sible,[11d] since exposure of the vinylketene complex **10** to 3 atm of ^{13}C-labeled carbon monoxide at ambient temperatures resulted in incorporation of the label at the ketene carbon (**10′**).[20] At this point we can only suggest a mechanism for the furan formation which involves a migration of methoxy to the metal (**19** → **20**),[5k] reductive elimination of methoxy and acyl (**20** → **21**), and addition of the ester carbonyl to the carbene carbon (**21** → **22**).[11c] Further studies on this mechanism will be reported later[8] (Scheme III).

The synthetic utility of the reaction of cobalt carbene complexes with acetylenes is illustrated by the synthesis of bovolide, a naturally occurring butenolide isolated from several sources,[21] which was first characterized as a component of butter flavor (Scheme IV).[22] The α-methoxy-*n*-pentyl complex **24** was prepared by the standard Fischer synthesis from the organolithium generated from the α-stannyl ether **23** and triphenyltin cobalt tetracarbonyl.[10,23] The cobalt carbene complex **24** was heated with 3 equiv of 2-butyne in benzene under an inert atmosphere. The crude reaction mixture was then treated with 3 equiv of trimethylsilyl iodide[24] to give bovolide in 48–52% yield.

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Supplementary Material Available: Spectral and physical data for all new compounds and the details of the X-ray analysis of compound **10** (8 pages). Ordering information is given on any current masthead page.

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Demonstration of Contact Induced Ion Exchange in Zeolites

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Zeolites are of considerable practical importance and current interest because of their sorptive and catalytic properties.[1] They are framework aluminosilicate species, usually highly crystalline in nature, with well-defined pore and channel structures.[2] The structures can be considered as formally being derived from crystalline silica by the replacement of SiO_2 units by AlO_2 units and have a general formula $M_x^+(AlO_2)_x(SiO_2)_y$. Because of the difference in nuclear charge between Al and Si, a single positive charge (usually present as metal cations in the cavities) must be present for each aluminum moiety in the structure. The framework structures confer a size and shape selectivity toward sorbed organic molecules and catalytic activity results when the cationic charges are protonic in nature (H_3O^+ etc.).

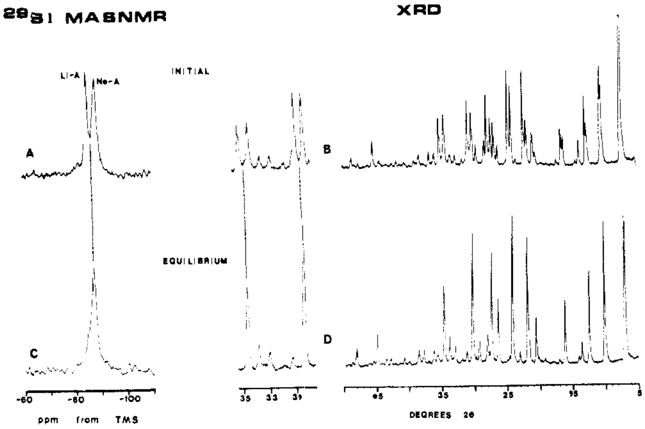

Figure 1. ^{29}Si MAS NMR spectra, obtained at 79.5 MHz, of a mixture of Li$^+$A and Na$^+$A: (A) immediately after mixing and (C) at equilibrium as well as the corresponding powder XRD patterns (B) and (D).

In general, the nature of the cations present in a given zeolite exerts a very considerable influence on the physical and physicochemical properties of the system. Thus, the lattice dimensions may change as, for example, in the case of zeolite X where the lattice parameter of the cubic unit cell varies from 24.99 Å for the Na$^+$ salt to 24.88 Å for the Li$^+$ salt. The free space in the cavity is controlled by the variation in ionic radius of the cations. Thus, for zeolite A, which is commonly used as a "molecular sieve", when the cation is K$^+$ molecules of diameters up to 3 Å may be sorbed, when the cation is Ca^{2+} molecules of diameters up to 5 Å may be sorbed. In addition, certain metal ions may confer a very specific catalytic activity on the system by acting as the central metal atom in an organometallic complex in various chemical conversions.

