

Supporting Information

Insights into the Ceria-catalyzed Ketonization Reaction Mechanism for Biofuels

Applications

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1. Experimental Method

1.1 Materials synthesis

Cerium oxide was made through thermal decomposition of cerium (III) nitrate hexahydrate (Aldrich 99.99%) at 600 °C in air using a Carbolite AAF 1100 muffle furnace. A 2 °C/min heating ramp to 600 °C was used after which the temperature was held steady for 3 h. After cooling, the ceria was finely powdered using a mortar and pestle before being stored in a desiccator. A number of different cerium carboxylates were synthesized through reacting either cerium (III) nitrate hexahydrate (ROTH ≥99.5%) or cerium (III) carbonate hydrate (Aldrich 99.9%) with the respective acid, either acetic acid (Fluka 99.8%), propionic acid (AppliChem >99%), butyric acid (AppliChem ≥99%), isobutyric acid (Fluka ≥99.5%) or pivalic acid (Merck ≥99%). For cerium pivalate, this synthesis consisted of first neutralizing the acid with ammonium hydroxide before mixing with the aqueous metal nitrate solution and adjusting the pH to 6-7 in a fashion similar to that proposed by Khudyakov.¹ The solution was then heated to 60 °C and stirred for a short time before being cooled and stirred overnight. Finally the carboxylate was filtered and dried at 110 °C in air. For the synthesis of cerium acetate, cerium propionate, and cerium isobutyrate, cerium carbonate was mixed directly with a slight excess of the respective acid. This solution was then heated and stirred until the metal carboxylate gel was formed. After filtration the product was dried in air at 130 °C for 2 h.

1.2 Materials characterization

Thermogravimetric analysis of the metal carboxylates was performed on a Netzsch STA 449 Jupiter TGA-DSC under the flow of 70 mL/min argon with a ramp rate of 10 °C/min. Product evolution was evaluated with a connected mass spectrometer. BET surface area analysis was done on a Micromeritics ASAP 2020 at 77 K using N₂. Prior to analysis the ceria was degassed at 100 °C. XPS was used for the measurement of cerium oxidation states and was executed on a Physical Electronics 5500 Multi-technique system using an Al K α source and double-sided tape for mounting. Peak binding energies were obtained by placing the binding energy of the C 1s peak to a location of 284.6 eV. XRD characterization of ceria catalysts both before and after reaction testing utilized a Siemens D-500 with a 0.15 detector slit and Cu K α radiation source. In-situ XRD tests involved use of a STOE theta-theta diffractometer with a scintillation counter and Cu K α radiation. During the in-situ experiments the powdered sample was in an Anton Parr RK 900 high temperature reaction chamber. Scans during the tests were of a step size of 0.05 with a dwell time of 2 s. Acetic acid vapors were passed over the catalysts during these tests by bubbling 100 ml/min of He gas through acetic acid at 40 °C. Scanning electron micrographs (SEM) of the materials were obtained using a FEI Quanta FE-SEM. Temperature programmed decomposition (TPD) of spent ceria catalysts was performed on a Micromeritics Autochem (II) Chemisorption Analyzer connected to a Microstar mass spectrometer (MS). The tests used a 5 °C/min ramp from 80-700 °C under the flow of 20 ml/min argon. Finally transmission FTIR experiments were completed using a Bruker IFS 66 spectrometer. For the cerium acetate FTIR analysis, the sample was diluted in KBr, pressed into a self supporting wafer, and mounted in a heated quartz chamber under the constant flow of Ar. The sample was then dehydrated at 150 °C, cooled and the spectrum taken. A similar process was used for the in-situ cerium oxide FTIR experiments except the ceria was not diluted in KBr and was used by

itself to form the wafer. The ceria wafer was then exposed to small amounts of acetic acid vapor in flowing Ar at the given temperature and purged with pure Ar before cooling and taking the spectra.

1.3 Reaction testing

Reaction testing of the ceria catalyst was done at a variety of temperatures using 50 ml of toluene (Fisher 99.8%) as solvent, 1.0 g of acetic acid (Fisher 100%) or 1.7 g of pivalic acid (Aldrich 99%) as reactant, and 0.5 ml of 1,4 dioxane (Fisher 100%) as internal standard. The catalyst was then added along with the previously listed chemicals into a stainless steel Parr Series 4598 75 ml batch reactor. The reactor was subsequently pressurized with N₂ to 30 - 40 bar before heating in order to keep the reactants in the condensed phase. After pressurizing, the vessels were heated to the desired temperature while stirring at 400 rpm. A liquid nitrogen cold trap was used to collect samples and an Agilent 7890 GC-FID used for product analysis. Prior to characterization and after reaction, the catalysts were dried at 100 °C in air for 1 h.

