

# Triphase Catalytic Reactions Using Clay Intercalates

N. Shabestary\*, S. Khazaeli<sup>1</sup> and N. Long<sup>1</sup>

A naturally occurring clay mineral, hectorite, was used as the support for quaternary ammonium cations. The intercalation of the cations by the clay has the advantage of separation of the catalyst from the product by a simple filtration technique. Several quaternary ammonium cation clay intercalates have been used to investigate the effects of alkyl chain length, size and shape of these catalysts in converting *n*-butyl bromide to *n*-butyl chloride. It appears that the hectorite intercalates have a great tendency for emulsification in the presence of organic solvent (toluene) and water. In fact, the emulsification being facilitated by the clay intercalates helps to bring the nucleophile from the aqueous phase into contact with the substrate, which is contained in the organic phase. The rate of the reaction was measured for the biphasic reaction (no supporting clay) and for the triphase catalytic system (with supporting clay) for comparison. Relatively large differences in reactivity have been observed between the catalysts chosen in this research. The results have indicated that quaternary ammonium with certain carbon numbers has higher catalytic activity.

## INTRODUCTION

Phase-Transfer Catalysis (PTC) has emerged in the past few decades as an extremely useful methodology for the synthesis of various classes of compounds [1-4]. Increasing reaction yield, mild reaction conditions, safe and inexpensive solvents and reagents and the ability to conduct reactions on a commercial scale are some of the advantages that this technique offers. However, separation of the catalyst from the reaction mixture has been a challenge for this technique. Recently, Triphase Catalysis (TC) has been introduced [5-7] as a unique type of heterogeneous catalysis, in which the catalyst and each of a pair of reactants are located in different phases. Based on this technique, synthetic methods have been developed for aqueous-organic phase reactions using solid catalysts, such as synthetic polymers or various clay minerals. TC shows considerable potential for commercial application. Several commercially available ion-exchange resins, such as Dowex resins

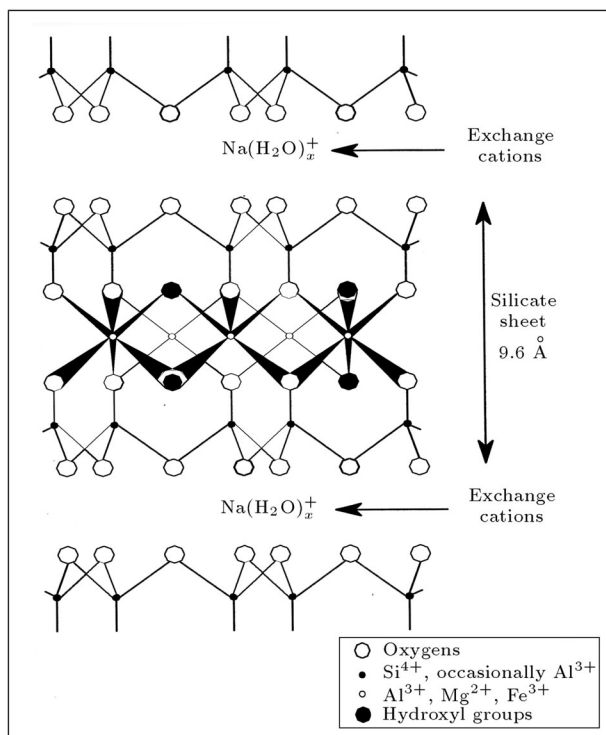
containing quaternary ammonium groups, have been studied as triphase catalysts [8].

In this research, a study is reported on the use of clay of the smectite family, hectorite, as support for various quaternary ammonium salts. Smectite clay minerals are among members of various layered silicates with 2:1 mica-like layer lattice structures. As illustrated in Figure 1, the negative charges on the clay layers are balanced by cations that are intercalated between the interlayers. It is interesting that the naturally occurring alkali and alkaline earth cations can be replaced by almost any cation. Cation exchange in this type of clay is very rapid and it takes about several minutes. It is interesting that the smectite clay has a great affinity towards water, as well as organic reagents. Therefore, this unique characteristic of smectite clay that combines hydrophilicity with hydrophobicity, makes it attractive to function as a triphase catalyst. Earlier work [9,10] has demonstrated that alkyl ammonium ions intercalated in smectite clay produce ordered structures, in which the alkyl chains and the ammonium groups form a specific orientation with respect to the clay layers. Thus, these structures depend on the length of the alkyl chains and the charge density of the clay layers.

