



Short Communication

Epoxidation of propene on vanadium species supported on silica supports of different structure

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ABSTRACT

Silica supports such as mesoporous materials (SBA-3, SBA-15 and MCM-41), silicalite and amorphous silica were used for accommodation of vanadium species introduced on the support surface by means of impregnation, with vanadium concentration from 1 to 7 wt.%. Catalysts were characterised by means of XRD, low temperature adsorption/desorption of nitrogen, DR UV–vis and Raman spectra and also H₂-TPR measurements. Isolated vanadium species dispersed in the channels of mesoporous SBA-3 with pores diameter related to micropores range, seems to be the most active for propene epoxidation.

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1. Introduction

Propylene oxide (PO) belongs to the most important intermediate chemicals and it is applied for the production of a number of consumer goods such as polyols used for polyurethane plastics manufacture, glycols, mono propylene glycol (MPG), and so on. The world propylene oxide production rate is always growing and currently it exceeds 6 million tons per year. Despite of the development of new modern technologies for PO production, based on direct propylene oxidation with hydrogen peroxide as an oxidant, nearly 50% of world production of PO stems from chlorhydrine method (CHPO). Considering the above, the research for development of clean, more convenient and safe technologies is still undertaken. The use of nitrous oxide as an oxidant for heterogeneous propene to PO oxidation was initiated by Duma and Hönicke [1] over iron modified silica. Zhang et al. [2] employed an iron modified high silica zeolite of ZSM-5 structure as catalysts for propene to PO oxidation conducted in the presence of N₂O. Iron modified zeolites ZSM-5 have been successfully applied for one step benzene to phenol oxidation [3] as well as they have shown promising activity for light paraffins oxidative dehydrogenation [4]. However, the main drawback of iron modified zeolite matrices, used for oxidation of propene to PO was relatively low selectivity to PO and the formation of many other oxygen bearing organic compounds, resulted from direct allylic propene oxidation or from further transformation of produced PO in the presence of acidic sites of zeolitic catalysts. Considering the special activity of gold [5] and copper [6] containing catalysts, for propylene

epoxidation in the presence of oxygen and hydrogen, and on the other hand the ability of copper catalysts in nitrous oxide decomposition [7] Chimentão et al. [8] revealed a new catalytic system, active for propene epoxidation with nitrous oxide, based on bimetallic Cu–Au alloy supported on TiO₂. The quoted authors evidenced that metallic particles dispersion dependent on copper contribution in bimetallic alloy, influences the catalysts activity for studied reaction. Recently, we have proved that not only iron modified silica supports [1,2,9,10], or bimetallic Cu–Au catalytic systems [8], reported in literature, but also vanadium cations introduced into mesoporous all silica molecular sieves channels, show high activity in propene oxidation as well as relatively high selectivity to PO [11]. The activity of the catalysts was influenced by vanadium distribution, vanadium ions coordination, oxidation degree and reducibility, as well as acidity of the support.

In the presented study, we have used silica based matrices (SBA-3, SBA-15, MCM-41, silicalite and amorphous silica) of different structure and porosity as supports for vanadium catalysts. Influence of the support features and vanadium species nature on oxidative ability of vanadium catalysts in transformation of propene to PO has been evaluated. The nature of vanadium species generated on the supports was estimated on the base of UV–vis and Raman spectra and from H₂-TPR measurements.

2. Experimental

2.1. Catalysts preparation

Mesoporous all silica supports (SBA-3, SBA-15, MCM-41) were synthesized according to literature description [12,13,14] and characterized by means of XRD technique and low temperature nitrogen adsorption/

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desorption. Silicalite and amorphous silica were commercial products from UOP and POCH, respectively.

Inorganic matrices were impregnated with aqueous solution of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ with different amount of vanadium (in the range of 1–7 wt.%). 10 g of particular support was impregnated with 0.1 M aqueous solution of VOSO_4 (pH equal to 4) by means of incipient wetness method (time of impregnation was equal to 4–6 hours), using the volume of solution relating to intended vanadium concentration (1–7 wt.% of V). After impregnation and drying (373 K) the catalysts were calcined in air at 823 K.

2.2. Catalysts characterization

The correctness of mesostructure of synthesized silica supports and vanadium modified samples were characterized by XRD patterns recorded on Bruker AXA D8 Advance diffractometer, $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm). The BET surface area was measured by nitrogen adsorption/desorption isotherms employing a Quantachrome NOVA 1000e analyser. Typically, 0.1–0.3 g of sample was used for the measurement and the sample was degassed at 575 K prior to nitrogen adsorption at 77 K. H_2 -TPR profiles were monitored (in the range of 300–1173 K and with heating rate 10 K/min. using 10% of hydrogen in argon flowing with 70 ml/min) using homemade equipment with TCD detector. Quartz microreactor was charged with 0.03 g of catalyst.

Diffuse reflectance (DR) spectra in the UV–visible region of dehydrated samples (calcination at 673 K) were recorded in the reflectance function mode (F(R)) at room temperature in the range of 800–200 nm on a Varian Cary 100 spectrophotometer.

