Reaction of Interstitial Cyanide Ions in a Hydrotalcite-like Material with Organic Chlorides

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A hydrotalcite-like material, $Mg_6Al_2(OH)_{16}Cl_{2-x}CN_x{\bullet}4H_2O$ (x= 1.53−1.94), was prepared and tested as a reagent for the nucleophilic substitution for chlorine atom of $C_6H_5CH_2Cl$, C_4H_9Cl, and C_3H_7Cl by the CN^- ions in the interlayer of the material. The corresponding organic cyanides were obtained at 353 K in a non-polar solvent, toluene.

Hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3{\bullet}4H_2O$, is a naturally occurring anionic clay mineral[1] and can be synthesized.[2] Isomorphously substituted materials, $Mg_6Al_2(OH)_{16}A^{n-}_{2/n}{\bullet}4H_2O$ (A^{n-}= Cl^-, NO_3^-, SO_4^{2-}, etc.), generally referred to hydrotalcite-like materials, can also be synthesized.[3,4] Here, Mg^{2+} and Al^{3+} cations constitute positively charged hydroxide layers between which interstitial A^{n-} anions and water molecules are located, the former being anion-exchangeable.[5] The anion-exchangeability offers an opportunity for introducing various interstitial anions into the interlayer space of hydrotalcite-like materials.

The interstitial anions are known to invoke a nucleophilic substitution of halogen atom of organic halides as demonstrated by Martin and Pinnavaia,[6] who reported that butyl bromide was converted into butyl iodide in a non-polar solvent such as toluene by the action of I^- ion in an interlayer of a hydrotalcite-like material, $Zn_2Cr(OH)_6I_2{\bullet}2H_2O$. The reactions of benzyl- and butyl bromides with interstitial Cl^- ion of a hydrotalcite-like material, $Mg_6Al_2(OH)_{16}Cl_2{\bullet}4H_2O$, affording the corresponding chlorides have also been reported.[7] These methodologies must be applicable to the preparation of a variety of organic compounds by using hydrotalcite-like materials with various interstitial anions.

In this work, a CN^--containing hydrotalcite-like material was prepared by the anion-exchanging method, and used for the conversion of organic chlorides such as benzyl- and butyl chlorides into the corresponding cyanides. According to this procedure, organic cyanides can be obtained using a solid cyanation reagent and even in a non-polar solvent.

The hydrotalcite-like material, $Mg_6Al_2(OH)_{16}Cl_2{\bullet}4H_2O$, was synthesized by adding dropwise an aqueous solution of NaOH into an aqueous solution of $MgCl_2{\bullet}6H_2O$ and $AlCl_3{\bullet}6H_2O$ at 353K for 18 h (Mg^{2+}/Al^{3+} molar ratio= 3), followed by filtration, washing, and drying in vacuo at 383 K for 12 h.[3] The material was then converted into the CN^--containing one by anion-exchanging Cl^- ions with CN^- ions in an aqueous solution of KCN (CN^-/Cl^-= 4.0, 12, 36) at 353 K for 18 h, followed by working up as above. The amount of residual chlorine in the anion-exchanged samples was determined by ion chromatography, and was 2.77wt%, 2.04wt%, and 0.37wt% for the samples anion-exchanged at CN^-/Cl^-= 4.0, 12, and 36, respectively. Using these chlorine contents, the degree of anion exchange was calculated to be 77%, 82%, and 97% at CN^-/Cl^-= 4.0, 12, and 36, respectively. At CN^-/Cl^-= 36, an almost complete anion exchange was performed. Powder X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku RINT2000 diffractometer using monochromatic Cu*K*α radiation, operating at 40 kV and 80 mA.

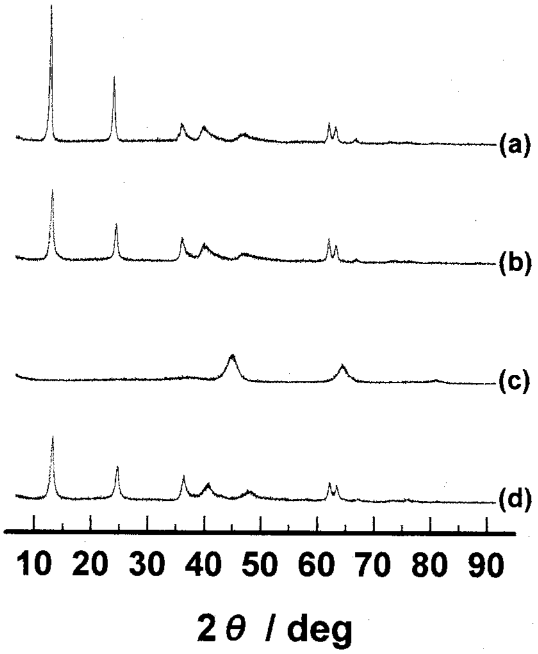

Figure 1. Powder XRD patterns of hydrotalcite-like materials and calcined hydrotalcite.
(a) parent Cl^--containing hydrotalcite-like material, (b) 97% CN^--exchanged sample, (c) hydrotalcite calcined at 823 K for 10 h, (d) rehydrated in aqueous KCN solution.