The rate of conversion of 1-butyl bromide to 1-butyl chloride was measured in the presence of various

\*. Corresponding Author, Department of Chemistry, College of Art and Sciences, Southern Illinois University at Edwardsville, Illinois 62026-1652, USA

1. Department of Chemistry, College of Art and Sciences, Southern Illinois University at Edwardsville, Illinois 62026-1652, USA



**Figure 1.** The 2:1 layer structure of a swelling (smectite) clay. Exchangeable  $\text{Na}(\text{H}_2\text{O})_x^+$  occupy spaces between the clay layers.

quaternary ammonium salts with different sizes and shapes. The rate of the reaction was measured for the biphasic catalytic system (no supporting clay) and for the triphase catalytic system (with supporting clay) for comparison. The results have shown an interesting behavior of this clay intercalates, which is related to the size and shape of the quaternary ammonium salts.

## EXPERIMENTAL

Unless stated otherwise, all reagents were obtained commercially and used without further purification.

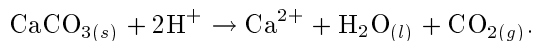
### Natural Hectorite

Naturally occurring sodium hectorite with a particle size  $< 2 \mu\text{m}$  was obtained in the pre-centrifuged and spray-dried form. The idealized anhydrous unit-cell formula of hectorite is  $\text{Na}_{0.66} [\text{Li}_{0.66} \text{Mg}_{5.34}] (\text{Si}_{8.00})\text{O}_{20} (\text{OH}, \text{F})_4$ , the experimentally determined cation-exchange capacity is about 73 meq/100 g and the surface area is about  $750 \text{ m}^2/\text{g}$  of air dried clay. The clay contains two major impurities that may interfere with the catalytic reactions. These are calcium carbonate and free (non-lattice) iron oxides, which can inhibit intercalation of the clay because they act as cementing agents, which prevent flocculation from occurring. The impurities also interfere with the determination of the Cation-Exchange Capacity (CEC)

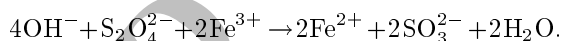
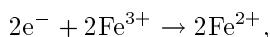
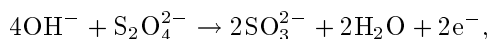
of the clay. These two major impurities are removed prior to intercalation, in order to promote flocculation of the freeze-dried clay.

The following cleaning procedures were conducted on a 20-g sample of hectorite:

a. Cleaning for calcium:



b. Cleaning for iron oxides:



c. Cleaning for organics by employing 30% hydrogen peroxide.

## Preparation of Clay Intercalates

Intercalation reactions of all cations were performed under similar conditions, since all the quaternary onium salts were quite stable and also soluble in water. To prepare the triphase catalysts, onium salts were added in excess of the clay Cation Exchange Capacity (CEC) and the clay intercalates have been washed several times with water to remove the excess onium salts. This was done to ensure that all the sodium cations can be replaced with the ammonium ions.

In a typical experiment, a 1.0 wt% aqueous suspension (e.g., 0.1 g of the mineral in 10 mL  $\text{H}_2\text{O}$ ) was added to a vigorously stirred aqueous solution of the quaternary onium salt containing about 1.2 meq/meq of clay. The reaction mixture was stirred over an hour. After an equilibration time of 24 hours, the clay was repeatedly washed with deionized water and then collected by centrifugation. The resulting homoionic quaternary onium cation exchanged forms of the minerals were air-dried or freeze-dried, as desired, and stored in a desiccator over anhydrous  $\text{CaCl}_2$ .

## Kinetics of Biphasic and Triphase-Catalyzed Displacement Reactions

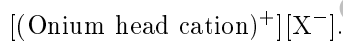
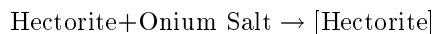
The halide displacement was conducted in 50-mL culture tubes using procedures described below. Rates of reactions were monitored by following the disappearance of the starting alkyl halides from the organic phase using gas liquid chromatography every half hour.

