



TOGETHER
for a sustainable future

OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

RESTRICTED

December 1988
ENGLISH

17606

DEVELOPMENT OF NOVEL SHAPE SELECTIVE ZEOLITE CATALYSTS

DP/IND/87/007/11-01

INDIA

Final Report*

Prepared for the Government of the Republic of India
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of Dr. Sigmund M. Csicsery
CTA

Backstopping officer: M. Derrough, Industrial Operations Technology Division

United Nations Industrial Development Organization
Vienna

* This document has been reproduced without formal editing

TABLE OF CONTENTS

UNDP PROJECT DP/IND/87/007/11

SUMMARY OF ACHIEVEMENTS IN 1988	1
AGENDA FOR TRIPARTITE REVIEW MEETING OF NOV. 14, 1988.	2
A : FOLLOW UP REPORT	2
B : PROJECT CONCEPT AND DESIGN	6
C : PROGRESS	6
D : OPERATIONAL ISSUES AND PROBLEMS	6
JOB DESCRIPTIONS	9
Experts in Zeolite Chemistry & Catalysis:General	10
Background Information	11
Other "Experts"	14
E : WORK PLAN FOR YEARS 1989-1992	19
Work schedule	23
F : DECISIONS AND RECOMMENDATIONS	27
PROJECT DOCUMENT	28
SUMMARY OF WORK DONE UPTO OCTOBER 1988	29
Annexure 1 (Isomorphous Substitution of Fe in Faujasite)	31
Annexure 2 (Isomorphous Substitution of Fe in ZSM-23)	31
Annexure 3 (Isomorphous Substitution of Fe in Beta-Zeolite)	33
Annexure 4 (Novel Zeolite with unknown Structures UN-1 & UN-2)	36
Annexure 5 (Direct Synthesis of High Si Large Pore Mordenite)	44
Annexure 6 (Preparation of EU-1 Zeolite with high Si content)	45
Annexure 7 (Scientific papers published during Sept.87-Oct.88)	46
Annexure 8 (Patents List)	48
Annexure 9 (Letter, Prof. Y. Ono, Oct., 7, 1988)	49
OUTPUTS : Schedule of Project Review, Judgement and Evaluation	50
STUDY TOUR REPORTS	51
Dr. Paul Ratnasamy	51
Dr. S.Sivasanker	53
Dr. B.S. Rao	53
FELLOWSHIP REPORTS	60
Dr. Joseph Kuruvilla	60
Dr. A. N. Kotasthane	62
Dr. MS A. J. Chandwadkar	62

- TABLE I : PROJECT BUDGET COVERING UNDP CONTRIBUTION
- TABLE II : PROJECT BUDGET COVERING UNDP CONTRIBUTION
- TABLE III : PROJECT BUDGET COVERING UNDP CONTRIBUTION
- TABLE IV : 1988 ACCOMPLISHMENTS
- TABLE V : 1988 ACTIVITIES
- TABLE VI : EXPERTS CONTACTED
- TABLE VII : EXPERTS CONTACTED
- TABLE VIII: SCHEDULE OF EXPERTS
- TABLE IX : 1989 ACTIVITIES (PROPOSED)
- TABLE X : EQUIPMENT
- TABLE XI : ADDRESSES OF EXPERTS
- TABLE XII : ADDRESSES OF EXPERTS
- TABLE XIII: ADDRESSES OF EXPERTS

UNDP PROJECT : DP/IND/87/007/11-01

SUMMARY OF ACHIEVEMENTS IN 1988

1. NCL HAS ACCOMPLISHED THE OBJECTIVES SET FOR 1988 :
 - : SUBSTITUTED FE INTO THE LATTICE OF FAUJASITE
 - : MADE TWO NEW ZEOLITE STRUCTURES

2. IN ADDITION, NCL MADE SEVERAL SIGNIFICANT NEW DISCOVERIES :
 - FE IN ZSM-20
 - FE IN BETA
 - FE IN ZSM-23
 - DIRECT SYNTHESIS OF HIGH SILICA MORDENITE
 - DIRECT SYNTHESIS OF HIGH SILICA EUJ-1
 - NEW, LESS EXPENSIVE AND SIMPLER SYNTHESIS OF BETA

POTENTIAL COMMERCIAL APPLICATIONS :

- * CUMENE PROCESS WITH HIGH SILICA MORDENITE
- * HYDRODEWAXING WITH FE BETA
- * XYLENE ISOMERISATION WITH FE BETA

3. THE WORK DONE SO FAR HAS RESULTED IN :
 - 11 SCIENTIFIC PUBLICATIONS
 - 11 PATENT APPLICATIONS

DEVELOPMENT OF NOVEL SHAPE SELECTIVE ZEOLITE CATALYSTS

PROJECT : DP/IND/87/007/11-01

Agenda for Tripartite Review, Nov. 14, 1988

A : Follow-up Report

NCL has completed the 1988 plans of this Project, ahead of schedule. Furthermore, NCL has made significant progress in many areas of this UNDP Project in addition to what was planned for 1988. Dr. Ratnasamy's Report "Summary of Work done upto October 1988" and Annexures 1-8 (Pages 29-49) describe the accomplishments in detail. Here we summarise NCL's accomplishments.

Tables I and II show the Project Budget. Table III details the 1988 and 1989 section of the original Budget and the actual expenditure.

Objectives of the Project

1. Synthesis and characterization of zeolites with faujasite structure and containing iron (Fe) in the lattice framework.
2. Characterization of the structural, physicochemical and catalytic properties of a new zeolite material of unknown structure.

The Project Document is shown on Page 28.

Accomplishments

Table IV summarises NCL's Accomplishments in 1988.

1. A series of faujasites, containing various amounts of Fe in the framework has been synthesised. The presence of Fe in the framework has been demonstrated by more than one techniques. Some

extra framework Fe is also present. Catalytic activities have been determined. NCL is now exploring potential commercial applications.

NCL has written 14 papers on these accomplishments (Annexure 7), and filed 11 Patent Applications (Annexure 8). Eleven of the papers have been published or under publication. Three are being reviewed.

2. Two new zeolite structures (UN-1 and UN-2) have been made at NCL. Preliminary characterizations show that both materials are so-called "small pore" zeolites; that is the pores are surrounded by 8 overlapping MO₄ tetrahedra (where M = Si or Al).

* Zeolite crystal structures may be determined from powder XRD spectra. This is a very difficult task; at present, only a handful of laboratories scattered around the world can do it. The Project's CTA has negotiated with some of these Institutions. One of these (Prof. Gallen Stucky's Laboratory at the University of California at Santa Barbara, California, USA) is willing to do the work for us. Delays in UNIDO authorizations have, however, prevented the full characterization of UN-1 so far.

Experts disagree at present whether UN-2 is a pure or a mixed phase zeolite. Its powder XRD spectrum has features resembling both Phi and a mixture of analcime and gmelinite. We need more studies here.

Because they are small-pore zeolites, UN-1 nor UN-2 have only limited commercial potential as catalysts (e.g. dewaxing, or Selectoforming). Non-catalytic applications are also possible (e.g. adsorbents).

3. NCL's accomplishments in addition to the 1988 Work Plan:

a : Iron has been incorporated into the framework of ZSM-20. The new zeolite has been characterized. The crystals are 100% pure. NCL has also evaluated the catalytic properties (activity, selectivity, stability) of this new material.'

b : Iron has been incorporated into the framework of zeolite beta. Its properties have been characterized. The crystals are 100 % pure.

c : NCL has synthesised a high-silica mordenite. High-Silica mordenite has great commercial potential. This is the first successful direct synthesis of this material. Its properties have been characterized. The crystals are 100 % pure.

d : NCL has synthesised a high silica EU-1 zeolite. Again this is the first successful direct synthesis of this material. Its properties have been characterized. The crystals are about 100 % pure.

e : NCL has found a better and less expensive process to synthesize zeolite beta.

The scientific importance and commercial potential of these accomplishments are obvious and need not be emphasised. Some of the many possible commercial applications already investigated are :

f : The iron-containing beta zeolite may be a better Xylene Isomerization Catalyst than those used commercially today. It combines the advantages of Mobil's HZSM-5 (high ethylbenzene conversion of high LHSV) and Engelhard and UOP's mordenite (hydro-isomerisation of ethylbenzene to xylenes). If further aging studies confirm initial trends, this may be a major breakthrough. We should then exploit all potentials of this

promising discovery !

g : NCL is currently evaluating the high-silica mordenite as a solid Cumene Manufacturing Catalyst. All present commercial processes use liquid phosphoric acid catalyst. Lower capital expenses, elimination of environmentally hazardous sludge disposal, and non-corrosive catalyst are just few of the advantages of the new solid catalyst. NCL has applied for patent coverage.

4. Equipment status

Of the \$ 332,318 scheduled for expendable and non-expendable equipment, \$ 129,478 has been spent. The purchasing of a Geomecanique reactor for \$ 203,032 is scheduled for later this year. Thus by the end of this year, we will spend about \$ 192 more than scheduled.

5. Study Tours and Fellowships

Table V summarises 1988 Study Tours, Fellowships, and Experts Visits.

The planned 3 study tours and 3 fellowship tours, plus an additional study tour by the Project Director have been completed. Reports of the participants are submitted separately. Out of the projected \$ 102,000, only \$ 92,000 was spent. The remaining \$ 10,000 is transferred to 1989.

Annexures 10, 11, 12 and 13 contain th Reports of the participants in the Study Tour and Fellowship Programme. (Pages 50-70.

6. Experts visits

The visits of Mr. H. Lovink, Prof. Ono and Dr. Csicsery

(Project CTA) have used up or will use up by the end of the year only 2.3 months of the projected 7.3 months. 5 months will be transferred to 1989. The causes of the problems of Experts' visits, and their possible solutions are discussed in Chapter D.

CONCLUSION

NCL has fulfilled its 1988 research objectives. In addition, it has discovered four more new zeolites, two of which have significant commercial potential. Furthermore, a simpler and more economic route has been found to make zeolite beta.

B: PROJECT CONCEPT AND DESIGN

The original concept and relevance of the Project to the priorities of the Government as envisaged in the project document are still appropriate.

C: PROGRESS

1. There has been substantial progress in achieving the Project objectives and production of the Project outputs. See Section A.

2. The Project, as being implemented, still remains very much relevant to the development efforts of the Government in the sector.

3. The environment of the Project has not changed. The development and application of novel shape selective zeolites still remain desired objectives for the advancement of the chemical industry.

D : OPERATIONAL ISSUES AND PROBLEMS

This project is proceeding smoothly, well ahead of its schedule on every front except one; the visits of Experts. In 1988 only 2.3 months have been utilized of the scheduled 7.3 months. Three factors contribute to this situation,

(a) We would like to have Experts who are the World's best in their respective fields. Most of these people are very busy. Teaching schedules, sabbaticals arranged several years in advance, organisation and attendance at international conferences, government duties, etc. fill their schedules for the forthcoming two or three years. (Second-rate experts would be

available at short notice, but we do not need them).

(b) : Some of the best potential Experts work in industry. Conflict of interest problems do not allow participation in this UNDP project for several of these people. This is especially true in the "Zeolite Synthesis" category.

We recommend to combine the "Zeolite Synthesis" category of this Project with that of "Physicochemical Characterization : I. General:" and rename it "Zeolite Chemistry and Catalysis, General". We believe that the elimination of this narrow category will make it easier for our best potential Experts to obtain the consent of their Corporations.

(c) Slow processing of UNIDO delays scheduling of the visits of Experts. It could also inconvenience some of our Experts already committed to visit NCL (e.g. see Prof. Ono's letter of October, 7, 1988, Annexure 9, Page 49 .Please speed up the processing of paperwork at UNIDO. Please be sure to send the proper job description (Pages 11-12) for the visiting Experts. (The 1988 Job Descriptions sent to the Project CTA contained an outdated, incorrect job description).

Job descriptions for the various "Expert" categories are shown on the following pages.

Tables VI and VII list the Experts contacted by NCL or the CTA. Tables XI -XIII give the addresses of each Expert.

Table VIII shows the Schedule of Experts for the duration of the whole Project.

Notes for 'Job Descriptions'

1. The following sections are the same for each 'Job Description' :

Duty Section

Purpose of Project

Reporting

Language

Background information.

The 'Background Information' section is attached only to the first Job Description.

2. The Experts in 'Zeolite Chemistry and Catalysis : General' subcategory is combined with the 'Zeolite Synthesis' category.

The new Post Title is 'Experts in Zeolite Chemistry and Catalysis : General'.

3. Note that all dates required are for between September and March of 1989, 1990 and 1991.

Names of Experts contacted and recommended are listed in Tables VI and VII. The full addresses are shown in Tables XI, XII and XIII.

JOB DESCRIPTION : Project : DP/IND/87/007 - II-01

Post title : Experts in Zeolite Chemistry & Catalysis : General.

Duration : 3-4 weeks, with possibility of extension in subsequent year(s).

Date required:

Several such experts are needed. They would come in three consecutive seasons, between September and March in 1989, 1990 and 1991. The first one or two expert should come before the end of March 1989, therefore recruitment is urgent.

Duty station : Pune (India).

Purpose of project

The long term objective of the project is to develop new shape selective zeolites and their applications in the petroleum and organochemical industries. The immediate objectives are (a) to support NCL research schemes for the development of new shape selective zeolites and catalysts, (b) establish a competent research and development team of scientists and engineers at NCL capable of developing new shape selective zeolite catalysts and of developing their applications.

Duties

The expert will be assigned to the National Chemical Laboratory, Pune, and in consultation with appropriate government authorities UNDP and UNIDO, he will be expected to carry out the following tasks:

- Review NCL's zeolite and catalyst programme, and suggest improvements and new methods.
- Review equipments and instruments available and the instruments proposed for further work.
- Give directions for laboratory work.
- Advise on establishing short and long-term research objectives.
- Indicate priorities.

Reporting : The expert will submit a report on his findings and recommendations.

Qualifications : High level scientist with extensive experience with zeolites.

Language : English

**Background
information :**

The Indian Government is keen to use the facilities of the National Chemical Laboratory (NCL) to develop SHAPE SELECTIVE CATALYSTS, e.g. zeolites. These relatively new catalysts have already brought dramatic improvements in a number of refinery and petrochemical processes. The Indian National Chemical Laboratory has a proven record of invention, research and development in this area.

