Cobalt Sorption in Silica-Pillared Clays

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Silicon pillared samples were prepared following conventional and microwave irradiation methods. The samples were characterized and tested in cobalt sorption. Ethylenediammine was added before cobalt addition to improve the amount of cobalt retained. The amount of cobalt introduced in the original clay in the presence of ethylenediammine was the highest. In calcined pillared clays the cobalt retention with ethylenediammine was lower (ca. 40%). In all cases the presence of ethylenediammine increased twice the amount of cobalt sorption measured for aqueous solutions.

Introduction

The study of cobalt sorption is relevant to understand either cobalt retention as a waste material or cobalt-supported catalysts. The interaction between cobalt and metal oxide supports (zeolites, silica, and alumina, among others) depends on factors such as pH of the adsorption surface, cobalt complex formed, and exchange capacity as well as textural and steric factors. For instance, cobalt has to be positioned in a suitable electronic environment to carry out $DeNO_x$ reaction.[1,2] Furthermore, differences in activity and selectivity of systems such as Co/ferrierite and Co/ZSM-5 may be related to the channel features:[1] smaller channels may provide Co^{2+} coordination that is less favorable for oxygen adsorption.[3] It seems that the traditional properties associated with zeolites, such as acidity and shape selectivity, are not important for this reaction; the electronic influence of zeolites on the cations may be more important. Of course, the overall activity of a catalyst is proportional to the number of exchanged Co^{2+} in the corresponding zeolite.[2] In the same trend, cobalt retention may be used to eliminate it from nuclear wastewaters.

Therefore, new supports, as clays or pillared clays, should provide materials with an original cobalt electronic environment. The amount of retained cobalt should be sensitive to ethylenediammine (EDA) addition as it is in zeolites.

Zeolites and ferrierites are not the only promising supports or adsorbers. Similar solids may be prepared from clays. To enlarge the interlamellar space between clay layers, nanometrical ionic complexes may be intercalated. Pillared clays are, in this way, frequently prepared with zirconium, titanium, chromium, and iron, among other polyoxocations.[4−7] Aluminum, which is a component of montmorillonite clays, is the most frequently reported. The other major component of montmorillonite, silicon, presents the disadvantage that no Keggin ions are formed. If a sol of silicon oxide particles is introduced in the clay, poor pillaring is observed.[7−9] With silicon oligosilsesquioxanes the pillaring is noticeably improved.[10−13] Microwave irradiation of the pillaring solution has been proposed to disperse the intercalating entities.[14] In the same way, microwave irradiation during the intercalation step provides better dispersion and more homogeneous pillar distribution.[14,15] These features are clearly observed in aluminum pillared clays. With this procedure, the concentration of aluminum pillaring solution has been increased and the resulting intercalation time is much shorter.[16]

However, the silica pillaring effect on cobalt sorption behavior has not been studied. Furthermore, the effect of organic compounds such as EDA observed in zeolites has not been established. Cobalt is known to form a hexahydrated ion in the presence of water or an ethylenediammine complex when this organic matter is present.[17−20] The ability of montmorillonite to sorb cobalt from aqueous solutions has been measured in previous works.[21,22]

In this work, we study the effect of the addition of an organic compound before the cobalt exchange. As silicon pillars are

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hydrophobic,[6] if an organic cationic complex is formed, the sorption of cobalt should be improved. We have chosen to prepare silicon pillared samples by the microwave irradiation method and, for comparative purposes, the conventionally prepared samples are also presented.

Experimental Section

Materials. A Sigma clay, $Na^+-Ca^{2+}-$montmorillonite, whose cation exchange capacity (CEC) and surface area were 90 mequiv/100 g of clay and 37 m^2/g, respectively, was used to synthesize silica-pillared clays (Si-PILCs). The silane precursor was 3-aminopropyltrimetoxysilane (APTMS) from Fluka Chemika and the solvents used were methanol and acetone, both from Baker.

The chemical composition of the montmorillonite (wt % on humid basis) was SiO_2, 59.6; Al_2O_3, 18.5; Fe_2O_3, 2.70; MgO, 2.07; Na_2O, 2.78; K_2O, 0.32; CaO, 1.54; H_2O, 12.49.

