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CATALYTIC BEHAVIOUR OF $VMoO_x$ CATALYSTS SUPPORTED ON HEXAGONAL MESOPOROUS SILICA IN PARTIAL OXIDATION OF BUTANE

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The vanadium oxide, molybdenum oxide and mixed vanadium-molybdenum oxide supported catalysts (1-2.5 wt % of vanadium and/or 1-2 wt % molybdenum on HMS (hexagonal mesoporous silica) were prepared by impregnation method. The prepared catalysts were studied by means of XRF, N_2-BET, UV-Vis spectroscopy, H_2-TPR and studied oxidative dehydrogenation (ODH) activity of butane. The mixed V-Mo oxide units were determined on the catalyst surface by H_2-TPR. The UV-Vis spectroscopy proved the presence of isolated tetrahedrally coordinated monomeric VO_x species and isolated tetrahedrally coordinated dimeric MoO_x species. The catalyst containing only VO_x species had the highest activity. The catalyst containing only MoO_x species was selective but of a very low activity. The highest selectivity (60 %) and productivity (0.35 $g_{prod}\, g_{kat}^{-1}\, h^{-1}$) were obtained with mixed $VMoO_x$ catalysts with the molar ratio 1 : 1.

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Introduction

The main task of today's chemical industry is production of a great amount of organic compounds. In the recent years it is very important to find alternative processes of production of these compounds from more economical raw compounds and with a smaller impact on environment. An example of such production is the usage of alkanes instead of alkenes. Alkanes are cheaper by half compared with alkenes and they are easily available [1].

The aim of this work is to study oxidation dehydrogenation (ODH) of butane to butenes and 1,3-butadiene. The industrial demand for these compounds shows a long term increase throughout the world. In the year 1984 the world production of butenes was 28.1 mil. tons [2]. In the year 2004 was production of butenes already 44 mil. tons [3]. Similar situation is in the case of 1,3-butadiene the production of which was 1.3 mil. tons in the year 1983 in USA [2] and nearly 2.1 mil. tons in 2000 [4].

The oxidation dehydrogenation (ODH) of butane is a possible alternative to dehydrogenation of butane avoiding its thermodynamic limitations. The ODH reaction can by written as

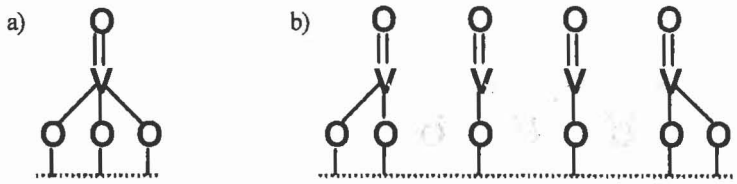
$$C_nH_{2n+2} + \frac{x}{2}O_2 \Rightarrow C_nH_{2(n-x+1)} + xH_2O$$

This reaction still has several unresolved problems which hinder its industrial application. The molecule of butane contains four carbon atoms enabling a lot of consecutive reactions. This makes it possible to form a lot of products, such as butadiene, butenes, furane, maleic anhydride, crotonaldehyde, acetic acid and many others as described in Ref. [5]. Moreover, the formed alkenes are approximately four times more reactive then butane [6], and this fact causes a selectivity decrease of desirable products with increasing butane conversion.

Vanadium-oxide based catalysts are very often used as catalysts in ODH reaction. Their employment offers several advantages: the lowest temperature for the activation of C-H bonds of reactants (limitation of cracking and combustion reactions), acceptable geometric and electron structure of VO_x (tunable with the used matrix, pressure or temperature). Hence, the vanadium-oxide catalysts are suitable for insertion of an oxygen atom into molecule hydrocarbon. But, vanadium-oxide catalysts cannot be used in their bulk form (this leads to noselective reactions) but as VO_x supported on an acceptable support (by us HMS – see below) [6,7].

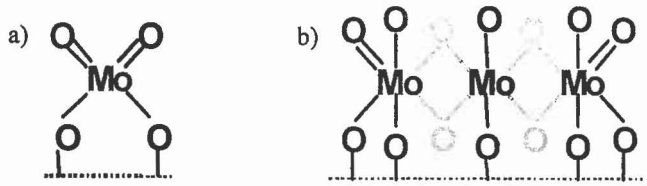
The VO_x particle can be present at the surface of catalysts in four different forms: highly dispersed isolated monomeric units with tetrahedral coordination $(sup–O)_3V=O$ (sup – atom of support) (type I — see Scheme 1), one-dimensional

oligomeric units connected by V–O–V bonds in distorted tetrahedral coordination (type II — see Scheme 1), two-dimensional polymeric units in octahedral coordination called oxide-like species (type III) and bulk three-dimensional V_2O_5 oxide (type IV). Tetrahedrally coordinated VO_4 species are usually considered as active and selective particles. The strength of the sup-O bond and, hence, acid base properties of the support significantly influence the selectivity [6,8].



