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Metal ion-exchanged zeolites as highly active solid acid catalysts for the green synthesis of glycerol carbonate from glycerol

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Abstract

The application of metal ion-exchanged zeolites as highly efficient catalyst for the synthesis of glycerol carbonate from glycerol carbonylation is reported. The catalysts were prepared by ion exchange method and characterized by XRD, py-FTIR, AAS, NH_3TPD, N_2 sorption and SEM. The Na, H and Zn form of different zeolites were screened for the reaction. The Zn-FAU zeolite exhibited high glycerol carbonate yield compared to other Zn-zeolites such as Zn-ZSM5, Zn-MOR and Zn-beta. The acidity of Zn-HY zeolite was correlated with the amount of zinc and catalytic activity of the reaction. As the amount of zinc content increased in HY zeolite, glycerol conversion and selectivity for glycerol carbonate increased due to increase in Lewis acidity. Among different metal ion-exchanged HY zeolite, Zn^{2+} showed higher catalytic performance. Zn-Y catalyst with 0.79 mmol/g of zinc content gave 94.6 % glycerol conversion with 98 % selectivity for glycerol carbonate. The degree of zinc loading, reaction temperature, catalyst amount, mole ratio and catalyst reusability were investigated.

Keywords: Carbonylation; Glycerol; Glycerol carbonate; Urea; Ion-exchange; Zeolites

1. Introduction

The utilization of biomass, in particular biodiesel production has received much attention in last two decades. Its potential application as alternative fossil fuels establishes a green alternative route to reduce carbon emissions. One of the major drawbacks of the biodiesel industry is the production of large amount of glycerol as a byproduct by trans-esterification of fatty acids with methanol. In other words, around 10 kg of glycerol is formed per 100 kg of biodiesel produced, which is the cause for the surplus amount of glycerol present in the current market. Therefore, conversion of glycerol to value added chemicals is a desirable and has become broad area of research.[1-5] In this regard plenty of research has been dedicated to convert glycerol into several important chemicals such as acrolein, propylene glycol, 1, 3-propanediol, glyceric acid, glycerol carbonate, solketal and ethers etc.[1-5] Among these glycerol derivatives, glycerol carbonate (GC) is one of the value-added product with many potential applications.[6] Glycerol carbonate has interesting properties that lie between the cyclic alkylene carbonates and glycerol, making its direct use as solvent, curing gent in cement, plasticizer, humectants, and nail lacquer gel remover in cosmetic industry, liquid membrane in gas separation and an electrolyte in lithium- ion batteries. It also finds indirect applications in the synthesis of surfactant, polymers and chemical intermediates in organic synthesis.[6]

The glycerol carbonate is synthesized by different routes such as reaction of glycerol with phosgene, carbonation of glycerol with dimethyl carbonate or ethylene carbonate, carbonylation of glycerol by urea, reaction of glycerol with carbon dioxide**.**[7-20] The major drawback of phosgene as carbonating agent is, its toxicity and environmentally unfriendly nature. The use of carbon dioxide as carbonating agent requires high temperature and pressure and the yields for glycerol carbonate are too low for practical purpose.[9] The use of ethylene carbonate as carbonating agent is also attractive approach. However, the separation of formed glycerol carbonate from its byproduct (ethylene glycol) is difficult.[10] The use of dimethyl carbonate as carbonate source requires basic catalyst. Nevertheless, these basic catalysts lose their activity after first use and easily get affected from moisture, making their practical applications away from industry.

One of the versatile routes for synthesis of glycerol carbonate from glycerol is the use of urea as carbonating agent. The major advantage of this method is use of urea, which is an inexpensive readily available carbonate source and the by-product (ammonia) produced in the reaction can be again utilized for the synthesis of urea, making it an atom economy process. With insight of green chemistry, different type of heterogeneous catalyst such as ZnO, γ-zirconium phosphate, mixed metal oxides, HTc-Zn derived from hydrotalcite, Co_3O_4/ZnO, Sm and Zn exchanged heteropoly tungstate, Au supported ZSM-5 and $ZnSn(OH)_6$ have been studied for glycerol carbonylation reaction.[17-28]

The presence of AlO_4 in zeolite framework induces a negative charge and compensation of this charge by proton generates the Brönsted acidity. Different metal cations are introduced into zeolites by ion-exchange method, which creates new Lewis acidic and red-ox active sites in the zeolites. The transition metal ion-exchanged zeolites have been broadly studied for the various organic transformations such as reduction of NO by ammonia, steam reforming of ethanol, isomerization and ring opening of styrene oxide, oxidative dehydrogenation of propane and epoxidation of alkenes.[29-38] The zinc ion-exchanged zeolite effectively catalyzes hydroamination reactions, aromatization of ethylene, dehydrogenation of propane and for the synthesis of 2-methyl pyrazine. The ion-exchange of zinc in zeolites generates Lewis acid sites, by replacing strong Brönsted acid sites.[39-41]

We recently reported the metal ion-exchanged zeolites for the Prins condensation of biorenewable feedstock.[41] In continuation of our research endeavors devoted to the development of simple, efficient and environmentally friendly heterogeneous catalytic protocols for biomass derived molecules, herein we report catalytic activity of metal ion-exchanged zeolites for the synthesize glycerol carbonate from glycerol and urea. To the best of knowledge, zeolites and their ion-exchanged forms have not been studied so far for glycerol carbonylation reaction. The current study describes the synthesis of glycerol carbonate from glycerol and urea using zinc exchanged zeolites such as Zn- BEA, Zn-ZSM-5, Zn-MOR, Zn-Y and Zn-X catalysts. The effect of different metal cations and different loading of zinc by ion exchange on Y zeolite have been studied. The physicochemical properties of the catalyst were correlated with the activity and selectivity of the reaction.

2. Experimental Section

2.1 Catalyst preparation

The metal ion-exchanged zeolites were prepared by ion-exchange method using 0.5 molar solutions of respective metal salts.[41] In a typical method, zeolite was treated with 0.5 M aqueous solution of metal salts keeping the liquid to solid weight ratio of 10. The solution was refluxed for 8 h, followed by filtration, washing and drying at 120 °C for 8 h. The above described procedure was repeated twice to achieve maximum ion-exchange. Finally, the catalyst was calcined at 540 °C for 4 h. These calcined metal ion-exchanged catalysts were designated as M-HZ, where M represents the exchanged metal ion, and Z represents the type of zeolite. In case of silver, the ion- exchange was carried in a dark environment using 0.1 M silver nitrate solution. Furthermore, a series of zinc exchanged H-Y zeolites with different zinc content were prepared by ion exchanging with 0.05M solution of zinc acetate repeatedly and designated as Zn-HY-M, where M is the number of ion-exchange step.

2.2 Catalyst Characterization techniques

The phase purity of all the ion-exchanged zeolites were determined by the X-ray diffractometer instrument (Bruker D-2 Phaser) with Cu K-α Source (λ-1.54 A˚). The catalysts were analyzed in the 2θ range of 5-60° with scanning rate of 1.2 degrees per minute. The metal contents of Zn^{2+}, Cu^{2+}, Fe^{2+}, Na^{+}, Ca^{2+}, K^{+}, Mg^{2+} ion-exchanged zeolites were determined by Perkin Elmer AAnalyst 200 atomic absorption spectrophotometer (AAS) using standard solutions. Metal contents of Ag^{+}, Ni^{2+}, Ba^{2+} and Mn^{2+} ion-exchanged zeolites were determined by ICP-OES using Thermo-iCAP 6000 series. N_2 sorption measurements were carried out for Zn-HY zeolites at -196 °C in a nova 1000 Quantachrome instrument and the specific surface area, micropore volume of the zeolites were determined.

