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Selective oxidation of formaldehyde to formic acid over supported vanadia catalysts

E.V. Danilevich [a,*], G.Ya. Popova [a], T.V. Andrushkevich [a], V.V. Kaichev [a,b], I.G. Danilova [a], Yu.A. Chesalov [a], V.A. Rogov [a,b], V.I. Bukhtiyarov [a,b], V.N. Parmon [a,b]

[a] Boreskov Institute of Catalysis of SB RAS, Lavrentieva Ave. 5, Novosibirsk 630090, Russia
[b] Novosibirsk State University, Pirogova St. 2, Novosibirsk 630090, Russia

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ABSTRACT

The effect of support and different vanadia species present at different vanadium loadings on the catalytic performance of supported vanadia in the oxidation of formaldehyde to formic acid was examined. The catalysts with vanadium supported on SiO_2, Al_2O_3, ZrO_2, and TiO_2 were prepared by impregnation. The catalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy, UV–vis diffuse reflectance spectroscopy, and the temperature-programmed reduction technique. All catalysts and supports were tested in the oxidation of formaldehyde at 120 °C. It was found that activity in the oxidation of formaldehyde to formic acid is determined by the structure of vanadia species and the selectivity is determined by the coverage of support surface by these species. TiO_2 (anatase) is the most suitable support for the formation of monolayer vanadium species which are the most active in the oxidation of formaldehyde to formic acid.

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1. Introduction

Supported vanadia catalysts form an important class of heterogeneous catalysts that are active toward the selective oxidation of benzene to maleic anhydride [1], ortho-xylene to phthalic anhydride [2], methane to formaldehyde [3,4], methanol to formaldehyde [5] and methyl formate [6]. These catalysts are also active in the oxidation and ammoxidation of alkyl pyridines [7–11], the oxidative dehydrogenation of alkanes [12–14], and the selective catalytic reduction of nitrogen oxides by ammonia [15,16]. In recent years, vanadia-titania catalysts were found to be highly efficient in the gas-phase oxidation of formaldehyde to formic acid at low temperatures [17–19].

Among various selective oxidation reactions catalyzed by supported vanadia catalysts, the oxidation of formaldehyde to formic acid is of special interest. This reaction is one of the simplest reactions among the partial oxidation of organic substances and can serve as a convenient model for selective oxidation studies. Such a gas-phase route to formic acid production by the oxidation of formaldehyde is attractive for industry, because formaldehyde is a cheap and readily available feedstock, whereas formic acid is a midscale chemical commodity, which is currently synthesized by complex multistage methods.

Many studies have demonstrated the dependence of activity and selectivity of various reactions, catalyzed by supported vanadium oxide, on the nature of supports and its coverage by different vanadia species [20–24]. For instance, V_2O_5/TiO_2 showed nearly a 10-fold higher activity as compared to V_2O_5/Al_2O_3 catalysts in the oxidative dehydrogenation of ethane and propane [22]. Vanadia supported on anatase is more active than that supported on Nb_2O_5 in the ammoxidation of 3-picoline [24]. The order of activity (TOF, number of molecules converted per active surface site per second) in dependence on the chemical composition of support was determined in the following reactions [25]:

The methanol oxidation to formaldehyde: V_2O_5/ZrO_2, V_2O_5/TiO_2 » V_2O_5/Al_2O_3 » V_2O_5/SiO_2;
The oxidation of CO: $V_2O_5/ZrO_2 > V_2O_5/TiO_2 > V_2O_5/Al_2O_3$;
The reduction of NO_x: $V_2O_5/ZrO_2 > V_2O_5/TiO_2 > V_2O_5/Al_2O_3 > V_2O_5/SiO_2$.

However, Baldychev et al. [26] reported that the TOF for the methanol oxidation over sub monolayer VTi, VZr, and VAl catalysts containing primarily isolated vanadia species does not depend strongly on the support.

