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Preparation of Highly Dispersed Cobalt Clusters in Zeolites via Microwave Discharge Methods

A microwave discharge has been used to prepare highly dispersed and reduced cobalt metal atom clusters in zeolites and other solid substrates such as alumina, silica, activated carbon, and polymers. Spectroscopic data show that the microwave discharge approach offers several advantages over other activation procedures for the preparation of small metal particles on solid supports. Scanning electron microscopy, ferromagnetic resonance, and X-ray line broadening experiments indicate that these particles are smaller than 30 Å. © 1986 Academic Press, Inc.

INTRODUCTION

The activity of a catalyst in a particular catalytic reaction depends on several factors including the choice of metal and the particle size of the metal. Several methods (*1–5*) including thermal, photochemical, H atom reduction, Cd vapor reduction, and metal atom vaporization, have been used to produce small metal particles.

Microwaves can split H_2 into H atoms which can reduce Ni^{2+} ions in zeolite samples (*5*). Microwaves have also been used to dehydrate zeolites (*6*). Radiofrequency methods can preferentially heat a metal at a temperature different from the support (*7*).

This paper describes the use of a microwave discharge to decompose metal-containing compounds on zeolites. This procedure leads to the formation of small *pyrophoric* cobalt(0) particles in various zeolites. Results concerning the preparation and characterization of superparamagnetic cobalt(0) particles on various zeolites are described here.

EXPERIMENTAL

MICROWAVE SYSTEM

The apparatus used for the deposition of metal carbonyls on solid supports are given in Fig. 1. A Raytheon PGM-10 microwave power generator operating at a frequency of 2450 ± 25 MHz was used as the radiation source. An Evenson quarter wave, coaxial cavity incorporating both tuning and coupling adjustments was used. All sample holders placed in the microwave cavity were made of quartz. Plasmas were generated using gas pressures of 0.1–0.5 Torr and powers of 5 to 75 W. Further details can be found elsewhere (*14a*).

MATERIALS

Zeolites NaY, NaX, and NH_4Y and $Co_2(CO)_8$ were obtained from Alfa Products. α-Alumina, activated carbon, and amorphous silica were purchased from Illinois Minerals Company. All the above supports were activated by heating to 375°C under a vacuum of 1×10^{-4} Torr and stored in sealed vials in a nitrogen-filled drybox.

PROCEDURES

Microwave effects on the various supports were studied by loading approximately 0.1 g of support into a straight 9-mm-I.D. quartz tube attached to two Teflon vacuum stopcocks (A and D, Fig. 1) using Cajon Ultra-Torr fittings (E and F, Fig. 1) in a N_2-filled drybox. The sealed sample tube assembly was then attached to the vacuum system and the support evacuated to 1×10^{-4} Torr before the introduction of Ar gas at a final pressure of about 0.3 Torr. The supports were then subjected to plasmas at low (0 to 10 W) and high (30 to 70 W) microwave powers. The irradiated supports were stored in a N_2-filled dry box. Further details can be found elsewhere (*14a*).

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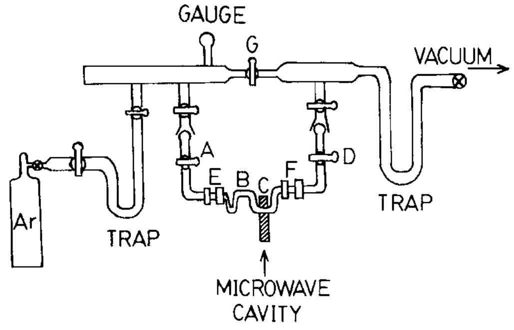

FIG. 1. Experimental apparatus for microwave discharge deposition.

STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION

Ferromagnetic Resonance

Ferromagnetic resonance (FMR) experiments were carried out using a Varian E-3 spectrometer. Spectra were recorded at an X-band microwave frequency of approximately 9.5 GHz. A DPPH sample was used as a standard for *g*-values. The FMR experiments were done between temperatures of −160 to 250°C.

