

A DSC Study of Intrazeolite Copper(II) Phthalocyanine Formation

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Abstract. The template synthesis of copper(II) phthalocyanine by the condensation of dicyanobenzene within the supercages of Cu(II) exchanged X and Y type zeolites was studied using differential scanning calorimetry. The exotherms for intrazeolite and surface complexation have been resolved. These thermal events exhibit a dependence on the copper loading and hydration level which has been interpreted as a pressure effect.

Key words. Zeolite, phthalocyanines, DSC.

1. Introduction

The formation of zeolite encapsulated metal complexes of phthalocyanine (Pc) has been accomplished in synthetic faujasite type zeolites X and Y by a template synthesis [1–14]. This involves the condensation of four 1,2-dicyanobenzene (DCB) molecules around an intrazeolite metal ion to form the encapsulated metallophthalocyanine. The dimensions of the X or Y type zeolite are such that the DCB can diffuse through the ~ 8 Å apertures but the resulting MPc complex (~ 13 Å) is too large to escape the supercage. Since the MPc complex is slightly larger than the zeolite supercage (~ 12 Å), the phthalocyanine ring is probably distorted from planarity and formation of the intrazeolite complex should be energetically less favorable than outside the zeolite. The minimum deformation of the Pc ligand in NaY has been calculated to be 37.27° out of the plane [14]. We recently reported a method for studying the energetics of intrazeolite MPc formation based on differential scanning calorimetry (DSC) [15] and measured a significant increase in the formation temperature of phthalocyanine for Co(II) exchanged NaY compared with CoCl_2 . Another potential advantage of using DSC is the possibility of differentiating between the formation of encapsulated and surface complexes, since there are no steric constraints associated with the formation of the latter. The charge balancing metal ions in these zeolites can be quite mobile, and their migration to the surface to form complexes there is feasible. In this paper we present evidence for the formation of intrazeolite copper(II) phthalocyanine as well as surface complexes using synthetic faujasite type zeolites X and Y. Additionally, we have used DSC to study the effects of metal loading and pressure on the template synthesis.

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2. Experimental

Zeolites NaY (LZY-52) and NaX (13X) were obtained from Union Carbide. NaA and 1,2-dicyanobenzene were obtained from Aldrich. The zeolites were exchanged with copper(II) by slurring an aqueous solution (pH \sim 6) of CuCl_2 with the zeolite at 353 K for 24 h. The zeolites were filtered, washed with deionized water until the filtrate tested negative for chloride ion, and then dried in a vacuum oven at 353 K. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Thermal behavior was measured using a Perkin-Elmer DSC-2 differential scanning calorimeter in the temperature range of 290–600 K. The DSC was calibrated using indium and tin samples. Samples were loaded as 1 : 1 (w/w) mixtures of zeolite and DCB. The reaction mixtures ranging between 0.3 and 5 mg were sealed in Perkin-Elmer stainless steel pans. The advantages of this type of reaction vessel, which primarily involve containment of the volatile reagents, have been previously discussed [15]. Additionally, we have found that the first row transition metal halides react with aluminum pans, which would complicate results obtained in these vessels. All DSC data were collected at the same scanning rate of 20 K min^{-1} and with a sensitivity in the range of $5\text{--}20 \text{ mcal s}^{-1}$. The formation of intrazeolite MPc complexes by this method has been firmly established by several groups using a battery of techniques [1–14]. Therefore, the resulting samples were not characterized further.

3. Results and Discussion

The formation of copper phthalocyanines from dicyanobenzene has been studied by differential scanning calorimetry using aluminum pans [16]. The peak temperature for phthalocyanine formation varied over a 150 K range depending upon the source of copper. A peak temperature at 533 K for CuPc formation from $\text{CuCl}_2 \cdot 2 \text{ H}_2\text{O}$ was reported [16]. Our studies indicate the peak temperature of $451 \pm 1 \text{ K}$. We ascribe the difference to our use of sealed stainless steel pans which do not react with the metal halide. Since we have exchanged the zeolites with CuCl_2 we take the reaction of $\text{CuCl}_2 \cdot 2 \text{ H}_2\text{O}$ with DCB in SS pans as our reference for extrazeolite MPc formation.