ESR spectrometer of Radiopan equipped with X band was used for the recording of ESR spectra of vanadium containing catalysts. The spectra were collected at 77 K.

Raman spectra of the dehydrated samples were recorded at room temperature with laser excitation at 514 nm (14 mW) in the range of 200–1500 cm^{-1} , using LabRAM HR800 Horiba Jobin Yvon Raman spectrometer.

2.3. Catalytic performance

Catalytic tests in propene epoxidation were performed in a continuous flow reactor at 673 K. For laboratory tests a fixed-bed glass reactor (10 mm i.d.) was loaded with 0.5 g of catalyst. The temperature of the catalyst bed was measured by a thermocouple. The experiments were carried out under atmospheric pressure, with $\text{WHSV} = 4 \text{ h}^{-1}$ related to contact time of 1.1 s. Prior the measurements, the catalysts were heated in flowing helium at 723 K for 30 min. The composition of the reactor inlet was $15 \text{ ml min}^{-1} \text{ N}_2\text{O}$, 1 ml min^{-1} propene and 12.5 ml min^{-1} helium, controlled by a mass flow meters. Reaction products were analyzed using on-line GC analysis. A Varian CP-3800 Gas Chromatograph with a FID detector and WCOT Fused Silica capillary column (50 m x 0.53 mm) and a SRI 8610 C Gas Chromatograph with a TCD detector and HayeSep Q packed column were used. On the grounds of GC analysis, it was found that besides PO we recorded also propionaldehyde, acetone, acroleine and carbon oxides. The catalysts were characterized with activity measured after 30 min. on stream. During 3 h of catalytic test small decrease in activity was noted. The threefold regeneration at 723 K in the presence of oxidant restored the initial activity. To estimate the C balance, the amount of propene converted to heavy product was estimated on the grounds of elemental analysis of coke deposit cumulated during three hours of the reaction. Considering the amount of coke deposit and the presence of C_3 unsaturated compounds, the C balance was kept within 7% or below.

The catalytic activities are reported as conversion (%), selectivity (%) and yield (%) calculated as follows:

$$C = \frac{\% \text{Conversion}}{\text{total amount of X transformed into products}} \times 100$$

$$C = \frac{\text{amount of X transformed into products}}{\text{amount of X introduced}} \times 100$$

$$\% \text{Selectivity}$$

$$S_i = \frac{\text{amount of X transformed into } Z_i}{\text{total amount of X transformed}} \times 100$$

where Z = propylene oxide, propionaldehyde, acroleine, acetone, CO_x ; X = propylene

$$\% \text{Yield}$$

$$Y = \frac{S \times C}{100}$$

The propylene oxide TOF was calculated according to Wachs et al. [15] and it was defined as propylene oxide formed per exposed surface vanadium site per second.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. XRD, ICP characterization and BET measurements

The following silica supports: SBA-3, SBA-15, MCM-41, silicalite and amorphous silica were applied for accommodation of vanadium species and employed as catalysts for propene epoxidation. Silica supports differed with crystalline structure, surface area and pore diameter (Table 1). Correctness of the meso structure was confirmed by XRD measurements displayed in Fig. 1. Accommodation of vanadium species of different concentration resulted in some modification of XRD diffraction patterns, nevertheless the hexagonally ordered structure of mesoporous supports was still preserved.

Surface area of vanadium impregnated molecular sieves decreased along with the increase in vanadium concentration (Table 1), while the variation of pore diameter was less visible. The coverage of the

Table 1

BET values of vanadium free and vanadium modified silica supports, vanadia surface density (V/nm^2) and vanadium concentration.

Sample	S_{BET} (m^2/g)	Average pore diameter (nm)	Vanadium concentration (wt.%)	Surface density ($\text{V atoms}/\text{nm}^2$)
SBA-3	1641	1.7		
1 V/SBA-3	1330	1.8	0.83	0.08
2 V/SBA-3	1223	2.0	1.61	0.15
3 V/SBA-3	917	1.8	2.80	0.36
5 V/SBA-3	636	1.7	5.16	0.96
7 V/SBA-3	631	2.4	6.02	1.13
SBA-15	834	6.0		
1 V/SBA-15	667	5.5	0.82	0.14
2 V/SBA-15	593	6.2	1.60	0.32
3 V/SBA-15	589	5.7	2.80	0.56
5 V/SBA-15	552	5.0	5.00	0.92
7 V/SBA-15	552	5.2	6.84	1.49
MCM-41	803	4.2		
1 V/MCM-41	624	3.4	1.26	0.24
2 V/MCM-41	708	3.8	1.74	0.29
3 V/MCM-41	651	4.0	2.34	0.42
5 V/MCM-41	521	4.9	4.13	0.94
7 V/MCM-41	198	3.8	6.53	3.89
SiO_2	443	macropores		
1 V/ SiO_2	398		0.87	0.30
2 V/ SiO_2	344		1.84	0.60
3 V/ SiO_2	343	macropores	2.52	0.84
5 V/ SiO_2	344		4.40	1.51
7 V/ SiO_2	84		5.8	8.15
Silicalite	335	0.55		
1 V/Silicalite	333		0.85	0.30

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