Figure 1a shows an XRD pattern of $Mg_6Al_2(OH)_{16}Cl_2{\bullet}4H_2O$ used as a parent material for the anion-exchange. The 003 reflection appeared at 2θ= 11.1°, from which the basal spacing was determined to be 8.0 Å. Because the layer thickness of hydrotalcite-like materials is 4.8 Å,[3] the interlayer spacing is therefore 3.2 Å. The XRD pattern for the 97% CN^--exchanged sample is shown in Figure 1b. From the 003 reflection at 2θ= 11.4°, the basal spacing was determined to be 7.7 Å, the interlayer spacing being 2.9 Å. For the 77% and 82% CN^--exchanged samples, the interlayer spacing was also 2.9 Å.

A 0.5 g portion of the CN^--containing hydrotalcite-like material was suspended in 30 cm^3 of toluene. Benzyl chloride or butyl (or propyl) chloride (1.73 mmol) together with decane as an internal standard was added, and the temperature was kept at 353 K. The reaction mixture was analyzed by a gas chromatograph. Benzyl chloride was converted into benzyl cyanide, the time course of the benzyl cyanide yield is shown in Figure 2. For the 97% CN^--exchanged material, the yield increased monotonously and attained 0.79 mmol at 4 h. At 18 and 20 h, the yield did not change practically, the yield at 20 h being 0.97 mmol. Since a 0.5 g portion of the material contains 1.63 mmol of the interstitial CN^- ion, 59% of the CN^- ion was consumed by the reaction. For the 77% and 82% CN^--exchanged materials, the benzyl cyanide yield at 20 h was 1.00

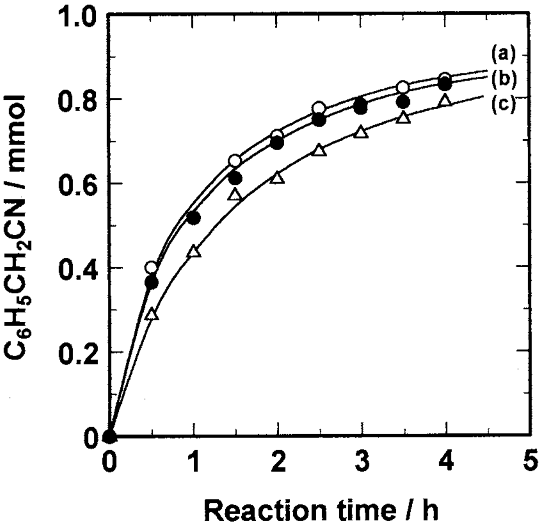

Figure 2. Time course of benzyl cyanide yield.
The degree of anion exchange with CN^- ion was 77% (a), 82% (b), and 97% (c).
Reaction conditions: $C_6H_5CH_2Cl$= 1.73 mmol, toluene (solvent)= 30 cm^3, hydrotalcite-like material= 0.5 g, 353 K.

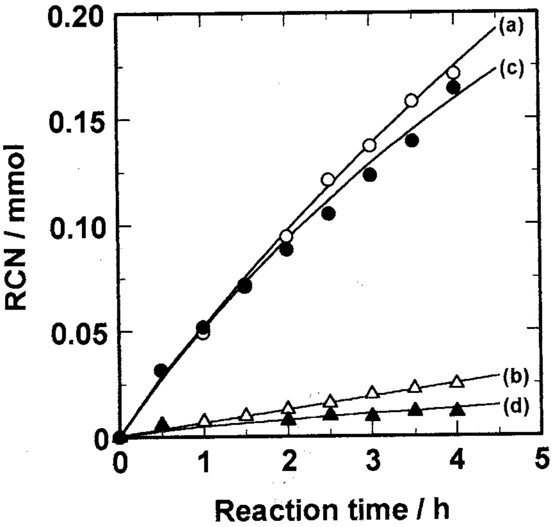

Figure 3. Time course of butyl (or propyl) cyanides yield.
The degree of anion exchange with CN^- ion was 97%.
Alkyl chloride= C_4H_9Cl (a), $^{i}C_4H_9Cl$ (b), C_3H_7Cl (c), $^{i}C_3H_7Cl$ (d).
Reaction conditions: alkyl chloride= 1.73 mmol, toluene (solvent)= 30 cm^3, hydrotalcite-like material= 0.5 g, 353 K.

and 0.99 mmol, and the materials used for the reaction contained 1.27 and 1.36 mmol of CN^-ion, respectively, 78% and 72% of the interstitial CN^-ion being consumed.