Preparation of the Pillaring Solutions. In the conventional method, 1 g of 3-aminopropyltrimethoxysilane was mixed with 3 mL of methanol at room temperature, and then 0.3 mL of an aqueous solution of HCl (16%) was added to the mixture. The solution was stirred for 27 h and then 7 mL of acetone was added to it. The solution was then heated to reflux for 1 h and cooled at room temperature with stirring for 3 h. The solution was stored in the dark for 24 h, known as the aging stage. This procedure for the hydrolysis of the silane was reported by Fetter et al.[11]

For preparation of the pillaring solution by microwave irradiation, the reagent ratios were the same as for the conventional method. The methanol/APTMS/HCl mixture was microwave-irradiated in a domestic oven (Philco) operating at 2.45 GHz and at 180 W of power. In this method the solution was not stored in the dark as the aging is very short, which is an important advantage of this method. The pillaring solution was first irradiated for 10 min, then acetone was added to the methanol/APTMS/HCl solution, and the resulting mixture was again microwave irradiated for 40 min.

Preparation of the Pillared Clays. In conventional preparations, the clay was not dispersed in water. The pillaring solution, prepared by the conventional method, was directly added dropwise to the clay powder and maintained under stirring for 36 h at room temperature. The final pH was 9.5−9.7; such a high pH has to be attributed to the species formed when APTMS is solved. Four samples were prepared with varying amounts of silicon (millimoles) per gram of clay (Si/clay = 2, 3, 4, and 5). The solids were filtered and dried at 60 °C.

In microwave-irradiated samples, the clay was added as a powder to the pillaring solution obtained previously by the microwave irradiation method. The slurries were stirred continuously to homogeneity and then microwave-irradiated for 10 min (final pH = 9.0−9.2). Again four samples resulted with the same Si/clay ratios as in conventional preparations. They were filtered and dried at 60 °C.

Note that for the preparation of the clays a small amount of water was used; however, most probably, the sample properties can be improved with a full washing.[13,22]

Thermal Treatments. To remove the organic matter present in the pillars, the intercalated clays were thermally treated in air at 600 °C as in ref 22. The air flow was about 100 mL/min with a heating rate of 60 °C/h. The calcination temperature was maintained for 5 h. Although the clay structure may be partially affected, only at such a temperature are most organics eliminated.

Characterization Techniques. A Siemens D500 diffractometer coupled to a copper anode tube, Cu Kα radiation, was used to study the nonoriented powder samples. The nitrogen adsorption isotherms at −196 °C were recorded on a Micromeritics Gemini 2360 automated gas adsorption system. The samples were previously outgassed at 300 °C for 3 h. Surface areas were calculated according to the BET equation. Atomic absorption (Perkin-Elmer 2280 spectrophotometer) was the method utilized to obtain the Si content of the initial and intercalated clays. Infrared spectra were recorded on a Nicolet Magna Infrared 500 spectrometer after the samples were mixed with KBr. Scans were taken in the mid-IR range (400−4000 cm^{-1}).

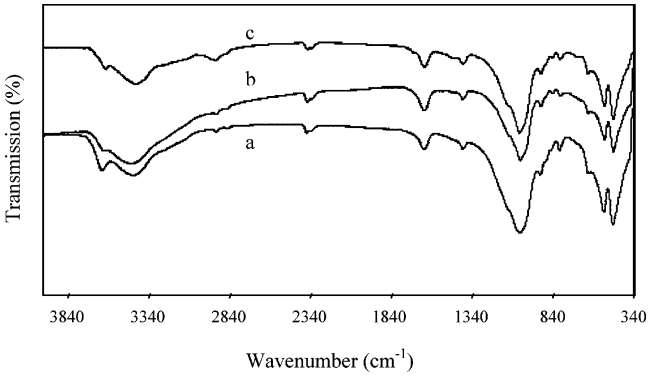

Figure 1. Infrared spectra of intercalated samples compared to the original clay: (a) original clay, (b) Si/clay = 2, conventional; and (c) Si/clay = 2, microwaved.

