(NH), 1751 (ester C=O), 1675 (amide I), 1633 (amide I), 1536 (amide II), 1500 (amide II) cm^{-1}; EI MS *m/e* obsd 202.0954, calcd for $C_8H_{14}N_2O_4$ 202.0954.

Growth of Crystals for Diffraction Studies. Prisms of triamide **1** were obtained by dissolving the material in hot CH_2Cl_2, adding hexane to saturation, and allowing the solution to cool to room temperature. Thin plates of **2** and **5** were grown by vapor diffusion of hexane into 1,2-dichloroethane solutions of the compounds at room temperature; the same procedure afforded prisms of **3**. Plates of **4** were obtained by vapor diffusion of hexane into a 1,2-dichloroethane of the triamide at −20 °C. Thin plates of **6** were grown by slow evaporation of a hexane/1,2-dichloroethane solution at room temperature.

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Note Added in Proof. Collins et al. (*Inorg. Chem.* **1991**, *30*, 4204) have very recently reported the crystal structure of a macrocyclic tetraamide that contains multiple *N*-malonylglycine skeletal units. In the solid state, this macrocycle displays two interwoven nine-membered-ring C=O···H—N hydrogen bonds.

Supplementary Material Available: Listings of literature references for crystal structures of malonamide derivatives and crystallographic details for **1–6**, including tables of atomic coordinates and bond lengths and angles (44 pages); listing of observed and calculated structure factors (45 pages). Ordering information is given on any current masthead page.

Size and Location of Cobalt Clusters in Zeolite NaY: A Nuclear Magnetic Resonance Study[§]

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Abstract: In this work, it is demonstrated how information concerning the size and location of Co clusters in the zeolite NaY can be obtained by measurements of the ^{59}Co spin-echo NMR spectrum. The critical temperature for the superparamagnetic/ferromagnetic transition was used to obtain an estimate for the average cluster size in Co/NaY samples which were prepared using different thermal treatments. In addition, a selective chemical treatment with triphenylphosphine was used to determine the location of the clusters. It was found that preparation of Co/NaY under "mild" conditions (decomposition and annealing carried out at 200 °C) resulted in the production of Co clusters with an average diameter of 6–10 Å inside the NaY cages, while preparation of Co/NaY under "extreme" conditions (decomposition and annealing carried out at 500 °C) resulted in larger clusters outside the NaY cages.

I. Introduction

Volatile transition metal complexes have been widely used for the production of zeolite-encaged metal catalysts.[1,2] For the first-row transition metals that are difficult to reduce from ionic precursors, severe reduction conditions can be avoided by using appropriate volatile precursors. Most carbonyl complexes can be introduced into zeolite cages via the vapor phase. They remain intact at low temperature and under CO pressure.[3,4] However, at elevated temperature or in vacuo, they decompose by releasing CO ligands. In the preparation of zeolite-supported Co catalysts, Co carbonyl [$Co_2(CO)_8$] is frequently used.[5,6] Since Co^{2+} ions in zeolite Y cannot be reduced below 750 °C,[7,8] the use of the volatile $Co_2(CO)_8$ precursor is advantageous because it decomposes at low temperature, leading to highly dispersed Co particles. In situ far-IR spectroscopy has shown that adsorbed $Co_2(CO)_8$ interacts with the accessible supercage cations in the NaY and CoY zeolites.[9] In the zeolite HY, Co atoms are oxidized to Co^{2+} ions by the zeolite protons. Therefore, the acidic form of zeolite is to be avoided. The final dispersion of Co in the zeolite cages is determined not only by the decomposition technique[10–12] but also by the properties of the zeolite supports and by the method with which the Co carbonyl complex is introduced into the zeolites. In this study, ^{59}Co nuclear magnetic resonance (NMR) spectroscopy has been utilized to determine the size and location of

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[§] We thank the National Science Foundation (Grant No. CTS11184) and the University of Connecticut Research Foundation for supporting this work.