The Project should help India to develop new SHAPE SELECTIVE CATALYSTS and those processes which will use these catalysts. Its main and foremost task is to evolve and demonstrate a procedure for the production of highly efficient zeolite catalysts. It is expected that many more novel applications will be discovered for these catalysts and they will facilitate many chemical reactions which presently cannot be practiced on an economic scale.

SHAPE SELECTIVE CATALYSTS are used for the production of gasoline from methanol, production of olefins, isomerization of aromatics, alkylation of olefins, alkylation of benzene and toluene and dewaxing of middle distillates and lube stocks.

NCL has been engaged in the synthesis, characterization and development of applications in the area of shape selective zeolite catalysts for the past 6 years. More than 60 publications in research journals, 25 patents and 15 presentations in international research conferences have been achieved in this area during this period. NCL is a recognized institution where graduate work leading to Ph.D's in chemistry and chemical engineering are carried out. Currently, about 60 students work there for their Ph.Ds in these two fields.

NCL's most important accomplishments are two catalytic processes used commercially in India. These are xylene isomerization and ethylbenzene production. The former has better yield than competing processes. The latter uses a completely new and unique route based on dilute ethanol instead of ethylene. NCL invented the catalysts, worked out their large-scale synthesis and developed the processes.

Today, these NCL catalysts are manufactured under license from NCL by M/s Associated Cement Companies Limited, Bombay and M/s United Catalysts India Limited, Bombay. Naphta reforming, production of methyl amines, toluene disproportionation, etc. are expected to be commercialised in the next few years.

NCL has well established facilities for the collection of kinetic data on catalytic processes using different types of micro-reactor systems. NCL's Instrumentation Centre has facilities such as ECSA, X-ray, SEM, etc. An internationally renowned experts team in chemical reaction engineering supports reactor and modelling simulation with special emphasis on the critical problem of dynamics and stability. However, NCL's current, more sophisticated objectives need UNDP assistance. New experimental and analytical facilities are needed and technical and scientific expertise should be built up in certain critical fields. Without this help NCL's work will not have the required and expected impact on the industrial development of India.

JOB DESCRIPTION
DF/IND/87/007/11.33 A

Post title : Experts in Physicochemical Characterization
of Zeolites and Catalysts :
II : Quantitative Powder X-Ray Diffraction.

Duration : Three to Four weeks, with possibility of
extension in subsequent year(s).

Date required :
One expert is needed. He should come between September and
March of 1989.

Duty station : Pune (India), of the Laboratory of the Expert.*

Purpose of Project :

The long term objective of the project is to develop new shape selective zeolites and their application in the petroleum and organochemical industries. The immediate objectives are (a) to support NCL research schemes for the development of synthesis, and characterization of new shape selective zeolites and catalysts, (b) demonstrate the preparation of suitable catalysts for refinery and petrochemical industries, (c) establish a competent research and development team of scientists and engineers at NCL capable of synthesising, characterizing and developing new shape zeolite catalysts and of developing their applications.

Duties :

The expert will be assigned to the National Chemical Laboratory, Pune, and in consultation with appropriate government authorities UNDP and UNIDO, he will be expected to carry out the following tasks :

- Help determine the structure of the new zeolite NCL discovered recently.
- Review NCL's zeolite and catalyst programme, and suggest improvements and new methods.
- Review the instruments available and the instruments proposed for further work.

Reporting : The expert will submit a report on his findings and recommendations.

Qualifications : High level scientist with extensive experience in quantitative powder X-ray diffraction structure determination.

Language : English.

* An Expert in quantitative powder X-ray diffraction needs his own instrument and computer in his own laboratory to accomplish his task. He need not come to NCL in Pune.

JOB DESCRIPTION

DF/IND/87/007 /M. 3 B

Post title : Experts in Physicochemical Characterization of Zeolites and Catalysts :
III : Transmission Electron Microscopy.

Duration : Three to Four weeks, with possibility of extension in subsequent year(s).

Date required :

One or two such experts are needed. They should come between September and March in 1989, 1990 and 1991.

Duty station : Pune (India).

Purpose of Project :

The long term objective of the project is to develop new shape selective zeolites and their application in the petroleum and organochemical industries. The immediate objectives are (a) to support NCL research schemes for the development of synthesis, and characterization of new shape selective zeolites and catalysts, (b) demonstrate the preparation of suitable catalysts for refinery and petrochemical industries, (c) establish a competent research and development team of scientists and engineers at NCL capable of synthesising, characterizing and developing new shape zeolite catalysts and of developing their applications.

Duties :

The expert will be assigned to the National Chemical Laboratory, Pune, and in consultation with appropriate government authorities UNDP and UNIDO, he will be expected to carry out the following tasks :

- Review NCL's zeolite and catalyst programme, and suggest improvements and new methods.
- Review the instruments available and the instruments proposed for further work. Suggest training programme in transmission electron microscopy for NCL staff.
- Help determine crystal size morphology and agglomeration of NCL's new zeolites.
- Advise on establishing short and long-term research objectives - indicate priorities.

Reporting : The expert will submit a report on his findings and recommendations.

Qualifications : High level scientist with extensive experience in Transmission Electron Microscopy.

Language : English.

JOB DESCRIPTION
DP/IND/87/007/M.03 C

Post title : Experts in Physicochemical Characterization of Zeolites and Catalysts : IV - ESCA & EPR

Duration : Three to Four weeks, with possibility of extension in subsequent year(s).

Date required : One or two such experts are needed. They should come between September and March in 1989, and 1990.

Duty station : Pune (India).

Purpose of Project :

The long term objective of the project is to develop new shape selective zeolites and their application in the petroleum and organochemical industries. The immediate objectives are (a) to support NCL research schemes for the development of synthesis, and characterization of new shape selective zeolites and catalysts, (b) demonstrate the preparation of suitable catalysts for refinery and petrochemical industries, (c) establish a competent research and development team of scientists and engineers at NCL capable of synthesising, characterizing and developing new shape zeolite catalysts and of developing their applications.

Duties :

The expert will be assigned to the National Chemical Laboratory, Pune, and in consultation with appropriate government authorities UNDP and UNIDO, he will be expected to carry out the following tasks :

- Review NCL's zeolite and catalyst programme, and suggest improvements and new methods.
- Review the instruments available and the instruments proposed for further work.
- Help in characterizing Fe in Fe-faujasite and Fe-pentasil zeolite not just qualitatively but also quantitatively.
- Advise on establishing short and long-term research objectives - indicate priorities.

Reporting : The expert will submit a report on his findings and recommendations.

Qualifications : High level scientist with extensive experience in EPR and ESCA techniques (Recommended Dr. J. Q. Adams, see list.

Language : English.

JOB DESCRIPTION
DF/IND/87/007/11.04

Post title : Experts in Catalytic Reactions, Chemistry and Engineering

Duration : Three to Four weeks, with possibility of extension in subsequent year(s).

Date required :
About five such experts are needed. They should come in three consecutive seasons, between September and March in 1989, 1990 and 1991.

Duty station : Pune (India).

Purpose of Project :

The long term objective of the project is to develop new shape selective zeolites and their application in the petroleum and organochemical industries. The immediate objectives are (a) to support NCL research schemes for the development of synthesis, and characterization of new shape selective zeolites and catalysts, (b) demonstrate the preparation of suitable catalysts for refinery and petrochemical industries, (c) establish a competent research and development team of scientists and engineers at NCL capable of synthesising, characterizing and developing new shape zeolite catalysts and of developing their applications.

Duties :

The expert will be assigned to the National Chemical Laboratory, Pune, and in consultation with appropriate government authorities UNDP and UNIDO, he will be expected to carry out the following tasks :

- Review NCL's zeolite and catalyst programme, and suggest improvements and new methods.
- Review the test reactors available
- Advise on potential applications of NCL's new zeolites. Select the most appropriate test reactor. Help designing the appropriate differential and/or integral test reactor.
- Advise on establishing short and long-term research objectives - indicate priorities.
- In later stages of the project help in scaling up the reaction.

Reporting : The expert will submit a report on his findings and recommendations.

Qualifications : High level chemical engineer as chemist with extensive experience in catalysis over zeolites and reaction engineering.

Language : English.

JOB DESCRIPTION
DP/ING/87/007 /11.05

Post title : Experts in Chemical Process Technology.

Duration : Three to Four weeks.

Date required :

About three such experts are needed. They should come between September and March of 1990 and 1991.

Duty station : Pune (India).

Purpose of Project :

The long term objective of the project is to develop new shape selective zeolites and their application in the petroleum and organochemical industries. The immediate objectives are (a) to support NCL research schemes for the development of synthesis, and characterization of new shape selective zeolites and catalysts, (b) demonstrate the preparation of suitable catalysts for refinery and petrochemical industries, (c) establish a competent research and development team of scientists and engineers at NCL capable of synthesising, characterizing and developing new shape zeolite catalysts and of developing their applications.

Duties :

The expert will be assigned to the National Chemical Laboratory, Pune, and in consultation with appropriate government authorities UNDP and UNIDO, he will be expected to carry out the following tasks :

- Advice on engineering problems associated with commercialisation
- Help in scaling up the process from pilot plant to commercial scale.
- Advice on establishing short and long-term research objectives - Indicate priorities.
- Give directions for laboratory and pilot plant work.
- Review the equipment available.

Reporting : The expert will submit a report on his findings and recommendations.

Qualifications : High level engineer with extensive experience in chemical process technology.

Language : English.

Recommendation : Dr. S. Khoobiar, the UNDP Expert of this project : 750 Ridge Rd., Kinnelon, N.J.07405, USA.

JOB DESCRIPTION
DF/IND/87/007/11.06

Post title : Experts in Process Control.

Duration : Three to Four weeks.

Date required :

Two or three such experts are needed. They should come between September and March of 1990 and 1991.

Duty station : Pune (India).

Purpose of Project :

The long term objective of the project is to develop new shape selective zeolites and their application in the petroleum and organochemical industries. The immediate objectives are (a) to support NCL research schemes for the development of synthesis, and characterization of new shape selective zeolites and catalysts, (b) demonstrate the preparation of suitable catalysts for refinery and petrochemical industries, (c) establish a competent research and development team of scientists and engineers at NCL capable of synthesising, characterizing and developing new shape zeolite catalysts and of developing their applications.

Duties :

The expert will be assigned to the National Chemical Laboratory, Pune, and in consultation with appropriate government authorities UNDP and UNIDO, he will be expected to carry out the following tasks :

- Advice on engineering problems.
- Help in scaling up the process from pilot plant to commercial scale.
- Advice on establishing short and long-term research objectives - Indicate priorities.
- Give directions for laboratory and pilot plant work.
- Review the equipment available.

Reporting : The expert will submit a report on his findings and recommendations.

Qualifications : High level chemical engineer with extensive experience in process control

Language : English.

Recommendation : Professor Ken. Bishop
University of Delaware
Dept. of Chem. Engg.
Newark, Delaware 19716.

E

WORK PLAN FOR YEARS 1989-92

(SECOND TO FIFTH YEARS OF THE PROJECT)

(GENERAL SUMMARY)

SECOND YEAR (1989)

See the work schedule for detailed quarterly break up of the work.

1: Synthesis of zeolites with new framework structures

Aluminosilicate zeolites with a 3 dimensional channel structure without cavities and with a pore diameter in the range 6-8 Å have great scientific and industrial potential. The absence of cavities will minimise coking, a shape selective reaction. The pore diameter is large enough to allow ingress of substituted aromatics and branched hydrocarbons. We propose to attempt synthesis of such zeolites using bulky long chain quaternary ammonium salts.

2: Modification of zeolites to enable them to exhibit new catalytic properties

We will modify several zeolites by steaming, silylation, acid treatment, and other techniques to change (1) Al distribution and thus, acid strength distribution and (2) accessibility. We will evaluate the performance of such modified zeolite in typical acid catalysed transformations.

Characterization of new zeolites

During the first year of this project, NCL has made two new crystalline zeolites. Since any new zeolite is of fundamental and potential technical interest, we are engaged in a major program to study the structure and physicochemical and catalytic properties of these two unknown materials. Two types of tests will be implemented:

a: Model compound test n-C₆ vs Me-C₅

Here we will need experts in zeolite reactions.

b: Commercial reactions (e.g. like Selectoforming) and devaxing)

In the first 3-4 months, further exploratory synthetic studies will be carried out to delineate and standardise conditions to get good quality zeolite crystals in high, reproducible yields. In the remaining months of the year, the physicochemical and catalytic properties of this new zeolite will be studied in a systematic and thorough manner.

3: Synthesis of zeolites with new chemical composition and lattice framework structure

We will try to introduce B, Fe, and other heteroatoms into the framework of new zeolites we discovered. We will use various physicochemical techniques (MAS NMR, ESR, XRD, etc.) to confirm the incorporation of heteroatom(s) in the lattice.

4. Catalytic applications of novel ferrisilicates

During 1988, many novel ferrisilicates like Fe-Y, Fe-beta, Fe-ZSM-23 and Fe-ZSM-20 were synthesised in the execution of the UNDP Project. During 1989, some of them, especially Fe-Y and Fe-beta, will be evaluated for potential application as hydrocracking and dewaxing catalysts. For this purpose, metals like Pt or Pd will be introduced in these zeolites. Due to the presence of Fe, the metal dispersion of in these ferrisilicate zeolites is expected to be more stable than in the corresponding aluminosilicate analogs.

5. Initiate studies on pelleting and binding framework-Fe zeolites.

Find suitable binders which do not contain aluminum to prevent Al exchange into the zeolite framework during preparation, use or regeneration.

Determine the effects of binders on catalytic activity, adsorption capacity, surface area, etc.

Determine Al exchange from Al-containing binders into Fe zeolites. Use catalytic activity tests, NMR, NH₃ TPD, IR, etc. Compare binder-free and bound samples before and after thermal and hydrothermal treatments.

6. Work schedule

The schedule of work along with UNDP inputs are summarised below. 1989 Study Tours and Fellowships are also summarized on Table IX. Equipment proposed for 1989 are summarized on Table X.

THIRD YEAR

We will evaluate at the bench scale level and over long time periods those new zeolites which were prepared during the first two years of this project. We will evaluate these materials for possible use in xylene isomerisation, naphtha reforming, hydrocracking, hydrodewaxing and for other important petrochemical, chemical and petroleum processing applications.

