

**Selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes over Pt supported on cerium–zirconium mixed oxide of different composition**

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Preparation of mixed  $x\text{CeO}_2\text{--}y\text{ZrO}_2$  oxide supports

The required amount of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  was dissolved in distilled  $\text{H}_2\text{O}$  at a ratio of 1 g of compound per 2.5 ml of water without heating. The resulting solution was diluted with isopropanol (99%) at a ratio 1.7 ml of i-PrOH per 1 ml of Ce-containing solution. Following dilution, the prepared solution was stirred for 1 h at room temperature. To prepare the Zr-containing solution, an aliquot of oxalic acid was first dissolved in deionized water at 60 °C to produce a solution with a concentration of 2.3 M. The required amount of  $\text{ZrO}(\text{NO}_3)_2$  was then added to the oxalic acid solution at a ratio of 45 mg/ml. The heating was switched off, and the resulting Zr-containing solution was diluted with i-PrOH at a ratio of 1 : 1. Following dilution, the solution was stirred for 1 h at room temperature. The solutions were mixed, and an ammonia solution was added to the mixture until pH 9.15. The prepared suspension was mixed for another 30 min, after that the precipitate was separated *via* centrifugation on 5000 rpm speed and washed with deionized water 3 times. The precipitate was dried for 12 h at 80°C and calcined in a closed crucible for 4 h at 400°C.

Synthesis of Pt-containing catalysts

The required amount of  $\text{H}_2\text{PtCl}_6$  solution (0.01 M) was diluted with deionized water in support/water ratio 10 mg/ml, and the solution was stirred for 10 min. Then the precursor was hydrolyzed by adding  $\text{Na}_2\text{CO}_3$  solution (0.1 M) to adjust the pH to 7 after which the support was added. The resulting suspension was vigorously stirred for 30 min without heating and for 3 h at 80°C. Then aqueous solution of  $\text{HNO}_3$  ( $C = 0.103$  M) was added to decrease the pH of the suspension to 4 and the suspension was stirred for additional 30 min. Finally, the degree of Pt deposition was checked by the indicator reaction for Pt ions in the parent solution. In the case of incomplete precipitation of Pt onto support the synthesis procedure was continued until the full platinum deposition was archived. The precipitate was separated *via* centrifugation and washed with deionized water twice, followed by drying under vacuum using a rotary evaporator for the complete removal of water. The obtained catalyst was reduced in hydrogen flow at the temperature 250 °C during 2 h.

### Catalyst characterization

TPR-H<sub>2</sub> measurements were carried out in a laboratory constructed flow system with a water trap cooled down to -100 °C. The detector (TCD) was calibrated by reduction of CuO (Aldrich-Chemie GmbH, 99%) pretreated in an Ar flow with a gas flow rate of 30 ml min<sup>-1</sup> at 300 °C. The 1%Pt/xCeO<sub>2</sub>-yZrO<sub>2</sub> catalysts with a weight of 140–170 mg were pretreated in an argon flow with an oxygen trap at 250 °C for 90 min. Prior to the TPR experiment, the sample was cooled in an Ar flow to -50 °C using a mixture of ethanol and liquid nitrogen as a cooling agent. Heating from -50 to 25 °C was carried out at the rate of 10 °C/min in a 5% H<sub>2</sub>-Ar gas mixture purified with an oxygen trap and supplied with a flow rate of 30 mL min<sup>-1</sup>. The sample was kept at room temperature (25 °C) for 30 min before the further linear sample heating.

Phase composition of supports and size of primary crystals of crystalline phases were determined by XRD. X-ray diffraction patterns were recorded on an ARL X'TRA device (Thermo Fisher Scientific) in CuK $\alpha$  radiation (40 kV, 40 mA) in a step-by-step scanning mode (with a step of 1.2 °/min) in the interval  $2\theta = 20^\circ\text{--}60^\circ$ . The phase composition was identified by correlating the position and intensity of the lines on the X-ray diffraction pattern with the ICDD data. The average crystallite size was calculated from the broadening of X-ray diffraction reflex lines of the most intensive peak on XRD curve in accordance with the Scherer equation.

Scanning electron microscopy with energy-dispersive X-ray spectroscopy were used to evaluate the uniformity of the distribution of support elements. Target-oriented approach was utilized for the optimization of the analytic measurements <sup>[19]</sup>. Before measurements the samples were mounted on a 25 mm aluminum specimen stub and fixed by conductive graphite adhesive tape. Samples morphology was studied under native conditions to exclude metal coating surface effects <sup>[20]</sup>. The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 20 kV accelerating voltage and at working distance 8-10 mm. EDX studies were carried out using Oxford Instruments X-max EDX system.

### Typical cinnamaldehyde hydrogenation reaction procedure

The liquid-phase cinnamaldehyde hydrogenation reaction was carried out at atmospheric pressure and room temperature (25 °C). The catalyst (50 mg) was placed in a two-necked glass flask and the system was pre-purged with hydrogen for 30 min. Then, a solution of cinnamaldehyde in EtOH (1.5 ml; C = 0.2 M) containing 0.020 ml of NaOH (6% mol) was poured into the reactor. The reaction was carried out with constant stirring at 1400 rpm for 2 h.

#### Reaction products analysis method

Liquid products of the reaction were analyzed using Chromatek Crystal 5000.2 gas-liquid chromatograph with FID and a capillary column with a CR-5 applied phase (2 mm × 25 m) with stepwise heating of the column at 80 - 190 °C. Signals identification was based on the experimentally obtained retention times of individual compounds (cinnamaldehyde, cinnamyl alcohol, hydrocinnamaldehyde, hydrocinnamyl alcohol, ethanol). The structure of the obtained compounds was determined by <sup>1</sup>H and <sup>13</sup>C NMR methods.