

Homogeneous catalytic systems for selective oxidation of methane: state of the art

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Homogeneous catalysts for methane oxidation are of a particular interest from scientific and economic points of view. The results show a great potential for activation and functionalization of CH bonds of unreactive methane. There are still gaps in the knowledge of how to rationally design catalysts for this process. In this paper state-of-the-art. in methane oxidation homogenous catalysis is presented.

Keywords: alkane functionalization, methane, methanol, catalytic systems, homogeneous catalytic systems.

INTRODUCTION

Hydrocarbons, like methane, are some of the most available energy sources, unreactive and inert to most reagents, as we know it. These properties have limited their usefulness. Methane is the main constituent of natural gas, the simplest alkane and the most abundant member of the hydrocarbon family.

Because of the enormous reserves of natural gas in the world ($1.8 \times 10^{14} \text{ m}^3$)¹, there is a strong economic incentive to develop a process that would convert methane into products such as syngas^{2, 3}, nanomaterials and hydrogen⁴⁻⁸ valuable chemicals or to more easily transported liquid fuel⁹.

Although methane can be applied as vehicle fuel, a good methane adsorbent is needed. Activated carbons are mainly investigated as a suitable material¹⁰⁻¹³.

Nevertheless methane is often difficult to use, because transportation of methane gas or even liquefied natural gas is expensive and dangerous.

Methane becomes a principal component of modern chemistry and, as such, plays a central role in our quality of life. As one of the most versatile raw material it is consumed by industry and household as an energy source. Methane can be a raw material for the chemical industry for the production of valuable chemicals, for example methanol. It has increasingly been viewed as a dependable and clean transportation fuel, powering urban mass transportation systems reliably and safely.

Catalytic oxidation of methane to produce oxygenates remains one of the challenges in catalysis field, and has attracted considerable interest since the 1907s due to its scientific and industrial significance. However, the selective oxidation of methane to methanol is a challenging problem for catalytic science. Methane is the most stable and unreactive hydrocarbon, has the highest C-H bond strength of all alkanes ($\Delta(\text{C} - \text{H}) = 438.8 \text{ kJ mol}^{-1}$), high ionization potential (12.5 eV), low proton affinity (4.4 eV) and low acidity ($\text{pK}_a = 42$) for which partial oxidation produces kinetically labile products^{14, 54, 61}. These points necessitate the design of a catalytic system that not only activates this inert substrate, but is able to do so under intrinsically mild reaction conditions so as to avoid deeper oxidation. However, although low-temperature routes have been reported to proceed with increased selectivity, they do not yet do so at economical catalytic rates¹⁵ and its direct conversion to useful chemicals is very difficult¹⁶.

This present work is a review with emphasis on recent advances of catalysis in liquid phase.

CATALYST DEVELOPMENT

Catalytic conversion of methane to methanol using solid catalysts

Methane oxidation in gas – phase, under atmospheric pressure on solid catalysts, was presented in numerous publications¹⁷⁻³⁴. Thus, a variety of compounds were used as contacts agents. The reaction was performed at 400–800°C and 0.1 MPa pressure, by insufficiency of oxygen (5–30% vol. O₂). Under these conditions formaldehyde was mainly obtained.

Particularly noteworthy was the publication of Yamada's group¹⁷, which shows results using 43 different oxides of elements supported on silica. The process was performed at 500°C. Contact time lasted 0.75 s. The oxygen content of the mixture was varied from 5 to 30% Vol. V, Fe, Sc, W, Mo and Os oxides were found to be good catalysts in these conditions.

There are known publications in which attempts were made to create a mixture of several oxides as a catalyst system, based on the experimental results obtained by using each of compounds alone. Pioneering work was done by Otsuka¹⁸, who studied oxide- catalysts supported on silica. With the increase in electronegativity of an oxide compound, the conversion first is growing up and then decreasing, while the selectivity of conversion into formaldehyde with grows the increase of electronegativity. Then two catalysts were used, one with high, and the other with average values of electronegativity. The highest degree of conversion was achieved for magnesium and boron oxides (Table 1).

Table 1 presents catalyst systems, the use of which has resulted in higher conversion into formaldehyde. Unfortunately, despite years of research, the problem of obtaining a higher yield of formaldehyde than a few percent is still unresolved.