FOURTH AND FIFTH YEARS

During the fourth and fifth years, those new zeolites which show promise in specific chemical applications will be identified. Further work will be focussed on two areas

- 1: Scale-up of the synthesis of the new zeolites to pilot plant and commercial batch levels. At this phase of the project we will collaborate with catalyst manufacturing companies.
- 2: Process development leading to preliminary process design packages for selected chemical processes of industrial importance.

We will also prepare and submit a Final Report containing all publications and internal reports from NCL in the area of zeolite catalysts prepared under this project during this period.

WORK SCHEDULE

PERIOD	ACTIVITY	PERSON IN-CHARGE	MANPOWER UTILISED M M	ITEM NO. IN PROJ. DOC.	EQUIPMENT TO BE PROVIDED BY UNDP (COST, S)	FELLOW- SHIP M M	STUDY TOUR M M
1989							
1.QR.	1. SYNTHESIS OF A ZEOLITE WITH NOVEL COMPOSITION	V.P. SHIRALKAR	50	8	GAS CHROMATOGRAPHS (70,000)		
23.	2. CHARACTERISATION	S.G. HEGDE	70	1	REACTORS FOR ZEOL. SYN. (50,000)		
	3. ACTIVITY TESTING	S. SIVASANKER	120	10	HIGH PRESS. VALVES (10,000)		
				13	GAS COMPRESSOR (50,000)		
				14	BACK PRESS REGULATORS (50,000)		
				15	PRESS. TRANS. (20,000)		

CONTD. 2/-

24.

2. QR. 1. SYNTHESIS OF NEW ZEOLITES	V.P. SHIRALKAR	50
2. CHARACTERISATION	J. KURUVILLA	70
3. ACTIVITY TESTING	S. SIVASANKER	120
3. QR. 1. ZEOLITE MODIFICATION	V.P. SHIRALKAR	50
2. CHARACTERISATION	J. KURUVILLA	50
3. ACTIVITY TESTING	S. SIVASANKER	120
4. QR. 1. SYN. OF ZEOL. WITH NEW COMP. AND STR.	V.P. SHIRALKAR	50
2. CHARACTERISATION	S.G. HEGDE	30
3. ACTIVITY TESTING	S. SIVASANKER	120

16	MOISTURE ANALYSER (10,000)		
	ACC FOR XRD (60,000)	24*	4**
	ELECTROBALANCE (25,000)	}	
	SURF. AREA ANAL. (20,000)		
	FUSION APP. (20,000)		
	VISCOSMETER (25,000)		
	MOSSBAUER SP. (25,000)		

TOTAL : \$ 435,000

* S.G. HEGDE, I. BALAKRISHNAN, P.N. JOSHI AND A.P. BUDHKAR
 ** P. RATNASAMY, R. KUMAR AND S.K. DATE

Period	Activity	Person In-charge	Man-power utilised man months	Item No (Ann. V of proj. document	Equipment to be provided by UNDP (Cost, \$)	Fellow- ships m/m person	Study tour m/m person
1990							
	1. Synthesis of zeolites containing Ni, Pd, Pt	- V.P. Shiralkar	200			18.0	6.0
	2. Characterisation	- S.G. Hegde	200				
	3. Bench scale evaluation	- S. Sivasanker	500				

Period	Activity	Person In-charge	Man-power utilised man months	Equipment to be provided by UNDP (Cost, \$)	Item No. (Ann. V of Proj. document)	Fellowships m/m	Study tour m/m
<u>1991</u>							
	1. Scale-up of zeolite synthesis to 1 kg. level at NCL	- G.R.V. Krishnan	200	-		18.0	6.0
	2. Characterisation	- S.G. Hegde	120	-			
	3. Process development	- G.R.V. Krishnan	580				
<u>1992</u>							
	1. Scale-up of zeolite synthesis to 50 kg. level at catalyst manufacturer's premises	- G.R.V. Krishnan	100	-		-	1.5
	2. Characterisation	- S.G. Hegde	50				
	3. Process design and semi-pilot plant tests	- G.R.V. Krishnan	300				
	Final evaluation :						
	GOI						
	UNDP						
	UNIDO						

F : Decisions and recommendations

The tasks and actions recommended are :

No.	Action recommended	Agency in-charge	Dateline
1.	Combine certain "Expert" classifications		
2.	Speed up the handling of "Expert" visits		
3.	Speed up authorization procedures of contracts for XRD (and other) analyses		
4.	Change some equipment order		
5.	Shift unused "Expert's Visits" and "Fellowship-Study Tour" funds to 1989		
6.	Authorization of Travel Agent in June for travel arrangements.		
7.			
8.			
9.			
10.			

UNITED NATIONS DEVELOPMENT PROGRAMME

PROJECT OF THE GOVERNMENT OF INDIA

PROJECT DOCUMENT

Title Development of Novel Shape Selective Zeolite Catalysts

Number DP/IND/87/007/P/01/37 Duration: 5 years

Primary Function Experimental/Pilot

Secondary Function Institution Building

Sector(Govt.Class)Chemicals

Sub-Sector (Govt. Class.) Petrochemicals

Sector(UNDP Class.) Development and Transfer of Technology 1620

Sub-Sector (UNDP Class.) Industrial Development Support Services/ Research and Development 0510

Government Implementing Agency Council of Scientific and Industrial Research through National Chemical Laboratory, Pune

Estimated Starting Date July 1987

Executing Agency United Nations Industrial Development Organization (UNIDO)

Government Inputs Rs. 22,200,000 (in kind) UNDP Inputs: US \$ 1,960,000

SIGNED

DEA's letter No. F8/25/85-UN
On behalf of the Government

19 November 1986
Date

UNIDO letter
On behalf of the Executing Agency

12 February 1987
Date

Henry J. Nardi
Resident Representative a.i.
On behalf of the United Nations
Development Programme

30 APR 1987
Date

Summary of work done upto October 1988

1. Work plan envisaged for 1988

(See CTA's report of Dec. 1987)

The work plan envisaged for 1988 in this project was

- (1) Synthesis and characterisation of zeolites with faujasite structure and containing iron in the lattice framework, and
- (2) Characterisation of the structural, physico-chemical and catalytic properties of a new zeolitic material of unknown structure.

2. Work accomplished upto October 1988

A. Synthesis and characterisation of novel zeolites

- (1) Zeolite with faujasite structure and containing iron in the lattice framework (Annexure - 1).
- (2) A ferrisilicate zeolite with the structure of ZSM-23 (Annexure - 2).
- (3) A ferrisilicate zeolite with the structure of beta (Annexure - 3).

(4) Two aluminosilicate zeolites with unknown novel crystalline structures (UN-1 and UN-2), (Annexure - 4).

(5) Direct synthesis of high silica, large port mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$), (Annexure - 5).

(6) Direct synthesis of high silica EU-1 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 120-530$), (Annexure - 6).

B. Publications

14 publications (Annexure - 7).

C. Patents

14 patents (Annexure - 8).

D. New and better methods of preparing known zeolites

Zeolite beta was prepared from commonly available silica gel rather than the silica sol or tetraethyl orthosilicate used so far (Annexure - 9).

Annexure 1.

Isomorphous substitution of Fe in the faujasite lattice

(See publication No. 10, a paper presented at the American Chemical Society, symposium on 'Advances in Zeolite Synthesis at LA, USA in September 1988).

Abstract

Crystalline faujasite Y zeolites containing iron have been prepared. Evidence for the presence of Fe in the lattice framework is obtained using XRD, solid state MASNMR, ESR, both framework and hydroxyl IR spectroscopies and DTA. Spin echo experiments (MASNMR) indicate that the spin-spin relaxation time of ^{29}Si is shortened due to Si-O-Fe interactions in the lattice.

Annexure 2.

Isomorphous substitution of iron in the ZSM-23 lattice

Starting from raw material free of Al a ferrisilicate zeolite with $\frac{\text{SiO}_2}{\text{Fe}_2\text{O}_3} = 110$ was synthesised whose XRD pattern matched with those of ZSM-23. Fumed silica (Cab-O-Sil) containing less than 10 ppm Al was used as the source of Si. Evidence for the structure and framework position of Fe has been deduced from a variety of techniques. The SEM photographs reveal the absence of amorphous matter.

1. Chemical composition

Chemical analysis (atomic absorption) showed values

of $\text{SiO}_2/\text{Fe}_2\text{O}_3 = 110$ and $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2000$, respectively. Al could not be detected by ESCA or MASNR.

2. XRD

The sample had the XRD pattern of ZSM-23. Due to the low concentration of Fe, any shift in 2 θ values could not be distinguished.

3. ESR

A peak at $g = 4.4$ indicating Fe^{3+} in T_d position has been observed.

4. Framework IR

All the peaks matched well with those of ZSM-23.

5. Adsorption At 25°C at $P/P_0 = 0.5$.

	<u>ZSM-23 (Al)</u>	<u>ZSM-23 (Fe)</u>
H ₂ O	5.6	5.8
n-hexane	7.2	8.5
Cyclohexane	3.2	3.5

The results indicate the absence of occluded oxides of Fe in the pores.

6. Catalytic activity in m-xylene isomerisation

The sample's activity in this reaction was similar to those of ZSM-23 (Al) though there significant

6. differences in selectivity. The catalytic activity indicates the presence of acid sites in the ferrisilicate which could arise only by the isomorphous substitution of Fe in the lattice since the concentration of Al was too low to account for the observed catalytic activity.

Conclusion

A novel ferrisilicate zeolite with the lattice structure of ZSM-23, wherein Fe^{3+} is isomorphously substituted in the lattice has been synthesised.

Annexure 3.

Isomorphous substitution of iron in the lattice of beta zeolite

Starting from raw material free of Al ferrisilicate zeolites have been synthesised whose XRD pattern matched well with those of beta zeolite. Fumed silica (Sigma) containing less than 10 ppm, Al was used as the source of Si. Evidence for the structure and framework position of Fe has been deduced from a variety of techniques.

1. Chemical composition

Zeolites with 2 composition were synthesised. Chemical analysis (atomic absorption) indicated values of $\text{SiO}_2/\text{Fe}_2\text{O}_3 = 22$ and 37, respectively in the two zeolites. In both zeolites, the value of $\text{SiO}_2/\text{Al}_2\text{O}_3$

was greater than 2000. Al could not be detected by ESCA or MASNMR.

2. XRD

Even though the XRD pattern indicated the structure to be similar to that of beta, the 2θ values were shifted to lower values as expected from Fe substitution (for Al) in the lattice.

3. DTA/TG

The exothermic peak due to lattice collapse was shifted to a value 60°C lower than the Al analog (813 instead of 873°C). Similar shifts are observed, for example, in the ZSM-5 system due to the lower thermal stability of ferrisilicate zeolites compared to their aluminium analogs.

4. ESR

A peak at $g = 4.4$ indicating Fe^{3+} in T_d positions has been observed.

5. Adsorption At 25°C and $P/p_0 = 0.5$.

	<u>Beta (Al)</u>	<u>Beta (Fe)</u>
H ₂ O	19.2	23.4
n-hexane	15.7	18.4
Cyclohexane	17.2	18.8
SiO ₂ /M ₂ O ₃	46	37

The results indicate the absence of occluded oxides of Fe in the pores.

6. MASNMR

The broadening of the ^{13}C and ^{29}Si peaks due to the paramagnetic susceptibility effect of Fe^{3+} is observed further supporting the hypothesis that Fe is in lattice positions.

7. Catalytic activity in m-xylene isomerisation

Even though the activity of beta (Fe) was similar to that of beta (Al), the former had better selectivity for isomerisation (vis-a-vis disproportionation) at equal conversion levels. The catalytic activity of beta (Fe) indicates the presence of acid sites which could arise only by the isomorphous substitution of Fe in the lattice since the concentration of Al was too low to account for the observed catalytic activity.

Conclusion

A novel ferrisilicate zeolite with the lattice structure of beta containing Fe^{3+} isomorphously substituted for Al in lattice has been synthesised.

1. Novel zeolite with unknown structure (UN-1)

A novel crystalline aluminosilicate of unknown crystal structure has been synthesised with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 300 using TMA as the organic guest molecule. The XRD pattern (Fig. 1), framework IR spectra (Fig. 2) and DTA/TG (Fig. 3) and adsorption properties (Table 3) indicate it to be a zeolite with low adsorption volume and unknown crystal structure.

Infrared spectra (Diffuse reflectance FTIR) in the hydroxyl vibration region reveals sharp bands at 3740, 3715, 3680 and 3520 cm^{-1} . The bands at 3740 and 3715 cm^{-1} are due to silanol groups. On exchange with D_2O , a fast H-D exchange occurred. All OH groups disappeared (in IR) and new bands appeared at 2760, 2740, 2724 and 2590 cm^{-1} confirming that the original bands are due to OH groups. Adsorption of methanol also results in the disappearance of all OH bands. However, on pyridine adsorption, all OH bands except that at 3520 cm^{-1} disappear and bands at 1450 and 1600 cm^{-1} due to coordinatively bound pyridine appear. On adsorption of NH_3 , all the OH bands disappear and bands due

to NH_4^+ and coordinatively bound NH_3 appear. Hence, it may be concluded that the band at 3520 cm^{-1} is due to bridged acidic hydroxyls ($\text{Si}(\text{OH})\text{Al}$), which are accessible to H_2O , CH_3OH and NH_3 but not to pyridine. Such behaviour is observed in small pore zeolites like erlonite and sodalite, UN-1 is, hence, likely to be a small pore zeolite. This is also consistent with the adsorption properties of UN-1.

2. Novel zeolite with unknown structure (UN-2)

In an attempt to synthesise NU-2, a oxide mole composition of :

1.47 (TEA)₂O : 16.46 Na₂O : Al₂O₃ : 30 SiO₂ : 600 H₂O

was tried for hydrothermal synthesis at 150°C. A typical batch composition was :

- NaAlO₂ : 2.32 g (43.68 % Al₂O₃, 39.0 % Na₂O)
- Sigma SiO₂ : 18.94 g (Sigma Chem. Co. No.S-5505)
- NaOH : 11.99 g (LR, Grade)
- TEA-Br : 6.17 g (Sisco, Bombay)
- Water : 110.00 g.

