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Comparative studies on the performance of immobilized quaternary ammonium salt catalysts for the addition of carbon dioxide to glycidyl methacrylate

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Abstract

The addition of carbon dioxide to glycidyl methacrylate (GMA) was investigated in a semi-batch reactor using immobilized quaternary ammonium chloride catalysts. Five different catalysts were prepared with the following supports: (1) soluble poly(ST-*co*-VBC)[C1], (2) insoluble poly(ST-DVB-VBC)[C2], (3) macroporous poly(ST-DVB-VBC)[C3], (4) poly(ST-*co*-VBC)-MMT[C4], (5) modified MCM-41[C5]. The addition of carbon dioxide to GMA can be considered as pseudo first-order with the concentration of GMA. The soluble poly(ST-*co*-VBC)-supported catalyst containing benzyltributylammonium chloride group showed the highest reaction rate. The order of the pseudo first-order rate constant for the catalysts was C1 > C3 > C2 > C4 > C5. The activation energy for the C1–C5 catalysts was 11.5, 28.1, 20.8, 36.6 and 39.3 kJ/mol, respectively. The immobilized catalysts can be reused for at least four successive runs without any considerable loss of their initial reactivities.

Keywords: Glycidyl methacrylate; Carbon dioxide; Immobilized catalyst; Quaternary ammonium chloride

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1. Introduction

Recently, the chemistry of carbon dioxide and the carbon dioxide fixation have received much attention from both an economical and an environmental point of view: utilization of the least-expensive carbon source and reduction of global-warming gas. The reaction of carbon dioxide with oxiranes to produce cyclic carbonates has been considered a useful method for its fixation by chemical processes [1,2]. These cyclic carbonates can be used as polar aprotic solvents, electrolytes for batteries and sources for reactive polymer [2]. The polar polymers obtained from cyclic carbonates and diamines are of interest for optical, magnetic and electronic applications.

The synthesis of cyclic carbonates by the reaction of CO_2 with oxirane has been performed using Lewis acids, transition metal complexes, and organometallic compounds as catalysts under high pressure [3]. Some articles reported the synthesis of five-membered cyclic carbonates under mild conditions in the presence of metal halides or quaternary ammonium salts [4–6].

The quaternary ammonium salts bound to polymer resins have been reported by several authors [7,8]. Most published works on resin-bound quaternary ammonium salts use styrene-divinylbenzene related resins because large amount of technology is available on these resins due to their use as ion-exchange resin support for the purification of water and various ionic chemicals [9]. Quaternary ammonium salts bound to cross-linked insoluble polystyrene, which is synthesized by the reaction between pendant chloromethyl groups in the polymer with tertiary amines, were used in many organic synthesis reactions [9–11]. The polymer-

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supported catalysts can be easily separated from reaction mixtures and can be reused, or they can be used in flow systems such as fixed-bed and fluidized-bed reactors.

However, the polymer-supported catalysts have yet some drawbacks such as diffusion limitations, high cost, tendancy to swell, and mechanical and thermal instability. Several inorganic supports involving metal oxides, zeolites and clays have been substituted for polymers. Clay material has high physical strength and chemical resistance towards acid and alkali treatment [12]. Montmorillonite is one of the most widely used supports for immobilized and anchored catalysts [13]. It is a naturally abundant material and available as an inexpensive material. Since the discovery of ordered mesoporous silica [14], there have been continuous efforts to improve their stability and catalytic performance. Recently, the incorporation of 3-choloro propyl methyl substituents on MCM-41 was reported [15].

