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THE MECHANISM OF LAYER CHARGE REDUCTION AND REGENERATION IN Li^+-EXCHANGED MONTMORILLONITE

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Thermally induced migration of Li^+-cations from the interlamellar region into the sheet structure of montmorillonite clays has long been known to lead to charge reduction which, depending on conditions, may be partial or virtually complete. Charge regeneration by treatment with strong base involves H^+-extraction from the sheets and detailed structural and interlamellar analysis establishes a 1 : 1 balance between Li^+ and H^+ arising from the structural exchange $-OH + Li^+ \rightarrow -OLi + H^+$. Such lithiated clays are substantially more thermally and solvent stable than their precursors.

Keywords: Clays, montmorillonites, charge reduction, charge regeneration, lithiation

Li^+-exchanged montmorillonites, such as Wyoming Bentonite, show little, if any activity as Bronsted acid catalyst. This is consistent with our experimental observation that the exchangeable (interlamellar) proton content of such Li^+-exchanged clays is extremely low. It is well known [1–5] that heating of Li^+-exchanged dioctahedral clays at ca. 200 ° C and above leads to progressive loss of cation exchange capacity (cec) to values as low as 8 meq/100 g dry clay [5]. This reduction in layer charge is widely accepted as due to migration of the interlamellar Li^+ ions into vacancies in the octahedral clay layer and has been used [5] to generate materials of controlled reduced charge. These then, following replacement of the residual interlamellar Li^+ by catalytically active cations, such as Al^{3+}, provided clays of interlamellar active cation content varying over a wide range. For typical test reactions such as alkanol dehydrations or alkene/acid esterifications, the catalytic activity was found to fall off dramatically at cec below about 50 meq/100 g, approaching zero at around 20 meq/100 g. We have discussed the implications of this behaviour earlier [5]. We now report a significant exception to the above which casts light on the mechanism of charge reduction by Li^+ migration.

The proton-catalysed conversion of primary to secondary amines viz.