Following a crystallisation kinetics at 150°C for 0, 20, 70, 112, 144, 168 and 312 h crystallisation time, samples with different crystallinity were obtained. Phase identification of each sample was done by XRD patterns. Samples obtained at 20, 70, 112 hrs exhibit unresolved multiple peaks in XRD pattern with comparatively lower crystallinity. A product obtained at 160-168 h of crystallisation is a fully crystalline material and most of the peaks in XRD pattern are well resolved. The XRD pattern apparently did not match in total with any of the known synthetic or natural zeolites. It was therefore thought to be

a new zeolitic (Table 1, shows the XRD pattern) phase of unidentified structure.

When heated upto 1000°C in a thermal analyser, TG and DTA data show occlusion of templating species and a total loss on ignition to be around 19.25 %. The XRD of the sample after thermal analysis treatment upto 1000°C showed sample to be amorphous indicating a total structural collapse. The templating species were decomposed at 400°C for 6 hrs. The sample in the Na form after removal of the template at 400°C shows the structure to be in tact by XRD pattern. Sorption measurements were carried out on sample in sodium form. When dehydrated upto 400°C under vacuum (10^{-6} mm) the % loss in wt. was 9. The sorption capacities for various probe molecules are listed in Table 2. Equilibrium sorption capacity for water upto 11 % indicates comparatively lower Si/Al ratio or higher aluminium concentration. 1-2 % equilibrium sorption capacity for n-hexane, cyclohexane and benzene suggests 8-membered pore opening.

Framework IR spectra in the region ($400-1200\text{ cm}^{-1}$) are shown in Fig. 1. The prominent absorption bands along with their frequency (cm^{-1}) are listed in Table 2. The characteristic absorption bands from

the IR spectra (540 cm^{-1} - double ring, 730 cm^{-1} - ELSS, 1050 cm^{-1} - ELSS, 1130 cm^{-1} - ITSS) indicate the product to be a zeolite having the double ring as a secondary building unit. The intensity of the structure sensitive bands (460 cm^{-1} - T-O bond and 10 cm^{-1} - ELSS) was found to increase with the increase in crystallinity.

MAS NMR of ^{29}Si spectra helped to identify chemical shifts for four silicon environments [Si(OAl), Si(1Al), Si(2Al), Si(3Al)]. ^{27}Al MAS NMR spectra single sharp peak with chemical shift (relative to AlCl_3 in H_2O) of 58.0-58.4 ppm in crystalline sample and a broad peak around 54.2 in amorphous sample. This indicated that all the aluminium is only in tetrahedral coordination. ^{29}Si MAS NMR and ^{27}Al MAS NMR spectra are shown in Fig. 3 and the chemical shifts are tabulated in Table 3.

The anhydrous chemical composition was found to 7.23 SiO_2 : Al_2O_3 : 0.8 Na_2O giving framework Si/Al to be 3.6. The value of $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ is less than one and this may be due to partial charge balancing on AlO_4 tetrahedra by templating species. The Si/Al ratio obtained by NMR is 2.5. This information on Si/Al ratio suggests the zeolite to be a low silica zeolite.

On prolonged hydrothermal treatment of the gel at 150°C for 312 h, the so-called new zeolitic phase, UN-2 gets completely transformed into the analcime phase. It was therefore thought the new phase obtained could either be a meta-stable phase prior to analcime or it could be a mixture of two phases. It seems that the so-called new zeolitic phase may be a mixture of gmelinite and analcime. Except 4-5 XRD reflections of $1/1 \cdot 10$, all the reflections are accounted either by gmelinite or by analcime XRD peaks. Although these peaks match roughly in 'd' values, they differ appreciably in $1/10$ values. Scanning electron micrographs showed the crystallite of 10-15 with a single crystalline habit of cuboids. This observation does not support the presence of two different phase.

Results on XRD, NMR, IR sorption, and chemical composition of this so-called new zeolitic phase, were supplied to Prof. Abraham Clearfield of USA and Prof. P. Jacobs of Belgium, to have their opinions. In his reply, Prof. Jacobs informed us that the XRD pattern of zeolite 'Phi' seems to match with that of our zeolite. He feels our zeolite to be a impure version of zeolite 'Phi'. However careful examination of XRD patterns of zeolite 'Phi' and UN-2 reveals

that they are not matching with each other. Zeolite 'Phi' shows the absence of XRD peaks corresponding to $d = 4.98$ (26), 4.07 (51), 3.21 (28), 2.96 (39), 2.90 (41), 2.85 (33), which are present in the XRD pattern of UN-2. Therefore it is very difficult to agree with his findings. Opinion from Prof. Clearfield is awaited.

UN-2 zeolite (the so-called new zeolitic phase) when calcined at 1000°C is converted into amorphous material. Careful calcination around 400°C for 4 hrs removes the template from the zeolite cavity. The ammonium form is obtained by twice NH_4NO_3 (5 % wt.) exchange at room temperature. XRD pattern of UN-2 in ammonium was almost identical to that in sodium and the as-synthesized form of UN-2. When ammonium form of UN-2 was deammoniated at $400\text{-}450^{\circ}\text{C}$ for 4 hrs, it was found by XPS to be transformed into analcime with some amorphous contribution. Such unstability of ammonium form is not surprising with low silica zeolites (for example, like type A). Barrer* and coworkers have reported synthesis of gmelinite at 205°C for 6 days from gel composition $\text{SrO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 4.4 \text{SiO}_2$. They found that the synthesis was reproducible. Analcime synthesis was carried out by them at 380°C from gel composition : $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{SiO}_2$.

* J. Chem. Soc. (1964), 2298, 485
(1959), 195
(1961), 983

Conclusion

UN-2 may either be a novel zeolite or a mixture of analcime and gmelinite. The former possibility is more probably.

Direct synthesis of high silica large port mordenite

(See also Annexure - 8, item 4, a patent application)

High silica, large port mordenites (HSLPM) find use as catalysts and adsorbents. Ethylbenzene hydroisomerisation to xylenes and toluene transalkylation with C₉ aromatics are two such applications. The direct synthesis of HSLPM with SiO₂/Al₂O₃ above 15 and capable of adsorbing more than 9 wt. % of benzene are unknown in the literature. HSLPM are usually prepared by the post-synthesis acid treatment of low silica mordenites (SiO₂/Al₂O₃ 15). However, this process has many limitations (zeolite crystal damage, amorphous matter in pores, special acid-resistant vessels for synthesis etc).

During this year, a process for the direct synthesis of mordenite having $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$ above 30 and a benzene adsorption above 9 % wt. has been developed. This material has promising potential application in the production of cumene from benzene and propylene. Initial results are quite promising. Its advantage over the conventional solid phosphoric acid catalyst are (1) avoidance of the acid sludge disposal and pollution problems and (2) regenerability.

Preparation of EU-1 zeolites with high silica content

(See also publication No.8 'Synthesis and characterisation of high silica Eu-1', accepted for publication in 'Zeolites').

Abstract

Both in the journal and patent literature, the maximum $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for EU-1 has been reported to be 120. In the present work, the synthesis of EU-1 zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios upto 525 has been accomplished. The factors influencing the synthesis of such zeolites have been systematically explored.

UNDP PROJECT ON "DEVELOPMENT OF NOVEL
SHAPE SELECTIVE ZEOLITES"

Scientific papers published/accepted/submitted and
under review during Sept. 87 - October 1988

1.	Papers published	:	5
	Papers accepted for publication	:	6
	Papers submitted but still under review	:	3
	Total	:	14

2. Publications

	<u>Title</u>	<u>Journal</u>
(1)	Naptha reforming over catalyts containing a ferrisilicate zeolite of the pentasil type.	Appl. Catal., <u>39</u> , 127 (1988).
(2)	Creation of acid sites by La ions in L zeolites	React. Kin. Catal. Lett., <u>36</u> (1), 173 (1988).
(3)	Catalytic dewaxing of petroleum oils over pentasil metallo- silicate zeolites	Proc. Intl. Congr. Catal., 1988, p. 120.
(4)	Catalytic dewaxing of petroleum lube fractions on pentasil zeolites	Proc. XI Ibero- Amer. Congr. Catal. 1988, p. 741.
(5)	Crystal symmetry and shape selectivity in ZSM-5 zeolites	Catalysis Today, <u>3</u> , 531 (1988).

3. Papers accepted for publication

(6)	Isomerization and formation of xylenes over ZSM-22 and -23.	J. Catalysis
-----	--	--------------

- | | | |
|------|---|---------------------------------------|
| (7) | Shape selective reactions over ZSM-48 | J. Catalysis |
| (8) | Synthesis and characterisation of high silica EU-1 zeolites | Zeolites |
| (9) | Influence of the pore geometry of ZSM-5, -22, -23, -48 and -50 on catalytic selectivity in reactions of aromatic hydrocarbons | 8th Intl. Zeol. Conf. (1989). |
| (10) | Isomorphous substitution of iron in the faujasite lattice. | ACS Symp. Adv. in Zeol. Synth. (1988) |
| (11) | Characterisation of zeolite beta by FTIR and TPD techniques | Zeolites |

4. Papers submitted for publication but still under review

- | | | |
|------|--|--------------------|
| (12) | Shape selectivity of EU-1 in reactions of aromatics. | Appl. Catal. |
| (13) | Location and configuration of dibenzyl dimethyl ammonium ion in EU-1 by ^{13}C -CPMASNMR spectroscopy | JCS. Chem. Commun. |
| (14) | Synthesis of zeolite beta using silica gel as a source of SiO_2 . | Zeolites |

PATENTS LIST

Sr.No.	Title	Application No. & Date of application
1.	An improved process for the preparation of high silica zeolite catalyst composite material	784/del/87 7-9-87
2.	An improved Naptha reforming process	222/DEL/88 21-3-88
3.	Process for the preparation of novel crystalline aluminosilicate	182/DEL/88 10-3-88
4.	Process for the preparation of high silica large port Mordenite	367/DEL/88 28-4-88
5.	Process for the preparation of crystalline ferosilicate catalyst composite material	475/DEL/88 30-5-88
6.	An improved reforming process for the catalytic conversion of petroleum fractions to a mixture of hydrocarbons rich in aromatics	526/DEL/88 16-6-88
7.	Process for the preparation of a novel crystalline aluminosilicate, Encilite-12	509/DEL/88 9-6-88
8.	Process for the preparation of novel crystalline aluminosilicate	Applied 28-9-88
9.	Process for the preparation of ferri-aluminosilicate	Applied 28-9-88
10.	Process for the preparation of catalyst composite material	Applied 9-8-88
11.	Process for the preparation of improved catalyst composite material suitable for hydrocarbon conversion.	Applied

TOKYO INSTITUTE OF TECHNOLOGY

FACULTY OF ENGINEERING
DEPARTMENT OF CHEMICAL ENGINEERING

O-okayama, Meguro-ku, Tokyo 152, Japan

Telephone: 03-726-1111
Cable: TITECHOOKAYAMA
Telex: 2466360 TITECHJ
FAX: 03-729-0425

October 7, 1988

Dr. P. Ratnasamy
National Chemical Laboratory
Pune 411 008
INDIA

Dear Dr. Ratnasamy:

As far as I understand, I am supposed to visit National Chemical Laboratory and also to join the National Catalyst Symposium at Madras in December through UNIDO program.

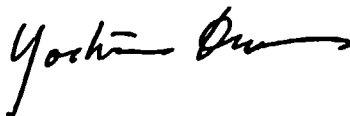
Yet I have heard nothing from you or an UNIDO authorities about the details of the program. To obtain the permission for a leave of absence from our Government, I need the formal document, which contains the detail of the schedule and tells that UNIDO supports the travel and living expenses.

I must return home by Dec. 20. Therefore, I have to leave India right after the Catalysis symposium. Please make up the schedule for me and let me know as soon as possible. I would also like to know if I have to reserve air-tickets by myself or they are prepared by UNIDO side.

Please respond me quickly because I have to apply the leave of absence by the end of this month at the latest.

I am looking forward to seeing you in Puna.

Sincerely yours,



Yoshio Ono

OUTPUTS : Schedule of Project Review, Judgement
and Evaluation

It is proposed that the project be reviewed annually during the visit of the CTA and UNDP Expert. The proposed dates are :

Mid-term Review	Nov. 1989
Review 3	- Nov. 1990
Review 4	- Nov. 1991
End of project Review	- Sep. 1992

An annual progress report will be submitted to the Review Committee members at least one month prior to the review meeting to facilitate the review process.

UNDP STUDY TOUR REPORT OF DR P. RATNASAMY

1. Objectives

The objectives of the study tour were (1) to discuss with Experts in the field of some of the recent advances in the area of zeolite synthesis and characterisation, (2) To discuss the program of work to be carried out by visiting NCL scientists during the tenure of their UNDP fellowship, and (3) to develop further contact with Experts in the field of Zeolite Chemistry and Catalysis.

2. Duration : April 19-June, 1988

3. Places visited

I visited and had discussions with the following persons :

- | | | |
|----|---|--|
| 1. | Prof. P. A. Jacobs
University of Leuven, Belgium. | Zeolite Characterisation |
| 2. | Prof. E. G. Derouane
University of Namur, Belgium. | Zeolite Chemistry |
| 3. | Prof. B. Delmon,
University of Louvain, Belgium. | Reaction Chemistry |
| 4. | Prof. G. Froment,
University of Glient, Belgium. | Chemical Reaction Engg. |
| 5. | Prof. S. Enzo,
University of Venice, Italy. | X-ray Characterisation of
Zeolites. |
| 6. | Dr. G. Fattore,
Enrlicherche, Milan, Italy. | |
| 7. | Dr. J. Vadrine,
Institute of Catalysis, Lynn, France. | |
| 8. | Dr. D. Barthomeuf, Univ. of
Paris, France. | |
| 9. | Dr. g. Martino, French Petroleum
Institute, Paris, France. | |

4. Activities during visits :

In addition to the discussions and visits to the labs., I also gave talks in the area of zeolite catalysis in most of the labs visited.

