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DEVELOPMENT OF NOVEL SHAPE SELECTIVE ZEOLITE CATALYSTS

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REPUBLIC OF INDIA

Expert's 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 Mr. J. C. Vedrine
Expert in Zeolite Synthesis

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Vienna

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EXPERT'S REPORT

The expert has been very favourably impressed by the high scientific quality of the laboratory of Dr. P. Ratnasamy with several brilliant scientists and by its very close relations with industry. Moreover the previously performed work has already found industrial applications in India in petrochemicals field, which is very encouraging for future.

The expert has not only visited NCL and discussed widely with all scientists working in the field of zeolites (synthesis, characterization, catalytic properties) but has also visited closely related laboratories or plants at Baroda (IPLC and United Catalyst) at Bombay (Hindustan Lever) and at DehraDun (IIP).

The expert has given three lectures at NCL, a lecture (n° 2) at IPLC (Baroda) and one (n° 2) at IIP (DehraDun). The lectures were entitled :

1. Adsorption and diffusion in zeolites. Influence of crystallite size.
2. Isomorphous substitution in MFI and AEL molecular sieves.
3. ESR technique and its use for Fe substituted zeolites.

The latter lecture was dealing with ESR technique (the expert being also competent in ESR and XPS techniques) with particular emphasis on Fe^{3+} (d^5) cations ESR spectrum and relation with isomorphous substitution. This was important since the indian patented catalyst designated ENCILITE contains iron in its zeolitic framework.

During my stay of ca 3 weeks in Pune I have been first acquainted about the previous works and about the UNDP programme. I noted how important is for the laboratory and subsequently for India to develop the iron type isomorphous substitution of many types of zeolites. Success has already been obtained for total substitution in ZSM-5 (ENCILITE), ZSM-23, β and partly in γ type zeolites. The present effort is placed upon iron substitution on as many zeolites as possible and this is a good scientific choice for future applications.

The laboratory had large success in synthesis new unidimensional zeolites as ZSM-22, - 23 ; - 48 ; - 50 ; EU-1 and should succeed in a near future to synthesise their iron forms. This is a difficult task but the expert thinks that the laboratory is well trained for it. The expert totally agrees with the present trend to focuss the effort on iron isomorphous substitution. He has tried by its own experience and its knowledge, particularly in ESR technique, to help the scientists to determine if iron is actually isomorphously substituted in such matrices or partly or not at all. The expert emphasized strongly upon the necessity to use various physical means including catalytic test reactions to fulfil the foregoing requirement.

The laboratory has also succeeded to synthesize new materials of unknown crystalline structure and chemical physical properties. An X ray powder analysis is conducted in USA under the UNIDO research programme but it is obvious that for powders the task is rather difficult. The expert strongly recommends a very well trained scientist about 50 years old in the field of powder in zeolites using X ray and neutron diffraction techniques. He is presently working at the University of Lyon I and his name is Dr. Bernard F. Mentzen. The expert will contact him to determine if he could be interested in a collaborative research programme under UNDP and UNIDO.

The expert has realized that UNIDO purposes not only consist in helping India to develop its own industrial processes on chemicals or petrochemicals but also to encourage basic type research and cooperation. As the expert has in his own laboratory some facilities such as particularly ESR, IR, UV-vis and Mössbauer techniques a collaboration research programme has been established for the near future. Some samples (ENCILITE and other Fe substituted zeolites) have been given to the expert to start some research work in common.

During the discussions with the different scientists many ideas have been shared and many suggestions made or advices given. It is impossible to summarize all of them. Let us concentrate on two cases. India being interested in middle distillates (kerosene, diesel) rather than in gasoline and LPG. Therefore hydro-cracking of naphta and aromatization of light paraffins could be interesting processes. In the former reaction as external acidity plays an important role by favoring branched paraffins against viscosity index, the idea was to neutralize such external acidity by some bulky basic molecules. As the laboratory has a large expertise in synthesis, the expert suggested to try to end the synthesis in an Al free medium in order to get zeolitic crystallites with Al free top layers. For the latter reaction Cyclar (Ga-ZSM-5 zeolite) and Aromex (Pt on BaK-L zeolite) processes are known and used commercially. As the laboratory has expertise in ALPO-5 and SAPO-5 (pore diameters ~ 0.8 nm) the expert suggested to start some experimental work on Pt on BaK-SAPO-5 materials.

The laboratory of NCL experienced an excellent training in zeolite synthesis and can be considered as mature in this field and is expanding its research in new type zeolites. Characterization of the materials is only possible, particularly for isomorphous substitutions, if a large variety of physical and chemical techniques are used. As it is impossible to have the expertise required for all techniques, the laboratory is, to my opinion, lacking high quality specialists in the different techniques. This is why several experts (ESR, Mössbauer, NMR, XRD on powders, XPS, etc.) are needed and collaboration research programmes have to be established to try to reach high quality characterization.

The group working on catalytic reactions (microreactor, micropilote units) is well trained, i.e. able to characterise catalytic properties of the new materials synthesized in the laboratory.

The laboratory seems to be well equipped although more physical techniques equipments (Mössbauer, microcalorimeter, EDX-STEM, etc.) are needed.

It is not possible to conclude this report without expressing my sincere thanks for all the people I have met, scientists, technicians, secretaries, car drivers, etc for their kind hospitality and kindness. All of them have tried to make my stay as pleasant as possible and to avoid any loss of time or any unpleasant event. They completely succeeded. I really and deeply thank them all, particularly the programme coordinator P. Ratnasamy with whom I had so many discussions, even in French. I thank also Mr Islam and Sat Pal at UNIDO in Delhi for their help to be acquainted to this programme and to India. Every thing was since and well organized.

February 7, 1989

A handwritten signature in black ink, appearing to read 'J.C. VEDRINE', written in a cursive style with a long horizontal stroke at the end.

J.C. VEDRINE