Scheme 1 Vanadium oxo-species on the surface a) isolated monomeric units with tetrahedral coordination (type I), b) one-dimensional oligomeric units connected by V–O–V bonds in distorted tetrahedral coordination (type II)

Albonetti [9] in his review describes the highly selective properties of molybdenum oxide. Molybdenum oxide is less reactive than vanadium oxide but it increases selectivity for ODH products. In the case of molybdenum oxide supported on the silica matrix, three different centers can be observed, analogous to supported vanadium oxide. The isolated tetrahedral coordinated particles can be taken as active and selective centers $(sup–O)_2Mo(=O)_2$ (see Scheme 2). The formation of dimeric and/or polymeric hexagonal coordinated species is expected to occur at higher oxide content.



Scheme 2 Molybdenum oxo-species on the surface a) isolated tetrahedral coordinated units, b) one-dimensional oligomeric units

It seems to be a good idea to connect benefits of both and create new catalysts with high selectivity and activity. Dejoz and Nieto [10] studied V-Mo oxide catalysts on the MgO support, and they found that molybdenum oxide induced a change of the number of active centers (vanadium content decreased with increased molybdenum content). Molybdenum oxide caused also a decrease in the reducibility of active centers on the support (decrease in activity). A better

activity over these catalysts was obtained at a higher temperature (molybdenum needs a higher operation temperature for its activation).

The mixed V-Mo-O catalysts anchored on the hexagonal mesoporous silica (HMS) were used for studying butane ODH reaction in this work. The HMS-supported catalysts have the following advantages: larger surface area (a good dispersion of active particles), thermal stability, good mechanical properties, weak acid centers (acceptable for our reaction), one-dimensional open channels with 35-40 Å pore diameter (easy delivery of products) [11,12].

We will try to prepare a new mixed vanadium molybdenum oxide with the following characteristics: The dimeric mixed oxide units will be composed of one vanadium atom (determining factor of activity) and one molybdenum atom (determining factor of selectivity) analogous to isomorphous MoO_x units.

Experimental

Preparation of Catalysts

The synthesis of hexagonal mesoporous silica (HMS) was based on the procedure reported by Tanev [13]. HMS was prepared by dissolving 19.3 g dodecylamine (DDA, Aldrich) in mixture of 225 ml absolute ethanol (abs-EtOH) and 200 ml re-distilled water (re-H_2O). The mixture was stirred for 20 min, whereupon 56 ml tetraethylorthosilicate (TEOS, Aldrich) was added dropvise. The reaction was performed at RT for 18 hours under static conditions. The reaction product was collected by filtration, washed two-times with 500 ml EtOH and dried at 120 °C for 14 hours. The dry products were finally calcined at 450 °C for 20 hours in dry air stream. The vanadium-based or molybdenum-based catalysts were prepared by impregnation of HMS with solution of vanadyl(IV) acetylacetonate ($VO(acac)_2$) or bis(acetylacetonato)-dioxomolybdenum(VI) ($MoO_2(acac)_2$) in 50 ml ethanol. The catalysts were collected by filtration and dried for 14 hours at 120 °C after impregnation. The calcination was carried out for 8 hours at 600 °C in air stream. The samples prepared were granulated at a pressure of 35 MPa and sieved to obtain the grain fraction of 250-500 μm after the calcination.

Characterization of Catalysts

The vanadium content was determined by means of XRF using Spectroscan V equipped with Pd anode (Spectron Optel, Russia); the samples were diluted with H_3BO_3 (p.a.) and pressed into pellets (for details, see Ref. [14]) before measurement.

The surface area was determined by nitrogen adsorption at 77 K using the

through-flow method at the relative pressure of nitrogen in the range of 0-0.33 [14].

The redox behaviour of VO_x and MoO_x species on V-HMS, Mo-HMS or V-Mo-HMS was tested by means of hydrogen temperature programmed reduction (H_2-TPR). A 100 mg granuled sample in a quartz U-tube microreactor was oxidized in oxygen flow at 450 °C for 2 hours. The temperature was increased from room temperature to 950 °C with a temperature gradient of 10 °C min^{-1} in the flow of reduction gas (5 vol % H_2 in Ar). The changes of hydrogen concentration were monitored by means of TCD detector (Regom). The data were evaluated in the OriginPro 7.5 software (OriginLab Corp.) [14].

