Catalysis Today 232 (2014) 127–133

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

# Catalytic performance of ion-exchanged montmorillonite with quaternary ammonium salts for the glycerolysis of urea

Sun-Do Lee[a], Moon-Seok Park[a], Dong-Woo Kim[a], Il Kim[b], Dae-Won Park[a,*]

[a] School of Chemical and Biomolecular Engineering, Pusan National University, Busan 609-735, Republic of Korea
[b] Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea

ARTICLE INFO

*Article history:*
Received 10 July 2013
Received in revised form 26 August 2013
Accepted 2 October 2013
Available online 28 October 2013

*Keywords:*
Glycerol
Glycerol carbonate
Ion-exchange method
Montmorillonite
Quaternary ammonium salt
Urea

ABSTRACT

Various quaternary ammonium salt (QX) ionic liquids immobilized onto montmorillonite clay (Q-MMT) were prepared by ion-exchange reaction between the tetra-alkyl ammonium salts and ions in the clay interlayer. The Q-MMTs were characterized by elemental analyses, nitrogen adsorption–desorption, XRD, $^{13}$C and $^{27}$Al NMR, TGA, FT-IR, and HRTEM. The *d*-spacing of the Q-MMTs increased with increasing alkyl chain lengths, however, the surface areas decreased by immobilizing QX onto MMTs. The Q-MMTs showed good catalytic activity for the synthesis of glycerol carbonate from glycerol and urea. The effects of the ionic liquid cation structure, and reaction parameters, such as temperature and degree of vacuum, on the performance of Q-MMTs were also discussed. The catalyst could be reused in up to four consecutive runs without any considerable loss of activity.

## 1. Introduction

The biodiesel has proved its value as a fuel for diesel engines and is renewable and clean [1–3]. Due to the rapid increase in the use of biodiesel and the sharp decrease in glycerol prices, glycerol has the potential to become a major platform chemical and has been identified as an important building block for future biorefineries by the DOE [4]. Glycerol carbonate (GC), which can be synthesized from glycerol, is a new and interesting material in the chemical industry [5]. It attracts much attention because of its low toxicity, good biodegradability, and high boiling point. It has been investigated as a novel component of gas separation membranes, polyurethane foams [6], a surfactant component [7], a nonvolatile reactive solvent for several types of materials, and a component in coatings, paints, and detergents.

The main methods for the preparation of GC involve the reaction of glycerol with (a) a carbon source (phosgene, a dialkyl carbonate, or an alkylene carbonate), (b) carbon monoxide and oxygen or carbon dioxide, or (c) urea. Traditionally, GC has been prepared by the reaction of glycol with phosgene; however, because of the high toxicity and corrosive nature of phosgene, alternative preparative methods for GC, such as glycerolysis of urea, have been explored [8–10].

The major advantage of the glycerolysis of urea is that the reactant, urea, is readily available and inexpensive. In addition, the ammonia formed can be easily converted to urea in the presence carbon dioxide. Several catalysts have been used, mainly based on metal oxides of variable basicity [8–10]. However, these catalysts are difficult to separate from the reaction mixture, because they dissolve in the reactants or are converted into micropowders.

Montmorillonite (MMT) is a 2:1 layer mineral of hydrated aluminum silicate, where the anionic charge of the aluminosilicate layer is neutralized by the intercalation of compensating, exchangeable cations (e.g., $Na^+$, $Ca^{2+}$, and $Mg^{2+}$), and their coordinated water molecules. Montmorillonites are highly reactive with a variety of organic molecules interacting through electrostatic interactions (e.g., ion exchange), secondary bonding (e.g., adsorption of neutral species), or covalent bonding (e.g., grafting) to produce novel compounds [11,12]. The interactions of MMTs with different organic molecules have been reviewed by Ruiz-Hitzky et al. [13]. In the modification of MMTs by ion exchange, the interlayer-accessible compensating cations can be exchanged with a wide variety of hydrated inorganic or organic cations including those of amines or quaternary ammonium salts, as well as oxonium, sulfonium, phosphonium, and more complex cationic species such as methylene blue and cationic dyestuffs [11,14,15]. Important incentives were the improvement of the thermal stabilities of the organoclays and the preparation of nanocomposites with enhanced flame retardant characteristics. However, only limited work has been reported for the

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* Corresponding author. Tel.: +82 51 510 2399; fax: +82 51 512 8563.
*E-mail address:* dwpark@pusan.ac.kr (D.-W. Park).