Cobalt Sorption. As in our previous works, we express the concentrations in normal units. The equivalent is formally defined as the mass in grams of a substance that will react with 6.022×10^{23} electrons (Avogadro's number). Or, the equivalent is the number of grams of a substance that will react with a gram of free hydrogen. Equivalents have an advantage over other measures of concentration (such as moles) in quantitative analysis of reactions. The best feature of using equivalents is that there is no need to study much about the nature of reaction, that is, no need to analyze and balance chemical equations. Equivalents of reactants react in equal number to yield the equal equivalents of products. And of course, 1 equiv of Co^{2+} is equal to 1 equiv of Na^+.

For the cobalt sorption determinations, 0.1 g of the original, intercalated, or calcined sample was in contact with 10 mL of a 0.05 N cobalt nitrate solution at room temperature. The mixtures were shaken for 3 h and the solids were separated by centrifugation. They were then washed with deionized water. All samples were dried in air at 60 °C overnight in an oven. Cobalt uptake in the solids was determined by neutron activation analysis. For these analyses, samples were irradiated in a Triga Mark III nuclear reactor for 15 min with an approximate neutron flux of 10^{13} neutrons/cm^2·s. The 1170 and 1330 photopeaks from ^{60}Co produced by the nuclear reaction ^{59}Co (n,γ) ^{60}Co were measured with a Ge/hyperpure solid-state detector coupled to a computerized 4096 channel pulse height analyzer.

A second set of measurements was carried out by adding 3 mL of ethylenediammine (EDA) to 0.1 g of clay before cobalt exchange. The mixture was maintained under stirring for 15 min. After each exchanging step the clay was washed with 15 mL of distilled water. All samples were dried in air at 60 °C overnight in an oven.

Results and Discussion

The infrared spectra of the original clay and the Si/clay = 2 intercalated samples, conventional and microwaved, are presented in Figure 1. No significant variations among the three samples are observed; hence the clay structure is not altered with the intercalation procedure only the hydroxylation degree diminishes.

In the conventionally prepared samples, the elemental composition of the original clay and the samples whose nominal Si/clay ratio was 2 and 5 provides Si/Al molar ratios of 2.58, 2.72, and 3.45, respectively. In the microwaved samples these ratios are different as they are higher: 2.90 for the Si/clay = 2 and 3.60 for the Si/ clay = 5. More pillars seem to be incorporated between the layers during the microwave procedure.

Figure 2 compares the X-ray diffraction patterns of the materials with Si/clay ratios of 2 and 5. As the Si/clay increases, the 001 peak turns out to be sharper and well-resolved in the conventionally prepared materials. Instead, in the microwaved samples, the sharp peak appears for the Si/clay = 2 sample. Hence, in conventionally prepared samples a large amount of silicon species propitiates a better intercalation with an interlamellar distance

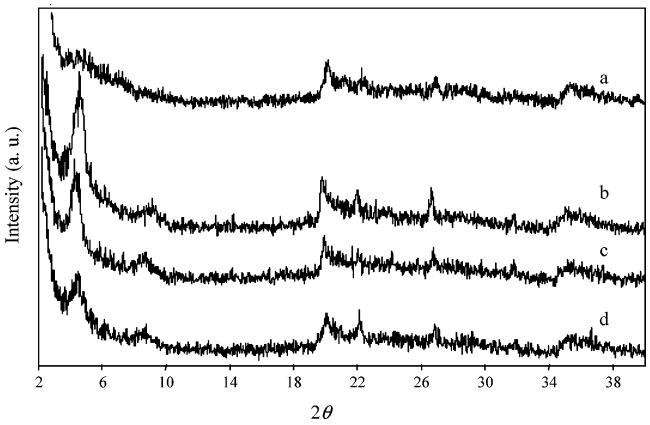

Figure 2. X-ray diffractograms of the intercalated samples: (a) Si/clay = 2, conventional; (b) Si/clay = 2, microwaved; (c) Si/clay = 5, conventional; and (d) Si/clay = 5, microwaved.