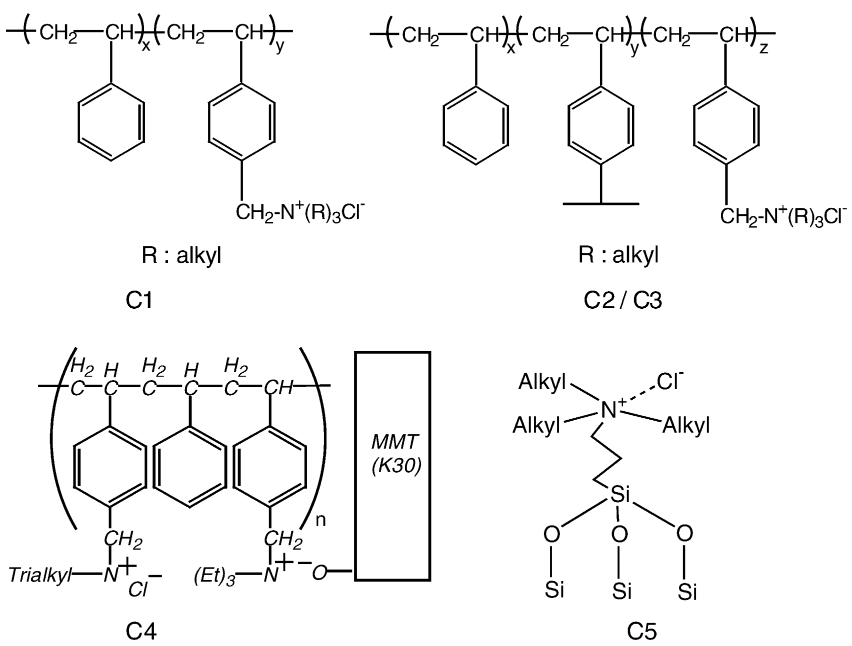
In our previous work [16], we studied the synthesis of (2-oxo-1,3-dioxolane-4-yl)methyl methacrylate [DOMA] from CO_2 and glycidyl methacrylate (GMA), using monomeric quaternary salt catalysts. In the present study, the same reaction was performed using immobilized quaternary ammonium salts as catalysts. We prepared five differently supported quaternary ammonium salt catalysts to compare their reactivity. The different supports used are: (1) soluble poly(ST-*co*-VBC), (2) insoluble poly(ST-DVB-VBC), (3) macroporous poly(ST-DVB-VBC), (4) poly(ST-*co*-VBC)-MMT and (5) chloro propyl methyl modified MCM-41. A comparative kinetic study on the reaction with the immobilized quaternary salt catalysts was carried out in a semi-batch reactor with a continuous supply of carbon dioxide into the reactor.

2. Experimental

2.1. Preparation of catalysts

Fig. 1 shows the schematic structure of the immobilized quaternary ammonium salt catalysts. The five immobilized catalysts were prepared by the same method described previously [17]. The synthesis of poly(ST-*co*-VBC) was carried out by the radical copolymerization of vinylbenzyl chloride (VBC) with styrene (ST) using 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator in toluene at 60 °C for 5 h and then at 80 °C for 2 h under nitrogen, followed by precipitation into methanol and two reprecipitations from tetrahydrofuran (THF) solution into methanol. The addition of the obtained polymer (10 mmol) with 15 mmol of tributylamine was performed in 15 mL of dimethylformamide (DMF) at 80 °C for 48 h. The resulting polymer was purified by reprecipitating twice from methanol solution into diethyl ether, and dried at 50 °C under vaccum to obtain C1 catalyst.

For the preparation of insoluble poly(ST-DVB-VBC)-supported catalyst[C2], a solution of gelatin (1.0 g) and 0.6 mL of 0.1% methylene blue in 100 g of water was added to a 500-mL four-neck flask with a reflux condenser. A mixture of 14.6 g of ST, 0.4 g of DVB and 0.1 g of AIBN was added drop-wise to the aqueous solution. The solution was partially polymerized at 70 °C for 4 h. Then 5.0 g of VBC was added slowly with vigorous stirring (600 rpm). The mixture charged with VBC was polymerized again for 17 h at 70 °C. The obtained polymer support was washed three times by stirring in refluxing methanol. After vacuum drying, the polymer support was placed in toluene and tributylamine was added to the solution.



C1 C2 / C3

C4 C5

Fig. 1. Schematic structures of the immobilized catalysts.