Parmaliana et al.³⁰ received formaldehyde at 650°C and SiO₂ as catalysts with a yield of 17%. The use of ZSM – 5³⁴, Fe – ZSM – 5^{35, 36} allowed to receive methanol with the yield of a few percent.

All research about oxidation of methane on solid catalysts by the high selectivity was characterized by low conversion and resulted low yield. The main issue regarding the yield of this reaction is the overoxidation

Table 1. Overview of solid catalysts in partial oxidation of methane at atmospheric pressure

Catalyst	Temperature [°C]	Conversion CH ₄ into HCHO [% Mol]	References
V ₂ O ₅ /SiO ₂	650	4.72	19
MoSn/ SiO ₂	700	4.66	20
Fe ₂ O ₃ (MoO ₃) _{2,25}	700	4.00	21
MoO ₃ / SiO ₂	650	1.70	22
FeNbBo	770	1.36	23
SiO ₂	620	1.15	24
FePO ₄ / SiO ₂	600	1.20	25
Zr – P – O	777	0.64	26
MgB – O/ SiO ₂	650	0.60	18
MgO	750	0.42	27
Cu – Fe/ ZnO	750	0.25	19
BMo – O/ SiO ₂	545	0.05	20
T, H, M form of Nb ₂ O ₅	350	0.4–0.6	28

to CO or CO₂. Under mild conditions the activation of methane was very difficult.

The above processes of methane oxidation take place at high temperatures (350–800°C). The first stage is C – H bond cleavage and the formation of the CH₃[•] radical^{20–22, 37, 38}. The construction of methane molecule and its properties limited the efficiency of oxidation for only few percent. Furthermore, dissociation energy of the C – H bond in methane molecule is higher than the energy in methanol or formaldehyde molecule. Products are more reactive than their substrates.

In 1972 Shilov et al. showed that platinum ions can activate C – H bond under mild conditions without radical reaction. This involves interaction of the metalorganic complex and sigma bond electron pair. The intermediate compound is the so – called “sigma complex”. The mechanism of C–H activation by molecular complexes for homogeneous processes has been extensively investigated; four mechanisms involving at least one metal center have been documented: oxidative addition (usually for late transition metal), σ-bond metathesis for their

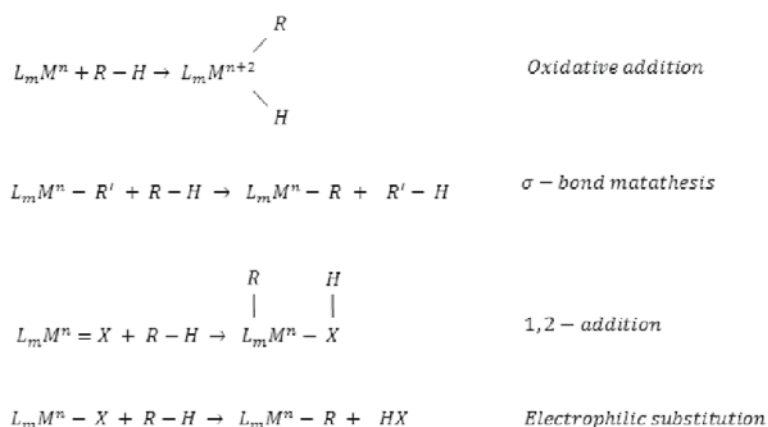
early counterparts, and, in a few cases, 1, 2-addition or electrophilic activation^{39, 40}.

Basset, Sun et al. presented an overview of heteropoly compounds in catalytic oxidation of light alkanes (C₁–C₄), mechanism of the reaction and the impact of various factors⁷¹.

Methane oxidation in the aqueous systems or similar

In 1972 Shilov`s group⁴¹ were able to oxidize methane at 120°C and 3.7–4.3 MPa methane pressure. The reaction was performed in the aquatic solution of H₂PtCl₆ and Na₂PtCl₄. The products in liquid phase were methanol and halogenoalkanes – mainly methyl chloride.