X-Ray Powder Diffraction

X-Ray powder diffraction experiments were carried out using a DIANO-XRD 8000 diffractometer equipped with a Philips Electronic source. Copper $K\alpha$ radiation was used and sample scans were done at 2°2θ/min.

Scanning Electron Microscopy and Microanalysis

Scanning electron microscopy experiments were performed at magnifications of 43,000 to 98,000 on an AMRAY Model 1000 A SEM with an EDAX 9100/60 system.

Fluorescence Studies of Microwave Discharge

The fluorescence spectra of excited-state atoms and molecules that are created during the microwave discharge were recorded with a fiber optic, scanning monochromator, and a photomultiplier tube.

Standard experiments. A plasma was formed by introducing CO gas into the vacuum line shown in Fig. 1. The color of this plasma was blue. The identity of the CO peaks in the 350- to 400-nm region was confirmed by referral to published CO emission lines (*8*). These CO emission lines are given in Fig (2a).

A series of experiments with various amounts of $Co_2(CO)_8$ decomposed by the Ar plasma to CO were done in order to establish a calibration curve to determine the amount of CO released from the $Co_2(CO)_8$. We chose the region of 482 to 485 nm for these quantitative experiments because the CO emission intensity peak was large and the Ar background intensity was low.

Determination of amount of CO released from zeolite during discharge. A weighed amount of $Co_2(CO)_8$ was placed in one side of the quartz tube in a glovebox. A dehydrated NaX zeolite was placed in the other well of the quartz tube. The sealed-off tube was brought out of the glovebox and attached to the vacuum line. The $Co_2(CO)_8$ was frozen and then a background emission of the pink Ar plasma was monitored at 482.79 nm.

The Ar flow was then stopped, the plasma was extinguished and the $Co_2(CO)_8$

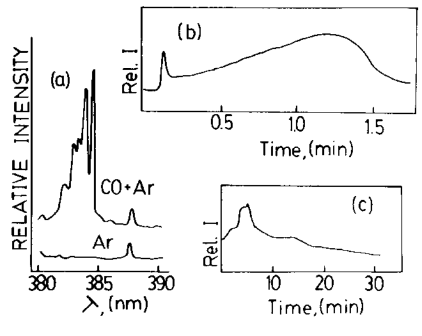

FIG. 2. Fluorescence emission spectra of (a) CO plasma, 380–390 nm; (b) $Co_2(CO)_8$ in an Ar plasma, 384 nm; (c) $Co_2(CO)_8$ in NaX zeolite in an Ar plasma, 384 nm.

was sublimed into the NaX zeolite with no external heat. Ar gas was introduced into the system and the plasma was ignited at 3 W power. A blue color was then observed. The microwave power was turned off when the blue color faded and the pink color of the Ar plasma appeared. The wavelength region at 228.8 and 240.7 nm was scanned to determine if Co atoms could be observed in the plasma.

BET Measurements

A three point BET measurement was done with N_2 gas for the dehydrated NaX zeolite and for the dehydrated NaX zeolite which was treated with $Co_2(CO)_8$ and subjected to the microwave plasma.

RESULTS

MICROWAVE EFFECTS ON SUPPORTS

If a thermally dehydrated zeolite (375°C) is placed in an argon plasma at low power (<10 W) a dark-pink glow characteristic of hydrogen emission (from OH groups) is observed. Microwave radiation provides an effective method for dehydrating zeolites (*6*). Sodium zeolites placed in an argon plasma at high power (>50 W) resulted in regions of a bright yellow glow, characteristic of sodium atomic emission. X-Ray powder diffraction of the zeolites treated with a low power plasma showed no apparent loss of crystallinity. After high-power treatment X-ray diffraction data show loss of some diffraction lines, a broad background and at times new lines consistent with bulk Al and Si.

