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**ROLE OF METHODS AND CONDITIONS
OF PREPARATION OF VANADIUM SPECIES
SUPPORTED ON LAMELLAR ZEOLITE MCM-36
IN THEIR CATALYTIC BEHAVIOUR IN OXIDATIVE
DEHYDROGENATION OF PROPANE**

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In this work, we report successful preparation of hierarchical VO_x-MCM-36 catalysts. Lamellar pillared zeolitic support (MCM-36) was prepared from layered precursor of MCM-22P zeolite by swelling and pillaring. Vanadium was introduced into MCM-36 support by different methods (including conventional impregnation and ion exchange) by means of different precursors and synthesis conditions. Textural properties of prepared catalysts were characterized by nitrogen adsorption-desorption isotherms, the concentration of vanadium was

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determined by X-ray fluorescence and vanadium complex speciation was investigated by diffuse reflectance UV-vis spectroscopy, hydrogen temperature programmed reduction (H_2 -TPR), electron paramagnetic resonance (EPR) and Fourier transform infrared (FTIR) spectroscopy. Effect of synthesis method and conditions on catalytic behaviour was tested in the oxidative dehydrogenation of propane at 540 °C. The vanadium is present in oxidation state IV, instead of usual oxidation state V, in the cases of the catalyst with low content of vanadium. The best selectivity to propene with 13 % of conversion (43.9 %) was obtained when the acid center was neutralized with potassium cations and the content of vanadium was 2 wt %.

Introduction

The wide availability and low price (e.g., actual price of propane is 860 USD per ton, while the price of propene is 1105 USD per ton [1]) of light alkanes and the fact that they generally have smaller impact on environment, are incentives for their use as raw materials in the chemical industry. One of the most important utilizations of alkanes is their transformation to unsaturated hydrocarbons, because the chemical industry uses olefins as starting compounds.

The oxidative dehydrogenation (ODH) is a suitable option to obtain those materials, because it is a thermodynamically feasible way. A lot of work was published in the last years on this topic [2-10]. Metals, such as vanadium and nickel supported on silica and aluminum silicates, are most frequently used for this type of reaction. In these systems, deposited material nature, the interaction between the active phase and the support, as well as physico-chemical properties of the support, such as surface area and acidity, strongly affect catalytic results.

Control of the selectivity towards desired product is one of the main problems in catalytic oxidation of hydrocarbons, in which the kinetics and thermodynamics are involved [11]. Generally, an increase in the conversion is accompanied by a decrease in the selectivity to the alkene. It is, therefore, necessary to develop highly structured materials with tailored activity and selectivity [3]. For this purpose, the knowledge of how the support influences the active phase and its speciation, how it is influenced by the method of synthesis, nature of precursors used and pre-treatment of the material is necessary.

Many catalysts investigated in the ODH reaction are based on the vanadium oxides as the main component [12-14]. Different authors relate the catalytic activity to the nature of vanadium species supported in the different materials [15-17]. Bulky vanadium pentoxide is not a good catalyst for the ODH reactions, because it exhibits low selectivity to alkenes (desirable product in this reaction). Bulánek *et al.* show in their work [14] that VO_x isolated tetrahedrally coordinated species leads to a higher selectivity to alkenes in the reaction of light alkanes

ODH; on the contrary, bulky vanadium pentoxide species are not a good catalyst for the ODH reactions, because it exhibits low selectivity to alkenes. For that reason, a specific support with large surface area or providing specific sites for chemical bonding of monomeric vanadyls is necessary for fine dispersion of vanadium species. From this point of view, mesoporous silicas belong to the good candidates for support. Zeolitic materials should be other promising type of catalysts due to the presence of cationic sites in their framework where vanadium species can be coordinated to the framework in monomeric form and stabilized by negative charge of zeolite framework. Albuquerque *et al.* [6,7] reported successful ion-exchange of vanadyl groups into MCM-22 zeolite (three-dimensional form zeolite with MWW framework structure) and predicted potential application of this material in the ODH reaction of propane due to its oxidation/reduction behaviour. Wannakao *et al.* studied the reaction mechanism of propane ODH over VO₂-exchanged MCM-22 theoretically by means of DFT method [5] and found that the formation of propene is preferred over the competing oxygenated product on the VO₂-MCM-22 nanocatalyst.

Lamellar zeolites, affording both cationic sites for anchoring vanadium species and mesoporosity for fast mass transport as mesoporous silica supports, are another group of promising supports allowing the deposition of a large number of well-defined vanadium species. To the best of our knowledge, no papers dealing with the possibility to use of vanadium modified lamellar form of MWW zeolite have been published up to now. Therefore, we turn our attention to the study of preparation and properties of VO_x-MCM-36 materials. In this present work, we report successful preparation of VO_x-MCM-36 catalysts. Lamellar pillared zeolitic support (MCM-36) was prepared from layered precursor of MCM-22 zeolite by swelling and pillaring. Vanadium was introduced into MCM-36 support by different methods (including conventional impregnation and ion exchange) by means of different precursors and synthesis conditions. Textural properties of prepared catalysts were characterized by nitrogen adsorption-desorption isotherm, the concentration of vanadium was determined by X-ray fluorescence and vanadium complex speciation was investigated by UV-vis diffuse reflectance spectroscopy, hydrogen temperature programmed reduction (H₂-TPR), EPR and FTIR spectroscopy. The effect of synthesis method and conditions on catalytic behaviour was tested in the oxidative dehydrogenation of propane at 540 °C and the obtained catalytic results were correlated with their surface and structural characteristics.

Experimental

Materials

The MCM-22 precursor (MCM-22P) was synthesized by the following procedure: 1.16 g NaOH was dissolved in 251.2 g water and mixed with 1.68 g sodium aluminate (40-45 % Na₂O, 50-56 % Al₂O₃). Then, 62 g LUDOX (AS 30) was added. The mixture became thick and was stirred until homogeneous gel was formed. Then, 17.2 g hexamethylenimine (HMI) was added and the final mixture was stirred for 2 h. The reaction mixture was charged into Teflon-lined steel autoclaves (4×90 ml). Crystallization proceeded at the temperature of 150 °C under agitation and autogeneous pressure for 5 days. Solid product was collected by filtration, washed with distilled water and dried in an oven at the temperature of 60 °C overnight.