The UV-Vis spectroscopy was used to distinguish different vanadium and molybdenum oxo-species in the catalysts. The UV-Vis diffuse reflectance spectra of dehydrated granulated samples were recorded using CINTRA 303 (GBS) spectrometer equipped with a diffuse reflectance attachment with a $BaSO_4$-coated integrating sphere against a $BaSO_4$ reference. The reflectance was re-calculated to the Kubelka-Munk units using the equation $F(R_\infty) = (1-R_\infty)^2/2R_\infty$, where R_∞ is the diffuse reflectance from a semi-infinite layer. The dehydration of samples was carried out in two steps: 120 °C for 30 min at reduced pressure ($p < 70$ Pa) and 450 °C for one hour at a low pressure of oxygen (13 300 Pa). After the dehydration, the samples were cooled down to room temperature and transferred into the optical cell of 55 mm thickness under vacuum.

Catalytic Tests in ODH Reaction

The butane oxidative dehydrogenation (ODH) reaction was carried out in a glass plug-flow fixed-bed reactor at atmospheric pressure at steady state conditions. Typically, 400 mg catalyst (grains 0.25-0.50 mm) was diluted with 3.17 g inert SiC to avoid the catalytic bed overheating. The catalysts were pre-treated with a flow of oxygen at 450 °C for 2 hours before each reaction run. The input feed composition was $C_4H_{10}/O_2/He$ = 10/10/80 vol.% - with a total flow rate of 100 ml min^{-1} (W/F = 14.94 g_{cat} h $(mol\text{-}C_4)^{-1}$). The catalytic activity was compared in the range of 460-540 °C at the steady state conditions. The composition of the input feed and the reaction products was analyzed by on-line gas-chromatograph CHROM-5 (Laboratorní přístroje Prague) equipped with a thermal conductivity detector (TCD). Butane and the products of ODH reaction (butadiene, 1-butene, *cis*-2-butene, *trans*-2-butene, propene and propane) were separated using a packed column with *n*-octane on Durapak (3 mm × 3.5 m) (Restek) cooled with water to 20 °C. The packed column Porapak Q (3 mm × 3,5 m) (Supelco) was used for the analysis of ethane, ethene, CO_2 and acetaldehyde. The molecular sieve 13 X (3 mm × 3,5 m) (Supelco) was used for the separation of permanent gases.

Results and Discussion

Catalyst Characterization

The correct value of metal (V, Mo) content of several catalysts was determined by means of XRF technique and the values obtained are summarized in Table I. The observed discrepancy between theoretical and experimental values is probably caused by the loses of vanadium during the annealing procedure.

Table I Physico-chemical properties of V and/or Mo oxides supported on hexagonal mesoporous silica (HMS); metal content, specific surface area of support and catalyst, surface density of active particle and characteristic of H_2-TPR reduction profile

Sample	V content		Mo content		S_{BET}
	wt %	mol. %	Wt %	mol %	$m^2 g^{-1}$
HMS_1	0	0	0	0	704.67
HMS_2	0	0	0	0	620.93
1.22V-HMS	1.20	1.41	0	0	648.43
2.03Mo-HMS	0	0	2.03	1.28	632.08
1.08V-2.05Mo-HMS	1.08	1.28	2.05	1.29	631.29
1.13Mo-HMS	0	0	1.13	0.71	628.37
1.11V-1.05Mo-HMS	1.11	1.31	1.05	0.66	447.18
2.36V-1.01Mo-HMS	2.36	2.78	1.01	0.63	352.24
2.55V-HMS	2.55	2.99	0	0	615.68

Sample	θ^a, particle nm^{-2}		TPR results[b]	
	V	Mo	T_M, °C	AOS
HMS_1	0	0	–	–
HMS_2	0	0	–	–
1.22V-HMS	0.22	0	562.4	2.09
2.03Mo-HMS	0	0.20	901.6	–
1.08V-2.05Mo-HMS	0.20	0.20	568.2	2.31
1.13Mo-HMS	0	0.11	941.8	–
1.11V-1.05Mo-HMS	0.29	0.15	554.0	1.79
2.36V-1.01Mo-HMS	0.79	0.18	564.6	2.09

Table I — Continued

2.55V-HMS	0.49	0	564.6	1.50

[a] VO_x and MoO_x surface density was calculated as in Ref. [25]

[b] temperature of the maximum hydrogen consumption (T_M) and change oxidation state (COS) at reduction

The specific surface area values (given also in Table I) were measured by the N_2 adsorption and calculated by the Brunauer–Emmet–Teller (N_2-BET) method. The specific surface areas of HMS matrixes were 704 and 621 $m^2 g^{-1}$. These values are comparable with those literature [15], namely 650 $m^2 g^{-1}$. However, some papers give higher values of specific surface area, 866 $m^2 g^{-1}$ [16] and 1 021 $m^2 g^{-1}$ [17]. It can be observed that surface areas of catalysts decrease with increasing coverage metal amount. The maximum decrease was observed in the case of the sample 2.36V-1.01Mo-HMS (352 $m^2 g^{-1}$), 42 % compared to the pure matrix (621 $m^2 g^{-1}$). This area reduction is less than in the catalysts containing only vanadium (3.2 wt % — decrease about 53 % [18]). These values show that changes of the surface area were induced mostly by vanadium oxide particles. VO_x species more likely form various clusters and bulk oxides which cause blocking of pores in HMS, as compared with the molybdenum oxide particles. This theory is in agreement with the following experimental data: for 1.2 wt % vanadium the decrease is about 8 %, but an almost double amount of molybdenum (2.03 %) causes the decrease of only 10 %, and this value is in good agreement with results in Ref. [19] where 2 % of anchored molybdenum oxide caused a 9.3 % decrease in the surface area of the MCM-41 support.

