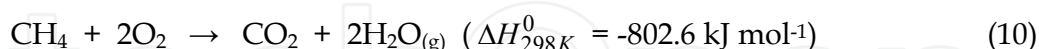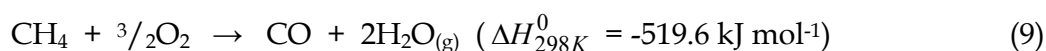
At the moment, oxygenates such as methanol and formaldehyde are produced via a multi-step process involving first the conversion of methane to syngas followed by the oxygenate formation in a second step. Although this multi-step process is highly efficient, the syngas production is very expensive due to high capital costs and it is therefore only economically viable if it is conducted on a large scale. Thus, a more convenient and economically viable process for small scale methanol production (e.g. at remote locations) would be the direct methane partial oxidation to methanol. Furthermore, it should be noted that methanol, being a precursor to ethylene and propylene, is a primary raw material for the chemical industry (Olah *et al.*, 2009; Beznis *et al.*, 2010a, 2010b). It is produced in large quantities as an intermediate for the production of a wide range of chemicals including formaldehyde, methyl *tert*-butyl ether and acetic acid, most of which are subsequently used to produce many important industrial products such as paints, resins, adhesives, antifreezes and plastics (Olah *et al.*, 2009). Thus, the direct catalytic synthesis of methanol from methane

would open up the possibility of producing a wide range of important chemicals by the chemical industry. Apart from catalytic direct conversion route, an alternative method is the biochemical production of methanol from methane, a process which occurs under mild conditions and atmospheric pressure. This bio-catalytic route is based on the ability of some bacterial species such as methanotrophs and methane monooxygenase (MMO) to oxidize methane to methanol and deeper oxidation products.

Another significant greenhouse gas is carbon dioxide which is considered to be harmful pollutant of our atmosphere and a major source of human-caused global warming (Olah *et al.*, 2009). On the other hand, carbon dioxide is an ubiquitous carbon source from which methanol, dimethyl ether and efficient alternative transportation fuels and their derivatives can be produced (Olah *et al.*, 2009). Thus, it has been suggested that an effective feasible approach for the disposal and recycling of carbon dioxide is its chemical conversion to important chemicals such as methanol, dimethyl ether and liquid fuels (Olah *et al.*, 2009). This approach is considered to have the potential to provide solution to the environmental problem of increasing levels of carbon dioxide in the atmosphere and the accompanying global warming. The chemical transformation of carbon dioxide also makes possible the production of renewable and inexhaustible liquid fuels and other important carbon chemicals, thus allowing an environmentally neutral use of carbon fuels and derived hydrocarbon products (Olah *et al.*, 2009).

The catalytic reductive conversion of carbon dioxide using hydrogen at non-ambient conditions appears to be the most studied direct route to methanol and other oxygenates from carbon dioxide (Eqn. 6). Such catalytic reactions have traditionally been heterogeneous catalytic, photocatalytic and electrocatalytic pathways (Lu *et al.*, 2006). These methods require high temperatures and pressures or additional electric or luminous energy, but both selectivity and yields are usually low. Besides these traditional routes, novel biocatalytic systems have also been shown to be capable of catalysing the reduction of carbon dioxide at ambient conditions (Lu *et al.*, 2006). Such biocatalytic pathways are attractive because they occur with high yields and selectivity at milder reaction conditions without pollution and the processing involves the use of low purity reactants and is very tolerant to many impurities that are toxic to chemical catalysts (Lu *et al.*, 2006; Lu *et al.*, 2010). For example, formate dehydrogenase (FateDH) immobilized in a novel alginate-silica hybrid gel was previously used as the biocatalyst to reductively convert carbon dioxide into formic acid and reduced nicotinamide adenine dinuncleotide (NADH) as the terminal electron donor for the enzymatic reaction (Lu *et al.*, 2006). A combination of biocatalysts has also been used for the reduction of CO_2 to methanol (Lu *et al.*, 2006).

This chapter presents a general overview of recent advances in the development of catalytic and biocatalytic systems for both the direct partial oxidative conversion of methane and the hydrogenation of carbon dioxide to produce methanol and other oxygenates. The review will cover both homogeneous and heterogeneous catalytic systems that have been developed so far. The electrochemical and photocatalytic reductive conversions of carbon dioxide are covered in the review. The chapter also presents a discussion of the progress that has been made on the development of chemical systems like MMO that are capable of oxidizing methane at ambient conditions. One interesting observation in our previous work on catalytic oxidative methylation of aromatics with methane that is directly relevant to the conversion of methane to methanol is that it is possible to inhibit the complete oxidation of

methane to carbon dioxide in the presence of an additive (Adebajo *et al.*, 2000; Adebajo *et al.*, 2004). This chapter also provides a brief summary of such oxidative methylation reaction and its significance to methanol conversion.

2. Conversion of methane to oxygenates

2.1 Recent advances in the catalytic conversion of methane to oxygenates

The direct conversion of methane to oxygenates such as methanol (CH$_3$OH), formaldehyde (HCHO) and acetic acid (CH$_3$COOH) has great potential for producing liquid fuels and petrochemicals from natural gas and CBM. This direct conversion route involves partial oxidation at 300-500 °C under fuel-rich mixtures to minimize the extent of the more thermodynamically favourable combustion reaction which produces unwanted CO and CO$_2$ (Zhang *et al.*, 2003; Navarro *et al.*, 2006; Alvarez-Galvan *et al.*, 2011). Several reviews which provided valuable discussions of various aspects of, and the progress already made in, the direct partial oxidation of methane to methanol and other oxygenates have been published (Foster, 1985; Gesser *et al.*, 1985; Edwards & Foster, 1986; Pitchai & Klier, 1986; Fujimoto, 1994; Yang *et al.*, 1997; Adebajo, 1999; Lunsford, 2000; Tabata *et al.*, 2002; Zhang *et al.*, 2003; Taniewski, 2004; de Vekki & Marakaev, 2009; Holmen, 2009; Alvarez-Galvan *et al.*, 2011). The selective partial oxidation of methane has been carried out in four ways, namely high temperature non-catalytic gas-phase homogeneous oxidation, heterogeneous catalytic oxidation, low temperature homogeneous catalysis in solution and enzymatic or biological catalytic oxidation (Zhang *et al.*, 2003; Holmen, 2009).

The gas-phase non-catalytic reactions usually occur via a free radical mechanism at high temperatures which are unfavourable with respect to the control of selectivity of the desired oxygenates (Navarro *et al.*, 2006; Alvarez-Galvan *et al.*, 2011). Thermodynamic and kinetic analyses have shown that the rate-limiting step of the partial oxidation of methane is the first H-abstraction from the C-H bond to form methyl radicals (Navarro *et al.*, 2006; Alvarez-Galvan *et al.*, 2011). Thus, initiators and sensitizers have been incorporated into the reaction mixture for the purpose of lowering the energy barrier of this H-abstraction (Navarro *et al.*, 2006; Alvarez-Galvan *et al.*, 2011). In particular, nitrogen oxides have been used to promote gas-phase reactions with methane (Otsuka *et al.*, 1999; Tabata *et al.*, 2000; Babero *et al.*, 2002; Tabata *et al.*, 2002). The presence of higher hydrocarbons, especially ethane, in small quantities has also been observed to lower the initiation temperature and increase methanol selectivity and yield (Gesser *et al.*, 1985; Fujimoto, 1994). High selectivities of up to 80% for methanol at up to 10% methane conversion have already been achieved under non-catalytic conditions by Gesser et al. (Yarlagadda *et al.*, 1988; Hunter *et al.*, 1990; Gesser & Hunter, 1998). It is generally accepted that high pressure favours the formation of methanol and high methane/oxygen enhances methanol selectivity but lowers methane conversion in gas phase homogeneous partial oxidation of methane (Zhang *et al.*, 2003, 2008). Most results indicate a selectivity of 30-40% at a conversion of 5-10% under the best conditions which are mainly temperatures of 450-500 °C and pressures of 30-60 bars (Holmen, 2009). The experimental and theoretical evidence obtained so far indicates limited possibilities of producing high yields of methanol in the gas-phase system (Holmen, 2009). The presence of catalysts in such gas-phase reactions carried out at high pressure appears to have no beneficial effect on the reactions. In fact, it has been observed that reactor inertness is critically important for obtaining high selectivity of methanol and that even the feed gas

should be isolated and not be allowed to make contact with the metal wall. Thus, Quartz and Pyrex glass-lined reactors have been shown to yield the best results (Zhang *et al.*, 2008).