When dehydrated NaY zeolite (375°C) was subjected to an argon plasma for about 4 s at a power of 3 W, portions of the surface became red in color. The color persisted for a period of about 1 min. When dehydrated NaX zeolite (375°C) was subjected to similar conditions a purple color was generated on the surface of the zeolite. Attempts to stabilize the colored materials for analysis were not successful.

MICROWAVE DECOMPOSITION OF $Co_2(CO)_8$ ON ZEOLITES

When bulk $Co_2(CO)_8$ was irradiated with microwaves under vacuum, no decomposition was observed even at powers of 70 W. When radiated at 5–10 W and with an Ar (0.3 Torr) plasma, a bright light-blue glow characteristic of CO emission and a sharp increase in pressure occurred along with the decomposition of the $Co_2(CO)_8$. A metallic mirror and brownish-black film coated the surface of the sample tube at the edge of the discharge near points B and F of Fig. 1.

When $Co_2(CO)_8$ was adsorbed onto dehydrated NaX zeolite and subjected to the microwave plasma (5 W, 0.3 Torr Ar), a bright light-blue glow and an initial increase in pressure was observed. The microwave treatment was continued until the emission from CO was no longer visible (about 45 min). The gray–brown colored product was pyrophoric in air. Similar microwave treatment of NaY, HY, and HZSM-5 zeolites resulted in dark-colored materials.

MICROWAVE DECOMPOSITION OF $Co_2(CO)_8$ ON OTHER SUPPORTS

Similar procedures were used to prepare small cobalt clusters on other supports such as Al_2O_3, TiO_2, SiO_2, activated carbon, and polystyrene. In the case of polystyrene, the polymer had to be placed outside the microwave discharge in order to avoid decomposition of the polymer.

In all cases, except the experiments with activated carbon and polystyrene, the qualitative observations were very similar to that of the zeolite system. When placed in the microwave field, polystyrene showed visual signs of degradation. Activated carbon glowed red when the discharge started.

FERROMAGNETIC RESONANCE EXPERIMENTS

Table 1 shows the apparent *g*-values and FMR line widths for zeolite NaX, Al_2O_3, SiO_2, TiO_2, and polymer samples that were exposed to the microwave discharge. Plots

TABLE 1

Cobalt Particles in Various Supports: FMR Linewidths and Apparent g-Values

Support	Temperature of FMR Expt (°C)	ΔHpp (G)	g_{app}
Zeolite NaX	−160	1600	2.26
	25	1150	2.18
	100	1100	2.18
	150	1050	2.18
Al_2O_3	−160	1100	16.25
	25	950	7.36
	50	900	5.80
	100	850	5.65
TiO_2	−160	3250	3.34
	25	2100	2.55
	50	2050	2.41
	100	1750	2.36
SiO_2	−160	1150	2.49
	25	850	2.22
	50	800	2.15
	100	750	2.16
Polystyrene	25	[a]	[a]

[a] No signal observed.

of the apparent g-value versus temperature for all materials follow a parabolic function with high g-values at low temperature. Plots of the FMR linewidth (kG) versus temperature were found to be linear.

MICROANALYSIS AND X-RAY POWDER DIFFRACTION EXPERIMENTS

X-Ray powder diffraction experiments show that the zeolites, Al_2O_3, and TiO_2 show no change in crystallinity after exposure to the microwave discharge as long as low-power microwave conditions (<50 W) are used. High-power microwave experiments led to degradation of the supports as indicated by color changes, new diffraction lines (due to Si, Al), and broadening of the background. This occurs whether cobalt is present or absent.

Results of a typical energy dispersive X-ray analysis for cobalt deposited on dehydrated zeolite NaX indicate the presence of 0.8% cobalt. Results of this microanalysis indicate the following overall composition: Co = 0.8%, Si = 10.7%, Al = 7.7%, Na = 5.9%, O = 73.8%. Similar cobalt loadings were observed for NaY, HY, and HZSM-5.

