

## The Catalytic Isomerisation of Cyclopropane over NaCoX Zeolites using a Pulsed Microreactor

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*The catalytic isomerisation of cyclopropane was investigated over a series of NaCoX zeolites using a pulsed microreactor. First order kinetic parameters were calculated for the surface reaction from measured enthalpies of adsorption and apparent activation energies. Surface activation energies were not very dependent on the extent of ion exchange of Co(II) for Na(I) ions. Rates of reaction did not increase significantly with Co(II) concentration until after about 30% exchange. At levels of ion exchange greater than about 30%, rates of reaction increased with cobalt concentration due to an increase in the number of active sites. In agreement with previous reports the active sites were presumed to be hydroxyl groups and the increase in rate at higher concentrations of cobalt was attributed to dissociation of coordinated water molecules, during dehydration, to produce protons. Location of these protons on oxygens in the large cages provides the active sites.*

### Introduction

Transition-metal ion-exchanged zeolites are of interest as potential oxidative catalysts [1] and in catalysis via carbocations [2]. Reactions proceeding via carbocations are frequently catalysed by Brønsted acid centres and such centres can also influence oxidative reactions [3]. Consequently when considering transition metal catalysts for oxidative reactions it is useful to examine the Brønsted acidity of the catalysts. The pulsed microreactor [4] provides a convenient method for catalytic studies, although exact analysis appears to be limited to first and zero order reactions [5, 6]. However, the isomerisation of cyclopropane has been shown to be first order over zeolite catalysts [5, 7, 8] and since the reaction mechanism involves protonation of the cyclopropane [8], this reaction provides a convenient test for Brønsted acidity.

In this work a pulsed microreactor is used to measure kinetic parameters for the isomerisation of

cyclopropane over NaX zeolites exchanged with cobalt ions.

### Experimental

The pulsed microreactor was described in a previous study [1]. Catalysts were prepared by ion exchange of Linde X zeolite (NaX) using a solution of analar cobalt nitrate buffered at pH 6.99. Prior to ion exchange the NaX zeolite was treated with a solution of sodium chloride to replace protons and any exchangeable calcium ions with sodium ions. Analysis of the  $\text{Co}^{2+}$  and  $\text{Na}^+$  ions in the solution after ion exchange confirmed the stoichiometry of the exchange process [9].

### Results

The determination of kinetic parameters for the isomerisation of cyclopropane over zeolites has been studied by Basset and Habgood [5] who provided an analysis for a first order process in which the surface reaction is rate controlling.

$$kK = F^0/273RW \ln[1/(1 - X)] \quad (1)$$

In equation (1)  $k$  is the first order surface rate constant,  $K$  is the adsorption equilibrium constant for cyclopropane,  $X$  is the fractional conversion of cyclopropane to propene,  $F^0$  is the carrier gas flow rate (at 273 K) and  $W$  is the weight of catalyst. The analysis was extended by Stevens and Squires [10] to include cases in which axial dispersion may be either very slow or very rapid compared with chemical reaction rate. These authors used the expression

$$\ln[1/(1 - X)] = k_{\text{app}}(Z/u) \quad (2)$$

where  $Z$  is the length of the column,  $u$  is the linear velocity of the carrier gas in interparticle space and  $k_{\text{app}}$  is the apparent first order rate constant. Stevens and Squires showed how  $k_{\text{app}}$  could be related to various rate controlling steps.

