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Synthesis of ethylene carbonate from cyclocondensation of ethylene glycol and urea over $ZnO\bullet Cr_2O_3$ catalyst system controlled by co-precipitation method

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ABSTRACT

$ZnO\cdot Cr_2O_3$ catalyst has been synthesized by low temperature, pH controlled co-precipitation route and characterized employing techniques of Brunauer, Emmett, and Teller (BET) surface area measurement, ammonia desorption technique, X-ray diffraction (XRD) and scanning electron microscopy (SEM). These characterizations reveal the catalyst to possess $ZnO\cdot ZnCr_2O_4$ composition. The catalysts have been tested for their performance for the first time, in the synthesis of ethylene carbonate from cyclocondensation of ethylene glycol and urea. Effect of catalyst concentration, temperature and molar ratio of reactants has been studied to obtain the optimum conversion and selectivity of ethylene glycol and urea to ethylene carbonate. A maximum yield of 85.75% of ethylene carbonate was obtained at a temperature of 423 K and urea: ethylene glycol molar ratio of 1:1.5. A tentative mechanism of the reaction is proposed on the basis of analysis of reactants, products and modeling of the transition state for the reaction under density function theory using Gaussian09W software. Our studies suggest a consecutive mechanism for the reaction. In the first step, urea and ethylene glycol react to produce 2-hydroxyethyl carbamate, which undergoes further reaction to produce ethylene carbonate (EC) and ammonia.

1. Introduction

Carbon dioxide is a greenhouse gas and renewable source of carbon. In the current decade attempts have therefore been made to transform it into valuable chemicals. However, because of its high thermodynamic stability, it is almost inert to large variety of chemicals and only highly strained molecules can react with it under elevated temperature and pressure. This is the reason why only limited chemical processes utilize it as a raw material. In spite of this drawback, success has been obtained to transform carbon dioxide into dimethyl carbonate, cyclic carbonates, polycarbonates, urea and urethane derivatives, carboxylic acids, esters, lactones, isocyanates and many more chemicals [1].

Cyclic carbonates find applications as reactive intermediates and as inert solvent. These can be used to prepare monomers, polymers, surfactants, plasticizers, cross linking agents and solvents [2]. Cyclic carbonates are also used as electrolytes in the lithium ion rechargeable batteries [3-5].

An important field in green chemistry is to find solvents which can replace the traditional hazardous solvents. Owing to their biodegradability and biocompatibility [6,7], low odour level, low toxicity, high dipole moment, and high boiling and flash point, cyclic carbonates are emerging as promising environmental benign solvents for future. Recently, Wang *et al.* [8] have used ethylene carbonate as a unique solvent for palladium-catalyzed Wacker oxidation using oxygen as sole oxidant.

Traditionally, these carbonates are prepared by reacting toxic phosgenation with alcohols at about room temperature in an anhydrous solvent containing excess of pyridine. Although the process is accompanied with very high yield of carbonates, the main drawback of the process is the use of toxic and hazardous chemicals like pyridine and phosgene [9].

Reaction of CO_2 with epoxides is another green process for synthesis of cyclic carbonates and fixation of carbon dioxide [10-23]. Drawback with this process is that it requires high pressure and uses epoxide as the starting material. A better route for the synthesis of cyclic carbonates is to transform CO_2 into urea and then react urea with diols, at about atmospheric pressure.

Chromite spinals formed due to close packing of O^{2-} anions have the general formula $A^{2+}[B_2^{3+}]O_4$ and posses tetrahedral and octahedral interstitial sites filled by A^{2+} and B^{3+} ions, respectively. Ferrite, spinals have been found to be very selective catalysts for alkylation of aromatics [24-28].

There are reports on the synthesis of ethylene carbonate (EC) [29-36]. Many of them use ethylene oxide as raw material [29-31]. Su *et al.* [32] described reactions of alkylene glycols and urea to synthesise alkylene carbonates using Tin containing catalysts. Masaharu *et al.* [33] have described a method for synthesis of alkylene carbonates from alkene glycols and urea under reduced pressure using a catalyst containing at least one metal selected from zinc, magnesium, lead and calcium; and reported a yield of EC reached 92.6 %.

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Table 1. Effect of precursor on catalytic composition of Zinc/Chromium oxide.

