Vanadium dispersion and catalytic activity of Pd/VO_x/SBA-15 catalysts in the Wacker oxidation of ethylene

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Abstract

Transmission electron microscopy (TEM), X-ray diffractometry (XRD), in situ diffuse reflectance ultra violet - visible (UV-vis) spectroscopy, and temperature-programmed reduction by hydrogen (H_2-TPR) were used to identify the vanadia forms in vanadium-containing SBA-15 preparations (VO_x/SBA-15). Wacker type supported Pd/VO_x/SBA-15 catalysts were obtained by introducing Pd into VO_x/SBA-15 samples using conventional impregnation method. The activity of the catalysts was tested in the gas phase partial oxidation of ethylene by O_2 in the presence of H_2O (Wacker oxidation). VO_x/SBA-15 sample was obtained by micelle-templated synthesis using vanadium-containing synthesis gel. The vanadium became incorporated in the silica structure from the gel in near to atomic dispersion. This catalyst was quite active in ethylene oxidation to CO_2 but had low Wacker activity. Isolated, polymeric and bulk vanadia species were identified in the VO_x/SBA-15 prepared by wet impregnation/calcination method. The specific surface area of the sample was found to be smaller than that of the neat SBA-15 support because some pores were blocked by vanadia agglomerates. The corresponding Pd/VO_x/SBA-15 catalyst showed high selectivity for acetaldehyde formation but the activity was relatively low due to low accessible active surface. A third VO_x/SBA-15 sample was obtained by applying directed surface reaction between silanol groups of dehydrated SBA-15 and anhydrous solution of vanadyl acetylacetonate. Large number of accessible Pd/VO_x sites were present in the corresponding Pd/VO_x/SBA-15 catalyst. Latter catalyst induced ethylene oxidation to acetaldehyde with high yield at temperatures <~160 ^oC and with good yield to acetic acid at temperatures >~160 ^oC.

Keywords: Wacker oxidation, SBA-15, Pd/V catalysts, H_2-TPR, UV-vis

1. Introduction

In the late 1950s Smidt et al. [1] discovered that the aqueous solution containing HCl, $PdCl_2$ and $CuCl_2$ can effectively convert ethylene to acetaldehyde by O_2. Shortly after its discovery the method was patented and used for production at industrial scale by the Wacker and Hoechst companies. The oxidation occurs in a catalytic process, wherein the Pd^{2+} and Cu^{2+} ions, getting transitionally in reduced state, provide a route to electrons of ethylene to pass over to dioxygen. In other words the role of Pd^{2+} ions is to oxidize the olefin molecules, whereas the role of Cu^{2+} ions is to re-oxidize of Pd^0 to Pd^{2+}. The oxidation of Cu^+ ions, formed in the step of Pd^0 oxidation, to Cu^{2+} ions by dioxygen closes the catalytic cycle. The result of the processes is that electron pair is transferred from the ethylene to the dioxygen. The oxidation of Pd^0 by Cu^{2+} proceeds only at high of HCl and $CuCl_2$ concentrations. Under such reaction conditions chlorinated by-products are formed from ethylene, the handling of which is troublesome. The corrosive reaction medium, appearance of noxious copper waste, formed in the process, precipitation and aggregation of Pd, and the inevitable loss of Pd requires attention and cause extra expenses [2-4]. It was discovered that by selecting proper solvent and ligands even internal olefins can be converted to carbonyl compounds in copper-free medium. In absence of copper O_2 must directly re-oxidize Pd^0. The olefin oxidation in Pd-containing copper-free medium is usually referred to as direct O_2-coupled Wacker type oxidation [5,6].

In attempt to circumvent the disadvantages of the homogeneous liquid phase catalytic systems the active complex was transferred from solution to solid surface [7]. The immobilization of the active complex was assumed to result in a catalyst, showing the advantages of both the homogeneous and heterogeneous catalytic systems. Several attempts have been made to heterogenize the homogeneous Wacker catalyst system. In early attempts different oxides [8-10], zeolites [11] and activated carbon [12] were used as solid support. It was recognized that besides copper, also vanadia can successfully act as co-catalyst of the crucial Pd^0 to Pd^{2+} oxidation step [8,9,13].