2. Fresh ceria characterization.

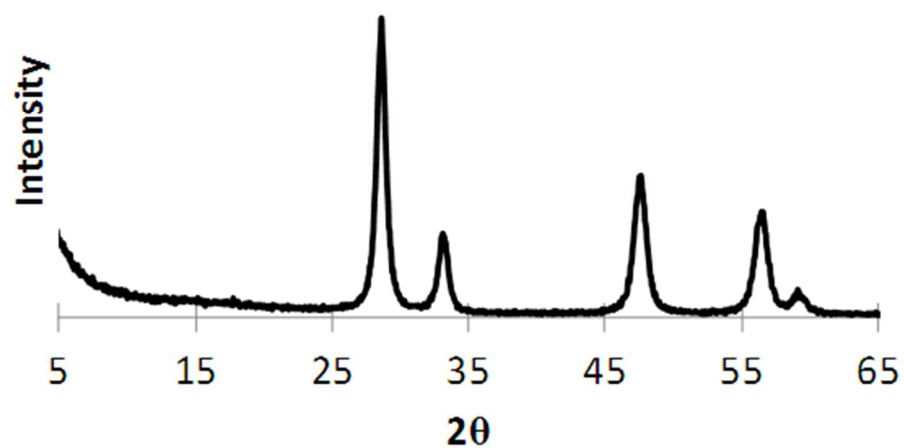


Figure S1. XRD profile of the fresh ceria catalyst demonstrating the cerianite structure.

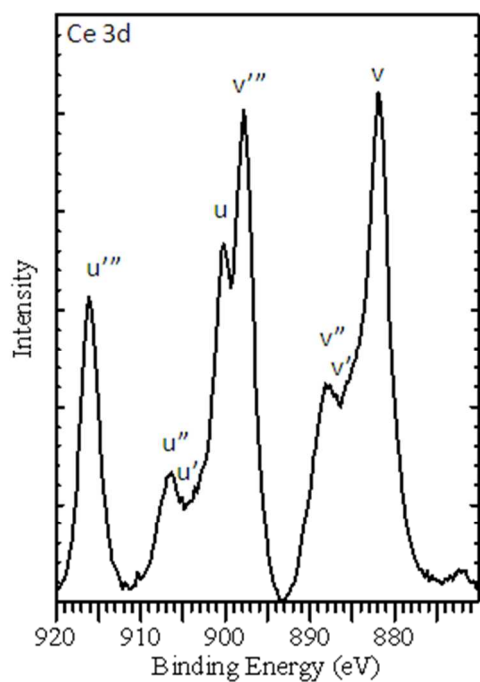


Figure S2. XPS of the ceria catalyst before reaction testing demonstrating the prevalence of the 4+ cerium oxidation state.

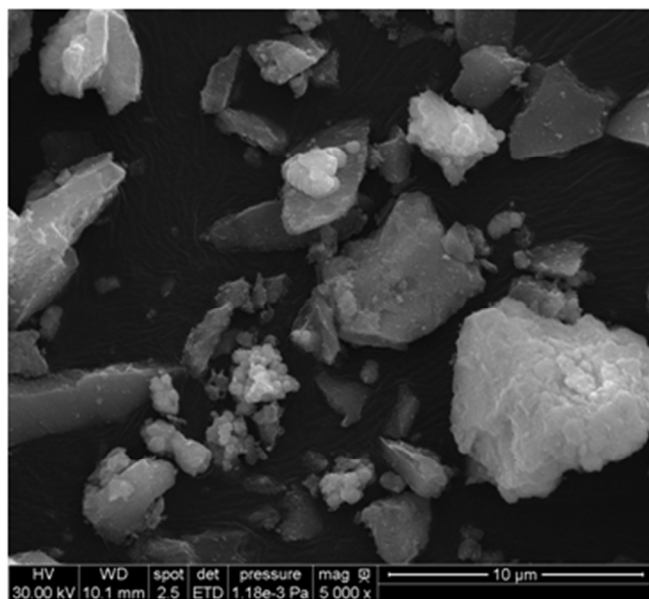


Figure S3. SEM image of fresh ceria catalysts showing a non-uniform macro morphology.