The origin of the influence of the support is still not well understood. However it is generally thought that the nature of V–O—support bonds determines the catalytic performance [5,27–29]. Some studies have reported the effect of support on the

* Corresponding author. Tel.: +7 383 3269713; fax: +7 383 3308056.
E-mail address: yelenasem@catalysis.ru (E.V. Danilevich).

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dispersion of surface VO_x species as well as the redox and acid-base properties of the supported catalysts [30,31].

The possibility of the selective heterogeneous oxidation of formaldehyde to formic acid and methyl formate on oxide catalysts was first demonstrated by Ai [32]. Ai studied the catalytic properties of various oxides (V_2O_5, SnO_2, Al_2O_3, Fe_2O_3, TiO_2, and WO_3) and their binary mixtures (V—Mo, V—K, V—Fe, V—Ni, V—Sn, and V—Ti oxides) in the oxidation of formaldehyde. The reaction was carried out at 180–300 °C. The maximum yield of formic acid (~25 mol%) was obtained on a mixture of vanadium and titanium oxides with the composition $V_2O_5/TiO_2 = 90/10$ at a reaction temperature of 205 °C. The maximum yield of methyl formate was observed on a mixture of tin and tungsten oxides $SnO_2/WO_3 = 67/33$ [32]. Later it was found that the supported vanadia–titania catalysts (10–90 wt% $V_2O_5/90$–10 wt% TiO_2) exhibited a high selectivity in the oxidation of formaldehyde to formic acid at 120–140 °C [17]. The selectivity with respect to formic acid achieved 95–90% at 120 °C at a conversion of formaldehyde in the range 10–85%.

Data on the influence of the support upon the catalytic properties of vanadium catalysts in the selective oxidation of formaldehyde are limited [19,32]. In contrast to the previously mentioned reactions of the oxidation of hydrocarbons and the reduction of NO_x over supported vanadium catalysts where supports such as Al_2O_3, ZrO_2, and TiO_2 are inert, these supports are not inert with respect to the oxidation of formaldehyde. Bare Al_2O_3, ZrO_2, and TiO_2 are active in the formation of methyl formate from formaldehyde in the temperature range when the supported vanadia demonstrates a high selectivity in the oxidation of formaldehyde to formic acid (100–140 °C) [19].

In this work some aspects of the reaction of the formaldehyde oxidation to formic acid, catalyzed by supported vanadium oxide were studied. Specifically, the effect of the nature of supports and the vanadia loading on activity and selectivity has been investigated. We have shown that activity of supported vanadia catalysts in the oxidation of formaldehyde to formic acid is determined by the structure of vanadia layer while selectivity is determined by the degree of coverage of the support by different vanadia species.

2. Experimental

2.1. Catalyst preparation

Supported vanadia catalysts of composition 2–25 wt.% V_2O_5 and 98–75 wt.% support were prepared by the impregnation of support (SiO_2, γ-Al_2O_3, ZrO_2, and TiO_2) with an aqueous solution of the calculated amount 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 calcined in an air flow (50 ml/min) at 400 °C for 4 h.

A commercial aerosil SiO_2 (>99.6%, Reachim, Russia) with the specific surface area S_{BET} of 200 m^2/g and TiO_2 (anatase, catalog Alfa Aesar) with S_{BET} of 350 m^2/g were used. γ-Al_2O_3 was synthesized by calcination of boehmite AlOOH·nH_2O ($n = 0.3$–1.0) in air at 550 °C for 4 h ($S_{BET} = 250$ m^2/g). ZrO_2 was prepared by the precipitation of Zr(OH)$_4$ from $ZrOCl_2$ solution with aqueous ammonia at 50 °C and final pH of 8.5. The resulting zirconium hydroxide was dried in air at 110 °C for 12 h and calcined at 400 °C for 4 h. The ZrO_2 obtained ($S_{BET} = 120$ m^2/g) is a mixture of the monoclinic (85%) and cubic (15%) phases.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were performed using a D500 diffractometer (Siemens) with monochromatic Cu Kα

radiation. Data were recorded in a 2θ range of 5–70° (step size 0.02°, time 5 s). The specific surface areas of the samples were determined by Brunauer–Emmett–Teller method (BET) from nitrogen adsorption isotherms measured at liquid nitrogen temperature using an automatic ASAP 2400 Sorptometer (Micromeritics).

