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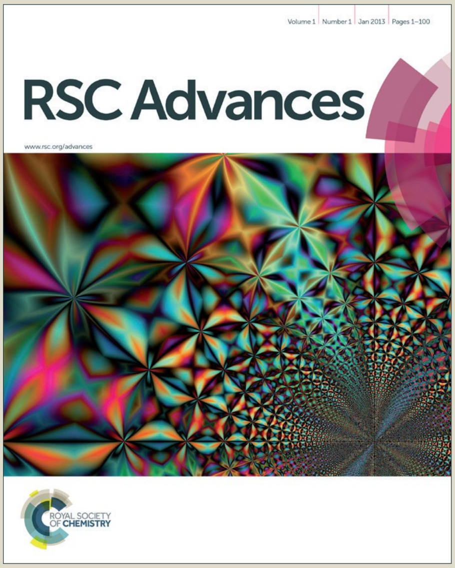

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Versatile Boiler Ash Containing Potassium Silicate for the Synthesis of Organic Carbonates

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In this study, boiler ash containing potassium silicate (BA 900) and potassium silicate (K_2SiO_3) were proven to be a feasible Lewis acid catalysts for the synthesis of different organic carbonates (glycerol carbonate, ethylene carbonate, propylene carbonate) from different polyol (glycerol, ethylene glycol, propylene glycol) feedstock. Additionally, the developed catalytic reaction has the ability to produce propylene carbonate at milder reaction temperature. BA 900 and K_2SiO_3 were reusable for three consecutive cycles of reaction without the loss of activity. The reusable characteristics of catalysts were confirmed through several characterisation techniques, i.e. XRD, FTIR, XRF, N_2 physisorption, FESEM-EDX, and Hammett Test. All organic carbonates synthesised had similar synthesis mechanistic pathway, which involved decomposition of intermediate carbamates into their respective carbonates.

Introduction

In our previous report, it was found that the boiler ash from palm oil industry was introduced as catalyst for the synthesis of glycerol carbonate (GC) from glycerol and urea as a bio-renewable feedstock.[1] In present study, the feasibility of the catalyst to synthesise ethylene carbonate (EC) and propylene carbonate (PC) is discussed. This specific carbonates were chosen due to their adverse use in many industries. Ethylene carbonate and propylene carbonate have variety of applications in many major industries such as polymers, gas separation membranes, paints, agrochemicals, batteries as well as supercapacitors.[2-4] Apart from that, previously identified element in boiler ash, i.e. potassium silicate (K_2SiO_3), which was responsible for the catalytic behaviour of boiler ash is also introduced as a new catalyst for the synthesis of glycerol carbonate. There are various routes of synthesising glycerol carbonate. One of the very common and known routes is through direct carbonylation of glycerol using carbon dioxide.[5] The reaction was conducted at higher temperature of 180 °C with the pressure of 5 MPa. However, this catalytic process is less feasible due to low conversion of glycerol as well as poor yield of glycerol carbonate due to the stability of CO_2. Besides, the direct carbonylation reaction requires very high energy input and very effective catalyst for conversion to occur.[6] Another way of synthesising glycerol carbonate is through the use of glycerol and dimethyl carbonate (DMC) with the aid of catalyst. Even though this synthesis route is highly employed by many, the reaction requires higher ratio of DMC to glycerol and it also causes shift in chemical equilibrium.[7] Recent synthesis proposes the use of glycerol and urea as feedstock for the synthesis of glycerol carbonate.[8,9] The use of relatively cheaper bio-renewable feedstock and catalyst derived from industrial waste has gain our interest to conduct the study. On the other hand, previous study conducted by our group using gypsum in glycerolysis reaction with urea to produce glycerol carbonate also suggest proper utilisation of industrial waste.[10]Though there have been studies reported on the use of catalyst containing K-zeolite derived from fly ash for the transesterification reaction of glycerol with DMC, the catalyst preparation involved deposition of synthetically derived potassium ions involving several pre-treatment stages.[11] Therefore, waste boiler ash is deduced herein as a catalyst for a greener and cost effective reaction operation. Hence, similar to glycerol used as a feedstock,[1] the cyclisation of ethylene glycol and propylene glycol to form their respective carbonate was possible through the use of boiler ash as catalyst and it was reported for the first time herein.

