



Short communication

Zinc oxide as a solid acid catalyst for esterification reaction



Anjani Nagvenkar, Sajo Naik, Julio Fernandes*

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

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ABSTRACT

Zinc oxide and its composites with H β 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 the structural features of the catalysts.

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1. Introduction

Solid acids have a tendency to donate a proton or to accept an electron pair in heterogeneous acid catalysis reactions such as alkylation and acylation. Esterification is an important reaction in the chemical industry where 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 $_2$ SO $_4$, HF, and H $_3$ PO $_4$, 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 catalysts as a replacement to homogenous catalysts 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. Pure ZnO and ZnO based catalysts have been already used for esterification and trans-esterification reactions [5–7]. The present investigation 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/H β 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, known amounts 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/H β composites were prepared by performing precipitation over H β 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 K α radiation ($\lambda = 1.5406 \text{ \AA}$).

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 for 12 h. After cooling to 25 °C, dry ammonia gas (20% NH $_3$ balance He (UHP);

* Corresponding author.

E-mail address: julio@unigoa.ac.in (J. Fernandes).

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

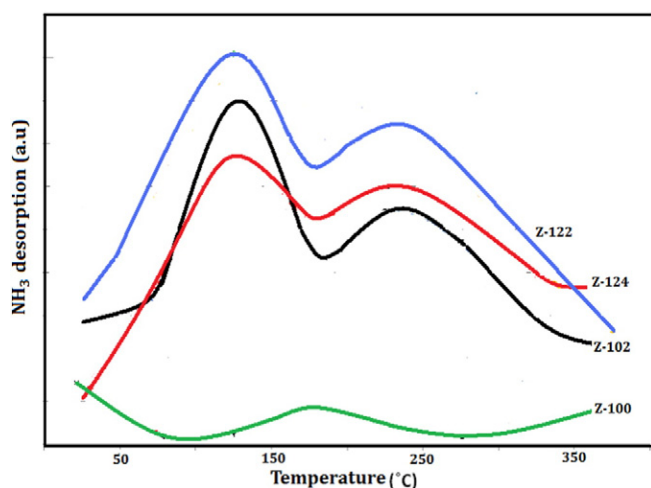


Fig. 1. TPD profiles of different ZnO catalysts.

20 mL/min) was passed over the sample for 15 min. 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 the surface acidity of the samples was determined by FTIR study. About 0.1 g of the samples was activated at 120 °C for 1 h prior to the experiment and exposed to pyridine vapours for 4–5 h. The samples were dried at 110 °C and degassed and FTIR spectra of each were recorded on a 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 N₂ as a probe molecule at 77.3 K. The samples were appropriately pre-treated and degassed to clean the surfaces from moisture and volatiles.

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 °C–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

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 glass 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 = $[C_i - C_t / C_i] \times 100$ 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] structure. The acid–base characteristics of a solid acid catalyst such as ZnO have been established earlier [6,8,10]. ZnO/SiO₂ is recently investigated for esterification of fatty acids, mediated by acid sites [11]. As the 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 to 30 m²/g. The average particle size of Z-102, Z-122, and Z-124 calculated by the Scherrer equation was ~34 nm. Z-100 showed a significant value of surface area due to large crystallite size. The surface area increased for Z-102 due to calcination in the presence of oxalic acid. Further, sample Z-122 prepared by using urea in addition to oxalic acid has significantly increased surface area from ~19 m²/g to 29 m²/g. The higher surface area resulted due to the porogenic properties of urea and oxalic acid. The presence of urea resulted in ZnO particles being of lower crystallite size, as well as enhanced porosity and surface area [8]. The 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 m²/g. This effect is interpreted from the point of view that excess oxalic acid acted as a fuel particularly in the presence of urea and resulted in local rise in temperatures, causing sintering of some particles with a consequent decrease in surface area.

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