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DEVELOPMENT OF NOVEL SHAPE SELECTIVE ZEOLITE CATALYSTS

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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 Prof. L. V. C. Rees
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DEVELOPMENT OF NOVEL SHAPE SELECTIVE CATALYSTS

INTRODUCTION

As stated in the 'Job Description' paper sent to me by UNIDO it is necessary to submit a report on my findings and recommendations following my 3 week visit to NCL from 19th January, 1989 as an Expert in Physicochemical Characterization of Zeolites and Catalysts. The following is my report as requested.

SUMMARY OF ACHIEVEMENTS BY NCL DURING 1988

NCL has made very significant progress in the areas of research proposed under the UNDP Project and seems to be ahead of schedule in many of these areas. NCL must be congratulated on the successes achieved so far. These successes include the substitution of Fe into the faujasite lattice and the synthesis of two new zeolite structures. In addition, NCL has been able to synthesise the zeolites ZSM-20 and -23 and BETA with Fe in the tetrahedral framework sites. The direct synthesis of high silica mordenite would seem to be a very interesting new development. This zeolite should be capable of being developed into a very useful catalyst and should also be important for fundamental catalytic studies. Similarly, the direct synthesis of high silica EU-1 and a less expensive and simpler synthesis of the zeolite Beta could lead to successful further developments in catalysis using these materials.

The publication of (or the acceptance of) 11 scientific publications in reputable journals in 1988 clearly indicates that the work at the NCL is of a high quality and of interest to the International Zeolite community. 11 Patents have also been applied for which demonstrate the ideal marriage of fundamental research and industrial application that zeolites provide.

The above achievements in the short time that the project has been running, are to be complimented.

SUMMARY OF MY FINDINGS AND RECOMMENDATIONS

NCL has rightly established itself as one of the leading laboratories in the world in the synthesis of metal substituted zeolite frameworks. The laboratory was the first to demonstrate the introduction of Fe into the framework of ZSM-5. This interest in Fe substitution in zeolite framework is continuing unabated and is a major part of the present research programme. This interest is understandable considering the successful industrial application of Fe substituted ZSM-5 in xylene isomerization and ethyl benzene production from dilute aqueous solutions of ethanol and benzene. Recent studies in this area of research have been concerned with the substitution of a variety of other elements, e.g. Zn, Ti, Zr, P into zeolite frameworks. The use of

metal alkoxides as precursors of metal oxides in the synthesis of metal substituted framework seems to be successful and interesting and should be encouraged.

NCL has also clearly demonstrated shape selectivity in catalytic reactions. The paper to be presented at the next IZA meeting in Amsterdam in July 1989 gives a clear understanding of this selectivity as demonstrated by the zeolites, ZSM-5, -22, -23, -48 and -50 for the isomerization of m-xylenes and methylation of toluene. This paper summarises much of the thrust of the research in this area being conducted at NCL. The synthesis and catalytic activity of these five zeolites is being tackled in a thorough, scientific manner. The laboratory has an excellent group of scientists who are very knowledgeable in the area of substitution and catalysis. There should be no problems in carrying out the work planned in these areas of research over the remaining period of the project.

However, to obtain the maximum benefit/information from the research on these new materials which are being generated at NCL there is a need to improve some of the characterization facilities available to the zeolite group. As I see it, there is a need for the recruitment of experienced scientists in (a) X-ray diffraction, (b) Adsorption, (c) Ion-exchange, and (d) Theoretical Analysis. Because of the great interest in Fe substituted frameworks there is an immediate need for a Mossbauer spectrometer capable of measuring spectra at liquid He temperatures in the presence of an external magnetic field. Although ESR is a useful spectroscopic technique it is somewhat limited compared with Mossbauer spectroscopy in the information obtainable on the tetrahedral Fe species present in the samples. It is now clearly established that tetrahedral framework Fe has an Isomer Shift of 0.3mm s^{-1} and superparamagnetism which is a function of Fe concentration in the framework can be used to establish Fe-Fe separation distances. The expertise to interpret such spectra already exists at NCL and this expertise should be more fully used.

In the day-to-day routine analyses of the large number of zeolite samples being produced under the NCL synthesis programme a new X-ray diffractometer (e.g. SIEMENS D-500) with extensive back-up software (e.g. DIFFRAX 500) is required. However, a VAX computer is required to run this software which contains an extensive library of zeolites X-ray diffraction patterns for comparison purposes and for deconvolution of mixed zeolite samples. The VAX computer has adequate capacity for running extensive "Computer Graphics" software (e.g. CHEM X) which would be a useful, if not essential, addition to the facilities of the zeolite group.

Ion-exchange is a useful method for demonstrating or confirming the introduction of 3+ species into zeolite frameworks. The substituted frameworks being produced at NCL should have confirmatory ion-exchange evidence of 3+ substitutions. Ion-exchange is, also, useful in demonstrating the presence of OH defect nests resulting from the calcination of organic template cations in high Si/M ratio zeolites. Finally, my group at Imperial College is analysing the "Cut-offs" obtained in divalent cation exchange with Na-ZSM-5 zeolites. These limits to the degree of divalent exchange increase with increasing Al in the framework. These results are being analysed, using the CHEM X package reported on above, to give the distribution of Al-Al separation distances in the ZSM-5 lattice as a function of Si/Al ratio. Similar studies would seem to be useful to the catalyst group at NCL.

Adsorption is also a very useful method of determining the degree of crystallinity of zeolite materials. It is essential to confirm X-ray crystallinities with adsorption saturation capacities. However, adsorption is also useful in studying the strengths and concentrations of the electric fields which exist on the surfaces of the channels of zeolites and for gaining immediate information on the effective free diameter of the windows controlling access to the channel networks present in zeolites. As many of the reactions being followed in the NCL programme are diffusion controlled, rates of sorption/desorption should be used to screen samples for their usefulness in such reactions. There is a need for this area of research to be strengthened.

I do not believe that the zeolite group at NCL need much advice from myself on short or long-term research objectives. The group seems to have a clear understanding of its objectives and is more than successful in the areas of synthesis, modification and catalysis of zeolites. However, as one of the prime aims of the project is to provide a better understanding of the fundamentals of shape selective catalysts and their catalytic reactions, it is essential that the group acquire certain additional modern instrumentation to achieve this aim. There is also a need for the members of the zeolite group at NCL to be trained in some of these techniques, e.g. X-ray crystallography.

CONCLUSIONS

The zeolite group at NCL is achieving considerable success in the research proposed in the UNDP project definition. I have every confidence that the group will continue to produce excellent results over the remaining period of the project. With the help of some additional equipment, the group should continue to produce first class research papers which will provide new insights into zeolite catalysis and catalysts. There is no doubt that the Indian Petroleum Industry will benefit greatly from these studies.

The visit of expert advisors from other countries to the NCL laboratories would seem to be an essential feature of the project and well worth the costs involved. These advisors, however, need to be carefully chosen to help in developing the expertise needed with the new instrumentation and techniques suggested in this report.

I wish the zeolite group at NCL every success during the period 1989-1992.

PROFESSOR L.V.C. REES
PUNE
3RD FEBRUARY 1989.