



## Diverse impact of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with nano/micro-sized shapes on the catalytic fast pyrolysis of pinewood: Py-GC/MS study



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### ABSTRACT

The feasibility of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalyst addition in the *in-situ* catalytic fast pyrolysis of Pinewood was considered with the focus on the variation in its shape: nano-sized non-ideal spheres, nanotubes, hollow nano/microtubes, and octadecahedral crystals. Nano-sized spheres strongly promoted the formation of acetaldehyde, something that was also observed for the octadecahedral crystals. The formation of acids was primarily facilitated through the addition of nanotube catalysts and octadecahedral crystals. Newly formed alicyclic ketonic compounds were promoted through the addition of nano-sized spheres, hollow nano/microtubes, and octadecahedral crystals. The latter two catalysts also showed a moderate selectivity in the formation of furfural. All applied catalysts showed loss of activity, though at different degrees, on the formation of lignin derived phenolic compounds, which can be primarily attributed to favoring the formation of char with simultaneous release of CO<sub>2</sub>. All used  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalysts with different shapes maintained their original morphology after the rapid heating with the rate of 20 K/ms followed by catalytic fast pyrolysis at 500 °C, indicating that nanomaterials with targeted dimensions can be applied as catalysts in the catalytic fast pyrolysis of biomass to enhance conversion of undesired oxygenated compounds to higher quality bio-oil and valuable chemicals.

### 1. Introduction

Iron oxides have been considered as promising catalytic materials [1,2] due to their high efficiency, environmental friendliness and low cost. Among different iron oxide polymorphs,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) is the most stable under ambient conditions.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is intensively used in diverse areas of catalysis, especially in reduction/oxidation and acid/base reactions [3]. Hematite was found as an effective catalyst for the oxidation of CO [4], photocatalytic water oxidation [5], reduction of NO<sub>x</sub> to NH<sub>3</sub> in diesel exhausts [6], oxidative S–S coupling of thiols to disulfides [7].

Besides the traditional fact, that high catalytic activity derives mainly from the large surface area and diverse surface defects of the nanoparticles, several additional factors could contribute to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

high catalytic activity: phase evolution, morphology of grains, pore size, the width of a band gap [8]. Generally, there is no linear relationship between the particle size and the catalytic activity. Some reactions could be size insensitive within a specific range of particle size like oxygen reduction reactions [9] or hydrogenation, while another group of reactions (such as formation of CO or N<sub>2</sub> [10] or Fischer-Tropsch synthesis [11]) are extremely size sensitive. Not only the size, but also the shape of the iron oxide nanomaterials could greatly affect their catalytic properties. The shape is associated with the diversity of crystal facets exposed to a reaction zone that will define the surface density of catalytic sites and their activity [12]. Each type of shape can be considered as a unique combination of facets and their dimensionality. So far,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with various morphologies (particles, sheets, spindles, rods, tubes, wires, spheres, cubes, and flower-like shape)

**Abbreviations:** BET, Brunauer-Emmett-Teller; CFP, catalytic fast pyrolysis; FNMT,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nano/microtubes; FNT,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanotubes; FOC,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> octadecahedral crystals; FS054,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder with non-ideal spherical shape and ~54 nm particle size; Py-GC/MS, pyrolysis-gas chromatography–mass spectrometry technique; PW, pinewood; PW:FNT, PW:FNMT, PW:FOC, PW:FS054, catalysts after CFP with pinewood; Red/ox, reduction/oxidation; S.D., standard deviation; SEM, scanning electron microscopy; TEM, transmission electron microscopy; XRD, X-ray powder diffraction

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[13–21] have been successfully fabricated. There are several studies investigating their catalytic ability. Iron oxide nanotubes demonstrated the highest selectivity towards heavy hydrocarbons production in Fischer-Tropsch synthesis compared with iron oxide catalysts with other morphologies: nanorods, nanospheres, nanopolyhedra, and microspheres [22]. The addition of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanowires increased greatly the yield of urea produced through green magnetic reactions in contrast to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles [23]. The crystal morphology of hematite has a significant effect on its photocatalytic properties [24]. Therefore, both size and shape are critical factors that must be considered to fully investigate  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalytic activity.

Briefly, catalytic fast pyrolysis (CFP) is a combination of the traditional fast pyrolysis, where biomass is exposed to moderate temperatures, typically 500 °C, with a high heating rate in the inert atmosphere, and catalysts, which play a key role by increasing the selectivity and efficiency of the process [25]. To date, CFP has attracted extensive attention as promising research area in catalysis. CFP is one of the feasible approaches to produce bio-oil and it can be regarded as the potential future fossil fuels replacement, and a source for valuable chemicals [26]. Meanwhile, CFP is used to upgrade the produced bio-oil by reducing the fraction of oxygenated compounds as their presence in the bio-oil causes its instability, high viscosity, acidity, and corrosiveness. The fraction of the oxygenated compounds in the bio-oil can be decreased through promotion of decarbonylation, decarboxylation, and hydrodeoxygenation reactions [27].

