



## Isomerization of *endo*-tetrahydrodicyclopentadiene over clay-supported chloroaluminate ionic liquid catalysts

Ming-Yu Huang<sup>a,b</sup>, Jung-Chung Wu<sup>a</sup>, Fuh-Sheng Shieu<sup>b,\*</sup>, Jiang-Jen Lin<sup>b,c,\*\*</sup>

<sup>a</sup> Refining & Manufacturing Research Institute, Taiwan CPC Corporation, Chia-Yi 60051, Taiwan

<sup>b</sup> Department of Materials Science and Engineering, National Chung Hsing University, Taichung 40227, Taiwan

<sup>c</sup> Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

### ARTICLE INFO

#### Article history:

Received 15 June 2009

Received in revised form 3 September 2009

Accepted 3 September 2009

Available online 10 September 2009

#### Keywords:

Montmorillonite

Tetrahydrodicyclopentadiene

Chloroaluminate ionic liquids

### ABSTRACT

Various halide salts with different alkyl lengths were allowed to intercalate into the layer structure of sodium montmorillonite clay through an ion exchange reaction. Intercalation of 1-hexadecyl-3-methylimidazolium chloride, hexadecyltrimethylammonium bromide, dihexadecyldimethylammonium bromide, and tributylhexadecylphosphonium bromide could expand the spacing of the silicate layers from 12 to 37–41 Å (measured by X-ray diffraction). The modified clays were pretreated with the pyridine hydrochloride/ $\text{AlCl}_3$  mixture and used for suitably supporting a chloroaluminate ionic liquid catalyst for the isomerization of *endo*-tetrahydrodicyclopentadiene into the corresponding *exo*-isomer. Nearly quantitative conversion to the desired product and nearly quantitative selectivity were observed for the newly developed clay-supported ionic liquid catalysts, which were proven to be recyclable.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

A number of different applications have been reported for naturally occurring clays. These applications include catalysis [1], adsorbing materials [2,3], nanocomposites [4–7], organic light-emitting diodes [8], and encapsulating agents for biomacromolecules [9]. The generic structure of smectite clays such as montmorillonite (MMT) is a multilayered structure of two sheets of tetrahedra sandwiching a sheet of edge-sharing octahedra [10]. The inherent ionic character and hydrophilic nature may be altered when the metal ions are exchanged with cationic surfactants such as  $\text{C}_{18}$  alkyl quaternary ammonium salts [11–16]. Depending on the intercalated organics, the resulting modified organoclays can be tailored for their interlayer spacing and compatibility with hydrophobic polymers. Such organoclays can be made compati-

ble with various polymers, including polyamide [11], polystyrene [11,12], poly(caprolactam) [13], polypropylene [14], poly(ethylene oxide) [15], and poly(*l*-lactide) [16]. Ultimately, the blending of organic silicate clays with polymers affords polymer/layered-silicate nanocomposites [11–16] with advanced properties.

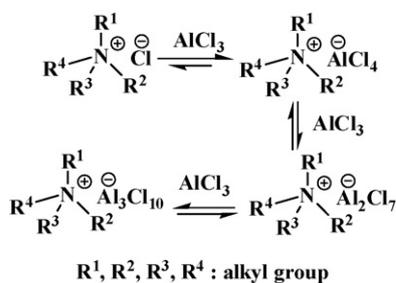
Ionic liquids (ILs), defined as salts with a melting point below about 100 °C, have been found to have unique chemical and physical properties [17]. With a low vapor pressure, adjustable hydrophilic/lipophilic solvating properties, high charge density, and high conductivity, ILs have been commonly used as catalysts, adsorbents, electrolytes, liquid supports, acid scavengers, and performance additives [17,18]. Recent developments in the field of ILs include the uses as supported catalysts for organic and electrochemical reactions [17], and as components of microemulsifiers for the synthesis of organic polymers [19] and inorganic nanoparticles [20]. The approach of supporting ILs on solid materials is expected to provide the advantages that heterogeneous liquid and solid phases offer, both for catalyst performance and for product separation. For example, ILs have been impregnated into silica gel [21,22], diatomic earth [23], molecular sieves [24], and MMT [25], and then used for catalyzing hydroformylation [21], the Heck reaction [22], hydroamination [23], and hydrogenation [24,25]. Conventionally, aluminum chloride ( $\text{AlCl}_3$ ) is widely used for catalyzing many organic reactions, but it has the serious drawbacks of being non-recyclable and of generating a corrosive waste stream during post-treatment. The chloroaluminate IL is one type of  $\text{AlCl}_3$  substitutes, prepared from quaternary ammonium chloride and  $\text{AlCl}_3$  (Fig. 1), and has shown similar acidity and efficacy for organic synthesis [17]. Furthermore, chloroaluminate ILs are effective for

**Abbreviations:** ADM, adamantane; BMIC, 1-butyl-3-methylimidazolium chloride; CEC, cation exchange capacity; DHDDMAB, dihexadecyldimethylammonium bromide; HDMIC, 1-hexadecyl-3-methylimidazolium chloride; HDTMAB, hexadecyltrimethylammonium bromide; I<sup>+</sup>, intercalated cation; IL, ionic liquid; MMT, montmorillonite; OMIC, 1-octyl-3-methylimidazolium chloride; PHC, pyridine hydrochloride; POP, poly(oxypropylene)diamine; TBHDPB, tributylhexadecylphosphonium bromide; TEM, transmission electron microscopy; THDCPD, tetrahydrodicyclopentadiene; XRD, X-ray diffraction.