MCM-22P (3.8 g uncalcined MCM22P sample) was mixed with 77 ml ion-exchanged cetyltrimethylammonium hydroxide (CTMA-OH), and the slurry was stirred overnight at ambient temperature. The product was separated by centrifugation, properly washed with distilled water and dried at 60 °C. Pillaring was carried out with 5 g swollen MCM-22 in 150 ml tetraethyl orthosilicate (1 g zeolite per 30 ml TEOS). The mixture was stirred and heated under reflux at 85 °C for overnight. The solid was isolated by centrifugation, dried at 40 °C and hydrolyzed by adding about 500 ml water to 5.013 g dried powder and stirred overnight at room temperature. The product was centrifuged again and dried at 60 °C. Final calcination was carried out at 540 °C for 6 h with the temperature ramp of 2 °C min⁻¹. The calcined product MCM-36 was ion-exchanged into NH₄ form by treating four-times with 1.0 M NH₄NO₃ solution for 4 h at room temperature (100 ml of solution per 1 g zeolite). The support was prepared also in potassium form by ion-exchange of H-MCM-36. The support was added to an aqueous solution of 0.1 M potassium carbonate at 50 °C for 24 h. After ion-exchange, the solid was filtered and kept overnight at 120 °C.

In this present paper, different methods and various precursors for the synthesis of vanadium based catalysts were used. The impregnation and ion exchange methods were applied for synthesis of catalysts and three precursors were used (vanadyl acetylacetonate, vanadyl vanadium sulfate and vanadyl acetate. The latter was synthesized from ammonium vanadate by heating with glacial acetic acid under reflux for 3 h, and then the resulting solid was filtered and calcined at 250 °C for 4 h in airflow. Impregnation method was conducted with the vanadyl acetylacetonate and vanadyl acetate on the both H-MCM-36 and K-MCM-36. The proper amount of precursor was dissolved in 100 ml ethanol. After that, the support was suspended in this solution and heated to boiling point of solution. Solvent was slowly evaporated under intensive stirring until some liquid remained in the beaker. Finally, the solid was dried overnight at 120 °C and calcined at 600

°C in airflow during 8 h.

The ion exchange was carried out with vanadyl acetate and vanadyl sulfate as precursors. In this case, the appropriate amount of precursor was dissolved in 150 ml water and the solution was kept together with the support at 50 °C for 24 h under vigorous stirring. Then, the solid was filtered and dried overnight at 120 °C and calcined at 600 °C in airflow during 8 h.

Synthesized materials are labeled as follows: the first letter, V, called the supported metal, followed by two subscripts, depending on the method of synthesis — (impregnation (i) or ion exchange (e)) —, and the precursor, vanadyl acetylacetonate (a), vanadyl acetate (c) or vanadyl sulfate (s). In the nomenclature is used K or H for potassium and acidic form of the original zeolitic material, respectively. For example, the catalyst synthesized by impregnation method using as the vanadyl acetylacetonate precursor and the support in potassium form is abbreviated as V_{ia} -K.

Characterization Techniques

The chemical composition of all the investigated samples was determined by X-ray fluorescence spectroscopy by an ElvaX spectrometer equipped with Pd anode (Elvatech, Ukraine). Samples were measured against the model samples (a mechanical mixture of pure SiO_2 and NaVO_3) granulated to the same grain size as the catalysts.

X-ray powder diffraction data were recorded on a Bruker D8 Advanced X-ray powder diffractometer equipped with a graphite monochromator and a position-sensitive detector (Vantec-1) using $\text{Cu K}\alpha$ radiation (at 40 kV and 30 mA) in Bragg–Brentano geometry.

Nitrogen was used as adsorptive and supplied by Messer (Griesheim, Germany — purity 99.999 vol. %). Sorption isotherms of nitrogen at 77 K were determined using an ASAP 2020 instrument. In order to attain a sufficient accuracy in the accumulation of the adsorption data, this instrument is equipped with pressure transducers covering the 133 Pa, 1.33 kPa and 133 kPa ranges. Before each sorption measurement, the sample was degassed for a slow removal of most pre-adsorbed water at low temperatures. This was done to avoid potential structural damage of the sample due to surface tension effects and hydrothermal alternation. Starting at ambient temperature, the sample was degassed at 110 °C (temperature ramp of 0.5 °C min^{-1}) until the residual pressure of 1 Pa was attained. After further heating at 110 °C for 1 h, the temperature was increased (temperature ramp of 1 °C min^{-1}) until the temperature of 350 °C was achieved. The sample was degassed at this temperature under turbomolecular pump vacuum for 8 h. The BET surface area was evaluated by adsorption data in the relative pressure between 0.05 and 0.25. Micropore volume (V_{micro}) was determined by using the t -plot method

employing Harkins–Jura equation. Mesopore size distribution was calculated from adsorption branch of isotherms by means of BJH methodology employing Harkins–Jura equation. The surface area obtained by the technique of adsorption and desorption of nitrogen, and the vanadium content of each catalyst are shown in Table I.

Table I Chemical composition and physico-chemical characterization of investigated VO_x-MCM-36 samples

Catalyst	V wt. %	S_{bet} m ² g ⁻¹	V_{micro} cm ³ g ⁻¹	S_{meso} m ² g ⁻¹
V _{ia} -K	2	540	0.0981	321
V _{es} -H	0.1	584	0.109	398
V _{es} -K	0.1	552	0.108	355
V _{ec} -H	7.2	408	0.066	287
V _{ic} -H	18.8	220	0.03	158
V _{ia} -H	1.9	481	0.078	344
MCM-36	-	612	0.092	454

Self-supporting wafers (ca. 5-8 mg cm⁻²) were prepared from the sample powder and treated directly in a glass IR cell. The cell was connected to a vacuum-adsorption apparatus with residual pressure of 10⁻³ mbar. The samples were activated by heating from ambient temperature to 450 °C with heating rate of 10 °C min⁻¹ and evacuated at the target temperature for 1h. The FT-IR spectra were recorded at room temperature using an FT-IR Nicolet 6700 spectrometer (equipped with an MCT/A detector) at a spectral resolution of 2 cm⁻¹ and accumulating of 64 scans. The spectra obtained through subtraction of the spectrum of the treated sample in vacuum from the spectrum in the presence of the probe molecules are reported here. The spectra are gas phase corrected.

