



# Selective oxidation of methane by molecular oxygen catalyzed by a bridged binuclear ruthenium complex at moderate pressures and ambient temperature

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## ABSTRACT

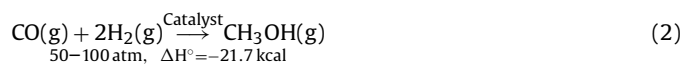
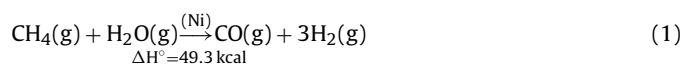
The oxidation of methane by molecular oxygen was found to be efficiently catalyzed by a binuclear bridged ruthenium complex, bis-( $\mu$ -acetato)( $\mu$ -oxo) bis-salen ruthenium (III), [L<sub>2</sub> Ru<sub>2</sub> ( $\mu$ -O)( $\mu$ -CH<sub>3</sub>COO)<sub>2</sub>] **1** (L = Hsalen), in which methanol was observed to be formed selectively with small formation of formaldehyde at moderate total pressure 10–15 atm and at 30 °C in a 1:1 (v/v) mixture of acetone–water solvent. In typical experiments conducted in a pressure reactor of 100 ml capacity at 30 °C and 15 atm pressure, 27 × 10<sup>-3</sup> M methanol and 2.4 × 10<sup>-3</sup> M formaldehyde were found to be formed with 5 × 10<sup>-4</sup> M catalyst. The employed partial pressures of methane and molecular oxygen in these catalytic experiments were at 10 and 5 atm, respectively. Complex **1** was synthesized, characterized and evaluated for catalytic oxidation of methane in detail as a function of total pressure, CH<sub>4</sub>:O<sub>2</sub> pressure ratio, concentration of the catalyst and the pressures of methane and molecular oxygen in which oxidation proved to be favorably effected by these parameters. The rates of the oxidation of methane to methanol were linearly increased on increasing the concentrations of the catalyst, methane and molecular oxygen under employed reaction conditions showing first order dependence kinetics in each concentration parameter. Based on the kinetics and experimental results, a non-radical, ionic mechanism is suggested for the oxidation of methane to methanol.

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## 1. Introduction

The direct oxidation of methane to an easily transportable liquid such as methanol has attracted great experimental and theoretical interests due to its importance as an industrial process and as model for alkane oxidation. The introduction of functional groups into the light paraffins requires severe conditions for selective reactions due to their chemical inertness. In recent years sustained efforts have been made to find a substitute for gasoline as a transportation fuel. Gasoline–alcohol blends/neat alcohols have been introduced [1] in many countries owing to its high octane number than normal fuels. Among all the gasoline substituents, methanol has several advantages as a liquid fuel [2,3] and can be prepared from a series of raw materials such as natural gas, coal, municipal solid waste, animal refuse and biomass. Catalytic conversion of methane to more useful chemicals and fuels [4,5] is one of the challenges of the century.

The existing commercial process [6] for the manufacture of methanol includes two-steps involving the steam reforming of methane to synthesis gas (reaction (1)), followed by the high-pressure catalytic conversion of synthesis gas to methanol (reaction (2)).



This process route has remained basically unchanged since its inception by BASF in 1923. The principal developments have been made (i) in catalyst formulation to increase productivity and selectivity and (ii) in process plant integration to improve output and energy efficiency to decrease the capital cost. The process suffers from high operational costs and thermal inefficiencies in the steam reforming step. Furthermore the methanol synthesis reactor is operated at relatively low conversions due to the highly exothermic nature of the reaction. Also the process needs to have clean synthesis gas free from sulfur.

Natural gas, a major source of methane using as a feed stock, has impurity gases like H<sub>2</sub>S, CO<sub>2</sub> and these impure gases effect the behavior of the catalyst during the oxidation of methane. It is of

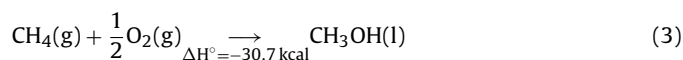
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interest to refer the issue of the effect of H<sub>2</sub>S and CO<sub>2</sub> on the catalytic behavior for methane oxidation. In the presence of H<sub>2</sub>S the behavior of the catalyst is explained in the terms of the formation of sulfur oxides from the oxidation of H<sub>2</sub>S at higher temperature. Catalyst poisoning by sulfur compounds have been identified due to very strong bonding of sulfur species [7] with the active sites of the metal of the catalyst, and such formed stable surface metal sulfides thereby prevent the reacting molecules from adsorbing at the surface. In the studied effect of H<sub>2</sub>S on the reaction of CH<sub>4</sub> with CO<sub>2</sub> over supported metal catalyst for the formation of syngas, it was found that H<sub>2</sub>S suppresses the formation of CO and H<sub>2</sub>. In the presence of H<sub>2</sub>S the amount of surface carbon formed in the reaction decreased significantly but its reactivity remained the same [8]. Sulfur has also been reported [9] for beneficial effect on the selectivity of methanol formation. In the homogeneous oxidation of methane [10], on increasing CO<sub>2</sub> levels in the feed, no adverse effect on methane conversion and methanol selectivity were observed, but selectivity of the formation of formaldehyde was increased to a small extent.

In order to overcome the drawbacks of existing commercial process [6], continuous efforts are directed towards investigating the catalytic routes under both heterogeneous [11,12] and homogeneous [13,14] conditions in which clearly a one step, direct conversion of methane to methanol (reaction (3)) is a promising alternative process.

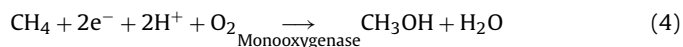


Under heterogeneous conditions the partial oxidation of methane by molecular oxygen performed on transition metal oxide catalysts [15,16] at high temperature (250–600 °C) gives <4% yield for methanol/formaldehyde. Methane oxidation [11,17] with *tert*-butylhydroperoxide and O<sub>2</sub> on iron-phtalocyanine complexes encapsulated in zeolites, gave <5% (CH<sub>3</sub>OH + HCHO) yield. Investigations are performed [18] to carry out methane oxidation at lower temperature and pressure with higher yield of methanol in heterogeneous conditions. Under homogenous conditions advances have been made for developing catalyst systems using acids viz. sulfuric [17,19] and trifluoroacetic acid [20,21] in which the reactions of methane with acid produce intermediate methyl bisulfate and methyl trifluoroacetate, respectively. These intermediates are further hydrolysed to produce methanol and acid. Methane oxidation in fuming sulfuric acid with Hg<sup>II</sup> salts [14,22] gives about 43% methanol and with Pt<sup>II</sup> complex [23] gives about 72% methanol both carried out at 150–220 °C. In strong acid solvents such as triflic or sulfuric acid, Au<sup>III</sup> cations [13] react with methane at 180 °C to selectively generate methanol at about 94% selectivity and 28% conversion.

