Preparation, Characterization and Catalytic Activity of MgO/ SiO₂ Supported Vanadium Oxide Based Catalysts

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Abstract Vanadium oxide-based catalyst obtained by grafting VOCl₃ on Florisil (MgO:SiO₂) with the molar ratio of 15:85 have been studied for the selective oxidation of cyclohexane in order to obtain cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone. The performances obtained have been compared with those of other catalysts in which vanadium oxide was supported on the same support by impregnation with ammonium oxalate. All the prepared catalysts have been characterized using XRD, FTIR, TEM, SEM, EDX, DRS and TGA in order to rationalize the differences in performance observed. The presence of magnesium oxide species (15 % MgO) on the surface of silica significantly modifies the molecular structure of the surface vanadium oxide species and changes their molecular structure from hydrated VO₅/VO₆ polymers to less polymerized VO₄ species and/or isolated $VO_2(OH)_2$ species. The catalytic activities indicate that the VO_x/Florisil catalysts show high conversions and TONs for those types containing isolated VO₄. Compared to previously studied VO_x/SiO₂ catalysts, the Florisil based systems show significantly improved leaching behavior.

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Institute of Chemistry and Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), University of Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany e-mail: pietschnig@uni-kassel.de **Keywords** Vanadium oxide \cdot Supported catalysts \cdot SiO₂ \cdot MgO \cdot Selective oxidation \cdot Hydroperoxide

1 Introduction

Supported vanadium oxide catalysts have attracted significant attention, because of their potential for catalyzing several oxidation reactions [1-11]. Especially the oxidation of lighter alkanes is promising with respect to alternative feedstocks for industrially relevant bulk chemicals [12–15]. The chemical environment on a molecular scale of the supported vanadium oxide species was found to depend on several parameters, e.g., metal oxide loading, oxide support material, and the degree of hydration [16-20]. The nature of the vanadium oxide species on several supports; i.e., Al₂O₃, Nb₂O₅, SiO₂, TiO₂, and ZrO₂, has been examined with various techniques [16, 17, 21-27]. Also pyrazine 2-carboxylic acid (PCA) acting as a co-catalyst has a significant influence on the conversion of hydrocarbons. It is anticipated that PCA coordinates to vanadium sites on the catalyst surface facilitating electron and proton transfer processes between peroxo/hydroxyl species and vanadium [24, 28, 29]. Our recent investigation on the oxidation of cyclohexane showed that the vanadium oxide catalysts supported on SiO₂ were very active however, their potential as heterogeneous catalyst was limited owing to significant leaching from the silica surface into the reaction medium which hampers recovering of the catalyst [24]. On the other hand MgO supported vanadium oxide showed substantially lower leaching rates but also variable catalytic activity which was attributed to the presence of different VO_x phases as confirmed by ⁵¹V-MAS-NMR, IR, UV-DRS and SEM/EDX [30]. The purpose of the present study is to investigate the effect of MgO in modifying the physicochemical characteristics and the catalytic behavior of silica supported vanadium oxide in the selective oxidation of cyclohexane by using readily available Florisil (15MgO/85SiO₂) as catalyst support.