To investigate the nature of acid sites present on the surface of zeolites, FT-IR pyridine adsorption technique was employed and spectra were measured in the range of 1600-1400 cm^{-1}. The samples were prepared in the form of pellets (35 mg) and saturated with small amount of pyridine followed by degassing at 150 °C for 30 minutes. The FT-IR spectra in absorbance mode after pyridine treatment were measured. The difference in FT-IR spectra before and after pyridine adsorption gives rise to spectra due to acid-pyridine interaction.

Temperature programmed desorption (TPD) of ammonia was performed in the temperature range of 100-550 °C with ramp rate of 10 °C /min followed by 15 minutes hold time at 550 °C. Before the TPD measurements, zeolite samples were calcined at 550 °C for 1 h in flow of helium gas. Then samples were saturated with anhydrous ammonia (10 % NH_3 + 90 %

He) at 100 °C for 45 minutes and finally helium gas was flushed for an hour to remove the physically adsorbed ammonia.

2.3 Catalyst testing

The carbonylation reaction was performed in a 100 ml two necked round bottom flask equipped with reflux condenser. The N_2 gas was purged through the second neck to remove the ammonia formed during the reaction. In a typical experiment, glycerol (2 g) and urea (1.30 g) were taken in a round bottom flask and catalyst (0.33 g) was added. The reaction was performed at 150 °C, after completion of reaction methanol was added to reaction mixture and the catalyst was separated by centrifugation. The products were analyzed using gas chromatography by separating the products on 60m X 0.25mm DB wax column. The products were identified by GC-MS analysis. The glycerol conversion and selectivity for glycerol carbonate were calculated using the following formulae.

$$\text{Conversion of glycerol}(mol\ \%) = \frac{\text{initial mol \%} - \text{final mol \%}}{\text{initial mol \%}}\ \text{X}\ 100$$

$$\text{Selelctivity for glycerol carbonate}\ (mol\ \%) = \frac{\text{mol \% of desired product}}{\text{total mol \% of all products}}\ \text{X}\ 100$$

3. Results and discussion

3.1 Characterization of catalysts

The X-ray diffraction patterns of the zeolites after ion-exchange with zinc showed the characteristic peaks in the 2θ range of 5 to 60°, which correspond to the respective zeolite pattern (Fig. 1.). The amount of metal content in the ion exchanged zeolite was determined by AAS and

ICP-OES. The amount of zinc exchanged in different zeolites was measured and are tabulated in the Table-1. The degree of ion exchange in HY zeolite differed based on the size and charge of the metal ions as shown in Table-2. The extent of the ion exchange of Zn^{2+} in HY zeolite increased with increase of the repetitive ion exchange steps. The amount of zinc exchanged was low (0.38 mmol/g) at first ion exchange and increased to 1.52 mmol/g after 5 reparative ion exchange steps.(Table-3) The surface area and micro pore volume of the H-Y and Zn-HY catalysts were measured by N_2 sorption techniques and are tabulated in Table-3. The increase of Zn content in Y zeolite decreased the surface area and micro pore volume due to the preferential location of exchanged Zn^{2+} inside the micropore of the zeolites.[41, 42]

The adsorption of pyridine on solid acid catalyst is one of the techniques to measure the nature of acid sites present on the catalyst. The interaction of pyridine molecule with Brönsted acid site give rise to a bending vibration at 1540 cm^{-1} and interaction with Lewis acid sites results into a vibration at 1450 cm^{-1}. The HY zeolite showed both Brönsted and Lewis acid sites as shown in Fig. 2. As the amount of zinc content increased in HY zeolite, the intensity of peak due to the Lewis acidity increased, where as the intensity of peak due to the Brönsted acidity decreased as shown in Fig. 2. The I_B/I_L ratio determined by measuring the intensity of the peaks due to Brönsted and Lewis acidity decreased with increase of zinc content. This clearly indicates that ion exchange with zinc increased the Lewis acidity in the catalyst. However, small amount of Brönsted acidity could be present even after multiple ion exchanges.

To determine the strength and amount of acid sites of zinc exchanged zeolites, temperature programmed desorption of ammonia (TPD- NH_3) of all the catalyst were measured. (Fig.3). The TPD profile of HY zeolite exhibited a major desorption peak at 250 °C with shoulder at 400 °C indicating the presence of two kind of acid sites. The peak at 250 °C could be due to the interaction of the NH_3 with weak Lewis and Brönsted acidity and a peak with maxima at 400 °C is due to strong Brönsted acidity. The TPD profile of all the zinc exchanged HY zeolite showed only major peak at lower temperature range of 200-250 °C, indicating the exchange of Zn^{2+} in HY zeolite decreased the strong Brönsted acidity and increased the Lewis acidity as supported by Py-FT-IR measurements. The total amount of acidity measured by TPD-NH_3 of all the Zn exchanged Y zeolites are presented in Table-3. The amount of acidity increased as the amount of zinc content increased up to 0.79 mmol/g, further increase of zinc content decreased the acidity. The decrease in the acidity above 0.79 mmol /g of zinc content could be due to the formation of ZnO.

The SEM images of H-Y and zinc exchanged Y catalyst (Zn-HY-3and Zn-HY-5) showed average particle size of 0.3 μm, with polygonal like morphology as shown in Fig. 4. Furthermore, SEM images of H-Y catalyst with higher Zn content of 1.52 mmol/ g (Zn-HY-5) confirmed the presence of ZnO in the form of flakes, on the contrary such flakes are not observed at lower Zn loading. This evidently indicates that at lower Zn loading (0.79 mmol/g), most of Zn is in the ion exchanged form and at higher loading (1.52 mmol/ g) results in the formation of ZnO.

3.2 Catalytic activity study

3.2.1 Screening of the zeolite catalyst

The carbonylation reaction of glycerol with urea was carried out over different unmodified and ion-exchanged ZSM-5, mordenite, beta and FAU(X & Y) zeolites. The reaction without catalyst resulted in 28.8 % of glycerol conversion and glycerol carbonate selectivity of 94 %. The H and Na- form of all the zeolites exhibited low glycerol conversion (< 50 %) and the selectivity for glycerol carbonate was in the range of 80-90 %. The residual selectivity could be attributed to the formation of minor side products such as glycerol urethane, glycedol, 5-(hydroxymethy) oxazolidin-2one and (2-oxo-1,3-dioxolan-4-yl) methyl carbamate. The H and Na form zeolite showed lower activity compared to the Zn^{2+} exchanged counter parts as shown in Fig.5. This evidently indicates the exchanged Zn^{2+} ion as a major active site in the reaction rather than H^+ or Na^+. Among the different Zn-exchanged zeolites, FAU (X and Y) catalyst showed higher yield for glycerol carbonate compared to Zn-beta, Zn-ZSM-5 and Zn-MOR as shown in Table-1. The yield for glycerol carbonate over different Zn-exchanged zeolites decreased in the following trend Zn-Y~ Zn-X > Zn-beta> Zn-ZSM-5 > Zn-MOR. The high catalytic activity of Zn-FAU (X and Y) catalyst compared to other zeolites could be due to its low Si/Al ratio and framework morphology. Owing to the low Si/Al ratio, FAU zeolites shows high ion-exchange capacity for Zn^{2+} ions which give rise to large concentration of Lewis acidity. Moreover, the relatively high aluminum content of FAU zeolite exhibits substantial framework negative charge resulting in generation Lewis basic sites. The presence of these acid-base pair in the Zn-HY zeolite along with super cage makes easy diffusion of reactants and products resulting in high yield for the glycerol carbonate. Whereas, high Si/Al ratio zeolites such as Zn-beta, Zn-ZSM-5 and Zn-MOR with very weak basicity, lower ion-exchange capacity and different framework morphology (lack of super cage) exhibited lower activity compared to Zn-FAU. The Zn-Y catalyst with 0.83 mmol/g of zinc content showed high glycerol conversion of 96.4% and glycerol carbonate selectivity of 97 %. Therefore, further optimization studies were performed over HY zeolite.

