Catalysis Letters 1 (1988) 191–194

PROBING STRUCTURAL CHANGES DURING THE ONSET OF CATALYTIC ACTIVITY BY *IN SITU* X-RAY DIFFRACTOMETRY

Peter J. MADDOX, Jaroslaw STACHURSKI and John M. THOMAS

Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street,
London W1X 4BS, U.K.

We demonstrate the feasibility of retrieving details of structural changes, in particular the migration of Ni^{2+} cations in the intrazeolite cavities of a faujasitic catalyst, during the development of activity for the trimerization of acetylene to benzene.

1. Introduction

Among the many reactions of organic compounds catalysed by transition-metal exchanged zeolites [1] is the facile trimerization of acetylene to benzene by Ni^{2+}-exchanged zeolite Y [2,3]. Circumstantial evidence [4,5] suggests that migration of metal cations from their original positions in the as-prepared solid is a pre-requisite to subsequent catalysis. X-ray powder diffractograms, shown below, clearly indicate that for the trimerization of acetylene significant structural changes occur coincidental with the onset of catalytic activity. These results, combined with those of earlier studies using Rietveld profile analysis [5a], demonstrate that with *in-situ* X-ray cells and on-line chemical analysis, it is feasible to chart the detailed structural changes during catalysis, and hence arrive at the nature of the active site in the 'uniform' heterogeneous catalysts for a variety of fundamentally and commercially important reactions.

Preliminary experiments into the trimerization of acetylene with Ni^{2+}-exchanged zeolite Y focused on the performance of various catalysts. A conventional flow reactor was employed for this purpose. When stringently purified acetylene (30 ml min^{-1} at 760 Torr) was passed over dehydrated zeolites of various Ni^{2+} loading at 100 °C, the trimerization proceeded efficiently, but the catalyst became inactive after approximately 2 hours because of coke formation [6]. These catalysts could be regenerated by heating in O_2 at 300 °C for several hours. Although lower partial pressures of acetylene resulted in smaller reaction rates of benzene formation, the catalyst life was extended, and hence these conditions were employed for an *in situ* X-ray diffraction study.

A sample of Ni^{2+}-exchanged zeolite Y, of approximate formula $Ni_{21}Na_{17}Al_{59}Si_{133}O_{384}$ from chemical analysis, was placed as a thin powdered layer on a porous quartz disc in a specially constructed flow-through cell fitted with mica windows and a tubular heated region. This was dehydrated for 15

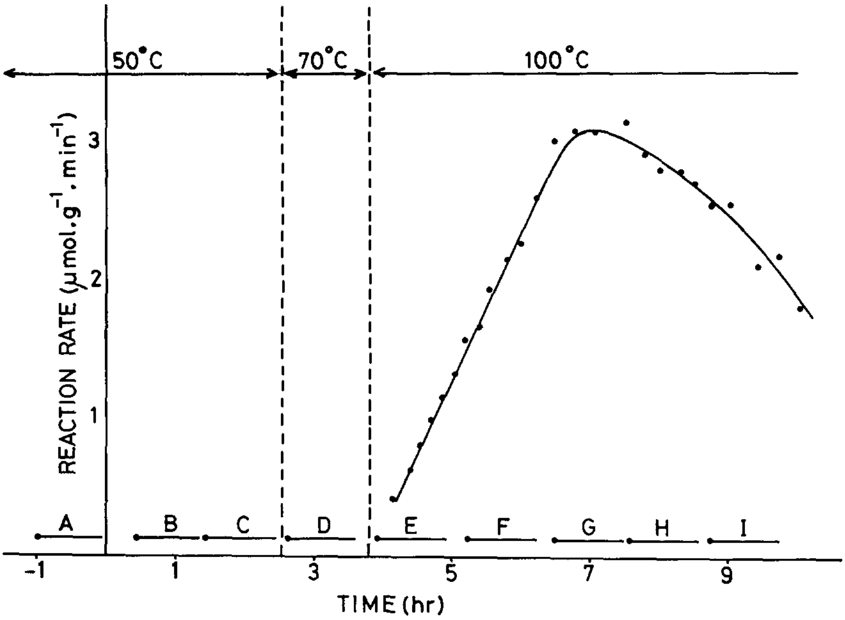

Fig. 1. Catalytic activity as a function of time and temperature. Reactant gases admitted at time = 0. Horizontal lines indicate the time and duration of the collected diffraction patterns *A* to *I*.

hours under a flow of dry O_2 (40 ml min^{-1}) at 400 °C. After cooling and standing at 50 °C, an X-ray diffraction pattern (Cu K_α radiation, conventional Siemens D500 diffractometer) was collected for the range of 2θ of interest. Acetylene was then admitted ($P_{C_2H_2}$ 225 Torr, balance N_2, 1 bar total pressure, flow rate 30 ml min^{-1}), and a series of eight X-ray diffractograms were collected, each pattern requiring 58 minutes. Concurrently the gas stream leaving the X-ray cell was analyzed by gas chromatography.

Figure 1 shows the manner in which catalytic activity develops as the temperature was increased and indicates when the X-ray diffractograms ($A - I$) were recorded. Below 100 °C no trimerization is detected, but at this temperature the formation of benzene begins. The diffractograms, shown in fig. 2, indicate clear cut changes in the (220), (311), (331), (333), (440), (531) and (533) reflections during this catalytic run, and these changes are most dramatic when the reaction commences (compare patterns *D* and *E*). Onset of catalysis also results in an increase of the unit cell dimension from 24.45 Å to 24.52 Å. In addition, we see no X-ray intensity attributable to Ni^0 species at $2\theta = 44.51$, (111) reflection [8].