Results and discussion

Catalytic Mechanism of Potassium Silicate Contained in Boiler Ash for the Synthesis of Glycerol Carbonate

Based on our previous study, potassium silicate (K_2SiO_3) contained in boiler ash was found to be the major element which influenced the catalytic behaviour of boiler ash in synthesising glycerol carbonate from glycerol and urea. The presence of potassium silicate in boiler ash was verified using XRD analysis[1] as well as through X-Ray Fluorescence (XRF) data, which is reported herein. Therefore, the detailed catalytic mechanism of potassium silicate contained in boiler ash for the synthesis of glycerol carbonate is

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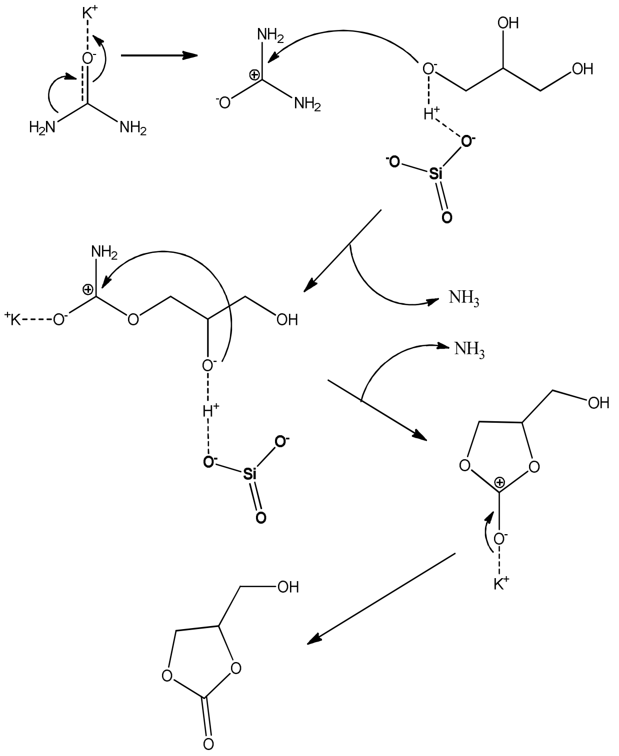
proposed. It can be inferred that the K$^+$ ion acts as a weak Lewis acid by activating the carbonyl group of urea. On the other hand, SiO_3^{2-} acts an effective conjugate basic site to activate the hydroxyl group of glycerol. Based on scheme 1, the activation of carbonyl group of urea grounds the carbonyl group to become positively charged and further acting as an electrophile. In contrast, the activated hydroxyl group of glycerol acts as a nucleophile. In step 1, the nucleophilic attack of hydroxyl group towards the electrophilic carbonyl of urea formed the carbamate intermediate while releasing ammonia gas. It is believed that the second step is the most anticipated reaction phase where the selectivity towards desired product formations is evidently observed due to the influence of the catalyst. The cyclisation is complete by the loss of more ammonia gas, followed by ring formation and rearrangement of the carbonyl double bond to form glycerol carbonate.



Scheme 1 Catalytic mechanisms of glycerol carbonate synthesis using K_2SiO_3

Reusability study of BA 900 and K_2SiO_3

In any fine chemical synthesis industry, the reusability of catalyst is one of the crucial parameters of concern. Thus, both boiler ash (BA 900) and K_2SiO_3 were subjected to reusability test that is being carried out under standard reaction conditions. As depicted in Fig. 1 and 2, the conversion, selectivity and yield were significantly comparable and showed optimum performance in all three cycles for both tested catalysts. The reusability of K_2SiO_3 catalyst is anticipated since the fresh and spent catalyst exhibits comparable characteristic through analysis conducted using FTIR, XRD, FESEM and N_2 physisorption.

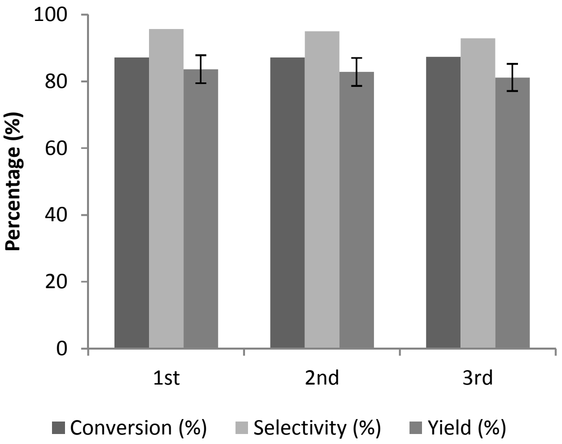


Fig. 1 Reusability study of glycerol carbonate using K_2SiO_3

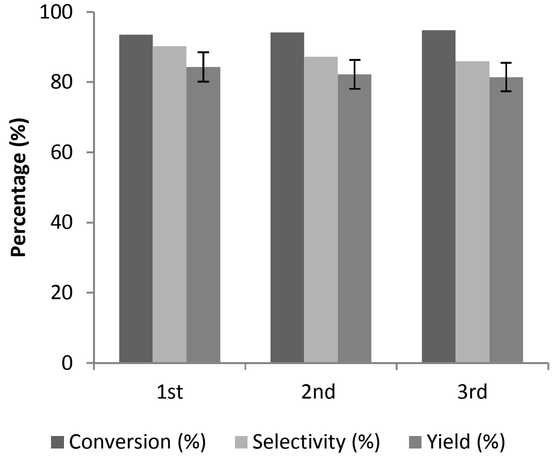


Fig. 2 Reusability study of glycerol carbonate using BA 900

However, unobserved FTIR peaks at range of 1200-1500 cm^{-1} for spent catalyst was found due to the presence of glycerol moiety that remained intact on the catalyst, which then interfered and broadened the FTIR signal (Fig. 3). For record, the spent catalyst was subjected to washing with deionised water, thus remaining glycerol is expected. In the meantime, a slight difference in XRD pattern as shown in Fig. 4 is due to dominant presence of SiO_2 in spent catalyst as an evident from EDX analysis (Table 1). More dominant amorphous SiO_2 is expected to be present due to the loss of some potassium ion, thus the XRD diffractogram will closely resemble the diffraction pattern of pure SiO_2.[12]

