Accepted Manuscript

Zinc oxide as a solid acid catalyst for esterification reaction

Anjani Nagvenkar, Sajo Naik, Julio Fernandes

Zinc Oxide as Solid Acid Catalyst for Esterification Reaction

Anjani Nagvenkar, Sajo Naik, and Julio Fernandes*

Department of Chemistry, Goa University, Taleigao Plateau, Goa, India, 403206

* e – mail: julio@unigoa.ac.in

1. Abstract

Zinc oxide and its composites with Hβ Zeolite were produced under different synthesis conditions. The synthesized catalysts were evaluated for performance in esterification of n-butanol with acetic acid.BET surface area, XRD, and acidity (using NH_3 and pyridine as probe molecules) were measured to correlate the activity with structural features of the catalysts.

2. Introduction

Solid acids have a tendency to donate a proton or to accept an electron pair in heterogeneous acid catalysis reactions such as alkylation, acylation, etc. Esterification is an important reaction in chemical industry where in an efficient acid catalyst is required to obtain good yields of ester at higher selectivity [1]. Esterification reaction can also be performed using homogenous catalysts such as H_2SO_4, HF, H_3PO_4, but use of such catalysts often causes serious issues in product separation and catalyst reuse and disposal [2].

The replacement of mineral acids by solid acids (metal oxides, zeolites, clays) has been a major research area as there is growing demand for environmentally benign processes using less hazardous chemicals [3,4]. The strong interest in the use of solid acid catalyst as a replacement to homogenous catalyst is because of their low corrosiveness, and the ease of regeneration and reuse. ZnO has been shown to have both acid and base characteristics which vary upon the method of preparation. Already, pure ZnO and ZnO based catalysts have been used for esterification and trans-esterification reactions [5-7]. The present investigation is aimed to develop a pure ZnO or ZnO based solid acid catalyst for direct esterification of carboxylic acids with alcohols under solvent-free conditions [8].

2. Experimental

2.1 Catalyst Synthesis

2.1.1 Synthesis of ZnO and composite ZnO/Hβ zeolite catalysts

A series of ZnO samples were prepared by using zinc nitrate as a precursor in the presence of urea and oxalic acid [8]. In general, a known amount of the three reactants were weighed in a molar ratio of 1: X: Y and designated as Z_{1XY} where 'X' is moles of urea and 'Y' is moles of oxalic acid. At first, calculated quantities of urea and oxalic acid were dissolved in a minimum amount of water and this solution was added dropwise to the zinc nitrate solution under stirring. The obtained precipitate was evaporated to dryness and then calcined at 450˚C for 4 h in air. Similarly, ZnO/Hβ composite were prepared by performing precipitation over Hβ zeolites suspended in water.

2.2 Catalyst Characterisation

2.2.1 X-ray diffraction(XRD)

XRD patterns were recorded on a Rigaku Ultima IV diffractometer, using Ni filtered Cu Karadiation (λ=1.5406A^o).

2.2.2 Temperature programmed desorption of ammonia (TPD-NH$_3$) and pyridine adsorption studies

TPD-NH$_3$ experiments were performed on a Chemisorb 2720, Micromeritics instrument. Typically, in a quartz tube, 25 mg of the sample was used for analysis. The sample was activated at 120°C, 12 h. After cooling to 25°C, dry ammonia gas (20 % NH$_3$ balance He (UHP); 20 mL/min) was passed over the sample for 15 minutes. The physically adsorbed ammonia was flushed out by He carrier gas at 25°C. The sample was heated from 25°C to 600°C at a heating rate of 5°C/min and the desorbed ammonia was measured using a thermal conductivity (TC) detector connected to the sample tube in a loop.The number and strength of acid sites in the catalyst were evaluated based on this measurement [14].

2.2.3 Pyridine adsorption studies

The nature of surface acidity of the samples was determined by FTIR study. About 0.1 g of the samples were activated at 120˚C for 1hr prior to the experiment and exposed to pyridine vapours for 4-5 hrs. The samples were dried at 110˚C, degassed and FTIRspectra of each were recorded on Shimadzu FTIR instrument.