\* Corresponding author. Tel.: +886 4 2285 4563; fax: +886 4 2285 7017.

\*\* Corresponding author at: Department of Materials Science and Engineering, National Chung Hsing University, Taichung 40227, Taiwan. Tel.: +886 2 3366 5312; fax: +886 2 3366 5237.

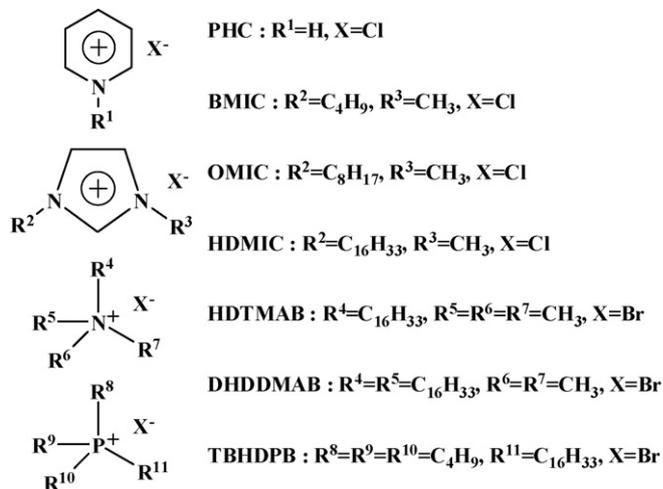
E-mail addresses: [fsshieu@dragon.nchu.edu.tw](mailto:fsshieu@dragon.nchu.edu.tw) (F.-S. Shieu), [jianglin@ntu.edu.tw](mailto:jianglin@ntu.edu.tw) (J.-J. Lin).



**Fig. 1.** Chloroaluminate ILs prepared from quaternary ammonium chloride and  $AlCl_3$ .

hydrocarbon cracking and isomerization with various feed sources of polyethylene [26], alkanes [27], fatty acids [28,29], and fatty acid methyl esters [29]. The separation of hydrogenation products could also be facilitated by impregnating chloroaluminate ILs on MMT [25].

The compound, *exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD), is valuable for high-energy density fuel, especially for short-range missiles and aircraft, and other industrial applications including solvent for paints, diluents for surfactants, waxes and washing agents [30]. The *exo*-THDCPD is derived from the corresponding *endo*-isomer which is the hydrogenation product of dicyclopentadiene from C5 fraction of stream cracker. For using as fuels such as Jet Propellant-10 (JP-10), *exo*-THDCPD of purity higher than 98.5% is required. Hence, the process of *endo*-THDCPD isomerization with a high conversion and selectivity is required. In the past, heterogeneous catalysts, zeolites [32,33] or



**Fig. 2.** Structures of various halide salts investigated in this work.

heteropolyacids [34], were studied for producing *exo*-THDCPD, but with a high processing temperature and byproduct formation. In the present work, we have first modified the natural clay by intercalation with various chloride salts. The organic-intercalated clays, with an expanded interlayer spacing and solvating ability, were further pretreated and impregnated with a chloroaluminate IL, and employed for the isomerization of *endo*-THDCPD into its *exo*-isomer.

**Table 1**  
Basal-plane spacing and dispersion properties for various halide salts embedded  $Na^+$ -MMT.

Intercalation agent <sup>a</sup>	Molar ratio of $I^+/(CEC \text{ of MMT})$	$d$ spacing XRD ( $\text{\AA}$ ) <sup>b</sup>	Wt fraction of intercalated MMT (org./inorg.) <sup>c</sup>	Dispersibility <sup>d</sup>	
				Water	Toluene
None		12		+	–
PHC	0.2	16	9/91	+	–
	0.5	13	10/90	+	–
	1.0	13	12/88	+–	–
BMIC	0.2	14	8/92	+	–
	0.5	14	14/86	+–	–
	1.0	14	17/83	–	–
OMIC	0.2	13	12/88	+	–
	0.5	15	16/84	+–	–
	1.0	16	21/79	–	+–
HDMIC	0.2	15	15/85	+	–
	0.5	16	23/77	–	+–
	1.0	37	35/65	–	+
	2.0	41	43/57	–	+
HDTMAB	0.2	14	15/85	+	–
	0.5	16	25/75	+–	+–
	1.0	18, 25	35/65	–	+–
	2.0	41	50/50	–	+–
DHDDMAB	0.2	14	21/79	+	–
	0.5	28	32/68	+–	+–
	1.0	35	48/52	–	+–
	2.0	37	63/37	–	+–
TBHDPB	0.2	14	17/83	+	–
	0.5	20	25/75	–	–
	1.0	25	39/61	–	+
	2.0	34	44/56	+–	+

<sup>a</sup> Intercalation agents: PHC, pyridine hydrochloride; BMIC, 1-butyl-3-methylimidazolium chloride; OMIC, 1-octyl-3-methylimidazolium chloride; HDMIC, 1-hexadecyl-3-methylimidazolium chloride; HDTMAB, hexadecyltrimethylammonium bromide; DHDDMAB, dihexadecyldimethylammonium bromide; TBHDPB, tributylhexadecylphosphonium bromide.

<sup>b</sup> Basal-plane spacing calculated from XRD results according to the Bragg equation ( $n\lambda = 2d \sin \theta$ ) with  $n = 1$ .

<sup>c</sup> Based on TGA measurements.

