

The effect of different ZnO precursors on the catalytic decomposition of ethanol

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Abstract

Three different samples of ZnO were prepared from the thermal decomposition, at 500°C in N₂, of three precursors, i.e. Zn(CH₃CO₂)₂·2H₂O, Zn₃(C₆H₅O₇)₂·2H₂O and Zn(NO₃)₂·6H₂O. These oxide samples were characterized by XRD and IR spectroscopy and their surface area were calculated using the BET method. The excess surface oxygen for each oxide was determined using the hydrazine method. Also, the basicity of such oxides were estimated thermogravimetrically using formic acid adsorption method. The catalytic decomposition of ethanol, as a test reaction, was studied over ZnO samples in a flow system. Ethylene and acetaldehyde were identified as the reaction products using gas chromatography. The activation energy for the decomposition process of ethanol over ZnO samples was calculated as ≈ 43 kJ mol⁻¹. Reaction mechanisms for the formation of ethylene and acetaldehyde as the decomposition products of ethanol are given.

Keywords: Basicity; Characterization; Ethanol; IR; *S*_{BET}; Thermal analyses; XRD; ZnO precursors

1. Introduction

Metals and metal oxides are excellent catalysts for the decomposition of different aliphatic alcohols [1,2]. Zinc metal is known as an extremely important trace mineral in the development of the fetus and in the nutrition of infants, since it is necessary for the synthesis of DNA, and the genetic material in the cell [3]. Vohs and Barteau [4–6] have carried out a number of surface studies on ZnO which is known to possess two types of polar surfaces, i.e. (0001)-Zn and (000 $\bar{1}$)-O surfaces. They studied the decomposition of acetic acid and propionic acid on ZnO using TPR, XPS and UPS. It was found that on the (0001)-Zn polar surface, the carboxylic acids adsorbed dissociatively to form the corresponding surface carboxyl

species which underwent (at temperatures ≥ 500 K) either net dehydration to form unsaturated aldehydes or net total oxidation to carbon oxides and water. The (000 $\bar{1}$)-O polar surface was, however, more active for the decomposition of these carboxylic acids. These studies [4–6] indicated the pronounced structure dependence of the acid–base reaction on the polar surfaces of zinc oxide.

ZnO has been used as a catalyst for the decomposition of methanol [7], ethanol [8] and isopropanol [9]. In addition ZnO incorporated with other oxides, such as CuO, was used for methanol synthesis [10–12]. Also, the dehydrogenation of substituted alcohols, to aldehydes, was studied over the ZnO–Cr₂O₃ system [13]. A similar study [9] has been carried out on the dehydrogenation of isopropanol on ZnO, prepared from different

precursors, as a structure-insensitive reaction, through the oriented texture of the oxide powders. Also, Nakajima et al. [14] studied the acid properties of zinc oxides prepared by several methods from different precursors.

The present work is intended to study the relationship between ZnO precursors and the catalytic activity of the ZnO produced. The catalytic decomposition of ethanol was chosen as a test reaction for the present study.

2. Experimental

2.1. Materials and techniques

Zinc oxide samples were prepared by the thermal decomposition of three different precursors, i.e. zinc acetate [$\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$], zinc citrate [$\text{Zn}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$] and zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], in N_2 at 500°C for 6 h. All these chemicals were analytical grade materials.

Thermal analyses measurements (TG and DTA) of zinc oxide precursors were performed using a Shimadzu Stand-Alone Thermal Analyzer instrument (TGA-50H and DTA-50), supplied with a data acquisition and handling system model Shimadzu Chromatopac C-R4AD, Japan. Thermal measurements were carried out at 5°C min^{-1} heating rate using ≈ 10 mg sample weight and in a stream of N_2 (40 ml min^{-1}). Highly sintered α - Al_2O_3 was the thermally inert reference material used in the DTA measurements.

X-ray powder diffraction (XRD) analysis of the three products ZnO (from the different precursors) were carried out by means of an X-ray Diffractometer Model JSX-60PA JEOL (Japan), with a Ni-filtered CuK_α radiation source ($\lambda = 1.5405 \text{ \AA}$).

IR absorption spectra of the final products of decomposition of zinc precursors as well as ZnO samples, which were exposed to formic acid, were recorded using a Perkin Elmer 1430 ratio recording IR spectrophotometer between $4000\text{--}200 \text{ cm}^{-1}$, using KBr discs.

The surface area for ZnO samples were determined by the BET method [15] using N_2 as an adsorbate with the aid of a conventional volumetric gas adsorption apparatus [16].

