

Copper-Exchanged Zeolite Catalysts for the Cyclodimerization of Butadiene

II. Catalyst Structure

I. E. MAXWELL, J. J. DE BOER, AND R. S. DOWNING¹

Koninklijke/Shell-Laboratorium (Shell Research B.V.), Badhuisweg 3, Amsterdam, The Netherlands

Received January 16, 1978; revised October 24, 1978

An X-ray structure analysis has been carried out on a single crystal of natural faujasite which has been exchanged with Cu^{2+} ions, dehydrated at 150°C, and then exposed to butadiene vapor at room temperature. Copper ions have been located at sites I', II, II', and III. The adsorption of butadiene is shown to induce a migration of copper cations to site III, located at the pore entrances to the supercages. The unsaturated coordination of the cations to the zeolite framework, and their ideal location for interaction with adsorbate molecules, suggests that these are most probably the sites where the butadiene cyclodimerization reaction occurs. Some comparative data on a novel homogeneous copper catalyst suggest that the role of the zeolite framework is simply to stabilize monovalent copper ions and is not responsible for the high selectivity toward 4-vinylcyclohexene.

I. INTRODUCTION

Part I of this series (1) dealt with the catalytic stability and regenerability of direct monovalent-copper-exchanged and reduced divalent-copper-exchanged zeolite Y for the cyclodimerization of butadiene to 4-vinylcyclohexene. The present paper is concerned with the structure of these catalysts as regards both the role of the exchangeable cations and the zeolite framework.

In a previous publication (2) we reported the results of single-crystal X-ray analyses of divalent-copper-exchanged natural faujasite. Perhaps the most interesting result was the identification of site III-type Cu^{2+} ions, located at the pore entrances to the supercage and bonded asymmetrically to the framework oxygen atoms O(1) and O(4) (see Fig. 1). The location and

highly unsaturated coordination geometry of these cations led to the suggestion that cations at these sites would be expected to play an important role in cation-adsorbate molecule interactions.

Recent ESR and phosphorescence studies have shown (3) that the adsorption of butadiene into Cu^{2+} -exchanged zeolites X and Y causes a cation migration, most probably in the direction of the supercage. Furthermore, on heating at 100°C the divalent copper ions are reduced to the monovalent form, the rate of reduction being second order in the Cu^{2+} ion concentration.

To gain more insight into these phenomena, particularly the possible role of site III-type cations in catalytic reactions, we have now carried out a single-crystal X-ray study on a sample of divalent-copper-exchanged natural faujasite which had been dehydrated at 150°C and then

¹ Part author.

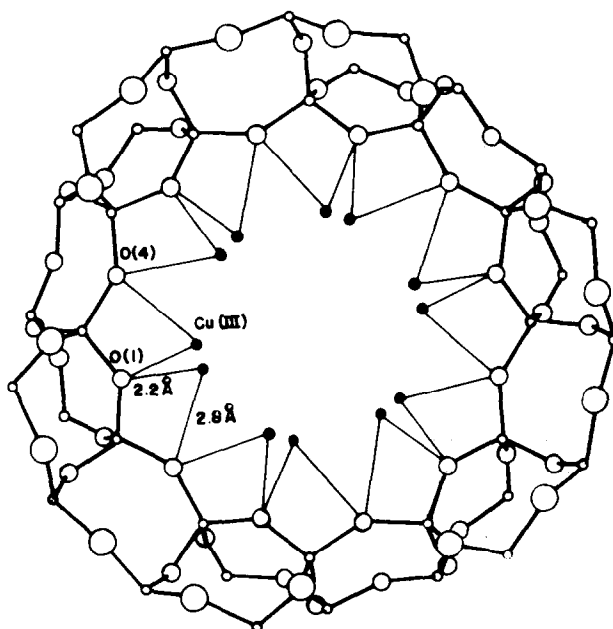


Fig. 1. Perspective view showing the siting of Cu (III) cations at the pore entrance to the supercage in dehydrated Cu^{2+} -exchanged faujasite. The occupancy factor is such that there is approximately one Cu (III) cation per five pore entrances.

exposed to butadiene vapor at room temperature.

In addition, we have investigated the possible influence of the catalyst support on the selectivity of the butadiene dimerization reaction, by comparing the heterogeneous catalyst system with a homogeneous analog.

II. EXPERIMENTAL SECTION

A. Single-Crystal X-Ray Data Collection

Crystals of natural faujasite which were initially exchanged with K^+ and then with Cu^{2+} , as previously described (2), were also used for the present structural analyses. The Si/Al ratio for this zeolite sample is 2.42; this figure was derived from the cell constant of the K^+ -exchanged form (2).