$$H^+ + 2RNH_2 \rightarrow R_2NH + NH_3 + H^+$$

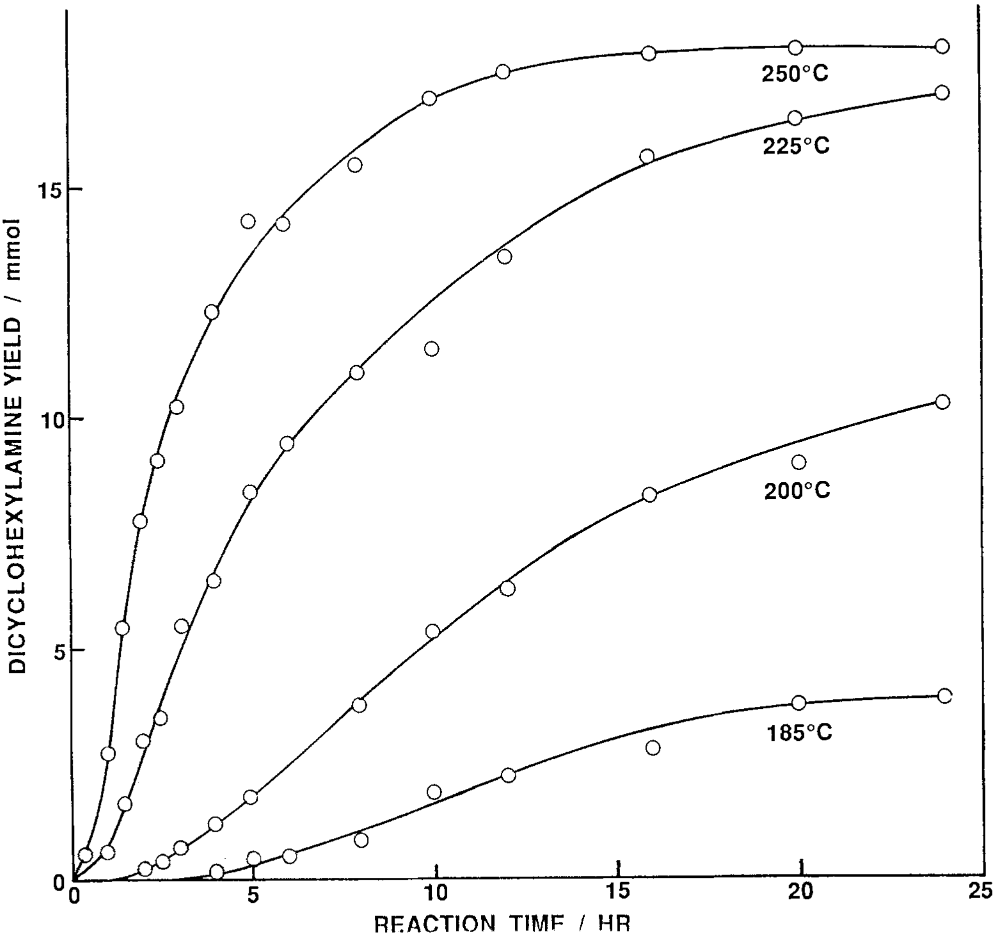

Fig. 1. Time-dependence for the production of dicyclohexylamine from cyclohexylamine as a function of temperature.

is catalysed by active clays with considerable facility [6] and has itself been used as a test reaction in activity comparisons. In this reaction, Li^+-exchanged clay, initially inactive, becomes progressively more active as reaction progresses and, eventually, reaches the level of activity characteristic of e.g. the H^+-exchanged analogue. Since the amine conversion is indubitably proton catalysed, while the original Li^+-exchanged clay has virtually no interlamellar proton content, it is clear that interlamellar protons are generated during reaction. We present here an outline of the experimental facts and their interpretation.

Fig. 1 illustrates rate plots for the formation of dicyclohexylamine from cyclohexylamine at temperatures in the range 185–250 °C. The reactions were carried out in stainless steel closed reactors of ca. 20 ml capacity containing 5 ml of amine + 0.5 g of Li^+-exchanged Wyoming Bentonite (BDH Ltd., Poole, U.K.) with product analysis by G.C. At 185 °C there is a very prolonged induction

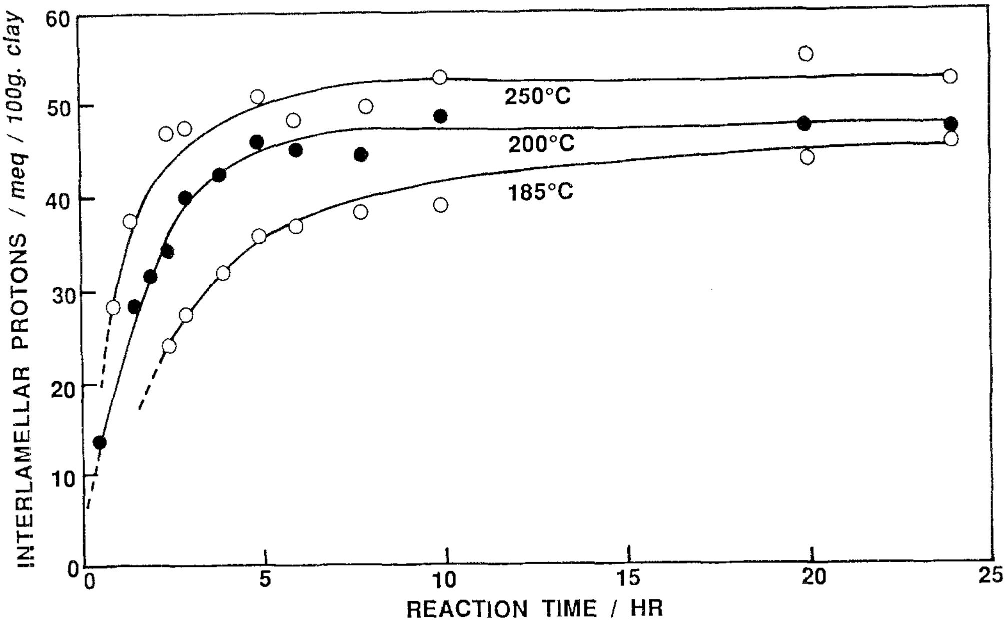

Fig. 2. Build-up of interlamellar protons with time (see text).

period before reaction commences. The induction period diminishes rapidly as the reaction temperature is raised and the curve for reaction at 250 ° C is closely similar to that obtained with the H^+ or Al^{3+}-exchanged clay.

Following rapid quenching of reactions at various times at each temperature the catalyst was removed and air dried prior to thermogravimetric analysis (TGA). The differential weight loss (DTG) peaks due to the thermal removal of the protonated primary and secondary amines have been well characterised by us previously [7] and so, in the present instance, the weight losses observed allow calculation of the number of interlamellar protons per unit weight of clay. Fig. 2 shows the growth curves of proton concentration with reaction time. For clarity of presentation we show only those for three of the reaction temperatures but this is sufficient to show the concordance between figs. 1 and 2. An Arrhenius plot of the estimated initial rates (post induction period) from fig. 2 yields an activation energy of about 47 kJ mol^{-1} for interlamellar proton growth.