<sup>d</sup> +, Dispersible; –, aggregated; +–, sedimentation after 5 min settlement.

## 2. Experimental

### 2.1. Materials

The sodium montmorillonite ( $\text{Na}^+$ -MMT) used was supplied by Nanocor Co. and had a cation exchange capacity (CEC) of 1.20 mequiv./g and a surface area of 750 m<sup>2</sup>/g. A series of halide salts ( $\text{I}^+\text{X}^-$ ), namely pyridine hydrochloride (PHC), 1-butyl-3-methylimidazolium chloride (BMIC), 1-octyl-3-methylimidazolium chloride (OMIC), hexadecyltrimethylammonium bromide (HDTMAB), dihexadecyldimethylammonium bromide (DHDDMAB), and tributylhexadecylphosphonium bromide (TBHDPB), were purchased from Fluka. 1-Hexadecyl-3-methylimidazolium chloride (HDMIC) and  $\text{AlCl}_3$  were purchased from Merck. *endo*-Tetrahydrodicyclopentadiene was purchased from Tokyo Kasei Kogyo Co. The structures of these halide salts are shown in Fig. 2.

### 2.2. Preparation of $\text{Na}^+$ -MMT ionic exchanging with halide salts to $\text{I}^+$ /MMT (Step I)

Various halide salts with different equivalent ratios were intercalated with  $\text{Na}^+$ -MMT and results are summarized in Table 1. A typical experimental procedure, using HDMIC as an example, was described as follows.  $\text{Na}^+$ -MMT (1.0 g, 1.2 mequiv./g) was placed in a 250 mL beaker and 100 mL of deionized water was added. The mixture was vigorously stirred with a magnetic stirrer and heated to 80 °C to become a swollen  $\text{Na}^+$ -MMT slurry. In a separate vessel, the IL (HDMIC, 0.41 g, 1.2 mmol) was dissolved in 20 mL of deionized water and then poured into the vessel containing the  $\text{Na}^+$ -MMT slurry. The mixture was stirred vigorously at 80 °C for 5 h and then allowed to cool to room temperature. The solid product was collected and washed thoroughly with deionized water to remove the excess organic salts. The product, HDMIC/MMT, was dried at 80 °C for 24 h before analysis.

### 2.3. Pretreatment of $\text{I}^+$ /MMT with $\text{PHC}/\text{AlCl}_3$ (Step II)

The pretreatment of  $\text{I}^+$ /MMT hybrids before impregnation with the chloroaluminate catalyst was carried out as follows. The prepared  $\text{I}^+$ /MMT hybrids were first dried at 100 °C under 0.06 Torr vacuum for 2 h. In a glove box filled with dried nitrogen, the pretreating reagent was prepared by mixing PHC (3.75 g, 32.5 mmol) with  $\text{AlCl}_3$  (7.50 g, 56.2 mmol) in a two-neck round-bottomed flask equipped with a magnetic stirring bar. After a period of agitation (5 min), the pretreated reagent became a homogeneous, viscous liquid, and then dichloromethane (20 mL) was added. The  $\text{I}^+$ /MMT (containing 3.8 g  $\text{Na}^+$ -MMT) was pretreated with the  $\text{PHC}/\text{AlCl}_3$  agent by stirring for 5, 30 or 60 min, filtered, and washed with several portions of dichloromethane. The pretreatment procedure with different time periods was performed for various  $\text{I}^+$ /MMT, as indicated in Tables 2 and 3. The reproducibility tests with HDMIC/MMT as the example were shown in Table 2.

### 2.4. Impregnation of $\text{PHC}/\text{AlCl}_3$ on pretreated $\text{I}^+$ /MMT (Step III)

The chloroaluminate IL was prepared from PHC and  $\text{AlCl}_3$  by the following procedures. In a glove box filled with dried nitrogen, PHC (0.529 g, 4.58 mmol) and  $\text{AlCl}_3$  (1.13 g, 8.5 mmol) were added in sequence to a round-bottomed flask with a magnetic stirrer. After dilution with dichloromethane (5 mL), the mixture was added to the pretreated  $\text{I}^+$ /MMT hybrid (containing 3.8 g MMT). The reaction vessel was then taken out of the glove box and fitted with a condenser under a nitrogen atmosphere. Dichloromethane was removed from the  $\text{I}^+$ /MMT-supported chloroaluminate catalyst under reduced pressure.

**Table 2**

Isomerization<sup>a</sup> of *endo*-THDCPD by  $\text{PHC}/\text{AlCl}_3$  catalyst impregnated into HDMIC/MMT supports.

Support <sup>b</sup>	Reaction time (min)	Conversion (%)	Selectivity	
			<i>exo</i> -THDCPD	ADM
None <sup>c</sup>	30	61.9	100	0
	60	83.2	99.8	0.2
	120	96.2	99.4	0.6
$\text{Na}^+$ -MMT	30	42.5	100	0
	60	61.4	100	0
	120	82.7	100	0
HDMIC/MMT <sup>d</sup>	120	0	0	0
HDMIC/MMT <sup>e</sup>	30	2.3	100	0
	60	4.7	100	0
	120	8.5	100	0
HDMIC/MMT <sup>f</sup>	30	47.1	100	0
	60	69.5	100	0
	120	84.6	100	0
0.5 <sup>f</sup>	30	92.3	100	0
	60	98.3	100	0
	120	99.3	100	0
1.2 <sup>f</sup>	30	93.1	100	0
	60	98.8	99.9	0.1
	120	99.2	99.9	0.1
1.2 <sup>f,g</sup>	30	92.5	100	0
	60	98.4	99.9	0.1
	120	99.1	99.9	0.1

<sup>a</sup> Reaction conditions: mole ratio of initial amount of PHC used for catalyst preparation in Fig. 3, Step III/*endo*-THDCPD = 1/12.8, reaction temperature 50 °C.