Catalyst	Precursors		Precursor (mol ratio)	Expected catalyst composition
	Zn	Cr		
ZC-1	$Zn(NO_3)_2{\cdot}6H_2O$	$Cl_3Cr{\cdot}6H_2O$	9:1	$8.5\ ZnO{\cdot}\ 0.5\ ZnCr_2O_4$
ZC-2	$Zn(NO_3)_2{\cdot}6H_2O$	$Cl_3Cr{\cdot}6H_2O$	7:3	$5.5\ ZnO{\cdot}\ 1.5\ ZnCr_2O_4$
ZC-3	$Zn(NO_3)_2{\cdot}6H_2O$	$Cl_3Cr{\cdot}6H_2O$	5:5	$2.5\ ZnO{\cdot}\ 2.5\ ZnCr_2O_4$
ZC-4	$Zn(NO_3)_2{\cdot}6H_2O$	$Cl_3Cr{\cdot}6H_2O$	3:7	$3.5\ ZnCr_2O_4{\cdot}0.5Cr_2O_3$
ZC-5	$Zn(NO_3)_2{\cdot}6H_2O$	$Cl_3Cr{\cdot}6H_2O$	1:2	$ZnCr_2O_4$

Table 2. Acidity, mean crystallite size, surface area and catalytic activity of $ZnO{\cdot}Cr_2O_3$.

Catalyst	Acidity (NH_3 uptake mmol/g)			Total acidity	Mean crystallite size (nm)	Surface Area (m^2/g)	Catalytic activity EC Yield (%)
	473-573 K	573-673 K	673-773 K				
ZC-1	0.3	0.2	0.1	0.6	31.34	20.89	59.90
ZC-2	0.5	0.3	0.2	1.0	7.49	58.64	56.00
ZC-3	0.4	0.2	0.3	0.9	4.87	66.30	40.50
ZC-4	0.4	0.2	0.2	0.8	4.08	157.67	34.54
ZC-5	0.4	0.3	0.1	0.8	4.89	148.32	31.88
ZnO						56.00	82.35

Reaction Conditions: Temperature: 423 K; Catalyst Concentration: 2 wt. %; Ethylene glycol/Urea mole ratio: 1.5; Duration of the reaction: 2 h.

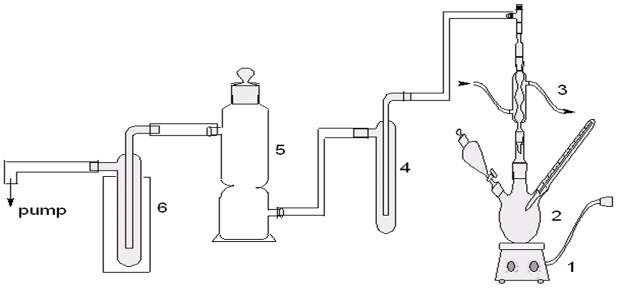


Figure 1. Experimental setup for lab. scale syntheses of EC. 1. Heater; 2. Reactor; 3. Condenser; 4. HCl trap; 5. Calcium chloride tower; 6. Ice cooled empty trap.

Li *et al.* [34] found that metal oxide catalysts with appropriate acidity and basicity were favourable for the synthesis of cyclic carbonate. Zhao *et al.* [35] and Jia *et al.* [36] prepared zinc/iron oxide and silica supported lead catalysts respectively for the synthesis of propylene carbonate via 1, 2-propylene glycol and urea.

There is one cursory study on the synthesis of ethylene carbonate from ethylene glycol and urea over $ZnO{\cdot}Fe_2O_3$ catalyst [37], to the best of our knowledge there seems to be no report on the synthesis of ethylene carbonate from ethylene glycol (EG) and urea using $ZnO{\cdot}Cr_2O_3$ as a catalyst system.

2. Experimental

2.1. Catalyst preparation

$Zn(NO_3)_2{\cdot}6H_2O$ and $Cl_3Cr{\cdot}6H_2O$ are taken in according to Table 1 and metal salts were dissolved in excess of distilled water (salt: water wt. ratio was kept nearly 1:300) and a dilute solution of NaOH was added with constant stirring until the pH of the solution was 8.5. The precipitate was further digested at 353 K for 2 h. and repeatedly washed with distilled water until free from chloride and nitrate ions. Finally the precipitate was oven dried and calcined at 723 K.

2.2. Characterization of the catalyst

The X-ray diffraction (XRD) measurements were performed using a Rigaku X-ray powder diffractometer equipped with a graphite-crystal monochromator (for the diffracted beam) and a scintillation counter: Cu$K\alpha$ radiation with wavelength 1.5406 Å was used in the 2θ range 10-95 Å. The mean crystallite size was determined by measuring the broadening of the peak and applying the Debye Scherrer equation [38].