A crystal (dimensions $0.07 \times 0.15 \times 0.22$ mm) was firmly wedged inside a tapered thin-walled Lindemann glass capillary, which could be attached to a vacuum line. The crystal was then heated to 150°C

for 20 h under a vacuum of 10^{-3} Pa (10^{-5} Torr). The capillary was then cooled to -10°C and butadiene (Matheson Instrument Grade, 99.6% pure) was slowly admitted into the system until a pressure of 120 kPa was obtained. Cooling was carried out as a precaution to prevent a temperature rise due to the evolved heat of adsorption. The capillary temperature was held at -10°C for some 2 h, after which the system was allowed to warm slowly to room temperature (ca. 20°C). After 3.5 days equilibration at room temperature the excess butadiene was pumped off to a residual pressure of 10 kPa and the capillary was sealed off for X-ray data collection.

The crystal was aligned about the $[110]$ direction during data collection, which was carried out using a Nonius three-circle automatic diffractometer equipped with a scintillation counter and a pulse-height discriminator. Least-squares cell refinement based on θ , $-\theta$ ($\theta \leq 15^\circ$) values measured for several reflections with $\text{CuK}\alpha$ radiation

($\lambda = 1.54182 \text{ \AA}$) gave the following lattice parameter, $a = 24.721(5) \text{ \AA}$.

Six equivalent data sets were collected,² using Ni-filtered $\text{CuK}\alpha$ radiation ($\theta \leq 50^\circ$). The θ - 2θ scan method was used with a scanning speed of $0.6^\circ/\text{min}$ (in θ) and a scan range of 0.8° . Backgrounds were measured for half of the scan time on each side of the reflection. Control reflections were monitored at regular intervals during data collection, and significant variations in the intensities of these reflections were not observed. Initial standard deviations in observed structure factors were calculated from counting statistics, but these were later found to be inadequate and were replaced by an empirical weighting scheme. Lorentz, polarization, and ϕ -dependent absorption corrections ($\mu_{\text{CuK}\alpha} = 5.2 \text{ mm}^{-1}$) were applied, the latter by means of a semiempirical method described by Furnas

² Observed and calculated structure amplitudes are available from the authors on request.

(4). The ϕ -dependent absorption corrections were obtained by averaging the intensities, measured as a function of ϕ from several reflections of the type hho. Since the variation in ϕ was found to be negligible, the ϕ -dependent part of the absorption correction was ignored. The data were then scaled and averaged to yield 211 unique reflections (observed more than once), with an estimated conventional R factor of 0.053.

B. Homogeneous Catalytic Cyclodimerization of Butadiene

The homogeneous monovalent-copper-catalyzed dimerization of butadiene was carried out in the following manner: butadiene containing 1% m of cuprous triflate (trifluoromethanesulfonate) in the form of the benzene adduct (5), $\text{F}_3\text{CSO}_3\text{Cu} \cdot 0.5\text{-}(\text{C}_6\text{H}_6)$, was heated for 16 h in an autoclave at 120°C under autogeneous pressure. The liquid product obtained following re-

TABLE 1
Positional, Occupancy, and Thermal Parameters for Dehydrated Divalent-Copper-Exchanged Faujasite with Adsorbed Butadiene

Atom	Position ^a	Occupancy factor ^b	X	Y	Z	B (\AA^2)
(Si, Al)	192 (i)	1	0.0360 (1)	0.3038 (1)	0.1241 (2)	1.07 (5)
O (1)	96 (h)	1	0	-0.1061 (5)	0.1061 (5)	2.6 (2)
O (2)	96 (g)	1	0.0020 (6)	-0.1423 (3)	0.0020 (6)	2.3 (2)
O (3)	96 (g)	1	0.0777 (5)	-0.0328 (3)	0.0777 (5)	2.2 (2)
O (4)	96 (g)	1	0.0713 (5)	0.3226 (4)	0.0713 (5)	2.0 (2)
Cu (I'A)	32 (e)	0.030 (15)	0.05 (2)	0.05 (2)	0.05 (2)	10.0 (66)
Cu (I'B)	32 (e)	0.098 (11)	0.070 (3)	0.070 (3)	0.070 (3)	1.5 (9)
Cu (I'C)	32 (e)	0.181 (15)	0.082 (2)	0.082 (2)	0.082 (2)	8.3 (11)
Cu (IIA)	32 (e)	0.131 (9)	0.007 (2)	0.243 (2)	0.007 (2)	3.2 (9)
Cu (IIB)	96 (g)	0.015 (5)	0.023 (7)	0.266 (5)	0.023 (7)	1.0 (30)
Cu (IIIA)	192 (i)	0.033 (6)	0.027 (3)	0.406 (3)	0.070 (3)	8.4 (21)
Cu (IIIB)	96 (g)	0.014 (4)	0.067 (8)	0.410 (5)	0.067 (8)	1.0 (32)
OW (1)	32 (e)	0.27 (4)	0.085 (5)	0.165 (5)	0.085 (5)	3.4 (16)
C (1)	48 (f)	0.19 (8)	$\frac{1}{2}$	0.45 (1)	$\frac{1}{2}$	10.0 ^c
C (2)	96 (g)	0.15 (6)	0.093 (13)	0.476 (9)	0.093 (13)	10.0
C (3)	32 (e)	0.15 (10)	0.53 (3)	-0.28 (3)	0.53 (3)	10.0