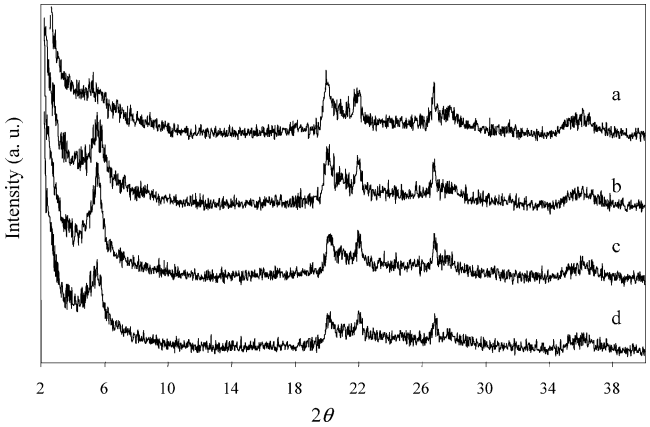

Figure 3. X-ray diffractograms of the calcined samples: (a) Si/clay = 2, conventional; (b) Si/clay = 2, microwaved; (c) Si/clay = 5, conventional; and (d) Si/clay = 5, microwaved.

d_{001} = 19.5 Å. The X-ray diffraction pattern of the low silicon ratio sample presents a broad 001 peak from distances d_{001} = 14.7 up to 19.5 Å, showing that only some layers are intercalated. Hence in anhydrous environment, the diffusion of cationic species is difficult as the clay is not well dispersed. In the low silicon-containing samples, this effect is enhanced by the low amount of silicon solution. The silicon pillars, then, are expected to diffuse only in some layers and to be located preferentially in the outer parts of the particles. Instead in the Si/clay = 5 sample the amount of solution is enough for an adequate diffusion and, hence, it provides a homogeneously intercalated sample.

For the nonconventional samples, microwave irradiation propitiates the easy diffusion of silicon species, hence a clear and sharp 001 peak is observed in the Si/clay = 2 samples. Instead, in the Si/clay = 5 sample, the irradiation combined with the silicon species in excess promotes the disorder of the clay, and the 001 peak then turns out to be less intense.

The 600 °C calcined samples show a lower interlaminar space, d_{001} = 15.8 Å, as the 001 peak is shifted toward higher angles (Figure 3). The difference between the intercalated and the calcined samples is the elimination of aminopropyltrimethoxy radicals; the final pillars could be, indeed, constituted by siloxane complexes, which were observed in a previous work by NMR.[11] However, it is difficult to believe that after a calcination at 600 °C any organic complex remains. Still, the presence of some silica-like phases cannot be excluded as the preparation procedure was not the same. Note that the initial features of the diffraction patterns (intercalated samples) are maintained in the calcined samples; therefore temperature (up to 600 °C) does not propitiate the diffusion or the delocalization of the pillars in the high Si-containing samples in both preparations.

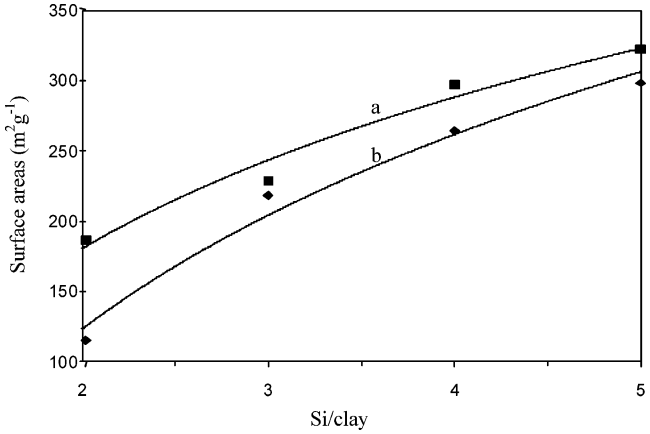

Figure 4. Surface areas as a function of the Si/clay molar ratios of the calcined samples: (a) microwaved and (b) conventional.

