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Monolayers and Double Layers of Vanadium Pentoxide on Different Carriers: Preparation, Characterization, and Catalytic Activities

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Reactions of vanadyl triisobutoxide with surface OH groups are used to immobilize mono- and double layers of V_2O_5 on Al_2O_3, SiO_2, MgO, and TiO_2 supports. The Al_2O_3 and SiO_2 carriers exhibit quantitative transformation of the surface hydroxyl groups into V=O species, as evidenced by OH group and V^{5+} determinations. In contrast, with MgO and TiO_2 only a fraction of the surface hydroxyls was found to react with the impregnant solution. Hydroxyl groups present on the surface of the calcined monolayer catalyst are utilized for immobilization of a second V_2O_5 layer. TPR profiles of the supported V_2O_5 catalysts exhibit one prominent peak and indicate that the reducibility of the V_2O_5 species depends mainly on the carrier, and only weakly on the V_2O_5 load. The temperature of maximum hydrogen consumption in the TPR profiles increases in the sequence $TiO_2 < Al_2O_3 < SiO_2 <$ MgO. The catalytic activity of the pure carriers and supported catalysts is tested for methanol and *n*-heptanol oxidation in the range 520–670 K. From the pure carriers, TiO_2 exhibits the highest selectivity to formaldehyde (22%), while MgO shows a selectivity of 95% to *n*-heptanal. From the monolayer supported systems, SiO_2—V^{5+} is most selective (90%) for formaldehyde formation, whereas for *n*-heptanal production MgO—V^{5+} was found to be most selective (>95%). Second-layer impregnation does not lead to enhanced activity and selectivity for methanol oxidation. However, it improves the selectivity to *n*-heptanal for Al_2O_3 and SiO_2 carriers.

INTRODUCTION

Considerable effort has been expended to develop methods for the uniform deposition of vanadium oxides as monolayers on support materials. Vanadium metavanadate (*1*, *2*), vanadium pentoxide (*3*), and vanadium or vanadyl chlorides (*4*, *5*) have been used as impregnating agents. Reactions of these compounds with oxide surfaces are often not specific, perhaps with the exception of TiO_2 supports. As a consequence, it is difficult to estimate the impregnation capacity of a carrier, and to assess the structure of the vanadium surface compounds. An effort toward more specific monolayer immobilization has been recently made by van Hengstum *et al.* (*6*) using $VO(acac)_2$ as the impregnating agent.

In this work, the reaction of vanadyl triisobutoxide with surface hydroxyls for the deposition of vanadium oxide species on a carrier surface is reported. By the selective immobilization of V_2O_5 mono- and double layers the influence of the support on the oxidizing characteristics of the surface vanadyl species is investigated; yields of partial and total oxidation products are compared for different carriers. The impregnation with solutions of corresponding alkoxides was previously applied for the immobilization of alkali metal ions on alumina surfaces (*7*). There a stoichiometric reaction between alcoholates and surface OH groups has been observed. In the

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present study we focus on the reaction of vanadyl triisobutoxide with the surfaces of alumina, silica, magnesia, and titania. The influence of the acid–base character of the support surface on the physicochemical and catalytic properties of monolayer and double layer catalysts is investigated. The oxidative and acidic catalyst functions are tested for methanol and *n*-heptanol oxidation.

EXPERIMENTAL

Catalysts. Alumina was obtained by hydrolysis of aluminum isopropoxide previously purified by destillation under vacuum (b.p. 413 K at 1.07 kPa). The hydrolysis procedure has been described elsewhere (*7*). Before calcination $Al(OH)_3$ was dried at 313, 353, and 393 K, for 24 h at each temperature.

Silica was prepared by hydrolysis of ethyl orthosilicate, previously purified by distillation (b.p. 441–442 K at 100 kPa). Freshly distilled ester (500 g) and doubly distilled water (1000 g) were stirred and heated at 318 k for several hours. The water layer was separated and the silica dried for 24 h at 333 and at 393 K.