In recent years, among different heterogeneous metal oxides catalysts, micron-sized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has been considered as a catalyst in CFP due to its multivalent nature, specific acid/base and reduction/oxidation properties as well as low cost, wider availability, and high stability [28]. For example, Fe<sub>2</sub>O<sub>3</sub> supported onto CaO was proposed as an effective catalyst for bio-oil upgrading leading to the decrease in acids and aldehydes/ketones fractions as well as the increase in the yields of furans, light and aromatic hydrocarbons [29]. Interestingly, Red mud (a mixture of 30–60% Fe<sub>2</sub>O<sub>3</sub> with TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, and SiO<sub>2</sub>), which is an industrial waste and a by-product in aluminum industry, has also been proposed as a promising catalyst for CFP with different types of biomass [30]. It was found that the addition of Fe<sub>2</sub>O<sub>3</sub> in CFP reduced heavy compounds in the bio-oil due to red/ox reactions at 500 °C [31]. Although iron oxide promotes decarboxylation reactions leading to the decrease in the overall liquid yield after CFP, the quality of the obtained bio-oil is significantly improved and better fulfils the requirements for practical applications. Despite the fact, that micron-sized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has been considered as a catalyst for CFP there is lack of studies focused on the application of the nano-sized catalyst. To date some limited results for nano-sized iron oxides were presented in the literature for pyrolysis of poplar wood [32], however, their effect on CFP product distribution has not been reported in details. From the published results, it is not clear whether  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> polymorphs were applied as a catalyst. Considering that several parallel and consequent reactions occur during the fast pyrolysis, one could expect the promotion of different pathways during the decomposition of biomass and more systematic analysis on the product distribution with the variation in shape and size of a catalyst will be required. Another important aspect is that since different types of wood have different ratios of their constituent biopolymers (lignin, cellulose, and hemicellulose) in their structure, the catalytic impact becomes unpredictable to some extent and individual studies will be essential to prove or disprove effectiveness of catalysts.

The present study explores the catalytic effect of nano/micro-sized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with different shapes (non-ideal spheres, nanotubes, hollow nano/microtubes, and octadecahedral crystals) on the products distribution in the fast pyrolysis of pinewood. Model compounds were not used in this study, as there are evidences that their properties become altered during extraction from wood and their usage for analysis results in the oversimplified decomposition mechanisms. The impact of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalysts with different shapes was analyzed by using the *in-situ* Py-GC/MS (pyrolysis-gas chromatography-mass spectrometry)

technique.

## 2. Materials and methods

### 2.1. Materials

All reagents were AR grade and were applied without further purification:  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanopowder (MACKUN, China),  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> submicron powder and NaF (Aladdin, China), FeCl<sub>3</sub>·6H<sub>2</sub>O and NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O (Shanghai Chemical Reagent Co., China). Distilled water was used throughout the experiments. Pinewood (PW) was chosen as the biomass feedstock, because it was considered as the optimal studying material with low ash formation [33]. PW was dried at 105 °C for 24 h in an oven before experiments and kept in a desiccator in a closed container.

### 2.2. Synthesis

Nano  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (commercial FNT) was calcined for 3 h at 800 °C to obtained non-ideal spherical nano-powder (FS054).

Both  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hollow nano/microtubes (FNMT) and octadecahedral crystals (FOC) were synthesized by the hydrothermal method. To produce FNMT, two 20 mL aqueous solutions of FeCl<sub>3</sub>·6H<sub>2</sub>O (0.42 g) and NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O (0.01 g), respectively, were mixed under stirring at room temperature and then dispersed uniformly by ultrasonic irradiation. The solution was sealed in the stainless steel autoclave followed by heating at 240 °C for 36 h. The obtained precipitants were separated by centrifugation, washed 3 times with distilled water, and dried at 60 °C in air overnight. To synthesize FOC, two 20 mL aqueous solutions of NaF (0.03 g) and FeCl<sub>3</sub>·6H<sub>2</sub>O (0.38 g), respectively, were mixed under stirring at room temperature, placed into the stainless steel autoclave and then hydrothermally treated at 220 °C for 60 h. The precipitants were separated by centrifugation, washed 3 times with distilled water, and finally dried at 60 °C in air overnight.

### 2.3. Characterization

The morphology of the catalysts before and after fast pyrolysis was analyzed on a JEOL JSM-6510 scanning electron microscope (SEM, JEOL, Japan) in 5–30 keV energy range and FEI Tecnai G20 transmission electron microscope (TEM, FEI, USA) with the acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer (Bruker AXS, Germany) in the reflection mode with Ni-filtered CuK $\alpha$  radiation equipped with a LYNXEYE detector at 40 kV and 40 mA. The XRD patterns were registered at room temperature under air atmosphere in the angular range of  $10 \leq 2\theta$  degree  $\leq 100$  with a step size of 0.01° and counting for 1 s in each point. The size of crystallites with spherical-like shape can be calculated by using the Scherrer equation [34].

The specific surface area and pore sizes of the selected catalysts were analyzed by a multi-point BET method using nitrogen adsorption/desorption isotherm measurements at –196 °C on a 3H-2000PS2 apparatus (BeiShiDe Instrument – S&T, China) in the static volumetric mode. Prior to the measurements, the samples were degassed at 120 °C for 4 h.

X-ray photoelectron spectra (XPS) were recorded to study the surface composition at few nanometer scale and surface chemical states of Fe, O, and C, using an ESCALAB 250xi spectrometer (Thermo Scientific, USA) with Al K $\alpha$  x-ray source ( $h\nu = 1486.7$  eV). The binding energies ( $E_{BE}$ ) were referenced to the C 1s peak at 284.6 eV and given with the precision of 0.1–0.2 eV. XPSpeak4 software was used to analyze spectra. The atomic concentrations of elements were calculated from the fitted peak areas using appropriate atomic sensitivity factors.

### 2.4. *In-situ* fast pyrolysis analysis

*In-situ* fast pyrolysis analysis was performed with the Pyrolyser

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