Elemental analysis was performed using an inductively coupled plasma atomic emission spectrometer (ICP, Baird). Raman spectra were obtained using a RFS 100/S BRUKER Raman spectrometer. A Nd:YAG laser, operating at 1064 nm with power of 100 mW at the sample, which gave a laser spot with a diameter 50 μm, was used for the excitation of spectra. Prior to recording the spectra, the samples were calcined in air at 400 °C for 30 min. Dehydrated samples were placed into sealed containers. The spectra were collected at ambient temperature. No background subtraction was applied for the spectral analysis.

The chemical composition of the catalyst surfaces was determined by X-ray photoelectron spectroscopy (XPS) using a photoelectron spectrometer (SPECS Surface Nano Analysis GmbH) equipped with an X-ray source XR-50M, an ellipsoidal crystal monochromator FOCUS-500, and a hemispherical electron energy analyzer PHOIBOS-150-MCD-9. The spectra were obtained using Al Kα radiation at a base pressure of approximately 10^{-9} mbar. The charge correction was performed by setting the C1s resulting from adventitious hydrocarbons at 284.8 eV. Fit XPS software was used for curve fitting. The core-level spectra were resolved into their components after a Shirley-type background subtraction. The line shape of each component was a convolution of a Lorentzian with a Gaussian function. Relative concentrations of elements were determined from the integral intensities of the XPS peaks using the cross-sections according to Scofield [33].

UV–vis diffuse reflectance spectra (UV–vis DRS) of the catalysts and the corresponding supports were recorded using an UV-2501 PC Shimadzu spectrometer with an IRS-250A diffusion reflection attachment in the range from 11,000 to 54,000 cm^{-1} using $BaSO_4$ as a reference. The samples were calcined in a 2 mm quartz cell at 400 °C for 4 h before measurement. After each treatment, the quartz cell was quickly sealed off and cooled to room temperature for the measurements.

The UV–vis spectra were transformed into the Kubelka–Munk function ($F(R_\infty) = (1-R_\infty)^2/2R_\infty$, where R_∞ is the experimentally measured reflectivity coefficient of the infinitely thick samples. The edge energy (E_g), or band gap, was determined by finding the intercept of the straight line for the low-energy rise of a plot of $[F(R_\infty)h\nu]^2$ versus $h\nu$, where $h\nu$ is the incident photon energy [34].

The temperature-programmed reduction in hydrogen (H_2-TPR) was performed with 100 mg of catalyst in a quartz reactor using a flow setup with a thermal conductivity detector. A fraction of the catalyst powder containing particles in the size range of 0.25–0.50 mm was used. Prior to the reduction, the samples were treated in oxygen for 0.5 h at 400 °C and then cooled to room temperature in O_2. The reducing mixture (10 vol.% H_2 in Ar) was fed at 40 ml/min. The rate of heating from room temperature to 900 °C was 10 °C/min.

2.3. Catalytic tests

The samples were tested in the oxidation of formaldehyde at 120 °C. Experiments were carried out at atmospheric pressure. The composition of the inlet mixture (vol.%) was as follows: 5% CH_2O, 10% H_2O in air. Experiments were carried out using a Pyrex glass reactor (i.d. 12 mm, length 50 mm) with a coaxial thermocouple pocket ($d = 4$ mm). The initial mixtures were supplied at a rate of 8.2 l/h. The compositions of reacting mixtures were analyzed by chromatography. The flow-type circulation setup maintained the