Methane oxidation has been reported [24,25] at atmospheric pressure and high temperature >400 °C using iron phosphate catalyst and gas mixture of H<sub>2</sub> and O<sub>2</sub> in which the presence of H<sub>2</sub> increased the selectivity of methanol. Atmospheric pressure oxidation of methane had been investigated [26] with N<sub>2</sub>O in Ar in plasma induced by low input power.

Investigations on developing metal complex based catalyst systems for direct oxidation of methane to methanol by molecular oxygen seems to be more promising. Oxidation of methane to methanol by O<sub>2</sub> is done in nature by enzyme oxygenases, cytochrome P<sub>450</sub> and methane monooxygenase (MMO) in homogeneous conditions. MMO reveals the highest activity towards methane which normally is the most inert among alkanes. In MMO the active centre contains binuclear  $\mu$ -oxo ( $\mu$ -hydroxo) iron complex which is bound to the protein molecule by imidazole and carboxylate groups of amino acids. Binuclear  $\mu$ -oxo iron complex in MMO contains non-heme iron centres in the active site [27–29].

The methane oxidation (reaction (4)) proceeds initially by two electron reduction of molecular oxygen. For reduction the electrons are supplied by either a sacrificial electron donor or by the oxidation of metal ion itself in the absence of the sacrificial reductant.



Synthetic [30–32] MMO selectively catalyzes the oxidation of methane to methanol with the same transition metal (iron) which is bound to the same protein and amino acid molecules. However in the chemical system the selectivity can be obtained by choosing among potential metals and ligands. Also in synthetic monooxygenase systems it is molecular oxygen rather than hydrocarbon molecule that is activated in the oxidation reaction. Hydrocarbon is kept near the active centre by so-called hydrophobic interaction. The experiences gained from these investigations suggest that the future catalyst for oxygen atom transfer to hydrocarbons must be capable to activate oxygen as well as hydrocarbons in order to get selective and better yield. A true catalyst would be the one which can bind oxygen as well as hydrocarbon via coordination. Ruthenium complexes catalyzed oxygen atom transfer to hydrocarbons seems to be more promising because their mechanism is found to involve heterolytic [33–35] (non-radical) activation and transfer of activated oxygen to the ligated hydrocarbon by ruthenium centre. Coordinating ligands in these ruthenium complexes are either nitrogen containing monodentate [35] or nitrogen and oxygen containing multidentate [33,34] ligands. Salen having two nitrogen and two oxygen donor atoms is a versatile quadridentate ligand. It can coordinate with metal in bidentate [36] to tetradentate [37] manner. Ruthenium, the next member of the Fe group having various oxidation states [38], forms salen complexes having potential to catalyze the oxidation of saturated hydrocarbons [39,40], which are attractive for the oxidation of methane to methanol by molecular oxygen.

In present investigation, a salen based binuclear ruthenium analogue of MMO complex is found to be an efficient catalyst for the oxidation of methane by molecular oxygen at moderate pressure of 15 atm and at ambient temperature in which methanol was found to be the major product with small formation of formaldehyde. In this article we report our investigations on the synthesis, characterization and catalysis of a binuclear ruthenium salen complex for the oxidation of methane by molecular oxygen involving catalytic, kinetic and mechanistic aspects of the reaction for the selective oxidation of methane to methanol.

## 2. Experimental

### 2.1. Materials

Methane (CH<sub>4</sub>, 99.95%) manufactured by manometric method was procured from Alchemie Gases and Chemicals Private Limited, pure grade oxygen (O<sub>2</sub>, 99.98%) and nitrogen (N<sub>2</sub>, 99.95%) for purging were procured from Inox Gas suppliers, India. RuCl<sub>3</sub>·3H<sub>2</sub>O was purchased from Johnson Mathey. Acetic acid, salicylaldehyde, disodium salt of ethylenediamine, ethanol, pyridine, ammonium hexafluorophosphate, acetonitrile, and acetone were procured from s. d. Fine Chemicals Ltd., India. Organic solvents were purified by reported procedures [41]. The double distilled milli-pore de-ionized water was used throughout the present study. All other reagents were of AR grade and were used without further purifications.

## 2.2. Physical measurements

Ruthenium complex bis-( $\mu$ -acetato)( $\mu$ -oxo) bis-salen ruthenium (III),  $[L_2 Ru_2 (\mu-O)(\mu-CH_3COO)_2]$  **1** ( $L = Hsalen$ ) used as catalyst was characterized by elemental (CHN) analysis, UV–vis, IR and NMR spectroscopy. Elemental analyses were carried out on PerkinElmer Series II, 2400 CHNS/O analyzer. Spectrophotometric characterizations were done on a Shimadzu UV-160 UV–vis spectrophotometer equipped with a temperature controller TCC-240, using matched 1 cm quartz cuvettes. For recording spectra under argon, solutions were transferred to cuvettes using Schlenk technique. IR spectra were recorded as KBr discs on a PerkinElmer FT-IR, GX-FTIR spectrophotometer. Initially the sample was mixed with KBr and was crushed to fine powder using mortar and pestle. Then the fine powder was pressurized to form pellets which fit the disc. The disc was allowed to scan in the range from 4000 to 400  $cm^{-1}$ . Number of scans used was 10 and the resolution was set to 2  $cm^{-1}$ .  $^1H$  NMR was carried out by FT-NMR, Bruker, DPX-500 (500 MHz) using  $CDCl_3$  as a solvent.

## 2.3. Oxidation of methane

Reactions for the oxidation of methane were carried out in 100 ml bench top stirred reactor, Parr model Number 4843 with controlling unit supplied by Parr Reactors, USA having provisions for, stirring, maintenance of temperature and sample withdrawing. All the high-pressure reactions were done in a high-pressure laboratory specially made for conducting the experiments at high pressure and temperature. The reactor was kept in a fume hood equipped with a strong exhaust fan. The required amount of the catalyst was dissolved in 60 ml of 1:1 (v/v) mixture of acetone and water and poured in the reactor. The reactor was fitted air tight. The reactor was flushed thrice with  $N_2$  and oxygen and methane gases were introduced at the desired pressures. The reaction was then initiated by starting the magnetic stirrer at 450 rpm. All the reactions were run at ambient temperature 30 °C at 450 rpm.

## 2.4. Reaction product analysis

Products' analysis was carried out by GC–MS (Shimadzu, GCMS-QP2010) and GC (Shimadzu 17A, Japan) equipped with 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.25 mm diameter) and a flame ionization detector (FID). The GC oven temperature was programmed from 40 to 200 °C at the rate of 3 °C/min till 100 °C and at 10 °C/min up to 200 °C.  $N_2$  was used as the carrier gas. The temperature of injection port and FID was kept constant at 200 °C. The retention time of different compounds were determined by injecting pure compounds under identical conditions. Before performing the product analysis, pure samples of acetone, methanol and formaldehyde were run separately. A mixture of 0.5 M concentration of each methanol and formaldehyde was also run, and under these conditions methanol and formaldehyde were easily separated. A total of 10  $\mu$ l of samples, withdrawn during the course of the oxidation, were analysed and the amount of the products formed was estimated by comparing the peak areas with the above run mixture.