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the small metallic Co clusters in the NaY zeolite (designated Co/NaY) and the influence upon these parameters by the sample-processing treatments.

Nuclear magnetic resonance spectroscopy is a technique by which the nuclear species that naturally occur in a material are used as probes to gain information concerning the atomic structure, electronic structure, and related interactions on a microscopic scale. Although NMR spectroscopy has been employed extensively in the study of the nonmagnetic supporting structures for catalytic materials,[13] its direct application to the small magnetically-ordered metallic clusters is in the pioneering stage.[12,14] There is a fundamental difference between NMR spectroscopy of nonmagnetic materials and NMR spectroscopy of magnetic materials. For nonmagnetic materials, the dc magnetic field at the nuclear sites, which is necessary for NMR spectroscopy, is obtained by the application of an external magnetic field. However, for magnetic materials, such as the Co clusters studied here, the magnetic field at the nuclear sites arises from the internal hyperfine field (HF) and the application of an external field is not required. This is known as "zero-field" NMR spectroscopy. In general, the HF can have three contributions, two from the on-site magnetic moment and one from the magnetic moments of the first nearest neighbor atoms. All three contributions are a result of an exchange coupling between 3d electrons and s electrons (either inner shells or s band). The contributions are intimately related to the local atomic environment as well as the electronic structure. (For a good review of the various contributions to the HF and their relationship to the atomic and electronic structures, see ref 15.) The connection between the HF and the atomic/electronic structure of 3d elements makes NMR spectroscopy an extremely valuable tool in the exploration of metallic and bimetallic catalysts.

Since the investigation reported here concerns the magnetic behavior of small Co clusters, there is one physical phenomenon which is particularly relevant.[16] For a magnetically-ordered material with a particle volume V, there is a critical temperature, T_c, such that the magnetic behavior is ferromagnetic for temperatures less than T_c and superparamagnetic for temperatures greater than T_c. The critical temperature is given approximately by

$$T_c \sim K_c V / k_B \qquad (1)$$

where K_c is the crystalline anisotropy constant and k_B is the Boltzmann constant. When the clusters are in the ferromagnetic state (i.e., $T < T_c$), the NMR line will be observable with the frequency for a particular nuclear species being determined predominantly by the internal hyperfine field at the nuclear site, as any external field is either relatively small or zero. When the clusters are in the superparamagnetic state (i.e., $T > T_c$), the NMR line will not be observable due to the severe broadening which arises from thermal fluctuations in the direction of the magnetization. However, with the application of an external magnetic field, the line can be recovered. Since the sizes of the metallic clusters that occur in zeolite-supported catalysts are in the range which yields superparamagnetic/ferromagnetic transitions at liquid helium temperatures, NMR spectra which are obtained for various temperatures and applied magnetic fields can be used to determine quantitatively the cluster size distribution. In addition, by observing the effect on the NMR spectrum observed for a sample which has undergone a chemical treatment that only quenches the magnetic moments of the clusters outside the zeolite cages, we can obtain information concerning the location of the clusters.