Based on the analysis being carried out using N_2 physisorption, it was found that the BET surface area of both fresh and spent K_2SiO_3 were comparable to each other (Table 2). However, spent catalyst contains larger pore volume and pore size. This scenario is expected to occur due to the loss of some potassium ion embedded to the silicate that allows larger pore of silicate to be present. As mentioned, it was found that potassium ion and silicate ions majorly plays an important role in the catalytic mechanism. Therefore, the variation of catalyst surface area, porous structure and morphology (Fig. 5) are less significant. The presence of K_2SiO_3 predominantly in calcined boiler ash (BA 900) was verified using XRF analysis (Table 3). It was also found that at higher heat treatment under static air environment, KCl that exist in dried boiler ash is later transformed into K_2SiO_3 where the loss of chlorine ion can be expected as reported by our group[1] (ESI 1). The presence of other elements such as MgO, CaO, Al_2O_3, Fe_2O_3, P_2O_5, ZrO_2 are at minor level that do not significantly affect the catalytic activity of boiler ash. Additionally, the presence of SiO_2 also does not affect the catalytic activity of boiler ash and gives the yield of glycerol carbonate amount to be comparable to uncatalysed reaction[1]. Indeed, it was found that potassium ion along with its conjugated basic site (i.e. KCl, KOH and K_2SiO_3) acted as the most effective metal element of interest. Apart from that, the XRF analysis conducted is in agreement with the ICP-MS and FESEM-EDX analysis reported earlier in which the dominant metal element detected in all three analysis was potassium.[1]

