Oxidation of methane and ethylene in water at ambient conditions

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ABSTRACT

Available spectroscopic, labelling and reactivity data show that stable μ-nitrido diiron phthalocyanine activates H_2O_2 to form a high-valent diiron oxo species. This species is a very powerful oxidant which oxidizes methane in pure water at 25–60 °C to methanol, formaldehyde and formic acid. The catalytic activity can significantly be increased in the presence of a diluted acid solution. Thus, a high turnover number of 209 was attained in 0.075 M H_2SO_4. Oxidation of ethylene resulted in the formation of formic acid as a major product and formaldehyde with high turnover numbers. Under optimal conditions, 426 mol HCOOH and 37 mol CH_2O per mole of catalyst were obtained in pure water. The practical and green features of this novel approach (H_2O_2 as the clean oxidant, water as the clean reaction medium, easily accessible solid catalyst) as well as the relevance to biological oxidation (binuclear structure of bio-inspired complex) are of great importance both from practical and fundamental points of view.

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1. Introduction

Transformation of methane, the most abundant and the least reactive component of natural gas is one of the most difficult chemical challenges of a great practical importance and of continuing interest [1–4]. Conversion of methane is particularly difficult compared to other alkanes because of very high dissociation energy of methane C–H bond (435 kJ mol^{-1}). Not surprisingly, current approaches to utilization of methane involve mainly high-temperature processes. For example, the use of CH_4 in the industry is based on the initial high-temperature conversion of methane to syngas (H_2 + CO) which further can be transformed into methanol or fuels [5–7]. During several decades a direct low temperature conversion of CH_4 to valuable products continues to be a major challenge in catalysis. This field has largely been inspired by the work by Shilov and co-workers [3,4]. They discovered CH_4 activation on platinum complexes via Pt–CH_3 intermediate followed by its oxidation by Pt(IV) complex. However, inactivation of the system occurred owing to irreversible formation of metal. This non-catalytic chemistry based on Pt compounds was transformed into a catalytic process by stabilization of species using appropriate ligands and strong acids [8–14]. The most efficient oxidation of CH_4 in oleum (terminal oxidant) containing Pt(II) bipyrimidine complex at 220 °C provided ~90% methane conversion and selective formation of methyl bisulfate [8]. Another interesting approach was proposed by Schüth and co-workers [14]. They covalently immobilized Pt(II)

within a triazine-based framework containing bipyridyl fragments. Heterogeneous catalysts showed catalytic activity comparable to the Periana's system at 215 °C in 30% oleum and were stable over at least five recycling steps. Activation of CH_4 at other transition metal centres (Pt, Pd, Hg, Au, Tl, and Ir) has also been published [15–20]. As can be seen from aforementioned examples, harsh conditions (strong concentrated acids and high temperatures) are usually applied in these processes. Perspectives and challenges in C–H bond activation on transition metal sites have been reviewed [21]. Several other systems involving V, Fe, Os and Rh compounds have also been reported [22–26]. An interesting approach of activation of methane in the gas phase using metal-free radical-cation oxides was published by groups of Schwartz [27] and de Petris et al. [28]. The most representative catalytic systems for transformation of methane are listed in Table 1.

Two catalytic systems are distinguished by their high catalytic activity. Homogeneous [8] and heterogeneous [14] (bipym)Pt^{II}Cl$_2$ complex in 9–30% oleum at 215–220 °C transforms CH_4 to CH_3OSO_3H with TON ∼ 200–500. Vanadium complexes with N,O- or O,O-ligands in trifluoroacetic acid in the presence of $K_2S_2O_8$ as oxidant initiate a radical oxidation of CH_4 into CH_3COOH with very high TONs up to 5600 [22]. The catalytic activity of other systems is significantly lower. Inspection of Table 1 shows that harsh reaction conditions (relatively high temperatures, strong concentrated acids) are generally needed to perform the oxidation of methane. Only few systems were reported on oxidation of methane in aqueous medium, but their efficiency was not very high.

In nature, methane monooxygenase (MMO) enzymes transform CH_4 to CH_3OH in water under mild physiological conditions [29]. A chemical system, capable of oxidizing CH_4 at ambient condi-

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Table 1
Catalytic systems for low temperature transformation of methane.