The oxidation of the simplest alkane with oxygen and carbon monoxide to acids in an aquatic solvent of 0.1 N HCl, at 70–200°C was developed by Sen and Lin. As a catalytic system the authors recommended metallic palladium⁴² or RhCl₃^{43, 44}. Using metallic palladium at 70–100°C on an active carbon support they obtained formic acid and methanol. The use of RuCl₃ as the catalytic system allowed to convert methane at 100°C and 5.52 MPa partial methane pressure. The main product was acetic acid; with formaldehyde and methanol.

**Scheme 1.** Various mechanisms belonging to the so-called organometallic C–H Bond activation^{40, 71}

Park et al.^{45, 46} oxidized methane in an aquatic solution of trifluoroacetic using metallic palladium on an active carbon support and $\text{Cu}(\text{CH}_3\text{COO})_2$ catalysts. The main product was trifluoromethyl acetate and formic acid was a by-product.

Methane oxidation in other organic solvent systems

Ellis et al.^{47, 48} developed an oxidation method of paraffins with molecular oxygen in the presence of porphyrins that contain cyanide groups and halogen atoms. Hydrocarbons, including methane, were oxidized by oxygen from air at 70–180°C and 0.2–5.2 MPa methane pressure. The reaction was performed in liquid phase, in organic solvents such as: C_6H_6 , CH_3COOH , acetonitrile, methylacetate, methyl acetate and others, which are inert in these reaction conditions. The catalysts used are transition metals Fe, Cr, Mn, Ru, Cu, Co. The corresponding alcohols were prepared in the reaction.

Süss-Fink et al.^{49, 50} investigated different types of similar catalytic systems. In the first case methane was oxidized by air in an acetonitrile solution, in the presence of $[\text{NBu}_4]\text{VO}_3$ – pyrazine – 2 – carboxylic acid used as the catalyst and 35% H_2O_2 used as the promoter. The main product under 35°C was methyl hydroperoxide, easily reduced to methanol. In higher temperature prevailed formaldehyde and formic acid. In the second case sodium orthovanadate was used as the catalyst and 35% H_2O_2 in water solution as the promoter were used – the only product was methyl hydrogen peroxide.

Lee et al.⁵¹ and Peng⁵² oxidized methane with oxygen in molten salts. The Lee group used sodium and potassium nitrate in 526–600°C at 0.1 MPa pressure. Mainly methanol and carbon oxides were obtained; the reaction yield was 0.47% with a degree of methane conversion at 8.2%. Peng et al. used a mixture of silver and sodium nitrate with other catalysts: $\text{Cu}(\text{CF}_3\text{CO}_2)_2$, $\text{Co}(\text{CF}_3\text{CO}_2)_2$, $\text{Ce}(\text{SO}_4)_2$, MnSO_4 and CuSO_4 . The reaction proceeded at 160°C under 3.5 MPa of methane and 0.5 MPa of oxygen pressure. The post – reaction gases contained methyl trifluoroacetate and propanone.

Sherman patented a method of methane oxidation in water, by a free radical mechanism⁵³. In a reactor of a special design, OH radicals were produced, which generated the production of CH_3^* .

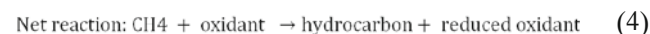
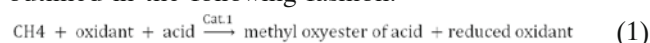
Stauffer developed a method of methane oxidation with oxygen at 200–375°C, using organic chlorine compounds⁵⁴. The process consisted of two phases and the only product was methanol. Copper (I) chloride was the reaction catalyst.

Seki et al.^{55, 56} investigated methane oxidation in the presence of heteropoly acids. The heteropoly acids and H_2O_2 were dissolved in the anhydride of trifluoroacetic acid, methyl cyanide and water. The reaction was carried out at 50–80°C and 5 MPa methane pressure. The reaction products were: CH_3OH , HCOOH , HCOOCH_3 , $\text{CF}_3\text{COOCH}_3$, C_2H_6 , CO_2 .