SCANNING ELECTRON MICROSCOPY

Photographs of the cobalt particles on zeolite X obtained during scanning electron microscopy experiments at 3500 and 30,000 magnification do not show cobalt particles on the surface. Energy dispersive X-ray analyses of zeolite X shows that cobalt is evenly distributed through the zeolite particles. Similar results were obtained with other cobalt zeolite NaY, HY, and ZSM-5 samples.

FLUORESCENCE DURING THE MICROWAVE DISCHARGE

The fluorescence emission spectra for CO gas, for the decomposition of $Co_2(CO)_8$ and $Co_2(CO)_8$ deposited on NaX zeolite are given in Fig. 2. The wavelength region of 350 to 400 nm yields three sharp lines for all three of these samples and a blue-colored plasma is observed. A major emission band occurs at 482.79 nm for all three samples and as shown in Figs. 2b and c the total amount of CO under this peak has been recorded for various amounts of $Co_2(CO)_8$ (Fig. 2b) and for the CO evolved from the decomposition of $Co_2(CO)_8$ on NaX zeolite. A calibration curve was made for the $Co_2(CO)_8$ samples such as from data of Fig. 2b and the amount of CO coming from the zeolite sample was determined with use of this calibration curve. The total number of moles of CO emitted from the $Co_2(CO)_8$/zeolite NaX system determined by this fluorescence procedure was 8.6×10^{-5} mol.

SURFACE AREA MEASUREMENTS

Before deposition of the cobalt onto dehydrated NaX zeolite the total surface area measured by BET was determined to be 595 m^2/g. After deposition of the cobalt by the microwave procedure the surface area decreased to 495 m^2/g. Similar results were found with a NaY support.

DISCUSSION

Microwave Discharges

Microwave discharges have been used to produce reactive H and O atoms (*9*), for polymerization (*10*), preparation of organic compounds (*11*), and for gasification of solid fossil fuels (*13*). Several researchers have used hydrogen atoms (*5, 13*) for reduction of metal oxides.

Microwave discharges have not been used to produce metal atoms which would then deposit on solid substrates (*14*). Researchers (*15*) have encountered problems concerning loss in activity in catalytic reactions due to migration of a metal complex from a solid support into solution. The microwave discharge experiments described here avoid the use of solvents.

Impetus for this research came from the fact that metal atoms can be formed from metal complexes which are decomposed in a microwave field. The metal atoms are in many states including ground and excited electronic and ionized forms. We have used microwave discharges to deposit metals onto silica for use in electrodeless discharge lamps (*16*). A number of decomposition mechanisms for the metal compound and excitation mechanisms for the metal are possible, including collisional excitation, radiative recombination, and collision exchange excitation. Details concerning these mechanisms, the possible states of the metal, the temperatures of the plasma, and a general discussion of microwave cavities can be found elsewhere (*17*).

Deposition of Cobalt(0) Clusters in Zeolites and Other Supports

High-power microwave plasma discharge experiments clearly cause degradation of solid supports whereas low power does not cause such degradation. Microscopic, spectroscopic, and X-ray powder diffraction data provide evidence that crystallinity and uniformity of these materials are lost when the microwave power is greater than 50 W. Experiments with high microwave power but no plasma show no such effects.

The color of the plasma is indicative of which particles are in the gas phase. The pink and purple color of the NaY and NaX zeolites, respectively, are indicative of sodium color centers such as Na_4^{3+} which have been generated in zeolites in metal liquid ammonia solutions (*18*) and by X-ray and γ-ray bombardment (*19*).

The procedure of depositing $Co_2(CO)_8$ in the pores of a large pore zeolite, before initiating the microwave discharge, should increase the chance of preparing small metal cobalt clusters in the zeolite pores. The microwave treatment of NaY, HY, and NaX yielded pyrophoric materials which remain stable when briefly exposed and sealed in a drybox.