II. Experimental Apparatus and Procedure

Zeolite NaY (Linde LZY-52) was first dehydrated at 500 °C for 2 h under ultra-high-purity Ar gas flow. Sublimed $Co_2(CO)_8$ was then carried by CO gas flow at room temperature via a separate line and adsorbed onto the dehydrated NaY. The sublimation process took approximately 12 h, resulting in a yellow color for NaY. The decomposition of $Co_2(CO)_8$, with the release of the CO ligands, was controlled by thermal treatment at a specified temperature (either 200 or 500 °C for 1 h) under H_2 flow. The use of H_2 was intended to avoid coke or carbide formation. The adsorbed hydrogen was then removed by an Ar gas purge which was carried out while the sample was being annealed for 1 h at the same temperature that was used for the $Co_2(CO)_8$ decomposition. Each Co/NaY sample was evacuated and then sealed in a Pyrex side arm of the reactor. The final Co loading was approximately 1 wt %. A loading of 1 wt % Co corresponds to an average of three Co atoms per unit cell. This loading is practical for catalytic applications. The choice of this loading was made in order to obtain small Co particles under the mild treatment conditions (200 °C). In order to distinguish between metallic Co clusters outside and inside the NaY cages, some of the samples were exposed to a chemical treatment with triphenylphosphine. Triphenylphosphine was heated to 190 °C in a separate bed. The vapor-phase molecules were carried to the catalyst bed by He gas. Since the triphenylphosphine molecules are too large to enter the zeolite channels, they will stay at the external surfaces of the zeolite crystallites and selectively quench the magnetic moments of only the Co clusters outside the cages. Triphenylphosphine molecules are well-known electron-donating ligands. The quenching of the magnetic moments occurs via an electron transfer to the unfilled d orbitals of Co atoms.

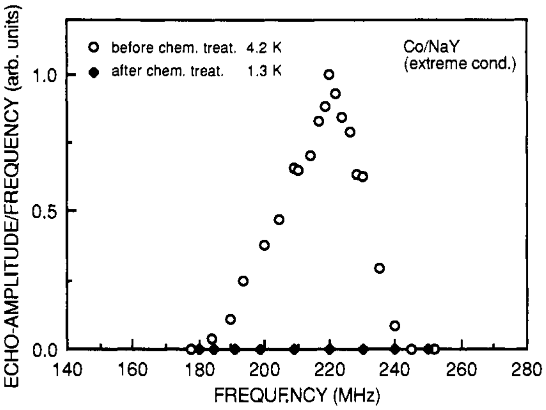

Figure 1. ^{59}Co spin-echo NMR spectra obtained from Co/NaY samples prepared under "extreme" conditions (decomposition and annealing temperature, 500 °C): open circles, untreated sample, spectrum obtained at 4.2 K; closed diamonds, sample treated chemically with triphenylphosphine, no signal observed at 4.2 or 1.3 K.

Spin-echo NMR measurements were carried out on a commercially available Matec Model 7700 pulse modulator and receiver (main frame), with a matching Matec Model 765 RF pulsed oscillator plug-in (90–300 MHz at 500 W). In addition, the resonance frequency was calibrated with a Hewlett Packard Model 608F signal generator and Fluke Model 1953A frequency counter, while the data acquisition was carried out with a Biomation Model 805 transient recorder and Nicolet Model 1072 time average computer. The spectrometer system was matched with a Varian Model V3400 electromagnet capable of fields up to 10 kOe. Operation at liquid helium temperatures was made possible with a conventional glass double-dewar system and pumping system. Two equal 120° pulses with lengths of 1.6 μs and a separation of 10 μs were used to obtain the spectra. The measured echo amplitude was normalized and divided by the first power of the frequency in the usual manner. Additional details concerning the pulsed NMR apparatus, single-coil arrangement, data acquisition procedure, and spectral analysis can be found elsewhere.[17]

III. Results and Analysis

Figure 1 shows the ^{59}Co spin-echo NMR spectrum obtained from a Co/NaY sample that was prepared under "extreme" conditions which were intended to form large Co clusters outside the NaY cages. As described in section II, the loaded $Co_2(CO)_8$ in the NaY was initially decomposed at 500 °C in H_2 and then the sample was annealed at 500 °C. For zero applied magnetic field, a somewhat broad spectrum with a central peak at 219 MHz was obtained (open circles). There is a very slight indication of a secondary peak at 229 MHz. A Co/NaY sample prepared