5. Benefits from the study tour

The following are some of the new ideas/concepts/techniques learned during the trip :

1. A technique for qualitatively estimating the Al distribution in zeolite crystals from the kinetics of water adsorption.
2. New insight into the interpretation of NMR spectra of zeolites.
3. The preparation of titanium pentasil zeolites and their catalytic applications.
4. Technique for obtaining better quality XRD pattern of zeolites.
5. Experimental technique for obtaining simultaneous IR/TG of zeolites under adsorption/catalysis conditions.
6. Stability and catalytic properties of boron substituted pentasil zeolites.

SUMMARY

Study tour to Japan, Mexico, USA and Canada

Submitted by Drs. S. Sivasanker and B.S. Rao
National Chemical Laboratory
Pune - 411 008, Maharashtra

Ref : UNDP Sanction, vide No.IND/87/007 (37) dtd 11-5-1988

A. JAPAN

We visited a number of research laboratories and had discussions with many professors during the period - 25th May to 7th June. The names of the professors and their organisations are listed below. During 8th and 9th June, we visited M/s Shimadzu Corporation's factory, at Kyoto.

(1) .Tokyo Institute of Technology, Ookayama Campus, Tokyo

Period : 25th May to 3rd June (except 30th and 31st May, and the afternoon of 2nd June).

Discussions were held with the following professors and their laboratories were visited.

<u>Name</u>	<u>Dept.</u>	<u>Topic</u>
(a) Prof. Y. Ono	Dept. of Chem. Engg.	Zeolite catalysis
(b) Prof. H. Niiyama	-do-	Computer automation of reactors.
(c) Prof. T. Yashima	Dept. of Chem.	Alkylation by zeolite catalysts.
(d) Prof. K. Otsuka	Dept. of Chem. Engg.	Methane conversion to olefins by oxidative coupling and using electro-chemical methods.
(e) Dr. E. Suzuki	-do-	PILLARED CLAYS.

(2) Tokyo Institute of Technology, Nagatsuta Campus, Tokyo
(2nd June)

- | | | | |
|-----|-------------------|------------------------------|--|
| (a) | Prof. Y. Morikawa | Resource
Utilisation Lab. | PILLARED CLAYS. |
| (b) | Prof. Y. Doi | -do- | Bio-polymers
CH ₄ oxidation. |

(3) Waseda University, Tokyo
(31st May)

- | | | | |
|-----|------------------|---------------------------|---|
| (a) | Prof. E. Kikuchi | Dept. of
Applied Chem. | (1) Selective
reactions
<u>deposited</u>
using metal
glass membranes
(2) coal gasi-
fication. |
|-----|------------------|---------------------------|---|

(4) Tokyo University
(30th May)

- | | | | |
|-----|-------------------|-----------------------------|------------------------------|
| (a) | Prof. H. Tominaga | Dept. of
Synthetic Chem. | F.T. synthesis |
| (b) | Prof. H. Misono | -do- | Heteropolyacid-
catalysis |

(5) Kyoto University, Kyoto
(4th and 6th June)

- | | | | |
|-----|--------------------|-------------------------------|--|
| (a) | Prof. T. Inui | Dept. of
Hydrocarbon Chem. | Isomorphous substi-
tuted zeolites,
synthesis and
applications. |
| (b) | Prof. Y. Watanabe | Dept. of
Hydrocarbon Chem. | Hydroprocessing of
heavy coal oils. |
| (c) | Prof. K. Yoshida | -do- | Catalysis by
amorphous metals |
| (d) | Prof. K. Hashimoto | Dept. of Chem. Engg. | Diffusion in
zeolites. |

(6) Osaka University, Osaka

(7th June)

- | | | |
|-----------------------------|-----------------------------------|---|
| (a) Prof. T. Imanaka | Dept. of
Chem. Engg. | Catalysis by evaporated
metal films. |
| (b) Prof. H. Miyake | Dept. of
Applied Chem. | Coal liquefaction
using metal salts. |

(7) Shimadzu Corporation, Kyoto

(8th and 9th June)

- | | | |
|----------------------------|--|---|
| (a) Dr. S. Hirayama | Gas chromato-
graphy, Analy-
tical Applica-
tion Lab. | Gas chromatography
PONA, SIM-DIST
methods, capillary
G.C |
| (b) Dr. Y. Nagai | -do- | -do- |

Lectures: (June 2)

Tokyo Inst. of Technology, Ookayama, Tokyo

- (1) Dr. S. Sivasanker : Hydrodewaxing over zeolites.**
- (2) Dr. B.S. Rao : Isomerisation of xylenes.**

Kyoto University, Kyoto : (June 6)

- (1) Dr. S. Sivasanker : Naphtha reforming over zeolites.**
- (2) Dr. B.S. Rao : Alkylation over zeolites.**

Osaka University, Osaka : (June 7)

- (1) Dr. S. Sivasanker : Catalysis research in India.**

B. MEXICO

(1) Guanajuato (12-15th and 17th June)

- (a) Attended XI Ibero-american symposium.
- (b) Dr. S. Sivasanker presented a paper titled 'Catalytic dewaxing of petroleum lube fractions on pentasil zeolites'.
- (c) Had discussions with representatives from the Mexican Petroleum Institute (IMP) on collaboration in zeolite catalyst development.

(2) Mexico D.F (16th June)

- (a) Visited the Mexican Petroleum Institute (IMP).

C. USA

Newark, Delaware : (19th to 25th June)

During our stay in USA, we had discussions with the following professors and visited their laboratories.

- | | | |
|------------------------|-----------------------------------|---|
| (a) Prof. B.C. Gates | Centre for Cat. Sci. & Technology | Heterogeneous catalysts |
| (b) Prof. G.A. Mills | -do- | Methane activation, alcohol utilisation and MTBE production |
| (c) Prof. M.A. Barteau | -do- | Surface studies of oxides |
| (d) Prof. A.H. Stiles | -do- | General discussion on industrial aspects of catalysis |

S. Sivasanker

(Dr. S. SIVASANKER)

On 23rd June, we attended the research review meeting of the Centre for Catalytic Science and Technology, USA. 14 papers were presented describing the work being carried out in the Centre.

D. CANADA

(Calgary, 27th June to 3rd July)

- (a) Attended IX International congress on catalysis.
- (b) Dr. S. Sivasanker, presented a paper titled 'Catalytic dewaxing of petroleum oils over pentasil metallosilicate zeolites'.
- (c) Had discussions with a number of scientists including Drs. S. Csicsery and S. Khoobiar.
- (d) We visited Waterton Sour-gas treatment plant on 29th June.
- (e) We visited Syncrude plant at Fort McMurray on 2nd July.

Remarks :

The tour was very useful in enhancing our knowledge of catalysis, specifically in the area of experimental methods of characterising and evaluating catalysts. The tour was highly educative and we have professionally benefitted from it.

SOME SPECIFIC BENEFITS

- (1) We learnt the techniques of estimating the acid centres (both Bronsted and Lewis) on the external and internal surfaces of zeolites using adsorption of amines and FT-IR spectroscopy (Univ. of Tokyo). The shape selective nature of zeolite is decreased by the presence of external acid centres. This can have detrimental effects in reactions like hydrodewaxing and alkylation reactions. We now plan to use this technique to estimate the amount and nature of the different acid centres and use this information to improve the shape selectivity of catalysts.

- (2) Prof. Inui's group at Kyoto University has synthesised vanadosilicates. These vanadium containing zeolites have exceptional oxidation activities. These zeolites burn off carbon deposited on them at relatively low temperatures. We propose to examine the idea of incorporating some vanadium ions (isomorphous substituents) in zeolites especial the Fe-analogues which need to be regenerated at low temperatures to prevent damage to them. Such incorporation should reduce regeneration temperatures significantly, thereby protecting the Fe-zeolites.

- (3) Our discussions with Prof. Ono (Tokyo Institute of Technology), on gallosilicates (gallium containing zeolites) was very educative. We propose to incorporate gallium zeolites and use these for oligomerisation of light hydrocarbons. We are already working on the use of Fe-zeolite as additives in reforming catalysts for incorporation of oligomerisation ~~function~~ ^{function} in these catalysts. We will now also examine the use of gallium zeolites or gallium-iron-zeolites for aromatization purposes.
- (4) Our visit to Prof. Gates's laboratory (Univ. of Delaware, Newark, USA), helped us to appreciate the importance of surface studies in establishing the identity of supported species on catalysts especially those prepared from complexes.
- (5) During our stay at Guanajato, Mexico, we discussed with representatives from PEMEX, Mexico, on the possibility of collaboration in zeolite catalysis. Collaboration in the area of isomerisation and dewaxing catalysts were identified.
- (6) We also learnt about the modern and accurate methods applied in the acquirement of experimental data and the application of on-line facilities like G.C, quadrupole M.S and FT-IR.

Annexure 12.

Summary of Report of Training under UNDP
project on 'Novel Shape Selective Zeolite Catalyst'

1. Name : Dr. Joseph Kuruvilla
2. Designation : Scientist EI, National Chemical Laboratory, Poona
3. Period of visit : Six months (18.4.88 to 17.10.88)
4. Programme under which deputed : Novel Shape Selective Zeolite Catalyst
5. Country visited : United States of America
6. Name of the Specialist/ and Laboratory visited : Prof. Bruce C. Gates
Centre for Catalytic Science and Technology
University of Delaware, DE 19716
7. Expertise of Laboratory visited : Center for Catalytic Science and Technology is a leading establishment in USA for the study of Catalysts and Catalyst Systems. The Laboratory is well equipped for characterization of supported catalyst.
8. Purpose of visit : Studies in characterization of supported catalysts.
9. Specific knowledge :
acquired

Many of the catalyst precursors are air and moisture sensitive. Hence it was necessary to familiarise with the procedures adopted for supporting precursors on active supports such as magnesium oxide, aluminium oxide, etc. In this connection Cannula techniques for manipulating air sensitive materials were practiced. These techniques involve use of a modern glove box and vacuum line. Simple devices for carrying out reactions in an inert atmosphere, filtration of product out of contact with air etc. are of paramount importance in synthetic work. These techniques were practiced to prepare supported catalyst and was characterised with the help of FTIR spectrometry and temperature programmed decomposition studies.

For example iridium carbonyl cluster was deposited on freshly calcined magnesia. The cluster undergoes changes on the surface and from the IR data it could be concluded that at least two species are present on the magnesia surface. One was strongly bound and could not be extracted with solvents. The other could be extracted and showed two sharp IR absorption bands at 1984 and 1978 cm^{-1} . This compound appears to be a new cluster unreported in the literature. Efforts are underway to fully characterize it by growing single crystal for X-ray analysis.

10. Impact of acquired knowledge in your work : The knowledge acquired will be helpful in preparing new organometallic catalysts and depositing them on supports. The methods to characterise the catalyst will be beneficial in understanding the mechanism of reaction on the catalyst surfaces.
11. Specific suggestions : A good vacuum line may be fabricated which is a prerequisite for any study in organometallic chemistry.
- A modern dry box may be procured. A liquid nitrogen tank with provision to tap gas as well as liquid may be procured for maintenance of glove box as well as vacuum line.

Josephik
10/11/88

Signature of Scientist

REPORT ON THE VISIT UNDER UNIDO PROGRAMME

1. Name **S** : DR. A.N. KOTASTHANE
DY. A.J. CHANDWADKAR
2. Designation : Scientist & C
3. Laboratory : National Chemical Laboratory
Pune - 411 008, India.
4. Project in which engaged :
DP/IND/87/007/31-01 UNIDO
Novel Shape Selective Zeolite Catalyst.
5. Period of visit :
From 7th March to 31st August 1988 (6 months).
6. Programme under which deputed :
UNIDO Project No. DP/IND/87/007/31-01.
7. Countries visited :
Belgium and France.
8. Name/s of specialist/s and laboratories visited :
 - (a) Prof. E.G. Derouane
Dept. de Chimie, Laboratoire de Catalyse
Facultes Universitaires, N-D de La Paix
Namur - BELGIUM
 - (b) Prof. D. Barthomeuf
Universite P Et M Curie
Lab. De Reactivite De Surface Et Structure
CNRS, Paris - FRANCE
 - (c) Prof. Peter A. Jacobs
Katholieke University, Leuven
Lab. Voor Opper Valaktheemie
Leuven - BELGIUM

9. Expertise of laboratory/ies visited :

- (a) Prof. E.G. Derouane
Facultes Universitaires, Lab. de Catalyse
Namur (Belgium).
- (b) Prof. D. Barthomeuf
Universite P Et M Curie, CNRS, Paris (France)
- (c) Prof. Peter A. Jacobs
Katholieke Univ. Leuven (Belgium)..

10. Purpose of the visit :

Synthesis and characterisation of high silica medium and large pore zeolite materials.

11. Specific knowledge/information acquired :

- Synthesis of high silica large and medium pore zeolites followed by kinetics of crystallisation under hydrothermal conditions.
- The high resolution solid state MASNMR of ^{29}Si , ^{27}Al and ^{23}Na nuclei characterisation in synthesised precursors of these zeolites having different Si/Al ratios.

12. Impact of acquired knowledge in your work :

- This certainly help to persue studies in the area of Novel Shape Selective Zeolite Catalysis, at National Chemical Laboratory, Pune 411 008, India.

13. Summary report of the visit :

- Please see attached sheets -

14. Specific suggestions : No

15. Remarks of the Director :

good

Atch...

[Handwritten signature]

Signature of the candidates

Signature of the Director, NCL-Pune 411 008.

Man of work

Synthesis and characterization of high silica medium pore and large pore zeolites.

Background :

Zeolites are crystalline microporous aluminosilicates and have been utilised as ionic exchangers, adsorbents and catalytic materials. Silica-rich zeolites exhibit unique and shape selective properties. By virtue of their novel thermal, hydrothermal and acid stabilities, having ability to resist coke formation they are widely employed to catalyse the hydrocarbon transformation reactions⁽¹⁻³⁾. High-silica zeolites are usually synthesized by incorporating organic compounds such as quaternary ammonium ions and/or various (poly) alkylamines during the hydrothermal treatment of aluminosilicate hydrous gel mixtures⁽⁴⁾. Zeolite ZSM-5, a well known member of the so-called pentasil family has been studied extensively during the past ten years.