Magnesia was obtained by hydrolysis of $Mg(NO_3)_2 \cdot 6\ H_2O$ with concentrated aqueous ammonia solution. After washing with doubly distilled water the $Mg(OH)_2$ precipitate was dried at 333, 353, and 393 K, for 24 h at each temperature.

Titania (P 25, Degussa, consisting of 68% anatase and 32% rutile) was treated with doubly distilled water and dried for 24 h at 333 and 393 K.

Before the impregnation all oxides were calcined in water-free and deoxidized nitrogen during 5 h at 873 K. Grains of 0.5–1.0 mm diameter have been used for the impregnation.

Vanadium ions were immobilized on the carriers by impregnation with vanadyl triisobutoxide. This reagent was prepared according to the procedure described in Ref. (*8*), and purified by vacuum distillation (b.p. 414–415 K at 1.07 kPa). The isobutyl alcohol derivative offers the advantages of higher stability, as compared to the ethoxide (*9*), and a monomeric nature, as compared to the methoxide (*10*). The carriers were impregnated with a solution of vanadyl triisobutoxide in water free *n*-hexane. After 24 h the solution was removed and the catalyst was washed several times with the solvent. Subsequently the impregnated catalysts were calcined during 3 h at 573 K in a stream of dry air. Catalysts with a second layer of vanadium ions were prepared according to the same procedure from the previously produced monolayer catalyst.

With some catalysts the stream of air passed through the precursor material during calcination was analyzed by gas chromatography (3-m column 3% SE-30 on Chromosorb P; Willy Giede apparatus GCHF).

Chemical characterization of carriers and catalysts. The number of OH groups on the pure carrier surfaces, and on the monolayer and double layer vanadium catalysts was determined by means of the sodium naphthenide titration method (*11*).

To determine the number of immobilized V^{5+} ions, the vanadium was extracted with HCl from the catalyst surface and titrated iodometrically. In addition, the total amount of vanadium ions was measured gravimetrically. A comparison of the results indicated that all vanadium ions immobilized were present as V^{5+} species after calcination in air.

Temperature-programmed reduction (TPR). The TPR apparatus used has been described in Ref. (*12*). TPR profiles were obtained under the following conditions: sample weight, 1 g; reducing gas, 6% hydrogen in nitrogen; flow rate, 75 cm^3 (NTP)/min; heating rate, 10 K/min.

Catalytic activity measurements. Methanol and *n*-heptanol oxidation were performed in a fixed-bed reactor. The conditions for methanol oxidation were: temperature range, 523–673 K; amount of catalyst, 1 g; methanol flow rate, 1.64 ×

10^{-5} mol s^{-1}; flow rate of air, 1.89×10^{-4} mol s^{-1}. For *n*-heptanol oxidation the following conditions were used: temperature, 573 K; amount of catalyst, 4.1 g; heptanol flow rate, 1.97×10^{-5} mol s^{-1}; flow rate of air, 5.09×10^{-5} mol s^{-1}.

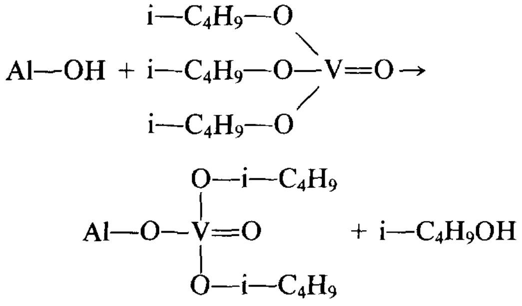
The products of methanol oxidation were sampled periodically with a Carlo Erba Bimatic sampling valve, and analyzed with a Carlo Erba gas chromatograph (Fractovap Linea G, Gl 452). Two columns of 2 m length have been used for the analysis: molecular sieve 5A for air analysis, and Poropak T for liquid products and CO_2. In addition CO and CO_2 were analyzed by Dräger test tubes.