The surface particles density (particle nm^{-2}) represents a parameter that allows comparing catalysts in a wide range of metal oxide concentration and specific surface area. It is possible to presume (understand) the type of coverage and dispersion of particle based on this value. Wachs [20] suggested a value 0.7 VO_x nm^{-2} for isolated monomeric units on the amorphous silica. The maximal surface density of VO_x particles in our catalysts was 0.77 particle nm^{-2}, which is an indication that all the vanadium species are well dispersed on the surface of the HMS support. These results were confirmed also by the H_2-TPR and UV-Vis spectroscopy. The surface density of MoO_x particles was comparable with the values shown by Lou [21] on the SBA-15 surface. Lou [8] also stated that a dispersed isolated monomeric species should dominate up to 0.45 MoO_x nm^{-2} and 5 wt. % Mo. Our samples contained less than 0.2 MoO_x nm^{-2} at 2 wt.% Mo and, hence, MoO_x should be present as isolated monomeric species.

The H_2-TPR profiles were measured to compare the redox properties and determine the amount (scale) dispersion and type of the present active species for all prepared samples. It can be seen in Fig. 1 that all V-containing catalysts have one sharp peak with a maximum around 560 °C. The results of the TPR

experiments are summarized in Table I including the calculated average change of the oxidation state of VO_x species. These results are in good agreement with the results presented in the literature [15], where the maximum first peak is around 570 °C. The VO_x TPR peak should be related to the reduction of highly dispersed tetrahedral vanadium species [22] reduced from oxidation state V^{5+} to oxidation state V^{3+}.

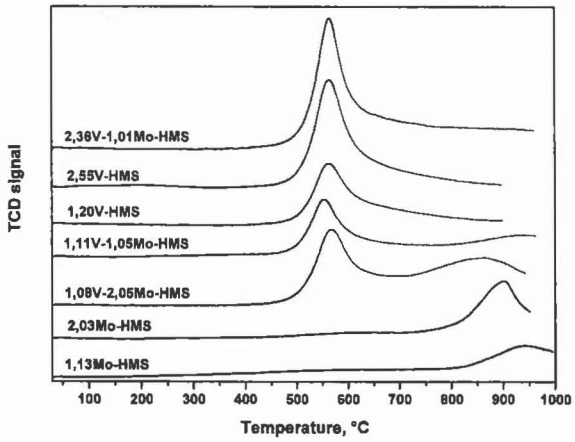


Fig. 1 The H_2-TPR spectra of VO_x, MoO_x and $VMoO_x$ catalysts on HMS supports

The samples containing only molybdenum oxide species have also one significant peak which can be attributed to the reduction of molybdenum species at intervals from 860 °C to 950 °C. The temperature of peak maximum decreases with increasing concentration of molybdenum species, see Table I. Lou [8] attributes these peaks to isolated monomeric MoO_x particles because theirs interaction with support are strongest. This was also confirmed by Arena [23], who suggested that reducibility progressively decreases in the order: polymolybdates (< 400 °C) > MoO_3 crystallites (500-800 °C) > isolated tetrahedral molybdates (T > 800 °C). The potential peaks of oligomeric or bulk particles which should be present at lower temperatures were not observed. Therefore, on the basis of TPR we presume that all the molybdenum is also well dispersed on the surface of HMS the matrix.

We can see a flattening of molybdenum peaks of mixed catalysts (Mo-V-HMS) compared to reduction peaks of only molybdenum catalysts with the same amount of molybdenum oxide. Moreover, there is a perceptible shift of molybdenum oxide peak maximum to the lower temperature but at retained position of vanadium oxide peak. This shift is probably caused by the formation of mixed $VMoO_x$ unit [24]. The reduction of molybdenum in these compounds proceeds after reduction of vanadium species, nevertheless at lower temperatures than the reduction of pure MoO_x species. The formation of this compound causes

a shift and flattening of reduction peaks of molybdenum oxide species.

Diffuse reflectance UV-Vis spectroscopy provides information about the nature and oxidation state of vanadium and molybdenum oxo-species. UV-Vis spectra of vanadium-based catalysts are characterized by charge-transfer transition of the $O \rightarrow V^{n+}$ type (typical for oxidized forms) and d-d transition of V^{n+} (typical for reduced forms) [25].