Catalyst	Conditions	Products (yield, %)	TON	Ref.
(Bipym)Pt^{II}Cl$_2$	oleum, 220 °C	CH$_3$OSO$_3$H (~90)[a]	~500	[8]
[(Mebipym)Pt^{II}Cl$_2$]$^+$ [H$_4$PV$_2$Mo$_{10}$O$_{40}$]$^-$/SiO$_2$	water, acid, O$_2$, 50 °C	CH$_3$OH, HCHO, CH$_3$CHO (0.51)[b]	33	[9]
(Bipym)Pt^{II}Cl$_2$	H$_2$SO$_4$ (96%), ionic liquid, 220 °C	CH$_3$OH (0.02–0.17)[b]	0.5	[10]
PtCl$_2$			3.5	
(Bipym)Pt^{II}Cl$_2$	30% oleum, 215 °C	CH$_3$OH (35–39)[b]	158–355	[14]
K$_2$[PtCl$_4$]-CTF		CH$_3$OH (72)[b]	201–246	
N-heterocyclic carbene	CF$_3$COOH, (CF$_3$CO)$_2$O, 80–100 °C	CF$_3$COOCH$_3$ (0.93–3.67)[b]	5–30	[16]
Pd complex, K$_2$S$_2$O$_8$				
PdSO$_4$	96% H$_2$SO$_4$, 180 °C	CH$_3$OH, CH$_3$COOH	5–18	[17]
		CO$_2$ (1–12)[a]		
Pd(OAc)$_2$, NaNO$_2$, O$_2$, benzoquinone	CF$_3$COOH, 80 °C	CF$_3$COOCH$_3$ (0.04–0.09)[b]	3–7	[18]
PdSO$_4$	96% H$_2$SO$_4$, 180 °C	CH$_3$COOH, CO$_x$ CH$_3$OSO$_3$H (1.4)[b]	14.2	[19]
Ir(6-phenyl-2,2'-bipyridine), NaIO$_4$	CF$_3$COOD, 180 °C	CF$_3$COOCH$_3$ (<5)[a]	6.3	[20]
V complexes with N,O or O,O-ligands, K$_2$S$_2$O$_8$	CF$_3$COOH, 80 °C	CH$_3$COOH (43–8.8)[a]	19.7–5600	[22]
[Fe$_4$(N$_3$O$_2$-L)$_4$(μ-O)$_2$]$^{4+}$, H$_2$O$_2$	H$_2$O, 50–80 °C	CH$_3$OH, CH$_3$OOH, HCOOH (no data)	19–24	[23]
OsCl$_3$, H$_2$O$_2$	H$_2$O, 90 °C	CH$_3$OH, CH$_3$OOH, HCHO, CO$_2$ (0.14)[b]	12	[24]
OsO$_4$, NaIO$_4$	D$_2$O, 50 °C	CH$_3$OH, HCHO, CO$_2$ (0.07)[b]	0.006	[25]

[a] Yield on the initial amount of methane indicated in paper.
[b] Yield on the initial amount of methane calculated from experimental data available in paper.

tions like MMO does, would be a significant achievement. However, chemical analogues for such a process are unknown despite considerable efforts [30]. An essential feature of MMO is an active site containing two iron centers in a non-heme environment. On the other hand, cytochrome P-450 enzymes, which efficiently catalyze a variety of reactions including oxidation of C–H bonds of alkanes, contain a mononuclear iron porphyrin active site [31]. We have proposed to use binuclear iron complexes with macrocyclic porphyrin-like ligands as catalysts for oxidation [32]. Although these and similar complexes have often been considered as inert in catalysis, we have shown that μ-nitrido diiron phthalocyanine complexes (Fig. 1) possess remarkable catalytic properties [32–36].

More data on preparation and characterization of N-bridged binuclear complexes can be found in selected original papers [37–40] and review [41]. Importantly, our available data indicate that μ-nitrido diiron tetra-tert-butylphthalocyanine (FePc^{t}Bu$_4$)$_2$N operates via oxo-transfer chemistry involving high-valent diiron oxo species. In this paper we resume the spectroscopic, labelling and reactivity data previously obtained under homogeneous conditions. We report on the preparation, characterization and use of heterogeneous (FePc^{t}Bu$_4$)$_2$N–SiO$_2$ catalysts for the oxidation of methane and ethylene by H$_2$O$_2$ in aqueous media.