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http://dx.doi.org/10.1016/j.cattod.2013.10.009

catalytic applications of the ionic liquids (ILs) immobilized on MMT [16].

Ionic liquids are proven to be environmentally benign media for catalytic processes or chemical extraction [17]. ILs have negligible vapor pressure, excellent thermal stability, and special characteristics as opposed to conventional organic and inorganic solvents. Quaternary ammonium salts are some of typical ILs. They can be widely used as catalysts in many organic syntheses [18–20].

We studied the performance of immobilized ILs on MCM-41 or Merrifield peptide resin for the synthesis of GC [21,22]. However, the use of expensive pore-directing agents and large amounts of organic solvents for template removal make these catalysts impractical for commercial production. Moreover, the ordering of the mesopores often decreases because of the use of such agents and solvents. These findings emphasize the need for a low-cost and commercially viable type of clay as a support.

In this study, ammonium salt type ILs were ion-exchanged with a commercial MMT to investigate the performance of this heterogeneous catalyst in the synthesis of GC from glycerol and urea. The effects of the ionic liquid cation structure, reaction time, temperature, and degree of vacuum are discussed for a better understanding of the reaction mechanism. A recycle test of Q-MMT was also performed to assess the stability of the catalyst.

## 2. Experimental procedures

### 2.1. Materials

$Na^+$-MMT, a hydrated aluminum silicate with sodium as the predominant exchangeable cation (trade name: Kunipia-F, Kunimine Industrial Company), is obtained in powder form with a typical particle size of less than 2 μm. The cation exchange capacity (CEC) of $Na^+$-MMT, as reported by the supplier, is 120 mequiv./100 g clay and the pH value of a 10% aqueous suspension is 10. Ionic liquids are used for the modification of MMT by ion exchange, which included tetrabutylammonium chloride (TBAC), tetrahexylammonium chloride (THAC), tetraoctylammonium chloride (TOAC), and tetradodecylammonium chloride (TDAC). They were obtained from Sigma–Aldrich and were used as obtained.

### 2.2. Preparation of Q-MMT

Quaternary ammonium salts embedded MMT hybrids (referred to hereafter as Q-MMT) with different alkyl chain lengths were prepared by the ion-exchange method. In a 250-mL beaker, MMT-$Na^+$ (1.0 g, 1.2 mequiv./g) was placed and 100-mL deionized water was added. The mixture was vigorously stirred with a magnetic stirrer and heated to 30 °C to obtain a swollen $Na^+$-MMT slurry. In a separate vessel, the quaternary ammonium salts (QX, 1.2 mmol) were dissolved in 20 mL ethanol and then poured into the vessel containing the $Na^+$-MMT slurry. The mixture was stirred vigorously at 30 °C for 12 h and then allowed to cool to room temperature. The solid product was collected and washed thoroughly with deionized water to remove unreacted QX. The end product, Q-MMT, was dried at 60 °C for 24 h before analysis.