## 2.5. Kinetic measurements

A series of kinetic experiments were carried out for the rate measurements. For each kinetic run an appropriate quantity of the catalyst was dissolved in 60 ml of 1:1 acetone–water (v/v) mixed solvent in the 100 ml bench top stirred reactor and then molecular oxygen and methane were pressurized at required pressures from the gas cylinders. The pressure of methane was always kept

more than that of molecular oxygen. The reactor has provision for withdrawing the samples under pressure through a liquid sampling valve, connected with a dip tube that extended up to the bottom of the reactor. The controlled aliquots were sampled with time through a valve in which only liquid aliquots came out with the help of pressure inside the reactor. The kinetics of methane oxidation reaction was followed gas chromatographically by directly estimating the amount of methanol formed with time. Rates in the form of concentration of methanol were computed from the slopes of the plots of the concentration of methanol versus time. The solubility of methane and molecular oxygen in 1:1 acetone–water (v/v) mixed solvent was computed from the solubility data of these gases in pure solvents of 1 atm [42,43] using Henry's law.

## 3. Results and discussion

### 3.1. Synthesis and characterization of the catalyst

Ruthenium complex **1** used as catalyst, was synthesized using complex  $[Ru_2 (\mu-O) (\mu-CH_3COO)_2 (py)_6](PF_6)_2$  and salen ligand, where salen = bis-salicylaldehyde ethylenediamine and py = pyridine. The starting ruthenium [44] complex  $[Ru_2 (\mu-O) (\mu-CH_3COO)_2 (py)_6](PF_6)_2$  and salen ligand [45] were prepared by reported procedures. For the synthesis of ruthenium complex **1**, 0.1 mM (0.1 g) of  $[Ru_2 (\mu-O) (\mu-CH_3COO)_2 (py)_6](PF_6)_2$  was dissolved in 10 ml degassed and cooled (0 °C) dichloromethane, which resulted into blue solution. After addition of salen (0.25 mM, 0.067 g) to the above solution the content was kept as such for 60 min at 0 °C under nitrogen atmosphere. The content was then mixed with cooled (0 °C) degassed petroleum ether and left in the refrigerator for 24 h. The greenish blue precipitate so formed on the addition of salen ligand was filtered using G4 filter funnel and washed with petroleum ether for few minutes. The washed material was dried under vacuum using desiccator. The complex being moisture and oxygen sensitive has chances of getting oxidized; hence all the procedures were carried out under nitrogen atmosphere using Schlenk technique.

In the elemental analysis of ruthenium complex **1** the calculated C, H, and N percentages were 49.88%, 3.69% and 6.46% respectively and the measured values were found to be C = 50.01%, H = 3.03% and N = 6.98%. The UV–vis spectrum of complex **1** given in Fig. 1 showed a strong absorption band at 585 nm ( $12 \times 10^3 M^{-1} cm^{-1}$ ) as characteristic peak [44,46] for the formation of  $\mu$ -oxo bridged binuclear (Ru–O–Ru) ruthenium complex. The IR spectrum (Fig. 2)

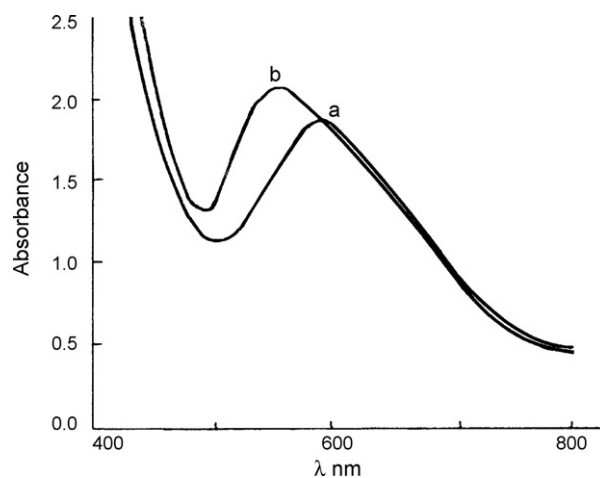


Fig. 1. UV–vis spectra of the complex **1** (a) under Ar and (b) under  $O_2$  bubbled for 1 h.

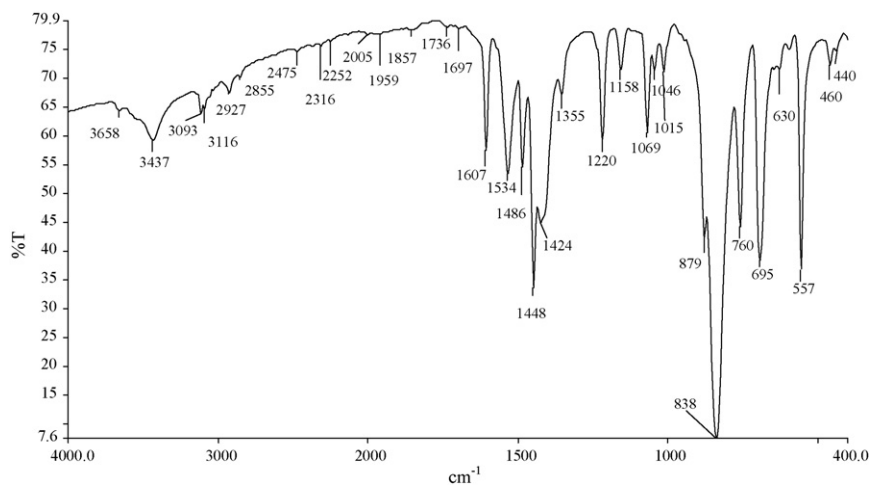
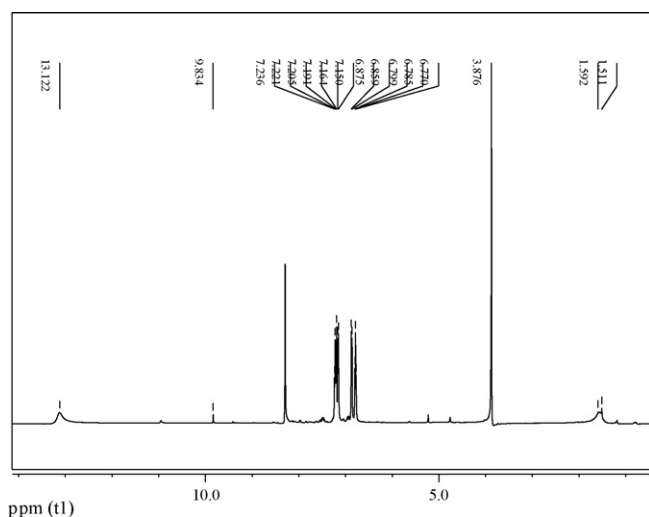


Fig. 2. IR spectrum of the complex 1.