Typical experimental results from several studies for the gas-phase partial oxidation of methane are shown in Fig. 1. This figure clearly demonstrates that any improvement in the direct conversion of methane to methanol via the gas phase homogeneous oxidation route must come from the enhancement of selectivity without reducing the conversion per pass which is a great challenge (Holmen, 2009; Alvarez-Galvan *et al.*, 2011). This challenge together with the need to operate the gas-phase reactions at high temperatures which make the control of selectivity to desired products extremely difficult has made it necessary for researchers to make considerable efforts to develop active and selective catalysts for the partial oxidation of methane. This review focuses on providing brief discussions of the progress that has been made in the conversion of methane to methanol and other oxygenates via the heterogeneous catalytic oxidation, homogeneous catalysis in solution and bio-catalytic oxidation routes. Such discussions are presented in the following sections.
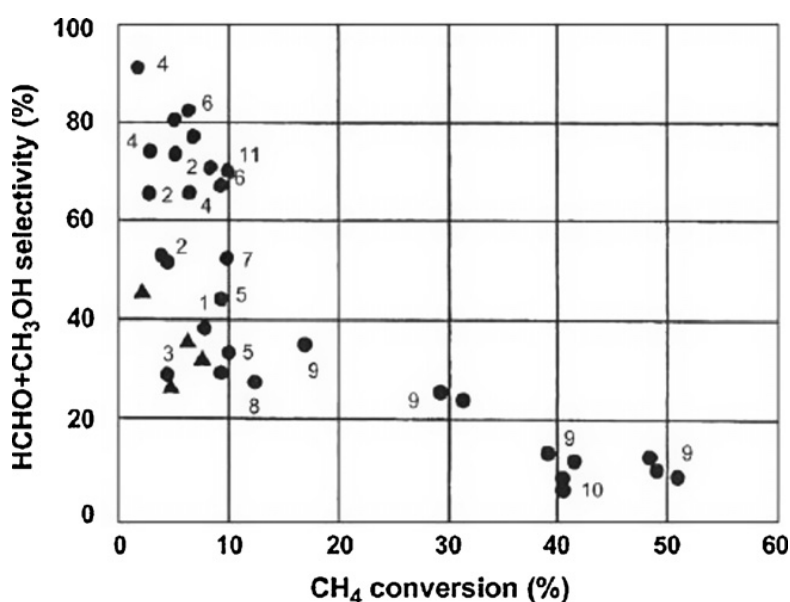

Fig. 1. Gas-phase partial oxidation of methane from several studies. From Tabata et al., 2002.

2.1.1 Heterogeneous catalytic partial oxidation of methane

At much lower pressures (i.e. as low as 1 atm.) than for gas-phase reactions, the catalyst becomes very important for the formation of oxygenates by direct partial oxidation of methane. In spite of the significant efforts that have been devoted to the development of active and selective catalysts, neither the product yield of C_1 oxygenates nor the complete mechanism of the reaction has been clarified (Navarro *et al.*, 2006; Alvarez-Galvan *et al.*, 2011). The selective O-insertion into CH_3 or other species obtained from the first H-abstraction of the CH_4 molecule is normally carried out on redox oxides of molybdenum and vanadium such as MoO_3 and V_2O_3 (Tabata *et al.*, 2002; Navarro *et al.*, 2006; Alvarez-Galvan *et al.*, 2011). In these catalytic systems, the catalytic performances are optimized by keeping isolated metal oxide structures isolated on a silica substrate in a slightly reduced state (Faraldos *et al.*, 1996; Chempath & Bell, 2007; Alvarez-Galvan *et al.*, 2011). The presence of these partially reduced oxides is believed to allow the redox cycles of catalytic surfaces to

proceed more rapidly and smoothly (Alvarez-Galvan et al., 2011). Most results reported to date were obtained at temperatures above 500 °C and formaldehyde has been the main oxidation product. When the reaction was carried out at 600 °C in the presence of excess water vapour on highly dispersed MoO_3/SiO_2, high selectivities (about 90 %) to methanol + formaldehyde oxygenates (or 20% yield) at methane conversions of 20-25% have been reported (Sugino et al., 2000). The improved selectivity which resulted from addition of water vapour was attributed to the formation of silicomolybdic acid (SMA: $H_4SiMo_{12}O_{40}$) over the silica surface.

The performance of V_2O_5/SiO_2 catalyst has been observed to change significantly by adding small amounts of radical initiator in the gas feed (Chempath & Bell, 2007). It was reported that up to 16% yields of oxygenates (methanol + formaldehyde) were obtained by adding about 1 vol.% NO to the feed in the presence of a low specific surface area V_2O_5/SiO_2 catalyst at 650 °C. The strong effect of NO was ascribed to a heterogeneous-homogeneous mechanism involving chain propagation of radical reactions in close vicinity of the catalyst bed (Chempath & Bell, 2007).

It has been reported that isolated molybdate species supported on silica have the highest specific activity and selectivity for the direct oxidation of methane to formaldehyde and a detailed mechanism of methane oxidation to formaldehyde was presented (Ohler & Bell, 2006; Chempath & Bell, 2007).

In addition to MoO_3/SiO_2 and V_2O_5/SiO_2 catalytic systems which have been most widely studied, many other metal oxides have also been investigated. It was observed that when 9.2% of various oxides were deposited onto silica, Ga_2O_3 and Bi_2O_3 which have medium electronegativities exhibited maximum conversion at 650 °C and $CH_4:O_2$ = 1:1 (Otsuka & Hatano, 1987; Navarro et al., 2006; de Vekki & Marakaev, 2009). The dependence of conversion on electronegativity was found to show extreme behaviour with maximum observed for gallium oxide (Otsuka & Hatano, 1987; de Vekki & Marakaev, 2009). In contrast, the selectivity for formaldehyde exhibited a steady increase with increase in the electronegativity of the additive elements. A possible arrangement of the oxides in decreasing order of selectivity was reported to be P_2O_5, WO_3, B_2O_3 (> 60%) > Sb_2O_3, Nb_2O_3, Al_2O_3, MgO (> 30 %), i.e. the acidic oxides are more selective than the basic oxides (de Vekki & Marakaev, 2009). A binary oxide mixture of Be and B supported on silica (i.e. B_2O_3-BeO/SiO_2) was found to exhibit optimum methane conversion and HCHO yield of 2.8% and 1%, respectively at 600 °C (de Vekki & Marakaev, 2009). The 1% yield corresponds to a selectivity of 35.7%.

Ono and co-workers have previously reported the partial oxidation of methane over various commercial silica catalysts and silica catalysts prepared from Si metal (Ono et al., 1993; Ono & Maruyama, 1996) and over ZSM-5 (MFI) zeolite catalysts (Kudo & Ono, 1997; Ono et al., 2000) at 600-650 °C and low CH_4 pressure of 8-8.5 torr using a closed circulation system and quartz reactor. These workers reported that H-ZSM-5 catalysts with SiO_2/Al_2O_3 ratio of 283 exhibited higher activities than the other commercial silicas. The rate was found to increase with increase in O_2 concentration. The selectivities to CH_3OH were also observed to be higher over NaZSM-5 while selectivities to HCHO were higher over H- and Cs-ZSM-5 catalysts. More recently, these workers investigated the partial oxidation reaction over Al doped silica catalysts and various commercial silica catalysts in a flow reactor system instead of a closed circulation system (Ono et al., 2008). They observed that not only HCHO
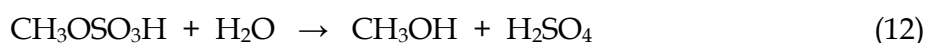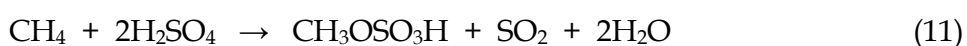
and CH_3OH but also other products such as C_2H_6, C_2H_4 and CO were formed over these catalysts and over a quartz reactor without catalysts. The presence of 0.1-0.5 wt% Al in silica enhanced methane conversions even at low O_2 concentrations. However, even over the Al/SiO_2 catalysts, the maximum selectivities to CH_3OH and HCHO obtained were only 3.5% and 7%, respectively. The enhancement of conversion observed over Al/SiO_2 catalysts was attributed to heterogeneous participation of O_2 on sites identified using MAS ^{27}Al NMR as isolated tetrahedrally coordinated Al ions.