The discovery of mesoporous micelle-templated silica (MTS) materials, such as MCM-41, MCM-48, and SBA-15 materials, opened a new field in heterogeneous catalysis research. These materials possess hexagonally arranged, channel-like, parallel mesopores of about uniform diameter, large specific surface area, and high silanol group concentration. Catalytically active species can be stabilized in high dispersion within the regular pore structure, providing very similar chemical environment for the active sites that is beneficial regarding the catalytic selectivity. Thanks to its thick pore walls the SBA-15 material is known to have excellent thermal, hydrothermal stability and outstanding acid resistance. Considering above benefits the SBA-15 material has been used widely as catalyst support. Unrestricted diffusion of reactants and products for MTS materials was observed even after the incorporation of large catalytically active species in the mesopore system [14].

MTS-material-supported vanadium oxide catalysts have received much attention recently because of their favorable structural properties and catalytic activity in industrially relevant oxidation reactions. Different gas phase oxidation reactions were investigated over vanadia-containing MTS-supported catalysts such as oxidative dehydrogenation of alkanes over HMS, MCM-41, MCM-48, SBA-15 and SBA-16 [15,16], epoxidation of propene over SBA-3, SBA-15 and MCM-41 [17]. Kuśtrowski et al. [18] studied oxidative dehydrogenation of ethylbenzene to styrene in presence of N_2O over VO_x/SBA-15 and observed that the catalytic activity paralleled the V content.

Thorough investigations were addressed to describe relationship between the nature of surface vanadia forms and the activity/selectivity in oxidation reactions. The conventional impregnation method results in samples containing mainly crystalline V_2O_5. Such preparations showed low catalytic activity because the bulk of the large vanadia particles was not accessible for the reactants [19].It was shown that better performing catalysts can be obtained by using more sophisticated synthesis methods.

Bulanek et al. [20] compared VO_x-containing hexagonal mesoporous silica (HMS) catalysts prepared by wet impregnation and direct synthesis. In the oxidative dehydrogenation of propane the synthesized catalyst was three times more active than the impregnated one. It was also shown that VO_x/SBA-15 catalysts prepared by grafting/ion-exchange method were better oxidation catalysts than the conventional VO_x/silica samples with the same vanadia loadings [21]. Van der Voort [22] grafted pure silica MCM-48 support with vanadyl acetylacetonate using gas-phase chemical vapor deposition. The final material contained 8.7wt% V, had narrow pore size distribution and a surface area of 800 m^2/g. The catalyst prepared by molecular designed dispersion, i.e., selective reaction of surface hydroxyls of MCM-41 with vanadyl acetylacetonate was active and stable for propane oxidative dehydrogenation even is absence of gas-phase oxygen [23]. Ying et al. [24] incorporated vanadia directly into SBA-15 silica framework applying acidic and peroxidic medium. They found that the synthesized materials had larger surface area, higher dispersion, easy-to-reduce

VO_x species, and superior catalytic performance for oxidative dehydrogenation of propane relative to the corresponding catalysts prepared by impregnation. The ordered mesoporous silica catalysts containing incorporated vanadia were active also in the vapor phase oxidation of diphenylmethane to benzophenone [25] and in the catalytic decomposition of dichloromethane to CO_2 [26].

The catalytic activity of the vanadium catalysts largely depends on the dispersion and structure of the supported vanadium-containing species. Depending on the isolation degree of vanadium atoms, surface vanadia sites can take up basically three different structures, such as, (i) isolated monomeric VO_4 species containing vanadium atom in tetrahedral coordination,(ii) one- or two- dimensional oligomeric species, having characteristic of V-O-V bridges, (iii) three-dimensional bulk, amorphous or crystalline vanadium oxide clusters [27]. The detailed structure-reactivity studies of Wachs et al [28] about the active oxidation sites of supported vanadia catalysts showed that the oxygen in terminal V = O bonds and the bridging oxygen in V–O–V bonds does not have significance in hydrocarbon oxidation reactions , but the oxygen atoms linking both to vanadium and support atoms establishing V–O–support bonds are active in the reaction.

By selecting the method a for vanadia introduction we can tune, which of the above species should have dominating presence on the surface of the SBA-15 support. In the present study we show that the most active Pd/VO_x/SBA-15 Wacker oxidation catalyst contains oligomeric VO_x species that is highly dispersed in mesopores and establishes intimate contact with Pd atoms.