### 2.3. Characterization

Fourier transform infrared spectra (FT-IR) of untreated clays, QX, and modified clays were obtained using a Bruker A.M GMBH (960981(A)). The percentage nitrogen in the untreated and modified MMTs was determined using a Vario-EL III CHN Elemental Analyzer, which involved combustion in a pure oxygen environment to convert the sample elements to simple gases such as $CO_2$, $H_2O$, and $N_2$. Wide-angle X-ray diffraction (WXRD) with a Rigaku D/Max 2500 diffractometer with Cu-Kα radiation (40 kV, 50 mA) was used to calculate the *d*-spacing of the samples. The pore morphology of the samples was examined by high-resolution transmission electron microscopy (HRTEM) on a Jem-3010 with an accelerating voltage of 200 kV. The samples were prepared by ultrasonic dispersion, using absolute alcohol as a solvent.

**Table 1**
Elemental analysis results of immobilized IL onto MMT.

| Catalyst | CHNO from elemental analysis | | | | N-content[a] (mmol/g) |
|---|---|---|---|---|---|
| | C (wt%) | H (wt%) | N (wt%) | O (wt%) | |
| MMT | 0.26 | 1.43 | 0.56 | 9.29 | – |
| TBA-MMT | 11.64 | 3.18 | 1.08 | 9.86 | 0.77 |
| THA-MMT | 20.40 | 4.44 | 1.20 | 8.18 | 0.86 |
| TOA-MMT | 30.94 | 6.19 | 1.36 | 7.34 | 0.97 |
| TDA-MMT | 39.17 | 7.40 | 1.20 | 6.97 | 0.86 |

[a] Amount of ionic liquid immobilized onto MMT.

Solid-state $^{27}Al$ MAS-NMR experiments were performed over a Bruker DSX-300 spectrometer at a frequency of 78.19 MHz. A standard 4-mm double-bearing Bruker MAS probe was used for all experiments. The nitrogen adsorption–desorption isotherms of the samples at the temperature of liquid nitrogen were measured by using a BET apparatus (Micromeritics ASAP 2020).

### 2.4. Synthesis of glycerol carbonate from glycerol and urea

In the synthesis of GC, the reaction of glycerol with urea was performed in a 50-mL *autoclave reactor* equipped with a magnetic stirrer. For each typical reaction, the Q-MMT catalyst, glycerol (50 mmol), and urea (50 mmol) were charged into the reactor. When the desired temperature was attained, the reaction was initiated by stirring under vacuum or under nitrogen purging. The products and reactants were analyzed by a gas chromatograph (HP 6890N) equipped with an FID and a capillary column (HP-5, 5% phenyl methyl siloxane). Tetraethylene glycol was used as an internal standard. The selectivity to GC was measured on the basis of glycerol as a limited reactant.

## 3. Results and discussion

### 3.1. Characterization of the Q-MMT

Elemental analysis data of MMT ion-exchanged with different tetra-alkyl ammonium chlorides (TBAC, THAC, TOAC, and TDAC) are listed in Table 1. The amount of attached QX was in the range of 0.20–0.88 mmol/g, indicating that the QX was effectively immobilized on the MMT by ion exchange. The amount of attached QX increased with an increase in the length of alkyl chains, for example, from butyl (TBA-MMT) to dodecyl (TDA-MMT), probably due to the increase in the interlayer distance of the MMT.

WXRD results for MMTs modified with ILs are presented in Fig. 1. Because the used samples were randomly oriented powders, the X-ray powder diffraction patterns showing the basal (0 0 1) reflection are one of the main identification sources for the clay group. Compared to the unmodified MMT, the *d*-spacing of the Q-MMT shifted to lower diffraction angles due to the presence of the quaternary salt. The angle $2\theta$ shifted to the left with the increasing alkyl chain length from TBA-MMT (d) to TDA-MMT (a). As indicated in Table 2, TDA-MMT having the bulkiest cation showed the largest interlayer distance of 3.51 nm. Kim et al. [11] also reported that the *d*-spacing increased from 1.28 to 1.61 nm when a propyl group was substituted with a butyl group in the case of MMT modified with alkyl-3-methylimidazolium halide.

The $N_2$ adsorption–desorption isotherm for THA-MMT is shown in Fig. 2. The presence of mesopores is confirmed. The BET surface