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CATALYTIC ACTIVITY OF SODIUM KAOLINITES

D. G. HAWTHORNE and D. H. SOLOMON
C.S.I.R.O. Division of Applied Chemistry, P.O. Box 4331 G.P.O., Melbourne, Victoria, Australia

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Abstract—Kaolinites, catalytically active for the polymerization of styrene, can be deactivated by treatment with 1N aqueous sodium chloride. Subsequent washing of the sodium kaolinite results in a facile hydrolysis yielding an active hydronium/aluminum kaolinite in which the exchangeable cations act as surface Brønsted acid initiation sites.

INTRODUCTION

THERE has been considerable discussion in the recent literature on the chemical activity of clays, particularly in connection with the acidity of the clay surface. Of particular interest has been the mechanism by which the aluminum silicate kaolin, after drying at moderate temperatures, can initiate the polymerization of styrene and other monomers susceptible to cationic polymerization (Solomon and Rosser, 1965; Solomon, Swift and Murphy, 1971). It is generally agreed that drying of kaolin results in the development of an acidic surface, but the question of whether the surface behaves as a Lewis acid (electron pair acceptor) or as a Brønsted acid (proton donor), or carries a mixture of these acid sites, has not been resolved. Similar problems exist with other aluminum silicate minerals, and with the related silica–alumina cracking catalysts.

One technique used for differentiation between Lewis and Brønsted acid activity in silica–alumina cracking catalysts has been the comparison of activity before, and after treatment with sodium salts (Shephard, Rooney and Kemball, 1962) or with sodium hydroxide. It was believed that only Brønsted sites would be "neutralized" by such treatments. This method has been applied to a natural acid clay, and the observed deactivation of the polymerization of styrene cited as evidence that the initiating species were Brønsted acid sites (Matsumoto, Sakai and Arihara, 1969). This is in contrast with other evidence which supported the hypothesis of initiation at Lewis acid sites (Solomon and Rosser, 1965).

Here we report on some problems which arise from a facile mineral surface hydrolysis when this technique is applied to kaolins.

EXPERIMENTAL

The kaolins

Natural kaolins from Mt. Egerton, Australia, St. Austel, Cornwell, and Dry Branch, Georgia were purified by sedimentation in distilled water. A benefitiated kaolin "Hydrite 10", supplied by the Georgia Kaolin Company, was used without further purification. The particular Cornish kaolin consisted of a clean-surfaced, principally calcium kaolinite, whereas electron microscopy showed that the other natural kaolin particles have a thin amorphous coating which, in the case of the Georgia kaolin masks a proportion of the cation exchange sites. The aluminum-rich coating on the Mt. Egerton kaolin could be removed by treatment with boiling 2% aqueous sodium carbonate without significant reduction in the clays cation exchange capacity. The Hydrite 10 is an aluminum-flocced derivative of the bleached, dispersed Georgia kaolin. Other properties of the kaolins are listed in Table 1. The exchangeable sodium contents were determined by atomic absorption analysis of N/10 hydrochloric acid extracts of the kaolins; the values agreed with those for total sodium after dissolution of the kaolins in hydrofluoric acid. Exchangeable aluminum was determined by atomic absorption analysis of neutral 1N sodium chloride extracts of the kaolins.

Sodium chloride treatment

Kaolin (10 g) was stirred for 10 hr at 20°C with aqueous 1N sodium chloride (200 ml) previously adjusted to pH 3·0, 7·0, or 10·0, as indicated in the Tables, by addition of dilute sodium hydroxide or hydrochloric acid. The mixture was centrifuged to recover the kaolin, and the treatment repeated twice. The treated kaolins were washed with either 5×300 ml, or 10×300 ml aliquots of distilled water, each washing being of 15 min duration, or they were dialysed in distilled water for 14 days; the kaolins were then dried in air at 50°C. Similar washing procedures were used for the 2% sodium carbonate-treated Mt. Egerton kaolin. Portion of the dialysed kaolin (0·5 g) was treated with 1N

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Table 1. Analyses of the kaolins, and effect of washing on the activity of sodium chloride (pH 7·0) treated kaolins

