

Osmania University



DC



Faculty of Science

This is to certify that B. Ramesh

son/daughter of B. Ramesh Rao having pursued a course of study prescribed by this University and having passed the requisite Examinations by thesis, has been admitted to the Degree of

Doctor of Philosophy

in the Faculty of Science

The subject in which he/she presented a thesis for the Degree was

" (Chemistry) "

Anchored Montmorillonite-palladium (II) Complexes:
Catalysis and Kinetics of Hydrogenation of some
Olefins."

Given under the seal of the University

Hyderabad

Dated MARGASHIRA 22, 1922
DECEMBER 13, 2000

DCM
Vice-Chancellor

No. 42/Ph.D/Exams/99

Dated 3-11-1999

P R E S S N O T E

The following candidates who had presented the thesis on the subject mentioned against each for the Degree of Doctor of Philosophy (Ph.D) are declared qualified for the award of Degree of Doctor of Philosophy (Ph.D) of Osmania University, Hyderabad.

Sl. No.	Name of the Candidate	Subject	T i t l e	Supervision/Regn./Date
1.	Mr. MUJEEB-UR-RAHMAN	Statistics	Variations in dietary pattern and the associated factors"	Dr.K.Visweswara Rao, Deputy Director, N.I.N.Hyd-7. (20-4-1990)
2.	Mr. V. RAMA KRISHNA	Physics	A Study of Elastic behaviour and magnetic properties of Polycrystalline barium Hexagonal ferrite with an addition of B_2O_3 content	Prof.S.Ramana Murthy, Dept.of Physics,O.U. (13-3-1989)
3.	Mr. TAJAMUL HUSSAIN	Bio-Chemistry	Evaluation of the thesis entitled 'Assessment of calpain and DNA in DMD: their importance in the diagnosis of disease and carrier states	Dr.Anandaraj MPJS Dept.of Genetics, Begumpet,Hyd. (30-4-1994)
4.	Mr. B. RAMESH	Chemistry	Anchored montmorillonite palladium (II) complexes: catalysis and kinetics of Hydrogenation of some olefins	Prof.P.K.Saiprakash Dept.of Chemistry, O.U. (24-4-1993)
5.	Mr. I. GANESH	Chemistry	Studies on supported vanadium oxide oxidation catalysts	Dr.B.M.Reddy, Scientist, I.I.C.T.Hyd. (27-11-1995)

S. Gouda
Addl. Controller of Examinations
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OSMANIA UNIVERSITY
MEMORANDUM OF MARKS

8087

No.

Dated 31 AUG 1994

Bsc Phd Examination, Feb 1994

D. D. No.

Dated. 199

Roll No. 94-2-209

Name B. Ramesh

No. Sl.	SUBJECTS	THEORY		PRACTICAL		TOTAL	
		Maximum Marks	Marks Secured	Maximum Marks	Marks Secured	Max. mum Marks	Marks Secured
	Chemistry	100	52	100	85	200	137

Aggregate ... 200 - 137

Aggregate in words... one Hundred Thirty Seven only

RESULT: Pass

Clerk-in-Charge.

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Controller of Examinations.

N.B. :- The Application and Fee of Rs. 20/- per Subject prescribed for the Recounting of Marks will be accepted only upto one Month from the date of Publication of Results.

(i)
date
JOINT

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9) MUST BE CLAIMED WITHIN 15 DAYS OF Y.

1. P&AO (EMR). The expenditure will be debitable to the Budget Head 'Grants-in-Aid Fellowship'.
2. Bill file.
3. Guard file.

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Note: (1) A booklet of CSIB Fellowship/Associateship is enclosed for guidance.
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UNIVERSITY OF SCIENCE

UNDERTAKING BY A RESEARCH FELLOW / ASSOCIATE ON ACCEPTANCE OF THE AWARD OF FELLOWSHIP/ASSOCIATESHIP

I B. Ramesh Son / Daughter / Wife of Shri B. Ramalingam residing at 2-3-645/4/2, PREMNASAR, AMBERPET, HYDERABAD

have been awarded the Junior/Senior Research Fellowship, / Research Associateship of the Council of Scientific & Industrial Research (hereinafter called Council). I accept the award and undertake that :