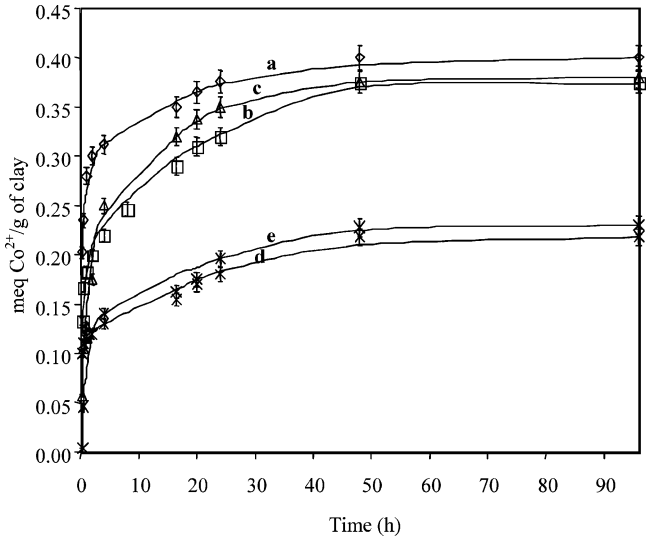

Figure 5. Cobalt sorption curves of samples: (a) original clay; (b) Si/clay = 2, intercalated, microwaved; (c) Si/clay = 5, intercalated, microwaved; (d) Si/clay = 2, calcined, microwaved; (e) Si/clay = 5, calcined, microwaved.

Specific surface areas of the calcined samples are compared in Figure 4; they are 115 and 187 m^2/g for the Si/clay = 2 samples and 298 and 323 m^2/g for the Si/clay = 5 samples in the conventional and microwave preparations, respectively. Pillared clays prepared following the microwave technique present systematically higher areas than the samples obtained conventionally. As the interplanar distance is independent of the Si/clay ratio, the variations in the surface area reflect the number of incorporated pillars and either the number of pillared layers or the regularity of the pillar location in the interlamellar space. Therefore, as previously stated, the microwave irradiation incorporates, one way or the other, more pillars than the corresponding conventional preparation and the number of pillars depends on the Si/clay ratio. These differences diminish as the Si/clay ratio increases.

The cobalt sorption curves of the original, intercalated, and calcined microwaved samples are compared in Figure 5. Cobalt present in the solution has been reported to be in the form of an octahedral aqueous complex $[Co(H_2O)_6]^{2+}$.[17] The curves reach the sorption equilibrium after 30 h. Although the exchange capacity (CEC) of the original clay is 0.90 mequiv/g of clay, it

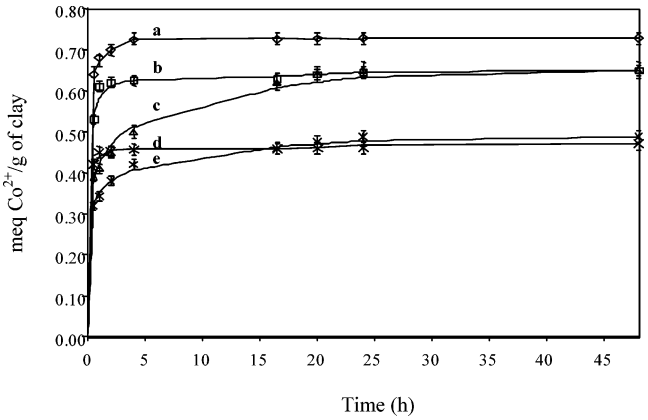

Figure 6. Cobalt sorption curves with EDA of samples: (a) original clay; b) Si/clay = 2, intercalated, microwaved; (c) Si/clay = 5, intercalated, microwaved; (d) Si/clay = 2, calcined, microwaved; (e) Si/clay = 5, calcined, microwaved.

retains only 0.40 mequiv of Co^{2+}/g of clay; the two intercalated samples retain 0.37 mequiv of Co^{2+}/g of clay, whereas both calcined samples 0.23 mequiv of Co^{2+}/g of clay, within the error range. Therefore, in the original clay only half of the sites are reached by cobalt. If the X-ray diffraction pattern is obtained after cobalt sorption, the interlamellar space 001 turns out to be 15.5 Å; it was 12.6 Å. The large hydrated cobalt species $[Co(H_2O)_6]^{2+}$, then, occupy the sodium and calcium ion sites, expanding the clay network, with the final effect being the hydration of the interlamellar space; the values correspond to a monolayer or a bilayer of water molecules.