Methane oxidation in the strong acids

Periana et al.⁵⁷ developed a method of hydrocarbon conversion into alcohols, thiols, esters and halogenoalkanes. Instead of using water, an acid was used. The main product was an ester, which was stable in this environment of reaction. The desired product was pre-

pared by reaction with a nucleophilic compound. The overall process, using methane as an example, may be outlined in the following fashion:



The first step involves contacting methane with an acid and an oxidizing agent in the presence of a catalyst. The acid may be an organic or inorganic acid such as HNO_3 , H_2SO_4 , $\text{CF}_3\text{CO}_2\text{H}$, $\text{CF}_3\text{SO}_3\text{H}$, H_3PO_4 or the like. The preferred acids are strong inorganic acids ($\text{pK}_a < 2.0$) and especially preferred are H_2SO_4 and $\text{CF}_3\text{SO}_3\text{H}$. The acids should be oxidation resistant: they should not be oxidized by the catalyst metal in the noted reaction medium. In addition to acting as a reactant, the acid desirably is used in excess and thereby acts as a reaction medium as well⁴¹. The preferred oxidizing agents are O_2 , H_2SO_4 , SO_3 , HNO_3 , H_2SeO_4 .

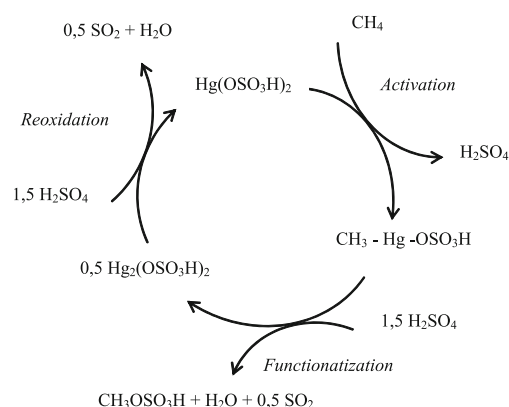
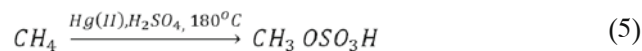
The catalysts used in Eq. 1 are transition metals, i.e., Cu, Zn, Pd, Ag, Cd, In, Sn, Sb, Te, Pt, Au, Hg, Tl, Pb, Bi, Ga, Ge, As, Po, Rh, Ir, Os and Ru^{58–62}. The authors recommended the following conditions: temperature at 50–30°C and 0.4–3.2 MPa of methane pressure.

Especially sulfuric acid at a high concentration was preferred. This substrate was not only a solvent or an oxidizing agent – basically water could remove itself from the reaction.

The second step is the conversion of methyl ester to methanol and regeneration of acid which was used in the first step. In each case the major product in liquid phase was methyl intermediate which e.g. could be hydrolyzed into methanol.

Mercury compounds as catalysts

Periana et al.⁶³ suggested a homogeneous catalytic system using Hg (II) salt as the catalyst in fuming sulfuric acid. The reaction took place at 180°C and 3.45 MPa methane pressure. Methane was oxidized to methyl bisulfate. $\text{CH}_3\text{OSO}_3\text{H}$ was further hydrolyzed to produce methanol.



Scheme 2. The possible mechanisms for the activation of methane C–H bond on the Hg^{2+} – H_2SO_4 catalyst⁶³

Gang et al.⁶⁴ applied a similar catalytic system as Periana's group but fuming sulfuric acid was more concentrated (65 wt% SO₃). The methane oxidation was studied at a temperature range of 150–200°C and of 4–10 MPa methane pressure.

Sen et al.^{65, 66} investigated the catalytic properties of HgSO₄ and other sulfates such as Ce(SO₄)₂, PdSO₄ in sulfuric acid. The reaction took place at 90°C and 160°C and 6.9 MPa methane pressure. In higher temperature methane was oxidized to methyl bisulfate, in lower temperature to methanesulfonic acid.

Bell et al.⁶⁷ investigated direct sulfonation of methane with SO₃ to methanesulfonic acid and methylbisulfate using Hg(I), Hg(II), and Rh(III)-salts as catalysts. The results of this investigation showed that after 5 h at 148°C and 2.5 MPa of methane pressure using fuming sulfuric acid as the solvent, the corresponding MSA selectivity was 87%. The authors proposed a mechanism for the formation of MSA and CH₃OSO₃H in the light of the experimental results.

Fu and co-workers summarized the possible mechanisms for the activation of methane C–H bond, which were calculated on the basis of model catalysts: V₃O₆Cl₃, Cr₃O₉, Mo₃O₉, and W₃O₉^{40, 68}.