Faujasite type zeolites have found wide acceptance as industrial cracking, isomerization and reforming catalysts. The thermal stability and catalytic performance of faujasites depend on Si/Al ratio. Increasing the relative silicon content in the faujasite framework may improve the stability of faujasite towards thermal and hydrothermal degradation. ZSM-20 is a faujasite like zeolite usually synthesized in the presence of tetraethylammonium ions. It is characterized by a unit cell with hexagonal symmetry and a higher Si/Al ratio ^(3,5). Thus, the latter feature could result in higher thermal, hydrothermal stability and acid strength with better resistance to deactivation relative to the known Y-type faujasite zeolites. Hence, ZSM-20, as a catalysts, may be useful for the polymerization of olefins or for an aromatization of olefinic/paraffinic liquids as well as in fluidized cracking of hydrocarbon feed stocks.

ZSM-23 is a medium pore zeolite belonging to the class of pentasil family. By virtue of its subtle structural differences ⁽⁶⁾ as well as the higher constraint index ⁽⁷⁾ compared with that of zeolite ZSM-5, it could be employed as a potential catalyst in xylene isomerization reactions for achieving improved para-selectivity.

The purpose of this work, is to prepare a series of silica-rich zeolites, preferably, other, than ZSM-5 thus, having different structural characteristics. Therefore, a more comprehensive study on the preparation of high-silica medium pore zeolite ZSM-23 and of large pore zeolite ZSM-20 has been undertaken. In addition, the present study is also aimed to investigate the possibility of isomorphous substitution of Fe^{3+} partly replacing Al^{3+} ions in faujasite type ZSM-20 zeolite framework.

In the first phase of this programme, we report the hydrothermal synthesis of zeolites ZSM-23 and ZSM-20 as well as ferrisilicate analogue of the latter. The kinetic features of the synthesis, the extent of crystallisation and quantitative phase identification by x-ray powder diffraction are also reported.

Experimental

Zeolite Synthesis :

Crystallisation of zeolite ZSM-23 was carried out in the system :

Pyrrrolidine - Na_2O - Al_2O_3 - SiO_2 - H_2O , in the temperature range 170° - 200° C in a Teflon cylindrical vessels with lid, fitted into a stainless steel autoclave. The autoclaves were heated in electrical ovens with a temperature control of $\pm 2^\circ$ C, consisting of an horizontally fitted rotating assembly. This provides more effective and constant stirring of hydrous gels under autogeneous pressure. The reagents used for the gel preparation were silica sol (IIS Ludox 40 %), sodium aluminate (Riedel de Haiën, 54 % Al_2O_3 , 41 % Na_2O and 5 % H_2O), sodium hydroxide (Janseen Chemica) and Pyrrrolidine (Pure > 98 % Fluka AG).

To investigate crystallization kinetics an initial hydrous gel having molar composition $40.0 \text{ R} : 1.7 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 130 \text{ SiO}_2 : 925 \text{ H}_2\text{O}$, where R represent pyrrrolidine, was heated in different autoclaves of identical dimensions with rotating speed of 40-50 RPM under controlled conditions. At different stages of the hydrothermal treatment an autoclave was removed from the oven and quenched to room temperature. The solid intermediate (gel + zeolite) or final (Pure zeolite) phases were separated by filtration, washed and dried at 100 - 110° C overnight. The product was then examined by X-ray diffraction (XRD) and, in appropriate cases, by Scanning Electron Microscopy (SEM).

Preparation of the hydrous gel

A consistent experimental procedure was adopted to obtain a good hydrous aluminosilicate gel. To a solution of 3.15 g of sodium aluminate and 0,81 g of an aqueous 50 % sodium hydroxide in 70 g of water, 42,68 g of pyrrrolidine was added dropwise, under constant stirring, the pH of which is recorded to be > 13. To this mixture was then added 296.59 g of silica-sol (Ludox 40 %) with vigorous stirring. A thick gel resulted, which after continued stirring for a few minutes thined to a smooth, even consistency. The pH was 11.0 immediately after mixing, rose to 12.0 after five minutes and stabilized at 12.5 after an hour.

Zeolite ZSM-20 and its ferrisilicate analogue :

Synthesis procedure for Al/ZSM-20 and Fe + Al/ZSM-20 was based on the recent published reports⁽⁶⁾. The typical composition adopted to synthesize these zeolites was 1.25 Na₂O : M₂O₃ : 30.2 SiO₂ : 26.4 TEA-OH : 267 H₂O, where M₂O₃ represents Al+Fe oxide and TEA-OH = tetraethylammonium hydroxide. The reactants used for the gel preparation were sodium aluminate (Riedel de Haën 54 % Al₂O₃, 41 % Na₂O₃ and 5 % H₂O), tetraethylorthosilicate TEOS (Aldrich), TEA-OH 40 % solution (Alfa-Ventron) and Ferric Sulphate Pentahydrate (Fluka A.G.). In case of ferrisilicate analogue of zeolite ZSM-20 the concentration of Fe³⁺ was taken as mole percent of total M₂O₃ required in the gel composition.

Characterization :

The nature and crystallinity of the products were determined by X-ray powder diffraction (XRD) using a Philips Pw1349/30 spectrometer fitted with Ni filtered CuK α , in the 5° - 50° 2 θ range.

The values of interplanar spacings (d°) and relative intensities (I/I₀ x 100) derived from x-ray powder diffraction patterns of both the zeolite ZSM-23 and ZSM-20 as well as the ferrisilicate analogue of the latter are essentially identical with those reported in the literature (8, 9-10).

Samples of zeolite ZSM-23 were typically scanned at 1° 2 θ min⁻¹ from 18°-27° 2 θ , for estimating the total crystallinity.

The 100 % crystallinity was arbitrarily assigned to the most crystalline material obtained during the kinetic studies.

The degree of crystallinity was estimated for zeolite ZSM-20 and its ferrisilicate analogue samples using the standard sample obtained from this laboratory⁽⁸⁾. In case of ferrisilicate analogue samples, it was observed that the crystallinity decreases on increasing the iron content > 10 mole weight percent in the reaction mixture.

Effect of temperature and SiO₂/Al₂O₃ ratios :

The reaction mixture with the composition SiO₂/Al₂O₃ = 130, Na₂O/SiO₂ = 0.013 and H₂O/OH⁻ = 280 was adopted to study the effect of temperature (range 170-200°) on the formation of zeolite ZSM-23. It was observed that increasing the reaction temperature enhances the rate of crystallisation and considerably reduces the induction period. At lower synthesis temperature the growth rate is lowered with greater induction period.

By varying the aluminium content in the reaction mixtures at constant synthesis temperature, it appeared that both the induction period and the crystal growth strongly depend on $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The crystallisation for zeolite ZSM-23 vary inversely with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the reaction mixture and the growth rate decreases with increased Al content. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the reaction mixture had a profound effect on the nature of the crystalline product. The reaction mixtures of low ratio (e.g. R = 66) yield zeolite ZSM-5 phase in the early stages of the crystallisation process, however, this phase slowly deviates and transforms to zeolite ZSM-23 on longer crystallisation. In addition, such low ratio values lead to only 80 % crystalline ZSM-23. On the other hand, at higher values of $\text{SiO}_2/\text{Al}_2\text{O}_3$ (e.g. R = 300-500) cristobalite was found to co-crystallize with ZSM-23, while at very high values (e.g. R = 1000 and above) ZSM-48 is the only phase formed.

Thermal analysis

Thermal analysis (TG/DTA) in flowing air was carried out with 30-40 mg sample at a heating rate of $10^\circ \text{C min}^{-1}$ using an automatic Stanton Redcroft STA 780 thermal analyser system. An endothermic weightloss of 20 % in the temperature range $40^\circ - 150^\circ \text{C}$ for zeolite ZSM-20 and about 2.0 % in the temperature range $40^\circ - 220^\circ$ for zeolite ZSM-23 is attributed to the loss of loosely held water in zeolite cavities. The strong exothermic effect in the temperature range of $150^\circ - 700^\circ \text{C}$ for zeolite ZSM-20 and $350^\circ - 560^\circ \text{C}$ for zeolite ZSM-23 are attributed to an oxidative decomposition of organic cations occluded in the zeolites frameworks. It is further confirmed that zeolite ZSM-20 and its ferrisilicate analogue as well as ZSM-23 are thermally stable varieties. The former is stable upto about 750°C , while the latter is stable upto 1000°C .

* The activities envisaged for the next phase of the programme (~~June-August-88~~) would cover a detailed characterization utilizing high resolution ^{13}C , ^{27}Al , ^{29}Si and ^{23}Na NMR MAS SPECTROSCOPY, electron paramagnetic resonance (EPR) spectroscopy and scanning electron microscopy with EDX analysis.

* As a part of the programme, we visited Prof. D. BARTHOMEUF, at Laboratoire De Reactivite De Surface Et Structure, Paris, on May 19 th and 20th, 88 for discussions and to exchange views on active research in the field of zeolite science.

* We attended a one-day meeting on "Advanced Methods In Zeolite Material Science Research", held at Katholieke Universiteit Leuven, on May 25, 88.

Acknowledgement

We acknowledge with thanks Prof. E.G. Derouane, Prof. J. B. Nagy and Dr. Z. Gabelica for valuable discussion and advice.

We gratefully acknowledge the UNIDO fellowship award and support by United Nations Industrial Development Organization, Vienna, Austria.

References

1. S.L. Meisel, J.P. Mc Cullough, C.H. Leachthaler, and P.B. Weisz
Chem. Tech. 1976, 86.
2. C.D. Chang and A.J. Silvestri
J. Catal. 1977, 47, 249.
3. Z. Gabelica, E.G. Derouane and N. Bloom in "Catalytic materials : Relationship between structure and Reactivity, Am. Chem. Soc., Washington DC, 1984, P. 219.
4. R.J. Argauer and G.R. Landolt
U.S. Patent 3 702 886, 1972 (Mobil Oil Corp. USA).
5. K.M. Barrer
Stud. Surf. Sci. Catal., 1984, 24, 1
6. P.A. Rohrman et al.
Zeolites 1985, 5, 352.
7. W.O. Hagg and R.M. Lago
Eur. Patent 0 034 444 (1981) (Mobil Oil Corp. - USA).
8. N. Dewaele, L. Maistriau, J. B.Nagy, Z. Gabelica and E.G. Derouane
Appl. Catal. 1988, 37, 273.
9. Theodare et al.
Eur. Pat. 136 133 (1985).
10. Valyosik et al.
Eur. Pat. 0178 847 A₂ (1985).

BENEFITS DERIVED FROM THE FELLOWSHIP PROGRAMME

1. Training in modern methods of synthesising high silica zeolites: Professor E. Derouane's laboratory is well equipped for synthesising and characterising high silica zeolites. We were trained in state-of art techniques for synthesising and characterising zeolites. This training will be useful in the programme of synthesising novel zeolites at NCL.
2. Training in the use of NMR as a tool for characterising the intermediates and final zeolitic products in the synthesis of zeolites : Solid state NMR is an extremely powerful tool which has emerged, during the last decade , as an indispensable technique for characterising zeolites. A solid state NMR spectrometer (Bruker model) has been purchased by NCL in 1988. However, there was no expertise available in the zeolite group at NCL to utilise this technique in the study of zeolites. The training acquired in Prof.Derouane's lab in the use of NMR will be of invaluable help in the fuller utilisation of the spectrometer available already at NCL.
3. A new ferrisilicate zeolite with the crystal structure of ZSM-20 was synthesised by us during our fellowship program. This is a novel zeolite whose catalytic applications will be further explored on our return to NCL .
4. As a part of the fellowship programme, visits were arranged to the laboratories of Professors.P.A.Jacobs(at the University of Leuven,Belgium) and D.Barthomeuf(CNRS, Paris, France). In Prof.Jacob's lab we learnt in detail the use of IR spectroscopy to characterise zeolite surfaces while at the lab of Prof.Barthomeuf, we acquired additional knowledge and insight in the potential of thermal analysis techniques in characterising the organic templates during zeolite synthesis .

COUNTRY : INDIA : DATE PRINTED: 30/04/89 : PAGE 1 :
 PROJECT NUMBER : IND/87/607/8/01/37 : SHADOW BUDGET
 PROJECT TITLE : DEVELOPMENT OF NOVEL SHAPE SELECTIVE ZEOLITIC CATALYSIS
 PROJECT BUDGET COVERING INMOP CONTRIBUTION (in U.S. dollars)

PROJECT COMPONENTS	TOTAL AMT M/M	1987 AMT M/M	1988 AMT M/M	1989 AMT M/M	1990 AMT M/M	1991 AMT M/M	1992 AMT M/M
010 PROJECT PERSONNEL							
011 Experts:							
011-010 CATALYSIS/CAT RES.ENG/CTA	41,000	4,490	10,710	7,400	7,600	7,600	3,800
	5.5	.7	1.3	1.0	1.0	1.0	.5
011-020 CATALYST PREPARATION	53,200		26,600	15,200	11,400		
	7.0		3.5	2.6	1.5		
011-030 PHYSIOCHEM. CHA.	45,400		15,200	15,200	7,600	7,600	
	6.0		2.0	2.0	1.0	1.0	
011-040 CATALYTIC REACTION	30,000		3,800	11,400	11,400	11,400	
	5.0		.5	1.5	1.5	1.5	
011-050 CHEM. PROCESS TECH.	22,800				7,600	7,600	7,600
	3.0				1.0	1.0	1.0
011-060 PROCESS CONTROL	22,800			7,600	7,600	7,600	
	3.0			1.0	1.0	1.0	
11-99 Subtotal (1)	224,200	4,490	56,310	57,000	53,200	41,800	11,400
	29.5	.7	7.3	7.5	7.0	5.5	1.5
015 Official travel:							
015-000 TRAVEL COST	4,425		1,200	1,125	1,050	825	225
15-99 Subtotal (1)	4,425		1,200	1,125	1,050	825	225
016 Mission costs:							
016-000 OTHER COST	30,000	8,279	3,721	6,000	6,000	6,000	
16-99 Subtotal (1)	30,000	8,279	3,721	6,000	6,000	6,000	
019 COMPONENT TOTAL (1)	258,625	12,769	61,231	64,125	60,250	48,625	11,625
	29.5	.7	7.3	7.5	7.0	5.5	1.5
030 TRAINING							
031 000 FELLOWSHIPS	286,375		72,000	80,000	80,000	46,375	