The macroporous polystyrene beads were prepared using the same method of synthesis for poly(ST-DVB-VBC). Isooctylalcohol was just added to the mixture of ST and DVB solution. The obtained polymer support was extracted by methanol to remove isooctylalcohol. After vacuum drying, tributylamine was attached to the polymer support to obtain the macroporous poly(ST-DVB-VBC)-supported quaternary ammonium salt catalyst, C3.

For the insoluble poly(ST-*co*-VBC)-MMT-supported catalyst[C4], poly(ST-*co*-VBC) was first dissolved in acetone and treated with 2% triethylamine by stirring overnight at room temperature to obtain a polymeric ammonium salt. A suspension of MMT in water was stirred overnight, and then a solution of the polymeric ammonium salt in acetone was added drop-wise and stirring was continued for 24 h at room temperature. The white precipitate product was filtered, washed several times with acetone and dried at 100 °C under vacuum to give the ST-VBC-MMT intercalate. The quaternization was carried out with tributylamine to produce the final poly(ST-*co*-VBC)-MMT-supported catalyst.

Organically modified MCM-41-supported quaternary salt catalyst[C5] was synthesized according to a previous report [6] using a mixture of 3-chloropropyl-dimethoxymethyl silane (ClPDMMS, Shin-etsu Chemicals) and tetraethyl orthosilicate (TEOS, TCI) as Si sources. Cetyltrimethylammonium bromide (CTMABr, TCI) was used as a template and tetra-methylammonium hydroxide (25% aqueous TMAOH, Aldrich) was used to provide alkalinity of the medium. A typical molar ratio of the various constituents in the synthesis mixture was: 4.0 (TEOS):1.5 (ClPDMMS):1.25 (C_{16}TMABr):2.5 (TMAOH):300 (H_2O). The quaternization of the 3-chloropropyl methyl modified MCM-41 was performed by the same procedure used for the other supported catalysts.

The amount of quaternary ammonium salt bound to polymer support was analyzed by an elemental analyzer (Perkin-Elmer 240). ^{1}H NMR was performed to identify the existence of $-N-CH_2-$ and $-CH_2-Cl$ groups in the catalyst. The pore size distribution and surface area of the MMT and MCM-41 supports were determined by a BET analysis (Micromeritics, ASAP 2000).

2.2. Addition of CO_2 to glycidyl methacrylate (GMA)

The syntheses of DOMA from GMA and CO_2 using polymer-supported catalysts were carried out under atmospheric pressure of CO_2. The catalyst was introduced to a 150-mL four-neck pyrex reactor containing the mixture of GMA (30 mmol) and solvent (50 mL), and the solution was heated up to the reaction temperature. Reaction was started by stirring the solution under a slow stream of CO_2 (10 mL/min), and continued for 6 h. Periodically, a small portion of reaction mixture was taken and analyzed by using a gas chromatograph (HP5890A) equipped with a 10 wt% OV-101/chromosorb W column. The identification of five-membered cyclic carbonates was performed by FT-IR (Mattson Polaris), ^{1}H NMR and ^{13}C NMR (Jeol PMX-60 SI, TMS as an internal standard).

3. Results and discussion

The synthesis of DOMA was carried out by the reaction of GMA with carbon dioxide using the immobilized catalysts of equal amount of attached quaternary salts. Therefore, 0.3 mmol of pendant quaternary ammonium chloride residues was used with 30 mmol of GMA. The formation of the five-membered cyclic carbonate was characterized by the FT-IR spectroscopy. The absorption peaks of C=O (1700 cm^{-1}) in the ester group and C=C (1800 cm^{-1}) in the cyclic carbonate were identified. The ^{13}C NMR and ^{1}H NMR analyses also confirmed the synthesis of DOMA. The composition of the different supports and the amount of attached quaternary ammonium chloride calculated by the elemental analyzer are listed in Table 1. BET surface area and pore volume of the inorganic supports, MMT and modified MCM-41 are also shown in this table.