The bands corresponding to d-d transitions (region 600-800 nm characteristic for reduced species) were not observed in our UV-Vis spectra. This is in good agreement with the H_2-TPR results (see above). All the catalysts containing only vanadium oxide exhibit absorption with a maximum in the range of 200-300 nm (Fig. 2). The UV-Vis spectra are a superposition of three bands with the maximum at 215, 250 and 280 nm. These bands could be attributed to the isolated monomeric tetrahedral vanadium species [9,12,26]. At a higher concentration (2.36 and 2.55 wt % of vanadium), a slight bathochromic shift of the bands can be observed. This can be explained by the presence of a small amount of oligomeric distorted tetrahedral VO_x species with the absorption band at 315 nm [9].

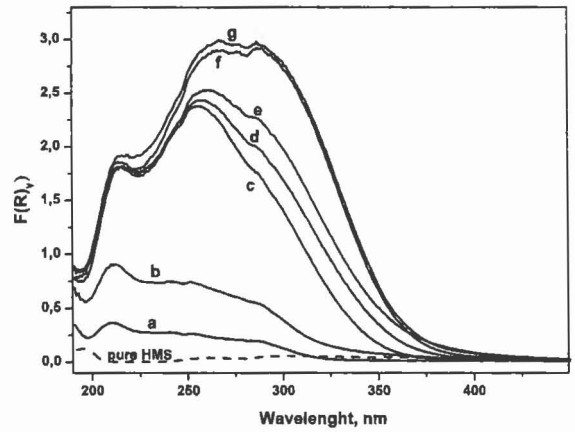


Fig. 2 The UV-Vis spectra of 1.13Mo-HMS (a), 2.03Mo-HMS (b), 1.11V-1.05Mo-HMS (c), 1.20V-HMS (d), 1.08V-2.05Mo-HMS (e), 2.55V-HMS (f), 2.36V-1.01Mo-HMS (g) and pure HMS matrix

In the case of samples containing only molybdenum oxides three absorption bands (Fig. 2) can be seen. Their maxima are at 213, 253 and 298 nm. The absorption bands between 215 and 300 nm can be attributed to isolated MoO_x species [8,27]. The bands above 300 nm show the presence of the oligomeric species with Mo-O-Mo bonds. Melero [28] and Weber [29] attributed the band about 250 nm to isolated dimeric tetrahedrally coordinated species. Graphic representation of Tauc's law [30] — the dependence of $(F(R_\infty)\, h\upsilon)^2$ (where $F(R_\infty)$

is Kubelka–Munk function) on energy (eV) can be used to determine the type of particles present on the surface of HMS matrix. It can be clearly seen in Fig. 3 (generated from Weber's [16] and our data) that our materials contain also mainly the dimeric tetrahedrally coordinated MoO_x. This observed fact is in contradiction to our results obtained from the H_2-TPR method and analysis of the surface density of molybdenum oxide. Therefore, we assume that the H_2-TPR technique is not sufficiently sensitive for determination of detailed character of molybdenum oxide species. Also unreliable is the determination of character of dispersed MoO_x species based on the surface density of MoO_x and wt.% MoO_x. The strong overlapping of molybdenum bands by more intense vanadium bands makes it impossible to correctly interpretate the V-Mo-O mixed oxides spectra by similar method.

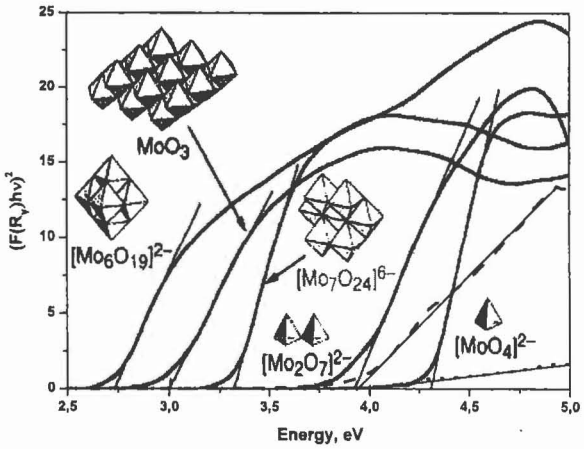


Fig. 3 The UV absorption edge of standard compounds given in Ref. [29] and two our catalysts 1.13Mo-HMS (•••••) a 2.03Mo-HMS, (- - -)

Oxidative Dehydrogenation of Butane

Several ODH measurements were carried out at three different temperatures to compare catalytic activity of the prepared catalysts. The activity of catalyst was stable at least 10 hours time-on-stream (TOS). No catalyst coking was observed during the catalytic tests.

