

# Direct conversion of corn cob to formic and acetic acids over nano oxide catalysts

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## Abstract

Considering energy shortage, large molecules in corn cob and easy separation of solid catalysts, nano oxides are used to transform corn cob into useful chemicals. Because of the microcrystals, nano oxides offer enough accessible sites for cellulose, hemicellulose and monosaccharide from corn cob hydrolysis and oxidant. Chemical conversion of corn cob to organic acids is investigated over nano ceria, alumina, titania and zirconia under various atmospheres. Liquid products are mainly formic and acetic acids. A small amount of other compounds, such as D-xylose, D-glucose, arabinose and xylitol are also detected simultaneously. The yield of organic acids reaches 25%–29% over the nano oxide of ceria, zirconia and alumina with 3 h reaction time under 453 K and 1.2 MPa O<sub>2</sub>. The unique and fast conversion of corn cob is directly approached over the nano oxides. The results are comparative to those of biofermentation and offer an alternative method in chemically catalytic conversion of corn cob to useful chemicals in a one-pot chemical process.

## Key words

corn cob; chemical conversion; nano oxides; biomass; formic acid; acetic acid

## 1. Introduction

The conversion of biomass gains unprecedented attention due to energy shortage and environmental challenge. It has been developed quite a few methods to utilize the renewable biomass to chemicals or to remit the short of fossil resource, such as microwave-assisted pyrolysis [1], co-firing with coal [2], steam reforming [3] and the importantly catalytic conversion [4]. Corn cob is one of the major byproducts of maize, containing ~32% cellulose, ~35% hemicellulose, ~20% lignin and 3% acetyl groups (oven-dry basis) [5,6]. It is commonly used as feed additives or as the resource of glucose by fermentation. The corn cob contains high content of xylans which could be transformed into xylooligosaccharides [7–9]. Xylan, the main component of hemicellulose, consists of a  $\beta$ -1, 4-linked D-xylosyl residues backbone branched with other pentoses, hexoses and uronic acids. It can be effectively converted into ethanol by simultaneous saccharification and fermentation (SSF) with *Saccharomyces cerevisiae* [10–13]. It has been reported that the combination of acidic and enzymatic hydrolysis converts lignocellulosic materials into bio-ethanol [14–16]. Although the utilization of fermentation process that relies on bacteria undoubtedly plays

a significant role in the process of biomass conversion, the requirement of specified bacteria which undergoes harsh environment for growth limits its further development to some extent. Hence, investigation on chemically fast conversion process is very important and beneficial to the better utilization of corn cob.

Chemical conversion of corn cob is commonly catalyzed by acids or bases and the distribution of products may be totally different due to the difference in the pH value of the reaction solution. Hemicellulose could be autohydrolyzed to sugars when the biomass was with water at high temperatures [17]. In addition, the distribution of products is also affected by various oxidants. It has been reported that ferulic acid (4-hydroxy-3-methoxycinnamic acid) and *p*-coumaric acid (4-hydroxycinnamic acid) are produced from alkaline hydrolysis of corn cob at room temperature [18]. Xylose has been also converted to formic and threonic acids as major products under the Ir(III)-catalyzed oxidation by potassium iodate [19]. Considering separation problems, solid catalysts have been widely studied instead of the traditional use of liquid ones in catalytic upgrading of biomass pyrolysis. For example, cellulosic and lignocellulosic biomass are hydrolysed by solid-supported Brønsted or Lewis acid reagent catalysts [20],

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zeolites [21,22], metal nano oxides [23,24] and modified heteropolyacids [25,26]. Multifunctional solid catalyst converts biomass to value-added fine chemicals, to be more exact, acid catalyst leads to sugars or polyols as major products and oxide catalysts result in organic acids such as levulinic acid, malic acid, lactic acid, acetic acid and formic acid. Solvents also influence the target products, but this degrading process in aqueous system is most desirable.

As an oxidation product, formic acid is non-toxic, of which concentrated solution is not flammable and diluted solution is on the US Food and Drug Administration list of food additives. The concentrated solution of formic acid used in the cells would be the best fuel for direct fuel cells and shows reasonable power densities at room temperature. It possesses far better electrocatalytic oxidation activity than direct methanol fuel cells (DMFCs) with relatively smaller crossover flux through Nafion<sup>®</sup> and higher electromotive force (theoretical open circuit potential 1.48 V) [27]. More recently, formic acid has been proposed as a suitable hydrogen storage compound [28]. This concept builds on the 4.4 wt% share of hydrogen in formic acid resulting in 53 g hydrogen per liter FA [29,30]. Glucose and xylose are also very valuable but further transformation of them is more popular and meaningful at present [31]. In McGinnis's research [32], the wet oxidation was used for the conversion of the model compounds, which are the primary parts of the lignocellulosic materials. At elevated temperature, the major products are mainly formic acid and acetic acid, and the yield could be improved by the addition of ferric sulfate at even reduced temperature.