The UV-vis diffuse reflectance spectra of dehydrated diluted samples were measured using a Cintra 303 spectrometer (GBC scientific Equipment, Australia) equipped with a Spectralon-coated integrating sphere using a Spectralon coated discs as a standard. The spectra were recorded in the range of the wavelength 190-850 nm. The samples were diluted with the pure silica (Fumed silica, Aldrich) in the ratio 1:100. All the samples were granulated and sieved to the fraction of size of 0.25-0.5 mm, dehydrated before the spectra measurement and oxidized in the glass apparatus under static oxygen atmosphere in two steps: 120 °C for 30 min and 450 °C for 60 min and subsequently cooled down to 250 °C and evacuated for 30 min. After the evacuation, the samples were transferred into the quartz optical cuvette 5 mm thick and sealed under vacuum. For additional details, see Ref. [18].

This procedure guaranteed a complete dehydration and defined oxidation state of vanadium for all catalysts. The obtained reflectance spectra were transformed into the dependencies of Kubelka–Munk function $F(R_\infty)$ on the absorption energy $h\nu$ using Eq. (1)

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (1)$$

where R_∞ is the measured diffuse reflectance from a semi-infinite layer [19]. All measured spectra were simultaneously fitted [16] by set of Gaussian curve shaped band using the fityk software [21]. Because all VO_x species exhibit the same or similar absorption coefficients [14], it is possible to make the semi-quantitative analysis of spectra.

Redox behaviour of VO_x surface species was investigated by the temperature programmed reduction by hydrogen (H_2 -TPR) using the AutoChem 2920 (Micromeritics, USA). Typically, 100 mg sample in a quartz U-tube microreactor was oxidized in oxygen flow at 450 °C (2 h) prior to the TPR measurement. The reduction was carried out from 100 to 900 °C with heating rate of 10 °C min^{-1} in the flow of reducing gas (5 vol. % H_2 in Ar). The changes in hydrogen concentration were monitored by the TCD detector.

The EPR spectra were measured on an Miniscope MS 300 spectrometer (ZWG Berlin) at X-band (ca. 9.5 GHz). Solid samples were measured in flat quartz cuvettes (width of 0.3 mm) at room temperature.

Catalytic Testing

The propane oxidative dehydrogenation (C_3 -ODH) reaction was carried out using a plug-flow fixed-bed reactor at atmospheric pressure in the kinetic region (independently checked) and steady state conditions of the reactions. The activity and selectivity of catalysts were tested at 540°C in the dependence on contact time (W/F 0.03, 0.06, 0.09, 0.12 and 0.15 $\text{g}_{cat} \text{min cm}^{-3}$). The demanded weight of catalyst (grains 0.25-0.50 mm) was mixed with 2 cm^3 of inert SiC. The catalysts were pre-treated in a flow of oxygen at 540 °C for 2 hours before each reaction run. The feed composition was $\text{C}_3\text{H}_8/\text{O}_2/\text{He} = 5/2.5/92.5$ vol. % with the total flow of 100 $\text{cm}^3 \text{min}^{-1}$ STP. The catalytic activity was analyzed at steady state conditions, and the products composition was analyzed by an on-line gas chromatograph Agilent 7890A Series equipped with TCD and FID detectors. The feed conversion, selectivity to products and productivity of the catalyst were calculated based on mass balance according to Sachtler and Boer [22]. The turn-over-frequency (TOF) values per V atom were calculated using Eq. (2)

$$\text{TOF}_x = \frac{n_{n-C}^0 X_{n-C} M_V}{m_{cat} w_V} \quad (2)$$

where n_{n-C}^0 is molar flow of propane (mol s^{-1}), X_{n-C} conversion of propane (%), M_V is atomic weight of vanadium (50.94 g mol^{-1}), m_{cat} is weight of catalyst (g), w_V is mass fraction of vanadium in catalysts.

Results and Discussion

Physico-chemical Properties of Catalysts

X-ray diffraction patterns of the materials obtained by XRD are presented in Fig. 1. In the case of MWW family of zeolites, the “fingerprint” region of the powder X-ray diffraction is between 5 and $10^\circ 2\theta$ when Cu $K\alpha$ radiation is used. Main reflections in this region centered at 7.2 , 8.1 and $10.2^\circ 2\theta$ are ascribed to planes (100), (101) and (102). Clear separation of (101) and (102) diffractions suggests well-ordered periodic structure. It is evident that the support structure (MCM-36) remains generally intact after vanadium deposition, except for the case of V_{ic} -36.

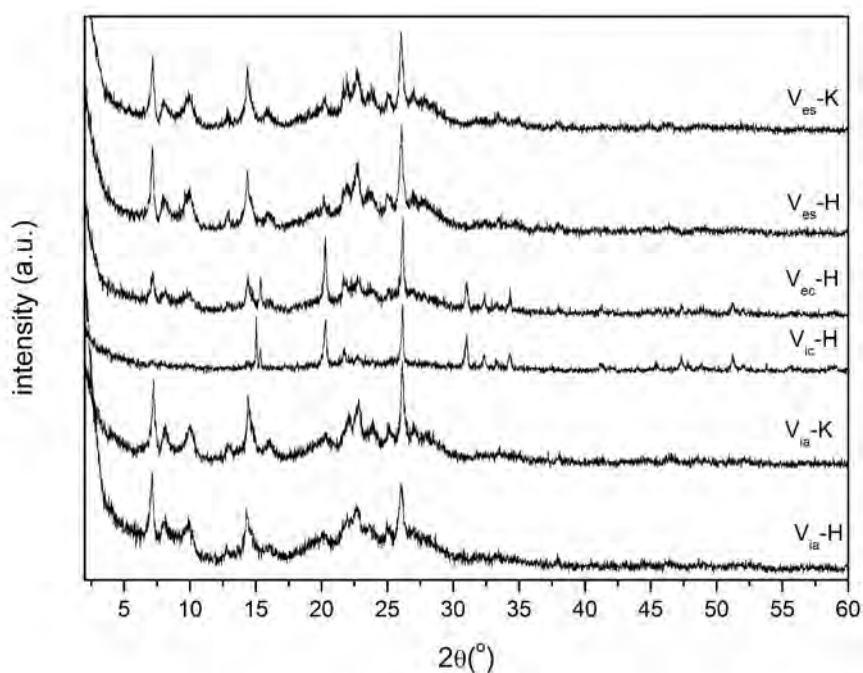


Fig. 1 X-ray diffraction patterns for VO_x -MCM-36 in different methods of synthesis

