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The effect of vanadium content and speciation on the activity of VO_x/ZrO_2 catalysts in the conversion of ethanol to acetaldehyde

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ABSTRACT

Catalytic conversion of ethanol to acetaldehyde under oxidizing conditions over VO_x/ZrO_2 catalysts with various surface VO_x densities has been investigated. Vanadium complexes anchored on the surface of zirconia oxide support are characterized in detail and their catalytic properties reported. The catalysts were prepared by incipient wetness impregnation from a peroxidic solution of ammonium metavanadate. The texture and crystallinity of the catalysts were investigated by N_2 physisorption and XRD analysis. The speciation and redox properties of the vanadium complexes were studied by dispersive Raman spectroscopy and the temperature programmed reduction (TPR) method. The effects of vanadium species distribution and ZrO_2 support crystallinity on the catalytic activity in the oxidative dehydrogenation of ethanol to acetaldehyde were analyzed and discussed in a broad context. A comparison of the catalytic results with details of the distribution of vanadium complexes has led to the conclusion that vanadium speciation has a great impact on catalytic behavior and that small oligomeric vanadium complexes dominate in the catalysts with vanadium content slightly above half of monolayer capacity, exhibiting the highest catalytic activity and very high selectivity to acetaldehyde (better than 93%). A comparison of the catalytic behavior of VO_x supported on tetragonal and monoclinic ZrO_2 phases has not revealed any differences in the activity or selectivity of the ethanol ODH reaction. Long-term catalytic experiments have shown good stability of the catalysts (stable conversion and selectivity for more than 600 h).

1. Introduction

In recent years, the production of bioethanol has tremendously increased due to the investments in renewable energy sources motivated by the depletion of fossil fuels [1–3]. The produced bioethanol is mainly applied as a fuel or in the beverage industry. Only a small percentage of the bioethanol is utilized for producing other chemicals and hydrocarbons [3–5]. Acetaldehyde is one of the important chemicals that could be produced from bioethanol via oxidative dehydrogenation [6–11], but the heterogeneous catalyst of this reaction should be further developed for industrialization.

As already mentioned, acetaldehyde is an important intermediate used for the production of various bulk chemicals, including acetic acid, acetic anhydride, ethyl acetate, peracetic acid, butanol, 2-ethylhexanol, pentaerythritol, chlorinated acetaldehydes, glyoxal, alkylamines, pyridines and others [3,10,12]. Nevertheless, this chemical can be synthesized from various starting materials, which are selected based on their price and availability. Nowadays, ethylene oxidation over $PdCl_2$ and $CuCl_2$ catalysts, the so-called Wacker process, is mainly used for acetaldehyde production [13,14]. Although this reaction has such advantages as the small amount of $PdCl_2$ required for the reaction and regeneration of the catalyst, there are some drawbacks that make this reaction economically quite demanding. Among others, it is necessary to i) use corrosion-resistant materials together with expensive titanium reactor tubing and ii) purify waste air and treat wastewater in order to remove acetaldehyde, unconverted ethylene and mainly chlorinated hydrocarbons, which are highly toxic and show antimicrobial activity. Therefore, they must be treated before entering the wastewater plant to become biologically degradable. As the demand for ethylene is expected to increase further due to the increasing requirements on the production of polymers and its production may decrease due to fossil fuel depletion, it is necessary to find new and alternative processes for the production of acetaldehyde. The acetaldehyde production via the oxidative dehydrogenation (ODH) of ethanol thus appears to be a

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promising alternative to the Wacker process [6,15,16]. The benefits of the ODH process can be seen in the implementation of bio-based renewable raw materials, in the preservation of ethylene for the processes where it cannot easily be substituted and in the removal of some of the negative aspects of the Wacker process, such as the treatment of a large amount of wastewater and the separation and disposal of chlorinated hydrocarbons.

Vanadium-containing porous solids are reported to be active heterogeneous catalysts for oxidative dehydrogenation reactions of various organic compounds, namely ethanol, methanol, light alkanes and other similar compounds. A key prerequisite for increased ODH catalytic efficiency is a high number of proper vanadium oxide species on the surface. Enormous efforts have been exerted by different research groups in the search for the best support for the high dispersion of vanadium with desired surface species and in its preparation [6,10,12,17]. Previous studies have demonstrated that titania and zirconia have a higher affinity to vanadium than other conventional supports (e.g. silica or alumina) and that it is possible to achieve high dispersion of vanadium on the surface of zirconia without the possible formation of V_2O_5 (higher than 7 V atoms/nm^2) [15,18–21]. Because of the 2D character of the complexes [22–27], the dispersed mono and polymeric vanadate species (VO_x) with tetrahedral coordination are more accessible and exhibit a higher catalytic activity for the ODH reaction of ethanol than the V_2O_5 clusters due to the inaccessibility of a portion of vanadium atoms inside the bulk oxide clusters. Titania-supported VO_x catalysts have been heavily investigated for this purpose [8,15,21,28–30], while VO_x/ZrO_2 catalysts have not been studied as thoroughly as titania and the conclusions have mostly been limited to the statement that zirconia-supported VO_x catalysts are slightly less active than VO_x/TiO_2 materials. For instance, the speciation of VO_x species on the surface of different phases of titania has been well studied by Fu et al., reporting that anatase is the favored phase for the formation of monomeric species [31]. For the ZrO_2 crystalline phase, on the other hand, similar studies are not available. Lin et al. [32] have reported high activity of catalysts prepared through the grafting of fumed silica by Zr-alkoxide and subsequently by vanadium oxytriisopropoxide. They have observed a very suitable catalytic performance on this $VO_x/ZrO_2/SiO_2$ catalyst (eight-time higher conversion and very high selectivity to acetaldehyde at temperatures below 200 °C as compared to the VO_x/SiO_2 catalyst). The effect of ZrO_2 as an additive was more distinct than that of TiO_2 used for the same purpose, especially in terms of selectivity. The formation of acetic acid over titania-supported VO_x catalysts was frequently reported in the past [8,33–38]. Despite the fact that both zirconia and titania catalytic systems have been operated in the same temperature window of 150–250 °C, suitable for the formation of acetic acid [33], only a few studies [18,21,39,40] have reported the formation of acetic acid over zirconia-supported VO_x catalysts. Since acetic acid is, according to Takei et al. [4], cheaper than ethanol, the low selectivity of VO_x/ZrO_2 catalysts to this byproduct can be an advantage of these materials over titania-supported materials. We have recently reported on the direct synthesis of the porous VO_x-ZrO_2 catalyst, exhibiting very high selectivity to acetaldehyde (more than 85% at all conversion degrees) and an activity comparable with the VO_x/TiO_2 catalytic system [6], which makes the VO_x-ZrO_2 system very promising. However, the study mainly focused on the investigation of the possibilities of synthesizing a high surface area porous catalytic system and not very much on the details of catalytic behavior and the role of the speciation of VO_x surface complexes. It thus seems to be reasonable to investigate the VO_x/ZrO_2 catalytic system in more detail.