2. Experimental

Nitrido-bis[tetra(tert-butyl)phthalocyaninatoiron] was prepared as previously described [33]. Supported catalysts were prepared as follows. (FePc^{t}Bu$_4$)$_2$N (28, 42 or 56 mg) was dissolved
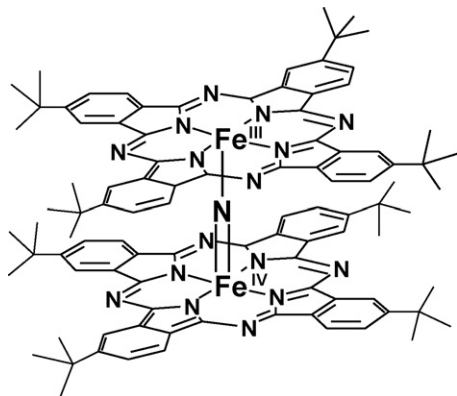

Fig. 1. Structure of μ-nitrido bridged diiron tetra-tert-butylphthalocyanine.

in 50 mL of CH$_2$Cl$_2$ and 1 g of silica (Degussa aerogel, 200 m^2/g) was added to the solution. The mixture was stirred at 25 °C for 2 h, then the solvent was removed under reduced pressure. The solid materials were dried in vacuum at room temperature for 1 h, then at 50 °C for 6 h. The complex loadings of solids were 17.5–20, 30 and 40 μmol/g.

Oxidation of methane and ethylene was performed in a 37 mL stainless steel autoclave with Teflon liner inside. The reactor was charged with 50 mg of (FePc^{t}Bu$_4$)$_2$N-SiO$_2$ containing 0.875–0.925 μmol of complex, 2 mL of water, 60 μL of 35% hydrogen peroxide solution in water (678 μmol of oxidant) and 32 bars of CH$_4$ or C$_2$H$_4$. The reactor was heated at desired temperature (25–60 °C) with magnetic stirring for 20 h. Hydrogen peroxide was consumed after reaction. The yield of formic acid was determined by GC–MS using isobutyric acid as an external standard and by HPLC. The HPLC determination of formic acid was made using an Agilent 1100 Liquid Chromatograph equipped with a 20 μL injection loop and multiple wavelength detector at 210 nm. Chromatographic analyses were carried out at room temperature using an ion exclusion Coregel-87H3 column with 0.004 M H$_2$SO$_4$ as eluent (flow rate of 0.8 mL/min). The yield of formaldehyde was determined by Nash method [42]. The labelling experiments were performed using approximately 1:1 mixture of ^{13}CH$_4$ (99 atom% ^{13}C, Sigma–Aldrich) and CH$_4$. Isotopic composition of products was determined by GC–MS.

3. Results and discussion

3.1. Spectroscopic characterization of intermediates generated from (FePc^{t}Bu$_4$)$_2$N and H$_2$O$_2$

The distinctive feature of (FePc^{t}Bu$_4$)$_2$N is its high stability which is an important requirement for the development of an oxidation catalyst. Phthalocyanine core is thermally and chemically stable. The stability of the binuclear structure is provided by the bridging nitrogen atom. The 1s N XPS spectrum showed a high-energy signal of bridging nitrogen of a low intensity at 402.4 eV compared with the signal at 398.7 eV due to 16 nitrogen atoms of two phthalocyanine ligands [32]. A strong molecular peak at m/z = 1599.8 was observed in the ESI-MS spectrum with no signals of monomer units also indicating a high stability of (FePc^{t}Bu$_4$)$_2$N [32]. UV–vis and EPR data indicated a slow reaction between (FePc^{t}Bu$_4$)$_2$N and H$_2$O$_2$ to form hydroperoxo (Pc^{t}Bu$_4$)Fe^{IV}=N–Fe^{III}(Pc^{t}Bu$_4$)–OOH complex [32,33]. It should be noted that the interaction of peroxides with iron complexes is an important subject of numerous studies and