The diffraction peaks located between 5 and $10^\circ 2\theta$ disappear for this sample, indicating the destruction of the support structure. Also in the case of catalyst synthesized with the same precursor, but through the ion exchange method, diffraction lines lose the intensity probably due to the partial destruction of the support. In both cases, the diffractograms of the catalysts show diffraction peaks between 30° and $35^\circ 2\theta$, typical of the bulk vanadium; no other materials showed these peaks. It must be noted that the vanadium content is high for both V_{ec} -36

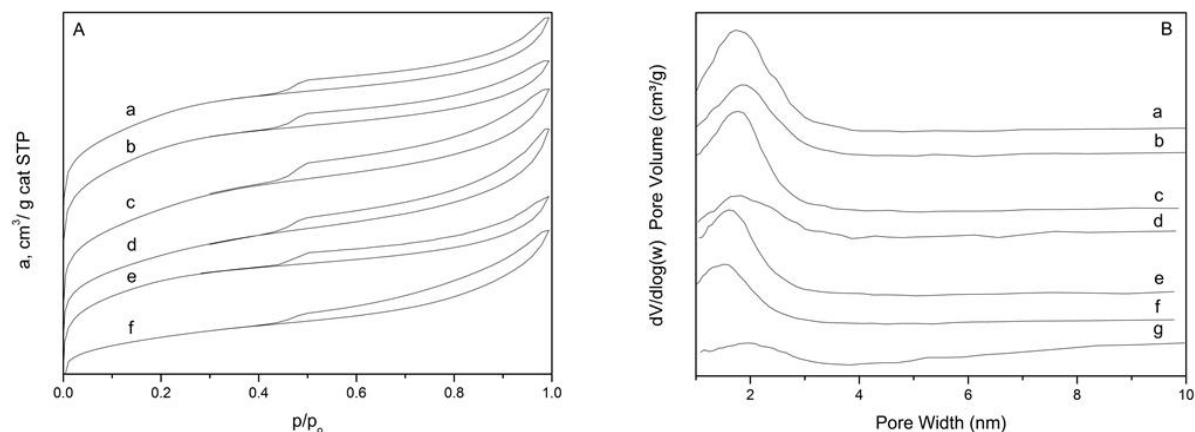


Fig. 2 (A) Nitrogen adsorption isotherms of vanadium catalyst: a – V_{es} -K; b – V_{es} -H; c – V_{ia} -H; d – V_{ic} -H; e – V_{ia} -K; f – V_{ec} -H. (B) pore size distribution calculated by BBJ of a – MCM-36; b – V_{ia} -H; c – V_{es} -H; d – V_{ec} -H; e – V_{es} -K; f – V_{ia} -K; g – V_{ic} -H

and V_{ic} -36 catalyst; therefore, the formation of V_2O_5 crystallites inside the micro/meso pores could be the reason for the blocking/destruction of the structure.

The textural data obtained from adsorption isotherms of nitrogen, e.g., the surface area, micropore and mesopore volumes and mesopore size distribution of each catalyst synthesized as well as the support are shown in Table I and Fig. 2. All isotherms exhibit an H4 hysteresis loop according to IUPAC classification. This type of hysteresis loop is usually related to slit-shape pores among plate-like particles (see Fig. 2A). This is in accordance with the morphology of studied samples (see SEM micrography in Fig. 3). The pore size distribution calculated by BBJ approach led to relative narrow distribution peak centered in the range from 1.8 to 2.2 nm for all samples (Fig. 2B); it agrees with typical distances of individual lamellas of MCM-36 obtained by pillaring. It is clearly seen that volumes of slit pores between lamellas substantially differ for individual samples depending on the methods of the synthesis and the content of vanadium. In the samples V_{ic} -H and V_{ec} -H, the intensity of the peaks is very low compared with the other samples, due to the destruction of support or obstruction of the mesopores by vanadium pentoxide. Very similar picture should be drafted for volume of micropores, which is decreasing with an increase in vanadium content. The highest volume of pores is found in the catalyst with 0.1 wt. % of content of vanadium. Change in pore volumes is in line with the changes in the specific surface area. Especially in the case of V_{ic} -H, the surface area drops drastically to $220 \text{ m}^2 \text{ g}^{-1}$, i.e., to 34 rel. % of original surface area of parent MCM-36 support (surface area $640 \text{ m}^2 \text{ g}^{-1}$).