For the addition reaction of CO_2 to GMA using supported catalysts, the following elementary reaction steps can be

Table 1
The composition and surface area of different supports and the amount of attached quaternary ammonium salt

Catalyst	Polymer support				Alkylamine	Attached amount (mmol N^+/g-support)
	ST (wt%)	VBC (wt%)	DVB (wt%)	*i*-Octoh (rel.%)		
C1	90	10	0	0	Butyl	0.894
C2	73	25	2	0	Butyl	1.087
C3	73	25	2	30	Butyl	1.326
C3-1	73	25	2	30	Ethyl	1.407
C3-2	73	25	2	30	Hexyl	0.972
C3-3	73	25	2	30	Octyl	0.756
	Inorganic support			Alkylamine	Attached amount (mmol N^+/g-support)	
	Support	BET area (m^2/g)	Pore volume (cm^3/g)			
C4	MMT	330	0.595	Butyl	2.200	
C5	Modified MCM-41	1037	1.083	Butyl	1.720	

proposed, where we set R = GMA, P = DOMA, and QX = quaternary ammonium salt catalyst [18].

$$\mathrm{R} + \mathrm{QX} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{RQX}^* \tag{1}$$

$$\mathrm{RQX}^* + \mathrm{CO_2} \xrightarrow{k_3} \mathrm{P} + \mathrm{QX} \tag{2}$$

where k_1, k_2 and k_3 are reaction rate constants. The rate of formation of P can be written as

$$\frac{\mathrm{dP}}{\mathrm{d}t} = k_3[\mathrm{CO_2}][\mathrm{RQX}^*] \tag{3}$$

The active intermediate RQX^* has a very short lifetime because of its high reactivity, and it is present only in low concentrations. Therefore, pseudo steady-state approximation, in which the rate of formation of RQX^* equals its rate of disappearance, can be applied. The net rate of RQX^* formation can be written as Eq. (4):

$$\frac{\mathrm{d}[\mathrm{RQX}^*]}{\mathrm{d}t} = k_1[\mathrm{R}][\mathrm{QX}] - k_2[\mathrm{RQX}^*] - k_3[\mathrm{CO_2}][\mathrm{RQX}^*] = 0 \tag{4}$$

Rearranging Eq. (4), the rate of formation of P can be written as

$$\frac{\mathrm{dP}}{\mathrm{d}t} = \frac{k_1k_3[\mathrm{R}][\mathrm{CO_2}][\mathrm{QX}]}{(\mathrm{k}_2 + \mathrm{k}_3[\mathrm{CO_2}])} \tag{5}$$

When the addition reaction of CO_2 to GMA is carried out in a semi-batch reactor with a constant flow of CO_2, the absorption rate of CO_2 into the solvent can be assumed much faster than the CO_2 addition reaction. Therefore, the concentration of dissolved CO_2 in the solvent can be assumed constant. The rate of product formation is:

$$\frac{\mathrm{dP}}{\mathrm{d}t} = k'[\mathrm{R}][\mathrm{QX}] \tag{6}$$

where k′ is $k_1k_3[\mathrm{CO_2}]/(k_2 + k_3[\mathrm{CO_2}])$. Since the catalyst concentration of RQX^* is very low compared to [QX] and it does not change during the reaction as assumed in Eq. (4), the concentration of [QX], initial concentration $[\mathrm{QX}]_0$ minus $[\mathrm{RQX}^*]$, can be considered constant. Therefore, a pseudo first-order rate equation can be applied.

$$\frac{\mathrm{dP}}{\mathrm{d}t} = \frac{-\mathrm{dR}}{\mathrm{d}t} = k[\mathrm{R}] \tag{7}$$

where $k = k'[\mathrm{QX}]$.

Integration of Eq. (7) gives Eq. (8).

$$\ln\left(\frac{[\mathrm{GMA}]_0}{[\mathrm{GMA}]}\right) = kt \tag{8}$$

From the slope of the linear plot of $\ln([\mathrm{GMA}]_0/[\mathrm{GMA}])$ versus time, one can estimate the pseudo first-order rate constant k.