3. Ceria exposed to acetic acid vapors.

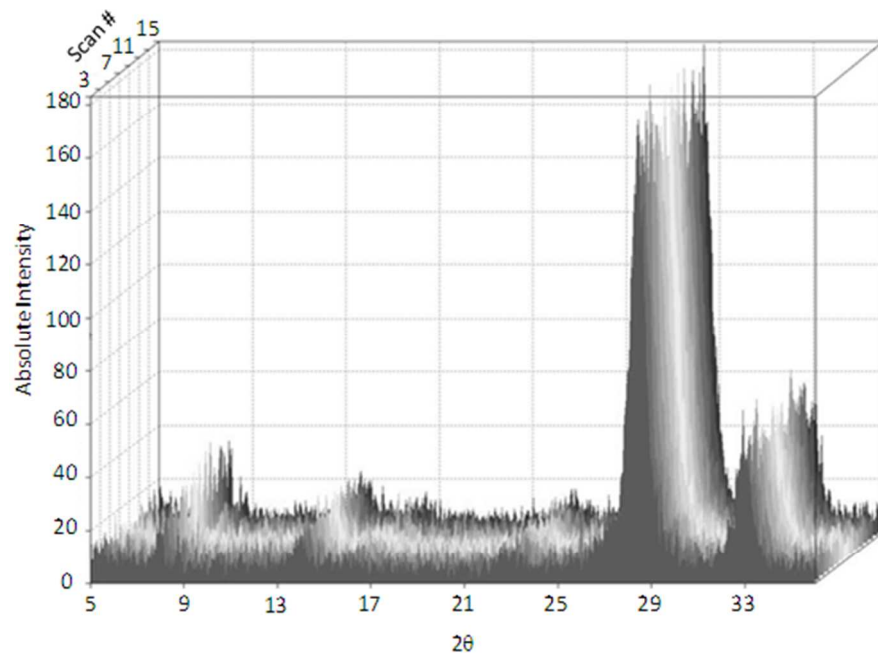


Figure S4. In-situ XRD of ceria exposed to acetic acid vapors at a constant temperature of 300 °C.

4. Ceria after reaction with pivalic acid.

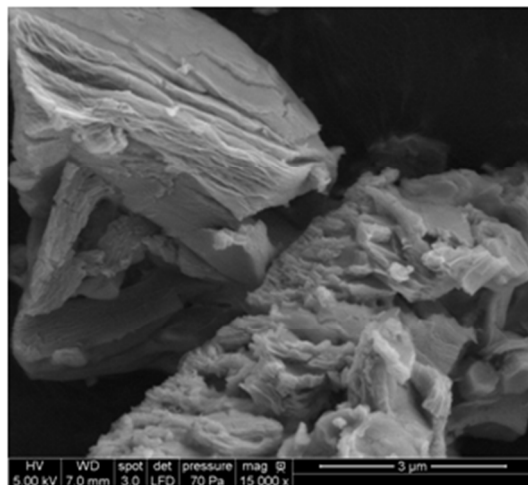


Figure S5. SEM image of the precipitate recovered after a 24 h pivalic acid reaction with ceria at 315 °C.

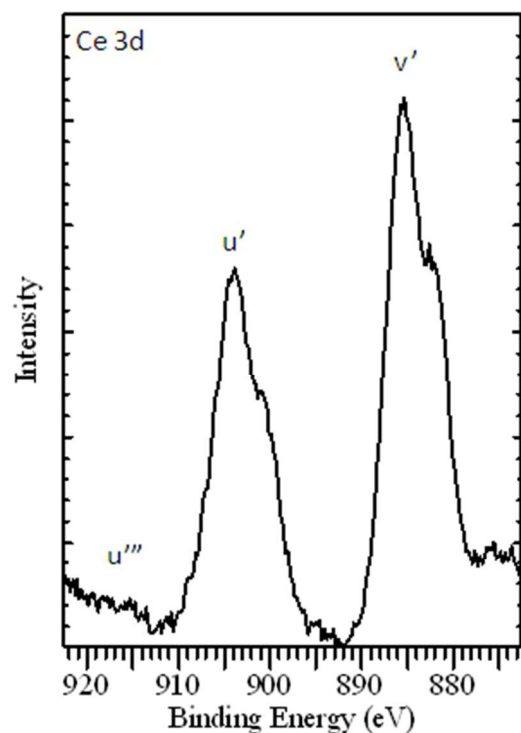


Figure S6. XPS spectra of ceria for the precipitate recovered after a 24 h reaction with pivalic acid at 315 °C. The u''' peak ≈ 916 eV corresponding to Ce⁴⁺ has fully disappeared, while the u' and v' features associated with the Ce³⁺ state are prevalent.

5. Reference

- (1) Khudyakov, M., *Russian J. Coord. Chem.* **2002**, 28, 521.