Potassium-modified silica-supported vanadium oxide catalysts applied for propene epoxidation

Agnieszka Held [a],*, Jolanta Kowalska-Kuś [a], Krystyna Nowińska [a], Kinga Góra-Marek [b]

[a] *Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*
[b] *Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland*

ABSTRACT

The influence of potassium ions on the structure and catalytic properties of silica-supported vanadium oxide catalysts was studied in the epoxidation of propene using N_2O as an oxidant. The combination of different techniques (XRD, DR UV–vis, Raman, FTIR, and H_2 TPR) for the characterization of potassium-doped V/SBA-15 catalysts reveals the formation of various types of vanadate species, including polyvanadates. Potassium changes the acid–base characteristics of the system and decreases the acidic character of surface vanadia. A decrease in the acidic character accounts for better selectivity in propene epoxidation; however, neutralization of active vanadium forms results in lower propene conversion. Textural, XRD and SEM/TEM, results indicate that the ordered hexagonal mesoporous structure with large pore diameters of the support is retained upon vanadium incorporation, although further modification with potassium ions results in a partial structure damage.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

The catalytic activity of a silica-supported vanadium oxide system for hydrocarbon oxidation reactions has been widely documented [1–3]. The oxidative dehydrogenation of ethane and propane to related olefins in the presence of oxygen or nitrous oxide as oxidants has been developed over silica [4,5]-, alumina [6,7]-, or titania [8]-supported vanadium oxides. Recently, we have found evidence of high activity of V_2O_5/silica systems (mesoporous materials SBA-3, SBA-15, and MCM-41 or amorphous silica) for propene epoxidation if N_2O is used as an oxidant [9]. However, selectivity toward propylene oxide (PO) was about 20% and significant amounts of propanal (PA), acetone (AC), and acrolein (ACR) were noted [10]. It has been shown earlier that iron-modified silica transforms propene to propylene oxide in the presence of nitrous oxide with a yield of PO not higher than 5% [11]. The authors demonstrated that the introduction of sodium ions into iron catalysts increased not only the propene oxidation rate but also the selectivity to PO. The effect of introducing alkaline ions into silica-supported iron catalysts for propene epoxidation with nitrous oxide as an oxidant has been reported by Moens et al. [12] and Ananieva et al. [13]. According to these authors, modification with alkaline ions resulted in an increase in activity for

propene epoxidation thanks to better iron dispersion and a reduction in catalyst acidity. The promotive influence of alkaline ions depended on the nature of the alkaline ion and also on the accompanying anions. Potassium chloride has been found to be especially beneficial [14]. Moreover, Zhang et al. [14,15], on the basis of band gap energy values (E_g) calculated from UV–vis absorption bands and from XANES spectra, indicated the favorable influence of potassium ions on the dispersion of iron species introduced into mesoporous silicas.

The effect of alkaline ions on the structure of vanadium catalysts and catalytic activity by modification of acidic and redox features has also been widely studied [16,17]. Grabowski et al. [16], investigating the propane ODH reaction with oxygen as an oxidant have shown, on the basis of kinetic calculations, that modification of silica-supported vanadium catalysts with potassium ions results in limitation of both propane and propene combustion. Alkaline ions also influence propane conversion and selectivity to propene. Chimentão et al. [17] have indicated the effect of alkaline ions on ethanol oxidation on V/SiMCM-41 catalyst. Interestingly, a small amount of sodium introduced into V/MCM-41 increased ethanol conversion and also enhanced the selectivity toward acetaldehyde, which was attributed to basicity promotion and an increase in vanadium dispersion. On the other hand, selectivity to ethylene diminishes. The decrease in selectivity to ethylene was due to the elimination of acidic sites by interaction with sodium ions.

* Corresponding author. Fax: +48 61 8291472.
  E-mail address: awaclaw@amu.edu.pl (A. Held).

Elimination of acidic sites also results in a diminution of carbonaceous formations.

Considering that the propanal and acetone formed during propene-to-PO oxidation constitute the propylene oxide isomers, it seemed likely that acidic sites present on vanadia/silica catalysts may be responsible for relatively high selectivity toward these chemicals. Taking the above into account, silica-supported vanadium catalysts for propene-to-PO oxidation were modified with potassium ions introduced in different amounts and tested in the studied reaction. The modified and unmodified samples were characterized by means of UV–vis spectra, H_2 TPR measurements, XRD profiles, low-temperature nitrogen adsorption desorption measurements, and FT-IR of adsorbed pyridine to estimate the acidity of the samples. Analyzing the influence of the potassium modifier on the catalytic results, the possible effect of potassium ions on vanadium species structure and distribution is discussed.

2. Experimental

2.1. Catalyst preparation

All silica mesoporous materials (SBA-3, SBA-15, MCM-41) used as a support for vanadium species were synthesized according to the procedures described elsewhere [18–20]. In the preparation of mesoporous supports, the following chemicals were used: cetyltrimethylammonium bromide (CTAB, ⩾98%, Aldrich) or tri-block copolymer, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Aldrich) as a template, tetraethyl orthosilicate (TEOS, Aldrich, 98%) as a source of silicon, hydrochloric acid (Chempur, 35–38%), and ammonia solution (Chempur, 25%).