These same species modify the intercalating complexes as the interplanar distance in the 001 direction diminishes from 19.5 to 18.4 Å with cobalt sorption. It seems that cobalt is incorporated into the intercalating species, diminishing their size, as it is sequestered into the pillar. Although the pillars block the original cation exchange sites of the clay, cobalt is now included in the pillar itself. One could speculate that the presence of cobalt in close interaction with the pillar walls alters the shape of the pillar. The resulting particle may be elongated in the direction of the layers. Nevertheless, in the calcined samples, the 001 peak position (d_{001} = 15.8 Å) remains the same before and after cobalt sorption, showing that cobalt interaction with the intercalating species does not alter their size. Still, as the retained cobalt is the same in the Si/clay = 2 and 5 materials, one has to assume that cobalt is adsorbed on the pillars and the free cationic sites of the clay.

If EDA is in contact with the clay before the cobalt solution addition, the curves (Figure 6) reach equilibrium in a much shorter period (equilibrium time = 4 h; the equilibrium time for Si/clay = 5 calcined and noncalcined samples is 18 h). The values of the plateau are twice as high as the corresponding values of the curves without EDA (Table 1). In the original clay the 001 interplanar distance was 12.6 Å before exchange, 15.5 Å after cobalt exchange, and 14.8 Å after EDA addition and cobalt exchange. As shown in previous works,[18] a coordination complex between cobalt and EDA is formed, $[Co(en)_3]^{2+}$, which in this work is labeled $[Co(EDA)_3]^{2+}$. Of course, in classic coordination chemistry the formation of tris-en is not favored. In this work

Table 1. Equilibrium Values for Cobalt Sorption with and without EDA

sample	Co retained in equilibrium (mequiv/g)	Co retained in equilibrium after EDA addition (mequiv/g)
original clay	0.40	0.73
Si/clay = 2, intercalated	0.37	0.64
Si/clay = 2, calcined	0.22	0.47
Si/clay = 5, intercalated	0.38	0.65
Si/clay = 5, calcined	0.23	0.49

the species are nanometrical and react with surfaces; therefore we are in a heterogeneous problem, and a catalytic effect of the surfaces is expected. According to Hutta and Lunsford,[24] the reactions that may occur in the Co montmorillonite when EDA is added at room temperature are the following:

$$Co^{2+}(H_2O)_6 + 3EDA \rightarrow Co(EDA)_3^{2+} + 6H_2O$$

$$Co(H_2O)_x^{2+} + 2EDA \rightarrow LCo(EDA)_2(H_2O)$$

where L = H_2O, clay oxygen, or monodentate ethylenediammine. Hence, with EDA addition, cobalt intercalates as the EDA complex, which is smaller than the hydrated cobalt. Therefore, on one hand, more EDA complexes can occupy the free exchange sites, and on the other hand, the EDA complexes diffuse easily. This observation is in agreement with the speed to reach the plateau in the sorption curves. Still, the EDA species interact with the silicon complexes present in the intercalated samples: for instance, in the Si/clay = 2 sample, it was 19.5 Å and it ends up equal to 15.6 Å, but when they are calcined, they are not altered; indeed, the 001 distances (d_{001} = 15.8 Å) are constant.

Conclusion

The microwave irradiation method, which eliminates the washing step in the synthesis procedure, was used to prepare the samples. It provided materials with more pillars. Furthermore, the pillars were distributed more homogeneously. The Si/clay ratio in the intercalated clays determines the interlamellar distance, the surface area, and the amount of retained cobalt. The amount of cobalt retained was independent of the Si/clay ratio, although the Si/clay = 5 sample presented the highest surface area.

With the addition of EDA, the capacity of cobalt sorption was improved up to 2-fold. A complex with EDA is formed that is smaller than the hydrated cobalt ions; hence the mobility and the stress introduced in the clay are more favorable. More exchange sites are reached. It has to be emphasized that cobalt species, either hydrated or as EDA complexes, interact with the Si pillars as well as with the exchange sites of the clay.

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