3.2.2 Effect of different metal ions

The effect of different metal ion-exchanged H-Y zeolite on the glycerol carbonylation reaction was performed. Only mono and divalent ion-exchanged zeolites were studied, as trivalent ions are not really exchanged and present in the form of oxide like clusters.[42] The various metal ions like alkali (Na^+, K^+), alkaline ($Mg^{2+,}$ Sr^{2+}, Ba^{2+}) and transition metal ions (Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}) were exchanged with protons of H-Y. Although same ion exchange procedure was applied, the degree of ion exchange was different for different metal ions due to the diverse degree of ion exchange and inherent properties of metal ions. Most of the metal ion-exchanged in HY zeolites exhibited glycerol conversion in the range of 40-61 % and selectivity for glycerol carbonate above 88 %. Among the different metal ions screened, Zn ion-exchanged catalyst with Lewis acidity showed higher conversion and selectivity in glycerol carobnylation reaction.

3.2.3 Effect of different zinc content

The influence of zinc content on catalytic activity of glycerol carbonylation was studied. The catalytic activity and physicochemical properties of H-Y zeolite with different zinc content were tabulated in Table-3. As the amount of zinc content increased, the conversion of glycerol and selectivity for glycerol carbonate improved due to the increase of Lewis acidity as supported by py-FTIR and TPD-NH_3.With increase of zinc loading from 0.38 to 0.79 mmol/g, conversion of glycerol increased from 57.3 % to 94.6 % and selectivity for glycerol carbonate from 90 to 98 %. Furthermore, at higher zinc loading (> 0.79mmol/g), the conversion decreased due to decrease in acidity as shown in Table-3.The measurement of I_B/I_L ratio of different zinc containing Y zeolite showed, decrease in Brönsted acidity with increase of zinc content indicating the Lewis acid sites (due to Zn^{2+}) are the major active sites of the reaction. The zinc content of 0.79 mmol/g in Zn-HY was enough to get high conversion of glycerol (94.6 %) and selectivity for glycerol carbonate (98 %). The pure zinc oxide as catalyst showed lower glycerol conversion (59.1 %) and selectivity for glycerol carbonate (75 %).

3.2.4 Influence of reaction conditions

The influence of reaction conditions such as effect of reaction temperature, mole ratio catalyst weight and reaction time were carried out. The effect of reaction temperature was studied using Zn-HY-3 catalyst with glycerol to urea mole ratio of 1:1 using 10 wt % of catalyst. The conversion of glycerol increased with increase of temperature as shown in Fig. 6a. With increase in reaction temperature from 130 to 150 °C, the glycerol conversion and selectivity for glycerol carbonate increased from 41.1% to 94.6 % and 92.2 to 98 % respectively. Further increase in reaction temperature to 160 °C there is no appreciable increase in the conversion and conversely selectivity for glycerol carbonate decreased. These results suggest that the optimum reaction temperature is 150 °C and hence selected for further study.

The effect of mole ratio of glycerol to urea was studied at 150 °C using Zn-HY-3 catalyst. The mole ratio of glycerol to urea was varied from 2:1 to 1:3 as shown in Fig. 6b. The glycerol conversion increased from 44.1 to 96.3 % with increase in the concentration of urea, at the same time selectivity towards glycerol carbonate decreased from 97 to 84 %. The decrease in selectivity with increase of urea concentration is due side products formed by reaction of glycerol carbonate with available urea. The glycerol: urea mole ratio of 1:1 is sufficient to produce high glycerol conversion of 94.6 % and glycerol carbonate selectivity of 98 % and hence glycerol: urea mole ratio of 1:1 is used for further studies.

The study of catalyst amount on glycerol carbonylaton was conducted by taking different weight % of Zn-HY-3 catalyst with respect to the total reactant weight as shown in Fig. 6c. As the catalyst concentration increased from 5 to 10 wt %, the conversion increased from 83.1 to 94.6 % and selectivity for glycerol carbonate increased from the 84.6 to 98 %. Further catalyst loading has marginal increase in the conversion with low selectivity for the glycerol carbonate.

The catalyst with 10 wt % of the total reactant weight is sufficient to produce high yield of glycerol carbonate.

Effect of reaction time for glycerol carbonylation with urea was carried out under optimized reaction conditions. The glycerol conversion and selectivity for glycerol carbonate increased with increase of reaction time as shown in Fig. 6d. The glycerol conversion was 70 % after 1 hr and then reached to 94.6 % after 3 h of reaction time. It shows that the conversion drops at higher reaction time due to the formation of products in the reaction mixture, which reduces the effective collision. The glycerol carbonate selectivity increased marginally with increase of reaction time.

3.2.5 The recycling and reaction mechanism

The Zn-HY-3 catalyst was studied for its reusability and results are presented in the Fig. 7. For recycling test, the catalyst was separated by adding methanol to the reaction mixture followed by filtration. The separated catalyst was washed with acetone, dried and finally calcined at 500 °C. It is then used in glycerol carbonylation reaction with fresh reactant mixture. The catalyst showed good recyclability with minimal decrease in the activity after 4 cycles. The yield for glycerol carbonate was 91.6 % after first cycle and it decreased marginally to 89 % after 4 cycles. In order to test Zn stability in the recycled catalyst, zinc content of the Zn-HY-3 catalyst after 4 cycles was measured by AAS. There was an insignificant decrease (~ 0.03 mmol/g) in zinc content of Zn-HY-3 catalyst after 4 cycles, indicating high stability of Zn in the catalyst.

It was established that catalysts with acid base properties were favorable for the selective synthesis of cyclic carbonates from urea and diols.[43, 44] Furthermore, the presence of solid acid catalyst with balanced Lewis acids and its conjugate base are found to be the active sites in glycerol carbonylation reaction.[10] Corma et al. studied in detail the carbonylation of glycerol with urea over different bi-functional acid-base catalysts and concluded that catalyst with Lewis acid sites activates the carbonyl group of the urea and the conjugate basic site activates the hydroxyl group of the glycerol resulting in high activity and selectivity.[10] Subsequently, Lingaiah et al. reported a series of papers on glycerol carbonylation and supported the requirement of Lewis acidity and its conjugate basic sites for the selective synthesis of glycerol carbonate.[12,23,26,27] Based on the above findings, plausible reaction mechanism for glycerol carbonylation with urea over Zn-Y zeolite has been proposed as shown in Scheme 1. It is speculated that Lewis acid sites activates (Zn^{2+}) the carbonyl group of the urea and weak conjugate base (framework oxygen) activates the hydroxyl group of the glycerol.[10] Presence of these sites in the Zn-Y catalyst exhibited high catalytic activity and selectivity for glycerol carbonate in carbonylation reaction.