2.2.4 BET surface area measurements

The BET surface areas of the samples were measured on a NOVA 2000e, Quantachrome surface area and porosity instrument using N$_2$ as a probe molecule at 77.3 K. The samples were appropriately pre-treated and degassed to clean the surfaces from moisture and volatiles. The multipoint Brunauer, Emmett and Teller (BET) method was used to measure total surface area.

2.3 Esterification of acetic acid with n-butanol

Typically, 25 ml of glacial acetic acid was taken in a three necked flask and heated to 95°C. After the desired temperature has been reached, 20 ml of n-butanol preheated separately was added into the reactor flask. The acetic acid : n-butanol molar ratio was 2:1 in all the experiments. An amount of 50 mg of catalyst was used in each case. Aliquots of the reaction mixture were analysed titrimetrically at regular time intervals to estimate the % conversion [9]. % Conversion of acetic acid = $[C_i - C_t /C_i]$ x 100 where C_i is in initial concentration of acetic acid and C_t is concentration after time t.

3. Results and Discussion

3.1. Synthesis and structural properties of catalysts

The XRD patterns (not shown here) confirmed the formation of ZnO from the observation of (100), (002), (101), (102) and (110) peaks indexed on the basis of hexagonal wurtzite [JCPDS no. 36-1451]. The acid-base characteristics of a solid acid catalyst such as ZnO has been established earlier [6,8,10]. ZnO/SiO_2 is recently investigated for esterification of fatty acids, mediated by acid sites [11]. As solid state properties and catalytic reactivity of ZnO are known to depend upon the method of preparation [9], in this investigation, ZnO samples were prepared by calcination of zinc nitrate with varying proportions of urea and oxalic acid.

Table 1 shows the list of prepared samples along with the corresponding surface areas and the activity in esterification reaction. It can be seen from Table 1 that the surface areas of zinc oxides ranged from 2-30 m^2g^{-1}. The average particle sizes of Z-102, Z-122, Z-124 were calculated by the Scherrer equation was ~34 nm. Z-100 showed significant value of surface area due to large crystallite size. The surface areas increased for Z-102 due to calcination in presence of oxalic acid. Further the sample Z-122 prepared by using urea in addition to oxalic acid, significantly increased the surface area from ~19 m^2/g to 29 m^2/g. The higher surface area resulted due to the porogenic properties of urea and oxalic acid. Presence of urea resulted in ZnO particles being of lower crystallite size, as well as enhanced porosity and surface area [8]. Z-124 catalyst was prepared in order to investigate the effect of excess oxalic acid during the calcination step, particularly because in the preceding sample Z-122, the presence of oxalic acid had resulted in enhanced surface area. However it was observed that excess oxalic acid did not cause further enhancement in surface area. On the contrary the surface area was significantly lower and was only about 17 m^2/g. This effect is interpreted from the point of view that excess oxalic acid acted as a fuel particularly in presence of urea and resulted in local rise in temperatures, causing sintering of some particles with a consequent decrease in surface area.

Table 1: *Percentage conversion of acetic acid during esterification reaction on various zinc oxide catalysts in relation to their surface area.*

Sample Code	Mole ratios of reagents			BET Surface area (m^2/g)	% Conversion of acetic acid
	$Zn(NO_3)_2$	Urea	Oxalic acid		
Z-102	1	0	2	19	23
Z-122	1	2	2	29	42
Z-124	1	2	4	17	31
Z-100	1	0	0	3	9
ZHβ-122	1	2	2	-	37
ZHβ-124	1	2	4	-	29

3.2. Reactivity of pure ZnO catalyst

The esterification activity in terms of % conversion of acetic acid and in relation to the number of acid sites is presented in Table 1. The reported conversions are equilibrium conversions. In all the experiments the equilibrium was reached at the end of ~ 2 hours. The catalyst Z-100 expectedly showed a minimum conversion of acetic acid (< 10 %). Furthermore, the catalytic activity showed dependence on surface area. Thus, as seen in Table 1, in comparison to Z-100, Z-102 showed a much higher conversion of 23.%. The activity of Z-122 was the highest with 42%. This was in agreement with its large surface area of 29 m^2/g. However, only ~ 31 % conversion was observed in case of Z-124 catalyst.