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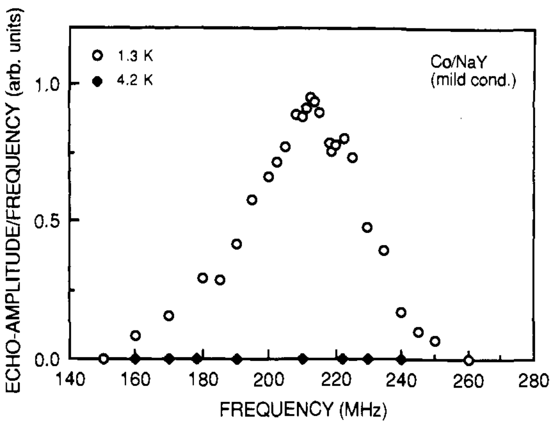

Figure 2. ^{59}Co spin-echo NMR spectra obtained from a Co/NaY sample prepared under "mild" conditions (decomposition and annealing temperature, 200 °C): closed diamonds, $T = 4.2$ °C (no signal observed); open circles, $T = 1.3$ °C. This sample has not been treated chemically with triphenylphosphine.

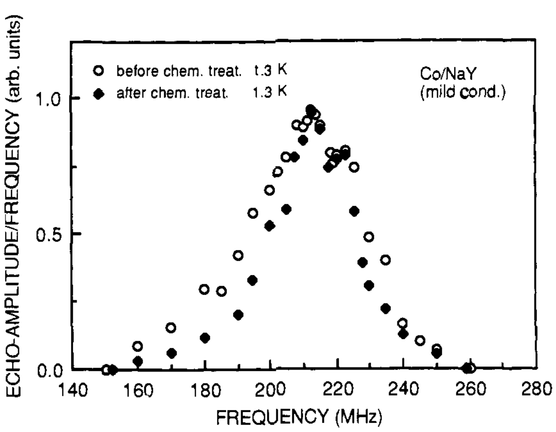

Figure 3. ^{59}Co spin-echo NMR spectra obtained at 1.3 K from Co/NaY samples prepared under "mild" conditions (decomposition and annealing temperature, 200 °C): open circles, untreated sample (replotted from Figure 2); closed diamonds, sample treated chemically with triphenylphosphine.

under the same extreme conditions but then treated chemically with triphenylphosphine was also investigated. As also shown in Figure 1, absolutely no NMR signal was observed at either 4.2 or 1.3 K (closed diamonds) for the chemically treated sample. This result reveals that the large metallic Co clusters which were formed by the extreme conditions indicated above are located outside the cages, as their magnetic moments were quenched by the triphenylphosphine.

Figure 2 shows the ^{59}Co spin-echo NMR spectrum obtained from a Co/NaY sample that was prepared under "mild" conditions which were intended to form small Co clusters inside the NaY cages. The loaded $Co_2(CO)_8$ in the NaY was initially decomposed at 200 °C in H_2, and then the sample was annealed at 200 °C. For zero external magnetic field, no NMR signal was observed at 4.2 K (solid diamonds). However, as the temperature was lowered from 4.2 to 1.3 K, a broad spectrum with a central peak at 212 MHz dramatically appeared (open circles). A secondary peak in the spectrum exists at approximately 222 MHz. A consideration of the signal-to-noise ratio indicates that this is indeed the result of a transition from the superparamagnetic state to the ferromagnetic state, not just the result of an increase in the signal intensity due to the Boltzmann factor. Qualitatively, the average size of the small Co clusters is such that $1.3 \text{ K} < T_c < 4.2 \text{ K}$. Also, not shown in Figure 2, the application of an external field of 9 kOe caused a reappearance of the NMR signal at 4.2 K. Figure 3 shows the ^{59}Co spin-echo NMR spectrum obtained a 1.3 K from a Co/NaY sample prepared under the same "mild" conditions described above except that it was treated chemically with triphenylphosphine. For comparison, the spectrum shown in Figure 2 for the untreated Co/NaY sample is reproduced in Figure 3. These results demonstrate that the vast majority of the (small) metallic Co clusters formed under the "mild" conditions indicated above are located inside the cages of the zeolite, as the ^{59}Co NMR spectrum was not significantly altered by the chemical treatment.