3.2.6 Comparison of Zn-Y zeolite with reported solid acid catalysts.

Table-4 shows the comparison of the catalytic activity of Zn-Y with other reported solid acid catalysts. The Sn-beta, Au/Fe_2O_3 and $Sm_{0.66}$ TPA showed good glycerol conversion with too low selectivity for glycerol carbonate.[26,45,46] SW21 (Sn-W mixed oxide), 2.5 % Au/Nb_2O_5 and Zn_1TPA exhibited good selectivity for glycerol carbonate but the conversion levels were low. Among the different catalyst zirconium phosphate, exhibited high glycerol conversion (80 %) and selectivity for glycerol carbonate (100 %).[9] It is observed that catalyst with high conversion showed lower selectivity and vice versa. The present catalyst Zn-HY exhibited high glycerol conversion and selectivity than the previously reported catalyst as shown Table-4.The Zn-HY showed glycerol conversion of 94.6 % with glycerol carbonate selectivity of 98 %. The catalyst designed in the present work was prepared by non toxic Zn metal ion with eco-friendly zeolites as its backbone and made the synthesis of glycerol carbonate, a green process. As most of the industrial process prefers the catalyst based on zeolite, the present study of selective synthesizing glycerol carbonate over metal ion-exchanged zeolite may possibly encourage its practical application in chemical industry.

4. Conclusions

Metal ion-exchanged zeolites are reported as highly active and selective catalyst for glycerol carbonylation reaction with urea to produce glycerol carbonate. The glycerol carbonate yield increased for the Zn-exchanged zeolites in the following trend Zn-MOR < Zn-ZSM-5 < Zn-beta < Zn-FAU. Among the different metal ion-exchanged HY zeolite, Zn^{2+} showed highest catalytic activity and selectivity for glycerol carbonate. The total acidity of HY catalyst increased with increase of zinc content up to 0.79mmol/g, further increase in zinc loading decreased acidity due to the formation of ZnO. As the amount of zinc content increased in HY zeolite, glycerol conversion and selectivity for glycerol carbonate increased due to decrease in I_B/I_L ratio. Zn-HY-3 catalyst with 0.79 mmol/g of zinc content gave 94.6 % glycerol conversion with 98 % selectivity for glycerol carbonate. The comparison of catalytic performances with other reported solid acid catalysts shows, the Zn^{2+} exchanged HY zeolite an inexpensive and highly active catalyst for glycerol carbonylation reaction to produce glycerol carbonate.

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6. References

[1] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 107 (2007) 2411.

[2] Y. L. Gu, A. Azzouzi, Y. Pouilloux, F. Jerome, J. Barrault, *Green Chem.* 10 (2008) 164

[3] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. D. Pina, *Angew. Chem. Int.* Ed. 46 (2007) 4434.

[4] C. H. Zhou, J. N. Beltramini, Y. X. Fan, G. Q. Lu, *Chem. Soc. Rev.* 37 (2008) 527.

[5] A. Behr, J. Eilting, K. Irrawaddy, J. Leschinski, F. Lindner, *Green Chem.* 10 (2008) 13.

[6] M. O. Sonnati, S. Amigoni, E. Givenchy, T. Darmanin, O. Choulet F. Guittard, *Green Chem.* 15 (2013) 283.

[7] J. H. Teles, N. Rieber, W. Harder, US Pat, 5 359 094, 1994.

[8] J. Hu, J. Li, Y. Gu, Z. Guan, W. Mo, Y. Ni, T. Li , G. Li, *Appl. Catal., A.* 386 (2010) 188.

[9] M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, *J. Mol. Catal. A: Chem*. 257 (2006) 149.

[10] M. J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty, P. Concepción, *J. Catal.* 269(2010) 140.

[11] A. Takagaki, K. Iwatani, S. Nishimura, K. Ebitani, *Green Chem*. 12(2010) 578.

[12] M. Malyaadri, K. Jagadeeswaraiah, P. S. Sai Prasad, N. Lingaiah, *Appl. Catal. A*. 401 (2011) 153.

[13] Z. Ilham, S. Saka, *Fuel,* 97 (2012) 670.

[14] S. Claude, Z. Mouloungui, J. Yoo, US Pat. 6 025 504, 2000.

[15] M. Okutsu, T. Kitsuki, *WO Pat*. 50415, 2000.

[16] Q. Li, W. Zhang, N. Zhao, W. Wei , Y. Sun, *Catal. Today*. 115 (2006) 111.

[17] F. Rubio-Marcos, V. Calvino-Casilda, M. A. Bañares, J. F. Fernandez, *J. Catal*. 275 (2010) 288.

[18] C. Hammond, J. A. Lopez-Sanchez, M. H. Ab Rahim, N. Dimitratos, R. L. Jenkins, A. F. Carley, Q. He, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Dalton. Trans.* 40 (2011) 3927.

[19] L. Wang, Y. Ma, Y. Wang, S. Liu, Y. Deng, *Catal. Commun*. 12 (2011) 1458.

[20] Y. T. Algoufi, B. H Hameed, *Fuel. Process. Technol.*126 (2014) 5.

[21] J. W. Yoo, Z. Mouloungui, *Stud. Surf. Sci. Catal*. 146 (2003) 757.

[22] M. Aresta, A. Dibenedetto, F. Nocito, C. Ferragina, *J. Catal*. 268 (2009) 106.

[23] K. Jagadeeswaraiah, Ch. Ramesh Kumar, P.S. Sai Prasad, S. Loridant, N. Lingaiah, *Appl. Catal. A: Gen.* 469 (2014) 165.

[24] M. J. Climent, A. Corma, P. Frutos, S. Iborra, M. Noy, A. Velty, P. Concepcion, *J. Catal.* 269 (2010) 140.

[25] F. Rubio-Marcos, V. Calvino-Casilda, M. A. Bañares, J. F. Fernandez, *J. Catal.* 275 (2010) 288.

[26] Ch. Ramesh Kumar, K. Jagadeeswaraiah, P.S. Sai Prasad, N. Lingaiah, *Chem.Cat.Chem.* 4 (2012) 1360.

[27] K. Jagadeeswaraiah, Ch. Ramesh Kumar, P. S. Sai Prasad, N. Lingaiah, *Catal. Sci. Technol*.4 (2014) 2969

[28] S. Swetha, G. V. Shanbhag, A. B Halgeri, *RSC Adv*. 4 (2014) 974.

[29] H. Inokawa, S. Nishimoto, Y. Kameshima, M. Miyake, *Int. J. Hydrogen Energy.* 35(2010) 11719.

[30] O. Bergadà, E. Boix, P. Salagre, Y. Cesteros, F. Medina,J. E. Sueiras, *Appl. Catal. A: Gen*. 368 (2009) 163.

[31] B .Qi, X. H. Lu, D. Zhou, Q. H. Xia, Z. R. Tang, S. Y. Fang, T. Pang, Y. L. Dong, *J. Mol. Catal. A: Chem.* 322 (2010) 73.

[32] J. Penzien, C. Haebner, A. Jentys, K. Köhler, T. E. Müller , J. E. Lercher, *J. Catal.* 221(2004) 302.

[33] A. Hagen, F. Roessner, *Stud. Surf. Sci. Catal.* 98 (1995) 182.

[34] J. A. Biscardi , E. Iglesia, *Phys. Chem. Chem. Phys*. 1 (1999) 5753.

[35] R. Anand, S. G. Hegde, B. S. Rao, C. S. Gopinath, *Catal. Lett.* 84 (2002) 265.

[36] D. Esquivel, A. J. Cruz-Cabeza, C. Jiménez-Sanchidrián, F. J. Romero-Salguero, *Microporous Mesoporous Mater.,* 179 (2013) 30.

[37] A. Goursot, B. Coq, F. Fajula, *J. Catal.* 216 (2003) 324.

[38] G. Qi, R. T. Yang, *Appl. Catal. B*. 60 (2005) 13.

[39] L. Barbosa, R. A. Van Santen, *Catal. Lett.* 63, (1999) 97.