Thermograms for the reaction of dicyanobenzene and $\text{CuCl}_2 \cdot 2 \text{ H}_2\text{O}$, CuNaY-3 (5.37% Cu), CuNaX (6.14% Cu) and CuNaA (5.17% Cu) are shown in Figure 1. The endotherms for CuCl_2 correspond to loss of water of hydration ($\sim 382 \text{ K}$) and the melting of dicyanobenzene. The presence of the zeolites is expected to have an effect on the colligative properties of the DCB which is manifested in the observed variance in DCB melting point. Although the zeolites are hydrated, an endotherm associated with dehydration is never observed in the sealed SS pans. A broad peak is observable, however, when the zeolites alone are placed in open pans. Apparently under the pressure generated in the sealed vessels the zeolite remains partially hydrated.

The exotherms in Figure 1 correspond to the formation of phthalocyanine complexes. The onset and peak temperature for these exotherms are listed in Table I and are reproducible within $\pm 1 \text{ K}$. As expected the formation of CuPc from CuCl_2 occurs at a much lower temperature than inside the zeolite or on the crystal

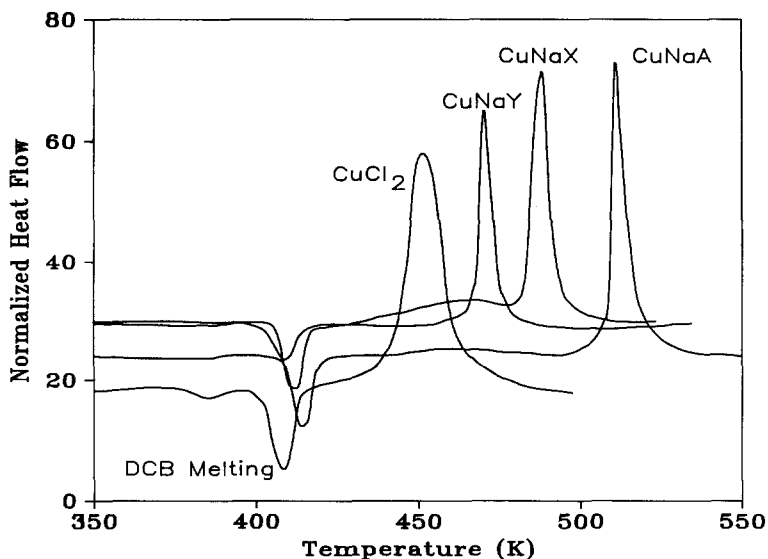


Fig. 1. DSC thermograms for the reaction of 1,2-dicyanobenzene with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CuNaY-3 , CuNaX and CuNaA .

Table I. Exotherms for CuPc formation

Sample	Onset (K)	Peak (K)	Amt of reactants (mg)
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	432	452	1.8
CuNaY-3	461	470	1.5
CuNaX	477	488	2.3
CuNaA	500	512	2.1

surface. The X and Y zeolites have the same structure but differ in their Si/Al ratios (1.2 vs. 2.4). The known increased mobility of Cu(II) ions in the Y zeolite compared to the X [17] is reflected in the lower peak temperature. The CuNaA was included because the A type zeolite has a similar size supercage to X and Y (11.4 vs. 12 Å in diameter) but the apertures to the large cavity are much smaller (4.1 vs 7.4 Å), thus prohibiting dicyanobenzene from accessing the interior of zeolite A. Hence the exotherm for MPC formation for CuNaA must be for the surface reaction. The higher temperature for this peak is expected since the mobility of the cations is controlled by Coulombic interactions at the smaller openings to the supercage which are defined by negatively charged oxygens.

For zeolites X and Y, there should be no more than one CuPc complex encapsulated per supercage. However, the Cu(II) exchanged zeolites contain several copper ions that could react to form surface species. This means the thermal events associated with formation of surface complexes could conceal the intrazeolite complexation if their transitions are energetically similar. We evaluated the effects of copper loading on the phthalocyanine reaction and the observed thermograms by

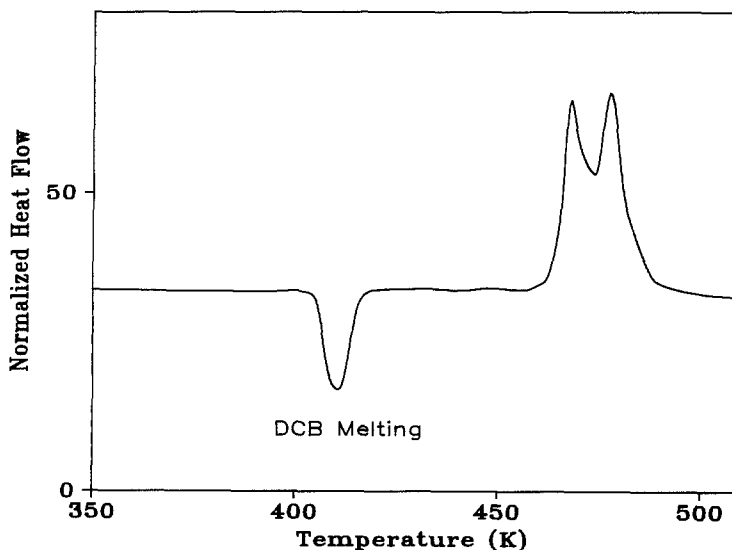


Fig. 2. DSC thermogram for the reaction of 1,2-dicyanobenzene with CuNaY-2.