^a Origin at center ($\bar{3}m$).

^b Standard deviations in units of the least significant digits of the corresponding parameters are given in parentheses in all tables.

^c Temperature factors fixed during refinement.

TABLE 2
Comparison of Sitings of Cations and Water Molecules in Divalent-Copper-Exchanged Faujasite after Various Treatments

	Hydrated (2)			Dehydrated (150°C) (2)			Dehydrated (150°C) and butadiene adsorbed					
	Atom	Coordinates	Number per unit cell	Atom	Coordinates	Number per unit cell	Atom	Coordinates	Number per unit cell			
Inside dense cage structure	Cu (I')	0.071 (1)	6.3 (2)	Cu (I)	0	1.5 (2)	Cu (I'A)	0.05 (2)	1.0 (5)			
				Cu (I'A)	0.0401 (7)	11.4 (2)				Cu (I'B)	0.073 (5)	2.8 (3)
				Cu (I'B)	0.073 (5)	2.8 (3)				Cu (I'C)	0.082 (3)	5.8 (5)
	OW (3)	‡	3.2 (3)	Cu (II')	0.203 (7)	0.8 (2)	OW (1)	0.165 (5)	8.6 (1.2)			
	OW (1)	0.168 (1)	26.9 (1.3)							Cu (IIA)	0.243 (2)	4.2 (3)
	Inside or on periphery of supercage structure	OW (2)	0.266 (2)	22.4 (1.3)	Cu (IIB)	0.244 (4)	1.5 (2)	Cu (IIB)	0.266 (7)	1.5 (4)		
					OW	0.263 (6)	5.3 (8)	Cu (IIIA)	0.027 (3)	6.3 (1.1)		
OW (4)		0.173 (3)	31 (4)	Cu (III)	0.017 (3)	3.3 (6)	Cu (IIIB)				0.067 (8)	1.3 (4)
								-0.197 (3)	0.418 (3)	0.406 (3)		
OW (5)		0.075 (2)	31 (4)	0.084 (3)	0.070 (3)	0.410 (5)	C (1)	‡	9.0 (3.6)			
										0.048 (3)	0.418 (3)	0.476 (9)
OW (6)		0.031 (6)	17 (3)	0.031 (6)	0.006 (6)	12 (2)	C (2)	0.093 (13)	14.0 (5.4)			
										0.427 (4)	0.386 (4)	0.476 (9)
OW (7)		0.006 (6)	12 (2)	0.006 (6)	C (3)	0.22 (3)	4.8 (3.2)	0.22 (3)	4.8 (3.2)			
										0.031 (6)	0.006 (6)	0.22 (3)
Total Cu ²⁺ located			6.3	24.8			23.2					
Total H ₂ O located			143.5	5.3			8.6					

action was analyzed by glc techniques. A blank experiment was carried out under the same conditions but in the absence of the catalyst.

III. STRUCTURE DETERMINATION

Using the framework parameters for natural faujasite (6) as a basis, full-matrix least-squares refinement was carried out. Copper ions, water molecules, and possibly carbon atoms were located from a series of difference Fourier syntheses and were included in subsequent cycles of refinement. Parameters with high correlation coefficients, such as occupancy and temperature factors, were varied separately in alternate refinement cycles.

In the final stages of refinement of the data three quite well-defined isotropic but low-intensity ($\sim 0.1 e/\text{\AA}^3$) residual electron density peaks were observed in difference

syntheses, corresponding to sites inside the supercage. The rather large distances of these sites from framework oxygen atoms and the relatively short distances to supercage-sited copper ions indicated that these peaks might be attributable to carbon atoms of the adsorbed butadiene molecules. When included as such in subsequent cycles, coordinate and occupancy factors (with fixed temperature factors) could be successfully refined. Unfortunately, since the occupancy factors are only two to three times higher than the estimated standard deviation, the assignment of these peaks to carbon atoms remains uncertain (see Table 1).