Previous studies [5a] allow us to build up a qualitative picture of Ni^{2+} cation migration during this experiment; in particular, the movement of cations away from site I in the hexagonal prisms [10] is indicated by the relative intensities of the (531) and (440) reflections. Rietveld analysis [11,12] on diffractograms with better signal to noise ratios will enable precise crystallographic data pertaining to

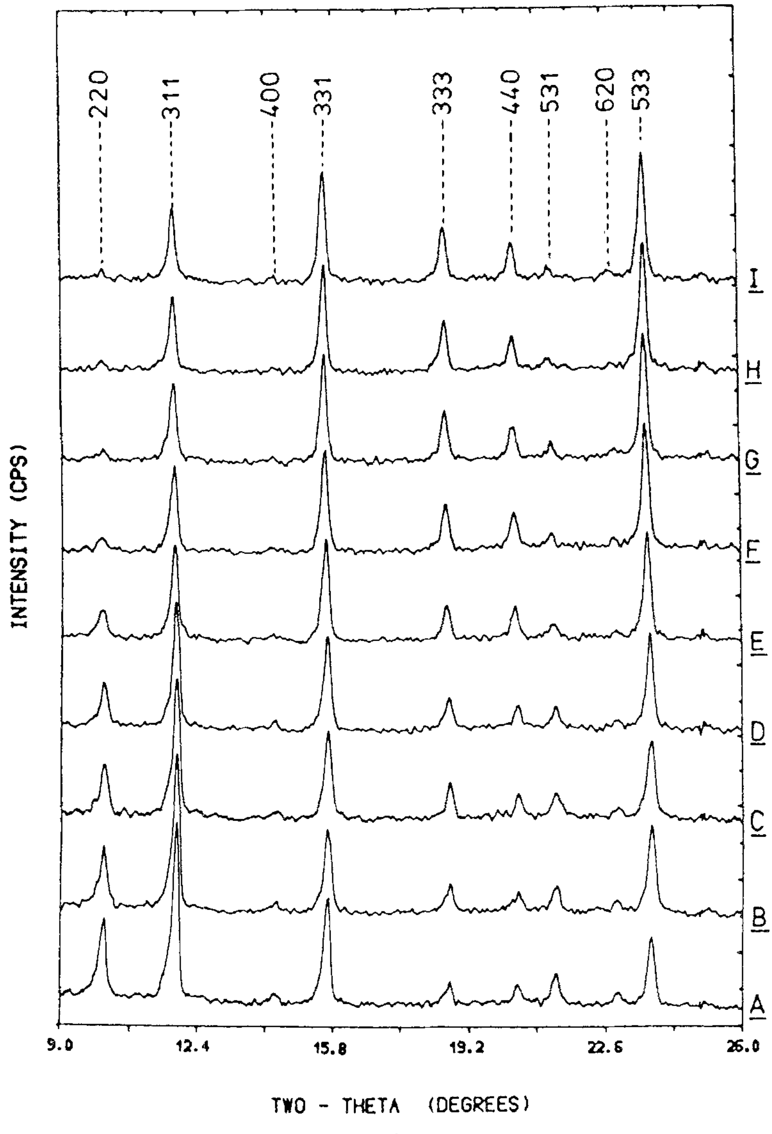

Fig. 2. The changes of diffraction patterns of Ni^{2+}-exchanged zeolite Y with duration of catalysis (refer to fig. 1). Miller indices are indicated at the top of the figure.

catalytically significant sites to be obtained, and will be the aim of future investigations.

We acknowledge, with gratitude, support from the Science and Engineering Research Council and practical assistance from Messrs. D. Madill and M. Sheehy.

References

[1] I.E. Maxwell, Adv. Catalysis 31 (1982) 1.
[2] U. Kruerke; as cited by J.A. Rabo and M.L. Poustma, Adv. Chem. Ser. 102 (1971) 297.
[3] P. Pichat, J.C. Vedrine, P. Gallezot and B. Imelik, J. Catal. 32 (1974) 190.
[4] W.J. Mortier and R.A. Schoonheydt, Progr. in Solid State Chem. 16 (1985) 1.
[5] For nickel:
  a. J.M. Thomas, C. Williams and T. Rayment, J.C.S. Faraday Trans. 1 (1988) in press.
  b. M. Sano, T. Maruo, H. Yamatera, M. Suzuki and Y. Saito, J.A.C.S. 109 (1987) 52.
[6] ^{29}Si and ^{27}Al MAS NMR spectra of the zeolites before and after reaction show that the framework is unchanged as a result of catalysis – chemical shifts are typical of zeolite Y [7].
[7] J. Klinowski, S. Ramdas, J.M. Thomas, C.A. Fyfe and J.S. Hartman, J.C.S. Faraday Trans. II 78 (1982) 1025.
[8] This observation does not rule out the possibility of small Ni^0 particles in the supercages. The dimerization of ethylene with Ni^{2+}-exchanged zeolite X seems to require prior reduction of Ni^{2+} ions to Ni^+ ions [9], a feature which could also be occurring in our experiment.
[9] L. Zheng, G. Wang and X. Bai, Proc. 7th Int. Zeolite Conf., ed. Y. Murakami, D. Iijima and J.W. Ward (1986) 965.
[10] J.V. Smith, Adv. Chem. Ser. 101 (1971) 171.
[11] H.M. Rietveld, J. Appl. Cryst. 2 (1969) 65.
[12] A.K. Cheetham and J.C. Taylor, J. Solid State Chem. 21 (1977) 253.