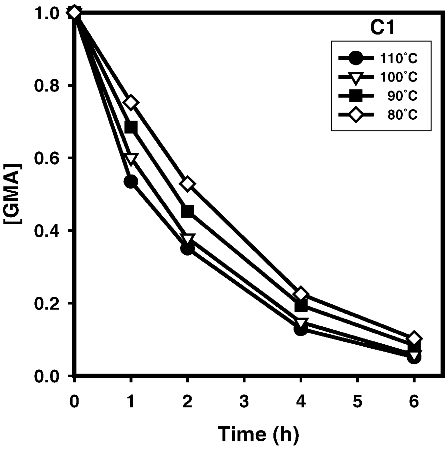


Fig. 2. Concentration of GMA vs. time with soluble C1 catalyst at various reaction temperatures.

The addition of CO_2 with PGE was carried out using 1 mol% of catalyst in dimethylacetamide (DMAc) at 80–110 °C. The variation of GMA concentration during the reaction with C1 catalyst at different temperatures is shown in Fig. 2. Fig. 3 is the plot of $\ln([\mathrm{GMA}]_0/[\mathrm{GMA}])$ versus time for C1 catalyst. The data fit well to pseudo first-order kinetics. The reaction rate constants are listed in Table 2.

When the initial concentration of the catalyst $[\mathrm{QX}]_0$ was varied from 0.5 to 1.0 and 1.5 mol%, we obtained k values of 0.312, 0.415 and 0.544 h^{-1}, respectively. The pseudo first-order rate constant k increased with increasing $[\mathrm{QX}]_0$. It confirms the validation of Eq. (6). The linear dependence of reaction rate with respect to the epoxide concentration was also observed by Kihara et al. [19]. They reported an increase of reaction rate as the initial catalyst concentration $[\mathrm{QX}]_0$ increased for the addition of CO_2 to phenyl glycidyl ether using metal halide and quaternary salt catalysts.

The effect of CO_2 pressure on the synthesis of cyclic carbonate was also reported by Kihara et al. for the addition of CO_2 to epoxides [19]. They reported zero-order relationship between reaction rate and CO_2 pressure. This can be expected from Eq. (5) when $k_2 \ll k_3\ [\mathrm{CO_2}]$.

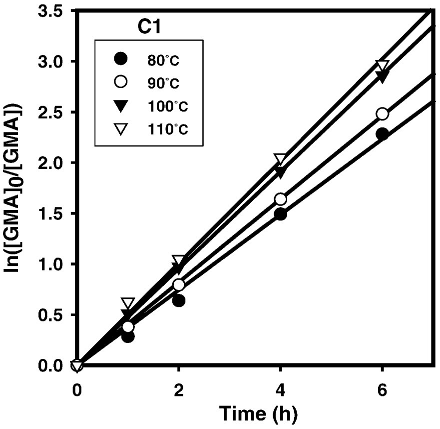


Fig. 3. First-order plots of $\ln([\mathrm{GMA}]_0/[\mathrm{GMA}])$ vs. time for C1 catalysts.

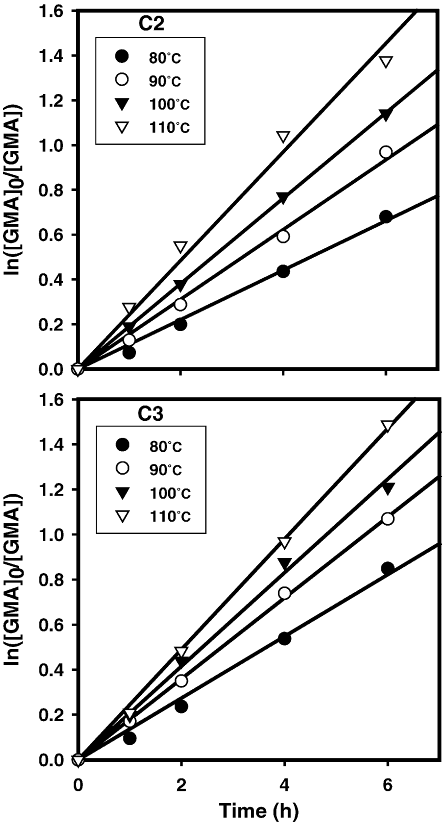


Fig. 4. First-order plots of ln($[GMA]_0$/[GMA]) vs. time for C2 and C3 catalysts.