<sup>b</sup> Pretreatment time 5 min for Step II.

<sup>c</sup>  $\text{PHC}/\text{AlCl}_3$  catalyst itself without MMT support.

<sup>d</sup> Control experiment—without impregnating the catalyst.

<sup>e</sup> Control experiment—without the pretreatment step.

<sup>f</sup> Mole ratio of HDMIC to the CEC of the silicate.

<sup>g</sup> Control experiment—reproducibility tests.

### 2.5. Catalytic isomerization of *endo*-THDCPD

Catalysts prepared in the manner described above were tested for the isomerization of *endo*-THDCPD. The supported chloroaluminate catalyst, containing the organic-salt intercalated silicates and added  $\text{PHC}/\text{AlCl}_3$  (0.529/1.13 g, 4.58/8.50 mmol), was placed in a glass-flask reactor equipped with a nitrogen line, stirrer, condenser, and heating oil-bath, and heated to 50 °C. Then, the feedstock, *endo*-THDCPD (8 g) in cyclohexane at 1/1 weight ratio, was added with a syringe. At intervals, samples were taken with a syringe for subsequent analysis by gas chromatography (GC).

Catalyst reusability of the supported chloroaluminate was performed by the procedures of withdrawing the liquid from the reaction system by a syringe and recharged a fresh feed for the next run (Table 4). Identical experimental procedures were applied for the recyclability and catalyst activity was monitored by sampling and analysis periodically.

### 2.6. Instruments and analysis

X-ray diffraction (XRD) patterns were obtained with a powder diffractometer (Shimadzu SD-D1) using a Cu target at 35 kV and 30 mA. The *d* spacing was calculated according to the Bragg equation ( $n\lambda = 2d \sin\theta$ ). Thermogravimetric analysis (TGA) was performed with a thermogravimetric analytical instrument (PerkinElmer Pyris 1) over the temperature range from 100 to 850 °C at 10 °C/min in air. Transmission electron microscopy (TEM)

**Table 3**  
Isomerization<sup>a</sup> of *endo*-THDCPD by PHC/AlCl<sub>3</sub> catalyst impregnated on I<sup>+</sup>/MMT.

Support <sup>b</sup>	Pretreatment time (min)	Reaction time (min)	Conversion (%)	Selectivity	
				<i>exo</i> -THDCPD	ADM
BMIC/MMT	0	30	1.2	100	0
		60	1.9	100	0
		120	2.2	100	0
BMIC/MMT	5	30	40.2	100	0
		60	62.0	100	0
		120	73.0	100	0
OMIC/MMT	0	30	1.0	100	0
		60	1.1	100	0
		120	1.2	100	0
OMIC/MMT	5	30	87.9	100	0
		60	98.2	99.9	0.1
		120	98.9	99.9	0.1
HDMIC/MMT	5	30	93.1	100	0
		60	98.8	99.9	0.1
		120	99.2	99.9	0.1
PHC/MMT	0	30	3.8	100	0
		60	8.7	100	0
		120	14.6	100	0
PHC/MMT	5	30	40.3	100	0
		60	52.0	100	0
		120	64.2	100	0
PHC/MMT	30	30	61.4	100	0
		60	78.6	100	0
		120	93.4	100	0
PHC/MMT	60	30	65.0	100	0
		60	81.8	100	0
		120	95.3	100	0

<sup>a</sup> Reaction conditions: mole ratio of initial amount of PHC used for catalyst preparation in Fig. 3, Step III/*endo*-THDCPD = 1/12.8; reaction temperature, 50 °C.

<sup>b</sup> The intercalated cation I<sup>+</sup> mole ratio relative to the CEC of the silicate was 1.2.

was performed with a Zeiss EM 902A instrument operated at 80 kV. The reaction mixture was analyzed with a gas chromatograph (HP6890) equipped with an automatic injector (HP7683) and a capillary column (Chrompack CP-Sil 5CB). The GC response factors (peak area divided by the substance weight) for *endo*-THDCPD/*exo*-THDCPD/ADM was 1.00:1.00:1.06 were assigned for the calculation.

### 3. Results and discussion

#### 3.1. Preparation of the organic-salt intercalated clays as the supports

Various alkylammonium, alkyipyridinium, alkyimidazolium, and alkylphosphonium halides, were allowed to intercalate into