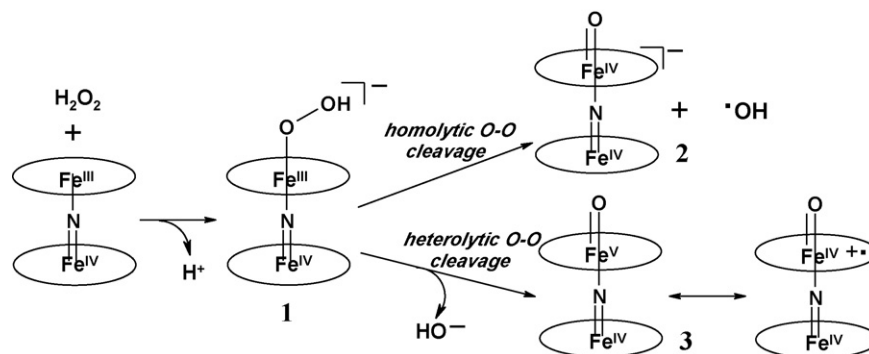**Fig. 2.** Proposed mechanism for activation of H_2O_2 by binuclear $(FePc^tBu_4)_2N$ complex.

debates in literature. Iron mononuclear complexes can initiate the formation of free radicals via homolytic cleavage of O–O peroxide bond resulting in free-radical oxidation. Otherwise, high-valent iron oxo species, e.g. $LFe^{IV}=O$ and $L^{•+}Fe^{IV}=O$ (L – ligand) are formed via heterolytic cleavage of O–O bond. In the latter case, these intermediates are oxidizing species. Activation of peroxides by binuclear porphyrin-like complexes is not yet well studied. Possible reaction pathways in the $(FePc^tBu_4)_2N$–H_2O_2 system are summarized in Fig. 2.

Hydroperoxo complex **1** formed from $(FePc^tBu_4)_2N$ and H_2O_2 can undergo homolytic or heterolytic O–O cleavage to generate complex **2** and hydroxyl radical or complex **3**, respectively. The complex **1** is negatively charged that should favour a formation of **3** with release of OH^-. Indeed, a high stability of phthalocyanine moiety, ^{18}O labelling data and analysis of kinetics were not consistent with participation of free radicals [33]. Under the electrospray ionization mass-spectrometry conditions complex **1** formed a high-valent diiron oxo complex **3** as evidenced by appearance of $m/z = 1615.9$ signal in ESI-MS spectrum. When $H_2^{18}O_2$ was used instead of $H_2^{16}O_2$ the spectrum exhibited a signal at $m/z = 1617.9$ corresponding to ^{18}O-containing complex **3** [33]. Isotopic distribution patterns of the molecular peak in both cases, with $H_2^{16}O_2$ and $H_2^{18}O_2$, were identical to the theoretical distribution patterns. Importantly, **3** retained the diiron structure. The complex **3** is formally Fe(IV)Fe(V) oxo species which can also be described as Fe(IV)Fe(IV) phthalocyanine cation-radical oxo form (Fig. 2). Such electrophilic species coordinated with electron-deficient phthalocyanine ligands should be a powerful oxidant. To prove this hypothesis we have investigated the oxidation of methane and ethylene using $(FePc^tBu_4)_2N$–H_2O_2 system.

3.2. Homogeneous oxidation of methane in organic solvents

Initial experiments of CH_4 oxidation were performed in CH_3CN containing 0.1 mM $(FePc^tBu_4)_2N$ and 67 mM H_2O_2. GC–MS analysis showed presence of formic acid and traces of methanol. When performing oxidation of CH_4 in organic solvents, a particular attention should be paid concerning the origin of products. Indeed, if the catalytic system is strong enough to oxidize CH_4, it could also be able to oxidize the organic solvent which concentration is much higher than that of methane. Furthermore, the products of oxidation of organic solvents (such as MeCN, acetone, etc.) might be the same as products of oxidation of methane. This problem has not usually been discussed in literature. Consequently, a closed control of the experiments should be performed in order to determine the origin of oxidation products and to confirm the occurrence of methane oxidation. In fact, such a control experiment is easy to perform by using of a deuterated solvent. If the oxidation of CH_4 is performed in CD_3CN, the products issued from CH_4 will contain H atoms and the products of solvent oxidation will be deuterated (Fig. 3).
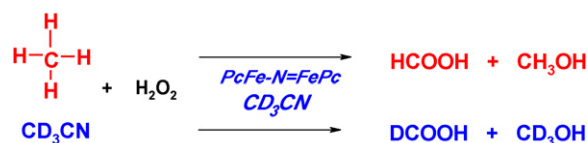

Fig. 3. Oxidation of methane in CD_3CN as a test on the origin of oxidation products.