The influence of HMS on the catalyst activity was checked using an unloaded HMS matrix in the reactor with silicium carbide. No activity was observed up to 540 °C. Only 5 % of activity was reached at 540 °C. This conversion is remarkably lower in comparison with the conversions reached on the catalysts used. Nevertheless, the presence of reactions in homogenous phase was proved after initialization by matrix, which is in accordance with the results

published previously [31].

The ODH reaction of butane the over investigated catalysts provided the following products: butadiene, but-1-ene, *cis*- and *trans*-but-2-ene, propene, propane, ethene, ethane, methane, acetaldehyde and carbon oxides.

It is evident from the temperature dependence (Fig. 4) of catalyst activity of 1.08V-2.05Mo-HMS in ODH of butane that the conversion was increased with increasing temperature as well as production of C_4-ODH hydrocarbons. The values of C_4-ODH selectivity are around 60 % and decline with increasing temperature. The C_4-ODH selectivity lowering is given by increasing selectivity to CO_x and cracking products, mainly propene, ethene and trace amounts of propane, ethane and methane. A similar dependence is also observed with the other catalysts — see Table II and Fig. 5.

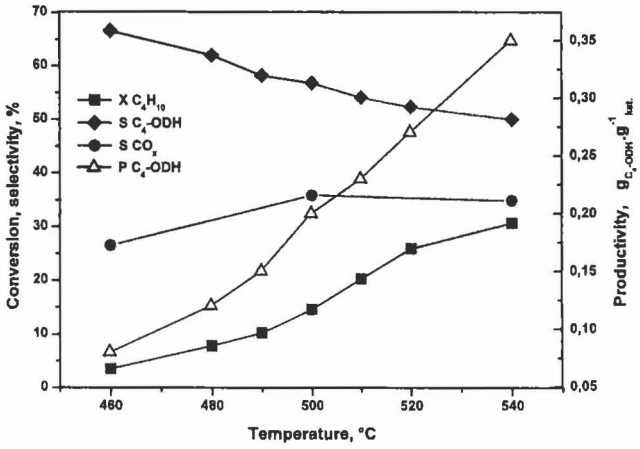


Fig. 4 Temperature dependence of catalyst activity for sample 1.08V-2.05Mo-HMS in ODH of butane

In Table II it can be seen that the highest activity (conversion) is observed at the catalysts based on vanadium oxide only, while the catalysts based on molybdenum oxide exhibited very low activity and, moreover, this activity can be caused by reaction in homogenous phase after activation of HMS matrix (see above).

Furthermore, it can be observed that the catalysts based on molybdenum oxide only show higher selectivity than those based on vanadium oxide only. However, the yields are low due to the low conversion (no reaction below 500 °C), which limits their potential application in the industry. The catalysts based on molybdenum can only be used in the production of butadiene from butenes by ODH where the activation energy of reaction is lower than that for butane [9]. The same behaviour was described by Dejoz [10] who studied a similar system on MgO matrix.

Table II Catalytic properties of Mo, V and V-Mo catalysts on HMS support in ODH of butane[a] at 460, 500 and 540 °C, respectively

Sample	Conversion, % butane	Selectivity, %				
		CO_x	C_2	C_3	1-C_4H_8	1-*c*-C_4H_8
T = 460 °C						
1.22V-HMS	4.5	45.5	2.0	1.5	17.4	7.4
2.55V-HMS	16.9	45.6	1.2	1.1	16.3	6.9
1.13Mo-HMS	0.0	0.0	0.0	0.0	0.0	0.0
2.03Mo-HMS	0.9	43.5	6.4	4.1	21.5	6.9
1.11V-1.05Mo-HMS	2.4	18.9	0.9	1.5	26.2	11.8
1.08V-2.05Mo-HMS	3.5	26.5	0.7	2.9	24.8	10.3
2.36V-1.01Mo-HMS	4.1	45.8	0.9	1.2	16.2	6.6

Sample	Selectivity, %			Yield, %	Productivity	
	2-*t*-C_4H_8	C_4H_6	∑ODH[b]	∑ODH[b]	C_4H_6	∑ODH[b]
T = 460 °C						
1.22V-HMS	2.6	18.9	46.3	2.3	0.03	0.07
2.55V-HMS	1.8	18.8	43.8	4.7	0.07	0.16
1.13Mo-HMS	0.0	0.0	0.0	0.0	0.00	0.00
2.03Mo-HMS	3.4	14.2	46.0	0.4	0.00	0.01
1.11V-1.05Mo-HMS	2.6	33.8	74.4	2.6	0.04	0.09
1.08V-2.05Mo-HMS	5.4	26.1	66.6	2.5	0.03	0.08
2.36V-1.01Mo-HMS	1.4	20.3	44.6	2.1	0.12	0.07