Modification of the mesoporous matrices with vanadium ions was performed by the wet-impregnation method using an aqueous solution of $VOSO_4$ (97%, Aldrich) with the amount required for 5 wt.% of V. A quantity of 5 g of silica support was impregnated with a 0.1 M aqueous solution of $VOSO_4$ (time of impregnation 4–6 h), using the volume of the solution required for the intended vanadium concentration. After drying at 373 K overnight, the samples were calcined at 823 K in air under static conditions for 1 h. The K-doped catalysts were prepared using an aqueous solution of potassium chloride (POCH), potassium bicarbonate (POCH), and potassium sulfate (POCH) by subsequent wet impregnation of vanadium catalysts. The concentration of potassium in this series corresponded to a K/V molar ratio of 0.2 and 0.5. The obtained samples were dried at 373 K and calcined at 823 K in air for 1 h.

2.2. Catalyst characterization and activity testing

2.2.1. X-ray diffraction

As-prepared nonmodified mesoporous matrices and vanadium- or vanadium/potassium-modified final catalysts were characterized by powder X-ray diffraction (XRD) measurements performed on a Bruker AXS D8 Advance diffractometer with $CuK\alpha$ radiation ($\lambda = 0.154$ nm) in the ranges of 2θ equal to $2°–10°$ and $10°–60°$.

2.2.2. Brunauer–Emmett–Teller

The BET (Brunauer–Emmett–Teller) surface area of the catalysts and the average pore diameter were measured with a Quantachrome Nova 1000e sorptometer. Usually, about 0.2 g of catalyst was degassed at 575 K prior to nitrogen adsorption. The N_2 adsorption/desorption isotherms were collected at 77 K.

2.2.3. H_2 temperature-programmed reduction

The reducibility of catalysts was studied by H_2 TPR (temperature-programmed reduction) in a fixed-bed quartz reactor using a homemade apparatus equipped with a thermal conductivity detector (TCD). The reduction of the samples was carried out using H_2/Ar (10 vol.% hydrogen) as a reductant (flow rate 70 cm^3 min^{-1}). A 0.03 g sample placed in the reactor was activated in a flow of helium at 723 K at a rate of 10 K min^{-1}. Subsequently, the sample was cooled to RT in helium and then heated at a rate of 10 K min^{-1} to 1123 K under a flow of the reductant mixture. The water produced during the reduction was condensed in a cold trap dipped in a mixture of propan-2-ol and liquid nitrogen.

2.2.4. Ultraviolet–visible spectra

Diffuse reflectance spectra in the UV–visible region of dehydrated samples (calcined at 673 K before UV–vis spectrum recording) were collected on a Varian Cary 100 spectrophotometer in the reflectance function mode (F(R)), in the range 800–200 nm. The spectra were recorded at room temperature (RT) using $BaSO_4$ as a reference material. The absorption edge energies for the presented UV–vis spectra were determined by finding the intercept of the straight line in the low-energy rise of a plot of $[F(R_\infty)h\nu]^{1/2}$ against $h\nu$, where $F(R_\infty)$ is a Kubelka–Munk function and $h\nu$ is the energy of the incident photon [21].

2.2.5. Elemental analysis

Chemical analyses of the catalysts were carried out by inductively coupled plasma analysis (ICP) measurements performed on a Varian ICP-OES VISTA-MPX spectrometer.

2.2.6. Fourier transform infrared spectra of adsorbed pyridine

Fourier transform infrared (FTIR) analysis was used for acidity measurements using pyridine as a probe molecule. The FTIR spectra were recorded on a Bruker Vector 22 spectrophotometer with a spectral resolution of 4 cm^{-1} by accumulating 75 scans. Self-supported wafers (ca. 20 mg/cm^2) of the catalysts were prepared and placed in a homemade quartz infrared cell with CaF_2 windows connected to a vacuum dosing system. Prior to the adsorption experiments, the samples were activated at 673 K in a vacuum for 2 h ($<10^{-4}$ Torr).

Pyridine vapors were contacted with the sample at RT for 15 min followed by evacuation at 373 K in order to remove physically adsorbed pyridine. IR spectra were recorded at room temperature after evacuation (for 30 min) at different temperatures (373, 473, 573, and 673 K).

The number of acidic centers was calculated with the following equation, according to [22,23]:

$$n_T = \frac{A_L C_d}{\varepsilon_L m} + \frac{A_B C_d}{\varepsilon_B m},$$

where n_T is the total number of acidic sites expressed as micromoles of pyridine per 1 g of catalyst, A_L and A_B are the integrated absorbances of IR bands related to Lewis and Brønsted sites, C_d is the cross section of the wafer in cm^2, m is the mass in g of the pressed pellet, and ε_L and ε_B are molar absorption coefficients for Lewis and Brønsted acid sites, equal to 1.5 and 1.8 [μmol^{-1} cm], respectively.

2.2.7. Fourier transform infrared spectra of adsorbed CO and CO_2

For FTIR studies, the samples were pressed into the form of self-supporting discs (ca. 5 mg/cm^2) and evacuated in a quartz IR cell at 623 K under vacuum for 1 h. Spectra were recorded with a Bruker Vertex spectrometer equipped with an MCT detector. The spectral resolution was 2 cm^{-1}. The measured doses of CO were sorbed at 173 K up to the saturation of all electron acceptor sites (the maximum intensity of 2206–2196 cm^{-1} bands) and the appearance of the band of CO bonded to Brønsted-type sites (the 2165–2156 cm^{-1}). The sorption of CO_2 was performed at room temperature. The excess of CO_2 was contacted with the catalysts for 10 min