Journal of Catalysis 338 (2016) 82–93

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Redox mechanism for selective oxidation of ethanol over monolayer V_2O_5/TiO_2 catalysts

Vasily V. Kaichev [a,b,*], Yuriy A. Chesalov [a,b], Andrey A. Saraev [a,b], Alexander Yu. Klyushin [c,d], Axel Knop-Gericke [c], Tamara V. Andrushkevich [a], Valerii I. Bukhtiyarov [a,b]

[a] Boreskov Institute of Catalysis, Lavrentieva Ave. 5, 630090 Novosibirsk, Russia
[b] Novosibirsk State University, Pirogov Str. 2, 630090 Novosibirsk, Russia
[c] Department of Inorganic Chemistry, Fritz Haber Institute of the Max Plank Society, Faradayweg 4-6, D-14195 Berlin, Germany
[d] Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Division Energy Material, Albert-Einstein-Str. 15, 12489 Berlin, Germany

ARTICLE INFO

Article history:
Received 27 November 2015
Revised 16 February 2016
Accepted 18 February 2016
Available online 16 March 2016

Keywords:
Heterogeneous catalysis
Ethanol oxidation
Acetaldehyde
Acetic acid
Vanadia

ABSTRACT

The selective oxidation of ethanol to acetaldehyde and acetic acid over a monolayer V_2O_5/TiO_2 catalyst has been studied in situ using Fourier transform infrared spectroscopy and near-ambient-pressure X-ray photoelectron spectroscopy (XPS) at temperatures ranging from 100 to 300 °C. The data were complemented with temperature-programmed reaction spectroscopy and kinetic measurements. It was found that under atmospheric pressure at low temperatures acetaldehyde is the major product formed with the selectivity of almost 100%. At higher temperatures, the reaction shifts toward acetic acid, and at 200 °C, its selectivity reaches 60%. Above 250 °C, unselective oxidation to CO and CO_2 becomes the dominant reaction. Infrared spectroscopy indicated that during the reaction at 100 °C, nondissociatively adsorbed molecules of ethanol, ethoxide species, and adsorbed acetaldehyde are on the catalyst surface, while at higher temperatures the surface is mainly covered with acetate species. According to the XPS data, titanium cations remain in the Ti^{4+} state, whereas V^{5+} cations undergo reversible reduction under reaction conditions. The presented data agree with the assumption that the selective oxidation of ethanol over vanadium oxide catalysts occurs at the redox V^{n+} sites via a redox mechanism involving the surface lattice oxygen species. A reaction scheme for the oxidation of ethanol over monolayer V_2O_5/TiO_2 catalysts is suggested.

1. Introduction

Over the past several years, the idea of using renewable resources in the chemical industry has become popular worldwide. In particular, a great many efforts have been made to develop technologies for the production of alternative fuels based on bio-oil, biodiesel, or bioethanol [1–4]. At the same time, bioethanol, or simply “ethanol,” which is produced from biomass by hydrolysis and sugar fermentation processes, can be used as a raw material for catalytic production of various useful chemical compounds. Depending on the catalyst and reaction conditions, ethanol can be transformed to acetaldehyde, acetic acid, butanol, or ethyl acetate with high selectivity [5–12]. A review of the major previous works on the transformation of ethanol to valuable chemicals has been published elsewhere [9]. In brief, the authors summarized that supported noble metal catalysts are active in the production of acetic acid, whereas base metal oxides favor acetaldehyde. High selectivity toward ethyl acetate has been observed only over Cu/ZnO and Pd-based catalysts [6,9].

Nowadays, special attention is paid to the development of novel catalytic technologies for industrial production of acetaldehyde and acetic acid via one-step gas-phase conversion of ethanol. As shown by Raich and Foley [6], the gas-phase dehydrogenation of ethanol to acetaldehyde can be competed by a Wacker process based on the oxidation of ethylene. Using a palladium membrane reactor, they achieved a selectivity toward acetaldehyde of 70% at a conversion of ethanol of approximately 90%. Afterward it was found that oxide catalysts are more effective in these reactions. For instance, Li and Iglesia [7] have shown that multi-component metal oxides Mo—V—Nb—O can catalyze the direct oxidation of ethanol to acetic acid with a selectivity of approximately 95% at 100% conversion. Mehlomakulu et al. [10] have found that ternary metal oxide catalysts $V_xMe_{1-x}SbO_4$ (Me = Fe, Al, Ga) are active in the gas-phase oxidation of ethanol to acetaldehyde with

---

[*] Corresponding author at: Boreskov Institute of Catalysis, Lavrentieva Ave. 5, 630090 Novosibirsk, Russia.

E-mail address: vvk@catalysis.ru (V.V. Kaichev).

http://dx.doi.org/10.1016/j.jcat.2016.02.022
0021-9517/

a selectivity of over 80%. The best catalytic performance was demonstrated by V_2O_5/TiO_2 nanoparticle catalysts that allowed producing acetaldehyde by the gas-phase oxidation of aqueous ethanol at approximately 180–185 °C with a selectivity higher than 90% at a conversion of ethanol above 95% [8]. Furthermore, a selectivity over 80% toward acetic acid could be achieved in this reaction at a low gas velocity at temperatures as low as 165 °C.

In this work we report the first results of our mechanistic study of the gas-phase selective oxidation of ethanol to acetaldehyde and acetic acid over titania-supported vanadium oxide catalysts. We used Fourier transform infrared spectroscopy (FTIR) and near-ambient pressure X-ray photoelectron spectroscopy, which allowed us to study the catalyst state and adsorbed species during the oxidation of alcohol [13,14]. The data are complemented by results of temperature-programmed reaction spectroscopy (TPRS) and kinetic measurements in a flow reactor.