Kaolin	Egerton	Cornish	Georgia	Hydrite 10
BET specific surface (m^2/g)	10	20	10	15
Cation exchange capacity (μequiv./g)	55	35	ca. 20	50
pH (20% aqueous slurry)	3·8	7·0	6·2	3·8
Hammett acidity* (kaolin dried at 120°C)	−5·6 to −8·2	−3·0 to −5·6	−3·0 to −5·6	$< -8·2$
Exchangeable Al (μequiv./g)	30	<2	5	28
Activity†	95	36	28	>99
NaCl-treated kaolins after:				
(a) 5-fold washing				
Loss, lattice Al (μmol/g)	—	—	0·3	0·2
Loss, lattice Si (μmol/g)	—	—	0·7	0·8
Exchangeable Na (μequiv./g)	55	33	35	35
Activity†	47	1	31	50
(b) 10-fold washing				
Loss, lattice Al (μmol/g)	—	—	0·7	1·4
Loss, lattice Si (μmol/g)	—	—	1·8	2·9
Exchangeable Na (μequiv./g)	42	28	30	32
Activity†	62	30	47	83
(c) 14-day dialysis				
Exchangeable Na (μequiv./g)	7	4	3	10
Exchangeable Al (μequiv./g)	14	6	11	14
Activity†	98	90	94	97
(d) NaCl-treated dialyzed kaolin				
Exchangeable Na (μequiv./g)	45	27	30	—
Activity†	50	71	72	—

*Method of Benesi (1956).
†Percentage conversion of styrene to polymer.

sodium chloride (100 ml, pH 7·0), then washed with 5 × 15 ml aliquots of water, and dried.

Sodium hexametaphosphate treatment

Kaolin (10 g) was stirred with aqueous 0·8% sodium hexametaphosphate (100 ml) at 20°C for 15 min, then again for 1 hr with a further 100 ml of the hexametaphosphate solution, followed by rapid washing with 3 × 100 ml aliquots of distilled water, and freeze-drying of the product. Alternatively, the phosphate-treated kaolins were washed with 10 × 100 ml aliquots of distilled water, or they were dialysed for 14 days, and then dried at 50°C.

Catalytic activity of the kaolins

Kaolin samples (0·5 g), previously activated by heating in air at 120°C for 18 hr, were each shaken for 5 hr in a bath at 30·0°C with a mixture of freshly-redistilled styrene (5 ml) and dry benzene (5 ml). The residual styrene concentrations were determined using gas chromatography, and the percentage conversion of the monomer to polystyrene calculated and used as a measure of the catalytic activity of the kaolins.

RESULTS AND DISCUSSION

The kinetics of the cationic polymerization of styrene by acidic mineral surfaces is complex (Bittles, Chaudhuri and Benson, 1964), and apparently only those sites having Hammett acidity values $H_0 < -5·6$ act as initiating species for the reaction. The percentage conversion values listed in Tables 1 and 2 are used as an empirical measure of the effect of the various treatments on the surface acidity of a particular kaolin and the related catalytic activity.

The tabulated results show that treatment with 1 N aqueous sodium chloride resulted in partial or complete deactivation of the kaolins towards the polymerization of styrene, and that the activity was regained on leaching with water, with concomitant loss of exchangeable sodium ions, plus some aluminum and a greater proportion of silica. In contrast, treatment of the kaolins with neutral

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Table 2. Effect of various treatments on the activity of kaolins

Treatment (Reagent; washing or dialysis with water, etc.)	Cornish kaolin Activity*	Cornish kaolin Assay (μequiv./g)	Egerton kaolin Activity*	Egerton kaolin Assay (μequiv./g)
Untreated kaolin	36	—	95	—
NaCl (pH 3·0); 5 washes	46	Na, 22	85	Na, 52
NaCl (pH 7·0); 5 washes	1	Na, 33	47	Na, 55
NaCl (pH 10·0); 5 washes	1	Na, 28	3	Na, 45
2% Na_2CO_3; 5 washes	—	—	4	Na, 56
2% Na_2CO_3; dialysis	—	—	97	Na, 11
$(NaPO_3)_6$; freeze-dried	2	P, 24	2	P, 36
$(NaPO_3)_6$; heat-dried	60	P, 19	94	P, 24
$(NaPO_3)_6$; dialysis	—	P, 15	—	P, 24

*Percentage conversion of styrene to polymer.

N/1000 sodium chloride only slightly reduced their activity; Mt. Egerton kaolin after such treatment gave an 86% conversion of styrene in the activity test. The loss of exchangeable sodium on washing or dialysis of the treated kaolins (Table 1) arose primarily from displacement by other ionic species, although there was also some reduction in the apparent cation exchange capacities of the dialyzed kaolins, as shown by a comparison of exchangeable sodium contents after sodium chloride treatment and minimal washing of the dialyzed kaolins (Table 1, treatment d), and the raw kaolins (Table 1, treatment b). After the fifth washing the wash liquors were chloride free, and the residual chloride assays of the washed kaolins were less than 2μ equiv./g. Electron microscopy showed that the dialyzed kaolins suffered some degradation of the particle edges, although there was no apparent alteration to their basal surfaces.