[40] M. Yadav, M. V. Patil, R. V. Jasra, *J. Mol. Catal. A: Chem*. 297 (2009) 101.

[41] V. S. Marakatti, A.B .Halgeri, G. V .Shanbhag, *Catal. Sci. Technol*. 4 (2014) 4065.

[42] A. J. Cruz-Cabeza, D. Esquivel, C. Jiménez-Sanchidrián , F. J. Romero-Salguero, *Materials*. 5 (2012) 121.

[43] P. Ball, H. Fullmann, W. Heitz, *Angew. Chem.,* 92 (1980) 742.

[44] Q. Li, W. Zhang, N. Zhao, W. Wei, Y. Sun, *Catal. Today,* 115 (2006) 111.

[45] C. Aille, J. W. Yoo, S. Pelet, Z. Mouloungui, *Catal. Lett.* 56 (1998) 245.

[46] Y. Ogasawara, S. Uchida, K. Yamaguchi, N. Mizuno, *Chem. Eur. J.* 15 (2009) 4343.

Figure Legends

Fig. 1. XRD patterns of Zn exchanged zeolites.

Fig. 2. Py-FTIR of Zn exchanged Y zeolites.

Fig. 3. TPD NH_3 profile Zn exchanged Y zeolites.

Fig. 4. SEM images of H-Y and Zn-exchanged Y zeolites.

Fig. 5. Catalytic activity and selectivity of zeolites in glycerol carbonylation reaction

Reaction conditions: glycerol= 2 g, urea =1.30g, catalyst amount = 0.33 g, reaction temperature = 150 °C, reaction time = 3 hr, z = zeolite.

Fig. 6. Influence of reaction conditions in glycerol carbonylation.

a) Effect of temperature: Reaction conditions: glycerol= 2 g, urea =1.30g, catalyst amount = 0.33 g , reaction time = 3 hr.

b) Effect of glycerol: urea mole ratio: Reaction conditions: catalyst amount = 0.33 g, reaction temperature = 150 °C, reaction time = 3 hr.

c) Effect of catalyst amount: Reaction conditions: glycerol= 2 g , urea =1.30g, reaction temperature = 150 °C, reaction time = 3 hr.

d) Effect of reaction time: Reaction conditions: Glycerol= 2 g, urea =1.30g, catalyst amount = 0.33 g, reaction temperature = 150 °C, reaction time = 3 hr.

Fig. 7. Reusability of Zn-HY-3 catalyst for carbonylation of glycerol reaction.

Reaction conditions: glycerol= 8 g, urea =5.2, catalyst amount = 1.32 g, reaction temperature = 150 °C, reaction time = 3 hr.

Scheme 1 Plausible reaction mechanism for the synthesis of glycerol carbonate over Zn-Y zeolite.

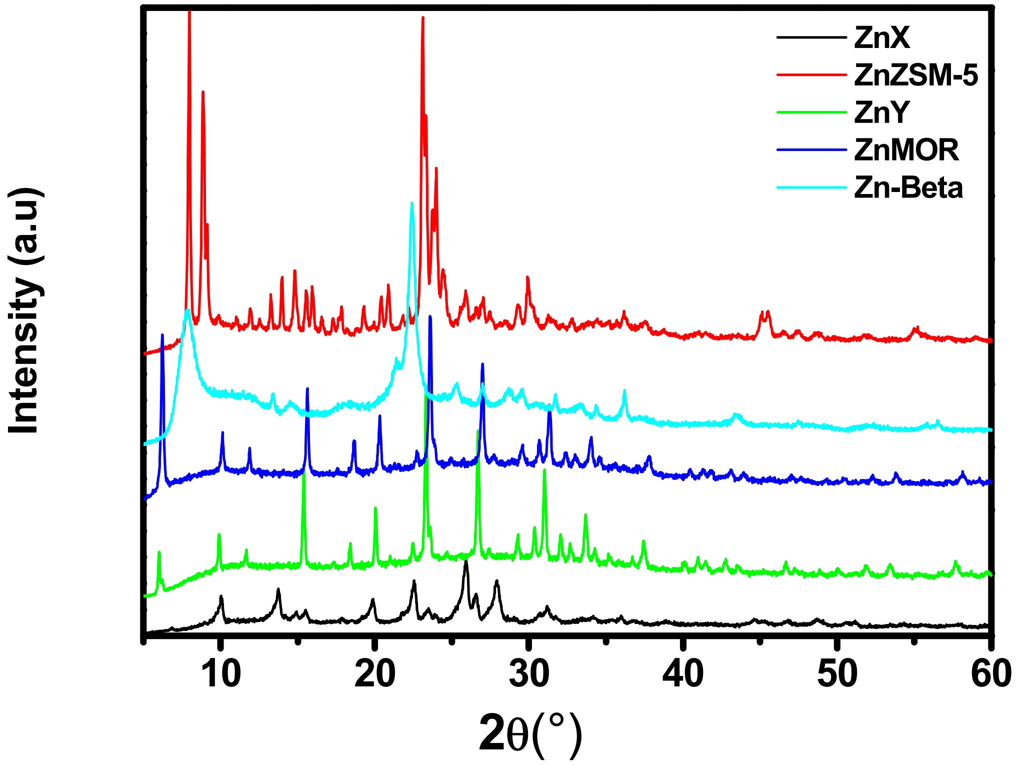


Fig. 1.

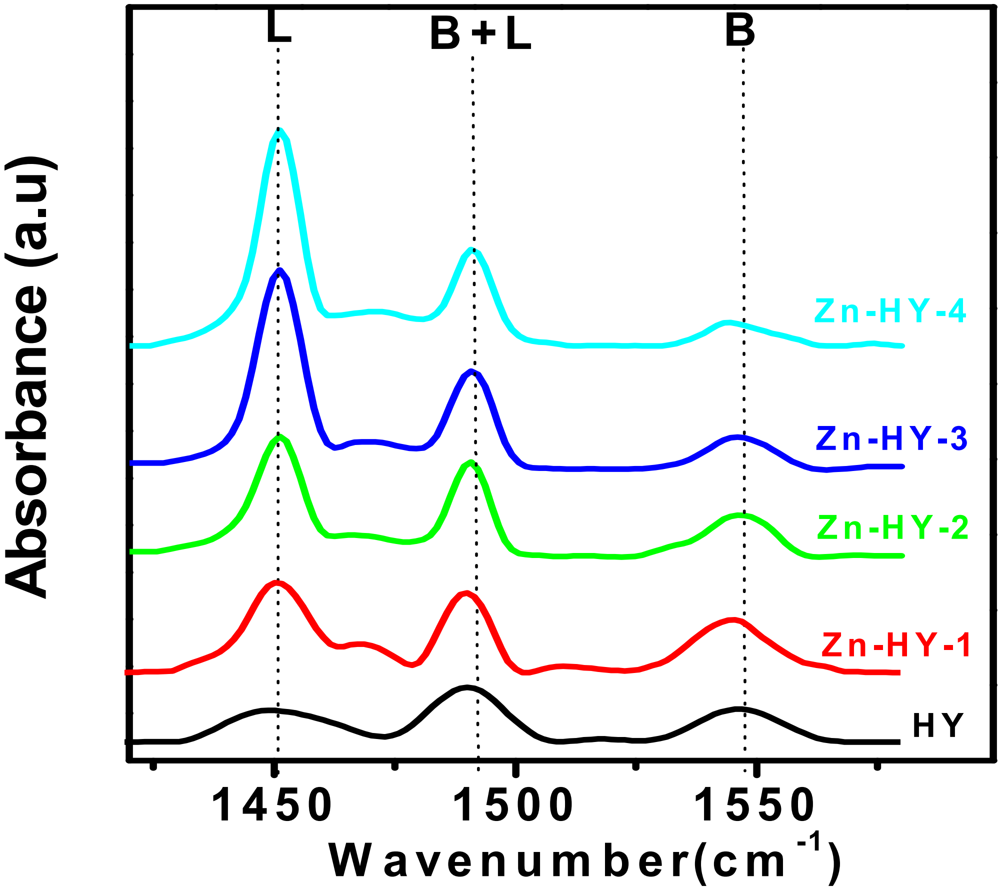

L
B+L
B
Absorbance (a.u)
Zn-HY-4
Zn-HY-3
Zn-HY-2
Zn-HY-1
HY
1450
1500
1550
Wavenumber(cm^{-1})

Fig. 2.

