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Clay Supported Catalysts: an Extension of Phase Transfer Catalysis

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The possible use of clay supported copper(II) dimers containing oxygen bridges and nitrogen-heterocyclic ligands to catalyse ring opening reactions of phenols is investigated. The materials are ineffective on montmorillonite, but physical data are presented to suggest that the complexes are taken onto the clay such that the plan of the pyridine ring is always perpendicular to the plane of the silicate layer of the clay.

The use of montmorillonite supported phase transfer catalysts such as the benzyltri-n-butylammonium ion is demonstrated. It is shown that such catalysts are effective for some organic and organometallic reactions and the advantages offered are greater ease of phase separation after the reaction together with, in some cases, shorter reaction times.

Introduction

Over the past few years we have been developing an interest in the geochemical aspects of waste disposal [1]. Since many sites selected as suitable for acceptance of domestic and/or industrial waste are located in strata rich in clay minerals, inevitably the need to consider the interaction of inorganic and organic species with clays has arisen.

One approach followed was to consider the possibility of supporting on clay minerals various catalysts that could initiate the chemical breakdown of selected components within effluent derived from a disposal site. Two aspects of our work afforded results which seemed to us to be of interest beyond the context of the investigation. Thus new results relating to copper(II) complexes on clays are reported in this paper, together with details of an attempt to utilise the interlamellar water of montmorillonite species as the aqueous phase in phase transfer catalysis.

Experimental and Results

Synthesis of Copper(II) Complexes

(a) Di-μ-methoxobis(chloropyridinecopper(II))

Anhydrous copper(II) chloride (1.35 g) in anhydrous methanol (50 cm^3) was added to a solution of sodium methoxide (0.54 g) in anhydrous methanol (15 cm^3). Pyridine (2 cm^3) was added and the reaction mixture was stirred and heated under gentle reflux over 2 h. A deep green *product* was formed. *Anal.* Found: C, 32.8; H, 3.00; Cu, 29.3; N, 6.86%. $C_{12}H_{16}Cl_2Cu_2N_2O_2$ requires: C, 24.4; H, 3.82; Cu, 30.3; N, 6.69%.

(b) Di-μ-methoxobis(bromopyridinecopper(II))

An exactly analogous method afforded the *product* as brown crystals from hot methanol which were filtered hot. On cooling the filtrate, green crystals of $\{Cu(py)_2Br_2\}$ deposited (py = pyridine). *Anal.* Found: Cu, 25.4; N, 5.15%; $C_{12}H_{16}Br_2Cu_2N_2O_2$ requires: Cu, 25.0; N, 5.52%.

(c) Di-μ-methoxo- and di-μ-ethoxobis (bis-2-aminopyridine copper(II)) dinitrate and di-μ-hydroxobis (2,2′-bipyridyl copper(II)) di-perchlorate

were prepared by the literature method [2]. These materials had analyses and spectra consistent with purity.

Data useful for the characterisation of the two pyridine complexes are gathered into Table I.

Transfer of Copper(II) Complexes to Montmorillonite

Montmorillonite used in this work was obtained from Berk Ltd. and was of the following stated composition: SiO_2, 52.2; Al_2O_3, 12.8; Fe_2O_3, 10.2; TiO_2, 0.6; MgO, 2.5; CaO, 2.2; K_2O, 0.4; Na_2O, 0.1; H_2O, 18.9%.

Three methods were evaluated to transfer the above copper(II) complexes to montmorillonite: (a) treatment of clay with a solution of the complex in an organic solvent; (b) synthesis of the complex in the presence of clay, and (c) pre-synthesis of the complex followed by addition of clay. In our hands method (c) was generally the most effective.

The synthesis of the appropriate complex was carried out as detailed above. The complex (10^{-2} mol) was then added to montmorillonite (5 g) in the presence of anhydrous methanol. The mixture was stirred at room temperature for 24 h.

The infra-red and electron spin resonance spectra of the clay supported complexes were recorded and compared with data for the pure complexes. The

(001) basal spacing of the silicate before and after uptake of the complex was determined by X-ray analysis using a sedimentation technique.