GC-MS analysis of the isotopic composition of formic acid using intensities of $m/z = 29$ (HCO^+) and $m/z = 30$ (DCO^+) signals showed that formic acid obtained in oxidation of CH_4 in CD_3CN contained 68% of HCOOH and 32% of DCOOH. Thus, one can conclude that oxidation of CH_4 does occur, but the reaction is masked by the oxidation of the MeCN solvent. In order to circumvent the oxidation of organic solvent the best option would be to perform the oxidation of CH_4 in water which is a clean and inert solvent. Since $(FePc^tBu_4)_2N$ is not soluble in water we supported this complex onto silica in order to carry out heterogeneous oxidation.

3.3. Preparation and characterization of $(FePc^tBu_4)_2N$–SiO_2 supported catalysts

$(FePc^tBu_4)_2N$ was supported onto silica (Degussa aerogel, specific surface – 200 m^2/g) by physical absorption from the solution in CH_2Cl_2. Three supported catalysts were prepared with the complex contents of 20, 30 and 40 μmol/g. Specific surfaces of supported catalysts were 180–185 m^2/g. The diffuse reflectance UV–vis spectrum of $(FePc^tBu_4)_2N$–SiO_2 in comparison with UV–vis spectrum of $(FePc^tBu_4)_2N$ in CH_2Cl_2 solution is shown in Fig. 4.

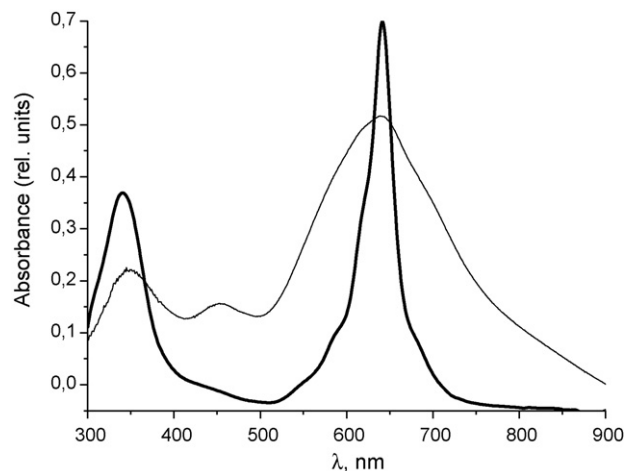**Fig. 4.** The diffuse reflectance UV–vis spectrum of solid $(FePc^tBu_4)_2N$–SiO_2 (thin line) and UV–vis spectrum of $(FePc^tBu_4)_2N$ in CH_2Cl_2 solution (bold line).

Table 2
Oxidation of CH$_4$ by H$_2$O$_2$ catalyzed by supported (FePc^{t}Bu$_4$)$_2$N.[a]

Run	T (°C)	[CH$_2$O] (mM)	[HCOOH] (mM)	CH$_2$O (mol/catalyst,mol)	HCOOH (mol/catalyst,mol)	TON[b]	Ref.
1	25	0	6.0	0	13.0	13	[33]
2	40	4.8	8.6	10.4	18.6	29	[33]
3	60	1.5	10.5	3.2	22.8	26	[33]
4[c]	60	n.d.	15.0	n.d.	19.6	20	This work
5[d]	60	n.d.	22.0	n.d.	21.7	22	This work

[a] *Conditions*: 2 mL of water, methane, 32 bars, 0.925 μmol of supported catalyst (18.5 μmol/g), 678 μmol of H$_2$O$_2$, reaction time – 20 h.

[b] TON – turnover number, number of CH$_4$ molecules transformed into the products by one molecule of catalyst.