Although comparing Z-102 and Z-124 we see that the surface area is almost similar (~18 m^2/g), their catalytic activity was widely different. Thus surface area was not the only criterion to determine the catalytic activity. In conclusion the activity of the various zinc oxide catalysts were in the following order : [Z-122] > [Z-124] >[Z-102] > [Z-100].

Since surface areas of the catalysts were not solely responsible for the esterification activity, the cause of enhanced activity of Z-124 as compared to Z-102 was explained considering the TPD profiles shown in Fig. 1.Z-100 showed a weak TPD profile indicating near absence of acid sites as compared to the other samples prepared with use of oxalic acid and/or urea. These later samples showed two distinct peaks in the temperature range 50 - 400˚C which may be classified as low temperature (150 - 200˚C) and medium temperature (200-350˚C) peaks. The magnitude of these peaks followed order:

Low Temperature (LT)   :   [Z-122] > [Z-102] > [Z-124]

Medium Temperature (MT) :   [Z-122] > [Z-124] > [Z-102]

4

Table 2: Percentage conversion of acetic acid during esterification reaction on various zinc oxide catalysts in relation to strength of their acid sites.

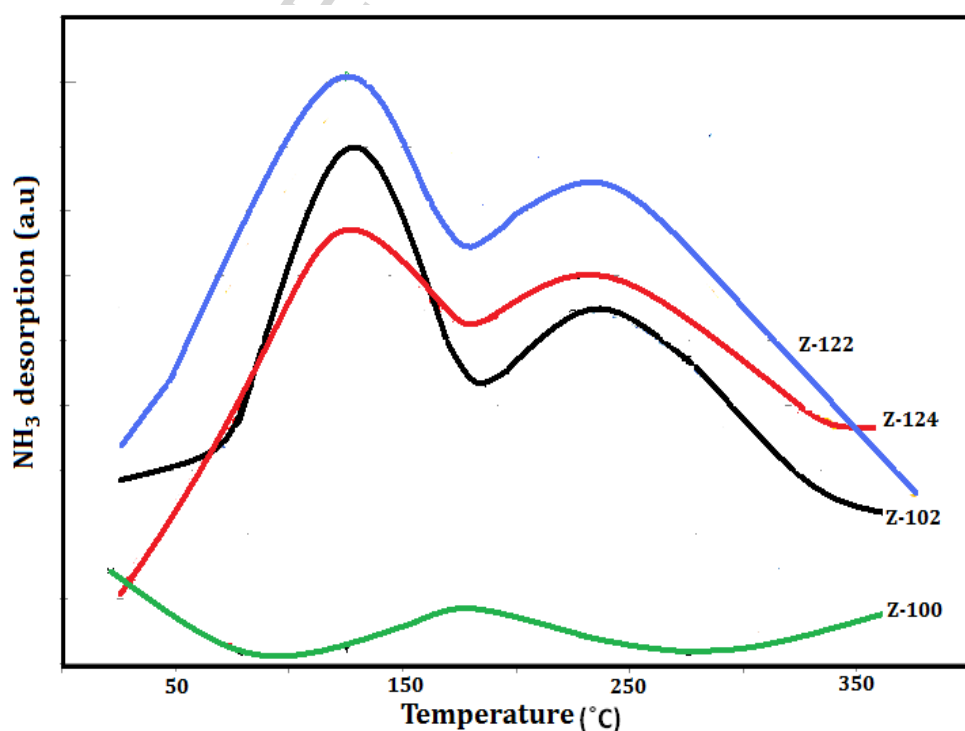| Sample	Total acidity (mmol/g)	Strength of acid sites (mmol/g)			% conversion of acetic acid
		Weak (RT - 150˚C)	Medium (150˚C - 300˚C)	Strong (300˚- 400˚C)	
Z-122	0.952	0.360	0.457	0.135	42
Z-124	0.720	0.232	0.335	0.157	31
Z-102	0.696	0.344	0.288	0.064	23
ZHβ-122	1.146	0.299	0.587	0.258	37
ZHβ-124	0.985	0.220	0.459	0.305	29

Fig 1. TPD Profiles of different ZnO catalysts.