RESULTS

(*A*) *Surface Hydroxyls and Deposited Vanadium*

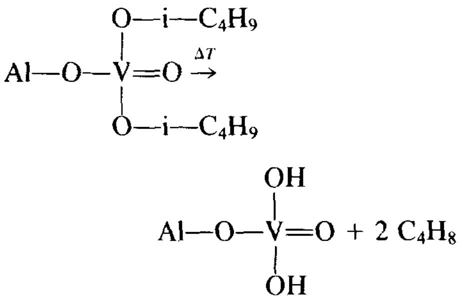
Supported monolayers. The numbers of surface hydroxyls and vanadium cations detected on carriers and surfaces impregnated with vanadium oxide monolayers and double layers are listed in Table 1. The valence of the V^{5+} cations is preserved during the impregnation and calcination in air. Hydroxyl groups detected on the impregnated catalysts originate from decomposition of the reacted alkoxide layer.

For *alumina* and *silica* the amount of vanadium deposited in the first layer corresponds closely to the number of surface hydroxyls on the pure carrier. This indicates an equimolar reaction of the surface hydroxyls and vanadyl alkoxide:

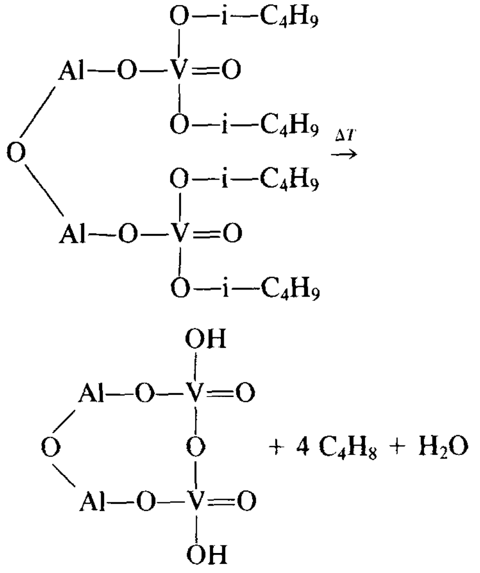


(1)

During the calcination of impregnated oxides the formation of butenes was detected. The formation of butene originates from reactions



$$\text{Al—O—}\overset{\displaystyle \text{O—i—C}_4\text{H}_9}{\underset{\displaystyle \text{O—i—C}_4\text{H}_9}{\text{V}}}\text{=O} \xrightarrow{\Delta T} \text{Al—O—}\overset{\displaystyle \text{OH}}{\underset{\displaystyle \text{OH}}{\text{V}}}\text{=O} + 2\,\text{C}_4\text{H}_8 \quad (2)$$



(3)

The number of secondary hydroxyls was found to depend on both the carrier material and its calcination temperature. For V_2O_5 on Al_2O_3 calcined at 573 K, the ratio of secondary hydroxyls to vanadium ions was about 2, which is consistent with the stoichiometry of reaction (2). For an Al_2O_3 carrier calcined at 873 K this ratio was about 1 (Table 1), indicating that reaction (3) was prevalent.

On *silica* the number of secondary hydroxyls is lower, as compared to Al_2O_3. For SiO_2 calcined at 573 K, the ratio of secondary hydroxyls to vanadium ions was about 1.5, consistent with an involvement

TABLE 1

Chemical and Physical Characterization of Pure Carriers and Supported Catalysts

Carrier or catalyst	Concentration of surface OH groups [mmol/g]	Concentration vanadium ions [mmol/g]	Surface area BET [m^2/g]	Pore volume [cm^3/g]	Most frequent pore radius [nm]
Al_2O_3	0.34	—	204	0.48	4.5/1.9
Al_2O_3—V^{5+}	0.36	0.34	—	—	—
Al_2O_3—$2V^{5+}$	0.13	0.63	206	0.44	4.1/1.8
SiO_2	0.28	—	448	0.48	2.3
SiO_2—V^{5+}	0.18	0.32	—	—	—
SiO_2—$2V^{5+}$	0.08	0.56	409	—	2.1
MgO	0.56	—	37	0.30	15
MgO—V^{5+}	0.20	0.22	—	—	—
MgO—$2V^{5+}$	0.24	0.29	41	0.29	15
TiO_2	0.17	—	38	0.37	17
TiO_2—V^{5+}	0.15	0.05	33	0.25	18
TiO_2—$2V^{5+}$	0.16	0.19	27	0.32	18

of both reactions (2) and (3). For SiO_2 calcined at 873 K a ratio of 0.5 was found (Table 1), suggesting that reaction (3) is extended to bridge more than two vanadium ions by V—O—V bonds.