Fig. 3.  $^1\text{H}$  NMR spectrum of the complex 1.

of complex **1** gave characteristic stretching vibrations at 1736, 1697, 1607 and an overtone peak at  $879\text{ cm}^{-1}$  (all  $\nu(\text{C}=\text{O})$ ) and a peak at  $1355\text{ cm}^{-1}$  corresponding to  $\nu(\text{C}-\text{O})$ . The peaks at 1448, 1486 and  $1428\text{ cm}^{-1}$  were obtained and assigned to C–H stretching of acetate and salen, respectively. Spectrum showed peaks at 1220 and  $838\text{ cm}^{-1}$  for C–N and C–C stretching, respectively. A broad peak exhibited at  $3437\text{ cm}^{-1}$ , assigned to  $\nu(\text{O}-\text{H})$  of phenolic-OH of salen ligand, indicated the presence of un-coordinated phenolic oxygen.  $^1\text{H}$  NMR spectrum of complex **1** and its chemical shift data is given in Fig. 3 and Table 1, respectively. Spectra gave a singlet at 3.87 ppm characteristic of the imine-protons of the coordinated salen ligand. The protons of the bridged acetates gave singlet at  $\delta = 1.51$  ppm. The spectra depicted a characteristic shift having a

Table 1

$^1\text{H}$  NMR spectral data for complex 1.

Assignments	Chemical shift
Salen (coordinated)	9.83 s (2H) –OH; 7.14–7.23 m (12H); 6.87–6.85 d (2H); 6.78–6.79 t (2H) –R; 3.87 s (4H) –CH–N–; 1.59 s (8H) –CH <sub>2</sub> –
Acetate (bridged)	1.51 s (6H) –CH <sub>3</sub>

Conditions:  $^1\text{H}$  NMR in  $\text{CDCl}_3$  with TMS as reference. Chemical shifts in ppm. Key: s = singlet; d = doublet; t = triplet; m = multiplet; –R = –C<sub>6</sub>H<sub>5</sub>.

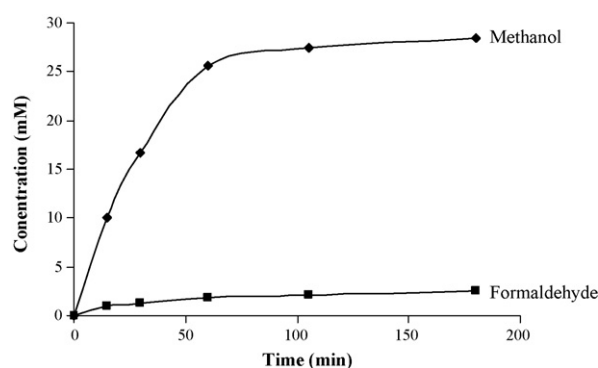
singlet at 9.83 ppm corresponding to the phenolic –OH of salen ligand. These characterization results indicated that the formulation of complex **1** involves the bridgings with two  $\mu$ -acetate and one  $\mu$ -oxo, and coordination with two salen ligands in which one phenolic group of each salen remained un-ionized [37].

### 3.2. Products of methane oxidation

In typical experiments performed for catalytic oxidation of methane with 10 atm pressure of methane and 5 atm pressure of molecular oxygen, at total pressure of 15 atm, at room temperature  $30^\circ\text{C}$  methanol was found to be the major product with small formation of formaldehyde. Under these conditions  $27 \times 10^{-3}\text{ M}$  methanol and  $2.4 \times 10^{-3}\text{ M}$  formaldehyde were formed with  $5 \times 10^{-4}\text{ M}$  catalyst. The initial rates for the formations of methanol ( $5 \times 10^{-4}\text{ M min}^{-1}$ ) and formaldehyde ( $0.45 \times 10^{-4}\text{ M min}^{-1}$ ) were found to be proportionate in the line of the amounts of the products formed.

### 3.3. Effect of the total pressure on the oxidation of methane

The effects of pressure on the oxidation of methane were studied in the total pressure range of 10.5–21 atm at  $30^\circ\text{C}$  by maintaining the methane:oxygen pressure ratio at 2 and the corresponding results are given in Fig. 4. At low pressure at 10.5 atm no product formation was observed. On increasing the pressure to 15 atm the formation of methanol as major product with a small amount of formaldehyde was observed. On further increasing the pressure at

Fig. 4. Effect of the total pressure on the oxidation of methane by molecular oxygen at  $30^\circ\text{C}$  and  $[\text{catalyst}] = 5 \times 10^{-4}\text{ M}$ .

**Table 2**  
Effect of methane:oxygen ratio on the formation of products.

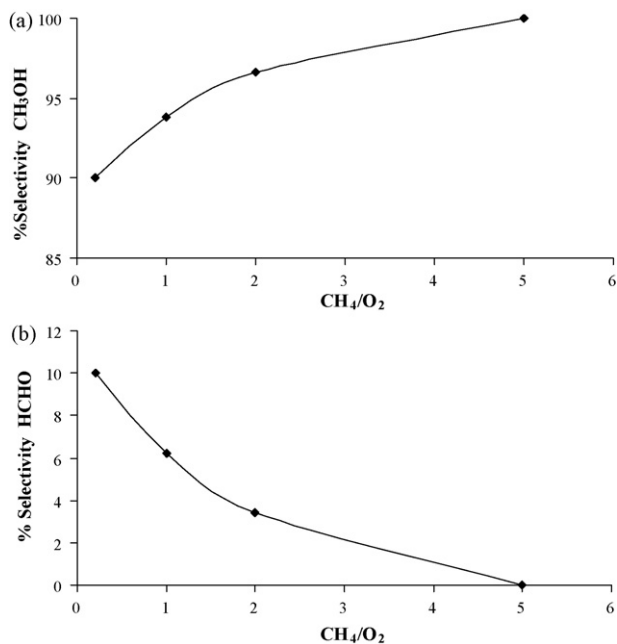
pCH <sub>4</sub> (atm)	pO <sub>2</sub> (atm)	CH <sub>4</sub> :O <sub>2</sub> ratio	% Selectivity CH <sub>3</sub> OH	% Selectivity HCHO
2.5	12.5	0.2	90	10
7.5	7.5	1	93.8	6.2
10	5	2	96.6	3.4
12.5	2.5	5	100	0

Reaction conditions: [Catalyst] =  $5 \times 10^{-4}$  M, total pressure = 15 atm, temperature = 30 °C.