The reactions of alkyl bromides with NaCl under triphase conditions were carried out as follows: Air dried [hectorite][onium head cation]<sup>+</sup>[X<sup>-</sup>] (0.037 meq of quaternary onium salt as catalyst) was dispersed in 3.0 mL aqueous 3.3 M NaCl in a 15 × 150 mm

Pyrex culture tube fitted with a Teflon-lined screw cap and magnetic stirring bar. The mixture was stirred for a few hours until a homogeneous suspension was obtained. To the suspension was added 1.0 mmol of the appropriate alkyl bromide in 2 mL of toluene. The tubes were sealed with a Teflon-lined screw cap and vigorously shaken for a minute. The kinetics experiment was then started by placing the tube in an oil bath maintained at the desired temperature. The reaction was followed by withdrawing 1- $\mu$ L samples of the organic phase at different times (no less than 30 minute intervals) and monitoring the disappearance of the reactant by gas chromatography. For sampling, the tube was removed from the oil bath, shaken, quickly cooled by ice water to a temperature below room temperature, opened, resealed and returned to the bath after sampling with a small syringe. The overall process took less than one minute. The temperature of the oil bath used for the kinetic experiments was controlled to  $\pm 1^\circ\text{C}$  with the aid of a temperature controller. The product mixture was analyzed by gas liquid chromatography.

## RESULTS AND DISCUSSION

As stated earlier, a naturally occurring sodium ion within the smectite clay interlayer is rapidly replaced by onium salt cations in aqueous solution. The exchange reaction may be represented as follows:



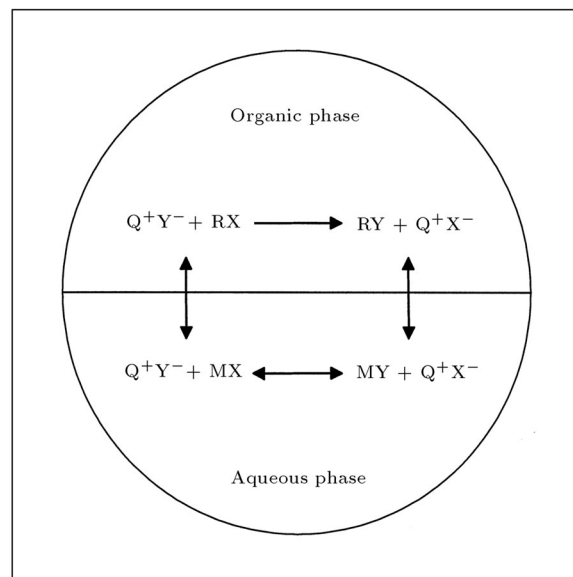
### Hectorite Clay Intercalate

The quaternary ammonium salts used in this study are different in the size, shape and length of their alkyl chains. The clay intercalates of the salts have been used to study triphase catalysis. Earlier investigations by Pinnavaia et al. [10] have shown that depending on the type and size of the alkyl chain of the onium salt, the thickness of the clay layer expands beyond a monolayer of onium ions. This results in a basal spacing of about 18 Å or more by x-ray powder diffraction, depending on the size of the alkyl group, since the van der Waals thickness of the clay layer is only about 9.6 Å. As the quaternary onium cations are sandwiched between the clay interlayers, it is expected that a larger cation will create a larger lateral surface. In general, a cation that creates a larger lateral surface area is also expected to result in higher catalytic activity.

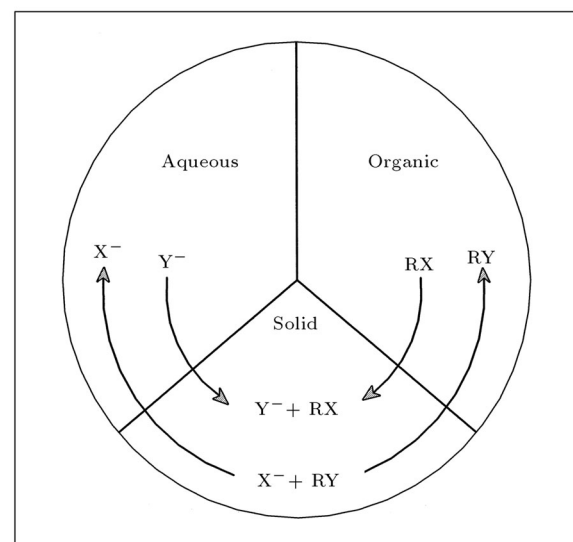
Various quaternary ammonium salts (see Table 1) were used as biphasic catalysts, as well as triphase catalysts, for side by side comparison. Schematic representations of biphasic and triphase catalytic systems

are given in Figures 2 and 3. All the catalysts are used in nucleophilic displacement reactions converting *n*-butylbromide to *n*-butylchloride.