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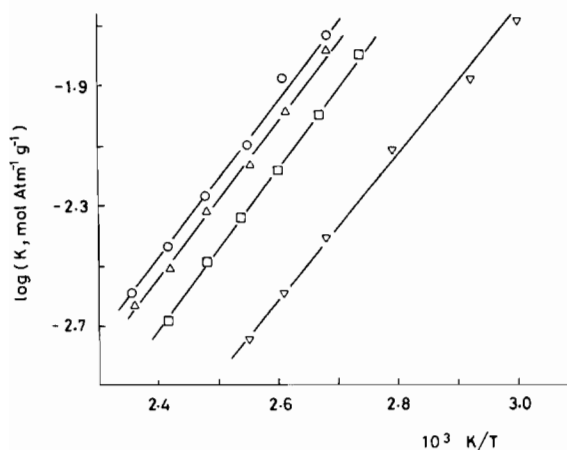


Figure 1. Temperature dependence of adsorption equilibrium constants for cyclopropane on:  $\nabla$  NaX;  $\circ$  NaCoX(8);  $\triangle$  NaCoX(16);  $\square$  NaCoX(25).

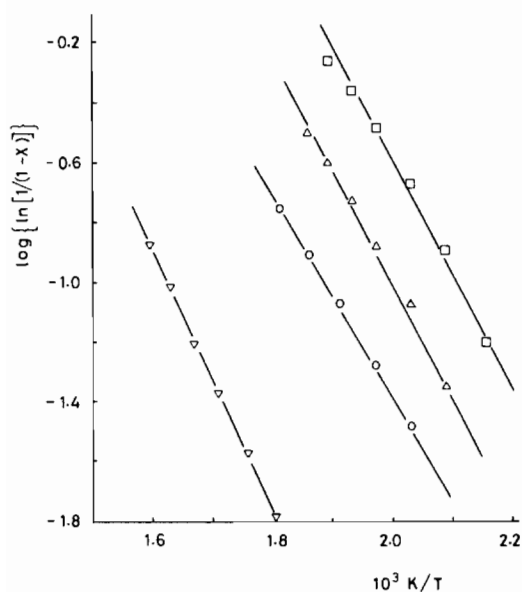


Figure 2. Arrhenius plots for isomerisation of cyclopropane on:  $\nabla$  NaX;  $\circ$  NaCoX(8);  $\triangle$  NaCoX(16);  $\square$  NaCoX(25).

As required by either of these approaches plots of  $\ln[1/(1-X)]$  against reciprocal flow rate gave straight lines passing through the origin. Adopting the approach of Basset and Habgood, equilibrium constants ( $K$ ) for the adsorption of cyclopropane were determined from measurements of retention volumes. For these measurements cyclopropane was pulsed onto the reactor at temperatures lower than reaction temperatures, and the exit gas stream was passed directly to the thermal conductivity detector. A small amount of nitrogen was introduced into each pulse to permit correction for dead space. Retention volumes were measured over a range of temperatures. Temperatures were selected randomly and between

temperatures the catalysts were re-activated at 400 °C (the temperature of initial activation) in flowing helium. The initial activation involved heating for 16 hours and subsequent reactivation involved heating for 1 hour. At least 30 minutes were allowed to establish thermal equilibrium before retention volumes were measured at any particular temperature. Heats of adsorption ( $-\overline{\Delta H}_s$ ) were obtained from plots of  $\ln(K/\text{mol Atm}^{-1} \text{g}^{-1})$  against reciprocal temperature (Fig. 1).

For measurement of activation energies, the reactor outlet was connected via a liquid nitrogen trap to a gas chromatographic analytical column. Products of reaction from a given pulse were collected in a product trap cooled in liquid nitrogen. Subsequently the products were vaporised by external heating and swept onto the analytical column by a stream of helium. The analytical column was seven feet long and 0.25 inches in diameter. It was packed with Poropak QS 80-120 mark and held at 120 °C for the analysis.

Apparent activation energies ( $E$ ) were determined from plots of  $\log\ln[1/(1-X)]$  against reciprocal temperature (Fig. 2). Measurements were made at constant flow rate and temperatures were selected randomly. At each temperature several pulses were applied and the average of three pulses was used when conversions were constant with pulse number.