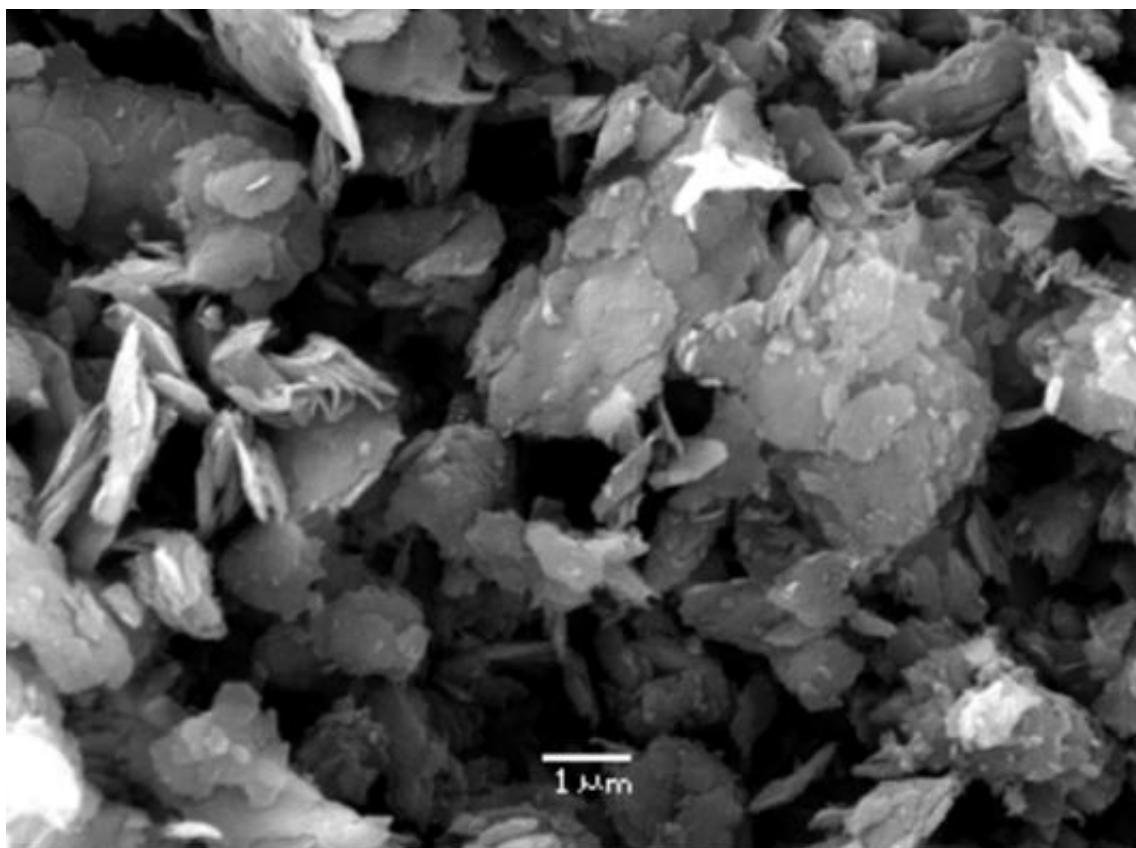


Fig. 3 SEM image of MCM-36 support

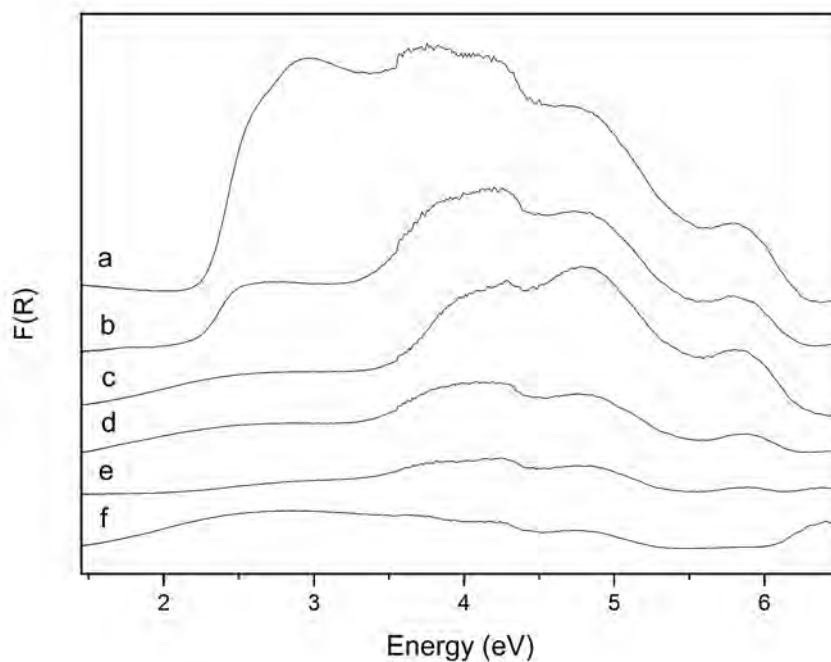


Fig. 4 Diffuse reflectance UV-vis spectra of vanadium based catalyst on MCM-36 prepared by various methods: a – V_{ic} -H; b – V_{ec} -H; c – V_{es} -K; d – V_{ia} -H; e – V_{ia} -K; f – V_{es} -H

The diffuse reflectance spectroscopy provides information on the oxidation state and the nature of the supported vanadium species. The different spectra obtained for the different synthesized samples are presented in Fig. 4. All the samples were analyzed in a dilution of 1:100 for obtaining a higher resolution of the spectra [19]. In the spectra, differences between the catalysts are observed. In the catalysts synthesized from acetate precursor and wherein the content of vanadium is higher (V_{ic} -H and V_{ec} -H), the spectrum is similar to those reported in earlier work on vanadium supported on various silica supports [23,24]. There are bands in the region 2.6-6.5 eV (460-190 nm), which are attributed to ligand to metal charge-transfer (LMCT) transition between O and V^{+5} . In the cases of samples with very high vanadium content, the spectra exhibit intense absorption bands at 2.6 and 3.1 eV attributed to the presence of 3D-octahedrally coordinated (group O) bulk-like units VO_x [19,25,26]. The samples with low content of vanadium (V_{ia-k} , V_{es} -H, V_{es} -K, V_{ia} -H) exhibited broad absorption bands or increase in background in the region of 1.55-2.07 eV, possibly caused by the d-d transition of the V^{+4} .

