



On the bifunctional nature of Cu/ZrO₂ catalysts applied in the hydrogenation of ethyl acetate



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ABSTRACT

The catalytic hydrogenation of ethyl acetate to ethanol was studied at ambient pressure in the temperature range from 463 K to 513 K using Cu/ZrO₂ catalysts obtained by co-precipitation as a function of the Cu loading. The hydrogenation was established as a reproducible probe reaction by determining optimal reaction parameters without deactivation or thermodynamic limitations. Power-law kinetics were determined yielding an apparent activation energy of 74 kJ mol⁻¹ and reaction orders of 0.1–0.3 for H₂ and –0.4 to 0.1 for ethyl acetate in the temperature range from 473 K to 503 K. Metallic Cu was found to be essential for the hydrogenation, but the catalytic activity was not proportional to the Cu surface area derived from N₂O decomposition and temperature-programmed H₂ desorption experiments identifying Cu/ZrO₂ as bifunctional catalyst. The acidic sites of the ZrO₂ matrix were probed by temperature-programmed experiments with ethyl acetate and NH₃. Cu⁰ is assumed to provide atomic hydrogen by dissociative adsorption and spillover, but the reaction rate is more affected by the tight contact between the embedded Cu nanoparticles and the X-ray amorphous ZrO₂ matrix.

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1. Introduction

Zirconium dioxide has numerous applications in heterogeneous catalysis due to its high mechanical and thermal stability [1], associated with suitable acid and base properties and high specific surface area [2,3]. Correspondingly, zirconia is frequently applied in acid-base catalysis or as catalyst support. Zirconia is able to prevent the sintering of supported metal nanoparticles under reaction conditions especially in case of strong interactions with an amorphous zirconia matrix [3–6].

Zirconia was investigated for redox reactions doped with other metal oxides, which changed its phase composition [3], and its utilization as active material was investigated in detail [7,8]. In particular, zirconia was used in hydrogenation reactions [9,10], hydrogen generation by direct oxidation of hydrocarbons [11], and CO oxidation [12]. Although there were many different doping materials tested, the focus was often on catalysts containing Cu as active component. Numerous investigations of Cu/ZrO₂ catalysts have dealt with the influence of the zirconia structure on the catalytic activity [3,9,10,13–16]. Cu supported on monoclinic zirconia was found to be active in methanol synthesis due to the presence of oxygen vacancies. It was reported that for materials with an equal

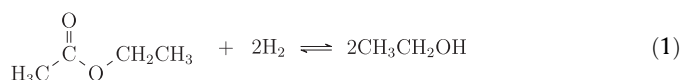
Cu surface area the catalyst with the monoclinic zirconia phase has a higher adsorption capacity for CO₂ and CO [15]. Furthermore, Bell and co-workers [14,15,17,18] demonstrated the bifunctional nature of this catalyst system in a detailed analysis of the synthesis of methanol from CO or CO₂ as well as the strong influence of the zirconia phase on the catalytic activity. According to the proposed reaction mechanism for methanol synthesis, CO or CO₂ was adsorbed on the zirconia surface, and metallic Cu was needed to adsorb H₂ dissociatively. The hydrogenation of the formate species occurred on the zirconia surface via hydrogen spillover. Similar observations were also reported by Otroshchenko et al. [19], who investigated propane dehydrogenation over Ru/ZrO₂ catalysts. The reaction was assumed to take place at zirconium cations (Zr_{cus}) located near anion vacancies. This hypothesis was supported by EPR and temporal analysis of products (TAP) reactor measurements. Metallic Ru is claimed to provide atomic hydrogen, which is comparable to the results of Bell and co-workers obtained with the Cu/ZrO₂ system [19]. Additionally, Wu et al. [10] reported that the catalytic activity of Cu/ZrO₂ cannot simply be attributed to the Cu surface area or the particle size of the metal, because it depends on the interaction between Cu and ZrO₂ and the interface between the two components. This conjecture was also supported by Copéret and co-workers [13], who combined kinetic investigations of CO₂ hydrogenation with IR and NMR spectroscopic and isotopic labeling studies. They postulated that the zirconia/copper interface

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is crucial for the conversion of the formate species as reaction intermediate in methanol synthesis. In addition, Sato et al. [4,20] related the high activity in the dehydrogenation of ethanol to ethyl acetate over Cu/ZrO₂ catalysts to their electronic properties. The zirconia phase was found to influence the ratio of Cu⁰/Cu⁺ due to the presence of oxygen vacancies in the monoclinic phase. The adsorption of ethanol took place either as ethoxy species on Cu⁺ and Zr^{δ+} sites and as acetyl species on metallic Cu. Accordingly, the formation of ethyl acetate was only possible by a combination of both adsorption sites [4,20]. The high activity in ethanol conversion as well as in methanol synthesis from CO₂ was also reported by Dumesic and co-workers [21], who observed an increase in turnover frequency by an order of magnitude due to the formation of Cu-ZrO₂ interfacial sites.

In recent years Cu has been frequently investigated in the hydrogenation of organic compounds. Cu was applied in several studies [22–25] because of its ability to hydrogenate C=O bonds selectively while leaving C=C bonds intact. First investigations of ester hydrogenation over Cu-containing catalysts were performed by Adkins et al. [22] at high pressure in the liquid phase with various esters. With Cu chromite as catalyst the reaction was carried out with an alcohol yield in the range from 80% to 98% requiring high pressures and temperatures [22]. In further studies, it was shown that several Cu-based catalysts have a high selectivity in the gas-phase conversion of simple esters to their corresponding alcohols such as ethyl acetate (EtOAc) to ethanol (EtOH) according to Eq. (1) [23–26]. The formation of a broader product distribution due to transesterification was reported [23,27,28].