In explaining our observations, reference can be made to the properties of the aluminum silicate montmorillonite which is similarly capable of initiating the polymerization of styrene. Sodium montmorillonite undergoes Donnan hydrolysis in dilute aqueous media, the exchangeable sodium ions being replaced in part by hydronium ions (Baron and Shainberg, 1970; Mitra and Kapoor, 1969). These can diffuse into the mineral surface, or to the layer edges, and attack the lattice structure, liberating aluminum ions which can preferentially reoccupy the exchange sites, even when the mineral is suspended in N/1000 aqueous sodium chloride (Kamil and Shainberg; 1968). These exchangeable aluminum ions, as well as adsorbed hydronium ions and lattice aluminum atoms exposed at the layer edges, are potential acidic initiation sites for the polymerization of styrene (Kusnitsya and Ostrovskaya, 1967; Solomon and Rosser, 1965). The loss of exchangeable sodium ions, and the accumulation of adsorbed aluminum species (Table 1) indicate that sodium kaolinite undergoes a similar hydrolysis on leaching with water. The spontaneous conversion of hydronium kaolinite into its aluminum form has recently been reported (Vasil'ev and Uskova, 1971).

The deactivation of the untreated kaolins, or the dialyzed sodium kaolinites on treatment with 1N sodium chloride, is consistent with the observed displacement of adsorbed aluminum (Table 1) and, in alkaline media (Table 2), the neutralization by deprotonation of ligand water associated with residual adsorbed multivalent cations and exposed lattice aluminum atoms which can act as Brønsted acids. It is significant that the larger amounts of aluminum were displaced from the more acidic of the untreated kaolins, although other exchangeable cations (Mortland and Raman, 1968) and surface defects would contribute to the surface acidity. There are marked differences between the various kaolins in the degree of deactivation caused by the sodium chloride treatment, and in the subsequent reactivation on leaching with water, the effects of treatment being most pronounced with the finer, clean-surfaced Cornish kaolin. Kaolins with a greater proportion of adsorbed amorphous aluminum silicate, or with degraded particle edges, show less sensitivity to sodium chloride treatment, consistent with their having a higher concentration of exposed, non-exchangeable, active aluminum atoms associated with lattice defects.

The facile hydrolysis of the kaolin lattice limits the deactivation which can possibly be achieved by treatment of the mineral with reagents which might be expected to form stable complexes with adsorbed or exposed aluminum atoms. For example although sodium hexametaphosphate treatment, followed by minimal washing and freeze-drying can yield an inert product (Table 2), heat-drying of the moist material, washing by prolonged dialysis, or even storage in a moist atmosphere

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vitiates the treatment. In contrast, no significant differences were found between the activities of heat-dried, and freeze-dried sodium kaolinites.

Our results show that repeated washing, used to remove chloride or other anions from homo-ionic clays prepared by ion-exchange with aqueous sodium salts, can actually generate strongly acid sites on the mineral surface. The apparent maintenance of catalytic activity, particularly after treatment with the more dilute sodium salt solutions, is thus not proof of the predominance of Lewis acid initiation sites. A pure, homo-ionic sodium kaolinite, like that prepared from the Cornish kaolin, is almost inactive for the polymerization of styrene, and a major part of the activity of the untreated kaolins, or their water-leached sodium derivatives would appear to be dependant on adventitious, adsorbed aluminum species which act as strong Brønsted acid initiation sites for the cationic polymerization of susceptible monomers.

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Résumé – Des kaolinites, dotées d'une activité catalytique pour la polymérisation du styrène, peuvent être inactivées par un traitement au chlorure de sodium aqueux 1 N. Un lavage ultérieur de la kaolinite sodique entraîne une hydrolyse facile qui fournit une kaolinite hydronium/aluminium, dans laquelle les cations échangeables agissent comme sites d'initiation superficiels par une acidité de Brønsted.

Kurzreferat – Kaolinite, die für die Polymerisation von Styrol katalytisch aktiv sind, können durch Behandlung mit 1 N wässriger Natriumchloridlösung deaktiviert werden. Nachfolgendes Waschen des Natriumkaolinits führt ohne weiteres zu Hydrolyse, bei welcher ein aktiver Hydronium/Aluminium Kaolinit gebildet wird, in welchem die austauschbaren Kationen Stellen zur Einleitung einer Brønstedsäure-Oberfläche bilden können.

Резюме — Каолиниты, являющиеся активными катализаторами при полимеризации стирола, лишаются своей активности при обработке 1N водным раствором хлорида натрия. Последующее промывание натриевого каолинита приводит к легкому гидролизу, дающему активный H_3O^+/Al-каолинит, в котором обменные катионы действуют как поверхностные кислотно-инициирующие центры.

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