IV. Discussion and Conclusions

Catalytic samples of the form Co/NaY were prepared by loading $Co_2(CO)_8$ into dehydrated NaY and then using two thermal treatments: (1) "mild", where both the decomposition and annealing temperatures were 200 °C, and (2) "extreme", where both the decomposition and annealing temperatures were 500 °C. It was anticipated that the "mild" conditions would result in small Co clusters residing inside the NaY cages, while the "extreme" conditions would result in larger Co clusters residing outside the cages. An indication of the size of the metallic clusters was obtained from the corresponding NMR spectra. The Co/NaY sample prepared under the "mild" conditions demonstrated a superparamagnetic/ferromagnetic transition between 1.3 and 4.2 K. A consideration of the crystalline anisotropy for Co ($K_c = 1.06 \pm 0.20 \times 10^6$ erg/cm^3) and eq 1 results in an estimate of the average cluster diameter between 6 and 10 Å, which is compatible with the size of the NaY cages. The above estimate is quite crude, and two points should be kept in mind. First of all, eq 1 is just an approximate relationship between the transition temperature and the average particle size. A detailed observation of the temperature and/or field dependence of the superparamagnetic/ferromagnetic transition would yield a better estimate of the average particle size and the distribution.[18] Secondly, it would be expected that the value for the crystalline anisotropy of the small Co particles is different from that of bulk Co. (In the estimate above, the value for K_c was obtained from a Mössbauer study that was carried out on 80-Å Co particles.[18]) The Co/NaY sample prepared under the "extreme" conditions contained Co clusters which were already ferromagnetic at 4.2 K and, therefore, had an average cluster diameter greater than 10 Å. A chemical treatment of two identically prepared Co/NaY samples with triphenylphosphine clearly demonstrated that the Co clusters prepared under the "mild" conditions were located inside the NaY cages, while the Co clusters prepared under the "extreme" conditions were located outside the cages.

Other explanations of the experimental results must be considered. Even if large Co particles are formed inside the zeolite crystallites by creating local voids, the triphenylphosphine molecules are not expected to totally quench the NMR signal because they are still unable to traverse the intact supercage windows at the exterior of the crystallites. It has been found that little loss of crystallinity occurs for the NaY support structure after heat treatments as high as 800 °C.[19] Therefore, the observation of a complete quenching of the NMR signal indicates that the large Co particles are located at the external surfaces of the zeolite crystallites, easily accessible to the triphenylphosphine molecules. On the other hand, a surface that is enriched with small Co particles would be very unstable even at 200 °C because of the large thermodynamic driving force for the coalescence of small Co particles to form larger Co particles.

The observation of the zero-field NMR signals clearly indicates that the Co clusters exist in a magnetically-ordered metallic state and not in an oxidation state characteristic of a paramagnetic salt.[12] Concerning the features of the NMR spectra, the larger Co particles were characterized by a somewhat broad spectrum with a central peak at 219 MHz and a very slight indication of a secondary peak at 228 MHz (see Figure 1). It should be noted that 219 and 229 MHz are close to the characteristic frequencies for bulk fcc Co and hcp Co, respectively. The broadening indicates

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that the Co clusters are sufficiently small that they are not truly bulk in nature. It is likely that these particles are single domain. The smaller Co particles were characterized by a spectrum with broader peaks than those of the large clusters and with a central peak located at 212 MHz. A secondary peak located at 222 MHz is clearly evident. Again, these two peaks might indicate fcc- and hcp-like short-range order, with the downward shift in frequency and the additional broadening being consequences of the fact that these clusters are also single domain and even further removed from the bulk situation.

The work presented here clearly demonstrates how NMR techniques can provide valuable information concerning the size and location of magnetically-ordered metallic clusters encaged in zeolite materials.