[c] With (FePc^{t}Bu$_4$)$_2$N–SiO$_2$ (30 μmol/g).

[d] With (FePc^{t}Bu$_4$)$_2$N–SiO$_2$ (40 μmol/g).

UV–vis spectrum of (FePc^{t}Bu$_4$)$_2$N in CH$_2$Cl$_2$ solution exhibits Soret and Q bands at 341 and 642 nm, respectively. Upon absorption of (FePc^{t}Bu$_4$)$_2$N onto silica the broader bands were observed at 348 and 639 nm. A novel absorption band of low intensity was detected at 453 nm. The origin of this band is not yet understood. When (FePc^{t}Bu$_4$)$_2$N was removed from the supported (FePc^{t}Bu$_4$)$_2$N–SiO$_2$ catalyst by the treatment with CH$_2$Cl$_2$, the solution showed the same UV–vis spectrum as was observed before absorption, indicating that (FePc^{t}Bu$_4$)$_2$N retained its binuclear structure during supporting onto silica.

3.4. Heterogeneous oxidation of methane in water

The initial experiments on heterogeneous oxidation of CH$_4$ were performed in pure water. The degradation of organic ligand of the catalyst under oxidation conditions is potentially a source of methanol, formaldehyde or formic acid that should be checked using labelled ^{13}CH$_4$. The oxidation of CH$_4$ was unambiguously evidenced using labeled ^{13}CH$_4$ in about 1:1 mixture with CH$_4$ [33]. ^{13}C NMR analysis of the reaction mixture showed the signals at 81.6 and 165.5 ppm attributed to hydrated formaldehyde ^{13}CH$_2$(OH)$_2$ and formic acid H^{13}COOH, respectively. Although no signal at 49 ppm due to ^{13}CH$_3$OH was seen in ^{13}C NMR spectrum, a small amount of methanol-^{13}C was detected by GC–MS. Noteworthy, the isotopic composition of methanol and formic acid corresponded to the isotopic composition of methane [32,33]. This experiment clearly demonstrates that these products originate from the oxidation of CH$_4$ but not from degradation of the catalyst. ^{13}C NMR analysis of the reaction mixture did not show the signal at 125 ppm due to possible ^{13}CO$_2$ formation during oxidation of ^{13}CH$_4$. The stability of HCOOH (major final product) was studied in the separate experiments. HCOOH was completely stable under reaction conditions (60 °C, water or 0.2 M H$_2$SO$_4$) during standard reaction time. These findings strongly suggest that CO$_2$ should not be formed in detectable amounts during oxidation of methane by (FePc^{t}Bu$_4$)$_2$N–H$_2$O$_2$ system.

The heterogeneous oxidation of CH$_4$ in water was studied at different temperatures (Table 2). Significantly, the (FePc^{t}Bu$_4$)$_2$N–SiO$_2$–H$_2$O$_2$ system was capable of oxidizing methane even at 25 °C in pure water, although with a moderate turnover number of 13. The catalytic system was more active at
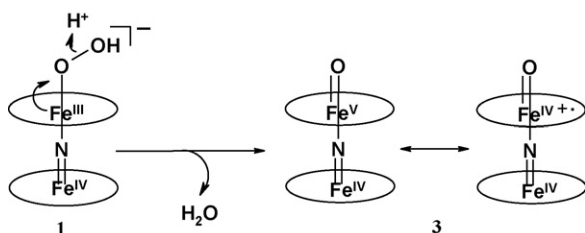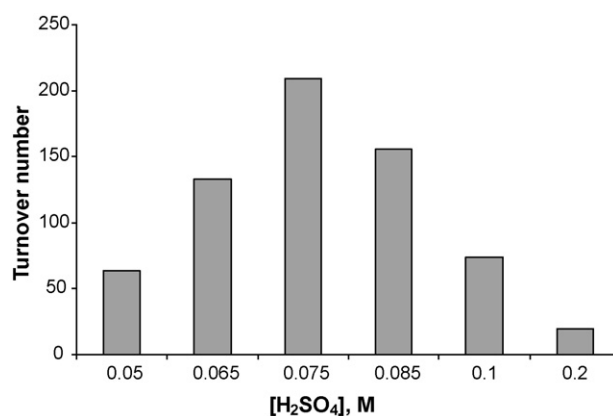