2 Experimental

Two different methods, grafting and wet impregnation, were applied to prepare supported vanadium oxide catalysts on Florisil (15MgO/85SiO₂) with different vanadium loadings ranging from 1 to 18 wt% following previously reported procedures [24]. The catalytic activity of the prepared catalysts was evaluated for the liquid-phase oxidation of cyclohexane with H₂O₂/molecular dioxygen (air) as described before [30]. The catalytic activities are reported as conversion (%), selectivity (%) and TON calculated following a published procedure [24]. The overall selectivity (OS %) is defined as sum of the selectivities for cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone. The vanadium concentration of the prepared catalysts was determined by flame atomic absorption spectroscopy (AAS) using a UNICAM 929 AA Spectrometer. The BET surface area of the catalysts was measured by nitrogen adsorption-desorption at 77 K using a NOVA 1200 surface area analyzer (Quanta-chrome). The isotherms were analyzed in a conventional manner in the region of the relative pressure, $p/p_0 = 0.05-0.3$. X-ray diffraction (XRD) patterns of all catalysts were performed on a Philips powder diffractometer PW1050/25 with Cu Ka radiation $(\lambda = 0.1542 \text{ nm})$ operating at 50 kV and 20 mA in a 20 range of 10-70° with step size 0.01° and time step 1.0 s to assess the crystallinity of the vanadium oxide loading. The diffractograms of the samples were compared with the powder diffraction patterns of reference samples. Fourier transform-infrared spectra of the samples were recorded on a Perkin-Elmer FT-IR spectrometer 1725X using KBr disks. Diffuse reflectance (DR) spectra in the UV-Vis region were recorded in the reflectance function mode (F(R)) at room temperature in the range 1,000–200 nm on a Varian Cary 500 spectrophotometer with a diffuse reflectance attachment to investigate the structures of V(V)containing oxide compounds under hydrated and dehydrated conditions. The plain oxide support was used as a reference for the corresponding supported catalysts. Thermogravimetric analyses using a Mettler TGA were performed on the support materials and all prepared catalysts. To evaluate the overall amount of surface hydroxyl groups available for anchoring reactions, the weight loss between 300 and 1,000 °C was determined. A heating rate of 10 °C/min under argon was applied to purge off gases from the TGA electronics and sample region. The reference material was α -alumina powder. The SEM analyses were done with a DSM 982 Gemini SEM with a maximum acceleration voltage of the primary electrons between 10 and 15 kV. The powder samples were prepared on double side adhesive carbon tape and covered with a gold layer in a Cressington sputter coater operated under vacuum conditions (0.5×10^{-1} mbar). Semi-quantitative EDX (Röntec, M-series, EDR288/SPU2) analysis was used for the characterization of element concentration and vanadium distribution within all prepared catalysts. The TEM examination of samples was carried out on a Philips CM10 microscope working at 100 kV. TEM specimens were prepared ultrasonically by dispersing the catalyst sample in ethanol, and then placing a drop of the suspension on a Cu grid covered with a lacey carbon film.

3 Results and Discussion

3.1 Catalyst Characterization

Table 1 summarizes the vanadium content of the catalysts determined from AAS analysis, BET surface areas, VO_x surface densities calculated with the use of these two parameters, and the concentration of surface hydroxyl groups of Florisil and VO_x/Florisil catalysts evaluated by TGA. Grafted catalysts Grf1F to Grf3F show vanadium loadings ranging from 1.1 to 5.1 wt%, while catalysts prepared by impregnation (Imp1F to Imp5F) show vanadium loadings from 1.1 to 17.8 wt% (Table 1). BET measurements indicate that the surface areas of the impregnated catalysts per gram of Florisil decrease with increasing vanadium loadings from Imp1F to Imp3F. A considerable increase of the surface area is found for high vanadium loadings (Imp4F) which may be explained by the presence of separate VO_x particles without pore blocking [31]. Both, the calcined or non-calcined catalysts (Ungrf1F and Grf1F) obtained from the initial grafting process exhibit high surface areas (559.44 and 288.19 m²/g Florisil). Repeating the grafting process decreases the surface area per gram of Florisil (Grf3F). In general, the surface area of the support material decreases by increasing the quantity of the active component until the monolayer coverage of the impregnated component is completed [32]. The VO_x/Florisil catalysts prepared by grafting and the impregnated catalyst with low V loading (Imp1F) do not differ significantly from the plain Florisil support in their XRD and FT-IR data. Nevertheless, in the diffuse reflectance UV-Vis spectra all catalysts exhibit characteristic LMCT transitions as broad absorption bands below \sim 550 nm for which the maximum of absorption shifts to higher wavelengths with increasing vanadium loadings (see ESI). The corresponding edge energy values have been calculated (Table 1) indicating isolated VO₄ species

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Catalyst	V conc. (mmol/g catal.)	OH groups (mmol/g catal.)	Surface area (m ² /g Florisil)	Pore volume cm ³ /g catalyst	VO _x surface densities (V atoms/nm ²)	V (wt%) (AAS)	${ m E_g}{ m (eV)^a}$	${\rm E}_{\rm g}({\rm eV})^{\rm b}$	Si (wt%) (EDX)c	O (wt%) (EDX)	Mg (wt%) (EDX)	V (wt%) (EDX)
Florisil	0.00	1.47	258.59	0.214	I	00.00	I	I	35.84 ± 07.49	58.11 ± 07.85	6.04 ± 0.56	0.00
Ungrf1F	0.21	1.97	288.19	0.220	0.44	01.07	3.44	3.43	41.03 ± 04.46	52.35 ± 04.46	6.00 ± 0.43	1.22 ± 0.78
Grf1F	0.21	1.26	559.44	0.449	0.23	01.06	3.48	3.43	34.32 ± 09.72	62.82 ± 17.48	5.71 ± 0.99	0.96 ± 0.47
Grf2F	0.68	0.93	I	I	I	03.49	3.41	3.22				
Grf3F	0.99	0.91	230.18	0.178	2.73	05.05	3.33	2.92	40.17 ± 07.78	54.73 ± 08.39	2.45 ± 2.21	3.13 ± 1.60
Imp1F	0.21	1.51	388.63	0.315	0.33	01.06	3.56	3.56	34.33 ± 07.23	59.28 ± 08.74	6.09 ± 1.37	1.43 ± 0.64
Imp2F	0.68	1.28	I	I	I	03.49	3.54	3.54	27.81 ± 10.55	62.23 ± 13.86	6.45 ± 3.32	3.97 ± 2.14
Imp3F	1.00	1.07	281.26	0.106	2.25	05.09	3.50	3.47	28.67 ± 08.76	56.03 ± 05.51	7.82 ± 6.83	7.46 ± 1.60
Imp4F	1.65	06.0	335.62	0.115	3.23	08.40	3.49	3.46	04.46 ± 04.83	80.75 ± 10.38	2.80 ± 1.30	8.92 ± 5.60
Imp5F	3.50	0.66	I	I	I	17.83	3.21	3.20	34.33 ± 07.23	59.28 ± 08.74	6.09 ± 1.37	1.43 ± 0.64
^a inert												