Antimony oxides (i.e. Sb_2O_3 or Sb_2O_5) highly dispersed on silica were also reported to be selective for the partial oxidation of methane to HCHO (Zhang *et al.*, 2004). SbO_x/SiO_2 catalysts with SbO_x loadings up to 20 wt% exhibited good HCHO selectivity, even at temperatures as high as 650 °C and the more oxidized Sb_2O_5/SiO_2 catalysts were found to be more selective than the reduced Sb_2O_3 counterpart (Zhang *et al.*, 2004). A HCHO selectivity of up to 41% was obtained for the Sb_2O_5/SiO_2 catalyst at 600 °C but this was reduced to 18% when the reaction temperature was increased to 650 °C

It is unfortunate that experimental studies on the partial oxidation of methane to methanol over a solid catalyst have up till now not been successful. The yield of HCHO on MoO_3/SiO_2 and V_2O_5/SiO_2 which are most widely studied does not exceed 3-4% (de Vekki & Marakaev, 2009). Higher yields have been reported for other catalysts but these could not be confirmed due to poor reproducibility (Zhang *et al.*, 2003; de Vekki & Marakaev, 2009) . Otsuka and Wang (Otsuka & Wang, 2001) have attributed the difficulty in producing methanol at the high temperatures required for activation of methane to immediate decomposition or oxidation of methanol to formaldehyde and carbon oxides. New catalysts that are capable of activating methane at lower temperatures should therefore be developed in future investigations for the direct synthesis of methanol. This is obviously a great challenge in view of the strong C-H bond in methane.

2.1.2 Homogeneous liquid phase catalytic oxidation at low temperatures

The activation of methane at low temperatures has been investigated using homogeneous catalysis. Such low temperature activation of C-H bond does not involve radicals and may lead to more selective reactions than those promoted by heterogeneous catalysts operating at high temperatures. However, the main challenge lies in finding a catalyst system that exhibits suitable reactivity and selectivity while tolerating harsh oxidizing and protic conditions. Shilov and his co-workers pioneered investigations in this area in the 1970s when they showed that methane could be converted to methanol by Pt(II) and Pt(IV) complexes because these complexes do not oxidize methanol to carbon oxides, CO_x (Gol'dshleger *et al.*, 1972; Shilov & Shul'pin, 1997, 2000). Subsequently, organometallic approaches to functionalization of C-H bonds in methane became a subject mainly after the work of Periana et al. (Periana *et al.*, 1993) who proposed a process involving a Hg(II) complex in concentrated H_2SO_4 as the catalyst. Methyl bisulphate is formed as an intermediate and this is then readily hydrolyzed to produce methanol (Eqns. 11 & 12):

$$CH_4 + 2H_2SO_4 \rightarrow CH_3OSO_3H + SO_2 + 2H_2O \qquad (11)$$

$$CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4 \qquad (12)$$

A bipyrimidyl platinum (II) complex and Tl(III), Pd(II) and Au have also been used as oxidation catalysts instead of the mercury complex (Periana et al., 1998). By using the Pt (II) complex, a methane conversion of 90% was obtained with a 72% one-pass yield and 81% selectivity to methylbisulfate at 220 °C and 35 bar. Pd(II) salts are not as effective as Pt(II) complexes because of the reduction of Pd(II) to Pd(0) species and the slow re-oxidation of Pd(0) (Alvarez-Galvan et al., 2011).

The major disadvantages of using H_2SO_4 as a solvent system include the difficulty of separating the methanol product from the sulphuric acid and the need for expensive corrosion-resistant materials and periodic regeneration of spent H_2SO_4 (Alvarez-Galvan et al., 2011). A complete cycle would require the costly regeneration of concentrated H_2SO_4 as indicated in the proposed catalytic cycle shown in Fig. 2 as reported by Periana et al. (Periana et al., 1998). More recent contributions have presented and discussed the key challenges and approaches for the development of the next generation of organometallic, alkane functionalization catalysts based on C-H activation (Periana et al., 2004; Bergman, 2007). One question that remains to be answered is whether a process consisting of several steps such as the ones shown in Fig. 2 can be developed and operated in an economical way. Nevertheless, it illustrates a system where the rate constant for breaking the C-H bond in CH_4 on Pt is much higher than the C-H bond in the methyl bisulfate product (Holmen, 2009).
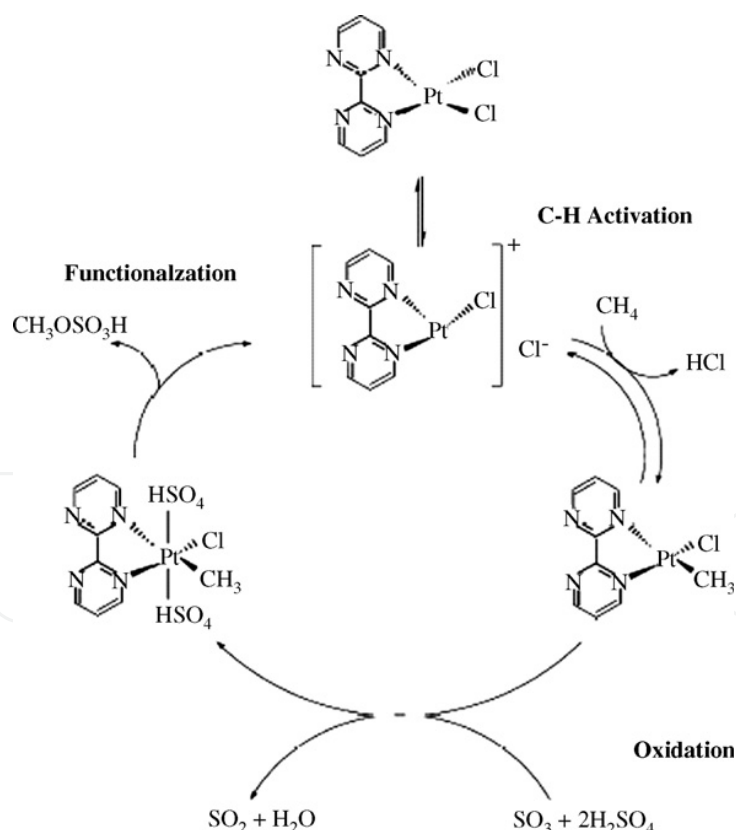

Fig. 2. Reaction mechanism for oxidation of methane to methyl bisulfate using a bipyrimidyl Pt(II) complex in concentrated sulphuric acid (Periana et al., 1998).

Schüth and co-workers (Palkovits et al., 2009) recently reported a new class of solid catalysts for the direct low-temperature oxidation of methane to methanol. The solid catalysts were

synthesized by immobilizing Pt(II) within a covalent triazine-based framework (CTF) containing bipyridyl fragments (Palkovits *et al.*, 2009). Such sold catalysts showed catalytic activity that are comparable to Periana's system at 215 °C in 30% oleum with selectivity to methanol above 75% and were stable over at least five recycling steps.

Most active catalytsts that operate at low temperature normally require the use of strong, environmentally unfriendly oxidizing agents such as SO_3, $K_2S_2O_8$ and $NaIO_4$ (Rahman *et al.*, 2011). Ishihara et al. (Rahman *et al.*, 2011) avoided the use of these oxidants in their very recent study of the synthesis of formic acid by partial oxidation of methane using H-ZSM-5 solid acid catalyst. The reaction was studied at 100 °C and 2.6 MPa pressure using the more benign hydrogen peroxide as the oxidant. They obtained a 13% yield and 66.8% selectivity of formic acid. Triphenylphosphene (Ph_3P) was used as a promoter in the reaction system. However, a fairly large amount of CO_2 was also observed as deep oxidation product. Another green chemical process, which uses gold nanoparticles on silica support as catalyst and ionic liquid (IL) as solvent, has just been reported for direct methane oxidation to methanol (Li *et al.*, 2011). The IL 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was used as the solvent, trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) as the acidic reagents and $K_2S_2O_8$ as the oxidant. The reaction was performed at 90 °C and 20 atm methane pressure. In the presence of 0.01g nano-Au/SiO_2 catalyst and 1g IL solvent, optimum methane conversion, selectivity and the yield to methanol obtained were 24.9%, 71.5% and 17.8%, respectively. The selectivity to CO_2 and H_2 obtained were 1.6% and 0.4%, respectively while the yield to these products were 0.6% and 0.1%, respectively. It was reported that 96.9% of the nano-Au/SiO_2 catalyst and the IL system could be recycled and the conversion of methane in the recycled system remained as high as 21.75%.