Zeolites seem like good catalysts for hemicellulosic biomass hydrolysis, however, limited pore size limits diffusion of biomass in zeolite channels. Heteropolyacids are moderate ones with glucose and methyl glucosides as main products [25,26]. Considering the large molecules in corn cob, nano oxides would offer enough accessible sites for transformation to oxidants and ensure fast and unique conversion. In the present work, the chemical conversion of corn cob to organic acids with a series of nano oxides as catalysts was performed under oxidative conditions. The yield of organic acids reached the maximum when the appropriate reaction condition was adopted. The yield of organic acids reached 25%–29% with 3 h reaction time under 453 K and 1.2 MPa O<sub>2</sub> over nano ceria, alumina, titania and zirconia.

## 2. Experimental

### 2.1. Materials

Corn cob. The corn cob was obtained from a plant of Inner Mongolia Autonomous Region of China and was ground to powders of ~75 μm in size and dried at 353 K overnight before reaction.

Nano ceria. The ammonium ceric nitrate (Ce(NH<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>) was chosen as the cerium source in the process of producing nano-CeO<sub>2</sub> with a hydrothermal method. Aqueous ammonia was added slowly into the aqueous solu-

tion of cerium source under stirring at room temperature. The resulting suspension was continuously stirred for another 30 min and then put into a Teflon lined stainless autoclave. The autoclave was kept at 393 K for 12 h. Both the centrifugation and wash steps were prerequisite to obtain the product after the autoclave cooled naturally to room temperature. The sample was calcined at 473 K in air for 4 h before participating in the catalytic reaction.

Nano alumina. The γ-Al<sub>2</sub>O<sub>3</sub> nanorods were prepared according to the following procedure. Alumina sol (18 g, ~10% dry alumina, Zhejiang Yuda Huagong Company) was added into a mixture of 1.4 g of oleylamine (Adrich) and 1 mL of NH<sub>3</sub>·H<sub>2</sub>O (25%) in 15 mL of distilled water at 353 K and maintained at 353 K for another 2 h. The resultant was transferred into the sealed autoclave and kept at 453 K for 72 h. The powder after hydrothermal treatment was washed with ethanol and dried at 373 K. The γ-Al<sub>2</sub>O<sub>3</sub> nanorods were obtained by calcination of the powder at 823 K in air for 4 h.

Nano zirconia. Nano ZrO<sub>2</sub> was prepared by the precipitation method using aqueous ammonia as the precipitating agent. The zirconyl chloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O) was selected as the zirconium source, and the pH of the precursor solution was adjusted to 10 by adding aqueous ammonia. Then, the solution was stirred at 323 K for 30 min. The resulted product was washed with deionized water until no Cl<sup>-</sup> was detected by AgNO<sub>3</sub> and then dried at 373 K in oven. The final sample was obtained by calcination at 673 K in air for 4 h.

Titania. The commercial sample of Degussa P25 was used as TiO<sub>2</sub> directly.

### 2.2. Characterization

Standard X-ray powder patterns were recorded on a vertical X-ray diffractometer (Philips X'pert-Pro) between 10° and 80°, using Cu K<sub>α</sub> radiation (λ = 0.15406 nm) generated at 40 kV and 40 mA. The identification of crystalline phases was made by matching with the JCPDS files.

The BET surface area was determined by nitrogen adsorption at 77 K using the automated gas adsorption analyzer Micromeritics ASAP 3020. FT-IR spectra of the prepared zirconium phosphates were recorded on Nicolet iS10 spectrometer using ATR accessory with a resolution of 4 cm<sup>-1</sup> and accumulation of 64 scans.

Transmission electron microscopy images were taken with a JEM-2100 using an accelerating voltage of 200 kV. The morphology of the oxides before and after the oxidation process of corn cob was investigated.

### 2.3. Catalytic test

The chemically catalytic conversion of corn cob was carried out in a bath-type autoclave reactor (total volume 60 mL). The powder of corn cob, catalyst and deionized water were added into the autoclave. Oxygen was introduced to the reactor at room temperature to a pressure set in advance. Then

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