The surface excess oxygen was determined using the hydrazine method as described elsewhere [17].

The basicity of ZnO samples was determined thermogravimetrically as follows: 100 mg of each sample was heated at 250°C in air for 2 h. The three oxide samples were kept in a desiccator together with a beaker containing formic acid at ambient temperature, for two weeks, prior to analysis. 15 mg of each oxide, after exposure to formic acid, was subjected to TG analysis in the temperature range between ambient to 200°C (at 20°C/min) in dry N_2 (20 ml/min). The TG curves were automatically recorded on the same apparatus mentioned above. The weight loss was calculated as the basicity of each oxide.

The catalytic activity of ZnO samples towards the decomposition of ethanol (PROLABO, France) has been investigated in a flow system under atmospheric pressure. A mixture of 2.3% ethanol in dry N_2 , obtained by passing N_2 through liquid ethanol held at 5°C , was used. The total flow rate was kept constant at 100 ml min^{-1} . The feed exit gases were analyzed by gas chromatograph, a Shimadzu GC-14A equipped with a data processor model Shimadzu Chromatopac C-R4AD (Japan), on a stainless steel column (PEG 20M 20% on Chromosorb W, 60/80 mesh, 3 m x 3 mm) at 110°C .

The reaction rate, catalytic activity, selectivity and the kinetic parameters of the decomposition of ethanol were determined as explained, in details, previously [18].

3. Results and discussion

3.1. Thermal analyses

Fig. 1 (I) shows the TG curves of the three zinc oxide precursors. Curve (a) represents the TG of zinc acetate, it shows two weight loss steps with

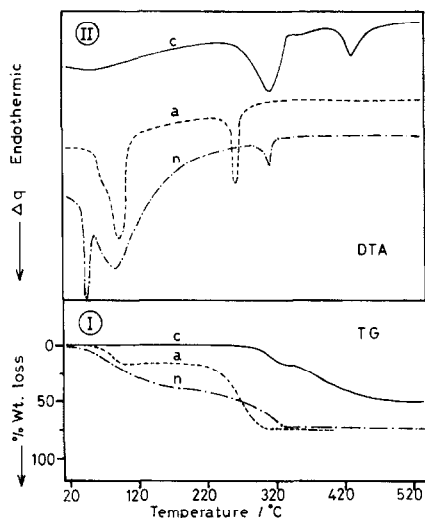


Fig. 1. TG and DTA curves for: (a) zinc acetate, (c) zinc citrate and (n) zinc nitrate, carried out at $5^{\circ}\text{C min}^{-1}$ in N_2 atmosphere (40 ml min^{-1}).

a total weight loss of 72.5% of the original sample weight. The first step, in the temperature range $50\text{--}95^{\circ}\text{C}$, is due to the dehydration of $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ [19]. The second step is located between $215\text{--}300^{\circ}\text{C}$ and corresponds to the decomposition of the anhydrous salt, $\text{Zn}(\text{CH}_3\text{CO}_2)_2$, to give ZnO as a final product. Zinc citrate, curve (c), shows two consecutive steps between $300\text{--}490^{\circ}\text{C}$ attributed to the dehydration and decomposition of $\text{Zn}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$, with total weight loss of 49.9% of the original weight. The calculated weight loss (ca. 49.9%) suggests the formation of ZnO together with the precipitation of some carbon (theoretical calculation for the decomposition of $\text{Zn}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ to give 3ZnO is equal to 60.3%). Finally, the TG curve of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (curve n) shows two successive steps of the dehydration and the decomposition of the nitrate to produce ZnO around 340°C with total loss of 72.4% of the original sample weight (theoretical calculation of % weight loss for the decomposition of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to give ZnO is 72.6%).

The DTA curves of zinc oxide precursors are shown in Fig. 1 (II). $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ (curve a) shows two endothermic peaks. The first, a broad and strong endotherm at 88°C , corre-

sponds to the dehydration step [19]. This is followed by the second peak at 254°C due to the decomposition of the anhydrous acetate. The DTA curve of zinc citrate (curve c) also shows two endothermic peaks at 300°C and 420°C which are ascribed for the dehydration and decomposition steps as shown in its TG curve. Zinc nitrate shows a sharp endotherm at 43°C (curve n) due to melting of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [19]. This is followed by a broad peak at 81°C which corresponds to the dehydration process. Finally, a relatively small endotherm appeared at 307°C which is attributed to the decomposition of the nitrate to give ZnO.