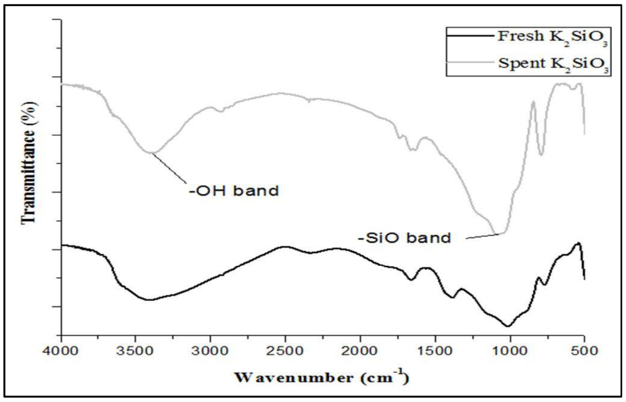


Fig. 3 FTIR spectrum of fresh and spent K_2SiO_3

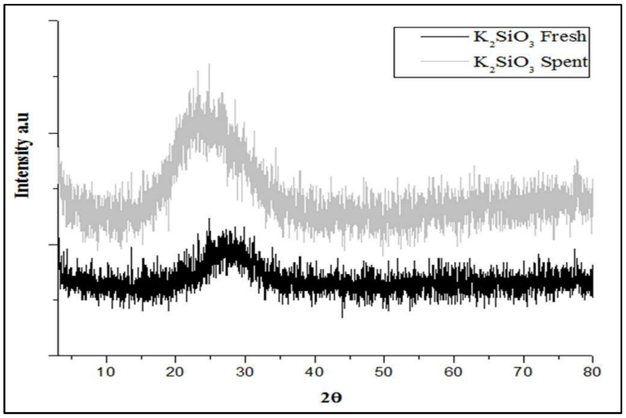


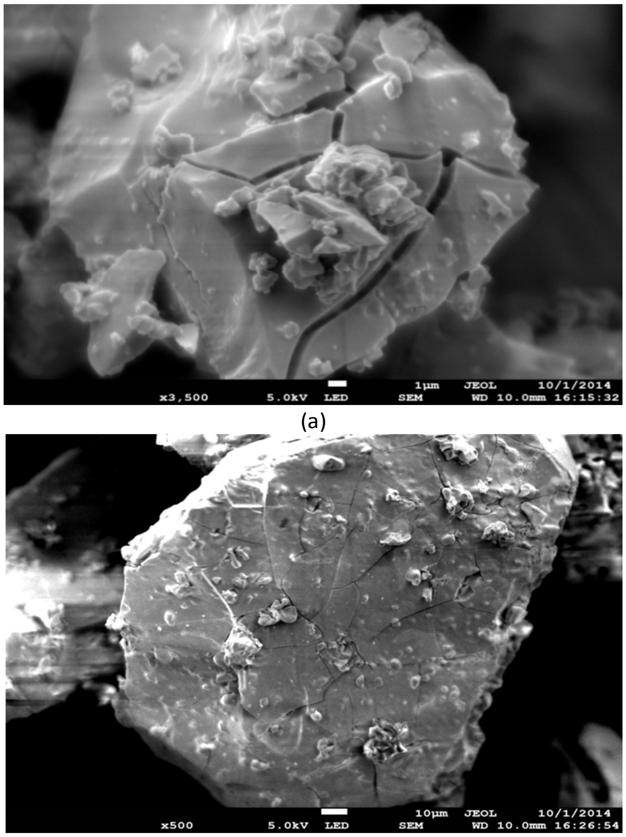
Fig. 4 XRD of fresh and spent K_2SiO_3

Table 1: Element and composition in weight percent of Fresh and Spent K_2SiO_3

Element	wt% (Fresh)	wt% (Spent)
O	56.11	57.27
Si	26.01	28.47
K	17.88	14.26
Totals	100.00	100.00

Table 2: BET Surface area, pore size and pore volume of fresh and spent K_2SiO_3.

Catalyst	BET Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
Fresh	2.50	0.003	45.14
Spent	2.54	0.021	342.06



(a)

(b)

Fig. 5 FESEM morphology of (a) fresh K_2SiO_3 (b) Spent K_2SiO_3.

Table 3: X-Ray Fluorescence of BA 900 (metal oxides)

Analyte	Mass %
K_2SiO_3	43.53
SiO_2	33.14
K_2O	7.17
CaO	8.98
MgO	2.41
Al_2O_3	1.93
Fe_2O_3	1.89
P_2O_5	0.73
ZrO_2	0.22
Total	**100**

Even though K_2SiO_3 demonstrated reusable property, only 56.3 wt % of catalyst was recovered after the third cycle. The partial recovery of the catalyst might be due to the delocalisation of potassium ions during reaction and washing procedure as well as contribution from systematic and random error during experimental work. Indeed, the minor amount of metal leached was confirmed through Energy Dispersive X-Ray (EDX) analysis of spent catalyst and ICP-MS analysis of reaction solution, where 2.4 % K and 18.21 % of Si were lost.

In similar trend to K_2SiO_3, only 31.7 wt % of catalyst was recovered after the third cycle. The higher weight percent of catalyst loss was observed from BA 900 compared to K_2SiO_3 that can be attributed to the loss of other present element in boiler ash as previously reported[1] apart from leaching of potassium ion. It is also notable that the FTIR spectrum (Fig. 6) of spent BA 900 and spent K_2SiO_3 showed almost similar patterns. This qualitative data indicated that major composition of boiler ash is predominantly existed in potassium silicate phase. Besides, there is also no significant difference between the FTIR spectrums (Fig. 7) of fresh BA 900 and spent BA 900. Moreover, Hammett test from Table 4 also indicate the basic property of all fresh and spent BA 900 as well as K_2SiO_3 as confirmed by changed in colour of phenolphthalein indicator. Hence, the activity of reusable boiler ash is expected to be comparable as the reusable K_2SiO_3. Indeed, the calculated turn over frequency (TOF) of K_2SiO_3 is 125.6 mmol/ g.cat.h^{-1}, which do not ideally deviate from the TOF value of BA 900, which were 126.5 mmol/ g.cat.h^{-1}.