Metal-containing zeolites (particularly Fe-ZSM-5 and Cu-ZSM-5) have also been observed to show great potential as catalysts for the direct partial oxidation of methane to oxygenates at low or ambient temperatures. Fe-ZSM-5 has been shown to be active for this reaction although the less attractive N_2O was required to be used as the oxidant and this oxidant was observed to lead to the formation of a special type of reactive surface oxygen species known as α-oxygen (Panov *et al.*, 1990; Sobolev *et al.*, 1995; Dubkov *et al.*, 1997). Co-ZSM-5 was also shown recently to be active for the conversion of methane to oxygenates using oxygen (Beznis *et al.*, 2010b). The activity and selectivity were found to be dependent on the nature of cobalt species present in the materials. Cobalt in ion-exchange positions was observed to be selective towards formaldehyde while larger Co-oxide species (CoO and Co_3O_4) prepared by impregnation were selective towards methanol (Beznis *et al.*, 2010b). CuZSM-5 has also been shown to be active for the conversion of methane to methanol at 100 °C using molecular oxygen as oxidant with selectivity >98% (Groothaert *et al.*, 2005; Smeets *et al.*, 2005). Reactivity was found to occur at a small fraction of the total copper sites in the zeolite. The oxygen-activated active site in CuZSM-5 was correlated to a UV-Vis-NIR diffuse reflectance spectroscopy (DRS) absorption band at 22,700 cm^{-1} (Groothaert *et al.*, 2003). Additional information was provided by Woertink et al. (Woertink *et al.*, 2009) on the origin of Cu species using a combination of resonance Raman (rR) spectroscopy and density functional theory (DFT). These workers confirmed that the oxygen activated Cu core is defined as bent mono-(μ-oxo)dicupric cluster (Cu^{II}-O-Cu^{II}) (Woertink *et al.*, 2009). Subsequent investigations by Beznis et al. (Beznis *et al.*, 2010a) have now established a linear relationship between the intensity of the UV-Vis-NIR DRS charge transfer (CT) band at 22,700 cm^{-1} and the amount of methanol produced irrespective of the synthesis route used.

The absolute intensity of the 22,700 cm^{-1} CT band was observed to be always low indicating a low number of active sites in the samples. At least two Cu species were identified to be present in all Cu-ZSM-5 zeolites, namely Cu-O clusters dispersed on the outer surface of ZSM-5 and highly dispersed copper-oxo species inside the channels which are only a minority fraction in the sample (Beznis *et al.*, 2010a). Catalytic experiments and FTIR measurements of adsorbed pivalonitrile revealed that the Cu-O species on the outer surface are inactive for methanol production while the copper species inside the channels are responsible for the selective oxidation of methane to methanol (Beznis *et al.*, 2010a).

2.2 Biological catalytic oxidation at low temperatures

It is well known that methane monooxygenase enzymes (MMO) naturally catalyze the selective oxidation of methane to methanol in water at ambient or physiological conditions. (Labinger, 2004) Two types of this enzyme that provide solution to harnessing methane as an energy source and for synthesis of molecules required for life exists in nature, namely (i) the soluble methane monooxygenase (sMMO) which is a complex of iron found in the cytosol of some methane-metabolizing bacteria and (ii) particulate methane monooxygenase (pMMO) which is a methanotrophic integral protein and a complex of Cu (Kopp & Lippard, 2002; Balasubramanian & Rosenzweig, 2007; Himes & Karlin, 2009). pMMO is a membrane metalloenzyme produced by all methanotrophs and is composed of three protein subunits, pmoA, pmoB and pmoC, arranged in a trimeric $\alpha_3\beta_3\gamma_3$ complex (Balasubramanian *et al.*, 2010; Bollinger Jr., 2010). It is well understood that the soluble enzyme sMMO uses a co-factor containing an active di-iron cluster to bind and activate oxygen in the two-electron oxidation of methane to methanol. In other words, an essential feature of sMMO is an active site containing two iron centres in a non-heme environment (Sorokin *et al.*, 2010; Alvarez-Galvan *et al.*, 2011). This active di-iron centre and the possible mechanistic pathways for sMMO catalysis have been well characterized and studied by Lippard, Lipscomb and their co-workers (Merkx *et al.*, 2001; Kovaleva *et al.*, 2007; Tinberg & Lippard, 2011). The mechanism of sMMO which involves creation of a very strong oxidizing di-iron species that is able to attack a C-H bond in CH_4 is quite different from organometallic CH_4 activation. In contrast to the studies on sMMO, the nature of the pMMO metal active site has been very controversial and was not established until very recently when it was shown that the methane-oxidizing co-factor was a di-copper cluster in the soluble domains of the extramembrane pmoB subunit (Balasubramanian *et al.*, 2010; Bollinger Jr., 2010; Himes *et al.*, 2010). These newly discovered soluble proteins may now be useful tools for investigating the mechanism of oxygen activation and methane hydroxylation at a copper centre (Bollinger Jr., 2010). This new discovery of a di-copper co-factor in pMMO is in agreement with earlier report of direct methane activation by mono-(µ-oxo)dicopper cores in inorganic Cu-ZSM-5 zeolite catalysts (Woertink *et al.*, 2009). Both of these new discoveries appear to have the potential to bring our understanding of copper-mediated methane oxidation to the level achieved for the better studied di-iron sMMO and relevant inorganic models (Bollinger Jr., 2010).

A chemical system that is capable of oxidizing CH_4 at ambient conditions like MMOs would be highly desirable. Complexes mimicking the structural organisation and spectral features of MMO have been reported but di-iron functional synthetic models capable of oxidizing

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methane have not yet been created in spite of considerable efforts (Tshuva & Lippard, 2004). However, previous studies have indicated that metallophthalocyanines (MPc), especially iron phthalocyanines (FePc) are good catalysts for clean oxidation processes (Sorokin *et al.*, 2008; Sorokin *et al.*, 2010; Alvarez-Galvan *et al.*, 2011). In particular, it has been shown that μ-nitrido diiron phthalocyanine complexes (Fig. 3) possess remarkable catalytic properties (Sorokin *et al.*, 2008; Sorokin *et al.*, 2010).
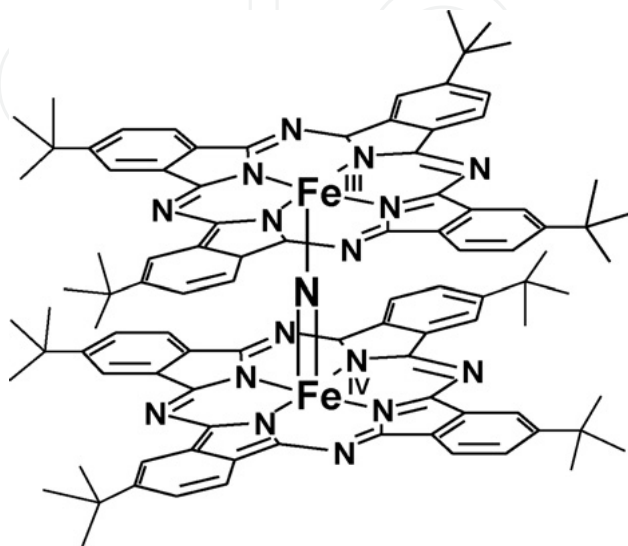

Fig. 3. Structure of μ-nitrido bridged diiron tetra-tert-butylphthalocyanine (Sorokin *et al.*, 2010).

Using ^{13}C and ^{18}O labelling experiments, μ-nitrido diiron tetra-tert-butylphthalocyanine, $(FePc^tBu_4)_2N$ (Fig. 3) supported on silica was shown to activate H_2O_2 to oxidize methane in water at 25-60 °C to methanol, formaldehyde and formic acid under the heterogeneous conditions (Sorokin *et al.*, 2008; Sorokin *et al.*, 2010). The use of H_2O_2 as the clean oxidant, water as the clean reaction medium and easily accessible solid catalyst makes this approach to be green and practical. These features together with the relevance of the binuclear structure of bio-inspired complex to biological oxidation are of great importance from both practical and fundamental points of view. Experimental data indicated that the stable μ-nitrido diiron tetra-tert-butylphthalocyanine complex operates via oxo-transfer mechanism involving a high-valent diiron oxo species which acts as a powerful oxidant in the methane oxidation reaction (Sorokin *et al.*, 2008; Sorokin *et al.*, 2010). The heterolytic cleavage of the O-O bond in $Fe^{IV}NFe^{III}OOH$ complex and the formation of very strong oxidizing $Fe^{IV}NFe^V=O$ species are favoured in the presence of acid by the protonation of peroxide oxygen (Sorokin *et al.*, 2008; Alvarez-Galvan *et al.*, 2011). Thus, significant improvement in catalytic activity was observed in the presence of 0.075-0.1 M H_2SO_4 (Sorokin *et al.*, 2008; Sorokin *et al.*, 2010).

