



Propane-to-propene oxide oxidation on silica-supported vanadium catalysts with N₂O as an oxidant



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ABSTRACT

Propane-to-propene oxide oxidation was carried out at 673 and 703 K and for different contact times on vanadium catalyst supported on mesoporous silica of SBA-3 structure in the presence of N₂O as an oxidant. For comparison, direct propene epoxidation was also investigated. Vanadium catalysts for propane oxidation undergo deactivation with time on stream. It was noted that the higher the reaction temperature the faster the deactivation. The very small amount of coke deposit in the spent catalyst would indicate that the vanadium reduction is responsible for catalyst deactivation. FT-IR spectroscopy was used to study the adsorbed surface species involved in the selective propane oxidation. Considering the alteration of selectivity toward oxygen-bearing products with propane/propene conversion influenced by reaction temperature and contact time, some tentative reaction paths for the selective oxidation of propane have been proposed.

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1. Introduction

Propene oxide (PO), one of the most important intermediates, is mainly produced by the multistep chlorohydrin method, which results in a large amount of useless chloride-containing waste, or by the organic hydroperoxide process. Recently, a new clean technology, based on the application of hydrogen peroxide as an oxidant, has been developed, with the first installation in Antwerp [1]. Nevertheless, considering the cost of highly concentrated hydrogen peroxide and also some risk of uncontrolled H₂O₂ decomposition, the search for a new and more effective technology for PO production still continues. Direct oxidation of propene to propene oxide was performed on various catalysts with oxygen [2–4], an oxygen–hydrogen mixture [5,6], and nitrous oxide [7–9] as oxidants. Depending on the applied catalyst as well as the oxidant used, propene conversion and selectivity to PO differed significantly. When iron-modified silica was applied, a decrease in propene conversion with time on stream was observed [7], while selectivity to PO remained stable. Reoxidation of the catalyst restored the initial activity. According to Nijhuis and Weckhuysen [10], the introduction of water vapor on gold–titania catalyst applied for propene-to-PO oxidation in the presence of hydrogen

and oxygen reduced the catalyst deactivation, even though somewhat lower conversion was noted.

Propene applied as a starting material for PO production is usually manufactured by steam cracking or fluid cracking of higher hydrocarbons. Both processes are energy-intensive, as they are performed at high temperature (usually at about 1000 K). Propene may also be obtained by oxidative dehydrogenation (ODH) of propane under much milder conditions on iron [11]- or vanadium [12]-containing catalysts with oxygen [12–14] or nitrous oxide [11,13,14] as oxidants. The application of N₂O as an oxidant for propane ODH, despite resulting in lower propane conversion, allows higher propene selectivity and lower selectivity to carbon oxides [15]. According to the quoted authors [15], propane-to-propene oxydehydrogenation occurs on vanadyl groups with oxygen removal and subsequent vanadium reduction. Oxidants (O₂ or N₂O) are responsible for vanadium reoxidation. Reoxidation of vanadium species by oxygen is very fast and results in the temporary formation of peroxovanadates, highly reactive to subsequent propene oxidation. The ability of N₂O to reoxidize the reduced vanadium species is less and occurs without the formation of peroxovanadates [16].

As both iron and vanadium catalysts on different silica supports in the presence of N₂O and under similar conditions (reaction temperature in the range of 573–723 K), showed activity both for propane ODH [11,14] and propene-to-PO oxidation [7,8,17], it seemed reasonable to perform the direct processing of propane to propene

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oxide. Bravo-Suárez et al. [18] indicated that a combination of two catalysts, Au/TiO₂ and Au/TS-1, may catalyze the direct synthesis of propene oxide from propane with a H₂ and O₂ mixture as an oxidant at a relatively low temperature, 443 K. On the other hand, Song et al. [19] have found that propene oxide is formed only from propene, not from propane, when silica-supported molybdenum oxide is used with oxygen as an oxidant.

In the present study we have used vanadium catalysts at different vanadium concentrations (1–7 wt.%) supported on mesoporous silica support (SBA-3) as catalysts for direct oxidation of propane to propene oxide using N₂O as an oxidant. It has been shown that depending on vanadium loading, various VO_x species (monomers, dimers, polymers, and bulk V₂O₅ crystals) are formed on the surface of catalysts. According to our earlier results [16], the presence of monomeric VO_x species formed up to monolayer coverage favors the propene epoxidation reaction. Kondratenko et al. [14,20] have also indicated that up to monolayer coverage with VO_x species (noted for about 5 wt.% of vanadium on MCM-41), an increase in the rate of propene formation in ODH was observed. Considering the above, we applied vanadium catalysts comprising 1–7 wt.% of vanadium with a density in the range of 0.08–1.13 V/nm² (near-monolayer coverage) as catalysts for direct oxidation of propane to propene oxide. The possible paths for the transformation of propane to propene and to related oxygen-containing products were also estimated on the basis of catalytic results and FT-IR spectra of adsorbed hydrocarbons (propane, propene), the mixture of reagents (propane/propene with N₂O), and propene oxide.