Other studies into the activation of dioxygen at transition metals and main group element surfaces⁶⁹ provided evidence for transient species and intermediates O[–] and O^{2–}, and of their reactions with C–H bonds. The oxydehydrogenation reactions, efficient at low temperatures, are inhibited by thermally induced ordering of oxygen states and the accompanying surface reconstruction⁷⁰.

Palladium compounds as catalysts

Kao et al.⁷² suggested a homogenous catalytic system using a salt of Pd (II) as a catalyst and H₂O₂ as an initiator in CF₃COOH medium. Trifluoroacetic acid was first oxidized to trifluoroperacetic acid. Then, a reaction between methane and trifluoroperacetic acid was catalyzed by Pd(II) and methyl ester of trifluoroperacetic acid was obtained. The ester can be hydrolyzed to produce methanol. The reaction was performed at a temperature equal to 80°C and 5.5 MPa of methane pressure.

Taylor and co-workers⁷³ reported that a reaction occurred between methane at 5.52 MPa and palladium (II) acetate in trifluoroacetic acid at 80°C. The product – methyl trifluoroacetate, was then hydrolyzed to produce methanol and trifluoroacetic acid.

The use of metallic palladium as the catalyst was very difficult because it is not soluble in sulfuric acid even after heating. Michalkiewicz et al.⁵⁹ studied the oxidation of methane to organic oxygenates over metallic palladium dissolved in oleum. The reaction was carried out under the following conditions: temperature 160°C, pressure of methane 3.5 MPa, time 2 h, content of sulfur trioxide in fuming sulfuric acid 30% and the catalytic system Pd(0) in the form of palladium powder dissolved in fuming sulfuric acid.

The catalytic process relies on the formation of an unstable metal-organic complex Pd²⁺–CH₃ which reacts with sulfuric acid. The carbon atom undergoes oxidation to methyl bisulfate while palladium is reduced to Pd(0). The methane conversion could not proceed in the case

of metallic Pd without free SO₃ because the first stage of the catalytic process would not take place.

As a result, the catalyst life as well as the reaction selectivity was higher than that when using palladium (II) sulfate.

Michalkiewicz⁷⁴ found, that the rate of ester formation depends on the partial pressure of methane, the concentration of free sulphur trioxide in sulphuric acid, and concentration of methyl ester. The palladium – oleum catalytic system was used (concentration of Pd powder in oleum, 1.55 wt%), which generate an ester of methanol by the low temperature process and 4.5 MPa of methane pressure. The experiments were carried out in two series: the first one in the constant reaction time of 2 hours and temperature range at 90–160°C; the second over the period from 1–20 hours at 160°C.

The kinetics of the partial methane oxidation process⁷⁵ in the Pd|oleum was investigated too. The methane esterification process was carried out at 180°C in an autoclave containing oleum, using palladium as a catalyst. Then methyl esters were converted into methanol. The influence of the pressure on methane conversion and product yields were studied. The methane pressure was either varied from 1.5 to 5 MPa or was kept constant at 3.0 MPa.

In the latter case, the partial pressure of methane was changed by the addition of nitrogen as the inert gas into the autoclave. At the constant methane partial pressure, the total pressure changes have no influence on the process. Only the methane partial pressure influences the process.

On the basis of the experiments it may be concluded that:

- the process of methane oxidation in the condensed phase can be conducted at the atmospheric pressure,
- at a constant methane partial pressure, the total pressure changes have no influence on the process,
- increasing methane partial pressure allows to extend the amount of methanol and carbon dioxide,
- elevating methane partial pressure in the autoclave does not influence the methanol yield but increases the carbon dioxide yield,
- the rate of the reaction of forming ester is proportional to methane partial pressure.

Other studies⁷⁶ focused on the impact of catalyst type on the esterification process. Michalkiewicz found that using the powdered palladium catalyst, methyl bisulphate and formaldehyde were obtained, which were subsequently oxidized to carbon dioxide. When platinum (IV) chloride was used as the catalyst of methane oxidation, after 2 hours methyl bisulphate was the only product. It was found too, that the addition of either carbon dioxide or ester into the reaction mixture did not slow down the reactions.