The surface morphology of the catalyst was observed with a JEOL JSM-5600 scanning electron microscopy system equipped with an energy-dispersive X-ray analysis (SEM-EDX). The samples were prepared by evaporating a drop of the sample on a carbon-coated copper grid. All images were obtained in the SEM mode with the emission gun operated at an acceleration voltage of 20 kV.

BET surface area measurements were made using a single point BET dynamic method employing a Smart Sorb 93 instrument supplied by Smart instrument Co., Bombay.

Ammonia desorption experiments were carried out to measure the acidity of the catalyst using ammonia as an adsorbate. 2.0 g of catalyst was packed in a Pyrex tube down flow reactor and heated to 673 K under a nitrogen gas flow rate of 0.5 cm^3/s for 3 h. The reactor was then cooled to 298 K and adsorption conducted at that temperature by exposing the sample to ammonia for 2 h. Physically adsorbed ammonia was removed by purging the sample with a nitrogen gas (flow rate 0.5 cm^3/s) at 353 K for 1 h. The acid strength distribution was obtained by raising the catalyst temperature from 373-773 K in a flow of nitrogen gas at 0.5 $cm^3\ s^{-1}$and absorbing the ammonia evolved in 0.1 N HCl. Quantitative estimation was made by titrating the unreacted HCl with 0.1 N NaOH in different temperature ranges. The results are presented in Table 2.

2.3. Experimental procedure

The reaction was carried out in a 100 ml, three-neck round-bottomed flask, equipped with a condenser and a thermometer. The condenser was connected to a vacuum pump through an HCl tower and an ice cold trape, to pump out ammonia gas produced during the reaction (Figure 1). The reactor was charged with ethylene glycol and urea and was put to reflux at 423 K. After the completion of reaction, the product was filtered to separate the catalyst. The filtrate was cool to room temperature.

2.4. Identification and analysis of product

About 10 g of solid sample was collected. Its melting point was determined to be 307 K. An IR spectrum of the solid sample recorded at Shimadzu R-460 spectrometer in the range 400-4000 cm^{-1} shows band at 1752 cm^{-1} which can be assign to C=O stretching mode. Quantitative analysis of the product mixture was made employing a Gas Liquid Chromatograph (Chemito Gas Chromatograph 7610) equipped with a Flame Ionization Detector. The conditions of GC analysis were: FID Detector, temperature = 473 K; Injector temperature, 473 K, and Column temperature ranges from 353 K to 473 K. Nitrogen was used as a carrier gas.

3. Results and discussion

3.1. Catalyst characterization

The XRD pattern of various catalysts is reproduced in Figure 2. Although, most of the XRD peaks corresponds to $ZnCr_2O_4$ spinel, peak at θ = 68.0 corresponds to ZnO, while that appeared at θ = 36.2 correspond to chromium oxide. Thus, our catalyst system is composed of ZnO [39], Cr_2O_3 and $ZnCr_2O_4$. The expected composition of all catalysts is listed in Table 1. The chromites composition increases with increasing amount of chromium chloride. This is also reflected in the XRD pattern. It is worth noting that XRD pattern of ZC-5 correspond to single phase $ZnCr_2O_4$ and match well with JCPDS card No. 73-1962.

The SEM images of three typical catalysts ZC-1, ZC-2, ZC-3 are reproduced in Figure 3. The SEM picture of Figure 3 (a) is typical to that of ZnO rods. With increasing content of Cr_2O_3 in the catalyst (Figure 3 (b) and (c)) the ZnO rods have vanished suggesting formation of spinel structure.

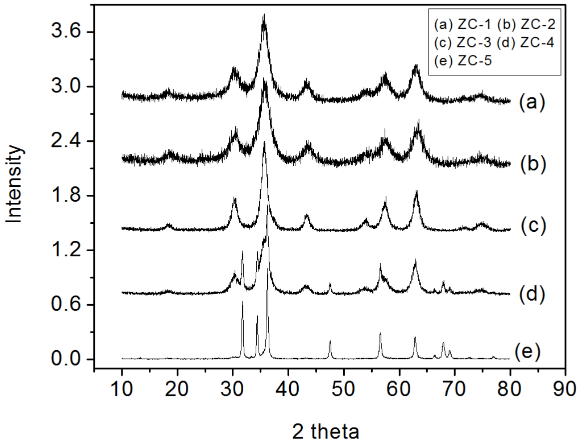


Figure 2. The XRD pattern of the various ZnO·Cr_2O_3 catalysts.