5

It is thus clear from Table 2 that the percent conversion of acetic acid can be directly correlated to the concentration of acid sites of medium strength. Thus Z-122 with highest concentration of medium strength acid sites showed maximum percent conversion.

Also Z-124 showed higher conversion than Z-102 because of increased number of medium strength acid sites and not necessarily the factor of surface area. Therefore it was inferred that this esterification reaction was essentially a moderate acid site dependent reaction. Solid zinc oxide prepared in this work could be one of the most desirable catalyst due to its high selectivity, reusability, activity and less corrosivity [12].

3.3. Reactivity of ZnO in relation to Hβ-zeolites.

Protonic zeolites are well known solid acid catalysts [13]. To assess the comparative potential of the synthesized ZnO catalysts, the reaction was also performed under similar conditions for pure Hβ zeolite and on ~15% ZnO supported on Hβ zeolite. Pure Hβ zeolite showed an activity of ~47% . This was a little higher than 41% activity of Z-122 that was obtained by a simple one step calcination method. It was therefore felt the ZnO-Hβ composite catalyst could possibly produce a synergistic effect to show higher activity.Hence the two additional catalysts Z-122(Hβ) and Z-124 (Hβ) with 15 % component of ZnO were prepared. These catalysts were designated as ZHβ-122 and ZHβ-124. When these two composite catalysts were used for esterification, contrary to expectation they showed lower activity of 37 % for ZHβ-122 and 29 % for ZHβ-124 than either of the pure catalyst ZnO or Hβ-zeolite. Hence it was concluded that the mechanisms of esterification could be different on Hβ zeolite and ZnO catalysts. Further investigation was carried out to elucidate the nature of acid sites by pyridine adsorption studies using FTIR as shown in Fig. 2.

It is well known that adsorbed pyridine shows characteristic IR absorptions at ~1450 cm^{-1} and 1510 cm^{-1} due to presence of Lewis and Bronsted acid sites respectively. The peak at 1490 cm^{-1} is a combination band due to Lewis and Bronsted acid sites. It can be seen from the figure that the ZnO samples (Z-102, Z-122, Z-124) showed the above absorptions due to the presence of both Lewis and Bronsted sites. Closer examination of these spectra suggests that the active sample Z-122 is rich in Lewis acid sites as compared to the other catalysts. Thus it is proposed that Lewis sites are preferable active centres on ZnO in esterification reactions [11,14]. The Hβ zeolite is predominantly Bronsted acid catalyst and esterification with these catalysts was primarily mediated through protons as active centres by protonation of the substrate leading to formation of ester. The lower activity of ZnO(Hβ) samples could be due to decrease in availability of protons as active centres [15].

Our reaction kinetics study indicated operation of Eley-Rideal mechanism (Fig. 3) for esterification on ZnO considering pre-adsorption of the carboxylic acid with Zn^{2+} acting as Lewis acid centres. All the esterification reactions in the present work were carried out with an acetic acid to n-butanol molar ratio of 2:1. Graphs were plotted of ln C_t v/s t