An attempt was made⁷⁷ to apply membrane distillation as the second step of conversion of methane to methanol. In this study the possibility of application of a LPMD (low pressure membrane distillation) for the separation of ester – oleum mixture was investigated. The efficiency of ester separation was close to 100%.

Michalkiewicz et al. investigated the hydrolysis process of methyl ester. The disadvantage of the conversion of methane to methanol in oleum via methyl bisulphate is

production of sulphuric acid and a very large amount of water consumption. The authors propose the extraction of the ester before hydrolysis in order to solve these problems.

Membrane distillation for the separation of ester – oleum mixture was applied.

Platinum compounds as catalysts

Platinum complex catalysts in fuming sulfuric acid (20 wt%) were reported by Periana et al.⁷⁸ for direct, oxidative conversion of methane to ester. The reaction was performed at 180°C and 3.45 MPa methane pressure. The catalysts were platinum complexes derived from the bidiazine ligand family that were stable, active, and selective for the oxidation of a carbon-hydrogen bond of methane to produce methyl esters.

Michalkiewicz et al.^{79, 80} studied the selective catalytic oxidation of methane in 25 wt% oleum to methyl bisulfate at ambient pressure and in the presence of PtCl₄ (Eq. 6). The study was directed toward methane esterification at ambient pressure. The reaction was performed at 130–220°C. It was shown that it is possible to functionalize methane at 0.1 MPa using a large surface area that was shown to facilitate liquid – gas contact.



Iodine compounds as catalysts

Gang et al.⁸¹ applied a new series of iodine compounds as catalysts for the selective oxidation of methane to methyl sulfates in oleum (65 wt%). A mathematical model for the relationship between the initial reaction rate and the iodine concentration and methane pressure was given. The reaction was performed in the range 170–190°C and 4 MPa methane pressure.

Periana et al.⁸² applied a similar catalytic system as Gang's group, but they used iodine dissolved in sulfuric acid (0.5–3 wt% SO₃). Several experiments were performed at 195°C and 3.4 MPa methane pressure.

Zarella and Bell⁸³ used Pt(II) cations as the catalyst and sulfuric acid as the solvent. The reactions were carried out at 180°C in a sealed batch reactor containing either fuming or concentrated (96 wt%) sulfuric acid and PtCl₂ in the liquid-phase, and with 2.75 MPa of CH₄ and CO pressure. Pt (II) in concentrated sulfuric acid catalyzed the oxidative carbonylation of methane to acetic acid but excessively high CO partial pressures had to be avoided, since they contributed to the reduction of active Pt(II) to inactive Pt(0).

Michalkiewicz et al.^{84, 85} performed methane oxidation to methyl bisulfate in the presence of iodine as a catalyst at ambient and higher pressure. In order to obtain high methyl bisulfate yield at 0.1 MPa high sulfur trioxide concentration and low methane flow is recommended. The optimum of temperature is equal to 130°C. It was showed that at methane pressure of 1–5 MPa the reaction is of the first order with methane pressure and sulfur trioxide concentration. In the temperature range 80–180°C, sulfur trioxide concentration 0–5.95 moldm⁻³ the reaction rate was well defined by an empirical equation.

Other compounds as catalysts

Vargaftik et al.⁸⁶ carried out research by using TFA and trifluoroacetate salts of Co (III), Mn (II), Fe(III), Cu (II), Pb (IV). At 100–200°C and 1–4 MPa of methane pressure only the methyl ester of trifluoroacetic acid were received. The best results were obtained for Co (II) salt (yield at 90% calculated as metal).

Otsuka et al.^{87, 88} proposed a catalytic system EuCl₃ – Zn – CF₃CO₂H which was used to oxidize methane with oxygen into methyl trifluoroacetate. Carbon dioxide was a by-product. Partial methane pressure was at 1.6 MPa and oxygen pressure at 0.4 MPa. After one hour the degree of methane conversion to 0.9% was obtained. The addition of TiO₂ increased methane conversion by 1.75%.

Sen et al.⁶⁵ used K₂S₂O₈ as the catalyst in fuming sulfuric acid. At 160°C under 6.9 MPa of methane pressure methyl bisulfate and at 90°C only the methanesulfonic acid, were obtained. A degree of methane conversion for each of the products reached a few percent.