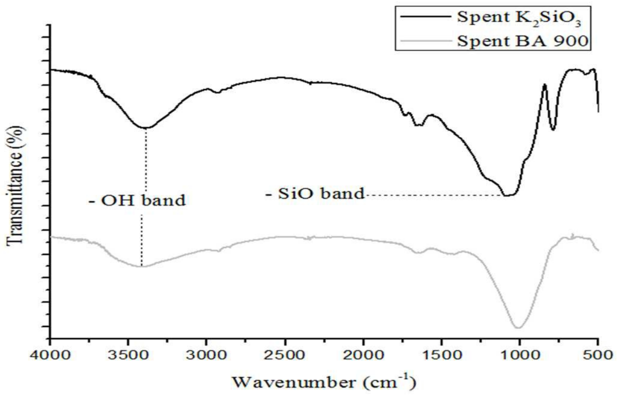


Fig. 6: FTIR spectrum of spent K_2SiO_3 and BA 900

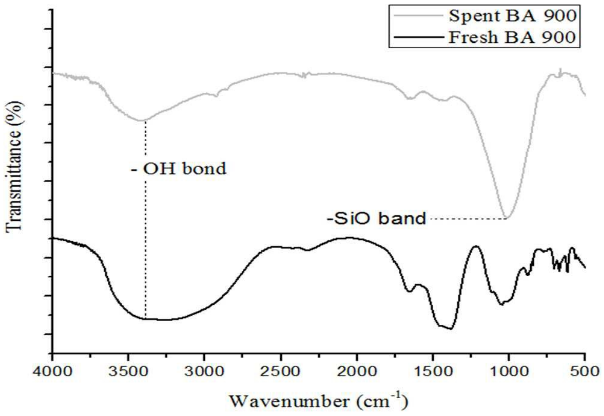


Fig. 7: FTIR spectrum of fresh and spent BA 900

Table 4: Hammett test of fresh and spent catalyst

Catalyst	Methyl Red (H_=4.8)	Phenolphthalein (H_=8.2)	2, 4 – Dinitroaniline (H_=15)	4 – Nitroaniline (H_=18.4)
Fresh BA 900	No changes	Colourless to pink solution	No changes	No changes
Spent BA 900	No changes	Colourless to pink solution	No changes	No changes
Fresh K_2SiO_3	No changes	Colourless to pink solution	No changes	No changes
Spent K_2SiO_3	No changes	Colourless to pink solution	No changes	No changes

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Catalyst Feasibility Study in Synthesis of Ethylene Carbonate (EC) and Propylene Carbonate (PC)

Waste boiler ash (BA 900) was used as the catalyst for a greener and cost effective reaction operation. Similar to glycerol as a feedstock,[1] the cyclisation of ethylene glycol and propylene glycol to form their respective carbonate was made possible through the use of boiler ash catalyst and it was reported for the first time herein. It was found that potassium silicate (K_2SiO_3) contained in boiler ash could aid in the selective carbonylation of ethylene glycol and propylene glycol to their respective carbonates. As shown in Table 5, the optimum yield of ethylene carbonate of 80.1 ± 0.6 % was obtained at 8 h reaction time while at 10 h, the yield of propylene carbonate was 73.8 ± 0.7 %. It is important to note that catalytic activity for both ethylene carbonate and propylene carbonate shows almost identical turn over frequency (TOF) indicating that the amount of active species responsible for the transcarbonylation reaction to be equal. Apart from that, reaction involving the use of K_2SiO_3 alone instead of boiler ash produced almost similar yield of respective carbonates of EC (79.9 ± 0.3 %) and PC (72.8 ± 0.7 %). Thus, it is suggested that the catalytic activity was due to the presence of K^+, which acted as a weak Lewis acid to activate urea while the conjugate basic site SiO_3^{2-} activated the hydroxyl group of the polyols to form the respective carbonates. Moreover, the current study proposes better yield of ethylene carbonates than previously reported study.[13,14] Besides, previous study reported the synthesis of propylene carbonate being operated at higher temperature (170 °C and 180 °C), which could contribute to relatively non cost effective process. [15-17] Indeed, the use of higher temperature, which is more than 150 °C was not favoured due to the reported decomposition of urea into isocyanic acid.[18] It is worth to note that there is no available study being reported on the use of potassium as an active catalyst for the cyclisation of polyols with the aid of urea.

Table 5: Reaction conditions and yield of ethylene carbonate and propylene carbonate

No.	Reaction/ Catalyst	Temperature (°C)	Molar ratio of Polyol to Urea	Conversion of polyol	Duration (h)	Yield % of Organic Carbonate	TOF (mmol/ g cat.h^{-1})
1	**Ethylene carbonate**	150	1.5:1 Ethylene glycol: Urea				
	Blank			60.5	8	17.9	-
	BA 900			92.7	8	80.1	120.2
	K_2SiO_3			92.7	8	79.9	119.8
2	**Propylene carbonate**	150	4:1 Propylene glycol: Urea				
	Blank			78.4	10	36.3	-
	BA 900			89.2	10	73.2	117.1
	K_2SiO_3			89.4	10	72.8	116.5

Reaction conditions: Catalyst mass, 0.25 g; gas, N_2; standard stirring rate, 340 rpm; TOF: calculated based on the yield of carbonate multiplied by mmol of initial polyols per gram catalyst per total reaction time (h). Quantitative analysis was carried out using Agilent Technologies A7890 Gas Chromatography-Flame Ionised Detector (GC-FID) equipped with DB-WAX (60m, 0.25mm, 0.25µm) column).

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Proposed Mechanistic Pathway of EC and PC using Boiler Ash as Catalyst

The cyclisation pathway of ethylene glycol and propylene glycol along with their by-products formation using boiler ash as a catalyst is proposed in Scheme 2 and 3. The mechanistic pathway for both ethylene carbonate and propylene carbonate through respective carbamate intermediate was confirmed via time online study monitored by ATR-FTIR (Fig. 8 and 9) and ^{13}C NMR (ESI 2). Both FTIR spectra showed the presence of C=O (1715 cm^{-1}) group of 2-hydroxyethyl carbamate and 2-hydroxypropyl carbamate, which later on transformed into carbonate compounds. There was also no sign of N-C-O stretching of isocyanic acid in peak observation at 2210 cm^{-1}, which indicates that the reaction is solely dependent on carbamate as an intermediate compound. In Fig. 8, the band at 1801 cm^{-1}and 1788 cm^{-1} indicate the symmetrical C=O stretching of EC.[19] The ring stretching peak of EC and PC were visible as duration or reaction is increased and was present at range of 770-785 cm^{-1}. In case of TOL of PC, the methyl group was also observed to be formed at 1352 cm^{-1} and 1380 cm^{-1}. The decomposition of urea from 0 h to 10 h is visible from being consumed in the reaction where the peak for urea is labelled in Fig. 8 and Fig. 9 that gradually disappeared.