2. Experimental

2.1. Catalyst preparation

SBA-3 was used as a supporting material for vanadium oxide species. The mesoporous material was prepared by hydrothermal synthesis according to a procedure described elsewhere [21]. The synthesis was performed under acidic conditions. The initial mole ratio of the reaction mixture was as follows: 0.11 TEOS:0.025 CTAB:1.94 HCl:9.17 H₂O. The SBA-3 support was prepared using the cationic surfactant cetyltrimethylammonium bromide (CTAB, ≥98%, Aldrich) as the template, and tetraethoxysilane (TEOS, ≥99%, Aldrich) as the silica source. TEOS (23 cm³) and 34 cm³ of hydrochloric acid (38%, POCH) were dissolved in 165 cm³ of deionized water followed by addition of 8.3 g of CTAB. The mixture was stirred at room temperature to obtain a homogeneous solution. After this, an additional 36 cm³ of hydrochloric acid was added, which resulted in the precipitation of a white gel. The mixture was stirred for up to 1 h at room temperature. The gel was crystallized at room temperature for 8 days. The product was then washed with deionized water, filtered, and dried at 373 K. Finally, the sample was calcined in air under static conditions at 823 K for 8 h (with a heating rate of 1 K/min). The modification of the SBA-3 matrix with vanadium ions was performed by the wet-impregnation method using an aqueous solution of VOSO₄ (97%, Aldrich) with the amount required for 1, 3, 5, and 7 wt.% of V. A quantity of 10 g of SBA-3 support was impregnated with a 0.1 M aqueous solution of VOSO₄ by the incipient wetness method (time of impregnation 4–6 h), using the volume of the solution required for the intended vanadium concentration. The obtained samples were dried at 373 K and calcined at 823 K in air under static conditions for 1 h.

2.2. Catalyst characterization

The correctness of the mesostructure of the as-synthesized and the vanadium-modified SBA-3 samples was checked by powder X-

ray diffraction (XRD), which was performed on a Bruker AXS D8 Advance diffractometer with Cu Kα radiation (λ = 0.154 nm). The Brunauer–Emmett–Teller (BET) surface area and the average pore diameter were estimated from N₂ adsorption/desorption isotherms collected at 77 K on a Quantachrome Nova 1000e sorptometer. Typically, about 0.2 g of sample was used for the measurement and the sample was degassed at 575 K prior to nitrogen adsorption at 77 K. The content of vanadium introduced into SBA-3 was estimated from ICP (inductively coupled plasma) measurements performed on a Varian ICP-OES VISTA-MPX spectrometer.

Diffuse reflectance spectra in the UV–vis regions of dehydrated samples (calcined at 673 K) were recorded in the reflectance function mode (F(R)) in the range 800–200 nm on a Varian Cary 100 spectrophotometer. The spectra were recorded at room temperature (RT) using BaSO₄ as a reference material.

H₂ TPR profiles were obtained by heating the catalysts from 300 to 1000 K at a rate of 10 K/min. under H₂/Ar flow (70 cm³/min) using a homemade apparatus equipped with a TCD detector. A quartz microreactor was charged with 0.03 g of catalyst (sieve fraction 0.3–0.5 mm).

The decomposition of propan-2-ol to propene was studied at 493 and 523 K by the pulse method using helium as a carrier gas. A quantity of 0.2 g of the sample and 0.5 μl of propan-2-ol were applied and the total flow rate of helium amounted to 30 cm³/min. Analysis of products was performed by gas chromatography with FID detection.

2.3. FTIR spectroscopy

IR spectra were recorded with a Bruker Vector 22 Spectrophotometer using a homemade quartz infrared cell with CaF₂ windows connected to a vacuum dosing system. This cell was designed and built at the Adam Mickiewicz University in Poznań. The catalyst powder was pressed into a self-supporting disc of around 20 mg/cm² and activated at 673 K under vacuum (<10⁻⁴ Torr) for 2 h before adsorption experiments. Adsorption of propane, propene, propene oxide, or reagent mixture (propane/propene and N₂O) was performed at room temperature (RT) for 30 min followed by subsequent heating to different temperatures: 373, 473, 573, 673, and 703 K (spectra were recorded after 30 min contact of the gas phase with the catalyst surface at selected temperatures and cooling of the sample to RT). Typical gas-phase partial pressures were 20 Torr of propane, 20 Torr of propene, 20 Torr of N₂O, and 2 Torr of propene oxide. After exposure of the catalyst surface to the substrates, products, or reagent mixture, it was evacuated at room temperature for 1 h and subsequently at 673 K for 1 h. All spectra were collected at room temperature with a resolution of 4 cm⁻¹ by accumulating 75 scans. In the paper the differential spectra are presented (after subtraction of the activated catalyst spectrum).

2.4. Catalytic tests

Catalytic tests for propane and propene oxidation were performed in the presence of N₂O as an oxidant in a continuous-flow reactor at two different temperatures: 673 and 703 K. The experiments were carried out under atmospheric pressure using different contact times: 0.5, 1, 1.5, 2.1, and 2.5 s. Propane or propene and N₂O (propane: 99.5 vol.% and propene: 99.5 vol.% from Linde and N₂O: 99.995 vol.% from Messer) were diluted with helium (≥99.9999 vol.%, Linde) and the flow rates of propane/propene:nitrogen oxide:helium were 1:15:x cm³/min, where x = 100, 41, 24, 12.5, and 8 cm³/min, related to different contact times. The total flow rate of the gases was equal to 116, 57, 40, 28.5, and 24 cm³/min, respectively. The composition of the reaction inlet flow was controlled by mass flow controllers (MFC Brooks). In the

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