



Influence of preparation method and doping of zirconium oxide onto the material characteristics and catalytic activity for the HDO reaction in nickel on zirconium oxide catalysts



Christian M. Pichler^a, Dong Gu^b, Hrishikesh Joshi^a, Ferdi Schüth^{a,*}

^a Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

^b The Institute for Advanced Studies, Wuhan University, Wuhan, Hubei 430072, PR China

ARTICLE INFO

Article history:

Received 19 February 2018

Revised 13 July 2018

Accepted 16 July 2018

Keywords:

Zirconium oxide

Surface casting

Hydrodeoxygenation

Oxygen vacancies

Lanthanum doping

ABSTRACT

Different Ni/ZrO₂ catalysts were prepared and tested for the hydrodeoxygenation (HDO) reaction of guaiacol. It was shown that the preparation mode of the ZrO₂ support has a significant influence on the catalytic results, as remaining elements like Si and Na from the preparation can change the material properties. The influence of Si and Na onto these material properties, which were especially surface acidity and oxygen vacancy concentration, could be clarified. It could be also rationalized, how the change of these properties affects the results of the HDO reaction. Furthermore, it was demonstrated that the oxygen vacancy concentration is an important factor for the catalytic performance, although this property has hardly been considered in the design of HDO catalysts so far. La doping was found to be an efficient strategy to tune the oxygen vacancy concentration, and by using this approach the catalytic performance of the catalyst could be improved remarkably.

© 2018 Published by Elsevier Inc.

1. Introduction

The use of lignocellulosic biomass as feedstock for the production of biofuels has attracted increasing research interests during the last years [1]. A promising approach to reach this goal comprises the fast pyrolysis of biomass, yielding bio-oil, which needs subsequent upgrading due to its high oxygen content, as the high oxygen content lowers heating value and reduces storage stability. During the upgrading process the oxygen content is lowered, resulting finally in a product that can meet specifications for transportation fuel [2]. The main element of the upgrading process is usually the hydrodeoxygenation (HDO) reaction, which is a hydrotreating process eliminating the oxygen from the bio-oil [3]. There exists several catalysts that are capable of performing this reaction, such as metal phosphides [4] and carbides [5,6], noble metals, such as Pt [7,8], Ru [9] or Pd [10], and also non-noble metals like Ni [11,12]. All of these active components can be combined with a variety of supports, mainly metal oxides (SiO₂, CeO₂, ZrO₂ etc.) or carbon [13–15]. A potentially suitable catalyst system that already suggested its suitability for the HDO reaction is Ni on ZrO₂ [13]. Beside an appealing catalytic activity, the Ni/ZrO₂ system possesses also an economic advantage,

especially compared to noble metal containing catalysts. A drawback of this catalyst is the relatively low surface area of the available ZrO₂ supports, especially when the reaction mechanism of the HDO reaction is considered. With guaiacol as a test substrate it could be shown that the hydrodeoxygenation proceeds in two steps: the hydrogenation of guaiacol to 2-methoxy-cyclohexanol, which is taking place on the metal nanoparticles, followed by the deoxygenation, producing cyclohexanol as intermediate and finally yielding cyclohexane [12]. For this second reaction part the support material plays a decisive role. The support material provides active centers for the deoxygenation reaction and it was shown that especially the surface acidity plays a determining role in this context [14]. Especially the medium-strength acidity of ZrO₂ is well suited for the hydrodeoxygenation reaction. A high surface area ZrO₂ support might therefore result in a significant advantage for catalytic reactivity. Recently we published a method for synthesizing high surface area ZrO₂ via a surface casting procedure [16]. We decided to use this high surface area ZrO₂ in combination with Ni as a catalyst due to its promising material characteristics. Furthermore, it should be investigated if the surface casting method in general influences the results of the catalytic tests compared to catalysts based on commercial ZrO₂. It is well known that beside the surface area also other parameters, such as surface acidity, strongly influence the outcome of the HDO reaction [17]. Another important factor, which was less considered until recently, is the

* Corresponding author.