Otsuka and Wang (Wang & Otsuka, 1994, 1995; Otsuka & Wang, 2001) have previously shown $FePO_4$ to exhibit a unique catalytic activity when H_2 is added to methane plus oxygen feed at atmospheric pressure. On this catalyst, both methane conversion and selectivity to methanol were enhanced in the presence of H_2 as a reductant. However, only up to 25.7% and 46% selectivities to methanol and formaldehyde, respectively, were obtained at very low conversion of 0.51% even in the presence of hydrogen. Only a trace

amount of methanol was obtained during the oxidation of methane in the absence of hydrogen (Wang & Otsuka, 1994, 1995).

The biochemical formation of methanol by the oxidation of methane was recently investigated using a biocatalyst based on the cells of the bacteria *Methylosinus sporioum B-2121* (Razumovsky *et al.*, 2008). The biocatalyst was suspended in a medium and immobilized in poly(vinyl alcohol) cryogel. It was observed that the use of the immobilized biocatalyst made it possible to enhance the productivity of the process more than 5-fold compared to that of the free cells and to achieve the highest methanol concentration of 62±2 mg L^{-1} in the medium (Razumovsky *et al.,* 2008). A brief review of the classification, characteristics and distribution of methanotrophic bacteria and discussion of the approach of biocatalytic mechanism of the selective oxidation of methane to methanol was presented recently by Liu et al. (Liu *et al.*, 2007).

2.3 Relevance of oxidative aromatics methylation to methane-to-methanol conversion

Recent investigations in our laboratory have demonstrated the formation of methanol intermediate in the oxidative methylation of aromatics in the presence of large excess of methane in a high pressure batch reactor at 400 °C (Adebajo *et al.*, 2000; Adebajo *et al.*, 2004). It appears that the methanol intermediate is formed homogeneously in the gas phase since it was only formed as the major product in the absence of solid catalyst. When zeolite catalysts were introduced into the reactor, the methanol was not detected but was used to methylate the aromatics reactants to produce methylated aromatic products or converted directly to aromatics in the absence of aromatic reactants (Adebajo *et al.*, 2000; Adebajo *et al.*, 2004). Gas phase analysis of reaction products failed to detect any CO_2, CO, H_2, or C_{2+} non-aromatic hydrocarbon products (Adebajo, 1999; Adebajo *et al.*, 2004). Thus, there appears to be no significant complete or incomplete combustion of methane due to failure to detect any CO or CO_2 deep oxidation products in the gas products. This observation implies that it is possible to inhibit the complete oxidation of methane to deep oxidation products in the presence of an additive such as aromatics. This observation is similar to earlier observation that the presence of small amounts of hydrocarbon additives (especially ethane) lowered the initiation temperatures of partial oxidation of methane to methanol and increased the methanol selectivity and yield (Gesser *et al.*, 1985; Fujimoto, 1994). This observation therefore extends the significance of the oxidative methylation reaction and we had earlier suggested that this avenue could be explored further for optimisation of the conversion of methane to methanol (Adebajo *et al.*, 2004).

This work has also demonstrated the possibility of achieving in-situ methylation using methane by combining methanol synthesis by partial oxidation of the methane with methylation of aromatics. This concept is very similar to earlier demonstration by Gesser et al. that methane partial oxidation could be combined with methanol conversion to gasoline in a two-stage continuous flow reactor (Yarlagadda *et al.*, 1987). In the first stage of the reactor, methane and oxygen reacted to produce methanol homogeneously while the methanol was converted by HZSM-5 catalyst in the second stage to produce aromatics (the major components of the liquid products), C_{3+} hydrocarbons, carbon oxides and water (Yarlagadda *et al.*, 1987).

3. Conversion of carbon dioxide to oxygenates

3.1 Recent advances in the catalytic conversion of carbon dioxide to oxygenates

Carbon dioxide is a renewable, non-toxic, abundant (cheap) and inflammable carbonaceous raw material. It is therefore considered attractive as an environmentally friendly chemical reagent or feedstock for the production of a wide range of value-added chemicals and fuels. However, CO_2 is rather inert and its chemical transformations are thermodynamically highly unfavourable. This is illustrated in Figure 4 (Zangeneh *et al.*, 2011). Its inertness is due to its being the most oxidized state of carbon. In other words, it is a raw material in its lowest energy level, thus constituting a major obstacle in establishing industrial processes for its conversion. A large input of energy is therefore required for its transformation into useful chemicals. Nevertheless, several exothermic reactions of CO_2 are known and have been investigated and many reviews of such transformations have been published recently (Jessop *et al.*, 2004; Jessop, 2007; Sakakura *et al.*, 2007; Yu *et al.*, 2008; Olah *et al.*, 2009; Zangeneh *et al.*, 2011). Reduction is the only possible route for the conversion of CO_2 since it is the most oxidized form of carbon. The chemical reduction of CO_2 can be either homogeneous or heterogeneous reduction. According to Sakakura et. al. in their review (Sakakura *et al.*, 2007), four main methodologies for transforming CO_2 into useful chemicals involve:

1. Using high-energy starting materials such as hydrogen, unsaturated compounds, small-membered ring compounds and organometallics.
2. Choosing oxidized low-energy synthetic targets such as organic carbonates.
3. Shifting the equilibrium to the product side by removing a particular compound.
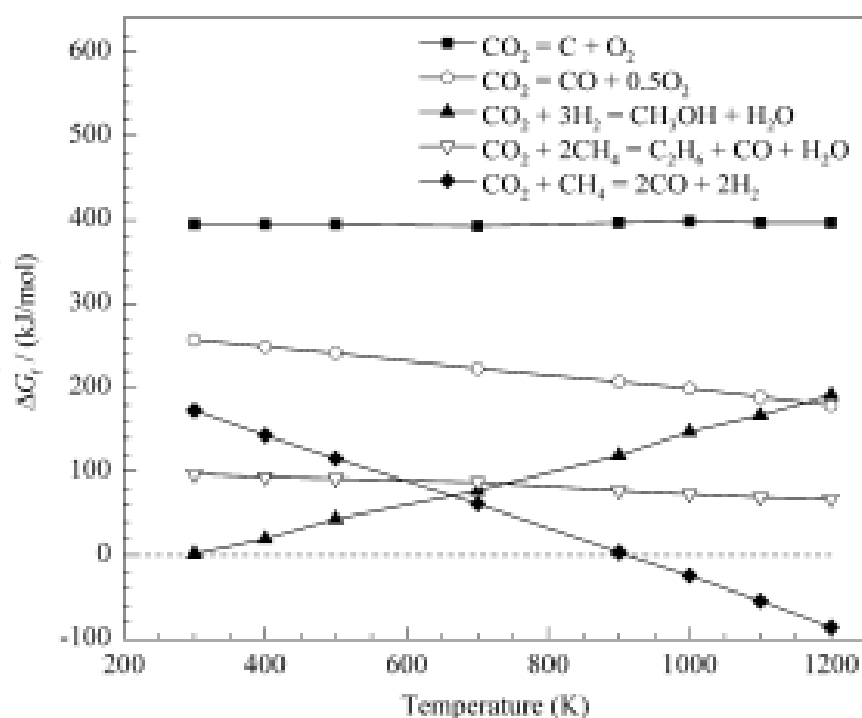4. Supplying physical energy such as light or electricity.

Fig. 4. Thermodynamics of some reactions of carbon dioxide ((Zangeneh *et al.*, 2011).

This review will cover mainly hydrogenation of CO_2 using homogeneous and heterogeneous catalytic and biocatalytic pathways. Photocatalytic and electrochemical reduction of CO_2 will also be discussed.