- (i) during the entire tenure of the Fellowship / Associateship, I shall abide by the rules and regulations of the Council for the award ;
- (ii) as a recipient of the Council's Fellowship / Associateship, I shall also abide by the rules/discipline of the Institution where I have been given the facility to work ;
- (iii) I shall devote whole of my time to research during the tenure of fellowship / associateship except as provided in the rules ;
- (iv) I shall obtain the approval of the Council before accepting any other award or allowance, if offered to me during the tenure of fellowship/associateship ;
- (v) I shall prepare the progress report of my work at the end of each year and communicate it to the Council through the guide/supervisor/Senior Faculty Member ;
- (vi) I shall send two copies of a detailed consolidated report of research work through the Supervisor on termination of the fellowship/associateship ;
- (vii) I also hereby declare that if the results of research are such that can be exploited commercially by taking a patent or otherwise, commercial exploitation and patent rights will rest exclusively with the Council (This clause is applicable for the guide also).

Date of joining 2/1/93 (Forenoon/Afternoon)



[Handwritten signature of Prof. P. K. Sai Prakash]

PROF. P. K. SAI PRAKASH
HEAD
Department of Chemistry

To
The Under Secretary
Extra Mural Research Division
Council of Scientific & Industrial Research
CSIR Complex, Pusa, New Delhi-110 012

Signature of the Research Fellow/Associate

[Handwritten signature of B. Ramesh]

Countersigned by the Supervisor/Senior Faculty Member

Date

PROF. P. K. SAI PRAKASH
HEAD
Department of Chemistry
Osmania University
HYDERABAD - 500 007.

Sir, I report myself on duty as Junior/Senior* Research Fellow/Research Associate on the Forenoon/Afternoon of 2/1/93 at Dept. of CHEMISTRY College/Department of OSMANIA UNIVERSITY (Name of University./Institute)

Date :

Yours faithfully,

[Handwritten signature of Prof. P. K. Sai Prakash]
Signature of the Head of the Dept./ Supervisor/Senior Faculty Member
PROF. P. K. SAI PRAKASH
HEAD
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[Handwritten signature of B. Ramesh]
Signature of the Research Fellow/Associate

*Delete whichever is not applicable.

Kinetics and mechanism of hydrogenation of some olefins catalysed by anchored montmorillonitebipyridinepalladium(II) acetate

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Abstract. Kinetics of hydrogenation of some olefins such as 2,5-furandione, *cis*-butenedioic acid, *trans*-butenedioic acid, *cis*-methylbutenedioate and *trans*-methylbutenedioate catalysed by anchored montmorillonitebipyridinepalladium(II) acetate have been studied in THF medium. The observed rate was found to be first order with respect to partial pressure of hydrogen and fractional order with respect to both [catalyst] and [substrate]. The rate of hydrogenation follows the trend: 2,5-furandione > *cis*-butenedioic acid > *trans*-butenedioic acid > *cis*-methylbutenedioate > *trans*-methylbutenedioate. Thermodynamic parameters were evaluated, the rate law and a probable mechanism have been proposed.

Keywords. Olefin; catalytic hydrogenation; anchored catalyst; montmorillonite; kinetics of hydrogenation.

1. Introduction

The second half of the twentieth century saw a breakthrough in the field of catalysis with the technique of heterogenizing homogeneous catalysts by anchoring them to insoluble supports (Pittman 1980). Enhanced reaction rates were obtained when metal complex homogeneous catalysts were attached to a suitable support (Ermakov 1981). Such catalysts also offer advantages in recovery and recycling of the active species as well as enhanced specificity, though leaching cannot be avoided. The inorganic supports that have been explored include silica, alumina, glasses, zeolites and clay (Pinnavaia and Welta 1978). Of all these, clays are shown to be good supports. Smectite clay, which includes hectorite and montmorillonite, has greater potential as providing better catalyst support (Quale and Pinnavaia 1979). The intra-crystal space of the clay can be swelled by various solvents and the degree of swelling depends upon the interlayer cations, the substrate and negative charge density on the silicate sheet (Hartley 1985). Successful attempts were made to synthesize a series of montmorillonite functionalised palladium(II) complexes (Choudary *et al* 1985; Choudhary and Bharati 1987; Shimazu *et al* 1993). Even though mechanistic studies of hydrogenation of olefinic compounds were explored (Turkovich *et al* 1950; Bailor and Itatani 1967; Nayak *et al* 1985) very little attention has been paid to the kinetic study for understanding the mechanism. Here we report the hydrogenation of a series of olefins, namely 2,5-furandione, *cis*-butenedioic acid, *trans*-butenedioic acid, *cis*-methylbutenedioate