E-mail address: schueth@kofo.mpg.de (F. Schüth).

concentration of oxygen vacancies in the support [18,19]. Therefore, this study also investigates the contributions of these factors to the catalytic activity. Special focus will be put on the fact how different material synthesis procedures or modifications influence the important characteristics, such as surface acidity and oxygen vacancy concentration, and how these modifications are linked to the performance of the catalyst.

2. Experimental and characterization

2.1. Catalyst preparation

All chemicals were purchased from commercial suppliers and used as received: tetraethylorthosilicate (Sigma-Aldrich, reagent grade 98%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 97%), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Sigma-Aldrich, 99.5%), Pluronic F-127 (Sigma-Aldrich), citric acid (Sigma-Aldrich, 99%), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Fluka, 99%), ZrSiO_4 (Acros 99%, 325 mesh) and zirconium(IV)butoxide (Sigma-Aldrich, 80 wt % in 1-butanol). Tetragonal ZrO_2 catalyst support was supplied by Saint Gobain NorPro (type SZ6*152 with an impurity of 3.3% SiO_2). ZrO_2 was crushed and milled with a mortar and then sieved. Only particles sized <50 μm were used.

The SiO_2 aerogel used as template was synthesized according to literature procedures [20]. In a beaker 20.8 g of tetraethylorthosilicate (TEOS) were added under stirring with a magnetic stirring bar to 99 mL ethanol, followed by the addition of 7.2 g water. The pH value was lowered to pH 3 by addition of 15 wt% HCl and the solution was stirred for 5 h 30 min. Then the pH of the solution was adjusted to pH 7 by adding 1 mol·L⁻¹ NH_3 solution, and stirring was stopped. The solution was aged for 16 h, and during this time a gel was formed. This gel was dried with supercritical CO_2 in a flow setup at 200 bar and 50 °C.

The procedure for synthesis of surface casted ZrO_2 is described in our previous report [16]. Briefly, 2.0 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and, if desired, 0.54 g $\text{La}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ were dissolved in 1.5 g of 1.07 mol·L⁻¹ HCl. 0.5 g of the aerogel was impregnated with the calculated amount of the respective solution (14.5 wt% calculated for ZrO_2). The as-treated material was sealed in a glass vial and aged at 50 °C for 24 h and at 90 °C for 48 h. The aging was followed by calcination at 800 °C or 400 °C for 5 h (heating ramp 1 °C·min⁻¹). The SiO_2 template was leached by treatment with 35 mL of 2 mol·L⁻¹ NaOH solution at 70 °C (repeated for two times). Finally the material was washed with water and ethanol.

The preparation of soft templated ZrO_2 was performed according to literature by the EISA method [21]. 1.54 g citric acid and 2.44 g F127 were dissolved under stirring in 74 mL ethanol. To this solution 3.67 g HCl (37%) and 5.85 g zirconium(IV)butoxide (and if desired 0.37 g $\text{La}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$) were added and stirred for 3 h. The solution became turbid and this dispersion was poured into a petri dish for evaporation of the solvent for 48 h at room temperature. Afterwards the sample was dried at 100 °C and the obtained yellow solid was calcined at 600 °C for 5 h (heating ramp 1 °C·min⁻¹).

The catalysts were prepared by incipient wetness impregnation of the ZrO_2 (commercial, surface casted, or soft templated) or ZrSiO_4 support with the desired amount of an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to reach a theoretical final Ni loading of 3.5 wt%. The impregnation was followed by drying at 90 °C for 16 h, calcination at 400 °C for 5 h (heating ramp: 1 °C·min⁻¹) and reduction at 500 °C under H_2 (flow: 33 mL·min⁻¹) for 4 h (heating ramp: 1 °C·min⁻¹).