2. Experimental

2.1. Catalyst preparation and characterization

All experiments were performed using a monolayer V_2O_5/TiO_2 catalyst, which was prepared as described in detail elsewhere [14,15]. In brief, a two-step procedure was used for synthesis of the catalyst. First, the TiO_2 support (anatase, 350 m^2/g) was impregnated with an aqueous solution of vanadyl oxalate via the incipient-wetness impregnation method and was subsequently dried at 110 °C for 12 h and then calcined in a flow of air at 400 °C for 4 h. According to chemical analysis, the catalyst consisted of 20 wt.% V_2O_5 and 80 wt.% TiO_2, and both polymeric surface vanadia species and supported V_2O_5 crystallites were detected by FTIR and X-ray diffraction (XRD) [14,15]. Second, to remove the V_2O_5 crystallites selectively, the catalyst was subsequently treated in a 10% aqueous solution of nitric acid at room temperature. After the washing process, the catalyst was calcined again in a flow of air at 400 °C for 4 h. This catalyst contained 12.5 wt.% V_2O_5, and no supported V_2O_5 crystallites were detected by XRD.

Earlier, it was found that vanadia might form different structures on titania surfaces, depending on the vanadia content and preparation techniques [16–22]. With the vanadia content under 10% of a monolayer, only isolated monomeric species with tetrahedral coordination exist under dehydrated conditions [17,20]. Polymeric structures such as chains and ribbons of VO_x units with octahedral coordination appear at a vanadia concentration above 20% of the monolayer [20]. The monolayer coverage of polymerized vanadia species on different oxides was measured by Raman spectroscopy and was found to be approximately 7–8 vanadium atoms/nm^2 for TiO_2 [18,19]. When the vanadium content exceeds what is necessary for the ideal monolayer, V_2O_5 crystallites are favorable. In our case the specific surface area of the washed catalyst was 115 m^2/g, which corresponded to the surface density of vanadia species of 7.3 V-atoms/nm^2. This means that polymeric vanadia species with a near-monolayer coverage exist mainly on the surface of the prepared catalyst. Such catalysts are usually referred to as monolayer catalysts [17].

2.2. Catalytic testing

The steady-state activity of the monolayer V_2O_5/TiO_2 catalyst was tested at atmospheric pressure in a differential reactor with a flow-circulating configuration [23]. 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 into 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 1:4:15 M ratio. The concentrations of reactants and products were determined with an online gas chromatograph equipped with thermal conductivity and flame ionization detectors. Ethanol, acetaldehyde, acetic acid, diethyl ether, ethyl acetate, crotonaldehyde, ethylene, water, and CO_2 were analyzed with a Porapak T column, while CO, oxygen, and nitrogen were analyzed with an NaA molecular sieve column. All gas lines from the reactor to a sampling valve were maintained at 120 °C to prevent the condensation of reactants and products. Ethanol (A.C.S. reagent grade, 99% purity) obtained from Aldrich was used in all the experiments. The conversion of ethanol was calculated on the basis of measured inlet and outlet concentrations of ethanol. The selectivity toward each product was calculated as the amount of the detected product divided by the amount of converted ethanol using corresponding stoichiometric coefficients. The carbon balance was 97 ± 2%.

When the dependence of selectivity on the conversion was studied, changes in the conversion of ethanol were provided by varying the catalyst loading and the feed flow [14]. Under the conditions used, the conversion of ethanol increased nonlinearly with the contact time. The rate of consumption of ethanol is described well by the first-order equation with respect to ethanol concentration. According to this equation, the dependence of the conversion on the contact time is described by a curve increasing to a plateau.

2.3. XPS, TPRS, and FTIR measurements

The in situ XPS and TPRS experiments were performed at the ISISS (Innovative Station for In Situ Spectroscopy) beamline at the synchrotron radiation facility BESSY II (Berlin, Germany). The experimental station is described in detail elsewhere [13]. In brief, the station was equipped with a PHOIBOS-150 electron energy analyzer (SPECS Surface Nano Analysis GmbH), a gas cell, and a system of differential pumping, which allowed us to obtain high-quality core-level spectra at pressures up to 1 mbar. A powder sample was pressed into a thin self-supporting pellet. The pellet was mounted on a sapphire sample holder between two stainless steel plates. The first plate had a hole of 5 mm diameter for measuring the core-level spectra of the catalyst surface. The second plate was used for heating by a near infrared semiconductor laser ($\lambda = 808$ nm). The sample temperature was measured with a K-type thermocouple pressed directly against the rear of the sample. The flows of ethanol vapor and oxygen into the gas cell were regulated separately with calibrated mass-flow controllers (Bronkhorst High-Tech BV). The flow rate of ethanol in all the experiments was approximately 2 sccm. The total pressure in the gas cell was measured with an MKS Type 121A baratron (MKS Instruments Inc.) and was kept at a constant level during the experiments with the help of a special pumping system. This was 0.25 and 0.5 mbar in the experiments with ethanol and with an equimolar C_2H_5OH/O_2 mixture, respectively.

The synchrotron worked in the multibunch hybrid mode, which provided a constant photon flux. The C1*s*, Ti2$p_{3/2}$, V2$p_{3/2}$, and O1*s* core-level spectra were recorded at a photon energy of 720 eV. On the one hand, this provided acquisition of the core-level spectra at the same photon flux, which guaranteed the constant charge effect. On the other hand, the analysis depths for C, Ti, V, and O atoms were different; however, this was unimportant in this study. Charge correction was performed by setting the Ti2$p_{3/2}$ peak at 459.0 eV. The curve fitting was done with the CasaXPS software. The core-level spectra were resolved into their components after Shirley-type background subtraction. The lineshape of each component was considered to be a product of Lorentzian and Gaussian functions.