From the thermal analyses results, it is concluded that the thermal treatment of zinc precursors at 500°C , for 6 h in N_2 atmosphere, is quite enough for the preparation of ZnO samples.

3.2. IR spectroscopy

The IR spectra of all prepared ZnO samples, from the three different precursors at 500°C , showed the characteristic absorption band of ZnO at $449\text{--}439 \text{ cm}^{-1}$ [20]. No absorption bands characteristic of hydroxyl groups appeared in the IR spectra of all three ZnO samples. This has indicated, however, that heating of the three precursors at 500°C for 6 h was enough to ensure complete crystallization of the product ZnO.

3.3. X-ray analysis

X-ray powder diffraction (XRD) analysis was used to characterize ZnO produced from the thermal decomposition of different precursors (i.e. acetate, citrate and nitrate) at 500°C in N_2 . The XRD data of these three oxide samples are summarized in Table 1. The XRD patterns of the three prepared oxides showed a group of diffraction lines that were identical with the pattern of pure ZnO (ASTM card no. 5-0664), especially those high intense lines at $d = 2.53, 2.66$ and 2.88 \AA .

From the results of IR and XRD analyses one can conclude that the obtained samples from the thermal decomposition of the different zinc precursors are all pure ZnO.

Table 1

X-ray powder diffraction data of the oxide samples produced from the thermal decomposition of three zinc precursors (acetate, citrate and nitrate) at 500°C, in N₂ for 6 h and the ASTM card data of ZnO

ZnO (acetate)		ZnO (citrate)		ZnO (nitrate)		ASTM (5-0664)	
<i>d</i> (Å)	<i>I</i> / <i>I</i> ⁰	<i>d</i> (Å)	<i>I</i> / <i>I</i> ⁰	<i>d</i> (Å)	<i>I</i> / <i>I</i> ⁰	<i>d</i> (Å)	<i>I</i> / <i>I</i> ⁰
2.88	49	2.86	54	2.89	42	2.82	70
2.66	46	2.64	40	2.67	35	2.60	60
2.53	100	2.51	100	2.53	100	2.48	100
1.94	28	1.93	26	1.94	26	1.91	30
1.64	46	1.64	47	1.65	39	1.63	40

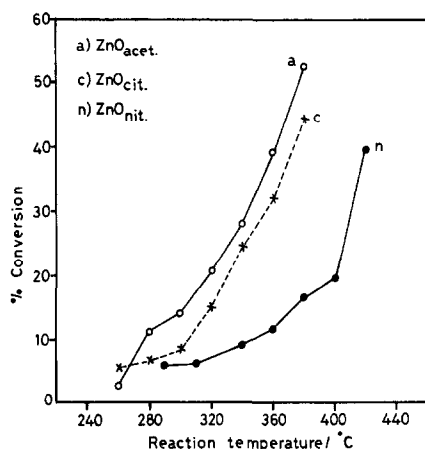


Fig. 2. Effect of reaction temperature on the activity of ZnO, prepared at 500°C from (a) acetate, (c) citrate and (n) nitrate precursors, during the decomposition of ethanol.

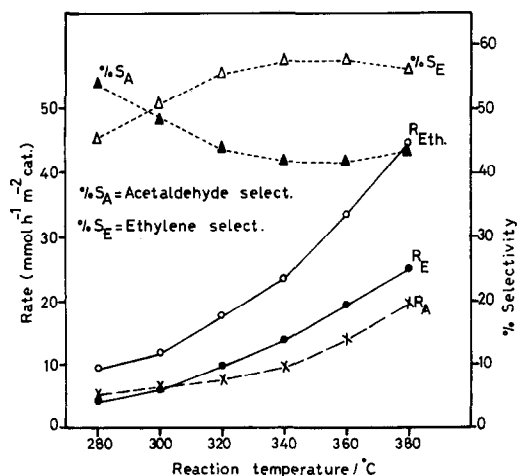


Fig. 3. Effect of reaction temperature on the activity and selectivity of ZnO, prepared from Zn(CH₃CO₂)₂·2H₂O at 500°C, during the decomposition of ethanol.

3.4. Surface area measurements

The S_{BET} values of ZnO samples, from the three different precursors at 500°C, were determined as 10.0 m²/g in case of ZnO_{acet} (from zinc acetate), 9.2 m²/g for ZnO_{cit} (from citrate salt) and 3.6 m²/g in case of ZnO_{nit} (from zinc nitrate).