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[33–35]. By increasing the V loading from Imp2F, Imp3F to Imp4F structural changes are evident which suggest the presence of MgO based on XRD and IR data. The latter may be derived from magnesium oxalate formed during impregnation with aqueous $(NH_4)_2[VO(C_2O_4)_2]$ upon calcination. For the catalysts with the highest vanadium loadings (Imp4F, Imp5F) a multiphasic composition may be derived from the XRD, IR and UV-Vis data indicative for polymerized vanadium oxide species (VO₅/VO₆) such as vanadium pentoxide, meta-MgV₂O₆ and pyro-Mg₂V₂O₇. Moreover, for the whole concentration range elemental composition and distribution have been examined using SEM, TEM, and EDX (Table 1) which confirm the even distribution of V as isolated VO₄ species for low loadings, increasing presence of MgO for intermediate loadings obtained by impregnation and a multiphasic mixture for the highest loadings (cf. ESI).

In summary these results show that the impregnation process also significantly affects the composition of the support material at and near the surface. During impregnation at intermediate vanadium concentrations Mg(OH)₂ is formed in addition to magnesium oxalate which incorporates VO_x in the bulk of the catalysts, resulting in lower than expected vanadium surface concentrations. At high vanadium loadings only magnesium oxalate is formed during impregnation, resulting in significant amounts of pyro-Mg₂V₂O₇, meta-MgV₂O₆ as well as V₂O₅. Similar results have also been observed in MoO_x/MgO catalysts [32, 36].

3.2 Catalytic Activity

hydrated

Measurements of the catalytic activity reveal cyclohexyl hydroperoxide (Cy–OOH) as the primary oxidation product of cyclohexane besides small amounts of cyclohexanol (Cy– OH) and cyclohexanone (Cy=O) resulting from subsequent reaction steps. The effect of various parameters such as vanadium loading, vanadium distribution, catalyst amount, hydrogen peroxide concentration and reaction time were investigated to achieve optimum reaction conditions.

At the same total vanadium content (11 µmol) per reaction batch, the influence of the nature of different (VO_x/Florisil) catalysts on conversion and selectivity to the primary oxidation product cyclohexyl hydroperoxide has been studied (Table 2). The VO_x/Florisil catalysts exhibit quite high conversions up to 78 % and selectivities to cyclohexyl hydroperoxide up to 90 %. Interestingly, the highest selectivities are obtained for the lowest conversion rates which indicates that the same factors that favor the initial oxidation also increase subsequent reactions of the resulting hydroperoxide like dehydration to (Cy=O) or O–O cleavage to (Cy–OH). This interpretation is in good agreement with the fact that the selectivity to cyclohexyl

Catalysts TON % (OS) % By-products % Conv. $\% S_{Cy-OH}$ % S_{Cy=O} % SCy-OOH Ungrf1F 58.40 1,442 00.00 08.46 90.00 98.46 00.90 Imp1F 04.26 10.46 82.50 98.40 00.93 58.59 1,446 Grf1F 56.94 1,385 09.55 16.17 71.22 96.94 01.74 Imp2F 74.51 1,785 09.64 18.55 64.32 95.51 03.34 Imp3F 1,798 04.47 19.60 67.35 95.42 03.44 75.13 Imp4F 74.04 1,736 10.02 22.80 60.38 93.50 04.81 Grf2F 1,677 18.20 61.36 08.52 75.14 09.60 88.65 Grf3F 77.50 1,671 15.25 18.69 52.22 85.96 10.88 Imp5F 77.59 1,650 19.81 21.06 43.92 84.79 11.80