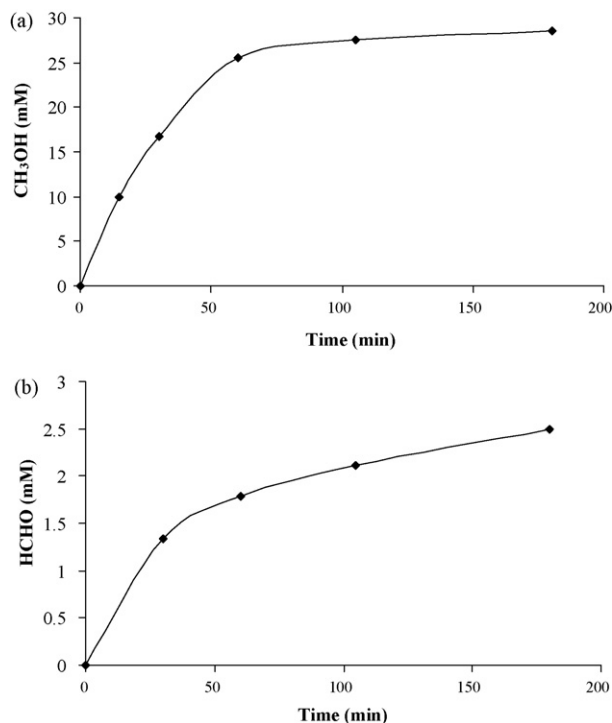
18 atm the product formations attained saturation. The product formation was decreased at higher pressure at 21 atm. The patterns of the formations of the oxidized products, methanol and formaldehyde were identical during the entire varied pressure range. At the pressures >10.5 atm the increasing tendency of methanol formation began gently and increased up to 15 atm indicating that a total pressure of 15 atm would be suitable for methane oxidation under present employed reaction conditions.

### 3.4. Effect of methane:oxygen ratio on the product formation

The ratio of methane to oxygen [47–49] plays an important role towards the product distribution to C1-oxygenates formed from methane oxidation. In order to observe the effect of the variation of the ratio of the pressure of methane to oxygen on the selectivity of products formed from methane oxidation, the ratio of methane:oxygen was varied in the range of 0.2–5.0 at total pressure of 15 atm and the corresponding results are given in Table 2 and in Fig. 5a and b. The selectivity of methanol formation was found to be increased on increasing the ratio of methane:oxygen. At a methane:oxygen ratio of 5:1 (Fig. 5a), methanol selectivity has increased to 100%. The selectivity for the formation of formaldehyde decreased on increasing the ratio and no formaldehyde was obtained at the ratio of 5:1. Higher methane/oxygen ratios provided higher methanol [47–49] selectivity suggesting that the concentration of the oxygen significantly influences the oxidation of methane to methanol. In the lower ratios the concentrations of molecular oxygen become higher and contribute towards the



**Fig. 5.** Plots of % selectivity of (a) methanol and (b) formaldehyde against the ratio of CH<sub>4</sub>/O<sub>2</sub> pressure at 30 °C, [catalyst] =  $5 \times 10^{-4}$  M, total pressure = 15 atm.



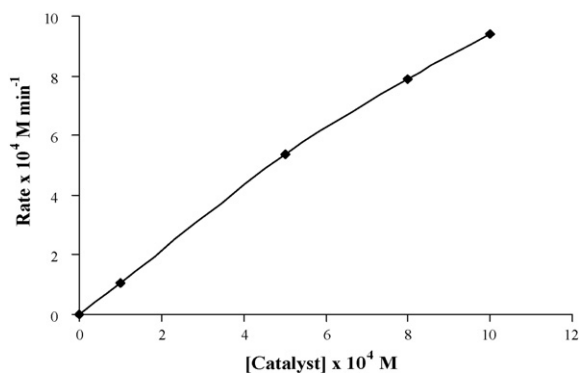
**Fig. 6.** The time-dependent plots for the formation of (a) methanol and (b) formaldehyde at 30 °C, [catalyst] =  $5 \times 10^{-4}$  M, pCH<sub>4</sub> = 10 atm, pO<sub>2</sub> = 5 atm and total pressure = 15 atm.

favorability for the formation of formaldehyde. The selectivity of methanol formation approached to be the maximum at the ratio of 2 and above. The ratio 2 is the required value of the stoichiometric reaction ( $\text{CH}_4 + (1/2)\text{O}_2 \rightarrow \text{CH}_3\text{OH}$ ) for the oxidation of methane to methanol. Formation of 1 mol of methanol from 1 mol of methane requires only 0.5 mol of molecular oxygen. However the formation of 1 mol of formaldehyde ( $\text{CH}_4 + \text{O}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}$ ) from 1 mol of methane requires 1 mol of molecular oxygen. The selective formation of methanol at the methane:oxygen ratios 2:1 and above is explainable in terms of the low concentration of molecular oxygen. In the ratios of 2:1 and above the concentration of oxygen was decreased and that of methane increased, which favored the selectivity for the methanol formation. This suggests that the controllability of oxygen pressure is remarkably effective for the selectivity of methanol formation at the methane:oxygen pressure ratios of 2:1 and above.

### 3.5. Kinetics of the oxidation of methane

The kinetics of the oxidation of methane to methanol was investigated in detail as a function of the concentration of the catalyst, pressure of methane and molecular oxygen at 30 °C. The time-dependent plots for the formation of methanol and formaldehyde are given in Fig. 6a and b, respectively. The formations of methanol (Fig. 6a) and formaldehyde (Fig. 6b) were found to be faster and linear in the beginning (1 h) of the oxidation reaction and after that the formations became slow. A similar trend of the products formations, being faster and linear in the beginning were observed in all the kinetics experiments conducted in the said conditions. The rates of the formation of methanol ( $d[\text{methanol}]/dt$ ) were suitably determined from the linear portions of such plots.

In order to see the stability of the catalyst, in the experiments conducted for longer time (24 h), it was found that an extremely slow increase in the formation of methanol and formaldehyde



**Fig. 7.** Effect of the catalyst concentration on the rate of methanol formation at 30 °C,  $p_{\text{CH}_4} = 10$  atm,  $p_{\text{O}_2} = 5$  atm and total pressure = 15 atm.

remained continued. This observation of no decay in the formation of the products indicated the stability of the catalyst for long time. The sustainability of the catalyst in the terms of the number of cycles (turn over number) was determined by the usual relation: TON = moles of the products (methanol + formaldehyde)/mole of catalyst, and was found to be 58 cycles.

### 3.6. Effect of the catalyst concentration on the rate of methanol formation

The oxidation of methane to methanol was studied by conducting the experiments at 30 °C at different initial concentrations of the catalyst with 10-fold variation in the range  $1 \times 10^{-4}$  to  $10 \times 10^{-4}$  M, while keeping the pressures of methane and molecular oxygen, methane:oxygen ratio, reaction volume and agitation speed constant. The results are depicted in Fig. 7. The rate of oxidation was found to be linearly increased on increasing the catalyst concentration under employed reactions conditions and also the plot of rate versus [catalyst] passes through origin indicating that the reaction is completely catalytic. The kinetic plot (Fig. 7) of the rate versus catalyst concentration ( $d \log(\text{rate})/d \log[\text{catalyst}] = 1$ ) indicated that the rate of oxidation of methane to methanol is first order dependent with respect to the concentration of the catalyst.