By decomposing a metal complex such as $Co_2(CO)_8$ in the flowing microwave discharge and by keeping the support out of the discharge, the metal atoms can be deposited on the external surface of supports.

Fluorescence Emission

The fluorescence emission experiments clearly show that CO molecules are being released from the metal carbonyl $[Co_2(CO)_8]$ complex either in the presence of the zeolite or alone. A pink glow means that CO is being released and a blue glow is indicative of only Ar being present. Spectral identification of Ar and CO lines has also been shown here, i.e., Fig. 2.

No lines (*8*) for cobalt atoms were observed in the plasma decomposition of $Co_2(CO)_8$ on zeolite NaX. From this observation we infer that cobalt remains on the zeolite since we are only observing the plasma species in these optical experiments.

The amount of CO detected during decomposition (8.6×10^{-5} mol CO) is very close to that expected (9.6×10^{-5} mol CO) based on the total amount of cobalt (from EDX experiment) adsorbed into the zeolite pores. The absence of infrared bands in the terminal CO and bridged CO region for the plasma decomposed $Co_2(CO)_8$/NaX zeolite system is further support for our belief that all cobalt carbon bonds are broken. Similar fluorescence emission results were observed for NaY zeolite.

COMPARISON OF MICROWAVE DISCHARGE TO CLASSICAL REDUCTION METHODS

It is useful to compare the microwave discharge method to more classical procedures for reducing metal systems. We (*20*) and others (*21*) have found it extremely difficult to prepare small iron clusters in zeolites. Thermal (*20*) and photochemical (*22*) procedures generally yield oxidized metal particles or larger (>30 Å) particles of the reduced metal on the external surface of the zeolite. Small Fe(0) particles (<13 Å) have been prepared by thermal treatment of $Fe(CO)_5$ in zeolite NaY (*23*).

In the case of cobalt, Fraenkel and Gates (*2*) have used cadium vapor to reduce Co^{2+} ions in zeolite A. Ozin and co-workers (*4*) have used metal atom vaporization (low temperature) methods to prepare highly reduced and dispersed cobalt clusters in the pores of zeolites. Thermal and photochemical methods can lead to sintering of the metal (*20*).

We have measured the temperature of the reactor immediately after the microwave discharge and have found no increase in the *thermal* temperature of the reactor which is in contact with the support. The *electronic* temperature, however, is undoubtedly much higher than room temperature. We cannot discount the effect of the light emission on the decomposition of the metal carbon bonds of the metal carbonyl although the intensity of this line emission is orders of magnitude lower than the intensity of a Xe photolamp.

FERROMAGNETIC RESONANCE

A general expression for the ferromagnetic resonance experiments is given below:

$$\frac{h\nu}{g\beta} = H_{\mathrm{RES}} + \alpha \mathrm{H}_{\mathrm{A}} + H_{\mathrm{SM}} + H_{\mathrm{ST}}$$
$$= H_{\mathrm{RES}} + H_{\mathrm{T}}.$$

In this equation h is Planck's constant, ν is the microwave frequency, g is the splitting factor, β is the Bohr magneton, H_{A} is the magnetocrystalline anisotropy field, H_{SM} is the shape anisotropy demagnetizing field, H_{ST} is the magnetostriction anisotropy field, H_{T} is the total anisotropy field, H_{RES} is the observed line position, and α depends on the particle orientation in the external magnetic field. Only the homogenous mode of the spin-wave spectrum is excited in the FMR experiment.

Several distortions of the lineshape can arise due to the various anisotropy terms. Single-domain magnetic particles have rapid thermal fluctuations when the anisotropy energy is on the order of kT and such particles are referred to as superparamagnetic (*24*). The thermal fluctuations prevent observation of the anisotropy.