2. Experimental section

2.1. Preparation of catalysts

The parent SBA-15 silica material was synthesized according to the well-known procedure of Stucky and co-workers [29]. The applied synthesis mixture had molar composition $PEO_{20}PPO_{70}PEO_{20}$:0.24HCl:0.04TEOS:6.67H_2O. The silica source and the micelle template was tetraethyortosilicate (TEOS, Aldrich, 98%) and $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H$ triblock copolymer (Pluronic P-123, Aldrich), respectively. The template was removed from the solid product of the synthesis by calcinations. The sample was heated up in air at a rate of 1 °C/min to 500 °C and kept at this temperature overnight.

A VO_x/SBA-15 sample was prepared by direct impregnation of the SBA-15 sample using decavanadate ($V_{10}O_{56}^{6-}$) solution. An aqueous decavanadate solution, having a vanadium concentration of 0.17 mol/dm^3, was made by dissolving NH_4VO_3 (VEB Laborchemie Apolda GmbH, Germany, 99.0 % purity). An aliquot was taken from the solution containing V in an amount that was 2.24 wt % of the SBA-15 material to be impregnated. The pH of an aliquot was adjusted to 4 by 1 molar HNO_3 solution and added to the SBA-15 sample. The wet sample was dried under continuous mixing and calcined in air at 500 °C overnight. The vanadia content of the preparation, expressed as V_2O_5, was 8 wt%. The preparation made by wet impregnation is designated as VO_X/SBA-15(i).

In order to get highly dispersed VO_x on SBA-15 support the grafting method, described by Sokolov et al.[23], was applied. Vanadyl acetylacetonate (VO(acac)$_2$, Acros Organics, Belgium, purity 99%) dissolved in dry toluene (Aldrich, anhydrous, purity 99.8%) was reacted with the silanol groups of previously dehydrated (3h, 180 °C) SBA-15 material. First, 253.6 mg VO(acac)$_2$ was dissolved in 100 cm^3 toluene, dried on activated molecular sieve 4A, by refluxing at 60 °C for about 1 h. Then 1 g of dehydrated SBA-15 was added to solution and the mixture was stirred at 60 °C for 4 h. Hereupon, the suspension was filtered and washed several times with warm anhydrous toluene to remove unreacted VO(acac)$_2$. The solid sample was dried at 120 °C overnight and calcined then in air at 400°C for 4 h. The amount of VO(acac)$_2$ and SBA-15 material was determined that the preparation should have 8wt% V_2O_5, provided that all the applied VO(acac)$_2$ remained bound to the silica material. The analysis of the preparation showed that this was not the case (vide infra). The sample made by grafting is designated as VO_x/SBA-15(g).

A V-SBA-15 sample, further on referred to as VO_x/SBA-15(s), contains V incorporated into the silica walls of SBA-15 material. It was prepared by direct synthesis following the method of Piumetti et al. [30]. A solution of template compounds was made by mixing of 612ml of 2 mol/dm^3 HCl, 16.33g Pluronic P-123 and 0.927g of cetyltrimethylammonium chloride (CTAC). The 25 wt% aqueous CTAC solution, obtained from Aldrich, was used. The mixture was intensely stirred at room temperature for 5 h. Also a vanadium-containing solution was made by mixing 0.870g V_2O_5 (Aldrich, purity 99.6+ wt%), 304.3g water and 27.52g aqueous hydrogen peroxide solution, containing 30 wt % H_2O_2 (Perhydrol, Merck, concentration 30 wt %). The mixture was stirred at 70°C until deep orange colored oxo-peroxo vanadium solution was obtained. Then, 37.16 ml of TEOS was added to the template solution, the cooled oxo-peroxo vanadium solution was admixed and the obtained mixture was stirred at room temperature for 5 h. A solid was obtained that was recovered by filtration, thoroughly washed with distilled water, dried at 120°C overnight and then calcined at 500 °C for 6 h. The Si and V contents of the synthesis mixture was determined that the V content of the solid product, expressed in V_2O_5, should be 8 wt %, provided that all the used V and Si appears in the product. The analysis of the preparation showed that this was not the case (vide infra).

Pd/VO_x/SBA-15 catalysts were prepared by impregnating the VO_x/SBA-15 samples applying 38 mmol Pd/dm^3 solution in an amount needed to get catalysts of about 1.0 wt% Pd content. The impregnation solution was made from a $Pd(NH_3)_4(NO_3)_2$ solution, containing 5.0 wt% Pd, obtained from Strem Chemicals Inc..