Table 2 Oxidation of cyclohexan	e using VO _x /Florisil	catalysts at equal '	V conc. (1	l μmol)
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Reaction conditions: cyclohexane (1.06 M, 27.56 mmol), H_2O_2 (0.40 M, 10.5 mmol), PCA (1.70 × 10⁻³ M, 0.044 mmol), CH₃CN (20 ml), 60 °C, 24 h. %; By-products: 1,4-cyclohexanedione, 1,3-cyclohexanediol, 4-hydroxy-cyclohexanone, 2-hydroxy-cyclohexanone, 2,4-dihydroxy-cyclohexanone

hydroperoxide decreases with increasing vanadium concentration within the catalyst (Tables 1, 2). From a structural point of view these findings suggest that the polymerized species of vanadium oxide present in catalysts with high vanadium loadings accelerate the oxidation of cyclohexyl hydroperoxide to unwanted by-products. Although the catalysts with the lowest vanadium concentrations (Ungrf1F, Imp1F, Grf1F) show the lowest conversion and TON values, there is no clear correlation between vanadium concentration and conversion $(\sim 75-78 \%)$ or TON $(\sim 1.4-1.8 k)$ for the catalysts with higher V loadings (0.7-3.5 mmol/g).

Under the reaction conditions described in Table 2, only slight leaching of vanadium (ca. 2-4 %, confirmed by UV analysis) is detected for impregnated catalysts (Imp1F, Imp2F, Imp3F, Imp4F) and for grafted catalysts with low vanadium loadings (Ungrf1F, Grf1F). The impregnated catalyst with the highest vanadium loading (Imp5F) shows significant leaching (ca. 15 %). This partial leaching likely is a consequence of the presence of V₂O₅ in this catalyst as confirmed by IR, SEM, TEM and DRS. Furthermore, the grafted catalysts such as Grf2F and Grf3F show a relatively high leaching (>50 %). Again this can be attributed to the presence of polymerized VO₄ or VO₂(OH)₂ species, which coordinate weakly to silica. Nevertheless, all investigated Florisil based catalysts especially those prepared by impregnation show significantly improved leaching behavior compared to SiO₂ supported VO_x for which complete leaching of vanadium has been reported [24]. In addition, the stability of the VO_x/Florisil catalysts upon exposure to air (3 h) has been explored by DRS (Table 1 and ESI) which confirms that hydration is not an issue for the catalysts with low V loadings (up to Imp1F and Imp2F). This is in marked contrast to their SiO₂ supported congeners [24] which may be explained by an increase of



Fig. 1 Variation of cyclohexane conversion and selectivity to cyclohexyl hydroperoxide using different $VO_x/Florisil$ catalysts with the same surface area (2.05 m²)

the surface pH at the point of zero charge owing to the presence of MgO in Florisil.

Since no simple correlation between the total vanadium concentration in the catalyst and its catalytic activity could be established, the catalytic performance with respect to the vanadium distribution on the surface has been explored. For this purpose the activity of impregnated or grafted VO_x /Florisil catalysts with the same surface area of catalysts (2.05 m²) per batch have been compared. The influence of the vanadium distribution (cf. Table 1) on the catalytic performance is illustrated in Figs. 1 and 2. The conversion of cyclohexane roughly increases with increasing V loadings for impregnated or grafted catalysts. However, the TON and the selectivity to Cy–OOH of these



Fig. 2 Variation of TON using different VO_x /Florisil catalysts with the same surface area (2.05 m²)

catalysts decrease with increasing vanadium loadings. This observation suggests that the highly polymerized species of vanadium oxide in catalysts containing high loadings such as Grf3F, Imp3F and Imp4F catalysts accelerate the overoxidation of Cy–OOH to unwanted by-products such as 1,4-cyclohexanedione, 1,3-cyclohexanediol, 4-hydroxycyclohexanone, 2-hydroxy-cyclohexanone and 2,4-dihydroxy-cyclohexanone, which could be identified by mass spectrometry.

Best selectivities for the monooxidation of cyclohexane have been obtained with the VO_x/Florisil catalysts Ungrf1F, Grf1F and Imp1F providing low vanadium loadings (0.2 mmol/g). Therefore conversion and selectivity for these catalysts as a function of different amounts of catalyst were studied (see ESI for details). By increasing the amounts of Ugrf1F, Grf1F and Imp1F catalysts, the conversion of cyclohexane generally increases. As the catalyst amount increases further, a considerable decrease in the conversion of cyclohexane is observed but no decrease of the selectivity for Cy-OOH. Moreover, the TON values decrease as well. This behavior may be explained by the presence of PCA free V^{5+} ("uncomplexed" V^{5+}) which decomposes H₂O₂ to H₂O and O₂ leading to low conversions. Interestingly, these three catalysts are also among those with the lowest leaching rates.