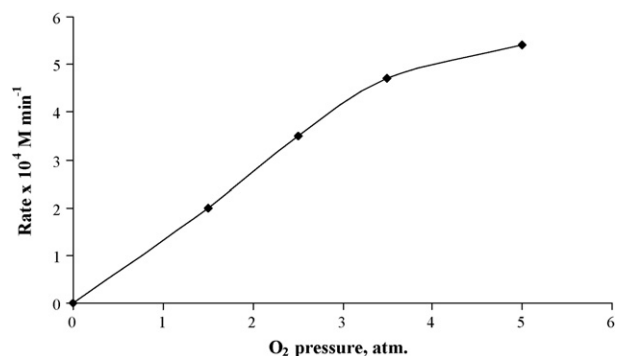
### 3.7. Effect of oxygen pressure on the rate of methanol formation

Kinetic experiments were conducted at different pressure (1.5–5 atm) of molecular oxygen at 10 atm constant pressure of methane. The total pressure in the reactor was maintained constant at 15 atm using nitrogen as balance gas. The rate of the formation of methanol was favored on increasing the pressure of molecular oxygen. In order to have an insight in to the solubility of molecular oxygen in 1:1 (v/v) water–acetone solvent at the different applied pressure of molecular oxygen in present investigations, the solubilities were calculated and given in Table 3. The solubility was calculated at 30 °C by using formula: solubility of molecular oxygen in mole/liter (M) =  $1000nv/V$ ; where  $n$  = pressure of O<sub>2</sub>

**Table 3**  
Solubility and concentration of oxygen at various pressures.

Entry	O <sub>2</sub> press. (atm)	O <sub>2</sub> solubility ( $\times 10^3$ M)	[O <sub>2</sub> ] ( $\times 10^3$ M)
1	1	4.4	40
2	1.5	6.6	60
3	2.5	11.06	100
4	3.5	15.41	140
5	5	22.02	200

Reaction conditions: temperature = 30 °C, total pressure = 15 atm.



**Fig. 8.** Effect of variation of pressure of O<sub>2</sub> on the rate of formation of methanol at 30 °C. [catalyst] =  $5 \times 10^{-4}$  M,  $p_{\text{CH}_4} = 10$  atm and total pressure = 15 atm. N<sub>2</sub> is used as a balance gas to maintain the total pressure at 15 atm.

(in atm),  $V$  = volume of 1 mol of gas at 30 °C at 1 atm pressure,  $v$  = solubility of O<sub>2</sub> (in ml/(ml atm)) in 1:1 (v/v) water–acetone solvent, and calculated as  $v = x(0.5) + y(0.5)$ ; where  $x$  and  $y$  are the solubilities (ml/(ml atm)) of molecular oxygen in water and acetone respectively at atmospheric pressure and were taken from the reported [42] data. Concentrations of molecular oxygen were calculated at different applied pressures at 30 °C by reported method [50] for the used reactor of 100 ml capacity and the values are mentioned in Table 3. The plot of the pressure of oxygen versus rate of the methanol formation depicted in Fig. 8 indicated that the rate was linearly increased with pressure showing first order dependence ( $d \log(\text{rate})/d \log[\text{O}_2] \sim 1$ ) with respect to the concentration of molecular oxygen.

### 3.8. Effect of methane pressure on the rate of methanol formation

Kinetic experiments were conducted at different pressure (3.5–10 atm) of methane at 5 atm constant pressure of oxygen. Similar to the variation of oxygen pressure, methane pressure was varied at the total constant pressure of 15 atm using nitrogen as balance gas. The rate of the formation of methanol was increased on increasing the pressure of methane. The solubility and concentration of methane gas at different employed pressures at 30 °C were evaluated, using calculations similar to oxygen gas as mentioned above, and are given in Table 4. The solubility data [42] of methane in water and acetone at atmospheric pressure were taken from the literature and the concentrations [50] were calculated using reported method. The plot of the pressure of methane versus rate of the methanol formation (Fig. 9) showed first order dependence ( $d \log(\text{rate})/d \log[\text{CH}_4] \sim 1$ ) with respect to the concentration of methane.

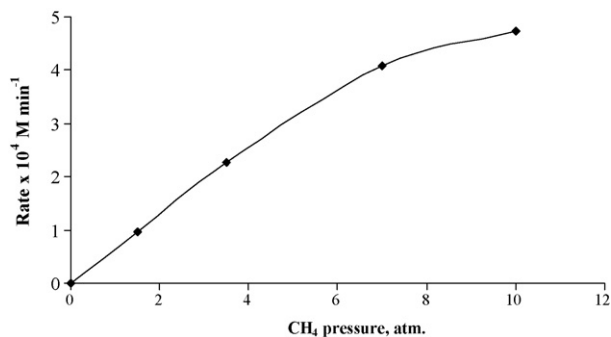
### 3.9. Mechanism for the oxidation of methane to methanol

On the basis of kinetic results, product analysis and other experimental results, a proposed mechanism on the reaction routes concerned for the catalytic oxidation of methane to methanol is given in Scheme 1. The detail kinetic studies performed for the oxi-

**Table 4**  
Solubility and concentration of methane at various pressures.

Entry	CH <sub>4</sub> press. (atm)	CH <sub>4</sub> solubility ( $\times 10^3$ M)	[CH <sub>4</sub> ] ( $\times 10^3$ M)
1	1	13.16	40
2	1.5	19.74	60
3	3.5	46.04	140
4	7	92.12	280