The final residuals were $R_1 = 0.055$ and $R_2 = 0.049$ (where $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$, $R_2 = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w |F_0|^2]^{1/2}$ and $w = \sigma^{-2} F_0$). The final value for the error in an observation of unit weight was 1.01. The final refined positional, occupancy,

and temperature factors are given in Table 1. Listings of observed and calculated structure factors are available from the authors on request.

IV. RESULTS AND DISCUSSION

A. Siting of Copper Ions

The sitings of cations and water molecules for the present structure, together with those for the previously determined structures of hydrated and dehydrated (150°C) divalent-copper-exchanged faujasite (2), are compared in Table 2. These assignments were made on the basis of the cation/H₂O-framework distances given in Table 3.

Assuming complete Cu²⁺ exchange (i.e., 28 Cu²⁺ ions per unit cell), then 83% of the copper cations were located. These cations are distributed over several different sites, i.e., I, I', II, II', and III.³

³The site nomenclature is as follows: site I, center of hexagonal prism; site II, six-membered ring face of sodalite cage on the supercage side; sites I' and II' lie on the other sides of the six-membered rings, opposites sites I and II, respectively, and inside the sodalite cage; site III, at the edges of the four-membered rings formed by O(3) and O(4) inside the supercage.

As previously observed, type I' copper ions are strongly bound to the zeolite framework, i.e., Cu (I'A)-O(3), 2.25 (11) Å (cf. $r_{\text{Cu}^{2+}} + r_{\text{O}^{2-}} = 2.09$ Å). Furthermore, the relatively high occupancy factors of this site (Table 2) confirm the preference of copper ions for site I' (2, 7). The less weakly bound cations in this region, i.e., Cu (I'B)-O(3), 2.56 (6) Å, most probably also interact with water molecules (see Fig. 2). This is in fact evidenced by the distances of some of these cations from water molecules located at site II', e.g., Cu (I'B)-OW(1), 2.39 (14) Å. A similar cation-framework coordination geometry exists near the single six-membered ring which faces onto the supercage, i.e., site II, the closest framework-cation distances being Cu (IIA)-O(2), 2.52 (5) Å, and Cu (II)-O(2), 2.49 (5) Å. Cation Cu (IIB) lies off the threefold axis and is close to, and almost equidistant from, O(4), i.e., Cu (IIB)-O(2), 2.21 (12) Å, Cu (IIB)-O(4), 2.18 (18) Å.

As previously found for the dehydrated Cu²⁺-exchanged faujasite (2), supercage-sited type III copper cations have been located in the present structure. Two site III cations, Cu (IIIA) and Cu (IIIB),

TABLE 3
Cation-Framework and Water-Framework Distances (Å) for Divalent-Copper-Exchanged Faujasite Dehydrated and Butadiene Adsorbed

Atoms	Distance	Atoms	Distance
Cu (I'A)-O (3)	2.25 (11)	Cu (IIB)-OW (1)	3.3 (3)
Cu (I'A)-O (2)	2.91 (2)	Cu (IIB)-O (4)	3.42 (8)
Cu (I'A)-OW (1)	3.2 (8)	Cu (IIIA)-O (1)	2.31 (9)
Cu (I'C)-OW (1)	2.04 (13)	Cu (IIIA)-O (4)	2.34 (8)
Cu (I'C)-O (3)	2.85 (7)	Cu (IIIB)-O (4)	2.16 (14)
Cu (I'C)-O (2)	3.30 (5)	Cu (IIIB)-O (1)	2.85 (7)
Cu (I'B)-OW (1)	2.39 (14)	OW (1)-OW (1)	2.8 (3)
Cu (I'B)-O (3)	2.56 (6)	OW (1)-O (2)	3.11 (15)
Cu (I'B)-O (2)	3.09 (5)	C (1)-C (2)	1.3 (2)
Cu (IIA)-O (2)	2.52 (5)	C (1)-Cu (IIIB)	2.2 (3)
Cu (IIA)-O (4)	2.99 (3)	C (1)-Cu (IIIA)	2.94 (12)
Cu (IIA)-OW (1)	3.4 (2)	C (2)-Cu (IIIB)	1.9 (3)
Cu (IIB)-O (4)	2.18 (18)	C (2)-Cu (IIIA)	2.4 (3)
Cu (IIB)-O (2)	2.21 (12)	C (3)-Cu (IIA)	1.6 (1.1)
Cu (IIB)-O (2')	3.19 (12)	C (3)-Cu (IIB)	1.9 (1.1)