BET surface area records are listed in Table 2. The surface area increased with increasing amount of Cr_2O_3. This can be correlated to decrease in the particle size of the catalysts. An inspection of Table 2 suggests all the catalysts to possess acidic nature. Acidity in ZnO has been shown by others also [40,41]. Presence of acidity is important for adsorption of reactants.

3.2. Performance of various catalysts in the cyclization of ethylene glycol and urea to EC

Catalysts with their performances are shown in Table 2. The order of catalytic activity of system toward overall conversion was observed to be ZC-1 > ZC-2 > ZC-3 > ZC- 4 > ZC-5. The best activity was shown by ZC-1. Therefore, further studies were performed on this catalyst.

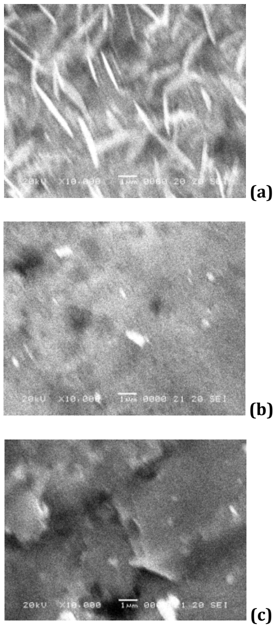


Figure 3. SEM images of (a) ZC-1 (b) ZC-3 (c) ZC-5.

3.3. Effect of temperature on the synthesis of EC

The effect of temperature on the cyclization of EC is shown in Figure 4. Conversion increased slowly up to 400 K reached a maximum of 70 % at 423 K. Thus, optimum temperature range of cycloaddition with Urea over ZC-1 catalyst seems to be 400-448 K. Maximum selectivity was also found in the same temperature range.

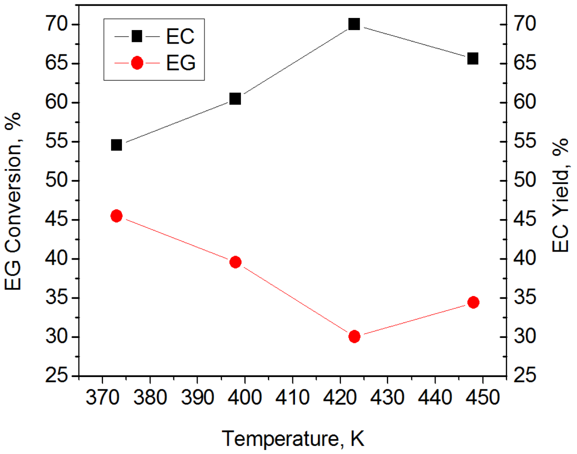


Figure 4. Effect of reaction temperature on EC yield. Reaction conditions: catalyst concentration: 6 wt.% (ZC-1), ethylene glycol/urea mole ratio: 1.5, duration of the reaction: 2 h.

3.4. Effect of catalyst Concentration on the reaction

Figure 5 presents the effect of catalyst concentration on the cycloaddition of urea with EG. It is found that initial increase in the catalyst concentration leads to increase in EG conversion until a limiting value is reached. A 6 wt% catalyst is found to be optimum EG conversion with an EC yield of 70%.

Table 3. IR observed bands (cm^{-1}) during syntheses of ethylene carbonate.

Sample No	Stretching	Ethylene glycol	Urea	2-Hydroxyethyl carbamate	Ethylene carbonate
1	-OH	3356	-	3666	-
2	C=O	-	1625	-	1800
3	C-O	-	-	-	1125

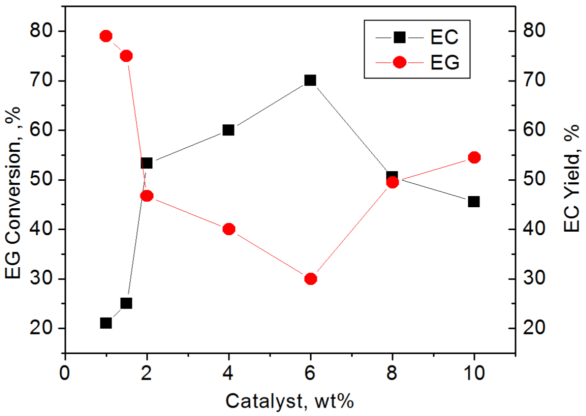


Figure 5. Effect of catalyst concentration on the EC yield. Reaction conditions: temperature: 423 K, ethylene glycol/urea mole ratio: 1.5, duration of the reaction: 2 h.