2.2 Characterization

X-ray patterns were recorded by Philips PW 1810/3710 diffractometer applying monochromatized CuKα radiation (40 kV, 35 mA). The patterns were collected between 3° and 65° 2Θ, by 0.02° steps for 0.5 sec at ambient conditions. X-ray patterns in the low angle range were measured by the CREDO instrument described elsewhere [31].

Nitrogen physisorption measurements were carried out at -195°C using Quantachrome NOVA Automated Gas Sorption Instrument. Samples were outgassed under vacuum at 150 °C for 24 h. The specific surface area was calculated by the BET method. The pore-size distributions of SBA-15 supported samples were calculated by the method of nonlocal density functional theory (NLDFT) applying the model of open cylindrical pores for the adsorption branch of the adsorption isotherms of samples VO_x/SBA-15(i) and VO_x/SBA-15(g), and the model of cylindrical/spherical pores for the adsorption branch of the isotherm of sample VO_x/SBA-15(s).

The morphology of synthesized samples was examined by Morgagni 268D Transmission Electron Microscope (100 kV, W filament, point resolution = 0.5 nm)

The palladium and vanadium content of samples was determined by means of inductively coupled plasma optical emission spectrometric (ICP-OES) measurement applying axial plasma observation (Spectro Genesis).

VO_x/SBA-15 and Pd/VO_x/SBA-15 samples were characterized by temperature-programmed reduction (H_2-TPR) measurements. About 100 mg of catalyst sample (particle size: 0.25–0.5 mm) was placed into a flow-through quartz tube (I.D. 4 mm) microreactor and was pre-treated in a 30 cm^3/min flow of O_2 at 350 °C for 1 h, cooled to room temperature in the O_2 flow, flushed by N_2 at room temperature for 30 min and then it was contacted with a 30 cm^3/min flow of 10% H_2/N_2 mixture. The reactor temperature was ramped up at a rate of 10 °C/min to 600 °C and held at this temperature for 1h. The reactor effluent was first passed through a liquid nitrogen trap and then a thermal conductivity detector (TCD) to monitor the hydrogen concentration of the gas. Data were collected and processed by computer. Calculation of hydrogen consumptions based on the peak areas. The TCD response was calibrated by measuring the H_2-TPR peak area of CuO reference material.

The in-situ UV-vis DRS spectra were collected by Thermo Scientific Evolution 300 UV-VIS spectrophotometer equipped with Praying Mantis Diffuse Reflectance Accessory and High Temperature and Pressure Reaction Chamber. The finely ground reference ($NaVO_3$, 99.9%, Na_3VO_4 99.98%, Aldrich products) and catalyst samples were diluted with an amount of $BaSO_4$ (Alfa Aesar, Puratronic 99,998%) to get Kubelka-Munk function $F(R\infty) < 1$ and measured against Spectralon® (Spectralon Inc., NH, USA) as background. In order to obtain spectra of dehydrated samples the absorbance data were collected at 400 °C after in-situ calcination at 400 °C in flowing oxygen for 30 min. The edge energy (Eg) for allowed transitions were determined by finding the intercept of the straight line fit to the low-energy rise of plot of $[F(R_\infty) \text{ x } h\nu]^2$ vs. hν [32].

2.3 Catalytic activity measurements

Catalytic test reactions were carried out at atmospheric pressure in a fixed-bed, continuous flow glass tube (∅ 8 mm) microreactor. Prior to the reaction the catalysts were activated in oxygen flow (20 ml/min) for 1h at 350°C. In the reaction 500 mg of sample (particle size 0.85-1.70 mm) was tested. The whole reacting mixture was fed into the reactor in gas phase. The molar composition of the feed was 3.3 % ethylene/12 % oxygen/24 % water/He. In some experiments the fed mixture was 1.5 % acetaldehyde or acetic acid/12 % oxygen/24 % water/He. The total flow rate was always 30 ml/min. All gas lines of the apparatus were heated to 120 °C in order to avoid the condensation of water and reaction products. The reaction products were analyzed by on-line Shimadzu GC-2010 gas chromatograph equipped with a 30-m HP-PLOT-U column and both TCD and FID detectors. The calibration of the GC for each reactant and product was carried out separately. The conversion of ethylene was calculated from the ethylene concentration of the feed and the reactor effluent. The selectivities were calculated from the molar yields of products.