In this paper, we demonstrate that exchange of these important cationic species can occur *between* different zeolite crystals based only on a simple physical contact between the crystallites. The structural changes accompanying the exchange have been monitored by powder XRD and ^{29}Si MAS NMR[3] studies which, because they are sensitive to long- and short-range ordering effects, respectively, complement each other and give a complete description of the structures. Zeolite A has been chosen for this work as it has a well-defined structure and XRD pattern and gives a single sharp absorption in its ^{29}Si MAS NMR spectrum.

Figure 1A shows the ^{29}Si MAS NMR spectrum of a mixture of crystals of Li$^+$A and Na$^+$A prepared separately (the Na$^+$A species ion exchanged thoroughly to the Li$^+$A form) and then mixed for 10 s in a "wigglebug" (as described in ref 4), the spectrum being recorded immediately after mixing. Figure 1B shows the corresponding powder XRD pattern. Since the replacement of Li$^+$ for Na$^+$ causes a shrinkage in the unit cell dimension, clear and predictable changes in the position of the absorptions in the X-ray diffraction pattern are observed. The XRD pattern of the mixture (Figure 1B) shows the superposition of the two patterns giving a "doublet" splitting of many of the peaks and indicating clearly that the sample consists of a simple physical mixture of the two sets of crystallites. This is confirmed by the ^{29}Si MAS NMR spectrum of the same sample (Figure 1A) which shows two sharp resonances at δ -85.1 and -88.9 due to there being *two* local silicon environments which do not exchange rapidly on the NMR time scale. This is again in agreement with there being two types of crystallites present as rapid diffusion within

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the pore structure is known to yield a single NMR resonance, even when more than one type of ion is present. It should be noted that the shift is probably due to local interactions involving the cations as the cubic symmetry of the unit cell is preserved and the local geometry of the silicon atoms is unchanged. Figure 1C,D shows the corresponding ^{29}Si MAS NMR spectrum and XRD pattern of the same system after allowing it to equilibrate for 18 h. Both spectra show single peaks indicative of there being a single species of average cation content present rather than a mixture. A previous report[4] of such a change has been made from XRD measurements and this is now confirmed for both the short- and long-range aspects of the structure. The species of average composition which results must have been formed from simultaneous migration of the different cations in opposite directions between the two sets of crystallites, purely from the macroscopic mechanical contact between the crystallites. The changes are reproducible, with the position of the NMR and XRD absorptions of the resulting "average" species depending, in a predictable manner, on the relative concentrations of the starting materials as would be expected. Scanning electron microscopy (SEM) confirms that the crystals remain intact unless severe conditions are used. In the present work a plastic ball was used to ensure that little or no degradation occurred when this apparatus was used.

Several variables are important in determining the rate of reaction: First, the rate depends on the amount of mechanical mixing of the sample. For example, mixing Li^+A and Na^+A, with particle size 1–2 μm, for 10 s in a wigglebug will give complete exchange although SEM indicates a small loss of crystallinity (<1%) due to the mechanical shock of mixing, while simply mixing the two sets of crystals by lightly stirring them together gives a system which takes 24 h to come to equilibrium with no loss in crystallinity. Second, the degree of hydration is important. For example, it can take several weeks for a mixture of dehydrated Li^+A and Na^+A (20–25-μm particle size) to reach equilibrium. However, when the same sets of crystals are fully hydrated, complete exchange will be attained after mixing for only 30 s in a wigglebug. Third, the reaction is very dependent on the crystallite size; small crystals (1–2 μm) reach equilibrium immediately while large (20–25 μm) crystals take 24 h to reach equilibrium under the same conditions (crystals partially dehydrated and mixed in wigglebug for 5 s). In general, although difficult to quantify, the reaction is surprisingly fast; for example, complete exchange occurs in approximately 5 min for a mixture of Li^+A and Na^+A (5-μm particle size) that has been mixed for 5 s in a wigglebug.