**Table 4**  
Recyclability<sup>a</sup> of PHC/MMT<sup>b</sup> supported catalyst for isomerization of *endo*-THDCPD.

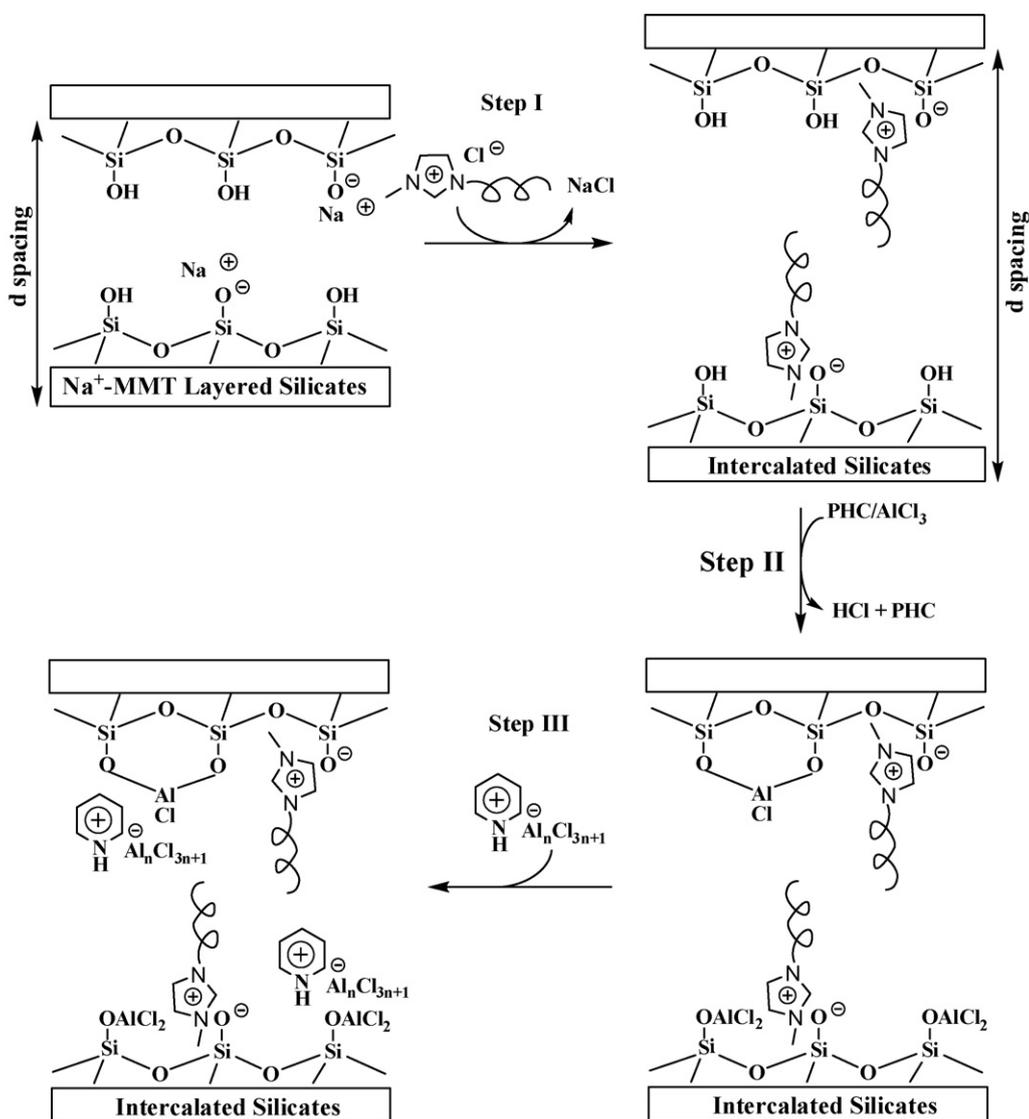
Cycle	Reaction time (h)	Conversion (%)	Selectivity (%)	
			<i>exo</i> -THDCPD	ADM
1	1	81.8	100	0
	2	95.3	100	0
2	1	82.8	100	0
	2	94.5	100	0
3	1	82.0	100	0
	2	94.0	100	0
4	1	80.0	100	0
	2	93.7	100	0

<sup>a</sup> Reaction conditions: mole ratio of initial amount of PHC used for catalyst preparation in Fig. 3, Step III/*endo*-THDCPD = 1/12.8, reaction temperature 50 °C.

<sup>b</sup> The PHC mole ratio relative to the CEC of the silicate was 1.2. Pretreatment time 1 h.

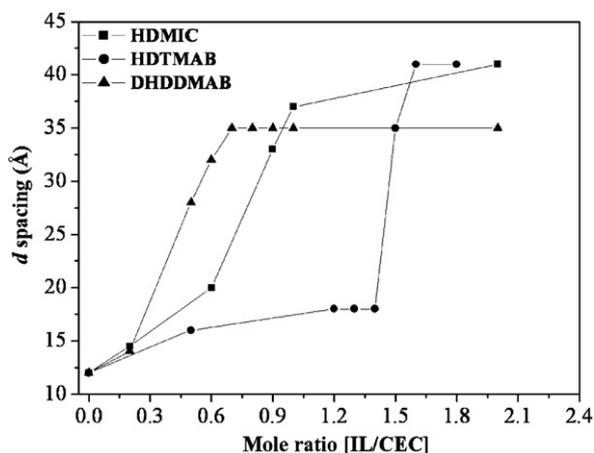
the Na<sup>+</sup>-MMT (*d* spacing = 12 Å by XRD analysis). The intercalation was performed through an ion exchange reaction with the example of HDMIC shown in Fig. 3, Step I. Other examples involving PHC, BMIC, OMIC, HDMIC, HDTMAB, DHDDMAB, and TBHDPB (structures shown in Fig. 2), were shown in Table 1. At an equivalent ratio of one with respect to the CEC of the clay, the resultant silicates were expanded to basal-plane spacings of 13, 14, 16, 37, 18–25, 35, and 25 Å, respectively. These results indicated that the embedment of alkylammonium and alkylphosphonium cations into the silicate layers enlarged the spacing. In the series of imidazolium salts, when the length of alkyl groups increased, from butyl to octyl to hexadecyl, the silicate *d* spacing expanded to 14, 16, and 37 Å, respectively. In addition to the size effect, the type of organic cations may also contribute to the interlayer expansion. We note that HDMIC, HDTMAB, and TBHDPB have the same hexadecyl, but that HDMIC expanded the basal-plane spacing of the clay more effectively, to over 37 Å at 1.0 CEC equivalent. In contrast, HDTMAB and TBHDPB required greater than 1.0 CEC equivalent of intercalating agent to expand the basal-plane spacing to 34 Å. In addition to the changes in the *d* spacing, the embedment of the lengthy alkyl cations could also affect the polar nature of the silicate plates. The pristine Na<sup>+</sup>-MMT is dispersible, or swells in water. With increasing amounts of organics in the galleries, the silicates lost their hydrophilic properties. In other words, with a significant amount of alkyl incorporation into the silicate galleries, for example, in the case of incorporation of HDMIC into MMT at a 37 Å *d* spacing and a 35 wt% organic composition, the hybrid became hydrophobic and dispersible in toluene.