COUNTRY : INDIA DATE PRINTED: 30/04/88 PAGE 2
 PROJECT NUMBER : IND/87/067/B/01/37 SHADOW BUDGET
 PROJECT TITLE : DEVELOPMENT OF NOVEL SHAPE SELECTIVE ZEOLITE CATALYSIS
 PROJECT BUDGET COVERING UNIP CONTRIBUTION (in U.S. dollars)

PROJECT COMPONENTS	TOTAL AMT	1987 AMT	1988 AMT	1989 AMT	1990 AMT	1991 AMT	1992 AMT
	N/N	N/N	N/N	N/N	N/N	N/N	N/N
032 000 GROUP TRAINING	90,000		30,000	18,000	18,000	18,000	6,000
039 COMPONENT TOTAL (**)	376,375		102,000	106,000	98,000	64,375	6,000
040 EQUIPMENT							
041 000 EXPENDABLE EQUIPMENT	150,000		35,000	35,000	55,000	25,000	
042 000 NON-EXPENDABLE EQUIPMENT	1,185,000	337,602	297,318	400,000	150,000		
049 COMPONENT TOTAL (**)	1,335,000	337,602	332,318	435,000	205,000	25,000	
050 MISCELLANEOUS							
051 000 MISCELLANEOUS	25,000	3,500	2,500	2,500	4,500	5,000	7,000
059 COMPONENT TOTAL (**)	25,000	3,500	2,500	2,500	4,500	5,000	7,000
099 BUDGET TYPE TOTAL (***)	1,995,000	353,951	498,049	607,625	367,750	143,000	24,625
	29.5	.7	7.3	7.5	7.0	5.5	1.5
999 UNIP TOTAL (***)	1,995,000	353,951	498,049	607,625	367,750	143,000	24,625
	29.5	.7	7.3	7.5	7.0	5.5	1.5

PROJECT BUDGET COVERING UNF CONTRIBUTION IN US DOLLARS

COUNTRY : INDIA

PROJECT NO : 87- 07/8/01/37

TABLE-III

TITLE : DEVELOPMENT OF NOVEL SHMPE SELECTIVE ZEOLITE CATALYSTS

YEAR	PROJECT COMPONENTS	TOTAL AMT M/M	1988				1989	
			ORIGINAL AMT M/M	ACTUAL 9.30 AMT M/M	EXPECTED BY YEAR END AMT M/M	SHIFTED TO 1989 AMT M/M	ORIGINAL AMT M/M	REVISED AMT. M/M
0610	PROJECT PERSONNEL							
	011 EXPERTS							
	011-010 CATALYSIS/CAT RES. ENG./CTA	41,000 5.5	10,710 1.3				7,400 1.0	
	011-020 ZEOLITE CHEMISTRY & CATALYSIS I : GENERAL	53,200 7.0	24,400 3.5				15,200 2.0	
	011-030 PHYSICOCHEM, CHMR.	45,400 4.0	15,200 2.0				15,200 2.0	
	011-040 CATALYTIC REACTION	38,000 5.0	3,800 .5				11,400 1.5	
	011-050 CHEN. PROCESS TECH.	22,800 3.0						
	011-060 PROCESS CONTROL	22,800 3.0					7,400 1.0	
	11-99 SUBTOTAL (01)	224,200 29.5	54,310 7.3	1.8	2.3	+ 5.3	57,000 7.5	
	(01)2 OFFICIAL TRAVEL							
	015-000 TRAVEL COST	4,425	1,200				1,125	
	15-99 SUBTOTAL (01)	4,425	1,200				1,125	
	016-MISSION COSTS:							
	016-000 OTHER COST	30,000	3,721				4,000	
	16-99 SUBTOTAL (01)	30,000	3,721				4,000	
	019 COMPONENT TOTAL (00)	258,625 29.5	61,231 7.3				64,125 7.5	
	0030 TRAINING							
	001-000 FELLOWSHIPS	284,375	72,000				88,000	
	002-000 GROUP TRAINING	96,000	30,000				10,000	
	009 COMPONENT TOTAL (00)	376,375	102,000	92,000	92,000	(+)10,000	106,000	
	0040 EQUIPMENT							
	041-000 EXPENDABLE EQUIPMENT	150,000	35,000				35,000	
	042-000 NON-EXPENDABLE EDUIP	1,185,000	297,318				400,000	
	049 COMPONENT TOTAL (00)	1,335,000	332,318	129,470	332,510	- (-)1192	435,000	
	0050 MISCELLANEOUS							
	051-000 MISCELLANEOUS	25,000	2,500				2,500	
	059 COMPONENT TOTAL (00)	25,000	2,500				2,500	
	099 BUDGET TYPE TOTAL (000)	1,995,000 29.5	498,049 7.3				607,625 7.5	
	999 UNF TOTAL (000)	1,995,000 29.5	498,049 7.3				607,625 7.5	

1988 ACCOMPLISHMENTS

DISCOVERY	FE-FALUASITE	FE-ZSM-23	FE-BETA	HIGH SI MORDENITE	HIGH SI EU-1	UN-1	UN-2	NEW SYN FOR BETA
SIGNIFICANCE	FE IN FRAMEWORK	FE IN FRAMEWORK	FE IN FRAMEWORK	FIRST DIRECT SYN. OF HIGH SI FORM	FIRST DIRECT SYN. OF HIGH SI FORM	COMPLE- TELY NEW STRUCTURE	COMPLE- TELY NEW STRUCTURE	SIMPLER AND LESS EXPENSIVE PROCESS
POTENTIAL USES	HYDRO - ISOM - CRACK	(1) HYDRO DEWAX (2) XYL. ISOM.	HYDRO DEWAX (2) XYL. ISOM.	CUMENE MFG.	-	(1) ADSORP (2) METHYL AMINES	ADSORP	HYDRO DEWAX
PROCESS DEVELOPMENT	-	XYLENE ISOM	HYDRO DEWAX	CUMENE MFG.	-	-	-	HYDRO DEWAX
OTHER FUTURE RESEARCH PLANS	-	-	SCALE UP	SCALE UP	-	STRUCTURE DETERMINA- TION FROM POWDER XRD	STRUCTURE DETERMIN- ATION	SCALE UP
PUBLICATIONS (REFERENCE NOS)	10	-	-	-	12	-	-	14
PATENT APPLIC- ATIONS (REFERENCE NOS)	9	5	10	4	7	3	8	-

PL

1988 ACTIVITIES

1. FELLOWSHIPS

SCIENTIST	INSTITUTION	TIME	TRAINING
1. A.N. KOTASTHANE	U. NAMUR, BELGIUM	6 MON.	ZEOL. SYN.
2. A.J. CHANDWADKAR	U. NAMUR, BELGIUM	6 MON.	ZEOL. SYN.
3. J. KURUVILLA	U. DELAWARE, USA	6 MON.	IR SPECTR.

2. STUDY TOURS

SCIENTIST	INSTITUTIONS VISITED	CONFERENCES ATTENDED	PAPERS PRESENTED	TIME
1. S. SIVASANKER	TOKYO INST. TECH.	(1) INTL. CONGR. CAT.	YES	6 WKS
2. B.S. RAO	" "	(2) IBERO AMER. CONF. CAT.	YES	6 WKS
3. P. RATNASAMY	LABS. IN BELG. ITALY, FRANCE	-	TALKS	6 WKS
4. L.K. DORAISWAMY	LABS. IN EUROPE, USA	-	TALKS	4 WKS

3. VISITING EXPERTS

EXPERT	AFFILIATION	SPECIALISATION	TIME
H.J. LOVINK	UNDP /AKZO	ZEOL. SYN.	FEB. 2 WKS
Y. ONO	UNDP/TOKYO, I.T.	CAT. REACT. ENG.	DEC. 2 WKS
SIGMUND CSICSERY	UNIDO	CTA - CATALYSIS	OCT. 15- NOV. 17

EXPERTS CONTACTED

EXPERT	INSTITUTION	SPECIALITY	TIME
<u>A. VISIT ARRANGED</u>			
J.B. NAGY	UNIV. NAMUR	ZEOL. CHAR.	DEC. 89
S. CSICSERY	UNIDO, CTA	CTA	OCT-NOV. 89
P.A. JACOBS	U. LEUVEN, BELG.	ZEOL. SYN.	JAN. 89
S. KHOOBIAR	UNDP	REACT. ENG.	?
J. LERCHER	U. WIEN, AUSTRIA	ZEOL. CHAR.	NOV. 89-JAN, 90
G. STUCKY	UNIV. CALIF. SB.	ZEOL. CHAR.	?
J. VEDRINE	CNRS, FRANCE	ZEOL. SYN.	FEB. 89

B. INVITATION SENT. UNDP SHOULD FOLLOW-UP

B. J.Q. ADAMS
 G. BELLUSSI
 Y. BEN TAARIT
 H. BEYER
 K. BISHOP
 A. CLEARFIELD
 A. CORMA
 R. COVINI
 S. M. CSICSERY (CTA)
 E. DEROUANE
 V. FATTORE
 E. FLANNIGEN
 J. GARCIA DE LA BANDA

EXPERT	INSTITUTION	SPECIALITY	TIME
--------	-------------	------------	------

B. GATES

W. HÖLDERICH

T.R. HUGHES

H. KARGE

A. KISS

H. KNÖZINGER

F. LYTLE

L. MAROSI

e. NACCACHE

D. PETRAKIS

J. RABO

L.V.C. REES

R. SZOSTAK

R.F. SULLIVAN

J. PETRO

C. EXPERTS CONTACTED BUT CONFLICT OF INTEREST OR OTHER
CAUSES INTERFERES WITH VISITS AT PRESENT. SHOULD BE
PERIODICALLY RE-CONTACTED BY NCL OR CTA.

W. HAAG

J. WEITKAMP

TABLE-VIII

SCHEDULE OF EXPERTS

Year	Zeolite Chemistry and Catalysis: General	Zeolite chemical Quant. Powder XRD	Physico-Characterization TEM	ESCA, EPR, NMR	Reactions, Chemistry and Engineering CIA	Chemical Process Technology	Process Control	M/M	Number of Experts
1987					1			1	2
1988	2*				1.3			2.3	3
1989	7	1	1	1	1 1			12	12
1990	4		1	1	1 1	1	1	10	10
1991	1				1 1	2	2	7	7
Total number of (4 week) visits	13	1	2	2	3 5	3	3	32	
Total number of Experts	8-12	1	1-2	1-2	3 1	3	2-3		20-25

* Two two-week visits of Dr. Lovink and Dr. Ono

78

TABLE-IX

1989 ACTIVITIES (PROPOSED)

FELLOWSHIPS

SCIENTIST	HOST INSTITUTION	TIME	STATUS
I. BALAKRISHNAN	U. OF LEUVEN, BELGIUM	6 MON	CSIR/UNDP APPROVAL AWAITED
S.G. HEGDE	VIRGINIA POLY., USA	6 MON	
P.N. JOSHI	U. OF NAMUR, BELGIUM	6 MON	
A.P. BUDHKAR	CHALMERS U., SWEDEN	6 MON	

STUDY TOURS

SCIENTIST	CONFERENCES TO BE ATTENDED	INSTITUTIONS TO BE VISITED	TIME
R. KUMAR	COURSE ON ZEOL. CHEM. INTL. ZEOL. SYMP. EUROP. CONGR. CATAL.	AKZO CHEMIE.	6 WKS
P. RATNASAMY		SHELL LABS.	4 WKS
		HALDOR TOPSOE	
S.K. DATE			U.LUB AND SAARBRUCK

TABLE-X

EQUIPMENT

ITEM	EQUIPMENT	\$	DELIVERY DATE	STATUS
A. 1.	GAS CHROMATOGRAPH. (ITEM 8)	70,000	1989	ORDERED
2.	REACTORS FOR ZEOL.SYN. (ITEM 1)	50,000	1989	
3.	HIGH PRESS. VALVES (ITEM 10)	10,000	1989	
B. 1.	ACCESSORY FOR XRD UNIT (INSTEAD OF ITEMS 5,6,9)	60,000	1989	SHOULD BE ORDERED
2.	BACK-PRESSURE REGULATORS (ITEM 14)	50,000	1989	
3.	GAS COMPRESSOR (ITEM 13)	50,000	1989	
4.	MOISTURE ANALYSER (ITEM 16)	10,000	1989	
5.	PRESSURE TRANSDUCERS (ITEM 15)	20,000	1989	
C. 1.	ELECTRO-BALANCE	25,000	1989	UNDP SHOULD AUTHORISE CHANGE TO ORDER THESE ITEMS INSTEAD OF ITEM 3 IN THE PROJECT DOCUMENT.
2.	SURF. AREA ANALYSER	20,000	1989	
3.	FUSION APPARATUS	20,000	1989	
4.	VISCOMETER	25,000	1989	
5.	MOSSBAUER SPECTROMETER	25,000	1989	
TOTAL		435,000		
BUDGET (1989)		435,000		

TABLE - XI

Visits of Experts in Zeolite Chemistry and Catalysis

1. Dr. J. Q. Adams,
C/O Dr. T.R. Hughes, 4 Keith, Orinda, California 94563,
U.S.A.
2. Dr. Giuseppe Bellussi, ENIRICERCHE/CATA,
26 Via Maritano, 20097 San Donato Milanese
(Milano) Italy. (Phone 039-2-520-33404 Telex, 310246-ENI-I)
3. Dr. Younef Ben Taarit, Institut de Catalyse,
2, Avenue Albert Einstein,
69626 Villeurbanne Cedex, France (Phone : 033-7-893-3471)
4. Dr. Herman Beyer,
Home Address: Martirok utja 8-10, H-1027 Budapest, Hungary.
Office address: Central Research Institute for Chemistry,
Hungarian Academy of Sciences, H-1025 Budapest
Pusztaszeri ut 59-67, Hungary.
5. Prof. Ken Bishop, Department of Chemical Engineering,
University of Delaware, Newark, Delaware 19716, U.S.A
6. Prof. J. B. Nagy,
Department of Chemistry,
Faculte's Universitaires Notre Dame de la Paix,
Rue de Bruxelles 61, B-5000 Namur, Belgium.
(Phone 032-81-229-061, Telex 59222 FACNAM B)
7. Prof. Abraham Clearfield,
Texas A and M University, Department of Chemistry,
College Station, Texas, 77843-3255, U.S.A.
8. Professor Anelinc Corma
Home address : Mesena 108, Madrid 28033, Spain.
(Phone: 1-202-9720)
9. Dr. Romano Covini,
Home Address : San Simpliciano 6,
I-20221, Milano, Italy. (Office Phone 039-2-6270-7944)
10. Dr. Sigmund M. Csicsery (Project CTA)
P.O. Box 843, Lafayette, California 94549, U.S.A.
(Phone 415-283-2750)
11. Prof. E. G. Derouane,
Department of Chemistry,
Universitaires Notre Dame
Rue de Bruxelles, 61 Namur, B-5000, Belgium.
(Phone 032-81-229-061, Telex 59222 FACNAM B)
12. Dr. Vittorio Fattore, ENIRICERCHE/CATA
26 Via Maritano, 20097 San Donato Milanese
(Milano) Italy (Phone 039-2-520-5657, Telex : 310246 ENI-I)