Based on TOL analysis conducted using ATR-FTIR and ^{13}C NMR, the mechanistic pathway for both EC and PC corresponds to the similar pathway observed for glycerol carbonate, where the formation of glycerol carbonate is originated through selective transformation of respective carbamate intermediate. Even though similar route was observed in related literature,[15,20] a slight difference was perceived with boiler ash as catalyst whereby the conversion of carbamate into respective carbonate occurred in an accelerated manner. However, some of the by-products detected in prior-art experiments were not detected in this study such as biuret which is also known as carbamylurea.[13] Similar finding on the reaction pathway involved decomposition of intermediate carbamate into EC.[13,20] On the other hand, Wang and co-researchers in 2014 proposed the formation of propylene carbonate that was due to decomposition of intermediate 2-hydroxypropyl carbamate, which was similar to the current findings.[14] However, they also reported the presence of isocyanic acid, which later forms the intermediate compound. This scenario is expected since the reaction was carried out at temperature higher than 150 °C, thus increasing the possibility of urea to decompose into isocyanic acid. Scheme 2 and Scheme 3 illustrate the reaction pathway of ethylene carbonate and propylene carbonate using BA 900 containing potassium silicate as catalyst.

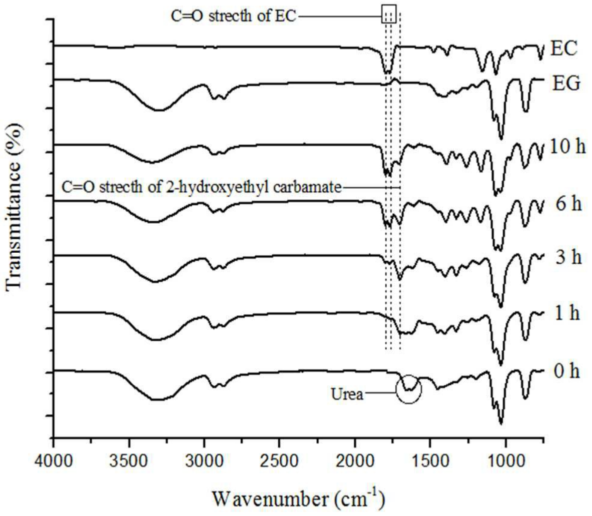


Fig. 8 ATR-FTIR time online analysis study of ethylene carbonate synthesis

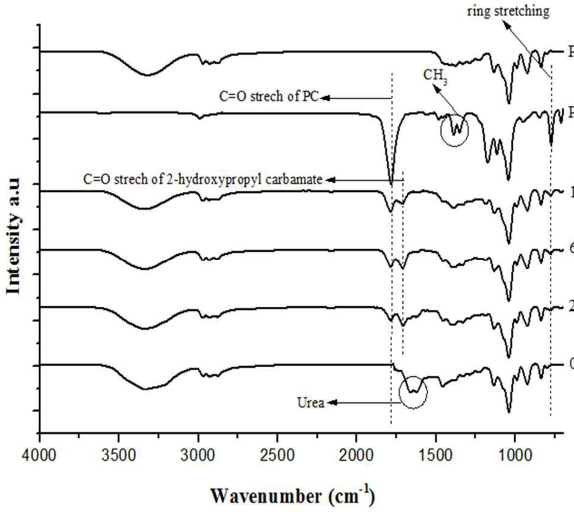
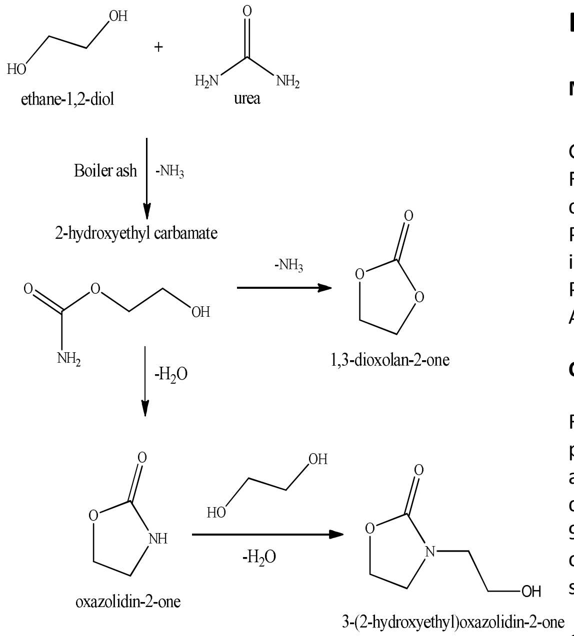
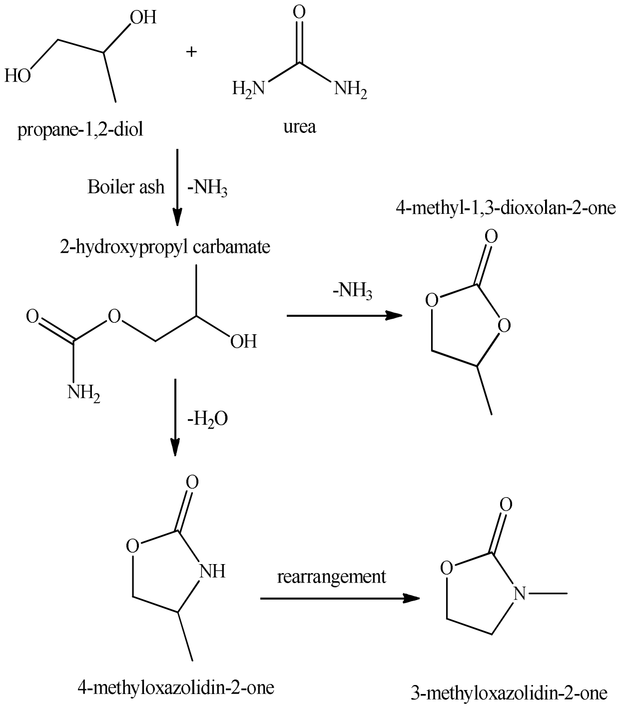