In the clay catalytic system, alkyl halide and halide anion from the organic phase and the aqueous phase, respectively, are transferred to the interface of the solid clay intercalate where they can react. It appears that these quaternary onium ion hectorite intercalates have a great tendency for emulsification in the presence of organic solvent (toluene) and water. In fact, the emulsification being facilitated by the clay intercalates helps bring the nucleophile from the



**Figure 2.** Schematic representation of a biphasic catalyst system.



**Figure 3.** Schematic representation of a layered silicate clay based triphase catalyst system for nucleophilic displacement reactions.

**Table 1.** Pseudo first order rate constants at 90°C for the chlorination of *n*-butyl bromide in the presence of a quaternary ammonium cation-hectorite intercalates as triphase catalysts and also under biphasic reaction conditions.

Quaternary Onium Salt	Biphase Rate Constant $k_{\text{obs}}, \text{hr}^{-1}$	Triphase Rate Constant $k_{\text{obs}}, \text{hr}^{-1}$
Tetrabutylammonium bromide	0.057	0.026
Tetraoctylammonium bromide	0.740	0.430
Tetrahexadecylammonium bromide	0.830	0.250
Tricaprylmethylammonium chloride	0.348	0.280
Tridodecylmethylammonium chloride	0.420	0.340
Tetrahexylammonium chloride	0.650	0.420
Tetrabutylammonium chloride	0.065	0.032
Octyltrimethylammonium bromide	No observable activity	No observable activity
Cetyltrimethylammonium bromide	No observable activity	No observable activity

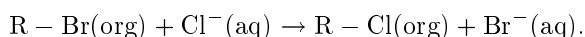
Note The observed rate constants had an error of < 1.0

aqueous phase into contact with the substrate, which is contained in the organic phase. It is anticipated that a higher degree of emulsification leads to higher catalytic activity. It seems that the degree of emulsification depends on the shape of the onium cation and the characteristics of the intercalates. In this study, only toluene has been used as solvent, however, a higher degree of emulsification is also expected if a more polar solvent than toluene, such as alcohol, is used or utilization of a co-solvent, which may change the emulsification properties of the intercalates.

It is interesting to note that once the onium cations are intercalated, their exchange with sodium ions in the aqueous layer is not favored, due to a great affinity that clay exhibits for this kind of catalyst. Therefore, this phenomenon prohibits biphasic catalytic reactions within the solution, since little or no leaching of quaternary onium cations out of the clay intercalates occurs despite the high concentration of sodium ion within the reaction mixture (sodium chloride concentration in the aqueous phase is about ten times higher than 1-butylbromide).

The quaternary ammonium catalysts have been used for intercalation to investigate the effect of alkyl chain length, size and shape of these catalysts, according to the equation below. For all of the catalysts used, a pseudo first order reaction was observed. The complete kinetic equation can be written in the following form:

$$-d[1 - \text{bromobutane}]/dt = k_{\text{obs}}[1 - \text{bromobutane}],$$



Also, the reaction rate constants are given in Table 1.

Relatively large differences in reactivity have been observed between the catalysts chosen in this research