3.5. Catalytic activity measurements

The decomposition of ethanol over these ZnO catalyst samples was studied in a flow system. Fig. 2 represents the effect of reaction temperature on the activity of ZnO towards the decomposition of ethanol. The oxide, ZnO_{acet}, prepared from the acetate salt was the most active one [% conversion at 380°C (reaction temperature) = 52.8%], while ZnO_{nit} prepared from the nitrate salt was the least active catalyst (% conversion at 380°C = 16.7% only). This can be correlated with the acidity of the oxide precursors, where the acidity of these precursors could be arranged in the following order: nitrate > citrate > acetate. From Fig. 2 it is evident that the lower the acidity of the precursor, the higher is the activity of ZnO towards the decomposition of ethanol. It is interesting to realize that this sequence of the precursor's acidity is parallel with the measured amount of excess sur-

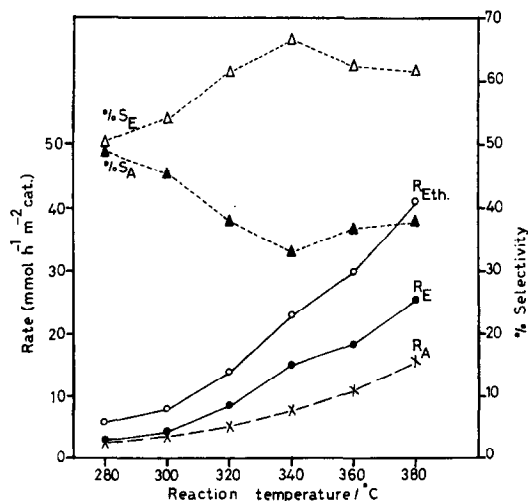


Fig. 4. Effect of reaction temperature on the activity and selectivity of ZnO, prepared from Zn₃(C₆H₅O₇)₂·2H₂O at 500°C, during the decomposition of ethanol.

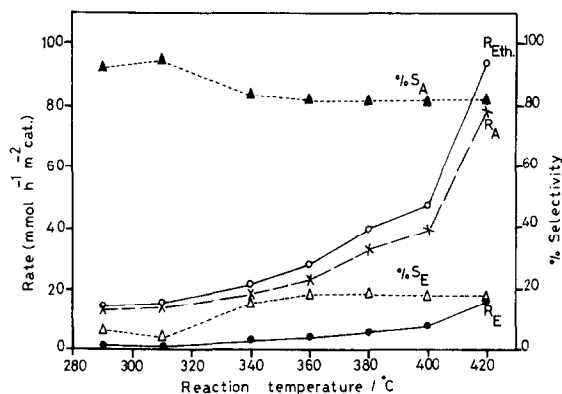
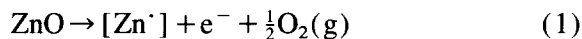


Fig. 5. Effect of reaction temperature on the activity and selectivity of ZnO, prepared from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 500°C , during the decomposition of ethanol.

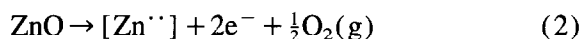
face oxygen for each catalyst. ZnO_{acet} has $0.3 \text{ mg O}_{\text{ex}}/\text{m}^2$ catalyst, ZnO_{cit} has $0.4 \text{ mg O}_{\text{ex}}/\text{m}^2$ catalyst while ZnO_{nit} gains $1.4 \text{ mg O}_{\text{ex}}/\text{m}^2$ catalyst.

Figs. 3 and 4 show the effect of reaction temperature on the activity and selectivity of ZnO, prepared from the acetate and citrate precursors at 500°C respectively, during the decomposition of ethanol. Both oxides have, almost, the same behaviour towards the decomposition of ethanol. The total rate of removal of ethanol (R_{Eth}) was calculated as $44.9 \text{ mmol h}^{-1} \text{m}^{-2} \text{cat.}^{-1}$ over ZnO_{acet} while a value of $41.3 \text{ mmol h}^{-1} \text{m}^{-2} \text{cat.}^{-1}$ was found in case of ZnO_{cit} . Values of both R_{E} (rate of formation of ethylene) and R_{A} (rate of formation of acetaldehyde), during the decomposition process of ethanol over the two oxides, are plotted in Figs. 3 and 4. At low temperatures, ZnO_{acet} was selective towards acetaldehyde formation, then it became selective towards ethylene formation at $\geq 300^\circ\text{C}$ reaction temperature. ZnO_{cit} showed considerable selectivity to both ethylene and acetaldehyde at temperatures less than 300°C (Fig. 4). Afterwards, the selectivity of ethylene increased with increasing the reaction temperature. On the other hand, ZnO_{nit} was mainly selective towards acetaldehyde formation ($S_{\text{A}} = 81.8\text{--}95.6\%$), see Fig. 5. The total rate of removal of ethanol, at 380°C , $R_{\text{Eth}} = 39.7 \text{ mmol h}^{-1} \text{m}^{-2} \text{cat.}^{-1}$, while the rate of formation of acetaldehyde, $R_{\text{A}} = 32.5 \text{ mmol h}^{-1} \text{m}^{-2} \text{cat.}^{-1}$. The rate of formation of ethylene (R_{E}) was also calculated to be $7.2 \text{ mmol h}^{-1} \text{m}^{-2} \text{cat.}^{-1}$.