Fig. 9 ATR-FTIR time online analysis study of propylene carbonate synthesis



Scheme 2 Proposed reaction pathway of ethylene carbonate synthesis using BA 900 containing K_2SiO_3



Scheme 3 Proposed reaction pathway of propylene carbonate synthesis using BA 900 containing K_2SiO_3.

Experimental

Materials

Glycerol (99.5%) and Urea (AR Grade) were purchased from Friendemann Schmidt Chemical. Waste boiler ash used as the catalyst was collected from a palm oil mill located in Lepar Hilir, Pahang, Malaysia. The boiler ash used is the ash obtained from incineration of palm fruits, palm kernel, palm shells and palm fibre. Potassium Silicate (K_2SiO_3) ≥99.9% used was purchased from Sigma-Aldrich.

Catalyst Preparation

Raw boiler ash was dried at 110 ˚C for overnight and then powdered using mortar and pestle. Then, the ash was sieved using a 200 µm sized sieve. Next, 2 g of the sieved ash was loaded on the combustion boat and calcined under static air at the temperature of 900 ˚C for 4 h in a horizontal tube furnace at temperature ramping of 5 ˚C/ min. The catalysts were later denoted as BA 900. Potassium silicate was directly used without any prior pre-treatment.

Catalytic Testing

The reaction of ethylene carbonate and propylene carbonate synthesis was carried out using a three-neck round bottom flask attached to a cycle condenser with water cooling system. The reaction parameters are as described in Table 5. For the reaction involving synthesis of ethylene carbonate, 18.6 g of ethylene glycol was allowed to heat up to 150 ˚C for 10 h under the flow of nitrogen gas for 20 min before adding urea and catalyst while the temperature and stirring rate was controlled using IKA@DTS-5 temperature controller. When the temperature reached 150 ˚C, 12.0 g urea and 0.25 g catalyst were added to the reaction and it was stirred using a magnetic stirrer under 340 rpm of stirring rate. The molar ratio of ethylene glycol to urea used was (1.5:1). For the reaction involving synthesis of propylene carbonate, 30.4 g of propylene glycol was allowed to heat up to 150 ˚C for 10 h under the flow of nitrogen gas for 20 min before adding urea and catalyst while the temperature and stirring rate was controlled using IKA@DTS-5 temperature controller. When the temperature reached 170 ˚C, 6.0 g urea and 0.25 g catalyst were added to the reaction and stirred using magnetic stirrer under 340 rpm of stirring rate. The molar ratio of propylene glycol to urea used was (4:1). Sampling was done from 0 h to 10 h with the time interval of 1 h. 50 µl of sample was transferred in 1450 µl of deionised water. The experiment was repeated three times for repeatability study.

The reaction setup was similar to the reaction of EC and PC for the reusability study of potassium silicate (K_2SiO_3). Glycerol was heated up to 150˚C for 20 min under the flow of nitrogen gas before adding urea and catalyst. The molar ratio of glycerol to urea was (1:1.5) and 0.5 g catalyst (K_2SiO_3) was added to the reaction and the sampling was done at 4 h. 50 µL of sample was transferred in 1450 µL of deionized water. The reaction mixture was immediately placed into a 100 mL centrifuge tube and centrifuged for 1 h at 8000 rpm. The catalyst deposited as residue at the bottom of the centrifuge tube was carefully transferred into a clean 100 mL centrifuge tube and washed with deionized water. The water was removed from the centrifuge tube after 30 min of centrifugation.

