

Catalysis

Zeolites under control

from Lovat V.C. Rees

ON page 589 of this issue of *Nature*, Haag *et al.* report a very nice example of the way in which zeolites can be used in the controlled catalysis of hydrocarbon cracking, which is best seen in the context of John Dwyer's brief but comprehensive overview of zeolites as acid catalysts in the 2 April issue of *Chemistry and Industry*.

Zeolites are crystals of aluminosilicates permeated by channels and cages of molecular dimensions. The active catalytic centres are hydroxyl groups — one for each Al atom — which are readily generated by deammoniation of ammonium-exchanged zeolites on heating to 400°C. On heating to temperatures greater than 550°C, however, these Brønsted acid sites are converted to Lewis sites by loss of H₂O. John Dwyer clearly indicates the importance of zeolites in elucidating the fundamental mechanisms involved in the catalytic conversion of hydrocarbons. Since zeolites can readily be synthesized over a very wide range of Si/Al ratios, it is possible to create catalysts with active centres whose average separation distance can be varied in a controlled way. Also, by choosing specific zeolite structures from a large list, channel and cage geometry can be varied. Specific channel geometries can also be modified by various techniques.

With this ability to finely tune zeolite catalysts, it is possible to observe the effect of increasing the acid strength on, for example, the product ratios resulting from the isomerization of butenes. The shape-selective behaviour of zeolite catalysts can be readily quantified. Thus reactant and product shape-selectivity and restricted transition-state-selectivity can be explained. The size and shape of the channels and cages exert both geometric and diffusional restrictions. The size of the crystals, coking, steam treatment and chemical modifications affect the products of a reaction in easily explained ways.

It is usually quite difficult to identify and count the number of active sites involved in a catalytic reaction but that is not the case for ZSM-5, the zeolite studied by Haag *et al.* and in which it is possible to have such a high ratio of SiO₂ to Al₂O₃ that the Al atoms are no longer a structure-determining constituent. Haag *et al.* varied the Al content of ZSM-5 from 20 to 10,000 p.p.m. such that the average distance between Al sites represented several to a very large number of atomic diameters and the distribution of the sites will have approached one of randomness. There is, thus, a substantial chemical uniformity to the catalytic sites.

The activity of these samples towards the cracking of *n*-hexane in controlled conditions was linearly related to the Al

content and extrapolated to zero activity at zero Al content. This quantitative correlation can be explained only if all Al atoms are in tetrahedral framework locations — which is exactly how they are shown to be arranged by high-resolution magic-angle spinning nuclear magnetic resonance.

With such accurate quantitative data it is possible to determine the number of active sites, the absolute molecular turnover rates and the turnover numbers. Haag *et al.* found an absolute turnover rate for *n*-hexane cracking of 2.8 molecules per minute per atom of Al over the entire Al concentration range. Since the reaction rate is first order, the fraction of occupied Al sites at 100 torr is less than 1 per cent of the total Al sites and the turnover rate per occupied active site (the turnover number) is greater than 300 molecules per minute per active Al site.

The reaction rates for other reactions, for example 1-hexane cracking and 1-hexene double-bond isomerization, have also been shown to be linearly dependent on the Al concentration. The olefin cracking rate is some 800 times the paraffin cracking rate while the olefin isomerization rate is some 1,300 times the olefin cracking rate. The Al concentration needed to achieve technically relevant reaction rates can be less than 1,000 p.p.m. for paraffin conversion and from a fraction of a p.p.m. to 100 p.p.m. for other conversions. Turnover numbers as large as 4×10^7 can be obtained with zeolite catalysts; not dis-

similar to the values in enzyme catalysis.

Ultra-stable zeolite Y is currently used as the cracking catalyst in oil refining. It cannot be synthesized with a ratio of SiO₂ to Al₂O₃ greater than 3, but this ratio can be increased by various de-alumination processes. These impart additional thermal stability but lower the crystallinity, and the resulting catalyst is still too active and requires dilution with catalytically inactive binder material. Even then, coking of the catalyst pellets occurs in a reactor in a time scale measured in seconds. The data of Haag *et al.* on ZSM-5 indicate how little Al is necessary for cracking reactions and should spur zeolite chemists on to discover a method to produce zeolite Y with very much less Al than used at present. Very interesting technical problems will have to be overcome to produce such a catalyst.

Finally, Martens *et al.* show that a relatively simple test can be used to obtain a detailed insight into the structure of the channels and cages of zeolites (*Zeolites* 4, 98; 1984). Using *n*-decane isomerization and hydrocracking reactions over platinum-loaded hydrogen zeolites as a fingerprint, five independent criteria can be found which give consistent and supplementary evidence on the structure and dimensions of the void space in zeolites. Voids that are characterized in terms of unidimensional pores made of 10-membered rings of oxygen atoms are readily distinguished from those that are cages of varied dimensions accessible through pores made of 8- or 12-membered rings. Surely the consistent reproducibility of these catalytic reactions indicates the uniqueness of zeolites as catalysts. □

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Immunology

T-cell development in the thymus

from Ken Shortman

MUCH of the development of T lymphocytes takes place in the thymus, away from the melee in bone marrow where B lymphocytes and other haematopoietic cells differentiate side by side. What is the purpose of this convenient packaging? Is the thymus an inductive environment for switching the differentiation of uncommitted stem cells into one of the T-cell lineages? Or is it an immunological finishing school, generating a diversity in the antigen receptors on the surface of T cells and selecting those most suitable for recognizing foreign antigens presented in the context of 'self' (major histocompatibility) antigens on the surface of cells. Or is it both? A careful study of what goes in and what comes out can set the limits of what might happen in the thymus itself.

Recently devised techniques^{1,2} for labelling cells within the adult mouse thymus and

for tracing labelled emigrants into the periphery have shown that emigrant cells are much like mature T cells, are already committed to one or other of the specialized T sublineages and are already functional. The essential development of the cells must have occurred within the thymus, or even before their arrival there. The output from the thymus is low, however: only about 3 per cent of the cells produced daily leave the thymus, the rest apparently dying within it. Although this high attrition rate suggests a stringent culling for appropriate specificity, it could equally well reflect a low efficiency in the formation of a functional T cell of any specificity.

The other part of the equation, the seeding of T cells in the thymus, is considered by Ezine, Weissman and Rouse on page 629 of this issue of *Nature*³. They have studied the reconstitution of the T-cell