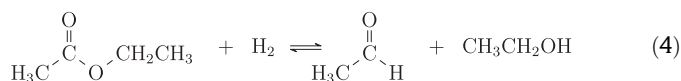
Structure-activity correlations as well as kinetic parameters have been derived for Raney Cu [23] or silica-supported Cu [24] at temperatures from 483 K to 553 K and different partial pressures. The hydrogenation mechanism for acetates was suggested by Yan et al. [29] and Evans et al. [23] to proceed via dissociatively adsorbed acetate yielding acyl and alkoxy species:



where * represents an active surface site. In further isotopic labeling studies, it was suggested that the alkoxy fragment is rapidly hydrogenated to its alcohol. In contrast, the acyl fragment is less reactive and can be partially hydrogenated to the aldehyde or fully to the alcohol. However, the hydrogenation of acetaldehyde was determined to be more than three orders of magnitude faster than that of ethyl acetate [26,30]. Thus, the amount of acetaldehyde being present is determined by the thermodynamic equilibrium constant of reaction (3):



Here, the hydrogenation of ethyl acetate over Cu/ZrO₂ catalysts was performed to establish a fast and reproducible probe reaction. Differently prepared Cu/ZrO₂ catalysts can be compared based on the conversion of ethyl acetate and the yields of ethanol.



This probe reaction is high suitable for Cu/ZrO₂ catalysts to investigate their bifunctional properties. The reaction kinetics of the hydrogenation was studied to evaluate the activity and stability in the used temperature range as well as to compare experimental data with literature data. Furthermore, this probe reaction was conducted to obtain structure-activity correlations for Cu/ZrO₂ catalysts with varied Cu content. The catalysts were

characterized by temperature-programmed reduction (TPR), X-ray diffraction (XRD), elemental analysis (ICP-OES), NH₃ temperature-programmed desorption (TPD) and by the determination of the Cu surface area using H₂ TPD in addition to N₂O frontal chromatography.

2. Experimental

2.1. Sample preparation

The Cu/ZrO₂ catalyst precursor was synthesized by coprecipitation at pH 10.5 using copper nitrate (Cu(NO₃)₂·3H₂O, Sigma Aldrich 99–104%), zirconium oxynitrate (ZrO(NO₃)₂·3H₂O, Sigma Aldrich 99%) and 25% NaOH as precipitating agent. The precursor was aged for 15 min, filtered and washed with HPLC water until the filtrate was free of nitrates. Subsequently, the precursor was dried over night and calcined at 763 K for 3 h in synthetic air. Samples with 0 wt%, 1 wt%, 5 wt%, 10 wt%, 18 wt%, 22 wt%, 31 wt%, CuO were synthesized.

2.2. Characterization

The metal content was determined by optical emission spectroscopy combined with inductively coupled plasma (ICP-OES) using an UNICAM PU 7000. XRD patterns were recorded in reflection geometry with an Empyrean Theta-Theta diffractometer (Panalytical, Almelo) using Cu Kα (λ = 1.5406 Å) radiation. The data was recorded from 5° to 80° in 2θ with 0.25° divergence slit, 0.5° anti-scatter slit, 0.04 rad incident, diffracted beam soller slits, and a position sensitive PIXcel-1d detector.

TPR experiments were performed using 100 mg of the catalyst sample with a sieve fraction of 255 μm to 350 μm placed in a glass-lined stainless steel U-tube reactor under plug-flow conditions. A thermocouple was placed directly in the catalyst bed to monitor the temperature. The catalyst was heated in diluted H₂ (2%, purity 99.9999%, 10 mL min⁻¹) to a maximum temperature of 573 K with 1 K min⁻¹ including an isothermal plateau at 398 K for 14 h. To achieve an adsorbate-free Cu surface after the reducing pretreatment, the catalyst was flushed with He at 573 K and cooled to room temperature in He.

N₂ physisorption measurements were performed with 200 mg calcined catalyst in a sieve fraction of 250–355 μm using a BELSORP-max (BEL Japan, Inc.). Prior to the measurement, the catalyst was heated to 473 K for 2 h under vacuum to remove adsorbed water.

To determine the specific Cu surface area of the catalysts two methods were used. First, the catalyst was treated with 1% N₂O at 296 K assuming an adsorption stoichiometry according to N₂O + 2Cu_s = Cu_s-O-Cu_s + N₂, that is, one chemisorbed oxygen atom requires two metallic Cu surface atoms.

A detailed description can be found elsewhere [31]. Surface determination was accomplished based on the total amount of N₂O consumed. Furthermore, the specific surface area was determined by H₂ TPD experiments. Pure H₂ was passed at room temperature through the catalyst bed with a 30 mL min⁻¹ flow rate and also during cooling with liquid nitrogen to 77 K. After holding this temperature for additional 20 min, weakly bound H₂ was flushed out in a He flow of 50 mL min⁻¹. Using this flow rate the reactor was heated to 573 K with a heating rate of β = 6 K min⁻¹.

NH₃ TPD curves were obtained after 2 h adsorption of 4000 ppm NH₃ at 323 K using a flow rate of 100 mL min⁻¹ and 100 mL min⁻¹ of sample. After flushing in He for 2 h the sample was heated in 100 mL min⁻¹ He at a rate of 5 K min⁻¹ up to 763 K. Additionally, the Cu/ZrO₂ catalyst with 18 wt% Cu was compared with pure ZrO₂ concerning the desorption and hydrogenation of adsorbed

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