



Selective oxidation of ethanol over vanadia-based catalysts: The influence of support material and reaction mechanism



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ABSTRACT

The catalytic performance of vanadia supported on silica, alumina, zirconia, and titania was investigated in the selective oxidation of ethanol. It was shown that the activity and product distribution strongly depend on the support material, which determines the structure of supported vanadia species. On silica and alumina, low-active V_2O_5 crystallites were mainly formed regardless of the vanadium content. These catalysts demonstrated high selectivity toward only acetaldehyde. In contrast, monomeric surface vanadia species and polymeric surface vanadia species were mainly formed over TiO_2 when the vanadium content did not exceed what is necessary for the ideal monolayer. Over zirconia, both the surface vanadia species and the V_2O_5 crystallites existed regardless of the vanadium content. It was found that the surface vanadia species are more active in the selective oxidation of ethanol than the V_2O_5 crystallites. The highest activity was observed for the polymeric vanadia species and, correspondingly, the best catalytic performance was achieved on the monolayer V_2O_5/TiO_2 catalyst. At low temperatures between 110 and 150 °C, this catalyst demonstrated high activity in the oxidation of ethanol to acetaldehyde with the selectivity ranging between 80% and 100%. At temperature near 200 °C, the same catalyst was active in the oxidation of ethanol to acetic acid with the selectivity of approximately 65%. The surface intermediates and the catalyst state were also studied in situ by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. It was shown that under reaction conditions near 100 °C, non-dissociatively adsorbed molecules of ethanol, ethoxide species, and adsorbed acetaldehyde exist on the catalyst surface, while at higher temperatures, V_2O_5/TiO_2 is mainly covered with acetate species. Titanium cations remained in the Ti^{4+} state, whereas V^{5+} cations underwent a reversible reduction under reaction conditions. On the basis of the in situ data complemented by the results of kinetic measurements, a reaction mechanism for the selective oxidation of ethanol to acetaldehyde and acetic acid over the monolayer catalysts was proposed.

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1. Introduction

Acetaldehyde and acetic acid are important reagents and industrial chemicals. The global demand for acetic acid, which is mainly used for the synthesis of vinyl acetate, acetic anhydride, and acetates, as well as a solvent for the production of purified terephthalic acid, is above 10 million tons per year [1]. Acetaldehyde is

also an industrially important solvent and an intermediate for the synthesis of a wide range of organic compounds, such as pentaerythritol, crotonaldehyde, and pyridine derivatives. The global market for acetaldehyde is forecast to reach 1.2 million tons by the year 2015. Currently, approximately 85% of acetaldehyde is produced from ethylene via the Wacker-Hoechst process, 75% of acetic acid for the chemical industry is produced by the catalytic carbonylation of methanol and 25% by classical fermentation [2]. All these processes are liquid-phase, and the development of more effective gas-phase technologies is one of the most important tasks of the large-scale chemical industry.

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To solve this task, the catalytic gas-phase oxidation of ethanol by molecular oxygen (from air) is more attractive because it is an economic and environmentally friendly process. Indeed, acetaldehyde, which is more expensive than ethanol, can be produced with high effectiveness by the gas-phase oxidative dehydrogenation (ODH) over supported transitional metal catalysts or by oxidation with O_2 over different vanadium and molybdenum based oxides [3–7]. A number of heterogeneous catalysts have been also reported for the formation of acetic acid by the oxidation of ethanol in the gas phase: $Mo_{0.61}V_{0.31}Nb_{0.08}O_x/TiO_2$ [7], Ce-meso TiO_2 [8], V_2O_5/TiO_2 [9], $Mo-CeO_x/SnO_2$ [10], $V_xM_{1-x}SbO_4$ ($M = Fe, Al, Ga$) [11], and Pt/Al_2O_3 [12]. Definitely, the development of new catalytic technologies requires the understanding of the mechanism for the selective oxidation of ethanol on the atomic level.

The oxide catalysts demonstrate high activity in the selective oxidation of ethanol to both acetaldehyde and acetic acid under mild conditions. The high selectivity toward acetaldehyde is usually observed at low temperatures ranging between 100 and 200 °C, while at 200–250 °C, because of the further oxidation of acetaldehyde, the reaction shifts toward acetic acid. For example, over Ce-meso TiO_2 catalysts, the selectivity toward acetaldehyde achieves 93% at 150 °C at the conversion of ethanol of 77% [8]. Similar selectivity toward acetaldehyde was observed over MoO_x/TiO_2 at 200 °C but at low conversions near 17% [7]. Over $V_{0.7}Mo_{0.3}SbO_4$ ($M = Fe, Al, Ga$), the direct oxidation of ethanol to acetaldehyde with the selectivity above 80% was observed in a wide temperature range from 150 to 230 °C [11]. Multi-component metal oxides ($Mo-V-Nb-O_x$) can catalyze the direct oxidation of ethanol to acetic acid at 240 °C with the selectivity up to 95% at 100% ethanol conversion [7]. A special attention has been paid to supported vanadia catalysts, which demonstrate excellent catalytic performance in the selective oxidation of ethanol [9]. Depending on reaction conditions, ethanol can be transformed to acetaldehyde, acetic acid, diethyl ether, ethyl acetate, ethyl formate, crotonaldehyde, ethylene, or carbon oxides (CO and CO_2). The product distribution is also dependent on the support material and vanadia surface density [10,13–17]; however, the reason for this effect is still a topic of debate. Recently, we have shown that the catalytic performance of supported vanadia catalysts in the selective oxidation of methanol to dimethoxymethane and methyl formate is mainly determined by the structure of vanadia species [18,19]. Herein, we demonstrate that this hypothesis is also applicable for the selective oxidation of ethanol.