3.1.1 Homogeneous catalytic hydrogenation of carbon dioxide

Transition metal complexes have been widely used for the homogeneous catalytic hydrogenation of CO_2. The mild conditions used for these reactions make the partial hydrogenation of CO_2 to formic acid and derivatives highly feasible (Eqn. 13) while further reduction of the formic acid is more difficult and only limited examples of formation of other products such as methanol and methane are known (Zangeneh *et al.*, 2011):

$$CO_2 + H_2 \rightarrow HCOOH_{(l)} (\Delta H^0_{298K} = -31.8 \text{ kJ mol}^{-1}) \tag{13}$$
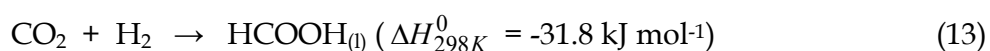
Homogeneous hydrogenation of CO_2 has been attracting a lot of interest and the major focus has been to develop active and selective catalysts for the production of valuable organics from this cheap and abundant resource. Two comprehensive reviews of advances in the developments of catalysts for homogeneous hydrogenation of CO_2 to formic acid, formamides, formates, methanol, methane and oxalic acid were published in 2004 and 2007 (Jessop *et al.*, 2004; Jessop, 2007). The earlier review published in 2004 (Jessop *et al.*, 2004) covered the advances in the field since 1995. This earlier review indicated that highly active and efficient catalysts which are mainly transition metal complexes had been developed for the homogeneous hydrogenation of CO_2 to formic acid and its derivatives such as formamides (Jessop *et al.*, 2004). These metal complexes are usually hydrides or halides with phosphines as natural ligands and complexes of Rh and Ru proved to be the most active metals (Jessop *et al.*, 2004; Zangeneh *et al.*, 2011). Such active catalysts were developed for CO_2 hydrogenation in water, organic solvents, supercritical CO_2 and ionic liquids (Jessop *et al.*, 2004). The 2004 review also indicated that the range of formamides that can be produced in high yield had expanded greatly. However, as of the time of this earlier review, very limited work had been done on the development of active and selective homogeneous catalysts for the production of other oxygenates (such as methyl formate, acetic acid, methanol and ethanol) and methane (Jessop *et al.*, 2004). This is so because these other products are more difficult to prepare by the homogeneously hydrogenation reaction. The synthesis of oxalic acid by this homogeneously catalyzed reaction was not yet reported prior to the 2004 review (Jessop *et al.*, 2004).

A novel non-metal-mediated homogeneous hydrogenation of CO_2 to methanol was recently reported by Ashley et al. (Ashley *et al.*, 2009) This was carried out using a Frustrated Lewis pairs (FLP)-based non-metal-mediated process at low pressures (1-2 atm) and a reaction temperature of 160 °C (Ashley *et al.*, 2009). In such FLP systems, the steric environment imposed on the donor and acceptor atoms by the substituents prevents a strong donor-acceptor interaction. The first step in the process involves heterolytic activation of hydrogen and subsequent insertion of CO_2 into a B-H bond of 2,2,6,6-tetramethylpiperidine (TMP) and $B(C_6F_5)_3$ to form $[TMPH][HB(C_6F_5)_3]$ complex (Ashley *et al.*, 2009). Introduction of CO_2 then produced the formatoborate complex $[TMPH]-[HCO_2B(C_6F_5)_3]$. Subsequent selective

distillation at 100 °C then resulted in the decomposition of the intermediate complex to produce methanol (Ashley *et al.*, 2009).

3.1.2 Heterogeneous catalytic hydrogenation of carbon dioxide

Heterogeneous catalysis is technically more favourable than the homogeneous reaction in terms of the reactor design and the stability, separation, handling and recycling of the catalysts. In spite of these practical benefits, there has only been limited number of compounds that have been synthesized from CO_2 through heterogeneous catalytic pathways and the equilibrium composition is complicated by the simultaneous chemical equilibria (Zangeneh *et al.*, 2011).

Metal-catalyzed heterogeneous hydrogenation of carbon dioxide generally produces methanol or methane directly depending on the reaction conditions. The syntheses of methanol and dimethylether (DME) are generally the most important heterogeneous hydrogenation reactions of CO_2 because of the potential of these oxygenates to become future energy carriers and major feedstock for petrochemical industries through C_1 chemistry (Lunsford, 2000; Olah *et al.*, 2009). Methanol is currently commercially produced on a large scale over heterogeneous catalysts from syngas (Eqns. 5 & 6) obtained from non-renewable natural gas or coal. Syngas contains mainly CO and H_2 along with a small amount of CO_2.

It is well agreed that the $Cu/ZnO/ZrO_2$ catalysts used for syngas production is also active for the direct synthesis of methanol from CO_2 and H_2 and in the steam reforming of methanol (Yu *et al.*, 2008; Olah *et al.*, 2009; Zangeneh *et al.*, 2011). This basic catalyst is often modified by addition of different oxides to improve its activity and stability. Apart from ZrO_2, other irreducible oxides such as Al_2O_3, TiO_2 and Ga_2O_3 have been investigated (Slocynski *et al.*, 2006). The effects of several other metal (e.g. boron, chromium, tungsten and manganese) and metal oxide (e.g. VO_x, MnO_x and MgO) additives have also been reported (Slocynski *et al.*, 2006; Yu *et al.*, 2008). Pd supported on several basic oxides including La_2O_3 and lithium-promoted Pd on SiO_2 have also been found to exhibit considerable activity and selectivity for methanol synthesis (Lunsford, 2000).

DME can be produced by dehydration of methanol (Eqn. 14) or directly from syngas over bifunctional catalysts (Lunsford, 2000; Arena *et al.*, 2004; Sun *et al.*, 2004). The direct synthesis of DME by CO_2 hydrogenation over bifunctional catalysts is a two-step process involving methanol synthesis followed by in situ dehydration of methanol (Eqn. 14) (Arena *et al.*, 2004; Sun *et al.*, 2004). Thus, the bifunctional catalysts contain functionally independent catalysts comprising of the methanol forming component based on CuO-ZnO and a methanol dehydration component based on suitable zeolites e.g. HZSM-5 and HY zeolites (Arena *et al.*, 2004; Sun *et al.*, 2004).

$$2CH_3OH \ \rightarrow \ CH_3OCH_3 \ + \ H_2O \ (\Delta H_{298K}^0 \ = -23.4 \text{ kJ mol}^{-1}) \qquad (14)$$
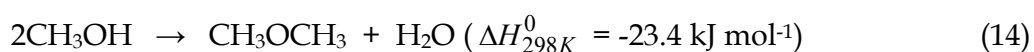
Very recently, Zhang et al. (Zhang *et al.*, 2009) reported that carbon nanotubes (CNTs) or CNT-based materials doped with some transition metals such as Co, Pd, etc., exhibited good catalytic activity and selectivity for some catalytic processes related to adsorption-activation

and spillover of hydrogen such as CO or CO_2 hydrogenation to alcohols. However, further detailed investigations of the interactions between CNTs and catalytically active host components and between CNTs and reactant molecules are needed in order to gain a better understanding of the nature of the promoter action by CNTs (Zhang *et al.*, 2009).

3.1.3 Photocatalytic reduction of carbon dioxide

Direct photoreduction of CO_2 has recently attracted much attention and many researchers have shown that CO_2 can be reduced in water vapour or solvent by photocatalysts. Photocatalytic systems utilizing semiconductor materials appear to be the most feasible of all the photocatalytic systems and processes that have been investigated. Inoue et al. (Inoue *et al.*, 1979) first reported the possibility of reducing carbon dioxide by photocatalysis in aqueous medium to produce methanol, formic acid, formaldehyde and trace amounts of methane. These workers used photosensitive semiconductors such as TiO_2, WO_3, ZnO, CdS, GaP and SiC. The efficient photoreduction of carbon dioxide in aqueous medium is one of the most challenging tasks due to the rather low solubility of CO_2 at ambient conditions (Sasirekha *et al.*, 2006). TiO_2 has been shown to be the most suitable semiconductor that offers the highest light conversion efficiency due to its excellent physico-chemical properties (Sasirekha *et al.*, 2006). This semiconductor is non-toxic and possesses high stability towards photo-corrosion and relatively favourable band gap energy. Thus, TiO_2 is currently the most widely studied. Two review papers were recently published on the photocatalytic reduction of CO_2 over TiO_2-based photocatalysts (Dey, 2007; Kočí *et al.*, 2008). One problem with TiO_2 is that their photosensitivity is limited to the ultraviolet (UV) region with absorption of only about 4-5% of solar energy due to their relatively large band gap, thus resulting in low quantum efficiencies. A lot of effort has therefore focused on doping TiO_2 with various metals and metal oxides in order to extend their absorption into the visible region (Slamet *et al.*, 2005; Wang *et al.*, 2005; Sasirekha *et al.*, 2006; Wu, 2009; Fan *et al.*, 2011; Wang *et al.*, 2011). In spite of these efforts, both recent reviews (Dey, 2007; Kočí *et al.*, 2008) indicate that the photocatalytic reduction of CO_2 is still in its infancy and that many questions still remain to be answered such as (i) how can the photocatalytic efficiency be improved?, (ii) what is the most suitable form of photocatalysts?, and (ii) how can the utilization of solar energy be greatly increased? Another review suggested that the efficiency of the photocatalytic process for CO_2 reduction can be improved by choosing semiconductors with suitable band-gap energies, developing suitable reductant and optimizing operating conditions such as temperature, pressure, light intensity and operating wavelength (Usubharatana *et al.*, 2006). This other review also suggested that further research should focus on the potential and economics of solar reactor and their design (Usubharatana *et al.*, 2006).