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Hydrogenation of some allylic alcohols catalysed by anchored montmorillonitebipyridinepalladium(II) acetate - A kinetic study

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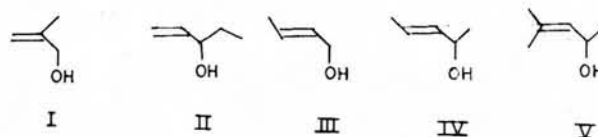
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Hydrogenation of some allylic alcohols like 2-methyl-2-propen-1-ol, 4-penten-3-ol, *trans*-2-buten-1-ol, *trans*-3-penten-2-ol and 4-methyl-3-penten-2-ol has been carried out by anchored montmorillonitebipyridinepalladium(II) acetate in THF medium. Under the reaction conditions 100% saturation of carbon-carbon double bond is observed and there is neither polymerisation nor isomerisation. The observed rate has been found to be first order each with respect to partial pressure of hydrogen and [substrate] and fractional order with respect to [catalyst]. The rate of hydrogenation follows the order: 2-methyl-2-propen-1-ol > 4-penten-3-ol > *trans*-2-buten-1-ol > *trans*-3-penten-2-ol > 4-methyl-3-penten-2-ol. Thermodynamic parameters have been evaluated, rate law and a plausible mechanism have been proposed.

One of the most intensively investigated research areas in recent years in the field of catalysis is immobilization of transition metal complexes on solid supports like organic polymers and inorganic oxides¹⁻⁶. Serious interest in these catalysts originated with efforts to develop industrially competitive homogeneous catalysts to supplant heterogeneous catalysts, which met with limited success due to the separation problem associated with homogeneous systems. In addition to providing a solution to this problem, the new anchored catalysts have attractive features of being reproducible, allowing control and knowledge of the nature of the incipient species immobilized on the support. Inorganic supports that have been used are silica, alumina, glasses, zeolites and clay. Of all these, clays are shown to be good catalyst supports. The clay used in our study is montmorillonite, a smectite clay. This clay possesses large amounts of highly reactive species which can be readily exchanged by inorganic complexes. Apart from this, the intra-crystal space can be swelled by various polar solvents⁷. The degree of swelling depends on the interlayer cations, the substrate and negative charge density on silicate sheet. Keeping these advantages in mind, Choudary *et al* synthesized a series of montmorillonite functionalised palladium(II) complexes^{8,9}. Number of attempts were made to hydrogenate the olefinic compounds, using anchored catalysts, however only in few instances detailed kinetic study has been undertaken¹⁰⁻¹⁸. We report a detailed kinetic study of hydrogenation of some allylic alcohols catalysed

by anchored montmorillonitebipyridine-palladium(II) acetate.

The influence of structure on reactivity is a topic of current interest in the study of the mechanism of alkene hydrogenation on supported metal catalysts^{19,20}. Therefore in this study, to determine as how olefin structure influences rate of hydrogenation, the catalyst was tested with a series of olefins of varying double bond substitution like 2-methyl-2-propen-1-ol (I), 4-penten-3-ol (II), *trans*-2-buten-1-ol (III), *trans*-3-penten-2-ol (IV) and 4-methyl-3-penten-2-ol (V)(Scheme.1)



Scheme-1

In all cases, the reaction is a function of substituents on the olefinic bond. The catalyst was very effective towards 100% selectivity in the hydrogenation of carbon-carbon double bond without any polymerisation and isomerisation. This is in contrast to the hydrogenation of allyl alcohols catalysed by other catalysts like polymer bound palladium catalysts where isomerisation is a side reaction^{15,16}.