Sample	Conversion, % butane	Selectivity, %				
		CO_x	C_2	C_3	1-C_4H_8	1-*c*-C_4H_8
T = 500 °C						
1.22V-HMS	12.5	51.6	2.3	2.1	14.5	5.8
2.55V-HMS	28.1	52.9	1.4	1.1	14.1	5.7
1.13Mo-HMS	2.5	21.9	4.5	9.0	17.4	7.0
2.03Mo-HMS	5.0	24.4	4.7	7.8	19.3	9.8
1.11V-1.05Mo-HMS	8.5	25.4	2.3	3.1	25.8	8.7

Table II — Continued

Sample	Conversion, % butane	Selectivity, %				
		CO_x	C_2	C_3	1-C_4H_8	1-*c*-C_4H_8
1.08V-2.05Mo-HMS	14.6	35.9	1.2	2.5	21.6	7.9
2.36V-1.01Mo-HMS	14.6	50.2	1.3	3.4	13.7	6.6

Sample	Selectivity, %			Yield, %	Productivity	
	2-*t*-C_4H_8	C_4H_6	∑ODH[b]	∑ODH[b]	C_4H_6	∑ODH[b]
T = 500 °C						
1.22V-HMS	3.1	17.4	40.8	4.3	0.06	0.14
2.55V-HMS	2.7	16.3	38.8	8.3	0.12	0.27
1.13Mo-HMS	12.5	27.7	64.6	1.2	0.02	0.04
2.03Mo-HMS	3.4	29.3	61.7	1.5	0.02	0.05
1.11V-1.05Mo-HMS	2.3	26.2	63.0	4.8	0.07	0.16
1.08V-2.05Mo-HMS	3.4	23.9	56.8	6.1	0.08	0.20
2.36V-1.01Mo-HMS	2.8	26.2	39.3	5.2	0.03	0.17

Sample	Conversion, % butane	Selectivity, %				
		CO_x	C_2	C_3	1-C_4H_8	1-*c*-C_4H_8
T = 540 °C						
1.22V-HMS	17.7	51.5	6.3	4.1	10.4	5.1
2.55V-HMS	35.9	49.7	3.5	1.5	11.8	6.1
1.13Mo-HMS	12.6	22.5	11.7	15.6	17.8	6.8
2.03Mo-HMS	10.4	14.1	15.7	21.2	19.9	7.0
1.11V-1.05Mo-HMS	23.9	21.1	6.1	6.3	23.8	8.1
1.08V-2.05Mo-HMS	30.7	34.9	5.5	4.0	19.5	6.5
2.36V-1.01Mo-HMS	27.4	43.2	5.4	4.2	14.1	6.3

Sample	Selectivity, %			Yield, %	Productivity	
	2-*t*-C_4H_8	C_4H_6	∑ODH[b]	∑ODH[b]	C_4H_6	∑ODH[b]
T = 540 °C						
1.22V-HMS	4.6	15.5	35.6	5.3	0.08	0.18

Table II — Continued

Sample	Selectivity, %			Yield, %	Productivity	
	2-*t*-C_4H_8	C_4H_6	∑ODH[b]	∑ODH[b]	C_4H_6	∑ODH[b]
2.55V-HMS	5.3	18.5	41.7	12.3	0.18	0.41
1.13Mo-HMS	3.3	21.5	49.4	4.1	0.06	0.14
2.03Mo-HMS	3.0	19.1	48.9	4.4	0.06	0.15
1.11V-1.05Mo-HMS	4.2	23.9	60.0	9.9	0.13	0.33
1.08V-2.05Mo-HMS	4.7	19.3	50.0	10.5	0.13	0.35
2.36V-1.01Mo-HMS	4.3	16.8	41.5	8.9	0.07	0.29

[a] reaction conditions: $W/F = 14.94\ g_{cat}\ h\ (mol\text{-}C_4)^{-1}$

[b] Total selectivity, yield or productivity to butenes and butadiene

[c] Productivity: $g_{prod}\ g_{cat}^{-1}\ h^{-1}$

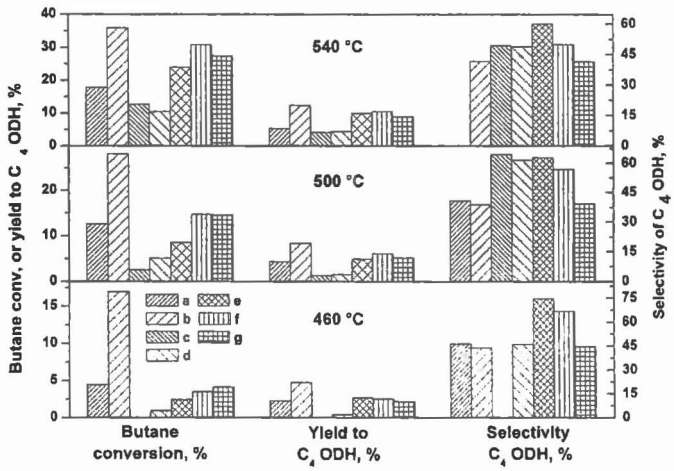


Fig. 5 The butane conversion and the yield and selectivity to C_4-ODH products for all investigated catalysts at three different temperatures. The input feed composition was $C_4H_{10}/O_2/He = 10/10/80$ vol % and $W/F = 14.94\ g_{cat}\ h\ (mol\text{-}C_4)^{-1}$