The profiles of the NMR and XRD spectra at intermediate times are complex and reflect the mechanism of the migration process. Since both long- and short-range orderings are being monitored by these experiments, it is hoped that a detailed picture of the mechanism will result from this data and such studies are currently in progress.

Preliminary results indicate that similar cation migrations occur between other pairs, for example, Li^+A and Na^+Y as well as between Li^+A and Na^+mordenite.

Further investigations of these systems are being carried out, but there are important implications in the semiquantitative results presented here concerning the practical use of zeolites in industrial processes: Often they are used together with "binders", usually natural clays, to increase the particle size and ease of handling. Those natural clays contain a number of cations, including transition-metal ions, and the present results suggest that migration of these species into the zeolite lattice is possible, especially if they are extruded under pressure with the binder. Thus the zeolite under reaction conditions may not have the same physical or physicochemical properties as the pure species used without additives.

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Pulse Radiolysis Studies of Alkaline Fe(III) and Fe(VI) Solutions. Observation of Transient Iron Complexes with Intermediate Oxidation States

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With the exception of some isolated studies on aqueous Fe(IV) in the 1960's,[1,2] the Fe(IV)/Fe(V) species have received little attention until quite recently.[3] Interest in these oxidation states has been stimulated by the finding that certain Fe(V) (or Fe(IV) cation radical) porphyrins[3,4] are the active intermediates in biological hydroxylation reactions. In nonbiological systems less exotic iron complexes such as $Fe(EDTA)^-$ perform silimar functions in the presence of H_2O_2. The intermediacy of Fe(IV), or the ferryl ion, FeO^{2+}, rather than the hydroxyl radical has been postulated to explain the specificity of these systems.[3,5] Recent thermodynamic calculations suggest that FeO^{2+} should be accessible in aqueous solution in the presence of suitable ligands.[6] In this paper we wish to report the first spectroscopic evidence for complexes containing iron formally in the IV and V oxidation states in the presence of a simple ligand, i.e., OH^- and $P_2O_7^{4-}$ in alkaline solution.

These transient species are obtained by pulse radiolysis of alkaline ferric (Fe(III)) and ferrate (Fe(VI)) solutions by using the hydroxyl radical or its conjugate base, O^-, and the aquated electron, e_{aq}^-, as the respective oxidizing and reducing agents. Dilute solutions containing monomeric Fe(III), as $Fe(OH)_3/Fe(OH)_4^-$,[7] and/or FeO_4^{2-} were prepared electrolytically in NaOH solutions (NaOH, 99.999%; G. F. Smith). A current of 500–1000 mA at 8–10 V was applied for 1–3 h to an iron anode (wire) in a 200-mL compartment that was separated from the cathode compartment (Pt wire) by a glass frit. Continuous evolution of dioxygen at the anode ensured the absence of Fe(II) in these solutions. Total iron concentrations were determined spectrophotometrically as the tris(*o*-phenanthroline)iron(II) complex following reduction with dithionite; ferrate (VI) concentrations were monitored by its absorption spectrum (vide infra). In chilled (~5 °C) 5 M NaOH, solutions of 50 μM Fe(VI) (60 μM total Fe) were obtained. In 1 M NaOH solutions 35 μM of Fe(III) were found after decomposition of any Fe(VI); the latter was not determined in these conditions because of its instability. These solutions were clear, stable, and free of colloidal iron. The only significant contaminant was a trace of carbonate which proved not to inhibit the reactions of interest. These solutions were pulse-irradiated with 2-MeV electrons from a Van de Graaf accelerator. The radiolysis of water is denoted by eq 1 where *G*

$$H_2O \rightsquigarrow e_{aq}^-\ (2.65),\ OH\ (2.75),\ H\ (0.65),\ H_2\ (0.45),\ H_2O_2\ (0.72) \quad (1)$$

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