A critical intercalation profile was previously reported for the intercalation of MMT clay by poly(oxypropylene)diamine (POP) salts [31]. The incorporation of the POP salts caused the clay interlayer spacing to widen from 12 to 20 Å and then sharply to 58 Å in a



**Fig. 3.** Schematic illustration of preparation procedures and catalyst species of clay-supported chloroaluminate IL catalysts—Step I: intercalation of Na<sup>+</sup>-MMT with HDMIC; Step II: pretreatment with AlCl<sub>3</sub> (in PHC) for a required time and solvent washed; Step III: impregnation of chloroaluminate IL catalyst (e.g., PHC/AlCl<sub>3</sub>).

two-stage manner. It was found in this work that the use of halide salts as intercalating agents may generate similar critical points in the expansion of the basal-plane spacing. Similar results were obtained for various organic salts, including HDMIC, HDTMAB, and DHDDMAB, intercalated into Na<sup>+</sup>-MMT. The intercalation profiles were generated by using a series of independent experiments that were performed with different stoichiometric amounts of organic salts relative to the clay, where the content was varied from 0.2 to 2.0 CEC, as shown in Fig. 4. The intercalation of HDMIC afforded a basal-plane spacing of 16–20 Å, which was observed throughout the addition of HDMIC from 0.2 to 0.6 CEC. Continuing addition of HDMIC beyond 0.6 CEC resulted in a sudden increase in the *d* spacing to 37 Å. When HDTMAB and DHDDMAB were intercalated into Na<sup>+</sup>-MMT, they led to a similar sudden increase in *d* spacing to 35 Å, at 1.5 and 0.7 CEC, respectively. The critical concentrations of the hexadecyl group for HDTMAB and DHDDMAB were similar, at about 1.4–1.5 CEC. The spatial enlargement can be expressed by plotting the basal-plane spacing against the amount of HDMIC, as illustrated in Figs. 4 and 5. It was observed that the silicate basal-plane spacing did not increase in a linear manner. The HDMIC may accumulate in the silicate galleries up to a critical concentration, similarly to the behavior of surfactants, which form micelles at a critical concentration.



**Fig. 4.** Intercalation profiles for incorporation of three representative halide salts into Na<sup>+</sup>-MMT.

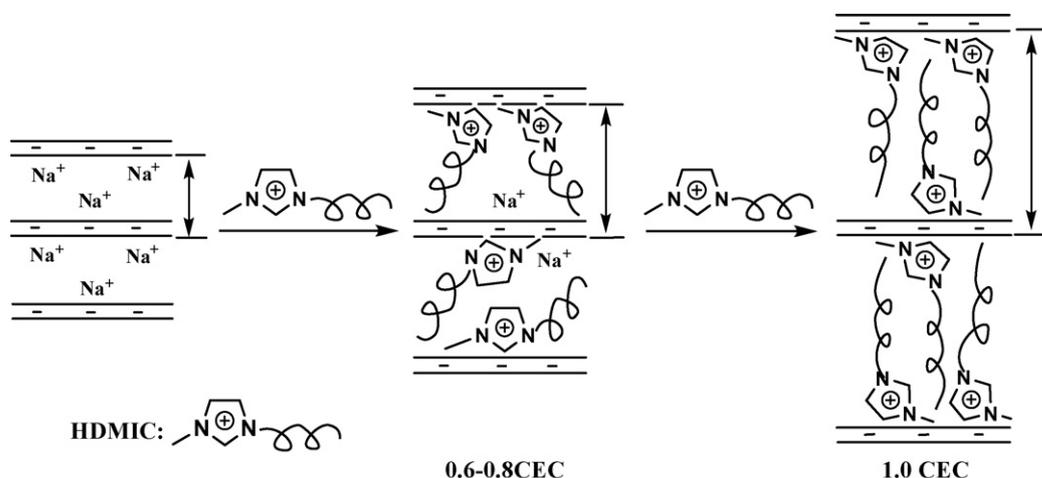


Fig. 5. Schematic illustration of HDMIC accumulation in galleries and generation of a new hydrophobic phase, which expands the basal-plane spacing.