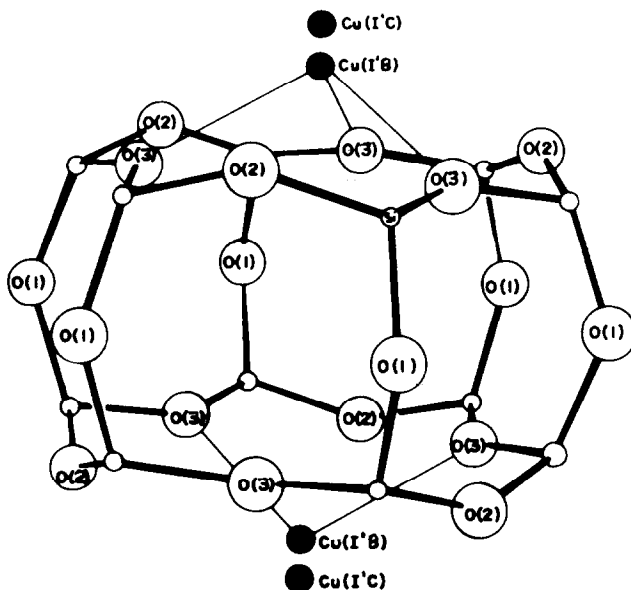


FIG. 2. Perspective view showing the siting of Cu (I') cations in crystal (Cu²⁺-exchanged faujasite, dehydrated at 150°C, butadiene adsorbed).

could be distinguished, the latter being sited on a mirror plane. The cation Cu (IIIA) is equidistant from framework oxygens O(1) and O(2), i.e., Cu (IIIA)-O(1), 2.31 (9) Å, and Cu (IIIA)-O(4), 2.34 (8) Å. These distances are remarkably close to those expected for monovalent copper ions (i.e., $r_{\text{Cu}^+} + r_{\text{O}^{2-}} = 2.36$ Å). Cu (IIIB) has an asymmetric interaction with the framework, being closer to O(4) than O(1), i.e., Cu (IIIB)-O(4), 2.16 (14) Å, and Cu (IIIB)-O(1), 2.85 (7) Å (see Fig. 3).

As regards the oxidation state of the copper ions it is not possible, from the X-ray analysis results, to arrive at a definite conclusion. The two shortest cation-oxygen distances, i.e., Cu(IIIB)-O(4), 2.16 (14) Å and Cu(I'A)-O(3), 2.25 (11) Å are suggestive of Cu²⁺-O²⁻ interactions (i.e., $r_{\text{Cu}^{2+}} + r_{\text{O}^{2-}} = 2.09$ Å), although to within 2 standard deviations these could also be attributed to monovalent copper (i.e., $r_{\text{Cu}^+} + r_{\text{O}^{2-}} = 2.36$ Å). It is quite possible that, despite the external cooling precautions taken during butadiene adsorption, the local heat evolved during adsorption was sufficient to cause complete or partial

reduction of copper ions to the monovalent form.

In Fig. 5 the sitings of copper cations and water molecules are compared for the three related structures of Cu²⁺-exchanged faujasite: hydrated; dehydrated (150°C); dehydrated (150°C) and adsorbed with butadiene. The comparison clearly demonstrates that the adsorption of butadiene on the dehydrated faujasite results in the migration of copper ions in the direction of the supercage, which is consistent with the results of ESR studies (3). The effect is in fact most pronounced for sites I' and III, the occupancy factor for the former being reduced by approximately a factor of 2, and that for the latter being increased by approximately the same amount (i.e., 7.6 per unit cell with butadiene and 3.3 per unit cell for the dehydrated structure). This cation migration in the direction of the supercage is most probably due to the fact that the butadiene molecules are too large to enter the sodalite cage.