3. Results and discussion

TEM images demonstrate that the vanadium-containing SBA-15 materials have highly-ordered mesoporous structure (Fig. 1, A-C), similar to that of the neat SBA-15 material (Fig. 1 D). On the surface of VO_x/SBA-15(i) sample aggregates could be observed (Fig. 1 A). Weak X-ray diffraction lines (Fig. 2a) suggest that crystalline V_2O_5 particles are present in this sample. These results substantiate that vanadia aggregates are located on the outer surface of the silica material. The other two VO_x/SBA-15 samples exhibit only a broad diffraction peak at around $2\Theta = 23°$, which peak comes from the amorphous mesoporous silica framework (Fig. 2, a-b). The insert of Fig. 2 shows the small-angle XRD patterns of the neat and vanadium-containing SBA-15 samples. These results suggest that the VO_x/SBA-15(i) and VO_x/SBA-15(g) and SBA-15 have about the same d-spacing and unit cell parameters, whereas the d-spacing and unit cell parameter of the VO_x/SBA-15(s) sample are significantly smaller (Table 1). The structural difference of these SBA-15 materials comes from the different methods applied for the synthesis of these materials. A hydrothermal treatment was applied to get SBA-15 material, whereas no hydrothermal treatment was involved in the synthesis of VOx/SBA-15(s), moreover, different template solutions were used in the two syntheses. The absence of crystalline V_2O_5 phase in samples VO_x/SBA-15(g) and VOx/SBA-15(s) suggests that the vanadium is highly dispersed both over the surface of pores or inside the silica framework. The V_2O_5 content of the mentioned samples is lower than that of the VO_x/SBA-15(i) sample (Table 1). That means that the vanadium precursor does not react quantitatively with the silica surface as it was reported by Segura et. al. [33] earlier, and, in harmony with the finding of Piumetti et. al. [30], can not incorporate quantitatively in the silica matrix of the SBA-15 material from the synthesis mixture. No reflections of PdO or Pd metal were found on the XRD patterns of Pd-loaded VO_x/SBA-15 samples.

Fig. 3, a-d shows type IV N_2 adsorption-desorption isotherms for neat and vanadium-containing SBA-15 materials, recorded at -196 °C. Mesoporous SBA-15 materials having perfectly ordered pore structure show perfect H1 type hysteresis loop characterized by vertical adsorption branch at higher and desorption branch at a lower relative pressure [34]. However, geometrical and chemical disorder in the linear pores can distort the hysteresis loop to type

H2, characterized by gradual saturation of the mesopores in the direction of increasing equilibrium N_2 pressure and emptying of the pores in a narrow N_2 pressure range in the direction of decreasing equilibrium pressures. This phenomenon was described as the consequence of the metastable states of the fluid inside the porous matrix having chemical and structural heterogeneity and the slow relaxation of the states under the conditions of the adsorption measurement [35]. The isotherm of the SBA-15 material shows hysteresis loop with relatively small deviation from the H1 character. All the vanadia-containing SBA-15 preparations have H2 hysteresis loop indicating enhanced heterogeneity of the pore structure relative to the neat SBA-15. The pore volume (PV), specific surface area (SSA), and pore diameter (PD) of the VO_x/SBA-15 samples are lower than the corresponding characteristics of the SBA-15 material (Table 1). Above mentioned textural parameters of VO_x/SBA-15(i), containing vanadia particles mainly on the outer surface of the SBA-15 particles, deviates to the smallest extent from the corresponding values of SBA-15 material. The VO_x/SBA-15(g) sample has smaller pore volume and average pore size indicating that the vanadium is mainly within the mesopores (Fig. 1, and Table 1). The desorption branch shows two distinct steps in the p/p_0 =0.45-0.75 range of relative pressure (Fig. 3b). Accordingly, the NLDFT calculation reveals bimodal pore size distribution with most frequent pore diameters of 7.27 and 4.95 nm (Table 1). It seems probable that the surface reaction of $VO(acac)_2$ with hydroxyls of SBA-15 proceeds mainly near to the orifice of some mesopores generating ink-bottle type pores with narrowed neck, whereas a large fraction of the mesopores remain virtually intact (Table 1). The unit cell parameter, a_0, calculated from the d-spacing, and the mesopore size allows estimating the thickness of the pore walls (Table 1). Data suggests that VO_x/SBA-15(s) has thicker pore walls between narrower pores than the SBA-15 and VO_x/SBA-15(i) samples. The smallest SSA of the VO_x/SBA-15(s) sample is in line with this structure. However , the VO_x/SBA-15(g) has also thick walls but large SSA suggesting that preparations might contain different amounts of mesoporous phase (Table 1). It was shown that the synthesis of SBA-15 material, not involving hydrothermal treatment of the synthesis mixture, resulted in a less ordered structure than synthesis under hydrothermal conditions [24]. This circumstance can contribute to the lower mesoporosity of the VO_x/SBA-15(s) preparation. According to TEM and XRD measurements there is no evidence for the formation of crystalline V_2O_5 phase either on the internal surfaces of the mesopores or on the external surface of the particles. These results suggest that the vanadium must have been incorporated into the silica framework of the VO_x/SBA-15 (s) material.