Natural montmorillonite and the clay supported copper(II) complex (1 g) were suspended separately in 0.1% sodium hexametaphosphate (50 cm^3) and shaken for 10 min, then set aside for 5 min. After this time some material was taken from the centre of the suspension by pipette and placed on a glass slide and allowed to dry in air. It was then analysed by X-ray diffraction. Relevant data for the clay supported complexes are gathered into Table II.

Phase Transfer Catalysis [3]

Normal phase transfer catalysis (PTC) involves an aqueous phase and an organic phase in which the catalyst, usually a large cation, will transport a nucleophile (X^-, say) from the aqueous layer across the phase boundary to attack a substrate (RY) in the organic layer. The product RX remains in the organic layer and the catalyst may then transport Y^- across the phase boundary into the aqueous layer and then recommence the cycle. It occurred to us that, under some circumstances, it might be possible to support the catalyst on an expandable clay and to use the water content of the clay as the aqueous phase. We illustrate the procedure using a few organic and organometallic reactions.

(a) The reaction of phenol with n-butylbromide [4]

Since the phenoxide ion was required, it was necessary to introduce some alkali. This was attempted in two ways: (i) Benzyltri-n-butylammonium bromide (Q^+Br^-) (5 g), the chosen catalyst, was mixed with water (100 cm^3) and excess of an anion exchange resin in the OH^- form. The resin was removed after the mixture had been stirred for 24 h and replaced by montmorillonite (10 g). After a further 24 h stirring the clay was filtered and air dried. In this instance the cation is exchanged onto the clay and we rely on the limited anion exchange capacity of the clay together with absorbed Q^+OH^- to provide hydroxyl ions for the reaction. (ii) Montmorillonite (10 g) was stirred with Q^+Br^- (5 g) in water (100 cm^3) over 24 h. The clay was filtered and air dried then mixed with sodium hydroxide solution (22.5 cm^3/4 *M*) (at this clay: water ratio all water in the paste may be considered clay bound [5]). The concentration of the sodium hydroxide may be adjusted according to the needs of the experiment.

Each of the clay preparations was added to a reaction mixture consisting of phenol (1.92 g) and n-butylbromide (10 cm^3) in dichloromethane (150 cm^3). Clay preparation (i) was stirred with the solution for 5 days, whereas preparation (ii) induced complete conversion of phenol to n-butyl-phenylether after 24 h. Reaction mixtures and products were identified by g.l.c. and mass spectroscopy. In both cases simple filtration of the clay followed by work up of the organic layer was required.

(b) The Reaction of Dichlorocarbene with an Alkene

It was in fact this reaction that awakened wide interest in the possibilities of PTC [6–8]. The dichloropropanation of cyclohexene was first carried out following the literature [7] and then by the following method.

Montmorillonite (10 g) was covered with a solution of $\{(PhCH_2)(Bu^n)_2N\}Br$ (5 g) in water (100 cm^3) and stirred for 24 h. The clay was filtered, air dried and then mixed with sodium hydroxide (21.5 cm^3, 50%). The paste thus formed was stirred with cyclohexene (17 cm^3) at 45–50 °C and chloroform (8 cm^3) was added dropwise over 30 min, after which stirring was continued for 1 h. Filtration of the clay paste followed by normal work up of the organic layer afforded a product identical (g.l.c., mass spectroscopy) with that obtained by the literature route [7].

(c) Applications to Organometallic Chemistry

We illustrate the methods with two examples.

(i) Synthesis of an organotellurium compound

A strong interest in organotellurium chemistry within our laboratory led us to this area. It has been demonstrated [9] that the nucleophile RTe^- (R = aryl) will react with various organic dihalides $X(CH_2)_nX$ (X = Cl, Br: n = 1–4). Improvements have been made to the reaction using phase transfer catalysis [10] hence the reaction was ideal for our purposes. Bis-p-ethoxyphenylditelluride (1 g), prepared following the literature [11], in benzene (25 cm^3) was treated dropwise with sodium borohydride (1 g) in sodium hydroxide (3 cm^3, 4 *M*). Montmorillonite (2 g), treated as in (b) above, was added together with 1,4-dibromobutane (3.5 cm^3) in benzene (25 cm^3). The container was protected from light and the contents stirred for 24 h. A good yield of [*p*-EtO·C_6H_4·Te⬠]Br was obtained in a considerably shorter time than using 'normal' PTC conditions when a 42 h reaction period was needed. The method also worked well with 1,4-dichlorobutane. *Anal.* Found: C, 41.3; H, 5.10; Cl, 10.9%. $C_{12}H_{17}ClOTe$ requires: C, 42.4; H, 5.00; Cl, 10.5%. *Anal.* Found: C, 36.7; H, 4.40; Br, 23.0%. $C_{12}H_{17}BrOTe$ requires: C, 37.5; H, 4.42; Br, 20.8%.