and $1/C_t$ v/s t where C_t is equivalent concentration of acetic acid after time t. From the resulting kinetic plots, it was observed that the correlation coefficient R^2 term for the first order reaction gave a better fit than the correlation coefficient for second order reaction. Thus the average R^2 values using the ZnO catalysts for esterification were 0.95 for first order and 0.84 if we considered second order kinetics. It was therefore concluded that the esterification of acetic acid and n-butanol followed pseudo first order reaction kinetics. Hence Eley-Rideal mechanism was proposed. Eley – Rideal mechanism was also recently proposed on ZrO_2 catalyst [16].
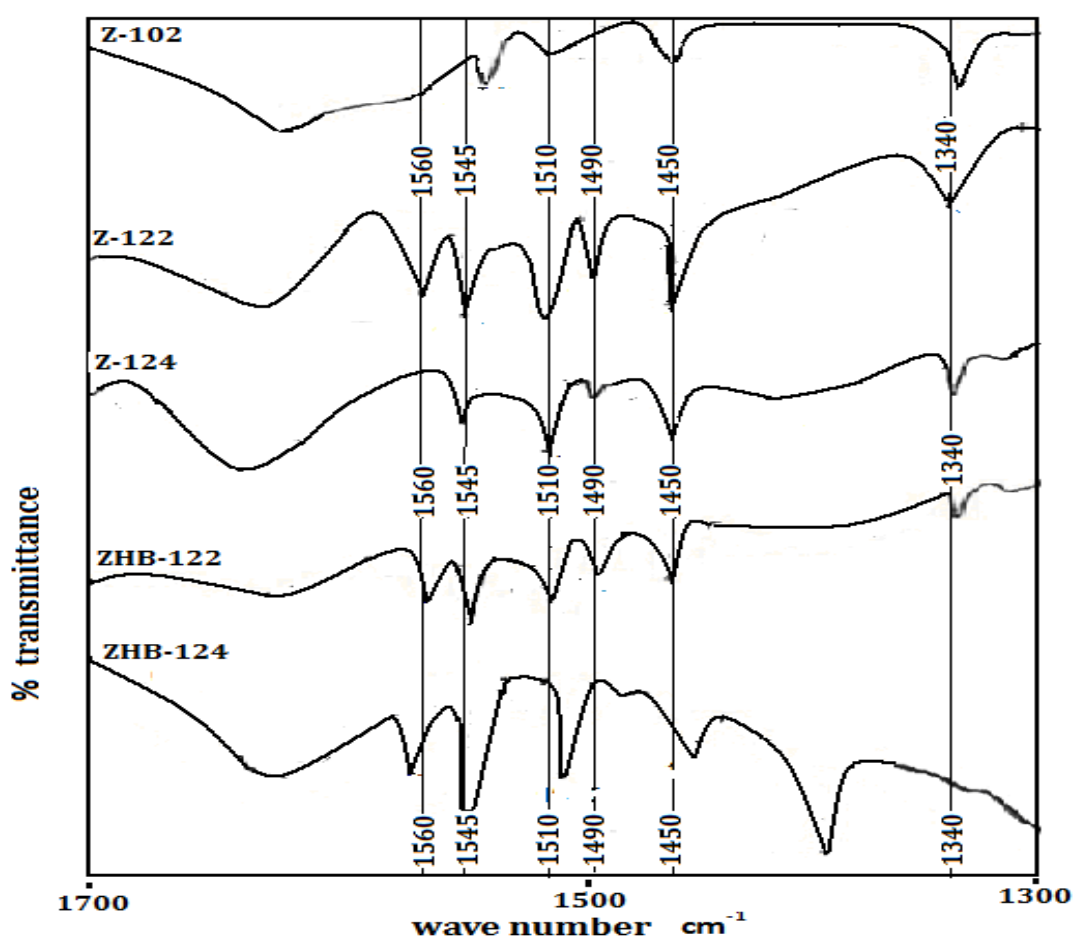