The plots of Eq. (8) for experimental data with C2 and C3 catalyst are shown in Fig. 4. They fit well to pseudo first-order kinetics. This result indicates that the assumed reaction steps (Eqs. (1) and (2)) are reasonable for the reaction mechanism. In order to study the structure of alkylamine on the reaction rate of GMA, four different amines (ethyl, butyl, hexyl and octyl) are used in the quaternization step for the preparation of C3 series catalysts. Fig. 5 shows the variations of the observed pseudo first-order rate constants with the carbon number of trialkyl groups on the pendant trialkylammonium chlorides at 110 °C. The catalyst quaternized with tributylamine showed the highest *k* value. The catalyst containing pendant benzyltriethylammonium chloride groups was relatively less lipophilic than the catalyst prepared by the tributyl amine. In our previous work [16] on the same reaction with unsupported liquid quaternary ammonium salt catalysts, the order of catalytic activity for the salt was tetraethyl- < tetrabutyl- < tetrahexyl- < tetraoctylammonium salt. Bulky quaternary salts, having longer distances between cations and anions, are generally known to exhibit higher activity in activating anions. However, the immobilized catalyst from trihexyl or trioctylamines showed lower catalytic activities than that of tributylamine. The result indicates that the steric hindrance of bulky alkyl structure of the immobilized catalyst inhibits the approach of GMA to the supported active sites. The similar results of the effects of alkyl chain length on the reaction rate of the addition reaction of phenyl glycidyl ether with *S*-phenyl thioacetate was reported by Nishikubo et al. [20].

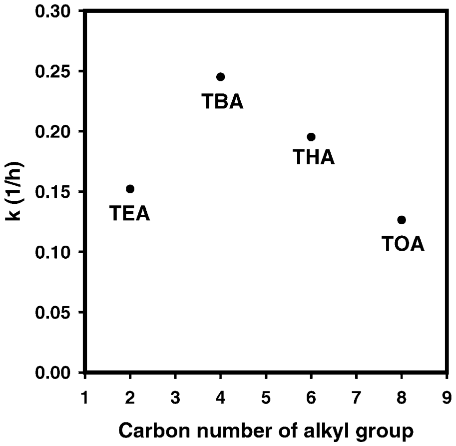


Fig. 5. Variation of *k* with carbon number of trialkyl amine.

The data for C4 and C5 catalyst in Fig. 6 also showed good linearity of pseudo first-order rate equation with respect to GMA concentration. The pseudo first-order rate constants and activation energies from the corresponding Arrhenius plot are summarized in Table 2. Soluble poly(ST-*co*-VBC)-supported quaternary ammonium salt showed the

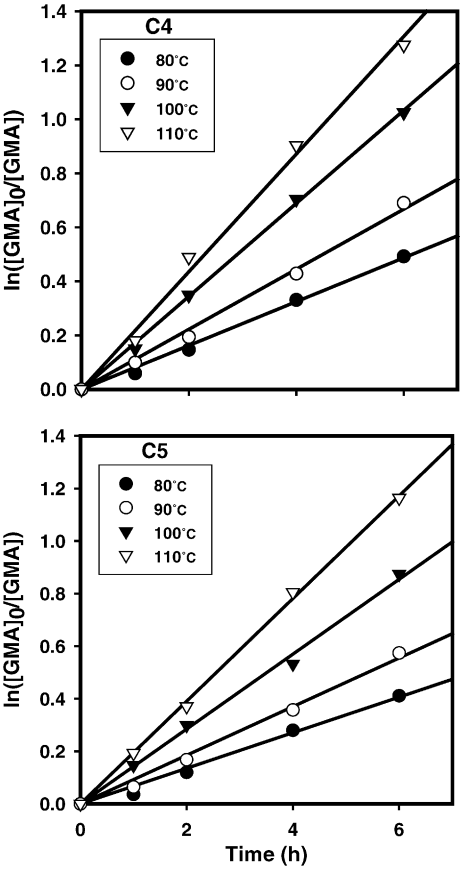


Fig. 6. First-order plots of ln($[GMA]_0$/[GMA]) vs. time for C4 and C5 catalysts.