Weighed amounts of the residual catalyst samples were then subjected to analysis for exchangeable (interlamellar) and unexchangeable (structural) lithium by flame emission spectroscopy (FES). The samples were first exchanged with NH_4^+ solution, the number of exchanges required to guarantee 2% analytical accuracy having been determined in test experiments with fresh Li^+-Bentonite. The supernatant solutions were collected, 2000 $\mu g \cdot cm^{-3}$ of K^+ (as KCl) were added as ionization suppressant and the whole progressively diluted in known amount to bring the FES response into the linear calibration region. These measurements provided values of the interlamellar Li^+ concentrations. Further

Table 1
Li^+ and H^+ analyses of Li^+-Bentonite clays recovered from the catalytic conversion of cyclohexylamine to dicyclohexylamine in 8 hr reactions at the stated temperatures. Concentrations in m.g. ion/100 g dry clay. Li^+ determined by flame emission spectroscopy; H^+ by TGA/cyclohexylamine titration.

	200 °C	225 °C	250 °C	267 °C
Exchangeable Li^+	40.9	38.5	36.2	26.4
Unexchangeable Li^+	44.4	47.7	49.0	57.6
H^+	44.7	50.5	49.0	57.6

weighed amounts of residual catalyst that had also been NH_4^+-exchanged and dried to remove amines were dissolved in the minimum of 40% (w/v) hydrofluoric acid in plastic containers and, following addition of KCl as above, were made up to 50 ml prior to FES analysis of structural Li content.

Table 1 lists typical results obtained with clays that had been used in 8 hr reactions of cyclohexylamine at temperatures in the range 200–267 °C. The results are unequivocal. While the amounts of exchangeable and unexchangeable Li fall and rise, respectively, with increasing reaction temperature, their sum remains essentially constant at a value very close to the cec of the original material. Significantly, we see also that the unexchangeable Li contents are, in each case, essentially identical to the independently determined proton concentrations. Thus, each Li^+ entering the structure is balanced by a H^+ leaving it.

The results leave no doubt that the sequence of events is (a) thermally induced migration of Li^+ into the octahedral layer, (b) interaction of Li^+ with the available –OH groups present there, (c) extraction of H^+ by the cyclohexylamine into the interlamellar space. Among several possibilities regarding the Li^+ migration process tentatively suggested in the past [3,4] was that described above, viz.

$$Li^+(i) \rightarrow Li^+(s)$$

$$-OH + Li^+(s) \rightarrow -OLi + H^+(s)$$

So far as we are aware, this proposal has never been followed up but our work evidently establishes that this is indeed what happens. When then Li^+ migration is associated with strong base availability in the interlamellar region, permanent introduction of Li into the clay structure occurs with total regeneration (by proton extraction) of the charge reduction that would occur in the absence of base. We propose to call this process *lithiation*. In an extended account we shall show solid-state infra-red and n.m.r. evidence that fully confirms the above view. It is worthwhile, however, to point out here that since the amounts of unexchangeable Li^+ and interlamellar H^+ are equal at all temperatures the rate determining process is Li^+ migration and not H^+ extraction; the estimated activation energy thus relates to the migration. In the light of this it is also clear that the use of strong bases in catalytic activity comparisons is liable to mislead since any free H^+ in the original clay structure will be extracted readily. That this is true is confirmed by the fact that natural Na^+-Bentonite, which is totally inactive in most reactions, shows a small but measurable activity in the cyclohexylamine reaction at 200 ° C.

The lithiation process described offers a route to the production of clays of general catalytic activity equal to those of their unlithiated analogues and in which the accessible –OH groups that contribute to clay instability are eliminated. Unfortunately, cyclohexylamine proves extremely difficult to remove entirely by ion-exchange of its protonated derivative, the residue acting as a catalytic poison. Our detailed study, which we shall report elsewhere, however, shows that while a strong base is necessary for successful proton regeneration ($pK_a > 9$), smaller amines can be entirely removed by heating and ion exchange following lithiation. Catalytic activity is then fully regenerated while, in addition, we observe improved solvent and thermal stability which then, in turn, provide the prospect of extension of the range of application of unpillared montmorillonite clays.

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