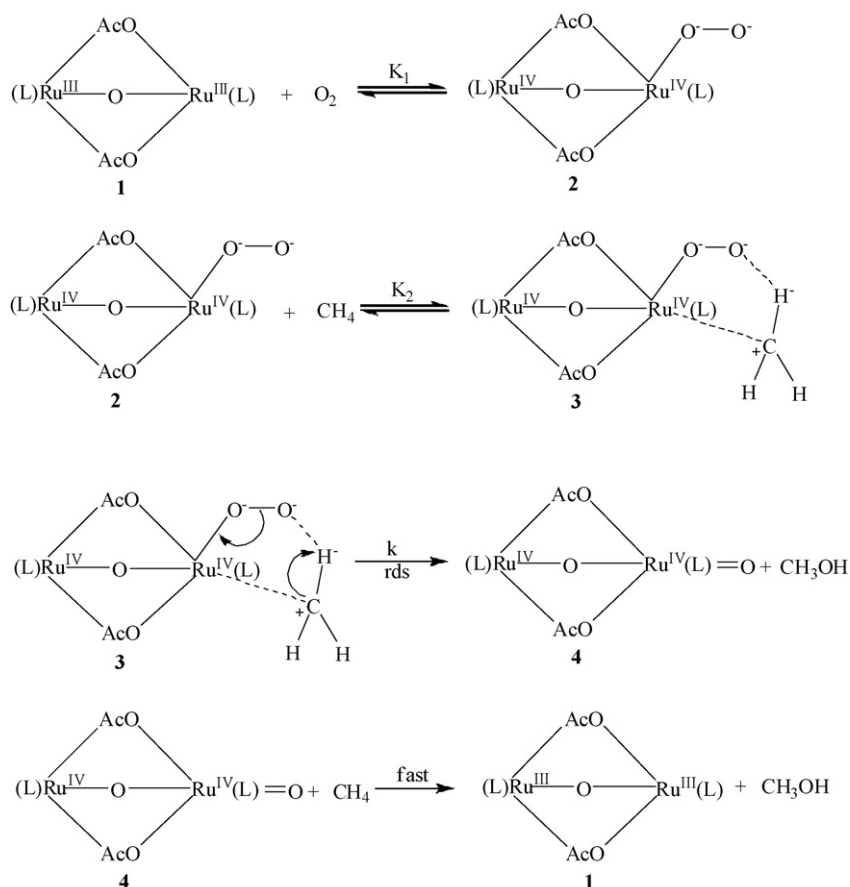
Reaction conditions: temperature = 30 °C, total pressure = 15 atm.



**Fig. 9.** Effect of the variation of the pressure of CH<sub>4</sub> on the rate of formation of methanol at 30 °C, [catalyst] =  $5 \times 10^{-4}$  M,  $p_{O_2}$  = 5 atm and total pressure = 15 atm. N<sub>2</sub> is used as a balance gas to maintain the total pressure at 15 atm.

ation of methane by molecular oxygen indicated that the rate of methanol formation was first order dependent in terms of the concentrations of the catalyst, molecular oxygen and methane, leading an involvement of over all third order kinetics in this oxidation under the employed reaction conditions. In line of these kinetic results of first order dependence in terms of concentration of catalyst and molecular oxygen in the proposed mechanism molecular oxygen first co-ordinates with catalyst **1** and forms an intermediate peroxy complex **2** with one of the ruthenium in equilibrium step  $K_1$ . The formation of the complex **2** in solution has been characterized and substantiated spectrophotometrically. Spectrum of complex **1** under O<sub>2</sub> (Fig. 1b) exhibited a shift in the  $\lambda_{max}$  from 585 nm ( $\epsilon = 120 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ ) to 560 nm ( $\epsilon = 56 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ ) which

evidenced [36] the interaction of O<sub>2</sub> with complex **1** to form peroxy complex **2**. The intermediate complex **2** reacts with methane in pre-equilibrium step  $K_2$  and forms kinetic intermediate complex **3** and its formation is proposed on the basis of first order dependence in methane concentration. In the complex **3** cleavage of the C–H bond occurred by forming a carbonium ion resulting from the hydride abstraction from one of the C–H bond of methane. The concerted cleavage of the O–O bond and transfer of one of the oxygen atoms to the carbonium ion centre to yield methanol followed by formation of ruthenyl oxo (Ru<sup>IV</sup>=O) complex **4**, take place in the rate determining step  $k$ . Complex **4** reacts further with another molecule of methane to give yet another molecule of methanol and the catalyst **1** in original form. The mechanisms involving the cleavage of the C–H bond of saturated hydrocarbons by hydride abstraction and the cleavage of O–O bond of molecular oxygen are reported [33,35] during the oxidation of saturated hydrocarbons to corresponding alcohols catalyzed by ruthenium complexes using molecular oxygen as oxidant in mixed aqueous organic solvents. In order to have an insight in to the nature of the mechanism, experiment conducted by adding a radical trapping agent, acrylonitrile in the methane oxidation reaction mixture did not give any positive evidence for the formation of radical intermediate, indicating that the mechanism follows non-radical route. With this observation a non-radical, ionic mechanism via formation of carbonium ion by hydride abstraction was found to be more reasonable to propose for the oxidation of methane to methanol. The mechanism is equivalent to oxygenation of organic substrates by oxygen atom insertion into the C–H bond by an ionic route reported by Sugimoto and Sawyer [51,52]. Experiments conducted with methanol as substrate, under identical conditions of methane oxidation, could not show the for-

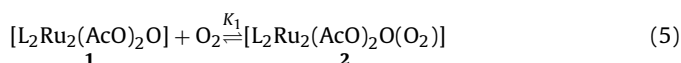


**Scheme 1.** Proposed mechanism for the catalytic oxidation of methane to methanol.

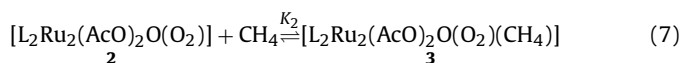
mation of any product indicated that the catalyst oxidizes methane selectively to methanol and prohibit deep oxidation.

### 3.10. Rate expression and evaluation of equilibrium constants for methanol formation

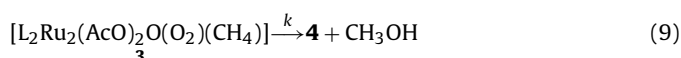
On the basis of kinetic observations and proposed mechanism the rate law for the oxidation of methane to methanol was derived and equilibrium constants  $K_1$  and  $K_2$ , and rate constant  $k$  corresponding to the rate determining step, mentioned in following Eqs. (5)–(8) and reaction (9) were determined.



$$K_1 = \frac{[\text{L}_2\text{Ru}_2(\text{AcO})_2\text{O}(\text{O}_2)]}{[\text{L}_2\text{Ru}_2(\text{AcO})_2\text{O}][\text{O}_2]} \quad (6)$$



$$K_2 = \frac{[\text{L}_2\text{Ru}_2(\text{AcO})_2\text{O}(\text{O}_2)(\text{CH}_4)]}{[\text{L}_2\text{Ru}_2(\text{AcO})_2\text{O}(\text{O}_2)][\text{CH}_4]} \quad (8)$$



By considering a steady-state concentration of the catalyst **1** ( $[\text{Cat}]$ ) the rate of the oxidation in terms of the formation of methanol is written as

$$\text{Rate} = d[\text{CH}_3\text{OH}]/dt = k[\mathbf{3}] = k[\text{L}_2\text{Ru}_2(\text{AcO})_2\text{O}(\text{O}_2)(\text{CH}_4)] \quad (10)$$

$$\text{Rate} = kK_2[\mathbf{2}][\text{CH}_4] = kK_2[\text{L}_2\text{Ru}_2(\text{AcO})_2\text{O}(\text{O}_2)][\text{CH}_4] \quad (11)$$

$$\text{Rate} = kK_1K_2[\mathbf{1}][\text{O}_2][\text{CH}_4] = kK_1K_2[\text{Cat}][\text{O}_2][\text{CH}_4] \quad (12)$$