Table 2
First-order reaction rate constant (*k*) and activation energy (*E*) for different catalysts

	Rate constant, *k* (h^{-1})				
	C1	C2	C3	C4	C5
Temperature (°C)					
80	0.3711	0.1109	0.1369	0.0820	0.0685
90	0.4104	0.1500	0.1790	0.1133	0.0936
100	0.4765	0.1900	0.2075	0.1693	0.1440
110	0.5039	0.2350	0.2449	0.2180	0.1955
E (kJ/mol)	11.5	28.1	20.8	36.6	39.3

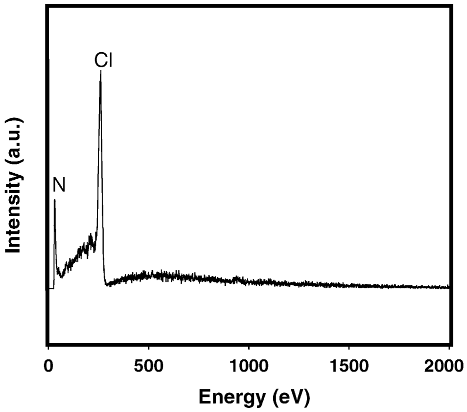


Fig. 7. EDS result of soluble C1 catalyst after 4th run.

highest reaction rate constants and the lowest activation energies. However, this catalyst has a drawback of separation after reaction, since it needs another precipitation step for the reuse of the catalyst. Macroporous poly(ST-DVB-VBC) catalyst[C3] showed higher rate constants than C2 catalyst, prepared without use of *i*-octylalcohol. Macroporous structure seems to favor the diffusion of GMA to the active site. One can also observe that poly(ST-*co*-VBC)-MMT-supported catalyst had higher rate constant than Cl-propyl-methyl-MCM-41 catalyst. The average pore diameter of the former and the latter was 5.5 and 4.0 nm, respectively. Even though the poly(ST-*co*-VBC)-MMT catalyst[C4] had lower surface area than the Cl-propyl-methyl-MCM-41 catalyst[C5], the pendant quaternary ammonium groups of C4 catalyst might be more easier for the contact of GMA molecules than those of C5 catalyst. The pores (or spacing) in the cross-linked polystyrene supports will be much higher than those of MMT and MCM-41. Therefore, the C1–C3 catalysts showed higher rate constant than C4 and C5 did.

The stability of the catalysts was tested by reusing them four successive times after separation from the reaction mixture at each experimental run. Insoluble catalysts were easily separated. However, the soluble poly(ST-*co*-VBC) was separated after precipitation in diethylether. All the catalysts maintained their catalytic activities showing less than 12% loss of their initial activity after 4th run. As shown in Fig. 7, surface analysis of the used catalyst by energy dispersive spectroscopy (EDS, Jeol JXA-8600) confirmed the maintenance of chloride group bound to the polymer support after 4th run.

4. Conclusions

Carbon dioxide can be effectively added to the epoxide ring of glycidyl methacrylate (GMA) to produce the corresponding five-membered cyclic carbonate (DOMA). The immobilized quaternary ammonium salts showed good catalytic activity even at atmospheric pressure of carbon dioxide. The addition reaction of CO_2 to GMA can be considered as pseudo first-order with respect to the concentration of GMA. The reaction rate constant increased linearly as the amount of catalyst increased. The order of the pseudo first-order rate constant for the immobilized catalysts was C1 > C3 > C2 > C4 > C5. The catalyst can be reused at least four successive times and considered to have high possibility of easy recovery.

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