(see Table 1). In this study, symmetrical, as well as non-symmetrical, quaternary ammonium salts with different carbon numbers were used to investigate the effect of shape and size of the intercalated cations on catalytic activity. The results have indicated that quaternary ammonium with certain carbon numbers has higher catalytic activity. For instance, tetraoctyl quaternary ammonium intercalate has shown higher catalytic activity than tetrabutyl quaternary ammonium and tetrahexyl quaternary ammonium intercalates, while their counterparts in the biphasic reaction have shown increased activity with higher carbon numbers. The results in biphasic reactions are consistent with the literature [11] on traditional phase transfer catalysis; however, the results in clay intercalates have shown a different trend. In the biphasic reaction, the effectiveness of a phase-transfer catalyst depends mainly on its organophilicity. However, in the case of clay intercalates, it appears that higher organophilicity or hydrophobicity is a limitation for emulsification, which is necessary for bringing the nucleophile to the surface of the clay. In the case of non-symmetrical quaternary ammonium, the same trend was observed both in the clay and the biphasic reaction for quaternary ammonium that has three long alkyl chains and one with a shorter alkyl chain. This may be due to quaternary ammonium structural orientation within the interlayer, which can affect the emulsification properties of the intercalates. For non-symmetrical quaternary ammonium that has one long alkyl chain and three short alkyl chains, no significant activity was observed in either the biphasic or the clay system. At present, there is no reasonable explanation for this behavior. It is important to mention that the reactivity of the catalysts in biphasic and triphasic reactions not only depends on the catalysts' structure, but also on the type of reaction as a whole.

Due to the relatively large size of onium ions, it is fair to assume that there are no interlayer surfaces available for catalytic reactions. Thus, the reactions are occurring only at the lateral surfaces of the clay intercalates rather than inside the interlayers. When the onium catalysts are small, such as tetrabutyl ammonium ion, they are unable to separate the clay layers to a great extent and, as a result, the lateral surfaces decrease considerably. This directly affects the rate of reaction, due to a decrease in the surface area of the intercalates.

All of the quaternary onium cations used in this study, when intercalated, show somewhat lower activity than in a biphasic system. This is characteristic of a triphase catalytic system, which has been documented in the literature [12].

### ACKNOWLEDGMENTS

The authors would like to acknowledge support from the NSF "Increasing the Minority Scientist Pool"; Graduate School, SIUE; Department of Chemistry, SIUE; and Senior Assignment Fund, Department of Chemistry, SIUE

### REFERENCES

1. Starks, C.M. "Phase-transfer catalysis. I. Heterogeneous reactions involving anion transfer by quaternary ammonium and phosphonium salts", *J. Amer. Chem. Soc.*, **93**(1), pp 195-199 (1971).
2. Starks, C.M. and Napier, D.R., United State patent 3,992,432 (1976), British patent 1,227,144 (1976), French patent 1,573,164 (1969), Australian patent 439,286 (1969) and Netherlands patent 6,804,687 (1968).
3. Starks, C.M. and Owens, R.M. "Phase-transfer catalysis. II. Kinetic details of cyanide displacement on 1-haloctanes", *J. Amer. Chem. Soc.*, **95**(11), pp 3613-3617 (1973).
4. Starks, C.M. and Liotta, C. "Phase transfer catalysis", *Principles and Techniques*, Academic Press, New York, USA (1978).
5. Regen, S.L. "Triphase catalysis", *J. Amer. Chem. Soc.*, **97**(20), pp 5956-5957 (1975).
6. Regen, S.L. "Triphase catalysis kinetics of cyanide displacement on 1-bromooctane", *J. Amer. Chem. Soc.*, **98**(20), pp 6270-6274 (1976).
7. Regen, S.L. "Triphase catalysis. Applications to organic synthesis", *J. Org. Chem.*, **42**(5), pp 875-879 (1977).
8. Ragain, V., Verzella, G., Ghignone, A. and Colombo, G. "Fixed-bed reactors for phase-transfer catalysis. A study of a liquid-liquid-solid reaction", *Ind. Eng. Chem.*, **25**(4), pp 878-885 (1986).
9. Lagaly, G., *Solid State Ionics*, **22**, p 43 (1986).
10. Kadkhodayan, A., Lin, C. and Pinnavaia, T.J. "Chemically modified surfaces in science and industry", Gordon & Breach, New York, USA, pp 221-238 (1987).
11. Landini, D., Maia, A. and Montanari, F. "Phase-transfer catalysis. Nucleophilicity of anions in aqueous organic two-phase reactions catalyzed by onium salts. A comparison with homogeneous organic systems", *J. Amer. Chem. Soc.*, **100**(9), pp 2798-2801 (1978).
12. Pinnavaia, T.J. et al. "Superamolecular architecture", *ACS Symposium Series*, **499**, p 99 (1992).