It is well known that vanadia can form different structures over the surface of oxide supports: monomeric and polymeric species as well as crystallites of vanadium oxide. As shown by Kilos et al. [14], the acetaldehyde formation rate during the oxidation of ethanol over VO_x/Al_2O_3 catalysts depends on the vanadia surface density. Polyvanadate surface species supported on alumina exhibit a somewhat higher rate of ethanol ODH than monovanadate surface species. In contrast, according to DFT calculations [20], vanadyl-terminated monomers on $CeO_2(111)$, that is, VO_2 , are the most active species. VO_x components in the $Mo_{0.61}V_{0.31}Nb_{0.08}O_x/TiO_2$ catalyst [7] are responsible for the high reactivity of this material in the selective oxidation of ethanol to acetaldehyde and acetic acid while V–O–Ti linkages are responsible for the unselective oxidation of acetaldehyde to CO_x . The contrary point of view was stated by Beck et al. [21] who suggested that the V–O–S linkages (where S is a cation of a support) take part in the selective oxidation of ethanol to acetaldehyde over vanadia supported on CeO_2 , Al_2O_3 , ZrO_2 , and TiO_2 . The authors suggested that the alcohol first adsorbs dissociatively, resulting in a breaking of the V–O–S bond to form ethoxide and S–OH species.

In order to elucidate these conflicting data and to develop the mechanism for the selective oxidation of ethanol, we synthesized a series of V_2O_5/SiO_2 , V_2O_5/Al_2O_3 , V_2O_5/ZrO_2 , and V_2O_5/TiO_2 catalysts and tested their catalytic activity in a flow reactor in a wide

temperature range. In addition, we carried out an in situ study of the oxidation of ethanol over the most active monolayer V_2O_5/TiO_2 catalyst using Fourier transform infrared spectroscopy (FTIR) and near ambient-pressure X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Catalyst preparation

Supported vanadia catalysts containing 2–22 wt% V_2O_5 were prepared by the impregnation of supports (SiO_2 , $\gamma-Al_2O_3$, ZrO_2 , and TiO_2) with an aqueous solution of vanadyl oxalate synthesized from V_2O_5 (>99.6%, Reachim, Russia) and oxalic acid (>97%, Reachim, Russia). The samples were dried in air at 110 °C for 24 h and then calcined in an air flow (50 ml/min) at 400 °C for 4 h. As support materials, we used commercial aerosil SiO_2 (>99.6%, Reachim, Russia) with the specific surface area S_{BET} of 200 m²/g and TiO_2 (anatase, AlfaAesar) with S_{BET} of 350 m²/g. $\gamma-Al_2O_3$ with $S_{BET} = 250$ m²/g was synthesized by the calcination of boehmite $AlOOH \cdot nH_2O$ ($n = 0.3–1.0$) in air at 550 °C for 4 h. ZrO_2 was prepared by the precipitation of $Zr(OH)_4$ from a $ZrOCl_2$ solution with aqueous ammonia at 50 °C; final pH was 8.5. The resulting zirconium hydroxide was dried in air at 110 °C for 12 h and then calcined at 400 °C for 4 h. Synthesized zirconia was a mixture of the monoclinic (85%) and cubic (15%) phases. The specific surface area of ZrO_2 , which was calculated by the Brunauer–Emmett–Teller (BET) method, was 120 m²/g.

2.2. Catalyst characterization

The catalysts were characterized by elemental analysis, Raman spectroscopy, N_2 adsorption and X-ray diffraction (XRD) techniques. The elemental analysis was performed using an inductively coupled plasma atomic emission spectrometer (Baird). Powder XRD measurements were carried out using a Siemens D500 diffractometer using monochromatic $CuK\alpha$ radiation. The 2θ scan covered a range of 10–70°. The specific surface area was calculated with the BET method using nitrogen adsorption isotherms measured at liquid nitrogen temperatures with an automatic Micromeritics ASAP 2400 sorptometer. Raman spectra were obtained on a RFS 100/S Raman spectrometer (Bruker) using a Nd:YAG laser as an excitation source ($\lambda = 1064$ nm, 100 mW). The laser radiation was focused onto a spot with a diameter 50 μ m. Before recording the spectra, the samples were calcined in air at 400 °C for 30 min.

2.3. Catalytic testing

The steady-state activity of the catalysts was tested at atmospheric pressure in a differential reactor with a flow-circulating configuration [22]. The reactor was constructed from a Pyrex glass tube with a 12-mm inner diameter and a 50-mm length. A coaxial thermocouple pocket with a 4-mm outer diameter was fitted in the catalyst bed to control the temperature. The reactor was placed inside an electric oven. The temperature was controlled within ± 0.5 °C by a K-type thermocouple. The feed consisted of ethanol, oxygen, and nitrogen in the molar ratios of 1:4:15 (5 vol.% C_2H_5OH in air). The catalyst fraction 0.25–0.50 mm was used in the experiments. Concentrations of the reactants and products were determined with an on-line gas chromatograph equipped with thermal conductivity and flame ionization detectors. Ethanol, acetaldehyde (CH_3CHO), acetic acid (CH_3COOH), diethyl ether ($(C_2H_5)_2O$), ethyl acetate ($CH_3-COO-CH_2-CH_3$), crotonaldehyde ($CH_3CH=CHCHO$), ethylene, water, and CO_2 were analyzed with a Porapak T column, while CO , oxygen, and nitrogen were analyzed with a NaA molecular sieve column. All gas lines from the reactor to

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