Rate expression (12) shows 1st order dependence in  $[\text{catalyst}]$ ,  $[\text{O}_2]$ , and  $[\text{CH}_4]$ . Under steady state and equilibrium conditions the total concentration of the catalyst ( $[\text{Cat}]_T$ ) is given by Eq. (13).

$$[\text{Cat}]_T = [\mathbf{1}]_T = [\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}] \quad (13)$$

Substituting **[2]** and **[3]** from Eqs. (5)–(8) we get

$$[\text{Cat}]_T = [\text{Cat}] + K_1[\text{Cat}][\text{O}_2] + K_1K_2[\text{Cat}][\text{O}_2][\text{CH}_4] \quad (14)$$

Hence,

$$[\text{Cat}] = \frac{[\text{Cat}]_T}{1 + K_1[\text{O}_2] + K_1K_2[\text{O}_2][\text{CH}_4]} \quad (15)$$

Now, the rate expression in terms of the total concentration of the catalyst, considering Eqs. (15) and (12) is written as Eq. (16).

$$\text{Rate} = \frac{kK_1K_2[\text{Cat}]_T[\text{O}_2][\text{CH}_4]}{1 + K_1[\text{O}_2] + K_1K_2[\text{O}_2][\text{CH}_4]} \quad (16)$$

Reversing Eq. (16) we get

$$\frac{[\text{Cat}]_T}{\text{Rate}} = \frac{1}{[\text{CH}_4]} \left( \frac{1}{kK_1K_2[\text{O}_2]} + \frac{1}{kK_2} \right) + \frac{1}{k} \quad (17)$$

$$\frac{[\text{Cat}]_T}{\text{Rate}} = \frac{1}{[\text{O}_2]} \left( \frac{1}{kK_1K_2[\text{CH}_4]} \right) + \frac{1}{kK_2[\text{CH}_4]} + \frac{1}{k} \quad (18)$$

According to Eq. (17), a plot of  $[\text{Cat}]_T/\text{Rate}$  versus  $[\text{CH}_4]^{-1}$  gave a straight line (Fig. 10) with a positive intercept on Y-axis and positive slope, hence supported Eq. (17). Similarly a plot of  $[\text{Cat}]_T/\text{Rate}$  versus  $[\text{O}_2]^{-1}$  depicted in Fig. 11 gave a straight line supporting the validity of Eq. (18). The constants  $k$ ,  $K_1$  and  $K_2$  were kinetically determined at 30 °C from the analysis of the kinetic data with help of the slopes and intercepts of the plots of Figs. 10 and 11, by substituting the required known concentration values. The rate constant  $k$  was found to be 2.5 min<sup>-1</sup>. The calculated values for the

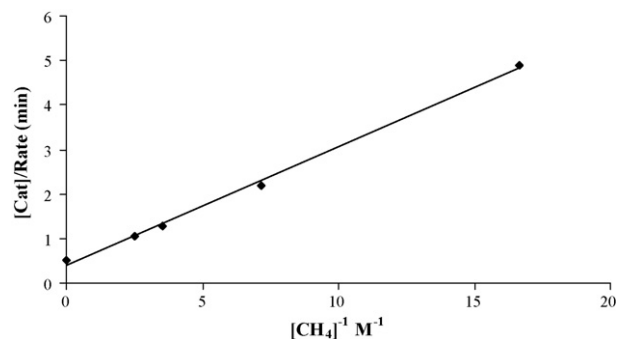


Fig. 10. Plot of  $[\text{Cat}]/\text{Rate}$  versus  $[\text{CH}_4]^{-1}$  for temp. = 30 °C,  $p\text{O}_2 = 5$  atm and total pressure = 15 atm.

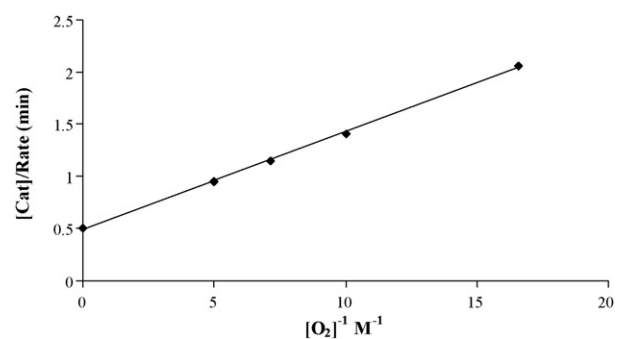


Fig. 11. Plot of  $[\text{Cat}]/\text{Rate}$  versus  $[\text{O}_2]^{-1}$  for temp. = 30 °C,  $p\text{CH}_4 = 10$  atm and total pressure = 15 atm.

formation constants  $K_1$  and  $K_2$  are 715 and 13 M<sup>-1</sup>, respectively. The formation constant  $K_2$  being 55 times lower than  $K_1$  indicated that the coordination of methane with ruthenium takes place only to a small extent in comparison to the coordination of molecular oxygen with ruthenium and this is in line of the fact that methane is highly saturated. The value of  $K_2$  for coordination of methane, though lower compared to molecular oxygen, is however sufficient to support that the reactants, molecular oxygen and methane, get coordinatively activated by the catalyst before the rate determining step. Similar observations of the higher formation constant for the coordination of molecular oxygen and lower formation constant for the coordination of saturated hydrocarbon, cyclohexane, have been reported [34,36] for the oxidation of cyclohexane to cyclohexanol by molecular oxygen using ruthenium complexes catalyst systems in mixed aqueous–organic solvents.

## 4. Conclusions

A binuclear bridged ruthenium (III) complex **1** has shown an efficient catalytic activity for the direct oxidation of methane by molecular oxygen in moderate conditions of pressure (10–15 atm) and at ambient temperature in which methanol was selectively formed with small amount of formaldehyde. The formation of methanol from methane oxidation was found to be favorable on increasing the reaction parameters: total pressure,  $\text{CH}_4:\text{O}_2$  pressure ratio, concentration of **1** and the partial pressures of methane and molecular oxygen. The ratio of  $\text{CH}_4:\text{O}_2$  pressure significantly contributed towards selective methanol formation and at a ratio of 5:1, only methanol was formed. The catalyst oxidizes methane selectively to methanol and prohibits deep oxidation. The rates of the methanol formation were found to be first order dependent with respect to the concentrations of catalyst, molecular oxygen and methane. The mechanism of the oxidation of methane to



methanol was observed to involve the formation of intermediate peroxy complex **2**, by interaction of **1** and O<sub>2</sub>, which on interacting with methane formed kinetic intermediate **3**. The cleavages of the C–H and O–O bond in complex **3** followed by transfer of one of the oxygen atoms to the carbonium ion centre yielded the product methanol. The catalyst is observed to activate both molecular oxygen and methane involving its mechanism equivalent to the insertion of oxygen atom into the C–H bond of methane by an ionic route.

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