For preparing the final catalysts, the  $I^+$ /MMT supports were first pretreated with  $AlCl_3$  (in mixing with PHC), washed with dichloromethane to remove the excess  $AlCl_3$  and followed by adding the designated amounts of the chloroaluminate IL catalyst, as illustrated in Fig. 3, Step II and III. For the pretreatment step, the PHC/ $AlCl_3$  mixture is conveniently used since it is an easily handled liquid and excess amount washable by dichloromethane.

### 3.2. Isomerization of *endo*-THDCPD

The clay-supported ILs, prepared by stepwise MMT intercalation, pretreatment and chloroaluminate IL catalyst impregnation, were evaluated for the isomerization of *endo*-THDCPD. The control experiments showed that an active catalyst required the  $I^+$ /MMT support to be pretreated and impregnated in two separated steps. As shown in Table 2, HDMIC/MMT without IL impregnation failed to catalyze the isomerization while the same HDMIC/MMT without going through the pretreatment step but directly impregnating with IL gave a low catalytic activity. The procedure of pretreatment described above was required for deactivating the silanol ( $\equiv Si-OH$ ) groups on the silicate plate surface. The reproducibility of catalyst preparations was demonstrated and shown in Table 2.

The HDMIC/MMT hybrids were used as the supports for the chloroaluminate IL catalyst. Three different clay hybrids, with 0.2, 0.5, and 1.2 CEC of organic salt with respect to the MMT, were selected for performing the isomerization of *endo*-THDCPD to the *exo*-product. As summarized in Table 2, the conversions after 30 min of reaction for these three different hybrids impregnated using the same initial amount of chloroaluminate IL were found to be 47.1%, 92.3%, and 93.1%, respectively. The basal-plane spacings for 0.2 and 0.5 CEC were very similar, but the reaction conversions were noticeably different. We observed further that HDMIC/MMT with 0.5 CEC or higher of the organic salt could be dispersed in a hydrocarbon solvent; however, the catalyst remained granular in appearance at 0.2 CEC. When the organic-salt content was over 0.5 CEC, the intercalation expanded the interlayer spacing of the silicate and caused the silicate to disperse well in the reaction mixture. The IL-impregnated HDMIC/MMT with 0.5 or 1.2 CEC of the organic salt demonstrated higher conversions than the values obtained without any support or with impregnated  $Na^+$ -MMT. It appears that the use of HDMIC/MMT as a support can provide an increased contact area between the catalyst and reactant and also phase compatibility for reaction feedstock that would otherwise be immiscible with unsupported catalyst, and that this ultimately accelerates the rate of the catalytic reaction.

Results for  $I^+$ /MMT catalysts based on PHC/MMT, BMIC/MMT, OMIC/MMT, and HDMIC/MMT for the conversion of *endo*-THDCPD are shown in Table 3. It is noteworthy that the pretreatment time of the support had an effect on the activity of the catalyst. The conversions for OMIC/MMT and HDMIC/MMT catalysts at 30 min reaction time were over 87.9% and 93.1%, respectively. The PHC/MMT and BMIC/MMT catalysts showed lower activities in comparison; the conversions at 30 and 60 min reaction time were 40% and 62%, respectively. It has been estimated [32] that *endo*-THDCPD molecules have dimensions of either  $0.67\text{ nm} \times 0.65\text{ nm}$  or  $0.58\text{ nm} \times 0.60\text{ nm}$ . The gallery widths of MMT intercalated with PHC, BMIC, OMIC, and HDMIC were estimated to be 0.3, 0.4, 0.6, and 2.7 nm by XRD analysis, and the platelet thickness was estimated to be 1 nm. The observed low conversion for the PHC/MMT and BMIC/MMT catalysts could be due to the difficulty of access for *endo*-THDCPD entering the layer structure. For OMIC/MMT (0.6 nm spacing), its ability to disperse in organic solvents may explain why its catalytic activity was similar to that of HDMIC/MMT.

When the period of pretreatment for PHC/MMT was increased from 5 to 30 and then 60 min, the conversion increased from 52.0% to 78.6% and then to 81.8%, respectively. It is expected that the effect of the pretreatment was mainly to avoid the presence of silanol groups on the surface of the MMT.

### 3.3. Catalyst recyclability

For demonstrating the catalyst recyclability, PHC/MMT was selected because of its easiness for product separation from the hybrid catalyst. The PHC/MMT hybrid was pretreated for 1 h, impregnated with PHC/ $AlCl_3$  catalyst and used for recycle studies. The results are summarized in Table 4. Clearly, the supported chloroaluminate IL catalyst remained similar activity for four cycles. At the fourth run, the catalyst showed 98% of the activity in comparison to the first run. Apparently, the clay-supported chloroaluminate ILs could be recycled a number of times before noticeable loss of activity.

## 4. Conclusions

Several different halides, including 1-hexadecyl-3-methylimidazolium chloride (HDMIC), have been intercalated into the layer structure of  $Na^+$ -MMT by an ion exchange reaction to generate effective supports for a chloroaluminate IL. The resulting organic-salt intercalation could expand the silicate interlayer spacing from 12 to 37–41 Å and rendered the clay hydrophobic and compatible with a hydrocarbon feedstock. When impreg-

nated with a chloroaluminate IL, the MMT-supported ILs became effective catalysts for the isomerization of *endo*-THDCPD. The rate was enhanced with the presence of clay supports, perhaps due to the increase in the gallery spacing of the clay and organic compatibility. An optimized  $I^+$ /MMT catalyst with 0.5 CEC equivalents of HDMIC affected the isomerization of *endo*-THDCPD with nearly quantitative conversion and selectivity. More importantly, the newly developed clay-supported ILs could be recyclable and practically used for the commercialization of the *exo*-THDCPD production.