Bell and Mukhopadhyay^{89, 90} carried out direct liquid-phase sulfonation of methane to methanesulfonic acid by SO₃ in the presence of cerium (IV) sulfate or metal peroxide. Methanesulfonic acid was obtained in fuming sulfuric acid, with a small amount of catalyst, which was added to the liquid phase. The selectivity achieved 99.9% for MSA product, using Ce(SO₄)₂ as the catalyst. Calcium peroxide proved the best initiator for the reaction conditions used. The peroxides of strontium and lead were only minimally more effective in promoting the sulfonation of methane.

The use of potassium peroxydiphosphate (K₄P₂O₈) as the initiator in a high-yield, direct sulfonation⁹¹ of methane with SO₃ in sulfuric acid led to obtaining MSA acid. The effects of initiator concentration, temperature, CH₄ pressure, the initial concentration of SO₃, and solvent acidity were investigated.

Periana et al.⁹² proposed selective oxidation of methane to methanol catalyzed, with C – H activation by cationic gold. In strong acid solvents such as triflic or sulfuric acid, Au(III) cations using Se(VI) ions as the stoichiometric oxidant (generated by dissolution⁹³ of Au₂O₃), react with methane at 180°C to selectively generate methanol, as a mixture of the ester and methanol, in high yield. The reaction does not appear to proceed through free radicals and DFT calculations indicate that Au(I) or Au(III) species are both viable catalysts that operate by mechanisms involving overall electrophilic C – H activation and oxidative functionalization.

Another publication by Periana's group⁹⁴ showed selective oxidization of mixtures of methane, ethane, and propane to alcohol esters. They reported that the electrophilic main-group cations of thallium (III) and lead (IV) oxidize methane and other alkanes to corresponding esters in a trifluoroacetic acid solvent. Esters were obtained with greater than 95% selectivity within 3 hours at 180°C. This experiment confirms a mechanism involving electrophilic carbon-hydrogen bond activation to generate metal alkyl intermediates.

In chemical literature we can find increasingly more information about the use of bromide compounds for selective oxidation of methane to methanesulfonic ester.

Wang group⁹⁵ synthesized acetyl bromide and acetic acid from methane. They developed Ru/SiO₂ catalyst

for the OBM reaction and a $\text{RhCl}_3\text{-PPh}_3$ system for the carbonylation of CH_3Br . Acetyl bromide could be hydrolysed readily to anhydrous acetic acid or alcoholised to produce esters.

Fengbo et al.⁹⁶ presented a novel bromine-mediated process over HgO supported nanophases for selective methane partial oxidation at a relatively low reaction temperature. The studies included synthesis of the catalysts, activity tests, the investigations about the role of bromine in the catalytic cycle and characterizations of the catalysts. The study found that the chemical composite changes of active species, which provide some direct information about the mediator role of bromine in the catalytic cycle and its influence on the mechanism for conversion of methane to C1 oxygenates.

Chan and co-workers⁹⁷ developed an efficient catalyst for controlled oxidation of small alkanes under ambient conditions. The tricopper complex $[\text{CuICuICuI}(7\text{-N-Etppz})]1+$, where 7-N-Etppz denotes the ligand 3,3'-(1,4-diazepane-1,4-diyl)bis[1-(4-ethyl piperazine-1-yl)propan-2-ol], is capable of mediating facile conversion of methane into methanol upon activation of the tricopper cluster by dioxygen and/or H_2O_2 at room temperature. This is the first molecular catalyst that can catalyze selective oxidation of methane to methanol without over-oxidation under ambient conditions.

Michalkiewicz et al.⁹⁸ investigated the catalytic properties of halogens in oleum. The reaction was performed with I_2 , KI, KBr, KCl, NaCl and HCl used as catalysts and at 160°C , 4.27 MPa methane pressure. It was found that Iodine (I_2) is the most effective catalyst.

Further studies revealed that KBr is a highly selective low temperature catalyst too, for homogeneous methane to methyl ester and then methanol conversion⁹⁹. Sulfur trioxide as an oxidant and sulfuric acid as an esterification agent were used. The increase of temperature, sulfur trioxide concentration or methane pressure resulted in TOF grow. More investigations about mechanism and kinetics of the reaction are needed – further research is in progress.