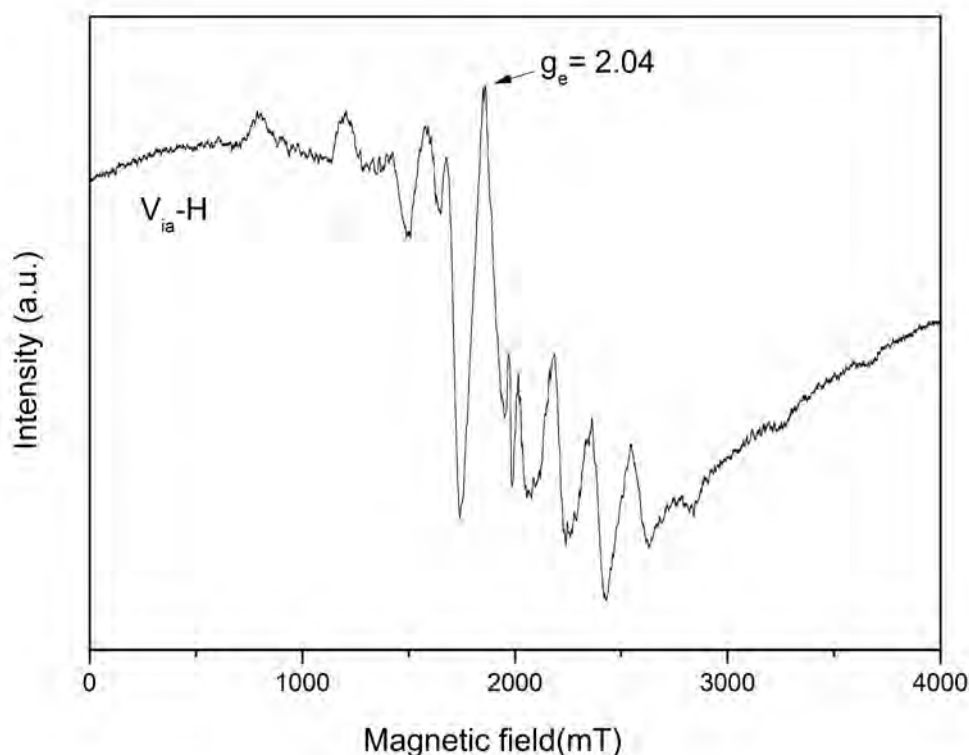


Fig. 5 EPR spectrum of V_{ia} -H sample

To confirm the existence of these species, EPR spectroscopy was performed on sample V_{ia} -H (Fig. 5). Anisotropic hyperfine structure with g value centered at 2.04 indicates the presence of the tetrahedrally coordinated V^{+4} atoms. The existence of V^{+4} ions in oxidized silica or alumina sample was sometimes mentioned in literature and explained by stabilization the vanadium oxidation state

when linked directly to the silicon or aluminum atoms [27,28]. Another explanation can be in suggestion of ion-exchange of vanadium into cationic sites of zeolite as a vanadyl cation $(VO)^{+2}$. For checking this possibility, IR spectra of OH group vibration were measured on selected samples exhibiting d-d transitions in their DR UV-vis spectra. As shown in Fig. 6, the blank spectrum of H-MCM-36 displays characteristic IR absorption bands at 3750 and 3627 cm^{-1} arising, respectively, from silanols and from bridged Si(OH)Al hydroxyl groups which constitute the zeolite Brønsted acid sites. The weak absorption band at 3675 cm^{-1} is ascribed to the AlOH species partially anchored to the zeolitic framework. After modification by vanadium, band at 3627 cm^{-1} almost completely disappears, which proves ion-exchange of vanadium into cationic sites instead of protons. Therefore, it is highly possible that presence of V^{+4} ions in the catalysts even after oxidation treatment is caused by stabilization of such oxidation state of vanadium by negative charged zeolite framework.

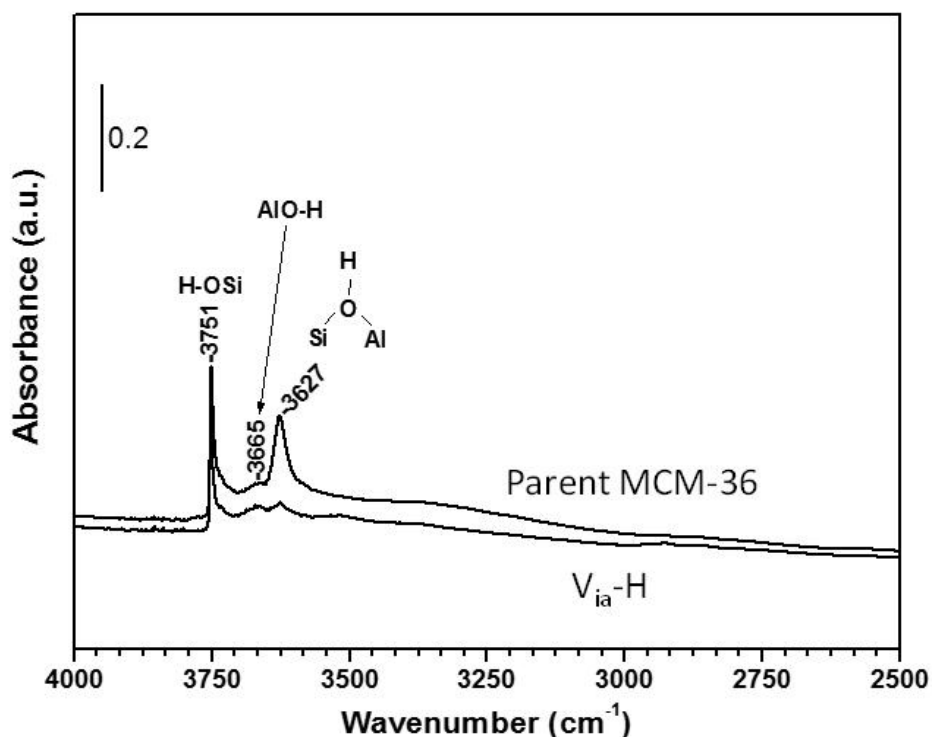


Fig. 6 FTIR spectra of OH group vibrations for parent MCM-36 zeolite and V-MCM-36 (V_{ia} -H)