Mixed oxide catalysts exhibited interesting behaviour in catalytic tests. The conversion degree was relatively high, roughly 30 % at 540 °C. High values of selectivity for the desiable C_4-ODH hydrocarbons (40 to 60 %) were reached over all tested mixed V-Mo-O samples. This behaviour can be explained as follows. Vanadium oxide in these catalysts operates as an active component on which activation of butane occurres. Less active MoO_x species are more selective for C_4-ODH products due to lower reducibility. They participate in following steps of reaction mechanism and, moreover, molybdenum species can stabilize vanadium

species within dimeric units preventing them to form higher oligomers.

We can see differences in values of conversion and selectivity with respect to the individual products as well as in catalyst productivity of the prepared mixed V-Mo-HMS catalysts. The highest selectivity was reached over 1.11V-1.05Mo-HMS catalyst. This could be caused by creation of mixed oxide of $VMoO_x$ which probably plays the role of most active and selective active species. The selectivity of this catalyst over C_4-ODH is 60 % at 540 °C, which is at least about 10 % more than for other our catalysts. Dejoz [10] indicates similar values of selectivity for his Mo-V catalysts on MgO matrix. Also selectivities to C_4-ODH over other mixed catalysts (1.08V-2.05Mo-HMS and 2.36V-1.01Mo-HMS) are relatively high — roughly 50 % and 43 % at 540 °C. These values are comparable to selectivity values reported in Ref. [10].

The C_4-ODH productivity, which gives the amount of products over the amount of the catalyst is another possible criterion for the comparison of various catalysts. In Fig. 6, the dependence of butane conversion and C_4-ODH productivity on the molar ratio V:Mo is presented. The highest conversion and yield was reached using the catalyst with molar ratio V:Mo equal to 1:1. The observed effect can also be ascribed to active site with the same amounts of active species $(sup–O)_3V{=}O$ and $(sup–O)_3Mo(=O)_2$, where VO_4 acts as an activating particle and MoO_5 puts double bond into the activated molecule.

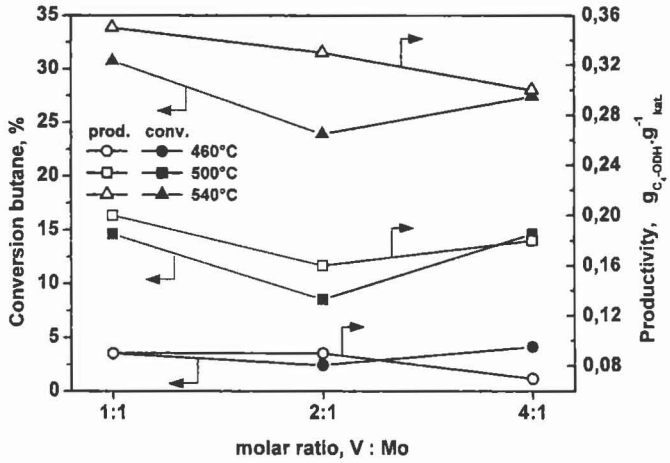


Fig. 6 Dependence of butane conversion and productivity C_4-ODH products of the mixed $VMoO_x$ catalysts at three different temperatures on vanadium-molybdenum molar ratio

Conclusion

- The vanadium-oxide species are anchored mainly as tetrahedrally coordinated units on the surface of HMS support. The catalysts containing only vanadium-oxide are very active in the C_4-ODH reaction.
- The addition of molybdenum has no radical influence on the HMS support structure properties. The MoO_x species are anchored to surface of the support mainly as dimeric tetrahedrally coordinated units. The tendency of vanadium-oxide to create oligomeric or bulk oxide species was not increased by the presence of molybdenum oxide at the mixed oxide catalysts.
- The formation a mixed V-Mo oxide can occur at a suitable molar ratio. The presence of this compound has positive influence on the reducibility of MoO_x.
- The catalysts based only on molybdenum oxide have very low activity in the ODH of butane.
- The C_4-ODH productivity and selectivity obtained with application of the mixed oxide catalysts is higher than that obtained with application of the catalysts based merely on vanadium oxide or merely on molybdenum oxide. The best results were obtained over the catalyst with the molar ratio V : Mo = 1 : 1.
- Monomeric vanadium oxide and mixed V-Mo-O species can by marked as active catalytic sites.

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