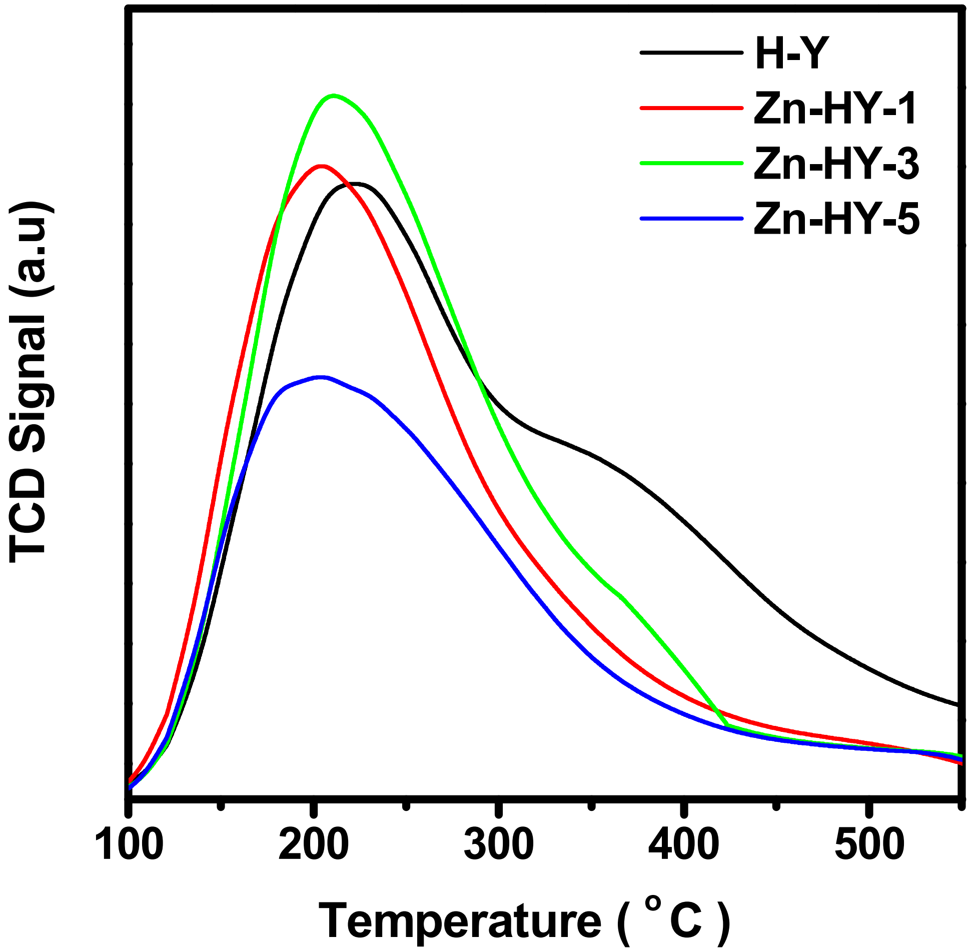

H-Y
Zn-HY-1
Zn-HY-3
Zn-HY-5
TCD Signal (a.u)
100
200
300
400
500
Temperature (°C)

Fig. 3.

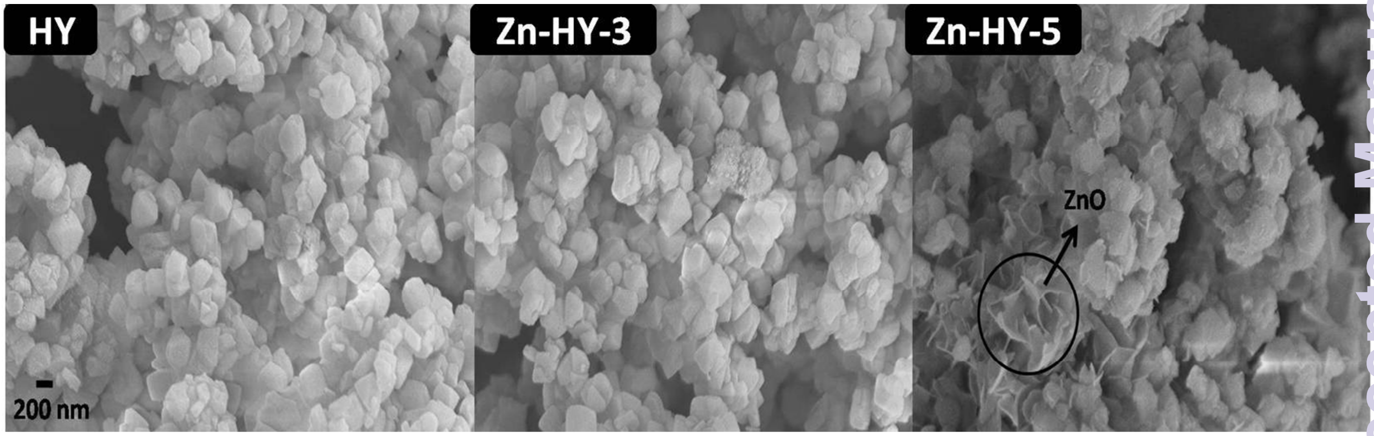


Fig. 4.

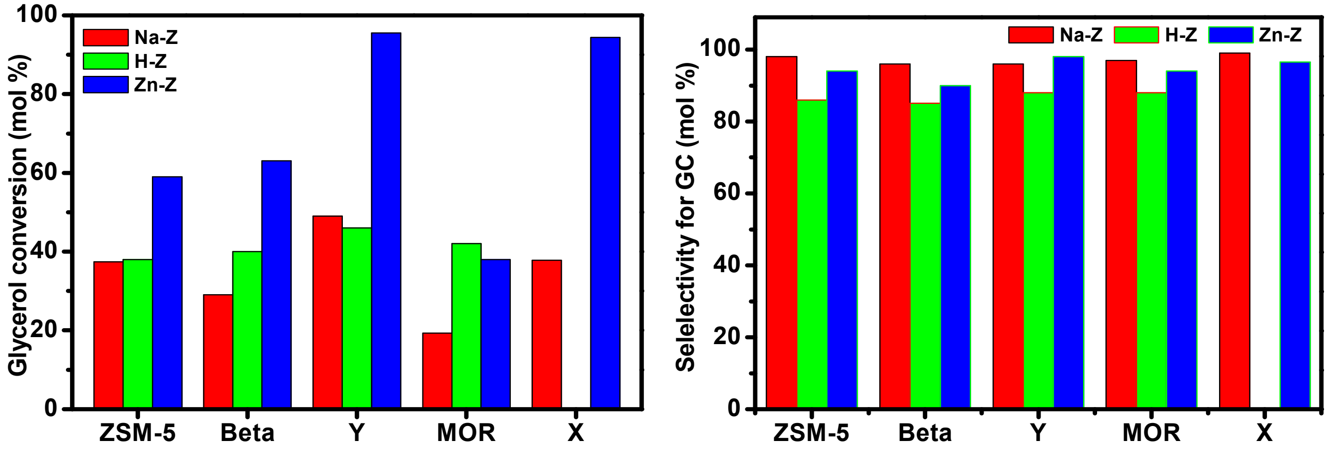

100
80
60
40
20
0
Glycerol conversion (mol %)
Na-Z
H-Z
Zn-Z
ZSM-5
Beta
Y
MOR
X
Selelectivity for GC (mol %)
100
80
60
40
20
0
Na-Z
H-Z
Zn-Z
ZSM-5
Beta
Y
MOR
X

Fig. 5.