In addition to TiO_2-based photocatalysts, $InTaO_4$ was recently reported to exhibit outstanding photocatalytic reduction of CO_2 into methanol under visible light irradiation (Pan & Chen, 2007; Chen *et al.*, 2008). More recently, the activities of a bifunctional N-doped $InTaO_4$ photocatalyst for the photocatalytic reduction of CO_2 to methanol was demonstrated (Tsai *et al.*, 2011). The photocatalyst was prepared by doping InTaO4 with nitrogen and incorporating a nanostructured Ni@NiO core-shell co-catalyst. Nitrogen doping produced visible-light-responsive photocatalytic activity which further enhanced absorbance. Thus,

methanol yield was enhanced when compared with undoped ones and the rate of the photoreaction was found to increase with visible light irradiation time (Fig. 5). Moreover, the introduction of the co-catalyst enhanced absorbance and methanol yield even further (Fig. 5) and efficiently prevented electron-hole recombination that would otherwise be caused by electrons and holes separated from the crystal (Tsai *et al.*, 2011).
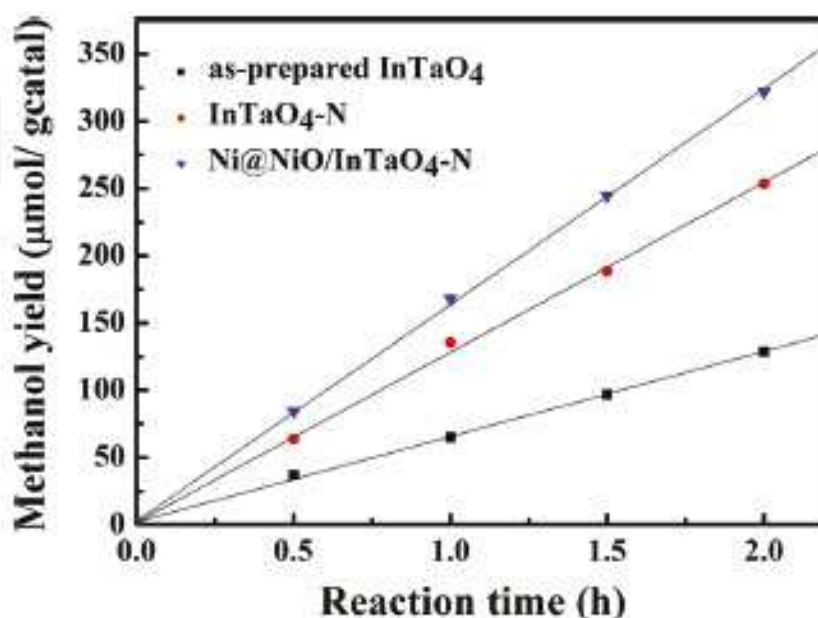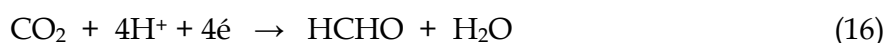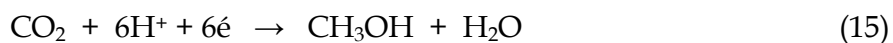

Fig. 5. The variation of methanol yield with reaction time for the as-prepared $InTaO_4$ and the N-doped and co-catalyst treated $InTaO_4$-based samples (Tsai *et al.*, 2011).

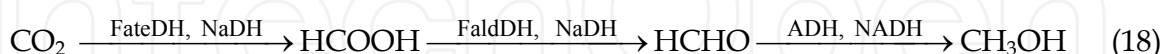### 3.1.4 Electrochemical reduction of carbon dioxide

Direct electrochemical reduction of CO_2 to produce methanol can be achieved but is rather kinetically complex and needs effective electrocatalysts (Olah *et al.*, 2009). Generally, during the electrochemical reduction of CO_2 to methanol, formaldehyde and formic acid are also produced as shown in Equations 15-17 (Olah *et al.*, 2009). Photoelectrochemical reduction of CO_2 to methanol has also been demonstrated by the use of solar energy at a semiconductor electrode such as p-GaP and such reductive reaction using light energy has been reported to show promise (Barton *et al.*, 2008). Secondary treatment steps for the conversion of formaldehyde and formic acid by-products to methanol over suitable solid catalysts have been developed to overcome the difficulties associated with the formation of product mixtures in the electrochemical reduction of CO_2. Such secondary treatment steps make it possible to significantly increase the overall efficiency of the electrochemical reduction of CO_2 to methanol. However, it is more desirable to develop more effective catalysts that are capable of increasing the selective electrochemical reduction of CO_2 to methanol so as to eliminate or reduce the secondary treatments.

$$CO_2 + 6H^+ + 6\acute{e} \rightarrow CH_3OH + H_2O \qquad (15)$$

$$CO_2 + 4H^+ + 4\acute{e} \rightarrow HCHO + H_2O \qquad (16)$$

$$CO_2 + 2H^+ + 2\acute{e} \rightarrow HCOOH \qquad (17)$$

The electrochemical reduction of carbon dioxide alone has also been found to produce oxalic acid and its derivatives such as glycolic acid, glyoxylic acid, etc., but these reactions have low selectivities (Sakakura *et al.*, 2007).

3.2 Biocatalytic or enzymatic conversion of carbon dioxide

Heterogeneous catalytic, photocatalytic and electrocatalytic routes which are most commonly used for reduction of carbon dioxide with hydrogen to produce methanol and other oxygenates require high temperatures and pressures since the reaction is not thermodynamically favoured at ambient conditions. The selectivity and yields of the desired products are also rather low. Most of the metallic catalysts also require highly pure feedstocks for them to maintain their activities. Thus, the thermochemical reduction of carbon dioxide is not economically viable for industrial use. In contrast to these traditional pathways, novel biocatalytic routes for reduction of CO_2 at ambient conditions have been demonstrated. Such biocatalytic reductions are attractive because they can be very efficient and can make use of low purity reactants and tolerate many impurities that are toxic to chemical catalysts (Lu *et al.*, 2010). For example, a combination of formate dehydrogenase (FateDH), formaldehyde dehydrogenase (FaldDH) and alcohol dehydrogenase (ADH) was used in sequential reduction of CO_2 to methanol (Obert & Dave, 1999; Jiang *et al.*, 2004; Wu *et al.*, 2004). Reduced nicotinamide adenine dinuncleotide (NADH) was used as the terminal electron donor for the enzymatic reaction. This sequential enzymatic conversion pathway is represented by Eqn. 18 below. In a later investigation by Lu et al. (Lu *et al.*, 2006), FateDH immobilized in a novel alginate-silica hybrid gel was used as the biocatalyst to convert CO_2 into formic acid in the presence of reduced NADH as the terminal electron donor (Eqn. 19). The gel was prepared by in-situ hydrolysis and polycondensation of tetramethoxysilane in alginate solution followed by Ca^{2+}-induced gelation (Lu *et al.*, 2006). The reduction of CO_2 by FateDH encapsulated in alginate-silica hybrid gel beads resulted in the high-yield production of formic acid (95.6%) and the relative activity of the immobilized FateDH after 10 cycles was as high as 69% (Lu *et al.*, 2006). Acetogenic bacteria microbes have also been investigated (Song *et al.*, 2011) as biocatalysts for the electrochemical reductive conversion of CO_2 with efficiency of 80-100% in phosphate buffer solution (pH 7) at -0.58 V vs NHE which was near the equilibrium potential of CO_2/formate. Direct bacterial use for electrochemical CO_2 conversion could eliminate expensive enzyme purification steps and widens the choice of catalysts to include the naturally developed and optimized microorganisms (Song *et al.*, 2011).