The Si, Na or La doped commercial catalysts were prepared by impregnation of the commercial ZrO_2 with precursors for the particular dopants, followed by drying and calcination. For Si doping 450 mg ZrO_2 were dispersed in 20 mL hexane, and the desired amount of SiCl_4 was added to the suspension. The suspension

was stirred at 60 °C for 16 h so that the SiCl_4 could hydrolyze and react with the ZrO_2 surface. This was followed by removal of the solvent on the rotary evaporator, and the resulting solid was dried at 90 °C for at least 8 h and calcined at 400 °C for 5 h (heating ramp 1 °C·min⁻¹). For Na or La doping, ZrO_2 was dry impregnated with the desired amount of an aqueous NaCl or $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution followed by drying at 90 °C for at least 8 h and calcining at 600 °C for 5 h (heating ramp 1 °C·min⁻¹). Then all the materials underwent the same incipient wetness impregnation procedure with Ni as described above for the other catalysts.

2.2. Catalyst characterization

STEM images and STEM-EDX mapping images were recorded on a Hitachi HD-2700 dedicated Scanning Transmission Electron Microscope operated at 200 kV and equipped with an EDAX Octane Ultra W EDX detector.

Temperature programmed oxidation (TPO) measurements were conducted on a Micromeritics AutoChem II (Chemisorption Analyzer). In the beginning 10 mL·min⁻¹ pure Ar was used to preheat ca. 100 mg support material to 750 °C. When the temperature was reached, the gas flow was changed to 30 mL·min⁻¹ H_2 and held for 270 min to reduce the sample and generate oxygen vacancies. After this reduction step the gas flow was switched back to pure Ar with a flow of 10 mL·min⁻¹, and the temperature was lowered to 550 °C and held at this temperature for 45 min to remove all adsorbed hydrogen. Then oxygen titration experiments were performed by pulsing pure O_2 over the sample until no further uptake was detected (at least 40 pulses). The amount of consumed oxygen was used to calculate the number of oxygen vacancies under the assumption that each O_2 molecule saturates two oxygen vacancies.

Ammonia temperature programmed desorption (NH_3 -TPD) measurements were conducted on a Micromeritics AutoChem II (Chemisorption Analyzer). In the beginning 10 mL·min⁻¹ of pure He was used to preheat ca. 100 mg catalyst to 500 °C for 60 min. Then the sample was cooled down to 120 °C and the gas flow was switched to 10 mL·min⁻¹ 10% NH_3 /He. The sample was held under this flow for 30 min, hereafter the gas flow was changed to 10 mL·min⁻¹ He and held for 60 min. Finally, the temperature was ramped to 650 °C (10 °C·min⁻¹) to desorb the NH_3 . The temperature was held at 650 °C for 30 min.

Hydrogen temperature programmed desorption (H_2 -TPD) measurements were conducted on a Micromeritics AutoChem II (Chemisorption Analyzer). In the beginning 50 mL·min⁻¹ pure Ar was used to preheat ca. 100 mg catalyst to 300 °C for 15 min. The gas was switched to 50 mL·min⁻¹ 10% H_2 /Ar and temperature was further increased to 450 °C and held there for 120 min for full reduction. This was followed by a gas switch to pure Ar (50 mL·min⁻¹), a temperature increase to 460 °C, and holding these conditions for 90 min to remove all adsorbed hydrogen. Subsequently, the temperature was lowered to 50 °C, and the gas was switched to 50 mL·min⁻¹ 10% H_2 /Ar, so hydrogen could chemisorb on the metal particles for 90 min. Then the gas was changed to pure Ar again and held for 60 min to remove physisorbed hydrogen. The measurement itself was performed by gradually heating the sample to 850 °C with a ramping rate of 10 °C·min⁻¹ to remove all the chemisorbed hydrogen from the metal surface. To quantify the amount of hydrogen desorbed during the heating of the sample, defined volumes of H_2 were injected in the TCD detector and plotted against the areas of the obtained peaks. The Ni particle size was determined by using the relation $I = 5/S \cdot d$ where I is the particle size, S is the metal surface area (calculated from the amount of desorbed hydrogen) and d is the density of nickel (8.9 g·cm⁻³) [22–24].

Powder X-ray diffraction (XRD) patterns were recorded on a Debye–Scherrer diffractometer (Stoe STADI P) operating in

Download English Version:

<https://daneshyari.com/en/article/6526541>

Download Persian Version:

<https://daneshyari.com/article/6526541>

[Daneshyari.com](https://daneshyari.com)