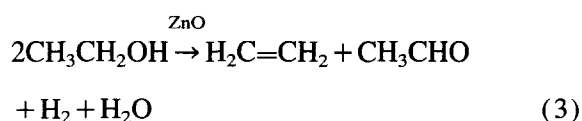
ZnO is known to be n-type semiconductor [21] and heating the oxide at 500°C for 6 h, during its preparation, may produce excess electrons according to the following mechanisms [22]:



or



$[\text{Zn}^{\cdot}]$ or $[\text{Zn}^{\cdot\cdot}]$ is an interstitial cation. Two chemisorbed ethanol molecules decomposed over ZnO surface to yield ethylene and acetaldehyde as follows:



The dehydrogenation of ethanol depends on the concentration of the Lewis base sites, while the dehydration depends on the concentration of the Lewis acid sites, as proposed previously [23].

ZnO is considered as a solid base [24,25] but some acidic properties have been reported [26]. The basicity measurements for ZnO catalysts, prepared from the three precursors, supported the experimental results drawn in Figs. 3–5. ZnO_{nit} has the highest basicity value ($15.7 \text{ mg H}_2\text{CO}_2/\text{m}^2 \text{cat.}^{-1}$) while ZnO_{acet} and ZnO_{cit} have lower values of basicity as 11.8 and $12.5 \text{ mg H}_2\text{CO}_2/\text{m}^2 \text{cat.}^{-1}$, respectively. ZnO catalysts, in our opinion, have both Lewis basic sites (as oxide ions) and Lewis acidic sites (as the coordinatively unsaturated zinc ion), which is very limited compared to the basic sites. The adsorbed formic acid on such Lewis basic sites was identified using the IR spectroscopy. The absorption bands of formic acid [27] at 3450 , 1730 , 1570 , 1395 , 1320 and 1180 cm^{-1} were observed in all the IR spectra of ZnO catalysts exposed to formic acid, as explained in the Experimental section.

It is worth noting here, that the increased concentration of excess surface oxygen over the catalysts as well as the higher basicity value of these catalysts can accelerate the dehydrogenation reaction (producing acetaldehyde) more than the dehydration reaction (to give ethylene). In case

Table 2

Kinetic parameters for the decomposition of ethanol over ZnO catalysts, prepared from the thermal decomposition of different precursors at 500°C for 6 h in N₂

Catalyst	Temperature interval, °C	ΔE kJ mol ⁻¹	lnA	Correlation coefficient
ZnO _{acet}	280–320	42.7	13.8	0.98
ZnO _{cit}	260–320	42.4	13.3	0.96
ZnO _{nit}	310–400	42.6	13.7	0.99

of ZnO_{nit} (see Fig. 5) where the catalyst is the most basic one and gains the highest concentration of excess surface oxygen, acetaldehyde is the main product with selectivity of 81.8–95.6%. In contrast, ZnO_{acet} and ZnO_{cit} which have lower concentration of surface excess oxygen (about one third of the value in case of ZnO_{nit}) and also lower basicity than ZnO_{nit} showed considerable yield of both ethylene and acetaldehyde at the same time, see Figs. 3–4 and Eq. 3.

Table 2 summarizes the kinetic parameters for the decomposition of ethanol over ZnO catalysts prepared from different precursors at 500°C, during the corresponding intervals of reaction temperatures. The activation energy was calculated to be 42.4–42.7 kJ mol⁻¹. Our results for the decomposition of ethanol over ZnO_{nit} is in close agreement with those previously published by Krylov and Fokina [28]. In addition, our calculated values of activation energy (ΔE) for the decomposition of ethanol over ZnO catalysts, Table 2, is consistent with the reported value by Srihari and Wiswanath [29].

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