Methane Monooxygenase (MMO)

The first reaction in this metabolic pathway is the conversion of methane to methanol catalyzed by the enzyme methane monooxygenase (MMO) as described in the report of Couderc and Baratti¹⁰⁰.

Because of this perceived limitation in heterogeneous catalysts, the Weakely's group undertook a program to take advantage of the selectivity already known to exist in a bacterial enzyme system. A group of aerobic soil/water bacteria called methanotrophs can efficiently and selectively utilize methane as the sole source of energy and carbon for cellular growth¹⁰¹. The synthesis of the chelating ligand HMeL was obtained by a five step procedure in 35% overall yield. Binuclear copper complexes of HMeL were prepared by dissolving 100 or 200 mole% of cupric perchlorate with 100 mole% HMeL and sodium acetate in methanol. The binuclear copper complex tested was capable of activating hydrogen peroxide and the presumed oxo-copper intermediate was able to oxidize alkanes.

Microorganisms can produce MMO in two distinct forms: a membrane-bound particulate form or a discrete

soluble form. The soluble form contains an oxygenase subunit, whose active site includes a binuclear iron center¹⁰²⁻¹⁰⁷.

In addition to inorganic catalysts that react with methane, it is well – known that a select group of aerobic soil/water bacteria called methanotrophs can efficiently and selectively utilize methane as the sole source of their energy and carbon for cellular growth¹⁰⁸.

The ability of MMO to selectively oxidize methane to methanol under ambient conditions is quite impressive. Understanding how the enzyme performs will demystify this marvelous natural phenomenon. Methane is generated from carbon dioxide by methanogenic bacteria under anaerobic conditions such as lakes, oceans, and wetlands. Since both methane and dioxygen are essential for methanotrophs, these bacteria thrive in the borderline region of the aerobic and anaerobic environments¹⁰⁹.

Michalkiewicz et al.¹¹⁰ applied the one-step method at very low temperatures (35°C) by the methane oxidation to methanol via bacteria. The role of copper was investigated in the one-step methane oxidation to methanol by utilizing whole cells of *Methylosinus trichosporium* OB3b bacteria. From the obtained results it was found that copper concentration in the medium influences the rate of bacterial biomass growth or methanol production during the process of methane oxidation to methanol. The presented results indicate that the process of methane oxidation to methanol by *Methylosinus trichosporium* OB3b bacteria is most efficient when the mineral medium contains 1.0×10^{-6} moldm⁻³ of copper. Under these conditions, a satisfactory growth of biomass was also achieved.

Hadt and co-workers presented Cu – ZSM – 5 as a biomimetic inorganic model for methane oxidation¹¹¹.

Sunney, Lu et al. developed a series of tricopper complexes that are capable of supporting facile catalytic oxidation of hydrocarbons. They investigated two tricopper complexes that are capable of facile conversion of methane to methanol: a tricopper-peptide complex derived from MMO and a biomimetic model tricopper complex. The biomimetic tricopper complex oxidizes methane efficiently at room temperature and can be formulated either as a homogeneous or heterogeneous catalyst¹¹².

Analysis of the available results on biomimetic and bio – inspired methane oxygenation demonstrated that assimilating of the experience of nature on oxidation of methane and other alkane significantly enriches the arsenal of chemistry and can radically change the character of the entire chemical production, as well as enables the solution of many material, energetic and environmental problems¹¹³.

CONCLUSIONS

The conversion of methane to value-added liquid chemicals is a promising answer to the imminent demand for fuels and chemical synthesis materials in the advent of a dwindling petroleum supply. Current technology requires high energy input for synthesis gas production and is characterized by low overall selectivity, which calls for alternative reaction routes. The limitation to achieve high selectivity is the high C – H bond strength

of methane. High – temperature reaction systems favor gas – phase radical reactions and total oxidation. The use of homogeneous catalysts that activate and functionalize the CH bonds of unactivated hydrocarbons is very important. This results from the strong potential for these catalysts to carry out oxidative hydrocarbon conversion with high atom and energy efficiency and under mild conditions.

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