3.5. Effect of molar ratio on the synthesis of EC

The effect of urea/EG molar ratio on the EG conversion and EC yield is depicted in Figure 6. A urea/EG molar ratio of 1:1.5 was found to be optimum. Further increase in the ratio led to decreased conversion due to insufficient availability of urea.

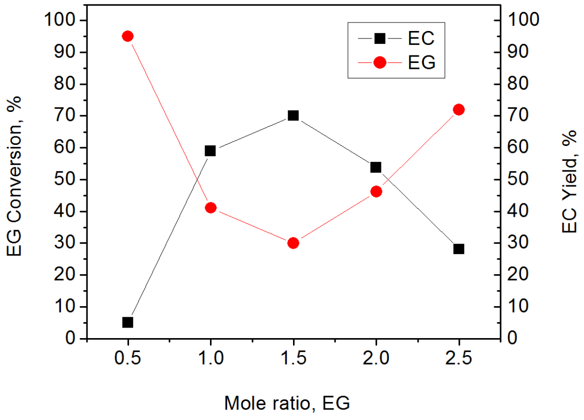


Figure 6. Effect of molar ratio urea/EC yield. Reaction conditions: catalyst: ZC-1, temperature: 423 K, duration of the reaction: 2 h.

3.6. Effect of time on stream on the synthesis of EC

To investigate the catalytic activity at different time, more experiments were conducted in the range of 1-4 h. The result presented graphically in Figure 7. It can be seen that the yield of EC increased with the reaction time, but the change was not significant after about 3 h. So, the optimum reaction time for the reaction is 3 h. In these experiments recovered catalyst were used. Therefore, these experiments demonstrate the reusability of the recovered catalysts as well.

4. Mechanism

The mechanism of the reaction being proposed is based on product analysis and infrared record of the reactants, product and reaction mixture at different interval of time on a Shimadzu IR spectrometer 460. The bands observed in the range 3000-4000 cm^{-1} and 1600-1900 cm^{-1} are listed in Table 3. The OH stretching mode of ethylene glycol appeared at 3356 cm^{-1}. In the reaction mixture a broad band centered around 3666 cm^{-1} appeared which loses its intensity with time.

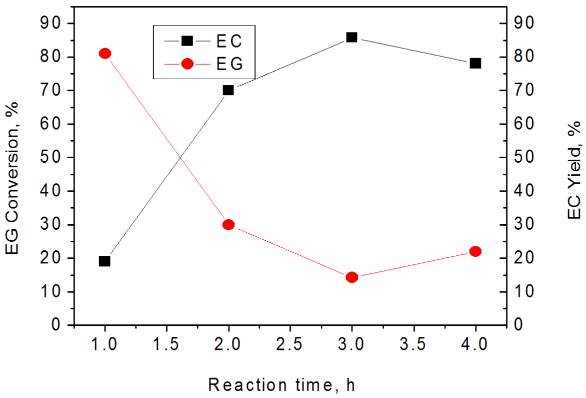
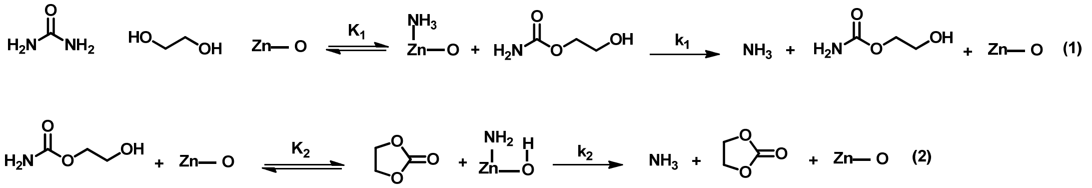


Figure 7. Effect of reaction time on EC yield. Reaction conditions: temperature: 423 K, catalyst concentration: 6 wt % ethylene glycol/urea mole ratio: 1.5.

This band has been assigned to OH stretching band of 2-hydroxyethyl carbamate.