This step was repeated for 4 times. The final catalyst was filtered and dried overnight at 110 ˚C and the synthesis of glycerol carbonate using dried catalyst was repeated for the second cycle. The same procedure was again repeated until the third cycle.

Product Analysis

GC-FID Agilent Technologies 7890A equipped with DB-WAX (60m, 0.25mm, 0.25µm) was used to analyse the product of ethylene carbonate and propylene carbonate. Helium gas was used as the carrier gas with a flow of 1.5 mL/min. The temperature of the injector and the detector were 225 °C and 250 °C respectively. The temperature of the column was programmed to have a 2 min initial hold at 80 °C and then 15 °C/min ramp from 80 °C to 250 °C at 5 min holding time. The split ratio was 1:10 and the injection volume was 1 µl.

ATR-FTIR Perkin Elmer USA was used to study the functional group present in the online time analysis of the product from 0 min to 10 h, which could attribute to the product and by product that is also present in the reaction mixture as a validation. A single drop of reaction mixture was placed on the liquid holder and the transmission data were collected in the range of 4000–700 cm^{-1}. NMR, BRUKER Ultra Shield Plus 500 MHz was also used to study the ^{13}C NMR of the products formed.

Inductive Coupled Plasma-Mass Spectrometer (ICP-MS) Agilent 7500c was used to study the potassium and silicate content in the reaction mixture using in-house method of CHEMITEL/WI/CHEMTM/001 that was based on AOAC999.10.

Catalyst Characterisation

XRD Rigaku Miniflex II was used to analyse the XRD pattern of the fresh and spent K_2SiO_3. Diffraction patterns were recorded with Cu Kα radiation (λ=1.5406 A), which was operated at 40kV and 30mA over the range of 3 degree to 80 degree at 2 Theta (θ) for crystalline phase determination at scan speed of 0.04 degree/s. The catalysts samples in powder form were then loaded individually on a glass sample holder for measurement.

FTIR transmission data were collected for pressed catalyst disk made with KBr with ratio of (1:10) catalyst to KBr in the scanning range of 4000–400 cm^{-1} for fresh and spent BA 900 as well as K_2SiO_3.

Shimadzu X-Ray Fluorescence 720 was used to analyse metal oxide content in boiler ash and it was conducted based on acceptable calibration range at CuKa 8.00-8.05 while the instrument was operated at 50 Kv and 30 µA.

Micromeritics' ASAP® 2020 Accelerated Surface Area and Porosity Analyser BET was used to analyse both fresh and spent K_2SiO_3. The procedures using BET instrument were initiated with the samples being dried with nitrogen purging. The volume of the gas being adsorbed at the surface of the particles is measured by referring to the boiling point of nitrogen at -196 °C. The number of gas adsorbed corresponds to the particles on total surface area, which includes the pores present on the surface.

FESEM-EDX, JEOL (JSM-7800f) with a spatial resolution up to 1 nm was used to study the surface morphology and elemental analysis of the fresh and spent K_2SiO_3.

The Hammett test were carried out on spent and fresh catalyst of BA 900 as well as K_2SiO_3 where phenolphthalein, 2, 4-dinitroaniline, 4-nitroaniline and methyl red were used as indicators to determine the qualitative acidic as well as basic properties of the catalyst. 25 mg of catalysts were weighed and prepared in three batches and 5 ml of methanol was added to the catalyst. Then, 1 ml of the indicator was added to 4 ml of methanol with the final volume of 5 ml indicators were added separately to the catalysts weighed in batches. The mixture was then let to equilibrate for 2 h and the colour changes were observed and noted.

Turn Over Frequency (TOF)

Equation 1

$$\text{Turnover Frequency, (TOF)} = \frac{\dfrac{\text{Mols of Polyol used} \times \text{yield \% of Organic carbonate}}{(\text{Mass of catalyst} \times 100)}}{\text{Duration of reaction (h)}}$$

Conclusions

In brief, boiler ash containing K_2SiO_3 (BA 900) and commercially available K_2SiO_3 demonstrates high selectivity and yield toward glycerol carbonate formation with no loss of activity up to three consecutive cycles. Besides, it is proven that boiler ash containing potassium silicate can act as an attractive catalyst to selectively convert polyols, ethylene glycol and propylene glycol into their desired cyclic organic carbonates. Therefore, the catalyst can serve as a Lewis acid catalyst for the synthesis of cyclic organic carbonates. In short, the catalyst derived from waste boiler ash can serve as an economical catalyst for the synthesis of GC, EC and PC.

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GRAPHICAL ABSTRACT