Furthermore, as previously mentioned, two peaks located in difference syntheses

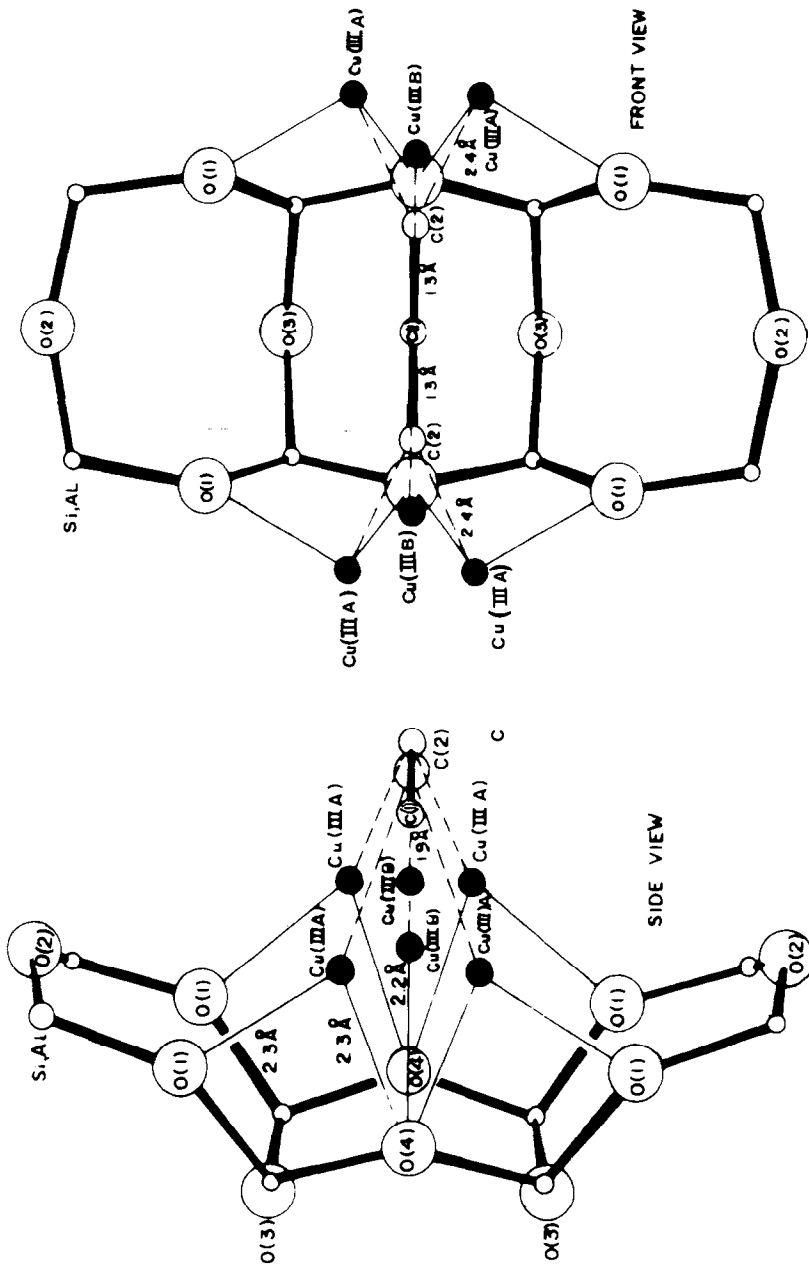


Fig. 3. Perspective views showing the siting of Cu (III) cations at the edges of the four-membered rings in the supercage (Cu^{2+} -exchanged faujasite, dehydrated at 150°C , butadiene adsorbed) and the interaction of these cations with a butadiene molecule.

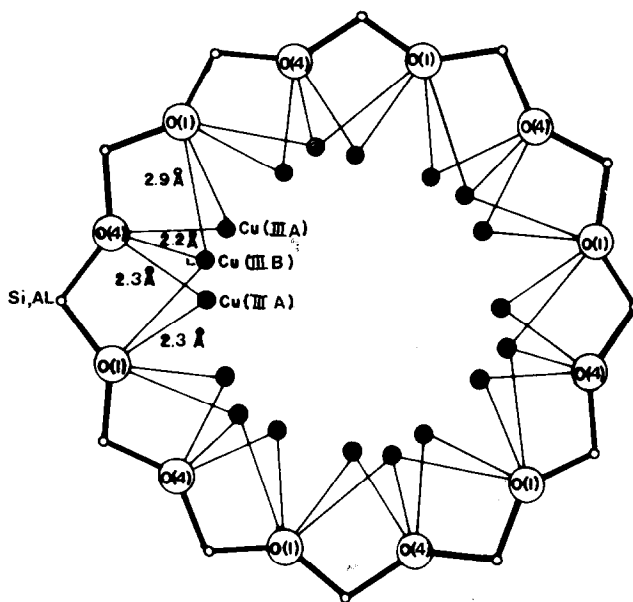


FIG. 4. Perspective view showing the siting of Cu (III) cations at the pore entrance to the supercage (Cu²⁺-exchanged faujasite, dehydrated at 150°C, butadiene adsorbed). The occupancy factors are such that there is approximately one Cu (III) cation per two pore entrances.