examining the following series of Cu(II) exchanged Y type zeolites: CuNaY-1 (1.72% Cu), CuNaY-2 (3.16% Cu), CuNaY-3 (5.37% Cu) and CuNaY-4 (5.78% Cu). At the lower loadings, corresponding to ~ 4 and 8 Cu^{2+} ions per unit cell, we observed a second exotherm associated with the phthalocyanine formation as illustrated for CuNaY-2 shown in Figure 2. The thermal event near 470 K appears to be independent of the concentration of copper ions in the zeolites, consistent with metallophthalocyanine formation on the zeolite surface, where there are no steric constraints on complexation. The higher temperature event is assigned to intrazeolite CuPc formation which is less favorable. The differences between samples containing different metal loadings must be related to the accessibility and mobility of copper ions to the supercage. The ratio of peak areas for intrazeolite complexation versus surface phthalocyanine formation on Cu^{2+} exchanged NaY is shown in Figure 3. If the areas under the exotherms are representative of the relative amounts of complex formed, then there is clearly a relationship between the copper loading and the intrazeolite CuPc synthesis. The more copper that is exchanged into the zeolite, the greater the level of encapsulation during reaction with DCB.

The condensation of dicyanobenzene to form the phthalocyanine macrocycle involves a large negative volume of activation (calculated $\Delta V^\ddagger \cong -37.32 \text{ mL mol}^{-1}$) [18] such that the rate of reaction should be sensitive to pressure [19]. It has recently been reported that high pressure improves the yields and rates of copper(II) phthalocyanine formation [20]. The zeolites used in our study contain $\sim 25\%$ water by weight and heating this water to 600 K in a sealed pan can generate considerable pressure. The stainless-steel pans used in this study are rated to 24 atmospheres which limits the amount of reactants that can be loaded into the pans. We found that upwards of 5 mg of reactants (1:1 w/w, zeolite:DCB) will

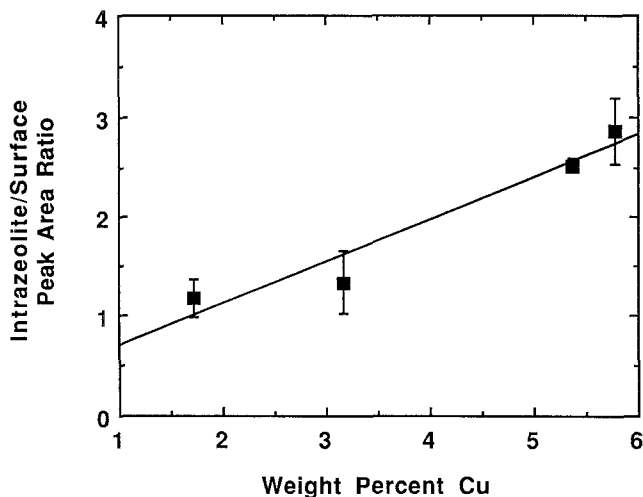


Fig. 3. A plot of weight percent copper exchanged in NaY versus the ratio of peak areas for the exotherms associated with intrazeolite and surface CuPc formation, respectively.

rupture the seals. In order to insure the integrity of the reaction vessels at high temperatures we began using smaller amounts of reactants (< 1 mg) and found that the exotherm for intrazeolite CuPc formation in the Y type zeolites was quite sensitive to the change in amount of reactants. As the amount of reactants was decreased, the exotherm for intrazeolite MPc formation shifted to higher temperatures. Table II lists the results for the series of CuNaY samples using < 1 mg of reactants. At this level even the zeolites containing the higher concentration of copper (CuNaY-3 and CuNaY-4) exhibit two exotherms for MPc formation.