The physicochemical properties of our samples prepared with $EO_{20}PO_{70}EO_{20}$ triblock copolymers are in the same range as it is reported in literature. Zhao et al. [30] obtained SBA-15 with SSA=850 m^2/g, PV=1.17 cm^3/g and WT= 3.1 nm (compare with data in Table 1.) The direct incorporation of vanadia into a silica framework resulted in a partial destruction of mesoporous structure. Santhanaraj et al. [20] reported SSA=570 m^2/g, PV=0.93 cm^3/g and WT= 4.3 nm for SBA-15 samples containing vanadia. These data are also near to the corresponding characteristics of our VO_x/SBA-15(s) sample.

Results of ethylene Wacker oxidation over Pd/VO_x/SBA-15 catalysts are shown in Fig. 4. Under identical reaction conditions the VO_x/SBA-15 preparations proved to be inactive, whereas the total ethylene oxidation prevailed over Pd/SBA-15 catalyst. In presence of Pd/VO_x partially oxidized products, such as, acetaldehyde and acetic acid were obtained proving that Wacker type reaction cycle operated. It is to be noted that, beside a similar Pd content (~1 wt%), the vanadia content of the catalysts is rather different. At comparable temperatures the Pd/VO_x/SBA-15 (g) and Pd/VO_x/SBA-15 (s) samples of lower vanadium content exhibit higher levels of conversion than the Pd/VO_x/SBA-15(i) catalyst having higher vanadium content(Table 1 and Fig. 4). The higher conversion is accompanied by higher CO_2 selectivity and yield. The highest acetaldehyde yields were 19-23 %. These yields were obtained using Pd/VO_x/SBA-15(g) catalyst in the 125-150°C temperature range. At temperature as low as 175 °C total conversion of ethylene occurs over Pd/VO_x/SBA-15(s) catalyst. At total conversion the acetic acid selectivity was as high as 40%. The Pd/VO_x/SBA-15(i) catalyst exhibits high acetaldehyde selectivities only at relatively low conversion levels at temperatures in the range of 125-175 °C.

Considering the consecutive reaction pathway of ethylene oxidation the conversion of the primary product of ethylene oxidation was also examined using acetaldehyde as reactant. The Wacker oxidation of acetaldehyde results in the formation of acetic acid and CO_2 in a molar ratio of about 1 to 2 (Fig. 5). It is worth to mention that the temperature dependence of acetaldehyde conversion and product selectivities are almost the same as those of the reactant ethylene (cf. Figs. 4 and 5). Interestingly when acetic acid was used as reactant no conversion was obtained in the temperature range of 125-200 °C.