Hydrogenation of 1-alkenes catalysed by anchored montmorillonite palladium(II) complexes: a kinetic study

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Abstract

Hydrogenation of 1-hexene, 1-heptene and 1-octene was carried out using anchored montmorillonitebipyridine-palladium(II) acetate (C_I), montmorillonitebipyridinepalladium(II) chloride (C_{II}) and montmorillonitediphenylphosphinopalladium(II) chloride (C_{III}) in THF. Under the reaction conditions 100% saturation of the carbon-carbon double bond was observed. The observed rates were first order with respect to the partial pressure of hydrogen and fractional order with respect to [substrate] and [catalyst]. The hydrogenation rates were found to be: 1-hexene > 1-heptene > 1-octene for all three catalysts. The reactivity order of various catalysts is: $C_I > C_{II} > C_{III}$. Thermodynamic and activation parameters were evaluated. A rate law and a plausible mechanism has been proposed.

Introduction

Palladium and rhodium complexes have been used as catalysts in many heterogeneous and homogeneous reactions [1–5]. The design of catalysts for heterogeneous reactions is not easy because the catalytically active sites are not well-defined. Although this problem is solved in homogeneous catalytic systems, inherent practical problems like corrosion, deposition of the catalysts on the walls of the reactor, and recovery of the catalysts from the reaction mixture remain, and the homogeneous catalysts have been applied in only limited number of chemical processes [6, 7]. The ideal union of the chemical advantages of homogeneous catalysis with the practicality of a solid heterogeneous system gave rise to anchored catalysis [8]. These new generation catalysts in which metal complexes are bound to insoluble organic or inorganic supports have advantages for both homogeneous and heterogeneous catalytic systems. Apart from enhanced activity, these anchored catalysts offer many advantages such as recovery and recycling of the active species as well as enhanced specificity and activity [9].

Platinum group metals have been widely used for decades as hydrogenation catalysts. The most effective metal varies with each substrate. Though palladium, platinum, rhodium and ruthenium have been anchored to a variety of supports, it appears that, except in some cases, palladium is the metal of choice. It is an extremely active catalyst for carbon-carbon double bond saturation, particularly in the presence of multiple unsaturation, as it is much more labile than other metals. The

activity and selectivity of a catalyst vary with the method of preparation, the type of metal atom or ion and the nature of ligands attached to metal [10–12].

Catalytic hydrogenation of organic functional groups is one of the most common steps in the synthesis of organic compounds. Unfortunately during the past few decades, there has been very little fundamental research into kinetics [13–19]. Therefore in order to understand the kinetics of hydrogenations of olefins using anchored catalysts, hydrogenation of 1-hexene, 1-heptene and 1-octene have been carried out using anchored montmorillonitepalladium(II) complexes such as montmorillonitebipyridine palladium(II) acetate, montmorillonitebipyridinepalladium(II) chloride and montmorillonitediphenylphosphinopalladium(II) chloride. Montmorillonite, the solid support used to anchor the palladium(II) complexes in the present study, is a naturally occurring clay [8]. It possesses large amounts of highly reactive surface consisting of two-dimensional polymeric silicate anions separated by layers of hydrated cations, normally Na^+ and Ca^{2+} . The most important property of montmorillonite from the standpoint of catalyst design is its ability to swell in different solvents to a different extent and, exert cation exchange capacity and intercalation. This paper describes the effect of increasing the chain length of olefins, the nature of ligands around the metal ion and the effect of interlayer spacing of the clay on hydrogenation rates.

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**ANCHORED MONTMORILLONITE-PALLADIUM (II) COMPLEXES:
CATALYSIS AND KINETICS OF HYDROGENATION OF SOME OLEFINS**



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B. RAMESH

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CERTIFICATE

This is to certify that the present work compiled in the thesis entitled "ANCHORED MONTMORILLONITEPALLADIUM(II) COMPLEXES: CATALYSIS AND KINETICS OF HYDROGENATION OF SOME OLEFINS" has been carried out by Mr. B.RAMESH, under my supervision in the Department of Chemistry, University College of Science, Osmania University, Hyderabad, for the award of degree of **Doctor of Philosophy** in Chemistry.

The results embodied in this thesis are original and no part of the thesis has been submitted to any other University for the award of any degree or diploma.


6/3/99
PROF. P.K. SAIPRAKASH
(Research Supervisor)