(ii) Acetato-tris(triphenylphosphine)rhodium(I)

Wilkinson's compound, chloro-tris(triphenylphosphine)rhodium(I) (0.1 g) prepared following the literature [12], was dissolved in benzene (50 cm^3) and treated with an aqueous solution (50 cm^3) of sodium acetate (1 g) and sodium hydroxide (0.6 g).

The reaction mixture was stirred for 24 h to afford, after work up, a yellow product. The reaction was then repeated by adding the catalyst in the montmorillonite exchanged form (1 g), the same yellow product was obtained after 24 h. *Anal.* Found: C, 70.6; H, 5.50; P, 9.22%. $C_{56}H_{48}O_2P_3Rh$ requires: C, 70.9; H, 5.06; P, 9.81%. IR ν_{as}(OCO): 1650 cm^{-1}.

Physical Methods

Infra-red spectra (4000–250 cm^{-1}) were measured using a Perkin Elmer 457 instrument. Mass spectra were obtained with an AEI MS9 instrument (70eV). Electron spin resonance data were obtained using a JEOL PE-1X instrument operating in the X band; g factors were measured using a manganese (II) standard. G.l.c. analyses were carried out using Pye Unicam equipment fitted with appropriate columns. Elemental analyses for carbon, hydrogen, nitrogen and halogen were obtained from the microanalytical service, Department of Chemistry, University of Aston. Copper was determined either volumetrically with EDTA or by atomic absorption spectroscopy.

Discussion

(a) Clay Supported Copper(II) Complexes

It has been reported that a copper(II) complex formulated as $\{(py)_2CuCl_2Cu(OMe)_2\}$ [13] is able to catalyse the ring opening reaction of some phenols. We decided to synthesize the catalyst and examine its effectiveness when supported on montmorillonite. The given formulation did however seem to us to be unlikely, hence we first attempted to characterise the complex.

TABLE I. Physical Data for $\{(py)(OMe)CuX\}_2$ (X = Cl, Br).

	$\{(py)(OMe)CuCl\}_2$	$\{(py)(OMe)CuBr\}_2$
Magnetic moment-μ_{eff} (B.M.)	1.30	1.40
E.s.r. data	$g_{\parallel} = 2.22$ $g_{\perp} = 2.06$	single broad resonance.
IR data - ν(CuO)	575 cm^{-1}	570 cm^{-1}

The low room temperature magnetic moment (Table I) suggested some degree of antiferromagnetic coupling of the unpaired electrons on adjacent copper(II) species and this would be consistent with a dimeric molecule. The e.s.r. data also support this view in that $G = (g_{\parallel} - 2/g_{\perp} - 2)$ is <4.0 (3.66) indicating considerable exchange coupling [14]. The broad unresolved resonance for the bromo-complex indicates exchange coupling in that case also. A major piece of diagnostic evidence is the observation of ν(CuO) at 575 cm^{-1} (chloro-complex) and 570 cm^{-1} (bromo-complex) in the infra-red spectrum. This is very characteristic of oxygen bridged dimers [15, 16], hence the correct formulation of the complex is $\{(py)XCu(OMe)_2Cu(py)X\}$ (X = Cl, Br).

The recognition that an oxygen bridged copper(II) dimer was the catalyst suggested to us that other similar complexes may be effective. We therefore considered the derivatives of 2-aminopyridine and 2,2′-bipyridyl first reported by [2]. These are ionic complexes and may therefore be exchanged onto the clay.