H_2-TPR curves of V-SBA-15 samples and their palladium doped derivatives are shown in Fig. 6. The H_2 consumptions, calculated by integration of the H_2-TPR peaks, are given in Table 2. The total H_2 consumption corresponds to H_2/V values varying between 0.85 to 1.03 substantiating that $V^{5+} \rightarrow V^{3+}$ reduction occurred in each sample. In absence of Pd the reduction of the samples begins above about 400 ^oC. In the presence of Pd in the sample the reduction process above about 400 ^oC gave a smaller TPR peak and new peaks at temperature lower than about 400 ^oC (Fig. 6). In contact with H_2 flow palladium is reduced already below room temperature. Therefore, no peak of H_2 consumption belongs to this process on the shown H_2-TPR curves. However, the palladium metal (Pd^0) can activate H_2 for the reduction of vanadium explaining the appearance of the low-temperature reduction peak on the TPR curve of the Pd/VO_x/SBA-15 samples. The negative spike at about 100 ^oC is to be noticed. This might belong to the sudden release of the H_2 dissolved in the palladium metal. The VO_x/SBA-15(i) has different reduction behavior than the other two VO_x/SBA-15 preparations. The H_2 consumption above 400 ^oC gives two distinct maxima that may suggest the presence of vanadium species of different reducibility. These can be easy-to-reduce smaller particles and/or surface of larger vanadia particles and hard-to-reduce larger vanadia particles and/or bulk of larger vanadia particles. A further difference is that the addition of palladium to the VO_x/SBA-15(i) sample resulted in an almost complete fade-out of the high temperature reduction peak present on the TPR curve of the Pd-free sample. Previously, XRD and TEM results verified that no bulk phase of vanadia is present in the VO_x/SBA-15(g) and VO_x/SBA-15(s) preparations. Accordingly, only a single, high-temperature peak appeared on the H_2-TPR curve of letter samples. The data of Table 2 suggest that about 70% and 84% of the vanadium in the VO_x/SBA-15(g) and VO_x/SBA-15(s), respectively, do not react with H_2 below about 400 $^\circ C$ even in the presence of palladium. The presence of high temperature reduction peak in the TPR curve of Pd/VO_x/SBA-15 catalyst indicates that Pd-activated hydrogen cannot reach a certain amount of vanadia atoms. In case of Pd/VO_x/SBA-15(g) the isolated vanadia isles, that could be located far-away from Pd particles, were reduced only at high temperatures, where also the thermally activated hydrogen can reactn with VO_x. The incorporation of vanadia into SBA-15 framework leads to higher vanadia dispersion and less intimate Pd-V connections. Reducibility of VO_x in Pd/VO_x/SBA-15(i) is the highest amongst three samples. This indicates that bulk VO_x can react more easily with activated hydrogen than polymeric or isolated VO_x species. In our opinion the low-temperature reducibility of vanadium is a catalyst property of primary importance if the catalyst is used to initiate a low-temperature catalytic redox reaction as the Wacker oxidation. For this reason the number of direct Pd-V linkages is also important.

The DR UV-VIS technique is capable to distinguish the surface vanadia forms. The sodium orthovanadate (Na_3VO_4) and sodium metavanadate ($NaVO_3$) compounds contain isolated VO_4 units and polymeric VO_4 chains, respectively [32]. The E_g values of $NaVO_3/Na_3VO_4$ mechanical mixtures show intermediate values. The E_g vs. molar ratio plot is linear. That means that after generating an E_g versus molar ratio calibration line the percentage of isolated and polymeric vanadia forms of a vanadia-containing catalyst can be obtained from the E_g edge energy. The edge energy (E_g) of pure $NaVO_3$ sample was found to be 3.06 eV whereas that of the Na_3VO_4 was 3.60 eV.

Fig. 7. shows that the VO_x/SBA-15(s) sample contains only isolated VO_4 units (E_g=3.64eV), while the VO_x/SBA-15(g) (E_g=3.30eV) and VO_x/SBA-15(i) (E_g=3.17eV) contains mixture of polymeric chains and isolated VO_4 units in polymeric/isolated ratios of 60/40 and 85/15. Since the impregnated sample contains a small amount of bulk V_2O_5 phase (E_g=2.18eV), which also effect on the resultant E_g value the amount of isolated VO_4 species is probably higher than 15%. The presence of linear VO_4 chains on surface of VO_x/SBA-15(g) sample suggests that in the calcination step of catalyst preparation the neighbouring vanadyl acetylacetonate groups get polymerized.

The results of UV-VIS, XRD and H_2-TPR measurements showed that the synthesis method generated only monomeric VO_4 species in catalyst Pd/VO_x/SBA-15(s). The vanadia is mainly incorporated into SiO_2 framework and only a small fraction thereof can be reduced even in presence of palladium. For Wacker-type reaction thorough cooperation of Pd/V redox couple is crucial. The relatively high acetic acid yields at lower temperatures suggest that Wacker oxidation occurs. However, at 175 ^oC and above the catalyst acts as supported palladium promoting total oxidation on high conversion level.