Iton (*25a*) and co-workers discussed what should happen in the case of small (less than 30 Å) cobalt particles in the FMR experiment. In short, the linewidth, ΔH_{pp}, and the apparent g-value can be used to establish a relative particle size if FMR experiments are done at high enough temperatures. At such high temperatures (25 to 400°C) the resonance line position approaches the true g-value when the magnetic anisotropy is small with respect to the linewidth. A value of $g = 2.18$ is obtained for fcc superparamagnetic cobalt particles. The lower the temperature at which this g value can be obtained, the smaller the particles. Except for the study by Iton and coworkers (*25a*) the use of FMR to study metal particles and sizes in zeolites has been limited to nickel (*24b, 25–28*).

Ferromagnetic resonance spectra for cobalt at X-band frequencies have been observed (*25a*). By comparison of our ferromagnetic resonance data to previous work (*22a*) it is observed that our cobalt particles are less than 30 Å. The data in Table 1 indicate that the superparamagnetic cobalt clusters on zeolite NaX are smaller than any of the other systems reported there. Even at temperatures of 275°C the apparent g-value for TiO_2 and Al_2O_3 does not reach the intrinsic value in the FMR experiment. The cobalt clusters on SiO_2 are also fairly small. The clusters on Al_2O_3 are the largest. No clusters were formed on polystyrene or activated carbon.

FMR spectra for NaX zeolite at various temperatures indicate some anisotropy as well as for supports like SiO_2, Al_2O_3, and TiO_2. Plots of the apparent *g*-values and linewidths each versus temperature are indicative of superparamagnetic cobalt clusters.

CHARGE, SIZE, AND COMPOSITION OF THE CLUSTERS

Charge

Ferromagnetic resonance experiments indicate that these clusters are metallic and have no charge. The pyrophoric nature of these clusters indicates a highly reduced state and discussions with several researchers in this field (*29*) indicate that none of their small particle clusters are pyrophoric with one exception (*22*). Liquid-helium EPR experiments do not show transitions expected for Co^{2+} or Co^{3+} suggesting that these cobalt species are extensively reduced to the elemental state. While transformations of $Co_2(CO)_8$ to $[Co(CO)_4^-]$ or $Co_4(CO)_{12}$ are believed to occur with NaX and NaY zeolite (*30*) it is suggested that if these species are present in our systems that microwave plasma treatment leads to decomposition of such species to cobalt(0) clusters.

Geometry

FMR data indicate that the cobalt clusters have a face-centered cubic geometry. Infrared spectra of the cobalt A, X, and ZSM-5 zeolites that have been treated with the microwave discharge do not show CO bands in infrared portion of the spectrum.

Size of Clusters

The SEM, FMR, BET, and X-ray line broadening results suggest that at least some of the cobalt particles are inside the pores of the X zeolite. The EDX data indicate that cobalt metal is not segregated to the external surface of the zeolite particles and the FMR, SEM, and X-ray results suggest that *all* of the cobalt particles are smaller than 30 Å. We also note from the FMR experiments that the ordering temperature for the zeolite X system is significantly lower than all of the other supports mentioned in Table 1 which suggests that the pore system does not allow the particles to grow as they do on SiO_2, Al_2O_3, and TiO_2 even under similar conditions in the discharge. BET data suggest that pores are at least partially filled with cobalt clusters after the microwave treatment.

CONCLUSION

Microwave discharge methods have been used here to prepare highly dispersed metal atom clusters in zeolites. Several advantages of this preparation method are now apparent (*14*). The method is general; several supports and types of metal species can be used for the deposition. Other metals, for example, Fe, have been used in our laboratory (*14*). The size of the metal particles can be controlled by optimizing the time of microwave discharge, amount of metal, location of the metal in the preparation apparatus, type of metal species, and type of support. Various forms of solids can be used including pellets, glasses, powders, single crystals, and films. With porous solids like zeolites, internal as well as external metal deposition can be controlled. High-power conditions lead to destruction of the supports and are probably less desirable in the case of molecular sieves if the pore structure needs to be retained.

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