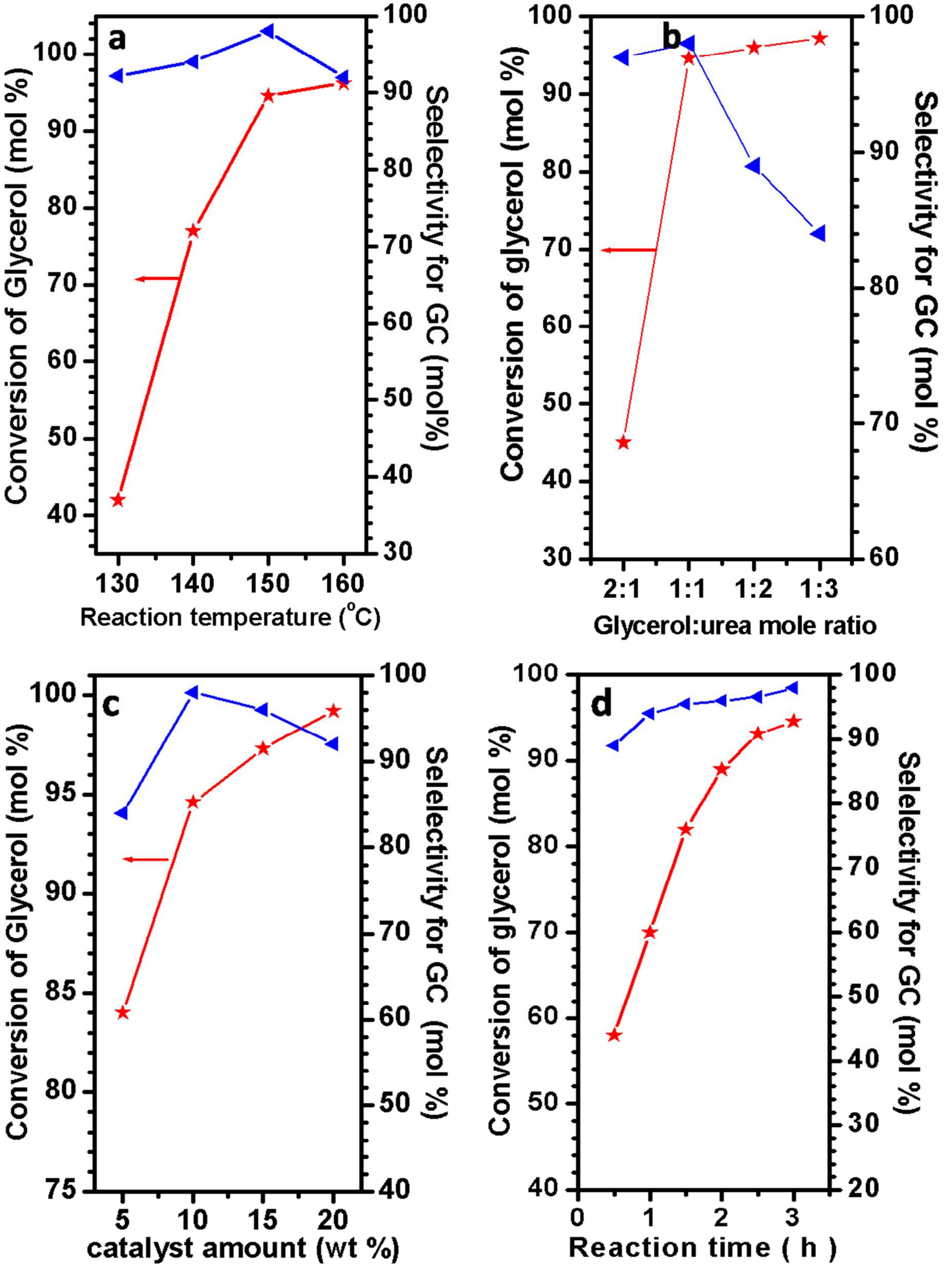

a
Conversion of Glycerol (mol %)
Seelectivity for GC (mol%)
Reaction temperature (°C)
130
140
150
160
40
50
60
70
80
90
100
30
40
50
60
70
80
90
100
b
Conversion of glycerol (mol %)
Selectivity for GC (mol %)
Glycerol:urea mole ratio
2:1
1:1
1:2
1:3
30
40
50
60
70
80
90
100
60
70
80
90
100
c
Conversion of Glycerol (mol %)
Selelectivity for GC (mol %)
catalyst amount (wt %)
5
10
15
20
75
80
85
90
95
100
40
50
60
70
80
90
100
d
Conversion of glycerol (mol %)
Selelectivity for GC (mol %)
Reaction time (h)
0
1
2
3
40
50
60
70
80
90
100
20
30
40
50
60
70
80
90
100

Fig. 6.