TABLE II. Basal (001) d Spacings for Complexes on Montmorillonite.

	d (001) Å	Δ (Å)[a]
$\{(py)Cu(OMe)Cl\}_2$	20.7	7.1
$\{(2\text{-ampy})_2Cu(OMe)(NO_3)\}_2$ [b]	15.7	2.1
$\{(2\text{-ampy})_2Cu(OEt)(NO_3)\}_2$ [b]	16.0	2.4
$\{(bipy)Cu(OH)(ClO_4)\}_2$ [c]	19.2	5.6

[a] d (001) for montmorillonite under the same experimental conditions was 13.6 Å. Δ is difference between this figure and those above. [b] 2-ampy = 2-aminopyridine. [c] bipy = 2,2′-bipyridyl.

The complexes were supported on the clay by the methods indicated in the experimental section. Small shifts in some fundamental vibrational frequencies were used to indicate that intercalation of the complexes was successfully accomplished [17] and X-ray diffraction measurement of the basal (001) d spacing confirmed that the compounds were indeed supported (Table II). Unfortunately, the clay supported copper(II) complexes were quite inactive as catalysts for ring opening reactions of phenols. However, one point of interest did emerge. In Table II the (001) spacings fall into two distinct classes: thus the 2-aminopyridine compounds give spacings of the order of 15–16 Å, whereas the pyridine and 2,2′-bipyridyl species give values of 19–20 Å. Such data must be treated with caution since montmorillonite itself will give differing (001) spacings depending on water content [18–20]. We have examined a sample of montmorillonite in parallel with the copper(II) complex containing material so that X-ray analysis of all species was carried out under identical conditions and we observe a (001) spacing of 13.6 Å for the 'free' clay indicating that water may indeed be taken up. However the data of Table II clearly indicate the greater experimental effect on the (001) spacing produced by uptake of the complexes which should in fact render the clay more hydrophobic [20–22].

We wish to advance the following suggestion to account for the observed basal spacings. In the case of the pyridine and 2,2′-bipyridyl complexes, we propose the molecular plane of the almost flat molecules to be perpendicular to the silicate sheets of the montmorillonite. Certainly, if in these cases more of the increase in the (001) spacing is due to water, the value of 19–20 Å is consistent with expansion of the clay structure by the approximate width of the complex molecules. In the case of 2-aminopyridine derivatives, it would appear that the molecular plane is parallel to the silicate layers of the clay. The observed basal spacing of ~15 Å is however close to that seen for intercalated pyridine [23] when the plane of the molecule was considered perpendicular to the silicate sheet on the basis of IR measurements. The proposals may be reconciled if it is noted that the 2-amino-group is likely to interact with copper(II) along a skewed tetragonal axis, this interaction will require the rotation of the plane of the pyridine ring out of the complex molecular plane and perpendicular to the silicate sheet. Thus it is suggested that in all the copper(II) complexes considered, the plane of the heterocyclic ring is perpendicular to the plane of the silicate sheet.

(b) Experiments in Phase-Transfer Catalysis

It is probable that our results here are of more general practical importance. The use of clay supported catalysts is not new [24] nor indeed is the concept of using a clay to facilitate reaction work-up. The idea for the present work stemmed from our reading of the use of montmorillonite supported thallium(III) for carrying out thallium promoted oxidations of organic substrates [25]. We have attempted to carry out standard phase transfer catalysis using intercalated water as the aqueous phase and supporting the quaternary ammonium cation on the clay. In practice it was often necessary to add extra water, particularly if hydroxide ion was required. However the water-clay ratio could be controlled to ensure that a coherent paste was produced [22], in this way both catalyst and 'aqueous phase' could be very conveniently separated after the reaction. In addition to this advantage of work up, we noted that in several cases satisfactory yields of product were obtained in shorter times than would apply to the conventional procedure.

The experimental data are almost self explanatory and it is necessary only to point out that the method is applicable both to organic and to organometallic reactions. The examples selected by us to illustrate the method reflect current interests within our laboratory and to that extent are not comprehensive, nor are they completely random.

The improved rate of reaction observed in some cases probably arises from the greater surface contact between the two phases and the large surface area of the clay doubtless is instrumental in achieving this.

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