Kinetic parameters were determined from the results shown in Fig. 1 and Fig. 2 by linear least squares. The models assumed are

$$K = K_o \exp\{-\overline{\Delta H}_s/RT\}$$

$$kK = k_o K_o \exp\{-E_a/RT\}$$

from which the first order rate constant is obtained

$$k = k_o \exp\{-E/RT\}$$

where  $E$  is the activation energy of the surface reaction ( $E = E_a + (-\overline{\Delta H}_s)$ ).

The 95% confidence limits for  $-\overline{\Delta H}_s$  and  $E_a$  were obtained from the data in Figs. 1 and 2 using pooled estimates of variance computed using residual variances from within individual runs. Prior to pooling, variance estimates were tested for homogeneity, and approximate 95% confidence limits for surface activation energies were obtained using the sum of the pooled variances for enthalpies of adsorption and apparent activation energies.

The pre-exponential adsorption factors  $K_o$  are seen from Table I to decrease progressively with increase in Co(II) concentration. This would seem to imply that adsorptive capacity for cyclopropane is reduced by ion exchange of Co(II) for Na(I) perhaps as a result of some loss of zeolite structure.

TABLE I. Kinetic Data.

	NaX	CoX(8)	CoX(16)	CoX(25)
% Ion exchange	—	18	37	58
$-\Delta H_a^0/\text{kJmol}^{-1}$	45.1	51.3	51.6	52.2
$E_a/\text{kJmol}^{-1}$	81.5	67.4	69.8	64.8
$E/\text{kJmol}^{-1}$	127	116	121	120
$10^{10}K_a/\text{mol atm}^{-1} \text{g}^{-1}$	18.2	12.1	9.68	5.32
$10^{-10}k_a/\text{s}$	5.4	2.5	21	63
$k_{613}/\text{s}$	0.88	3.2	9.5	40

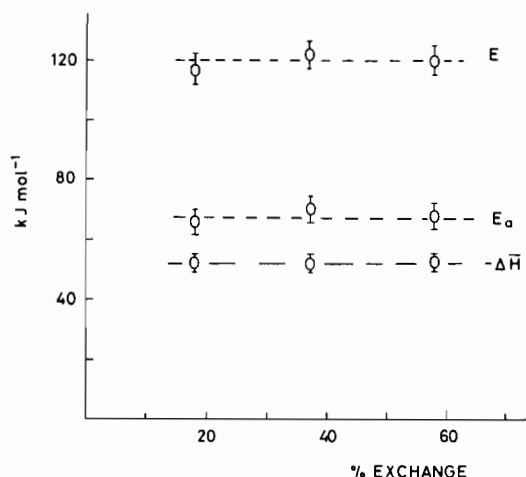
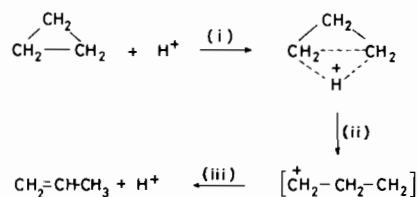


Figure 3. Adsorption enthalpies and activation energies for isomerisation of cyclopropane over NaCoX zeolites. Error bars represent 95% confidence limits.

## Discussion

Previous work on the isomerisation of cyclopropane over acidic catalysts, under conditions similar to those used in the present work, has established that reaction proceeds preferentially via a carbocation formed by interaction of cyclopropane and a Brønsted acid site [8, 11, 12]. This mechanism is almost certainly applicable to reaction over zeolites which have been activated at the temperatures used in this work [13]. It is generally believed that the reaction intermediate is a non-classical carbocation formed on the surface.



In the above reaction scheme all species are assumed to be adsorbed on the catalyst. In deriving

equation (1) step (i) was assumed to be slow compared with both the surface steps (ii) and (iii), and with the rates of reactant adsorption and product desorption. The measure of agreement between kinetic parameters determined by Basset and Habgood and those obtained in the present work suggests that step (i) is again rate determining, so that the surface kinetic parameters can be related to the rate of carbocation formation.