When primary and secondly butyl (or propyl) chlorides were used, the corresponding cyanides were formed. Reactions were carried out using the hydrotalcite-like material anion-exchanged by 97%, the results being shown in Figure 3. The reaction using these alkyl chlorides proceeded at far lower rate than that of benzyl chloride shown in Figure 2. This is similar to the observation in the reactions of butyl- and benzyl bromides with interstitial Cl^- ion of a hydrotalcite-like material, $Mg_6Al_2(OH)_{16}Cl_2{\bullet}4H_2O$, affording the corresponding chlorides.[7] The fact that the rate depends strongly on the kind of alkyl group indicates that the reaction is not controlled by the diffusion process of CN^-ion in the interlayer space but the reaction of CN^-ion towards the alkyl chlorides is a rate determining step.

A halide exchange between benzyl chloride and butyl bromide using $Mg_6Al_2(OH)_{16}Cl_2{\bullet}4H_2O$ as the catalyst has been reported.[8] Thus, butyl bromide undergoes a halide substitution by the interstitial Cl^-ion, leaving Br^-ion in the interlayer space; the intercalated Br^-ion, in turn, attacks benzyl chloride to yield benzyl bromide, leaving Cl^- ion in the interlayer space.[8] Repetition of this cycle establishes a catalytic process. In this work, a trial was made to convert catalytically benzyl chloride into benzyl cyanide using the CN^--containing hydrotalcite material in the presence of KCN as a cyanation reagent. However, no catalytic conversion was observed.

When hydrotalcite is thermally decomposed into an oxide and then rehydrated, the hydrotalcite-type structure is reconstructed by taking up anions present in the rehydration media.[9] This strategy was tested for the preparation of the CN^--containing material. Thus, after hydrotalcite was prepared from $MgCl_2$, $AlCl_3$, Na_2CO_3, and NaOH at 353 K,[2] it was calcined at 673, 773, or 823 K for 10 h: The calcined material was then stirred in an aqueous solution of KCN (CN^-/Al^{3+}= 3.0) at 353 K for 18 h, and then filtered, washed, and dried in vacuo at 383 K for 12 h. As shown in Figure 1c, the product of calcining hydrotalcite at 823 K for 10 h gave a diffuse XRD pattern assignable to MgO. Upon stirring this product in an aqueous solution of KCN at CN^-/Al^{3+}= 3.0, the XRD pattern changed to Figure 1d, which can be superimposed on Figure 1b. This shows that the calcined product is rehydrated and reconstructed into the hydrotalcite-type structure.[9] When the calcination was carried out at 623 or 723 K, the same XRD patterns as Figures 1c and 1d were obtained. The reconstructed materials were tested for the cyanation of benzyl chloride under the same reaction conditions as those in Figure 2. Benzyl cyanide was formed, the yields of which increased with reaction time and did not change at 3—20 h: The yields at 20 h were 0.46, 0.79, and 0.85 mmol for the calcination temperature of 623, 723, and 823 K, respectively. The benzyl cyanide yields using the reconstructed material do not reach those in Figure 2 where the anion-exchanged materials are used.

The hydrotalcite-like material containing interstitial CN^-ion is obtained by anion-exchanging interstitial Cl^- ion of $Mg_6Al_2(OH)_{16}Cl_2{\bullet}4H_2O$, the degree of anion exchange attaining 97%. Using the anion-exchanged material, cyanation of organic chlorides such as benzyl chloride proceeds.

References

1 Allmann, *Chimia*, **24**, 99 (1970).
2 S. Miyata, *Clays Clay Miner.*, **28**, 50 (1980).
3 S. Miyata, *Clays Clay Miner.*, **23**, 369 (1975).
4 S. Miyata, *Clays Clay Miner.*, **25**, 14 (1977).
5 S. Miyata, *Clays Clay Miner.*, **31**, 305 (1983).
6 K.J. Martin and T.J. Pinnavaia, *J. Am. Chem. Soc.*, **108**, 541 (1986).
7 E. Suzuki, M. Okamoto, and Y. Ono, *J. Mol. Catal.*, **61**, 283 (1990).
8 E. Suzuki, M. Okamoto, and Y. Ono, *Chem. Lett.*, **1989**, 1485; Y. Ono, E. Suzuki, and M. Okamoto, *Stud. Surf. Sci. Catal.*, **60**, 363 (1991); T. Matsui, E.L. Salinas, E. Suzuki, and Y. Ono, *Trans. Mat. Res. Soc. Jpn.*, **15A**, 145 (1994).
9 T. Sato, K. Kato, T. Endo, and M. Shimada, *React. Solids.*, **2**, 253 (1986); T. Sato, T. Wakabayashi, and M. Shimada, *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 89 (1986).