The temperature-programmed reduction (TPR) was carried out with all synthesized samples. Figure 7 shows the H_2 -TPR curve of VO_x catalysts; it can be noted that the parent silica support exhibits no reduction peaks and, therefore, is not reported here for the sake of brevity. Supported vanadium catalysts exhibit different reduction peaks between 550 and 750 $^{\circ}\text{C}$. In the cases of V_{ia} -K and V_{ia} -H, they show the maximum reduction peak of about 570 $^{\circ}\text{C}$, due to the monomeric species population as it described in literature [29]. On the other hand, the samples

V_{ic} -H and V_{ec} -H show reduction peaks at higher temperatures due to their higher content of oligomeric species as proved by high intensity of bands at 4.0 eV in DR UV-vis spectra (*cf.* Fig. 4). Quantitative analysis reveals that average change of oxidation state is far from value of 2 which should correspond to quantitative reduction of V^{+5} to V^{+3} . Only samples with the highest vanadium content reached values around 1.8. Other samples exhibit values close to one, which suggests the reduction of V^{4+} to V^{3+} . Therefore, the TPR experiments also confirmed a significant amount of vanadium preserving the lower oxidation state under the oxidation pretreatment of samples in a good agreement with UV-vis, FTIR and EPR characterization. In the cases V_{es} -H and V_{es} -K, the intensity of the peak is very low due to the low content of vanadium in the material (> 0.1 wt %), and it is difficult to obtain clear information from the TPR profile. We are vigilant in conclusions drawn from TPR of samples V_{es} -H and V_{es} -K, due to very low intensity of reduction peaks but UV-vis and ESR spectroscopies indicate the presence of vanadium species in these samples, mainly in the form of V^{4+} species.

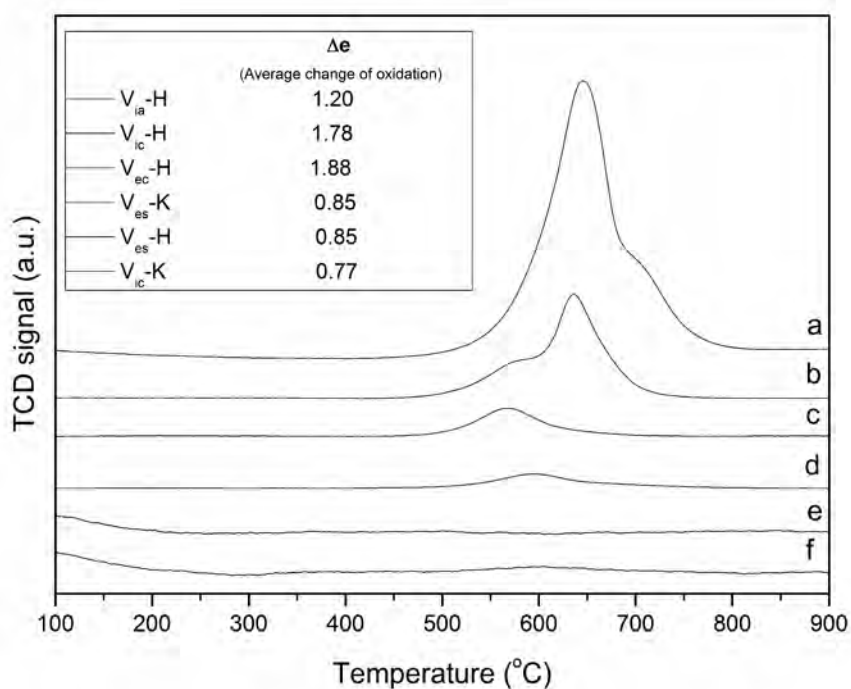


Fig. 7 H_2 -TPR patterns of VO_x -MCM-36 samples: a – V_{ic} -H; b – V_{ec} -H; c – V_{ia} -K; d – V_{ia} -H; e – V_{es} -H; f – V_{es} -K

Catalytic Activity in ODH of Propane

Oxidative dehydrogenation of propane over studied catalysts was investigated at 540 °C at various contact times realized by changes of catalyst weight. Main

results are presented in Table II. The main products of C₃-ODH were propene and carbon oxides. Traces of ethene and methane were detected as cracking products.