The relatively small changes in pressure that can be effected by adjusting the sample loading in the capsule should not have a significant impact on the surface reactions. There is very little variance in the lower temperature exotherm (~ 460 K) which has been assigned to the phthalocyanine formation on the outside of the zeolite crystals. This is supported by the lack of change in the peak position for the formation of CuPc from CuCl_2 using different amounts of reactants. Additionally, the exotherms for CuNaA + DCB, which can only form surface complexes, are similarly unaffected by changing the quantities of reactants. In contrast, the CuPc formation inside the zeolite occurs at a higher temperature if the amount of reactants is decreased. Thus, a high level of exchange coupled with high pressure

Table II. Exotherms for CuPc formation

Sample	Onset (K)	Peaks (K)	Amt of reactants (mg)
CuNaY-1	453	468,484	0.98
CuNaY-2	453	466,474	0.91
CuNaY-3	457	467,474	0.97
CuNaY-4	461	473,479	0.96

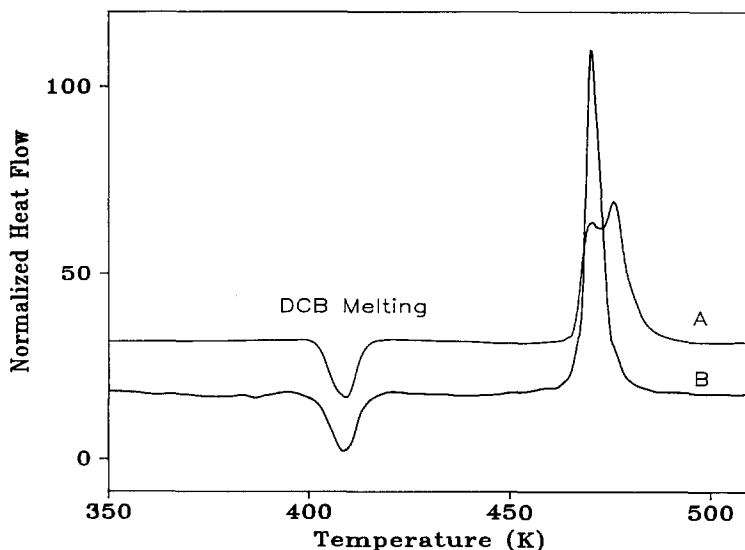


Fig. 4. DSC thermograms for the reaction of 1,2-dicyanobenzene with CuNaY-3 at pan loadings of (A) 1.1 mg and (B) 1.5 mg of reactants.

favors intrazeolite complexation. In Table II the amount of reactants was ~ 1 mg for all samples but the high loading CuNaY-4 had a peak separation of 6 K while the lowest loading CuNaY-1 had a separation of 16 K. The CuNaX sample which has the highest exchange level of the samples studied exhibited a single peak with as low as 0.7 mg of reactants. We plan to explore further the relationship between pressure and loading in X type zeolites.

The effect of water pressure in CuPc formation is apparently amplified inside the zeolites where the mobility of cations as well as a possible role in the mechanism may be enhanced. Figure 4 shows the thermograms for the reaction of 1,2-dicyanobenzene with CuNaY-3 with mixture loadings of 1 and 1.5 mg, respectively. At the lower loading the intrazeolite CuPc formation occurs ~ 7 K higher than the surface reaction. However, the addition of 0.5 mg more of the zeolite/DCB mixture to the pan results in the encapsulation process being energetically comparable to the surface reaction. The standardized areas under the peaks in thermograms A and B are the same within 10%. These results are reproducible with other loadings and samples which further supports our contention that at high pressure and metal loading the exotherm for intrazeolite MPC formation shifts to lower temperatures producing a single peak.

The lack of an endotherm for water desorption that can be observed in open pans suggests that in the sealed pans the water remains largely associated with the zeolite. These conditions appear to favor intrazeolite MPC formation. This is in contrast to the report that on a preparatory scale the zeolites should be partially dehydrated prior to reaction to insure access to the supercages [7]. It would appear from this study that zeolitic water is advantageous in a closed reaction system because the steam enhances cation mobility and may provide reducing equivalents during phthalocyanine formation.

4. Conclusions

We have further demonstrated the utility of differential scanning calorimetry (DSC) in the study of intrazeolite metallophthalocyanine formation. In the case of copper (II) we have resolved the exotherms for formation of surface and encapsulated complexes. The sensitivity of the exotherm associated with intrazeolite synthesis indicates the reaction improves with an increase in copper loading as well as an increase in pressure provided by zeolitic water. The peak temperatures for CuPc entrapped in NaY are considerably lower than for CoPc [15] which is consistent with reported formation constants for CuPc and CoPc [21]. Preliminary results with other transition metal exchanged X and Y type zeolites in this reaction are also in agreement with known MPc stabilities. We anticipate the application of DSC in the formation of intrazeolite metal complexes will be of significant value in determining optimum synthesis conditions.

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