### Acknowledgment

We acknowledge financial support from the National Science Council (NSC) of Taiwan and CPC Corporation, Taiwan.

### References

- [1] G. Sartori, R. Maggi, Chem. Rev. 106 (2006) 1077–1104.
- [2] K. Gopal, S.B. Srivastava, S. Shukla, J.L. Bersillon, J. Environ. Biol. 25 (2004) 469–475.
- [3] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Miner. Eng. 19 (2006) 463–470.
- [4] M. Alexandre, P. Dubois, Mater. Sci. Eng. 28 (2000) 1–63.
- [5] D. Porter, E. Metcalfe, M.J.K. Thomas, Fire Mater. 24 (2000) 45–52.
- [6] X. Fu, S. Qutubuddin, Polymer 42 (2001) 807–813.
- [7] A. Usuki, N. Hasegawa, H. Kasoura, T. Okamoto, Nano Lett. 1 (2001) 271–272.
- [8] H. Tetsuka, T. Ebina, T. Tsunoda, H. Nanjo, F. Mizukami, Nanotechnology 18 (2007) 355701.
- [9] M. Wei, S. Shi, J. Wang, Y. Li, X. Duan, J. Solid State Chem. 177 (2004) 2534–2541.
- [10] M. Zanetti, S. Lomakin, G. Camino, Macromol. Mater. Eng. 279 (2000) 1–9.
- [11] J.W. Gilman, W.H. Awad, R.D. Davis, J. Shields, R.H. Harris, C. Davis, A.B. Morgan, T.E. Sutto, J. Callahan, P.C. Trulove, H.C. Delong, Chem. Mater. 14 (2002) 3776–3785.
- [12] F.A. Bottino, E. Fabbri, I.L. Fragala, G. Malandrino, A. Orestano, F. Pilati, A. Pollicino, Macromol. Rapid Commun. 24 (2003) 1079–1084.
- [13] A. Usuki, A. Koiwai, Y. Kojima, M. Kawasumi, A. Okada, T. Kurauchi, O. Kamigaito, J. Appl. Polym. Sci. 55 (1995) 119–123.
- [14] M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, A. Okada, Macromolecules 30 (1997) 6333–6338.
- [15] N. Ogata, S. Kawakage, T. Ogihara, Polymer 38 (1997) 5115–5118.
- [16] N. Ogata, G. Jimenez, H. Kawai, T. Ogihara, J. Polym. Sci. B: Polym. Phys. 35 (1997) 389–396.
- [17] P. Wassercheid, T. Welton, Ionic Liquids in Synthesis, 2nd ed., Wiley-VCH, Weinheim, 2008.
- [18] H. Ohno, Electrochemical Aspects of Ionic Liquids, John Wiley & Sons, Hoboken, NJ, 2005.
- [19] F. Yan, J. Texter, Chem. Commun. 25 (2006) 2696–2698.
- [20] E. Rodil, L. Aldous, C. Hardacre, M.C. Lagunas, Nanotechnology 19 (2008) 105603.
- [21] A. Riisager, R. Fehrmann, S. Flicker, R. van Hal, M. Haumann, P. Wasserscheid, Angew. Chem. Int. Ed. 44 (2005) 815–819.
- [22] H. Hagiwara, Y. Sugawara, K. Isobe, T. Hoshi, T. Suzuki, Org. Lett. 6 (2004) 2325–2328.
- [23] S. Breitenlechner, M. Fleck, T.E. Müller, A. Suppan, J. Mol. Catal. A: Chem. 214 (2004) 175–179.
- [24] J. Huang, T. Jiang, H.X. Gao, B. Han, Z. Liu, W.Z. Wu, Y.H. Chang, G.T. Zhao, Angew. Chem. Int. Ed. 43 (2004) 1397–1399.
- [25] S. Miao, Z. Liu, B. Han, J. Huang, Z. Sun, J. Zhang, T. Jiang, Angew. Chem. Int. Ed. 45 (2006) 266–269.
- [26] C.J. Adams, M.J. Earle, K.R. Seddon, Green Chem. 2 (2000) 21–23.
- [27] P.N. Barnes, K.A. Grant, K.J. Green, N.D. Lever, WO Pat., 0040673, 2000.
- [28] G. Roberts, C.M. Lok, C.J. Adams, K.R. Seddon, M.J. Earle, J.T. Hamill, US Pat. 6255504 B1, to Unichema Chemie BV, 2001.
- [29] G. Roberts, C.M. Lok, C.J. Adams, K.R. Seddon, M.J. Earle, J.T. Hamill, US Pat. 6316643 B1, to Unichema Chemie BV, 2001.
- [30] E. Xing, Z. Mi, C. Xin, L. Wang, X. Zhan, J. Mol. Catal. A: Chem. 231 (2005) 161–167.
- [31] J.J. Lin, I.-J. Chen, C.C. Chou, Macromol. Rapid Commun. 24 (2003) 492–495.
- [32] E. Xing, X. Zhang, L. Wang, Z. Mi, Catal. Commun. 6 (2005) 737–741.
- [33] E. Xing, X. Zhang, L. Wang, Z. Mi, Green Chem. 9 (2007) 589–593.
- [34] B.H. Jeong, J.S. Han, S.W. Ko, J.H. Lee, B.J. Lee, J. Ind. Eng. Chem. 13 (2007) 310–313.