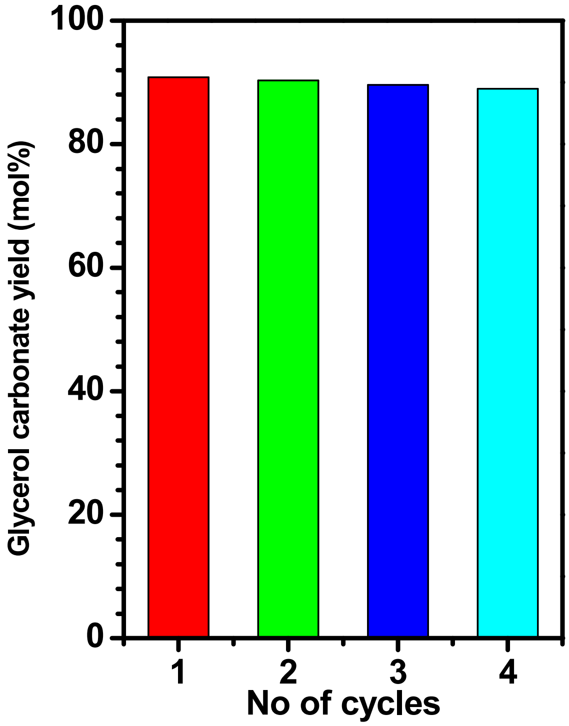
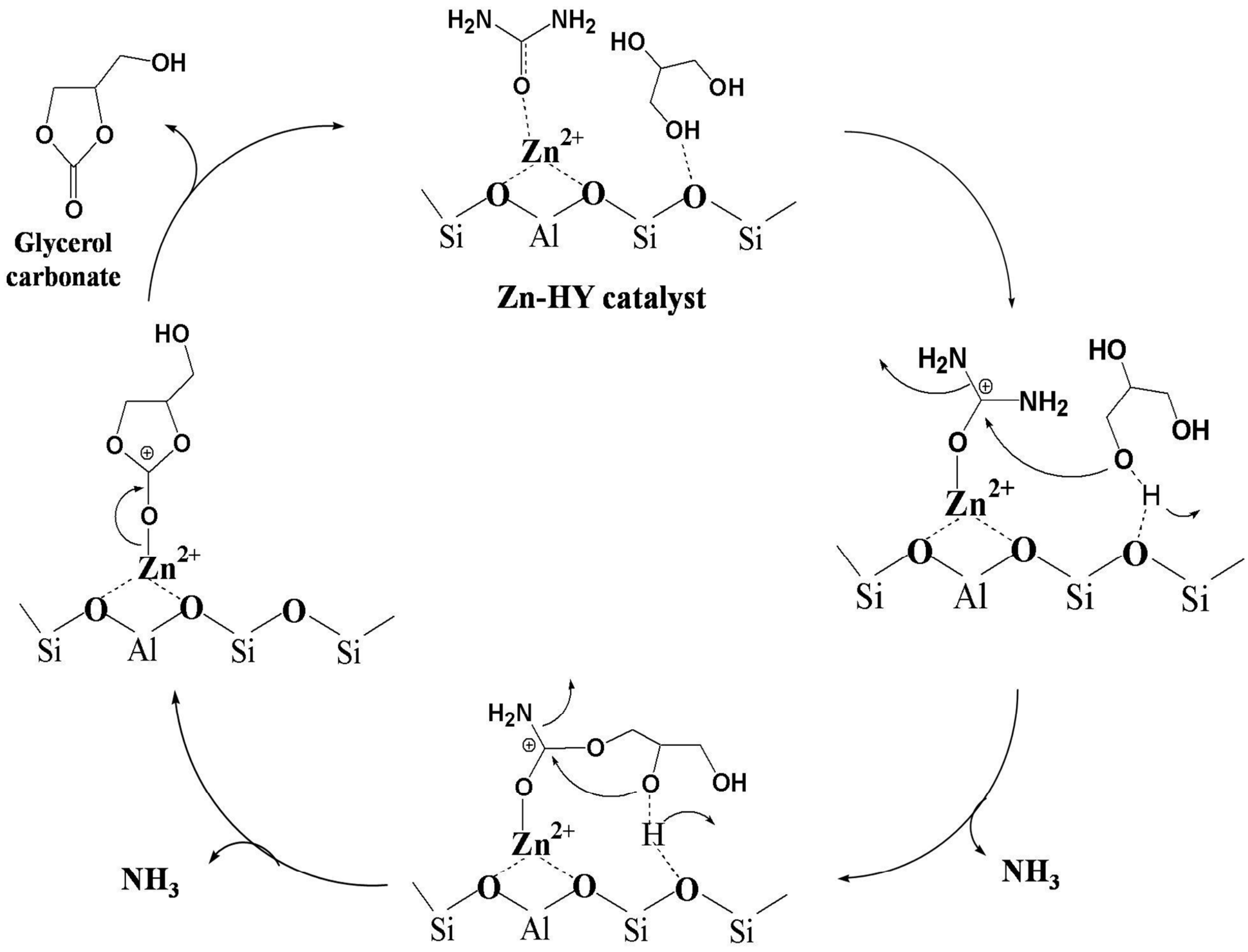

Glycerol carbonate yield (mol%)
100
80
60
40
20
0
1
2
3
4
No of cycles

Fig. 7.


Glycerol carbonate
Zn-HY catalyst
Zn^{2+}
Si
Al
O
NH$_3$
NH$_3$
H$_2$N
NH$_2$
HO
OH

Scheme 1

TABLE LEGENDS

Table-1 Physicochemical properties of Zn^{2+} exchanged zeolites and their catalytic activity.

Table-2 Catalytic activity of different metal ion-exchanged zeolites in glycerol carbonylation.

Table-3 Properties of Zn-Y catalysts and their catalytic activity on glycerol carbonylation reaction.

Table-4 Comparison of Zn-Y catalyst with reported solid acid catalysts.

Table-1 Physico-chemical properties of Zn^{2+} exchanged zeolites and their catalytic activity.

Zeolite	SAR (Si/Al)	Amount of Zn (mmol/g)	Pore size (Å)	Glycerol carbonate Yield (mol %)
Zn-Na-X	1.5	1.58	7.4*7.4	90.1
Zn-H-Y	8	0.83	7.4*7.4*7.4	93.5
Zn-H-Beta	15	0.31	5.6*5.6&7.7*6.6	57.8
Zn-H-ZSM-5	19	0.35	5.1*5.6	54.5
Zn-H-MOR	16	0.63	6.5*7&2.9*5.7	34.7

Reaction conditions: glycerol= 2 g, urea =1.3 g, catalyst amount = 0.33 g, reaction temperature = 150 °C, reaction time = 3 hr.

Table-2 Catalytic activity of different metal ion-exchanged zeolites in glycerol carbonylation.

Metal exchanged HY	Amount of metal (mmol/g)	Conversion of glycerol (mol %)	Selectivity for glycerol carbonate (mol %)
Ni^{2+}	0.65	41.1	90
Mn^{2+}	0.90	60.9	90
Ag^{+}	0.011	44.1	98
K^{+}	0.52	51.4	95
Na^{+}	0.86	48.1	96
Fe^{2+}	0.67	44	91
Cu^{2+}	0.42	41	85
Mg^{2+}	0.34	58	90
Sr^{2+}	0.42	55	88
Zn^{2+}	0.83	96.4	97
Ba^{2+}	0.48	53	88
H^{+}	--	45.1	88

Reaction conditions: glycerol= 2 g, urea =1.3 g, catalyst amount = 0.33 g, reaction temperature = 150 °C, reaction time = 3 hr.

Table-3 Properties of Zn-Y catalysts and their catalytic activity on glycerol carbonylation reaction.

Catalyst	Amount of zinc (mmol/g)			Specific surface area	Micropore volume	Py-FT-IR acidity	TPD acidity	Conversion of glycerol	Selectivity for glycerol carbonate
	Zn	Al	Zn/Al	(m^2/g)	(cm^3/g)	(I_B/I_L)	(NH_3 mmol/g)	(mol %)	(mol %)
HY	--	1.68	--	638.7	0.32	1.2	2.11	45.1	88
Zn-HY-1	0.38	1.66	0.22	434.6	0.21	0.75	2.23	57.3	90
Zn-HY-2	0.58	1.67	0.34	399.3	0.18	0.41	2.47	77.6	94
Zn-HY-3	0.79	1.65	0.47	312.8	0.14	0.20	2.64	94.6	98
Zn-HY-4	1.12	1.58	0.70	309.9	0.1	0.13	1.86	88.3	98
Zn-HY-5	1.52	1.54	1.01	300	0.06	0.10	1.32	83.2	97
ZnO	--			--	--	--	--	59.1	75

Reaction conditions: glycerol= 2 g, urea =1.3 g, catalyst amount = 0.33 g, reaction temperature = 150 °C, reaction time = 3 hr.

Table-4 Comparison of Zn-Y catalyst with reported solid acid catalysts.

Catalyst	**Reaction temperature (°C)**	**Reaction time (h)**	**Glycerol conversion (%)**	**Glycerol carbonate (%)**		**References**
				Yield	**Selectivity**	
SW21	140	4	52.1	49.7	95.3	[22]
Sn-beta	145	5	70	26	37	[44]
Zr-P	140	3	80	76	100	[9]
Au/Fe_2O_3	150	4	80	39	48	[45]
$Sm_{0.66}$ TPA	150	4	66	21	32	[25]
2.5 % Au/Nb_2O_5	140	4	49.5	42.3	85.4	[45]
Zn_1TPA	140	4	69.2	68.7	99.4	[26]
Zn-Y	150	3	94.6	92.7	98	Present work

Graphical abstract