Similarly the C=O stretching band of urea appears at 1625 cm^{-1}. IR spectrum of the reaction mixture showed a band at 1800 cm^{-1} and has been assigned to C=O stretching mode of ethylene carbonate. A shoulder appeared at 1850 cm^{-1} is assigned to C=O stretching mode of 2-hydroxyethyl carbamate. A plot of ethylene carbonate yield and concentration of ethylene glycol with time is shown in Figure 7. The yield increases with time and the concentration of ethylene glycol decrease with time. We could not observe any separate peak in our GC analysis for 2-hyroxyethyl carbonate. Idea of it concentration was therefore made from the time record of IR intensity of OH stretching mode of 2-hydroxyethyl carbamate. The records show decrease in the intensity of this peak. It seems 2-hydroxyethyl carbamate is rapidly formed in the beginning and then its concentration decrease with time. It seems urea is adsorbed on the acidic catalyst and EG remains in gas phase. Due to adsorption the ammine bond is weakened, reacts with EG and removed as NH_3 giving rise to the adsorbed specie 2-hydroxyethyl carbamate. 2-Hydroxyethyl carbamate is adsorbed on catalyst through nitrogen atom as well as undergoes a conformational change to the rotation about C-O bond to facilitate removal of second NH_3 molecule and formation of the ethylene carbonate.

Further clue to the reaction mechanism was obtained by modeling of the transition state for the reaction under QST2 option of the Gaussian-09 suite [42]. Details of QST2 option can be found elsewhere [43].



Scheme 1

The DFT molecular orbital calculations were performed using Becke's three parameter hybrid method with the Lee, Yang and Parr (B3LYP) gradient corrected correlation function [44 -45]. An inspection of Table 2 reveals that in the present catalyst system performance of the catalysts increased with increasing amount of ZnO in the catalyst and ZC-1 with maximum amount of ZnO came out to be the best catalyst. Li *et al.* [34] have studies a series of basic and acidic metal oxides for synthesis of cyclic carbonates from urea and diols and found ZnO to be most active catalyst for such reactions. These findings suggest ZnO as the active component of the catalyst. The function of $ZnCr_2O_4$ and Cr_2O_3 seems to be that of support / promoters. In view of these stoichiometric cluster Zn_4O_4 having least amount of dangling bond was chosen as the appropriate model of the catalyst [46-48] for Gaussian calculations.

Modeling of the reaction with flat adsorption of urea and ethylene glycol was so crowded that it did not converge even for reactant model. These rules out the single step reaction giving two moles of ammonia and one moles of ethylene carbonate. Attempts were therefore made to model these reactions as a two steps consecutive reaction in which urea and EG are adsorbed on neighboring sites and produce 2-hydroxyethyl carbamate (reaction 1). 2-Hydroxyethyl carbamate is further adsorbed in the second step to produce ethylene carbonate and ammonia (reaction 2). The potential energy surfaces for reaction 1 and 2 are shown in Figure 8.

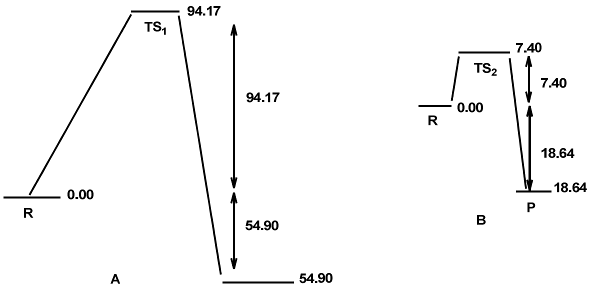


Figure 8. The potential energy surface for reactions (A) EG+ PG = 2-HEC + NH_3 and (B) 2-HEC = EC + NH_3. R= reactants, P = products.

The activation energies for reaction 1 and 2 were calculated to be 94.1 and 7.4 kcal/mol[1] respectively suggesting reaction 2 to be much faster than reaction 1. Thus, it seems 2-hydroxyethyl carbamate is formed in reaction 1 and is instantly converted to EC. The mechanism consistent with these is shown in Scheme 1.

5. Conclusions

$ZnO \cdot Cr_2O_3$ catalyst has been used for the first time for synthesis of ethylene carbonate from ethylene glycol and urea. The operation conditions have a significant influence on the EC yield. The experimental results indicated that the optimum reaction conditions over ZC-1 were urea/ EG molar ratio of 1:1.5, catalyst concentration of 6 wt.%, reaction temperature of 425 K, and reaction time of 3 h. A mechanism of the reaction assuming a consecutive reaction is proposed. Catalysts can be easily regenerated in situ by calcining with air at 773 K for 4 h.

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