Despite of the lower VO_x loading of the Pd/VO_x/SBA-15(g) catalyst relative to that of the Pd/VO_x/SBA-15(i) preparation, products of selective oxidation was obtained by higher yield over the former than over the latter catalyst in the whole applied temperature range. This finding can be explained by the higher vanadia coverage of the SBA-15 surface, attained in the selective reaction of the SBA-15 silanol groups and the $VO(acac)_2$ and, as a consequence of the higher vanadia coverage, by the obtained higher number of Pd-V linkages. Regarding the Wacker activity the number of the redox pairs, wherein the Pd and the VO_x is in intimate contact, is most important. The grafting reaction results in formation of V-O-support bonds in which the bridging oxygen atoms are more electronegative or basic than the vanadia oxygen atoms. These atoms were associated with the oxygen required for hydrocarbon oxidation [27]. As it was previously shown in oxidative dehydrogenation of propane only the highly dispersed surface VO_x species are selective while crystalline V_2O_5 particles induce the total oxidation of substrate [36]. Venkov et. al [37] demonstrated that release of oxygen from SBA-15 supported vanadia species is difficult and requires temperatures above 400°C. The rate constant of vanadium re-oxidation is 10^3-10^5 times higher than that of the reduction, which is activating the C-H bond [38]. In presence of palladium the reduction temperature of VO_x species shifts down to the range required for Wacker oxidation. We found that palladium over bulk V_2O_5 also exhibits activity in selective alkene oxidation (not shown). However, the activity is low due to small number of active sites (Pd-V linkages) caused by the low vanadia dispersity.

4. Conclusions

Three preparation methods of VO_x/SBA-15 were compared with regard to the structure of supported vanadia. Preparations were converted to Pd/VO_x/SBA-15 Wacker catalysts and tested in selective oxidation of ethylene to acetaldehyde and acetic acid, with oxygen, in presence of water. The introduction of VO_x in the silica matrix by direct synthesis resulted in mainly isolated vanadia species that poorly operated as co-catalyst of palladium. In virtual absence of active Pd/V redox couple this catalyst acted as a supported palladium, promoting total oxidation of ethylene at high conversion levels. The catalyst prepared by selective reaction of SBA-15 surface hydroxyls with vanadyl acetylacetonate led to formation of highly dispersed VO_x species on the inner surface of support and no bulk V_2O_5 clusters. After Pd impregnation large number of Pd/VO_x pairs formed, resulting in a high acetaldehyde yields at low temperatures. Impregnation of SBA-15 by decavanadate solution generated oligomerized VO_x structure, and crystalline V_2O_5 particles. Consequently, the Wacker activity of latter catalyst was low due to low VO_x dispersion and small number of active Pd/VO_x sites.

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Figure captions

Fig. 1. TEM images of samples (A) VO_x/SBA-15(i), (B) VO_x/SBA-15(g) (C) VO_x/SBA-15 (s), and (D) SBA-15.

Fig. 2. XRD patterns of (a) VO_x/SBA-15(i), (b) VO_x/SBA-15(g), (c)VO_x /SBA-15(s), and (d) neat SBA-15 samples. The inset shows the low 2 Θ region.

Fig. 3. N_2 adsorption isotherms of (a) parent SBA-15, (b) VO_x /SBA-15(i), (c) VO_x/SBA-15(g), (d) VO_x/SBA-15(s). Adsorption and desorption branches are indicated by full and open symbols, respectively.

Fig. 4. Catalytic conversion of 3 % ethylene/12 % oxygen/24 % water/He gas mixture as a function of temperature over different catalysts The measurements were carried out at atmospheric pressure, GHSV = 3,600 h^{-1}. Conversions and selectivities were calculated from the molar amounts of ethylene consumption and product formation.

Fig. 5. Catalytic conversion of 1.5 % acetaldehyde/12 % oxygen/24 % water/He gas mixture as a function of temperature over different catalysts. The measurements were carried out at atmospheric pressure, GHSV = 3,600 h^{-1}. Conversions and selectivities were calculated from the molar amounts of ethylene consumption and product formation.

Fig. 6. H_2-TPR profiles of VO_x /SBA-15 and Pd/VO_x /SBA-15 samples.

Fig. 7. UV–Vis DR spectra of VO_x/SBA-15 materials. The absorbance data were collected at 400°C after in situ calcinations of the sample at 400°C in flowing oxygen for 30 min.