Influence of Strain on Chemical Reactivity. Relative Reactivity of Torsionally Strained Double Bonds in 1,3-Dipolar Cycloadditions

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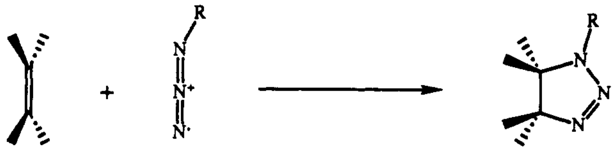
Abstract: The addition of picryl azide to a series of mono- and bicyclic olefins including *trans*-cycloalkenes and bridgehead alkenes is reported. Secondary reaction products were identified, and their mechanism of formation was explained by an analysis relating the transition state energies to the conformation of the reaction intermediates. Bridgehead alkenes showed reversed regiochemistry of cycloaddition when compared with model alkenes. It is proposed that the reversal of regiochemistry is caused by the out of plane bending of the bridgehead double bond. The kinetics of the cycloaddition reveals significant increases in reaction rate for the picryl azide addition to strained olefins. A good correlation was found in the plot of log k_{rel} vs ΔSE, where ΔSE values were calculated from differences of MM-2 steric energy between olefins and a model of the corresponding triazoline cycloadduct. This finding indicates that the strain relief in the transition state is a major factor affecting the reactivity of alkyl-substituted mono- and bicyclic olefins. The HOMO energy change did not affect the reactivity significantly in the picryl azide addition to alkyl-substituted olefins as evidenced by the absence of correlation in log k_{rel} vs ionization potential. Up to 60% of the steric energy difference (ΔSE) is found to be relieved in the transition state from the slope of the log k_{rel} vs ΔSE plots. By comparison of the reaction rates for the MCPBA epoxidation and the picryl azide addition, reactivity patterns were found to be similar among the olefins studied except for norbornene. An attempt was made to explain the norbornene anomaly by calling attention to the torsional interactions that develop between forming bonds and existing carbon–carbon bonds in the methylene bridge. An important outcome of this research is the quantification of the effect of strain on chemical reactivity and selectivity. The olefin strain changes both the rate of reaction and regiochemistry of the cycloaddition.

Introduction

In an effort to establish quantitative relationships between strain and reactivity,[1] we have undertaken a series of investigations of the rates of addition to torsionally distorted carbon–carbon double bonds. The present study examines the rates of azide addition to various strained alkenes. Organic azides react with olefins to form 1,2,3-Δ^2-triazolines, a reaction first reported by Wolff in 1912.[2] The reaction is an important synthetic route to triazolines and their derivatives.[3]



R = Aryl, Aryl sulfonyl, CN etc.

In 1931, Alder and Stein observed that norbornene derivatives have high reactivity with phenyl azide.[4,5] The ease of phenyl azide addition was subsequently employed as a measure of ring strain. Several studies have since attempted to identify the origin of the high reactivity of the norbornene ring system.[6]

Azide additions to double bonds were recognized as an example of a 1,3-dipolar cycloaddition reaction from the extensive research of Huisgen.[7,8] The general mechanistic features[3] are a concerted but nonsynchronous cycloaddition. Reactivity may be viewed in FMO terms as an interaction of the highest occupied molecular orbital (HOMO) of the 1,3-dipole (or dipolarophile) with the lowest unoccupied molecular orbital (LUMO) of the dipolarophile (or 1,3-dipole).

The substituent effect on reactivity follows from the frontier orbital interaction between the azide and the olefin (Figure 1). Olefins having electron-donating or conjugating substituents have their major interaction between the LUMO of phenyl azide and the HOMO of the olefin, but olefins with electron-withdrawing substituents have their major interaction between the HOMO of phenyl azide and the LUMO of the olefin.[9] The energy gap between the frontier orbital pairs becomes smaller as one progresses from parent ethylene to either electron-rich olefins or electron-deficient olefins, thus facilitating the reaction in both cases. When kinetic rate data are plotted against orbital energies (log k vs ionization potential), a characteristic U-shaped curve

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