Fig. 6. Dependence of the efficiency of oxidation of methane on the H$_2$SO$_4$ concentration, other experimental conditions being the same as in Table 2, run 3.

higher temperatures. However, the catalytic activity was kept almost the same in the range 40–80 °C (TON ∼ 26–29). At 40 °C the HCOOH/CH$_2$O ratio was about 2:1 while at higher temperatures the amount of CH$_2$O decreased [33]. When the supported catalysts more charged in (FePc^{t}Bu$_4$)$_2$N (30 and 40 μmol/g) were used, the turnover numbers were practically the same as those for supported catalyst with 18.5 μmol/g charge. By using more charged catalysts more concentrated solutions of formic acid can be obtained.
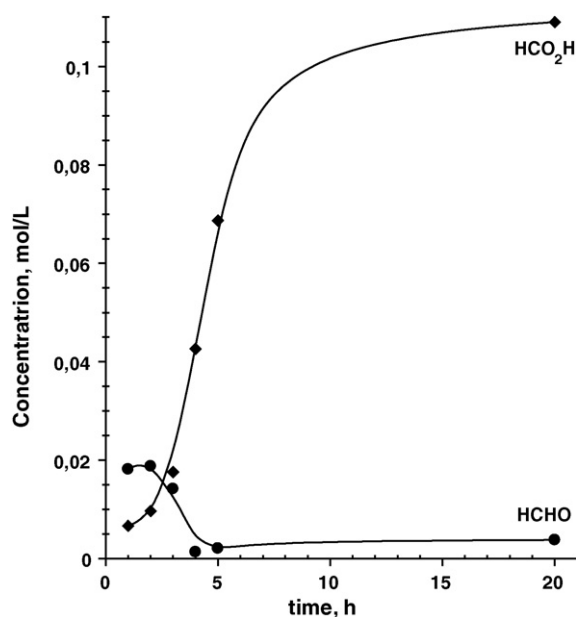

Fig. 5. Proposed mechanism of formation of complex **3** in the presence of acid.

Fig. 7. Time course for oxidation of methane by (FePc^{t}Bu$_4$)$_2$N–H$_2$O$_2$ system in 0.075 M H$_2$SO$_4$ at 60 °C.

Table 3
Oxidation of ethylene by H_2O_2 catalyzed by supported $(FePc^tBu_4)_2N$ complex.[a]

Run	T (°C)	[HCOOH] (mM)	[CH_2O] (mM)	HCOOH (mol/catalyst, mol)	CH_2O (mol/catalyst,mol)	TON[b]	Yield[c] on H_2O_2 (%)
Oxidation in water							
1[d]	25	Traces	n.d.	n.d.	n.d.	n.d	n.d.
2	40	50.3	23.1	115.0	52.8	83.9	36
3	60	86.3	14.3	197.3	32.6	115.0	51
4[e]	60	43.5	7.9	198.7	36.1	117.4	28
5[e]	70	93.3	8.1	426.5	37.0	231.8	57
Oxidation in 0.1 M H_2SO_4							
6[f]	25	40.7	8.3	92.9	19.0	56.0	26
7	60	107.6	17.9	246.1	41.0	143.5	69
8[e]	60	66.0	12.6	301.7	28.7	165.3	60

[a] *Conditions*: 2 mL of water or 0.1 M H_2SO_4, ethylene – 32 bars, 0.875 μmol of supported catalyst, 678 μmol of H_2O_2, reaction time – 20 h.
[b] TON – turnover number, number of C_2H_4 molecules transformed into the products by one molecule of catalyst; calculated as [(mol of HCOOH)/2 + (mol of CH_2O)/2]/mol of catalyst.
[c] Calculated supposing that four or two molecules of H_2O_2 are necessary to convert one C_2H_4 molecule to two HCOOH or CH_2O molecules.
[d] Reaction time: 48 h.
[e] Two times less of catalyst.
[f] Reaction time: 60 h.