The aim of the current study is to provide new information on the role of the speciation of the VO_x surface complexes and of the zirconia support structure of the VO_x/ZrO_2-based catalysts in the activity and selectivity in ethanol ODH to acetaldehyde. For this purpose, a set of catalysts differing in vanadium content and speciation was prepared by the impregnation of amorphous ZrO_2 with ammonium metavanadate. The structure and texture of the catalysts as well as the nature and properties of the surface VO_x complexes were thoroughly investigated by a combination of various experimental techniques (XRD, N_2 physisorption, Raman and IR spectroscopies, and H_2-TPR) and tested in the ethanol ODH reaction under various experimental conditions differing in reaction temperature and contact times. Furthermore, due to the presence of various crystalline phases of ZrO_2 in the catalysts and the variation of their content depending on the vanadium concentration in the catalysts, two additional ZrO_2 support-based catalysts have been prepared by the calcination of the amorphous $Zr(OH)_4$ at 400 and 700 °C, leading to the preparation of supports containing mainly tetragonal (ZrO_2-400) and monoclinic (ZrO_2-700) ZrO_2 phases. These catalysts were characterized and tested in the same reaction under the same conditions in order to elucidate the effect of the support crystal structure in VO_x/ZrO_2 catalysts on their catalytic activity and selectivity.

2. Experimental

2.1. The preparation of VO_x/ZrO_2 catalysts

VO_x/ZrO_2 catalysts containing various amount of vanadium were prepared by incipient wetness impregnation on amorphous ZrO_2, made from $Zr(OH)_4$ (Sigma Aldrich) by dehydration at 250 °C for 3 h, using ammonium metavanadate dissolved in hydrogen peroxide solution (with the ratio of hydrogen peroxide (30 wt. % solution) to water being 1:4) under the same conditions as the VO_x/TiO_2 catalyst in the previous study [10]. Briefly, 1 g of $Zr(OH)_4$ was dehydrated and then impregnated with 1 ml of the ammonium metavanadate solution of appropriate concentration to achieve the desired vanadium content in the resulting catalyst; subsequently, it was dried at 120 °C and calcined at 450 °C for 3 h to obtain the final catalyst. The catalysts are labeled as VO_x/ZrO_2-X, where X is the content of vanadium in the catalyst expressed in weight percent.

In order to study the effect of the ZrO_2 crystalline phase on the catalytic activity of VO_x/ZrO_2 catalysts, the amorphous $Zr(OH)_4$ powder was calcined at 400 and 700 °C before the impregnation procedure to obtain ZrO_2 with the majority of tetragonal and monoclinic phases, respectively. These two samples were named ZrO_2-400 and ZrO_2-700. These supports were impregnated under the same conditions as the above-described set of VO_x/ZrO_2 catalysts with an appropriate amount of ammonium metavanadate to reach the concentration close to the so-called monolayer capacity (which means the surface density of vanadium of ca 7 V atoms/nm^2 as reported in the literature [15,16,41]). The amount of vanadium for impregnation was determined based on the knowledge of the specific surface area of the ZrO_2 supports measured by N_2 adsorption. The catalysts were labeled VO_x/ZrO_2-400 and VO_x/ZrO_2-700.

2.2. The characterization of the samples

The elemental composition of the investigated catalysts was determined by X-ray fluorescence (XRF) using Philips PW 1401 equipped with an Rh RTG lamp. UniQuant software was used to evaluate the results. The particle morphology of the synthesized materials was evaluated by scanning electron microscopy using a JEOL JSM-7500F instrument with a cold-cathode field emission (parameters of the measurements: 1 kV, GB high mode). X-ray powder diffraction (XRD) patterns of the investigated samples were recorded on a Philips MPD 1880 diffractometer working with the Cu K_α line ($\lambda = 0.154$ nm) in the 2θ range of 4°–70° and the 2θ scanning rate of 2.4°/min. Quantitative phase analysis of the samples was performed via the Rietveld structure refinement method employing Materials Analysis Using Diffraction (MAUD) software (Version 2.26) [42,43].

The specific surface area and the pore volume of the investigated samples were measured by means of nitrogen adsorption/desorption at the temperature of liquid nitrogen by using ASAP 2020 equipment