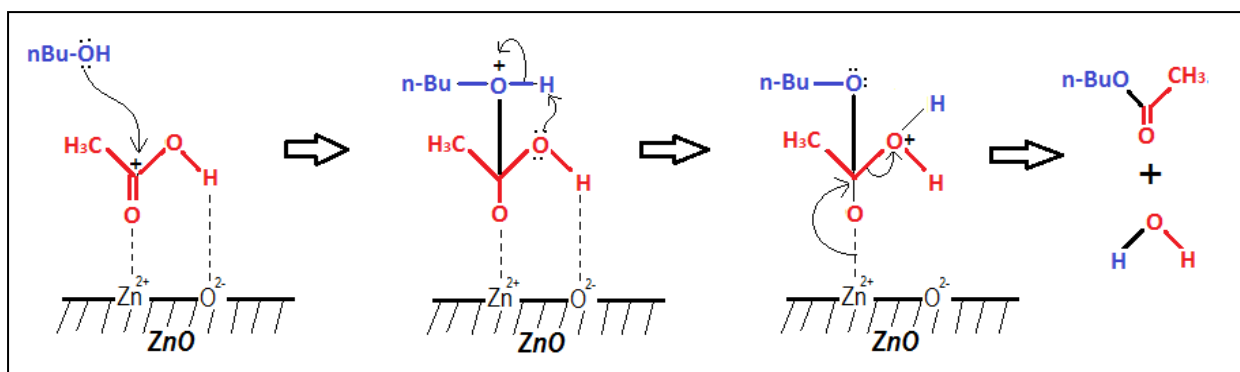**Fig. 2** : FT-IR spectra of pyridine adsorbed zinc oxide catalysts.

Fig. 3 : Proposed Eley-Rideal mechanism for esterification of acetic acid with n-butanol over zinc oxide catalyst.

4. Conclusions

Pure ZnO and ZnO/Hβ zeolites were synthesized and utilized as solid acid catalysts for esterification of acetic acid with n-butanol. ZnO synthesized by calcination of zinc nitrate in presence of urea and oxalic acid in molar ratio of 1:2:2 showed a high rate of esterification (% conversion of ~42 %) comparable to Hβ zeolite ~46%.

5. Acknowledgements

6. References

[1] N. Nagaraju, M. Shamshuddin, Indian J. Chem. 44A (2005) 1165-1170.

[2] Z. Qiuyun, Li Hu, Qin Wenting, Liu Xiaofang, China Petroleum Processing and Petrochem. Technol. Cat. Res., 15(2013) 19-24.

[3] R. Rajagopal, Sustainable Value Creation in the Fine and Speciality Chemicals Industry, Wiley, (2014).

[4] C. James, C. Duncan, Handbook of Green Chemistry and Technology, Blackwell Sci. Ltd, Oxford, London, (2002)321-335.

[5] Z. Mirjafary, H. Saeidian, A. Sadeghi, F. Moghaddam, Cat. Commun. 9, 2 (2008), 299-306.

[6] D. Singh, P. Patidar , A. Ganesh, S.Mahajani, Ind. Eng. Chem. Res.,52(2013)14776–14786.

[7] Hong-Bin Sun, R.Hua, Y. Yin, Molecules 11(2006) 263-271.

[8] S.P. Naik, J.B. Fernandes, Appl. Catal. A (Gen.) 20 (2001)195–199.

[9] O. I Peter , O. Chidi, Am. Chem. Sci. J. 2(2012)45-59.

[10] M.Sarvari, H. Sharghi, J. Org. Chem. 69, 20 2004) 6953-6956.

[11] G. Corro, U.Pal, N.Tellez, Appl. Cat. B: Environ. 129 (2013) 39– 47.

[12] M. Xianghe, P. Qiuyue, Y. Tiankui, J. Am. Oil Chem. Soc. 88(2011), 143.

[13] M. Bevilacqua, T. Montanari, E. Finocchio, G. Busca, Catal. Today 116 (2006) 132–142.

[14] G. Corro, F. Banuelos, E. Vidal, S. Cebada, Fuel 115 (2014) 625-628.

[15] X. Niu, Q. Mao, M. Dong, G. Wan, W. Fan, Z. Quin, J. Wang, Microporous Mesoporous Mater. 197 (2014) 252–261.

[16] H.Yang, H.Song, H.Zhang, P.Chen, Z.Zhao, J. Mol. Cat. A: Chem. 381 (2014) 54–60.

Highlights

- **Synthesized ZnO is active in n-butanol esterification reaction**
- **The activity of ZnO is comparable to that of Hβ Zeolite**
- **A reaction mechanism is provided from kinetics data**