Fig. 3 shows that enthalpies of adsorption, apparent activation energies and consequently values of surface activation energy ( $E$ ) do not change much with the extent of ion exchange. For example, in these NaCoX zeolites, values of  $E$  cover a range of about  $11 \text{ kJmol}^{-1}$  which may be compared with the estimated 95% confidence limits for a single estimate of  $E$  ( $\pm 4.7 \text{ kJ mol}^{-1}$ ). This result suggests that the reactive (Brønsted) site is similar on all the catalysts. Recent work [14] using infrared has established, in the case of HX zeolites, that the OH group giving rise to an absorption band centred around  $3650 \text{ cm}^{-1}$  is most reactive at temperatures above  $200^\circ \text{C}$ . The band at  $3650 \text{ cm}^{-1}$  has been attributed to OH groups associated with O(1) oxygens pointing into the large cavity [15]. Consequently it seems likely that the reactive sites in these NaCoX zeolites are the supercage hydroxyls and that differences in rate of reaction largely reflect differences in the number of active hydroxyls available for interaction with cyclopropane. Surface rate constants, calculated using the kinetic parameters in Table I, are plotted against % ion exchange (Co(II) for Na(I)) in Fig. 4. Rate constants are seen to increase with increasing Co(II) content. A similar pattern was reported by Hoser and Krzyzanowski [16] for the isomerisation of *n*-butene and 3,3-dimethyl-1-butene over NaCoX zeolites. Additionally these authors found a correlation between the catalytic activity and the concentration of tetrahedrally coordinated Co(II) ions. They concluded that the active centres were protons arising from the dissociation of residual water molecules from Co(II) ions in tetrahedral coordination (*i.e.* to three oxygens in a six oxygen ring and to one water molecule).

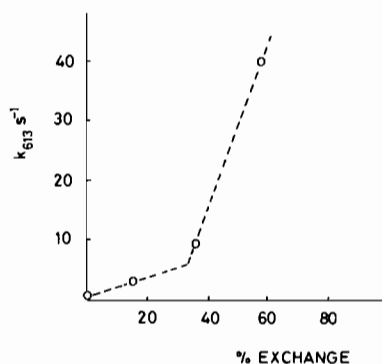
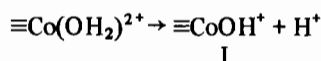


Figure 4. Calculated first order surface rate constants ( $k_{613}$ ) for the isomerisation of cyclopropane over NaCoX zeolites.



where I is attached to the lattice oxygens to give tetrahedral coordination and the proton liberated is attached to a lattice oxygen and forms the reactive site. As in the case of butane isomerisation Fig. 4 shows that rates are not greatly affected until the extent of ion exchange is around 30%. As pointed out by Hoser and Krzyzanowski among others, the initial exchanges lead to location of  $\text{Co}^{2+}$  ions in the small cage sites (I' and II') and only at higher levels of exchange are  $\text{Co}^{2+}$  ions found in supercage sites (for example site II). It is, presumably, the liberation of protons from partially hydrated  $\text{Co}^{2+}$  ions in supercage sites which gives the catalytically active sites. Reactive protons would be on O(1) oxygens in proximity to  $\text{Co}^{2+}$  ions.

An approximate relative measure of the concentration of active sites is provided from this work by the value of the pre-exponential factor of the surface rate constant ( $k_0$  in Table I). In Table I values of  $k_0$  are seen to be correlated with rate constants calculated at 613 K. Since values of  $k_0$  are obtained by extrapolation they are subject to relatively large experimental errors. However it seems clear that the

cyclopropane reaction can provide a relative measure of reactive sites which may be correlated with infrared intensities of OH groups or with UV intensities of four coordinated  $\text{Co}^{2+}$  ions, and work to this end is in progress.

With regard to the use of ion-exchanged zeolites as oxidation catalysts it is clear that in addition to the influence of protons produced during the ion-exchange process there is an additional source of protons in the unused catalysts, arising from dissociation of coordinated water during dehydration, which can influence oxidative activity [3].

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