We have proposed that the catalytic activity of $(FePc^tBu_4)_2N$–H_2O_2 system is associated with the formation of powerful oxidizing species **3** via heterolytic cleavage of O–O bond in hydroperoxo complex **1** and release of OH^- (Fig. 2). Since H_2O is a better leaving group than OH^-, it is reasonable to propose that the formation of **3** should be favoured by protonation of peroxide oxygen (Fig. 5).

In order to check this hypothesis we have studied the influence of concentration of acid on the catalytic activity of oxidation of methane to formic acid at 60 °C. Indeed, a significant improvement of catalytic activity was observed in the presence of 0.05–0.1 M H_2SO_4 (Fig. 6).

Even at low acid concentration of 0.05 M the TON_{HCOOH} was increased by factor 3 to attain 64 cycles. The maximal catalytic activity was observed in 0.075 M H_2SO_4. Under these conditions the catalyst showed a very high performance: 209 molecules CH_4 per catalyst molecule were oxidized to formic acid. Using 50 mg of the supported catalyst containing 1.6 mg of $(FePc^tBu_4)_2N$ complex, 2 mL of 0.11 M HCOOH solution was obtained after 20 h. This activity is far higher than that of the most published systems operating via CH_4 activation (Table 1) approaching to that of Periana's system based on Pt(II) bipyrimidine complex in oleum at 220 °C. Further increase of the H_2SO_4 concentration resulted in a progressive decrease of catalytic activity. In the 0.2 M H_2SO_4 solution the catalytic activity was almost the same as that in pure water. It should be noted that when the oxidation was performed in the presence of small amount of H_2SO_4, the catalyst was surprisingly stable. No appreciate decrease in blue colour of the catalyst was detected indicating the stability of phthalocyanine chromophore under reaction conditions.

The kinetics of oxidation methane was studied under the optimal conditions and presented in Fig. 7. The kinetic curve shows an induction period. This induction period can be explained by the initial formation of formaldehyde followed by its oxidation to formic acid.

3.5. Heterogeneous oxidation of ethylene

The scope of $(FePc^tBu_4)_2N$–H_2O_2 system was further checked in oxidation of ethylene in pure water and in 0.1 M H_2SO_4. The results are summarized in Table 3.

The main products of ethylene oxidation were formaldehyde and formic acid indicating the cleavage of C–C bond. Ethylene oxide or ethylene glycol were not detected in the course of the oxidation of ethylene. In contrast to oxidation of methane, the system in pure water was practically inactive at 25 °C. However, the oxidation in water was quite efficient at higher temperatures achieving TON of

231.8 at 70 °C (Table 3, run 5). The HCOOH/CH_2O ratio increases from 2.2 at 40 °C (Table 3, run 2) to 11.5 at 70 °C (Table 3, run 5). Using a half amount of the catalyst ~0.1 M HCOOH aqueous solution was obtained in the latter case. Interestingly, there was no such a strong influence of acid as was observed for oxidation of methane. In the presence of 0.1 M H_2SO_4 turnover numbers in HCOOH and CH_2O were 246.1 and 41.0, respectively (Table 3, run 7) as compared to 197.3 and 32.6 obtained in water (Table 3, run 3). It should be noted that the yields of products on H_2O_2 oxidant were quite high reaching 69%.

4. Conclusions

We have discovered a first bio-inspired catalytic system for the mild oxidation of CH_4 in water. The practical and green features of this novel approach (H_2O_2 as the clean oxidant, water as the clean reaction medium, easily accessible solid catalyst) as well as the relevance to biological oxidation (binuclear structure of bio-inspired complex) are of great importance both from the practical and fundamental points of view. N-Bridged diiron phthalocyanine complexes show a new unexpected reactivity and provide a novel promising approach in the field of oxidation. Importantly, available spectroscopic, labelling and reactivity data are consistent with involvement of a high-valent diron oxo species rather than with free-radical chemistry [32–36].

From the practical point of view, formic acid was proposed to be used as a raw material for hydrogen production [43]. Moreover, recent research has shown that formic acid has the potential to power fuel cells for electricity generation and automobiles [44]. The clean heterogeneous oxidation of methane and ethylene under mild conditions described in this paper presents a basis for a novel approach for the transformation of difficult-to-oxidize hydrocarbons to useful product.

Acknowledgment

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