TABLE - XII

13. Dr. Edith Flannigen, Union Carbide Corp.,
Tarrytown Technical Center,
Old Saw Mill River Road at Route 100 C,
Tarrytown, New York 10591, U.S.A.
14. Prof. Juan F. Garcia de la Banda,
Hilarion Eslava 28-5.C,
28015 Madrid 15, Spain. (Phone : 1-243-0683)
15. Prof. B. C. Gates, Department of Chemical Engineering,
University of Delaware,
Newark, Delaware 19716, U.S.A.
16. Dr. Werner Haag, Mobil Technical Center,
P.O.Box 1025, Princeton New Jersey 08540, U.S.A.
(Phone 609-737-3000, Ext. 4264)
17. Dr. Wolfgang Hölderich,
BASF Aktiengesellschaft, ZAK/Z Ammoniaklaboratorium,
D-6700 Ludwigshafen, West Germany.
(Phone 049-621-605-4072, Telex (17) 621-5934)
18. Dr. T.R. Hughes, 4 Keith, Orinda,
California 94563 U.S.A. (Phone 415-254-1711)
19. Prof. P. A. Jacobs,
Centre for Surface and Colloid Sciences,
Katholieke University at Leuven de Croylaan 42,
B-3030, Leuven, Belgium.
20. Prof. Helmut Karge,
Fritz Haber Institute, Faradayweg 4-6
1000 Berlin 33, West Germany (Phone 3305-281)
21. Dr. Akos Kiss,
Degussa A.G., Fachbereich Forschung Chemie, Postfach 1345,
Rodenbacher Chaussee 4, D-6450 Hanau 1, West Germany
(Phone : 049-6181-593-572, Telex 4 15200-0 dw D)
22. Prof. Helmut Knözinger, University of München,
Sophienstrasse 11, D-8000 München 2,
West Germany (Phone 0049-89-5902-319)
23. Dr. S. Khoobiar,
750 Ridge Road, Kinnelon, N.J. 07405, U.S.A.
(Phone 201-838-2931)
24. Professor Johannes Lercher
Institute für Physikalische Chemie
Technische Universität, WIEN A-1060 (Phone :0222-38801-4970)
25. Dr. Farrell W. Lytle, The EXAFS Company
10815 24th South Seattle, Washington 98168, U.S.A.
(Phone 206-242-9084)

TABLE - XIII

26. Dr. Laszlo Marosi,
Home Address : Leuschnerstrasse 32,
D-6700 Ludwigshafen, West Germany.
27. Prof. Claude Naccache, Institute de Catalyse,
2 Avenue Albert Einstein
69626 Villeurbanne Cedex, France
(Phone 033-7-893-3471)
28. Dr. D. L. Petrakis, Chevron Research Company,
576 Standard Avenue, Richmond, California, 94802
U.S.A. (Phone : 415-620-4648)
29. Prof. Jozsef Petro,
Department of Organic Chemical Technology,
Technical University, Muegyetem, Budapest,
H-1521 Hungary (Telex 22-5931)
30. Dr. Jule A. Rabo,
Union Carbide Technical Center,
Old Saw Mill River Rd at State Route 100C,
Tarrytown, New York 10591, U.S.A.
(Phone 914-789-2353)
31. Prof. L.V.C. Rees, Imperial College of Sci.
Technology, Chemistry Department, London SW7 2AY, U.K.
32. Prof. Rosemarie Szostak,
Zeolite Research Project, The Georgia Institute of Technology,
Atlanta, Georgia 30332, USA.
33. Prof. Galen D. Stucky,
Home Address : 973 W Campus Ln, Santa Barbara,
California 93117, U.S.A.
Office Address : Department of Chemistry, Univ. of Calif.
Santa Barbara, Santa Barbara, California 93106, U.S.A.
(Phone 805-961-4872)
34. Dr. Richard F. Sullivan, Chevron Research Co.,
576 Standard Avenue, Richmond, California 94802, U.S.A.
(Phone 415-620-2228)
35. Prof. J. Vadrine, Institute de Catalyse,
2 Avenue Albert Einstein
69626 Villeurbanne Cedex, France (Phone 033-7-893-3471)
36. Prof. Dr. Ing. Jens Weitkamp,
Univ. Stuttgart, Inst. Chemical Technol. I
Pfaffenwaldring 55, Postfach 80 11 40
D-7000 Stuttgart 80, West Germany (Phone: 049-711-685-4060,
Telex : 7-255-445, Telefax 049-711-685-3500)

ADDENDUM

FINAL REPORT AND COMMENTS, DP/IND/87/007

DECEMBER 1988

Introduction

The Final Report submitted in November, 1988 describes the accomplishments and status of the Project, the Work Plan and Work Schedule for 1989 plus the following years, and other relevant topics. The Report was prepared at the time of the First Tripartite Meeting, held in Pune, November, 14, 1988. The attached Table of Contents (Table I and II) shows the content of the November Report.

This December Report describes the decisions made at the Tripartite Meeting, and summarizes my own technical contributions to the Project.

The Tripartite Meeting of November 14, 1988

A Tripartite Meeting was held on November, 14, 1988 at NCL in Pune, India. Participants were :

NCL : Dr. L. K. Doraiswamy, Project Director,
Dr. Paul Ratnasamy, Project Coordinator,

UNDP Delhi : Mr. M. Islam,
Mr. Sat Pal,

CSIR, Delhi : Mr. K. N. Johry

UNIDO, Vienna : Mr. M. Derrough,

UNIDO : Dr. Sigmund M. Csicsery, CTA of the Project.

We concluded that the Project in 1988 has achieved its objectives. A number of additional accomplishments testify to the excellent performance and ability of the NCL task force. These accomplishments are described in detail in the November 1988 Final Report. Table III summarizes these results.

We made the following decisions at the Tripartite meeting:

No.	Action recommended	Agency in-charge	Dateline
1.	Combine certain "Expert" classifications	Tripartite meeting	November 14, 1988
2.	Speed up the handling of "Expert" visits	UNIDO VIENNA	December 1, 1988
3.	Speed up authorization procedures of contracts for XRD (and other) analyses	UNIDO (UNDP)	November 21, 1988
4.	Change some equipment order	NCL sends specs + vendors to UNDP	January 1, 1989
5.	Shift unused "Expert's Visits" and "Fellowship-Study Tour" funds to 1989		Done
6.	Authorization of Travel Agent in Pune for travel arrangements.	UNDP will authorize Air India to issue tickets	Whenever time is available
7.	Put more emphasis on "Expert" recruiting	CTA	continuously

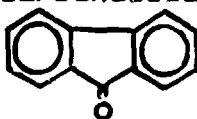
Technical Contributions of the CTA

The daily technical and scientific discussions with Dr. Paul Ratnasamy, Project Coordinator, and members of his Group need not be detailed here. The following illustrate the type of the recommendations of the CTA, and the nature of these discussions.

* Recommended to confirm the presence of Fe in the framework of zeolite beta (1) by comparing IR, etc. spectra of Fe-beta with those of Fe_2O_3 , $\text{Fe}(\text{OH})_3$, $\text{FeO}(\text{OH})$ etc. and (2) and to measure magnetic properties (susceptibility, Curie point, Curie Weiss point, etc., and Mossbauer spectra of Fe-beta zeolites). (Discussions with Dr. Kumar).

* Suggested a way to increase the acid strength and thermal stability of beta zeolites by removing all residual Na from the zeolite. Exchange first with Ag-acetate to make the silver form of the beta zeolite. Remove then all silver with ammonium thiocyanate exchange. Repeat these exchanges two or three times to remove the last traces of Na. Work in dark (Discussions with Dr. Hegde).

* Recommended the use of benzyldiethylamine instead of a mixture of benzylchloride and diethylamine to avoid the formation of unremovable refractory carbonaceous residues (probably



and anthracinone and related polycyclic aromatics) after calcining the beta zeolite (Discussions with Dr. Hegde).

Helped in the elucidation of the roles of various types of shape selectivities exhibited by medium-pore zeolites in xylene

isomerization, toluene disproportionation, and toluene alkylation (Discussions with Dr. Ratnasamy).

* Recommended operations at low conversion levels in all test reactions but especially in toluene alkylation to avoid complications by secondary reactions.

* Recommended seeding to improve reproducibility in zeolite syntheses (Discussions with Dr. Chandwadkar).

* Recommended to initiate studies on pelleting and binder selection to avoid unintended Al-exchange from binder to Fe-zeolites during catalyst preparation, use, or regeneration.

* Recommended the use of a test reaction for large-pore zeolites: a mixture of benzene (9 parts), o-xylene (1 part) and hydrogen (about 100 parts). The reactions are isomerization to m- and p-xylenes and transalkylation to toluene. Diffusion effects may be revealed by m-xylene/p-xylene ratios at constant low conversion levels. Catalysts with different activities need to be compared at the same temperature. Change LHSW's by diluting catalysts with inert material; (quartz or alpha-alumina of the same mesh size as the catalyst) rather than by changing flow rates. Compare apparent activation energies of isomerisation and transalkylation. Always try to operate at low conversion levels.

Other discussions involved possible applications of zeolites as catalysts in the formylation of phenol, photochemical reactions in the presence of water (with Dr. Pande), and chemical

engineering and diffusion phenomena associated with zeolites
(with Dr. Choudhary).

In addition, the CTA presented a Seminar for the Scientists
of NCL on the 4th of November, 1988. The title of the NCL's
seminar was "New Developments in Shape Selective Catalysis"

Enclosures : Tables I, II and II

Table I.

TABLE OF CONTENTS

UNDP PROJECT DP/IND/87/007/11

SUMMARY OF ACHIEVEMENTS IN 1988	1
AGENDA FOR TRIPARTITE REVIEW MEETING OF NOV. 14, 1988.	2
A : FOLLOW UP REPORT	2
B : PROJECT CONCEPT AND DESIGN	6
C : PROGRESS	6
D : OPERATIONAL ISSUES AND PROBLEMS	6
JOB DESCRIPTIONS	9
Experts in Zeolite Chemistry & Catalysis:General	10
Background Information	11
Other "Experts"	14
E : WORK PLAN FOR YEARS 1989-1992	19
Work schedule	23
F : DECISIONS AND RECOMMENDATIONS	27
PROJECT DOCUMENT	28
SUMMARY OF WORK DONE UPTO OCTOBER 1988	29
Annexure 1 (Isomorphous Substitution of Fe in Faujasite)	31
Annexure 2 (Isomorphous Substitution of Fe in ZSM-23)	31
Annexure 3 (Isomorphous Substitution of Fe in Beta-Zeolite)	33
Annexure 4 (Novel Zeolite with unknown Structures UN-1 & UN-2)	36
Annexure 5 (Direct Synthesis of High Si Large Pore Mordenite)	44
Annexure 6 (Preparation of EU-1 Zeolite with high Si content)	45
Annexure 7 (Scientific papers published during Sept.87-Oct.88)	46
Annexure 8 (Patents List)	48
Annexure 9 (Letter, Prof. Y. Ono, Oct., 7, 1988)	49
OUTPUTS : Schedule of Project Review, Judgement and Evaluation	50
STUDY TOUR REPORTS	51
Dr. Paul Ratnasamy	51
Dr. S.Sivasanker	53
Dr. B.S. Rao	53
FELLOWSHIP REPORTS	60
Dr. Joseph Kuruvilla	60
Dr. A. N. Kotasthane	62
Dr. MS A. J. Chandwadkar	62

TABLE II.

TABLE I : PROJECT BUDGET COVERING UNDP CONTRIBUTION

TABLE II : PROJECT BUDGET COVERING UNDP CONTRIBUTION

TABLE III : PROJECT BUDGET COVERING UNDP CONTRIBUTION

TABLE IV : 1988 ACCOMPLISHMENTS

TABLE V : 1988 ACTIVITIES

TABLE VI : EXPERTS CONTACTED

TABLE VII : EXPERTS CONTACTED

TABLE VIII: SCHEDULE OF EXPERTS

TABLE IX : 1989 ACTIVITIES (PROPOSED)

TABLE X : EQUIPMENT

TABLE XI : ADDRESSES OF EXPERTS

TABLE XII : ADDRESSES OF EXPERTS

TABLE XIII: ADDRESSES OF EXPERTS

TABLE III.

UNDP PROJECT : DP/IND/87/007/11-01

SUMMARY OF ACHIEVEMENTS IN 1988

1. NCL HAS ACCOMPLISHED THE OBJECTIVES SET FOR 1988 :
 - : SUBSTITUTED FE INTO THE LATTICE OF FAUJASITE
 - : MADE TWO NEW ZEOLITE STRUCTURES

2. IN ADDITION, NCL MADE SEVERAL SIGNIFICANT NEW DISCOVERIES :
 - FE IN ZSM-20
 - FE IN BETA
 - FE IN ZSM-23
 - DIRECT SYNTHESIS OF HIGH SILICA MORDENITE
 - DIRECT SYNTHESIS OF HIGH SILICA EU-1
 - NEW, LESS EXPENSIVE AND SIMPLER SYNTHESIS OF BETA

POTENTIAL COMMERCIAL APPLICATIONS :

- * CUMENE PROCESS WITH HIGH SILICA MORDENITE
- * HYDRODEWAXING WITH FE BETA
- * XYLENE ISOMERISATION WITH FE BETA

3. THE WORK DONE SO FAR HAS RESULTED IN :

- 11 SCIENTIFIC PUBLICATIONS
- 11 PATENT APPLICATIONS