As described before catalyst Ungrf1F showed the highest conversion and selectivity rates. Therefore it was chosen to explore the effect of the reaction temperature on the cyclohexane conversion as shown in Fig. 3. It can be seen that cyclohexane conversion increases with the reaction temperature. At higher temperatures (80 and 100 °C) decomposition of H_2O_2 to H_2O and O_2 may occur, which leads to a decrease of conversion. Moreover, these higher temperatures also accelerate the conversion of cyclohexyl



Fig. 3 Variation of cyclohexane conversion and cyclohexyl hydroperoxide selectivity with different reaction temperature, using Ungrf1F catalyst (11μ mol V)



Fig. 4 Variation of cyclohexane conversion and selectivity to cyclohexyl hydroperoxide with reaction time, using Grf1F catalyst (0.77 μ mol V)

hydroperoxide to cyclohexanol, cyclohexanone and unwanted by-products, which decreases the selectivity to the primary product cyclohexyl hydroperoxide significantly. Besides temperature also the reaction time is a straight forward parameter to modify the catalytic performance. The influence of the reaction time was explored for the catalyst Grf1F which shows especially low leaching rates. The catalytic activity in the oxidation of cyclohexane has been determined as a function of reaction time (Fig. 4). According to these measurements conversion and TON increase with the reaction time and reach a maximum after 48 h. By contrast the selectivity to Cy–OOH slightly decreases with time, however on a high level. Increasing the reaction time beyond 48 h also slightly decreases conversion, TON and total selectivity of the target products. This decrease may be a consequence of blocking active sites or pores on the catalyst surface by adsorption of reaction products or by-products at long reaction times. Similarly, also PCA has a significant influence on the conversion of cyclohexane. By increasing PCA concentrations the conversion of cyclohexane increases. A further increase of PCA slightly decreases conversion, selectivity to cyclohexyl hydroperoxide and the total selectivity to the target products (for details see ESI). Also here blocking of active sites or pores of the catalyst at high PCA concentrations may occur, which decreases the activity of the catalyst.

3.3 Conclusions

Structural characterization of VOx/Florisil (15MgO/ 85SiO₂) catalysts shows that the presence of basic MgO species significantly modifies the molecular structure of the surface vanadium oxide species and changes their structure from VO₅/VO₆ polymers to less polymerized species such as poly-VO₄ and/or isolated VO₂(OH)₂ species as compared to their SiO₂ supported congeners. According to XRD, IR, SEM, EDX and TEM measurements, VO_x/ Florisil catalysts either grafted (calcined or non-calcined) or impregnated (Imp1F) with low vanadium loading do not contain any bulk phase other than those characteristic for the Florisil support. The other impregnated catalysts (Imp2F, Imp3F and Imp4F) contain fine particles of MgO, while the catalyst (Imp5F) with high vanadium loading contains three different phases namely pyro-Mg₂V₂O₇, meta-MgV₂O₆ and V_2O_5 .

Our results show that the catalytic activity remarkably depends on the molecular structure of vanadium oxide species. High conversions at 70 % with an overall selectivity to the target products above 90 % are observed for catalysts (Ungrf1F, Grf1F, and Imp1F) containing isolated VO_4 or highly dispersed ortho-Mg₃V₂O₈. By contrast, catalysts containing polymerized species of vanadium oxide (Grf3F, Grf3F and Imp5F) gave high conversions but low overall selectivity. This suggests that the polymerized vanadium oxide species (VO₄, VO₅/VO₆) beside their high activities for the cyclohexane oxidation also accelerate the over-oxidation of Cy-OOH to unwanted by-products, thus reducing the overall selectivity to the target products. Also high concentrations of H₂O₂ should be avoided especially at high conversions, owing to increased over-oxidation of the primary cyclohexyl hydroperoxide to unwanted byproducts. Higher reaction temperatures increase the reaction rate but also accelerate the decomposition of H₂O₂. In terms of leaching, the presence of 15 % MgO besides SiO₂ on the surface of VO_x/Florisil catalysts significantly

improves the stability compared to silica (VO_x/SiO_2) supported catalysts. In summary, Florisil supported VO_x catalysts combine the high activity of SiO_2 and the improved leaching behavior of the MgO supported VO_x catalysts. Further improvement may be possible with other basic oxide modified support materials.

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