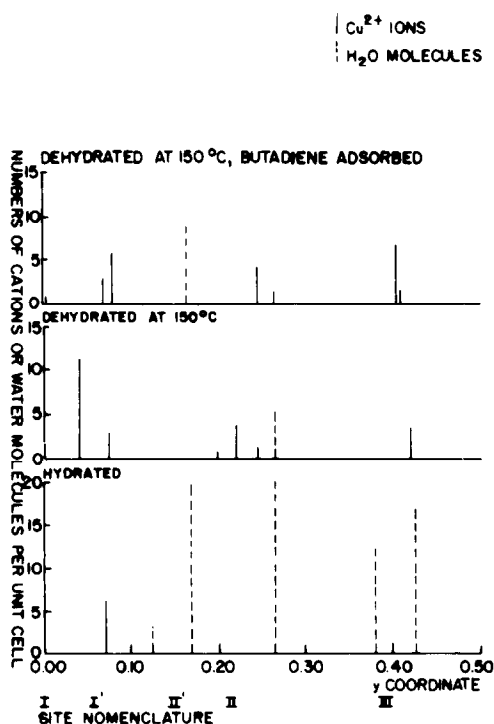


FIG. 5. Distribution of cations and water molecules in Cu²⁺-exchanged faujasite after various treatments.

have been tentatively assigned to carbon atoms of the adsorbed butadiene molecules. The coordination geometry as given by the refined coordinates of those atoms is shown in Fig. 3. Clearly, the stereochemistry and distances, i.e., C(1)–C(2), 1.3 (2) Å, C(1)–Cu (IIIB), 2.2 (3) Å, and C(2)–Cu (IIIB), 1.9 (3) Å, are such that an interaction between Cu (III) ions and butadiene molecules would seem to be indicated (although it must be stressed that the occupancy factors for the carbon atoms are not sufficiently precise to say with certainty that such an interaction exists). Thus, the favorable siting of these cations (i.e., at the pore entrances to the supercage, see Fig. 4), and their apparent highly unsaturated coordination geometry with respect to the zeolite framework, suggests that these cations are most probably the active sites for the butadiene cyclodimerization reaction.

B. Role of the Zeolite Framework

Framework bond lengths and angles, together with cell constants, are compared

for all three structures in Table 4. The cell constants are clearly quite sensitive to the presence of adsorbed species in the zeolite pores. Dehydration at 150°C results in a contraction of the lattice, i.e., $a = 24.713$ (5) Å hydrated, $a = 24.643$ (5) Å dehydrated, but it expands again after the adsorption of butadiene ($a = 24.721$ (5) Å). However, the variations in lattice dimensions cannot be related to any systematic distortion of framework bond lengths and angles; although, with the exception of the hydrated form, the Si(Al)-O(3) bond length is systematically the longest. This can most probably be attributed to the strong bonding of copper cations at site I' to the O(3) framework oxygen ions. In fact, it has been shown (2)

that for the dehydrated Cu²⁺-exchanged structure, an approximately linear relationship exists between the percentage of each oxygen atom in close contact with a copper ion and the Si(Al)-O bond distance. In the presence of adsorbed molecules (water or butadiene), however, this relationship no longer strictly holds, possibly because of the effect of framework-adsorbate interactions (e.g., H-bonding in the case of water).

A remarkable feature of the copper zeolite catalysts is their ability to give a very high selectivity to 4-vinylcyclohexene (almost quantitative) in the cyclodimerization of butadiene. Other known catalysts for this reaction are often considerably

TABLE 4
Comparison of Framework Bond Lengths and Angles in Divalent-Copper-Exchanged Faujasite after Various Treatments