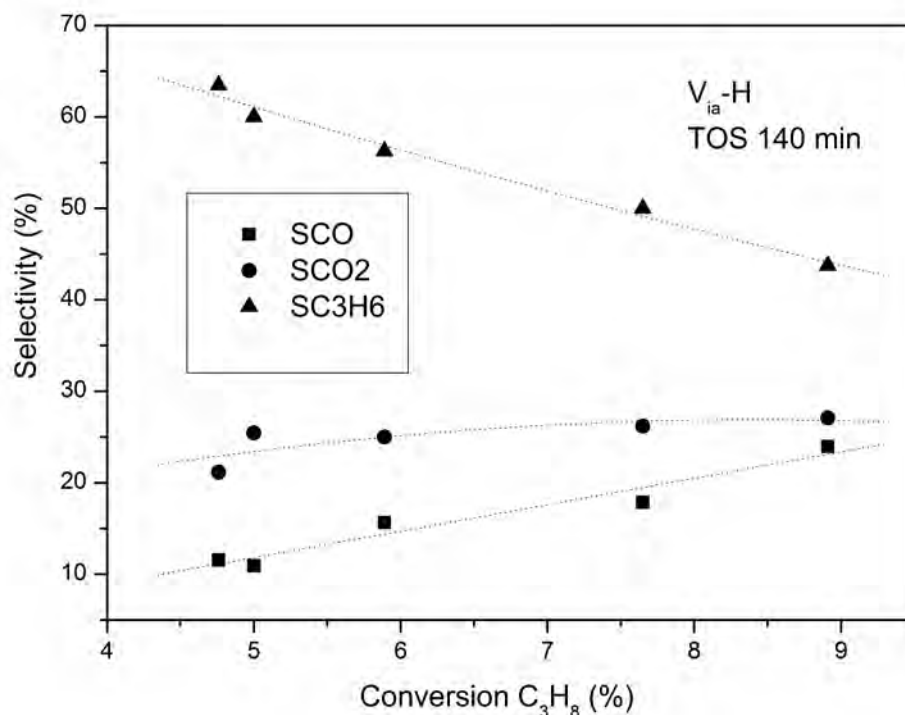


Fig. 8 Conversion versus selectivity of V_{ia}-H catalyst

No oxygenates were detected. The selectivity to CO, CO₂ and C₃H₆ is shown as a function of propane conversion over the sample V_{ia}-H in Fig. 8. The selectivity towards C₃H₆ slightly decreases with increasing propane conversion, whereas the selectivity to CO increases, as it is typical of a consecutive-parallel reaction net. Selectivity of CO₂ is almost constant with only minor changes. Such behaviour was observed by many researchers and is ascribed to the fact that carbon dioxide is formed by direct oxidation of propane, whereas CO originates from subsequent oxidation of propene. Similar behaviour was observed on all investigated catalysts. The samples with high content of vanadium, V_{ic}-H and V_{ec}-H, are the most pronounced cases of decrease in selectivity to propene; it passes from the 50 % of initial selectivity to C₃H₆ till around 20 % of selectivity at 13 % of conversion.

It is well-known that the selectivity is necessary to compare at the same degree of conversion for parallel-consecutive reaction such as the C₃-ODH reaction. Therefore, the catalytic behaviour of VO_x-silica catalysts with different vanadium loading and different texture of support was compared under iso-conversion conditions at propane conversion of 13 %. In addition, catalytic performance of the samples only slightly depend on time-on-stream (decline of propane conversion and propene selectivity was 1 and 2 %, respectively, within 4 hours in the stream).

The selectivity to propene is quite similar in all the cases, being about 25 %,

Table II Summary of catalytic performance of different systems in ODH reaction of propane to different products in iso-conversion at 13 %

Catalyst	X C ₃ H ₈	S CO	S CO ₂	S C ₃ H ₆	TOF	Yield
V _{ia} -H	13	35	31	26	4.1	5
V _{ic} -H	13	65.1	15	18.2	3.6	3
V _{ec} -H	13	52	19.7	23.3	8.3	3.1
V _{es} -H	13	36.6	29.2	26.5	88	3.5
V _{es} -K	13	43.4	18.2	25.6	88	3.3
V _{ia} -K	13	26.8	29.3	43.9	7.7	6

except for two cases. One, where the selectivity is somewhat lower than the rest, is sample V_{ic}-H, with the selectivity towards propene 18 %. The vanadium content in this catalyst is greater (18.8 wt %), and the original structure of the parent was destroyed during vanadium deposition leading to formation of a large amount of vanadium oxide clusters exhibiting very poor catalytic behaviour. The second case is the V_{ia}-K catalyst, which exhibits distinctively a higher selectivity to propene of 43.9 %. This is caused by the neutralization of the acid centers of the zeolite with the potassium cations by ion exchange, thus minimizing cracking processes, causing enhancement of diffusion of propene from the catalyst and probably some cooperation effect of vanadium and potassium; those cations can also be responsible for some interaction with the vanadium. For example, the temperature of reduction in the V_{ia}-K is lower than in the V_{ia}-H; maybe, the potassium prevents the agglomeration of vanadium species, but this is not clear, and more experiments and deepest study must be done for clear conclusion. Although this neutralization was also used in the sample V_{es}-K, in the lower concentration of vanadium in the resulting catalyst led to its worse catalytic performance.

The activity of VO_x-silica catalysts under these conditions was expressed by so called turn-over-frequency (*TOF*), describing the average number of catalytic cycles at one vanadium atom per time unit (h). Since we cannot be sure that all vanadium atoms are accessible from gas phase (especially in the case of high-content V-catalysts exhibiting frequent presence of oxidic clusters), here mentioned *TOF* values are “apparent *TOF*” — it means turn over frequency calculated by taking into account all vanadium atoms in the catalysts regardless of vanadium speciation and size of oxidic clusters. The *TOF* values obtained in the solids studied vary between 4.1 and 8.3, with two abnormal values with 88 h⁻¹, but these values are not real, since these samples were prepared by the method of ion exchange resulting in a very low content of vanadium. Therefore, the determination of vanadium content is inaccurate and, in addition, a lot of catalysts was used to reach the proper conversion, which can be a source of another effect,

e.g., not negligible activity of zeolite support and so on. All of these facts can be the reasons of a large error in the calculation of this term. The *TOF* value in MCM-36 catalyst type for ODH reaction of propane is around 6, in this present study, two samples were above this value, V_{ec} -H and V_{ia} -K, with 8.3 and 7.7 h⁻¹, respectively. In this study, the materials with vanadium in oxidation state IV, detected by UV-vis and EPR, obtained better results in terms of the yields of propene; in addition, the catalysts with high content in vanadium, V_{ic} -H and V_{ec} -H, have higher amount of oligomeric vanadium species, and the selectivity to CO₂ is higher than in the other cases. The decrease in selectivity with increasing VO_x concentration was most probably due to higher abundance of oligomeric species with T_d- and mainly O_h-coordination. These species contain the V–O–V bridging oxygen atoms and, according to the mechanism introduced by Kung [30], the presence of these units allows the formation of alkoxide intermediates which are further oxidized to the products of total oxidation.

Conclusion

Based on the data reported heretofore, we can conclude that insertion of vanadium ions into MCM-36 framework was successfully conducted, both *via* impregnation and ion-exchanging procedure of MCM-36 acid sites with VO²⁺ ions. Ion exchange of acid sites with VO²⁺ ions took place also in the case of impregnation method, probably during the thermal treatment (calcination), by means of solid state reaction between deposited vanadium compounds and Brønsted acid sites. Vanadium ions in ion-exchangeable sites retain lower oxidation states.

In the case of acidic MCM-36 catalysts, the ion exchange method gives better results for C₃-ODH catalytic reaction than the impregnation due to lowering of the Brønsted acid site amount and suppression of oligomeric and oxide-like species. The neutralization of acid sites by potassium before introduction of vanadium into MCM-36 support led to significant increase in selectivity to propylene with retaining the catalytic activity. This results in the catalyst with the highest yield of propylene. This increase in catalytic performance is ascribed to minimizing cracking processes, enhancement diffusion of propene from catalyst and probably some cooperation effect of vanadium and potassium.

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