$$CO_2 \xrightarrow{\text{FateDH, NaDH}} HCOOH \xrightarrow{\text{FaldDH, NaDH}} HCHO \xrightarrow{\text{ADH, NADH}} CH_3OH \quad (18)$$

$$CO_2 + NaDH \xrightarrow{\text{FateDH}} HCOOH + NAD^+ \quad (19)$$

One challenge for the realization of biocatalytic reduction of CO_2 at large scale is the efficiency of the reaction; the reported reaction rates and equilibrium yields are generally low. There is therefore need to develop faster and more efficient biocatalytic systems. Thus, recent research has been focusing on discovery of new enzymes and engineering of the reaction systems for improved catalytic efficiency (Baskaya *et al.*, 2010). Thus, Baskaya et al. (Baskaya *et al.*, 2010) recently investigated the sequential enzymatic conversion of CO_2 to methanol from a thermodynamic point of view with a focus on factors that control the reaction equilibrium. Their results showed that the enzymatic CO_2 conversion is highly sensitive to the pH of the reaction solution and that it is possible to shift the biological

metabolic reactions to favour the synthesis of methanol by conducting the reactions at low pHs (e.g. pH of 5 or 6) and ionic strengths and at elevated temperatures (Baskaya *et al.*, 2010). However, it may be very difficult to reach such favourable conditions with the currently available biocatalysts since native enzymes that catalyze such reactions tend to be denatured and inactivated at acidic and elevated temperatures (Baskaya *et al.*, 2010).

Another major concern for biocatalytic CO_2 conversions is the source of chemical energy used to drive the reactions forward. Lu et al. (Lu *et al.*, 2010) are of the opinion that since the reduced form cofactor NADH carries the energy required for the reactions in the enzymatic reduction of CO_2, a solar power driven regeneration of the co-factor would provide the avenue to use solar energy for production of chemicals and fuels. Thus, these workers believe that the integration of multi-enzyme systems on nanostructured electrodes will provide a unique approach to harvesting solar energy in the forms of renewable chemicals and fuels (Lu *et al.*, 2010).

4. Conclusions

It is evident that the direct conversion of methane to oxygenates such as methanol, formaldehyde and acetic has great potential for producing liquid fuels and petrochemicals while simultaneously reducing the global warming effect of the greenhouse gas. However, the major challenge that needs to be overcome before this can be realised is the difficulty in activating the strong C-H bond in methane at relatively lower temperatures and pressures to make the process economically viable and the problem of achieving high methane conversions without reducing product selectivities at these mild conditions. The homogeneous catalytic conversion of methane at low temperatures is thus highly desirable since the low temperature of activation of C-H bond does not involve radicals and may lead to more selective reactions than those promoted by heterogeneous catalysts operating at high temperatures. However highly active and selective catalysts under the strong oxidizing and protic conditions in which they operate still need to de developed in future investigations. Moreover, these harsh conditions are undesirable because they are environmentally unfriendly. Although, some other catalytic systems that do not operate under such strong oxidizing conditions have been used but their activities and product selectivities still need significant improvement. Among the catalysts that do not require harsh oxidizing conditions, metal-containing zeolites, especially Fe-ZSM-5 and Cu-ZSM-5, have been observed to show great potential for catalytic conversion of methane to oxygenates at low or ambient temperatures. In particular, since the active site in the highly selective CuZSM-5 has recently been identified to be a bent mono-(μ-oxo)dicopper cluster, its catalytic activity and selectivity for the partial methane oxidation should be optimized in future investigations. The biocatalytic oxidation of methane using MMOs or a chemical system that is capable of oxidizing methane at ambient conditions like MMOs is most highly desirable but such biocatalytic systems with desired high activities and selectivities are yet to be created in spite of considerable efforts. Nevertheless, now that the active sites in both pMMO and Cu-ZSM-5 have been identified to be soluble di-copper clusters, efforts should be directed to more detailed investigations of the mechanisms of copper-mediated oxygen activation and methane hydroxylation. A deeper understanding of the mechanism of this important reaction that will be gained from such studies will also underpin the design of novel catalytic systems with high activities and product selectivities, especially now that the active centres are known.

Important observations from studies in our laboratory indicate that it is possible to inhibit the complete oxidation of methane to deep oxidation products in the presence of an additive such as aromatics. It is suggested that this avenue should be explored further for optimizing the conversion of methane to methanol. Our work has also demonstrated the possibility of achieving in-situ methylation or production of aromatics using methane by combining methanol synthesis by partial methane oxidation with methylation of aromatics or methanol-to-aromatics conversion.

Carbon dioxide is a renewable, non-toxic, abundant and inflammable carbonaceous raw material and its reduction therefore also has great potential for both reduction of greenhouse gas emissions to some extent and production of value-added chemicals and fuels. Reduction is the only possible pathway for conversion of CO_2 since it is the most oxidized form of carbon. All types of catalysts (homogeneous, heterogeneous, photocatalysts, electrocatalysts and biocatalysts) are generally observed to play a major or important role in such reduction reactions. However, CO_2 is rather inert and its catalytic reduction and other transformations are highly kinetically and thermodynamically unfavourable. The greatest challenge common to all the different types of catalyst systems therefore lies in developing highly efficient and selective catalysts that do not undergo rapid deactivation and in overcoming the thermodynamic barrier. The thermodynamic limitation could be overcome by adopting either a physical approach (e.g. by using a suitable membrane reactor) or a chemical approach (e.g. by conversion to more stable products). The economic viability of the hydrogenation reactions depends on the sources of energy and hydrogen, thus these should also be taken into consideration in future investigations.

Among the different types of catalytic systems that have been investigated, photocatalytic reduction of CO_2 is highly attractive in view of the utilization of solar energy but the efficiency of the process still needs significant improvement by carefully choosing semiconductors with suitable band gap energy, developing appropriate reductants and optimizing reaction conditions. However, a recently reported bifunctional N-doped $InTaO_2$ photocatalyst containing a nanostructured Ni@NiO core-shell co-catalyst shows some great potential. Thus, other novel photocatalytic systems could be developed using this strategy in future investigations. The biocatalytic pathways for reduction of CO_2 are most attractive because they can operate at ambient temperatures and therefore highly economical. These biocatalytic routes can also be very efficient and can make use of low purity reactants and tolerate many impurities that are toxic to chemical catalysts. However, the reported reaction rates and equilibrium yields are still generally low, thus the efficiency of the reaction still requires significant improvement before it can operate at large scale. Faster and more efficient biocatalytic systems should therefore be developed. Another challenge for biocatalytic conversion is the source of chemical energy for driving the reaction forward. Some workers (Lu *et al.*, 2010) have suggested that the integration of multi-enzyme systems on nanostructured electrodes will provide a unique approach to harvesting solar energy in the forms of renewable chemicals and fuels.

In short, the goal of catalytically and/or biocatalytically converting methane and carbon dioxide to value-added chemicals and fuels while simultaneously reducing greenhouse emissions is far from being realised in terms of efficiency and economic and commercial viability. Nevertheless, the progress that has been made so far cannot be undermined.

5. Acknowledgment

6. References

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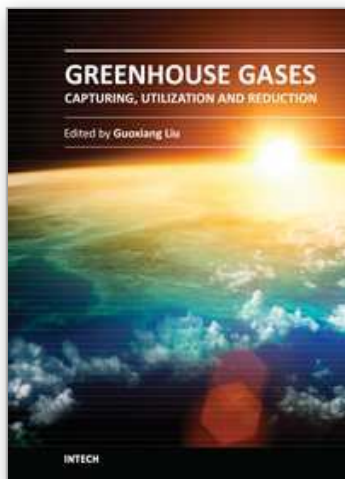
Greenhouse Gases - Capturing, Utilization and Reduction

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Understanding greenhouse gas capture, utilization, reduction, and storage is essential for solving issues such as global warming and climate change that result from greenhouse gas. Taking advantage of the authors' experience in greenhouse gases, this book discusses an overview of recently developed techniques, methods, and strategies: - Novel techniques and methods on greenhouse gas capture by physical adsorption and separation, chemical structural reconstruction, and biological utilization. - Systemic discussions on greenhouse gas reduction by policy conduction, mitigation strategies, and alternative energy sources. - A comprehensive review of geological storage monitoring technologies.

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