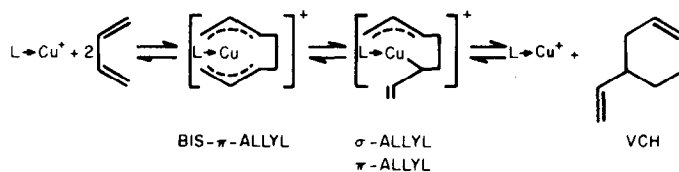
Atoms	Hydrated (2)	Dehydrated (2)	Dehydrated and butadiene adsorbed
(Si, Al)-O (1)	1.644 (6)	1.628 (7)	1.644 (7)
(Si, Al)-O (2)	1.643 (5)	1.640 (5)	1.639 (5)
(Si, Al)-O (3)	1.647 (4)	1.661 (5)	1.659 (4)
(Si, Al)-O (4)	1.644 (5)	1.629 (5)	1.638 (6)
Mean value	1.645	1.640	1.645
(Si, Al)-O (1)-(Si, Al)	138.5 (1.0)	138.3 (1.2)	139.4 (1.2)
(Si, Al)-O (2)-(Si, Al)	146.0 (7)	144.8 (8)	146.5 (9)
(Si, Al)-O (3)-(Si, Al)	141.8 (6)	137.9 (7)	142.6 (6)
(Si, Al)-O (4)-(Si, Al)	140.5 (7)	145.3 (8)	140.4 (9)
Mean value	141.7	141.6	142.1
O (1)-O (2)	2.702 (14)	2.696 (16)	2.725 (15)
O (1)-O (3)	2.714 (13)	2.696 (17)	2.734 (15)
O (1)-O (4)	2.648 (5)	2.655 (5)	2.648 (6)
O (2)-O (3)	2.669 (8)	2.649 (9)	2.648 (9)
O (2)-O (4)	2.667 (6)	2.650 (8)	2.672 (8)
O (3)-O (4)	2.710 (16)	2.717 (18)	2.688 (18)
Mean value	2.685	2.677	2.686
O (1)-(Si, Al)-O (2)	110.6 (7)	111.2 (8)	112.2 (7)
O (1)-(Si, Al)-O (3)	111.1 (6)	110.1 (8)	111.7 (7)
O (1)-(Si, Al)-O (4)	107.3 (6)	109.2 (7)	107.6 (7)
O (2)-(Si, Al)-O (3)	108.4 (6)	106.7 (7)	106.8 (6)
O (2)-(Si, Al)-O (4)	108.4 (6)	108.3 (6)	109.3 (6)
O (3)-(Si, Al)-O (4)	110.9 (8)	111.3 (9)	109.3 (8)
Mean value	109.5	109.5	107.5
Cell constant (a)	24.713 (5)	24.643 (5)	24.721 (5)

less selective toward 4-vinylcyclohexene, 1,5-cyclooctadiene being a common co-product. Heimbach and co-workers (8) have carried out detailed studies of the mechanism of reactions with the homogeneous (and isoelectronic) nickel(0) catalyst system.

The principal features of this mechanism are oxidative coupling of two molecules of butadiene to give an eight-membered chain which then rearranges to a

σ -allyl, π -allyl species, the precursor to 4-vinylcyclohexene.

A single strongly coordinated ligand favors the formation of the bis- π -allyl intermediate, whereas the presence of two ligands in the coordination sphere is required for the formation of the σ -allyl, π -allyl complex. By analogy, it is probable that for the isoelectronic Cu^+ system the intermediate species is also a σ -allyl, π -allyl complex:



(where L is most probably an oxygen from the zeolite framework).

We wished to investigate whether, for the copper-exchanged zeolite catalyst, the oxygen ions of the framework play a role in the selective formation of vinylcyclohexene similar to that of the strong ligands in the nickel system. To this end we prepared a Cu^+ complex having extremely weak ligands. This complex, cuprous triflate (= trifluoromethanesulfonate), is known (5) to form a complex with butadiene and we have now found it to be a highly active homogeneous catalyst for butadiene dimerization. The reaction, carried out as described in the experimental section, gave a 90% yield of vinylcyclohexene with only a trace of 1,5-cyclooctadiene. The blank experiment which was run under the same conditions, but in the absence of catalyst, gave only 6% vinylcyclohexene.

The above result shows that vinylcyclohexene is formed selectively, even in the

absence of strong ligands. It would therefore appear that this selectivity resides in the electronic structure of the cuprous ion and that in the case of copper-exchanged zeolite Y catalysts the role of the support (framework) is simply to stabilize monovalent copper ions on the surface, without having any specific effect on selectivity.

REFERENCES

1. Maxwell, I. E., Downing, R. S., and van Langen, S. A. J., *J. Catal.* **61**, 485 (1980).
2. Maxwell, I. E., and de Boer, J. J., *J. Phys. Chem.* **79**, 1874 (1975).
3. Maxwell, I. E., and Drent, E., *J. Catal.* **41**, 412 (1976).
4. Furnas, T. C., "Single Crystal Orienter Instruction Manual." General Electric Company, Milwaukee, 1957.
5. U.S. Patent 3,763,200 (to Esso Research and Engineering Co.), 1973.
6. Olson, D. H., *J. Phys. Chem.* **72**, 4366 (1968).
7. Gallezot, P., Ben Taarit, Y., and Imelik, B., *J. Catal.* **26**, 295 (1972).
8. Heimbach, P., Jolly, P. W., and Wilke, G., *Advan. Organometal. Chem.* **8**, 29 (1970).