For *magnesia* treated with vanadyl triisobutoxide the ratio of the hydroxyls on the pure carrier surface to the number of immobilized vanadium ions was about 2. This can be explained by the formation of surface alkoxide species with two bonds to the surface. The determined number of secondary hydroxyls was close to the number of immobilized vanadium ions.

The impregnation of *titania* with vanadyl triisobutoxide resulted in a considerably lower amount of vanadyl species, as compared to the number of surface hydroxyls on the titania carrier. In contrast to MgO—V^{5+}, the amount of secondary hydroxyls on TiO_2—V^{5+} was three times higher than the vanadium ion concentration. This result suggests that secondary hydroxyls detected are partly unreacted OH groups on the carrier surface.

Note that reactions (1)–(3) represent the stoichiometry of immobilization, but do not imply that the coordination of the surface vanadyl species is tetrahedral. Additional coordinative bonds with oxygen atoms on the surface may be formed during calcination as will be discussed below.

Supported double layers. The immobilization of a second V^{5+} layer on *alumina* yielded an increase in the number of vanadium ions which corresponded closely to the number of surface hydroxyls on the pure carrier. However, the concentration of OH groups was two times lower than the number of vanadium ions in the second layer. This is attributed to subsequent dehydration of vanadyl hydroxides leading to interconnection of vanadyl groups by V—O—V bonds. A similar behavior was found for the *silica*-supported catalyst.

On *magnesia*, the surface concentration of vanadium increases only by 0.07 mmol/g. Simultaneously, the surface hydroxyl concentration shows a slight increase from 0.20 to 0.24 mmol/g. These findings suggest that only a part of the surface hydroxyls present on the monolayer catalyst underwent reaction during the second impregnation. The newly introduced groups are only singly bound to the surface, and consequently carry two OH groups.

Second layer impregnation of *titania* results in a very pronounced increase of the vanadium ion concentration, whereas the hydroxyl concentration remains almost unchanged. This suggests that some of the unreacted hydroxyls present on the surface of the monolayer catalyst have gained a higher acidity during the calcination process. As a consequence they react with vanadyl triisobutoxide in the second impregnation step. The fact that the OH concentration remains constant suggests that the vanadyl groups immobilized in the second layer are doubly bonded to the surface; thereby they contribute only one OH group per vanadium ion.

(*B*) *Texture of Catalysts*

Textural properties of the prepared catalysts are listed in Table 1. The differences in the surface area between the pure carriers and doubly impregnated catalysts are relatively small, as expected. The *silica* and *titania* systems show a decrease in surface area after impregnation, whereas with *alumina* and *magnesia* the surface area increases slightly. For the pore volumina a small decrease is observed. A slight narrowing of the micropores by the deposition of the V_2O_5 is indicated with *alumina* and *silica*.

(*C*) *Reduction Behavior of Catalysts*

The reduction behavior of the impregnated carriers was investigated by temperature-programmed reduction and thermogravimetric measurements. Reduction profiles of the catalysts are presented in Fig. 1. The TPR profiles of all catalysts exhibited only one prominent maximum. The approximate onset temperatures of reduction, T_{on}, and the temperature of maximum hydrogen consumption, T_m, are listed in Table 2. The temperature of maximum hydrogen consumption depended on the carrier material and increased in the sequence $TiO_2 < Al_2O_3 < SiO_2 < MgO$. Note that for silica- and alumina-supported catalysts T_m was virtually not affected by the load of V_2O_5. In contrast, with magnesia T_m shifted to higher temperature by 20°C after second-layer impregnation.

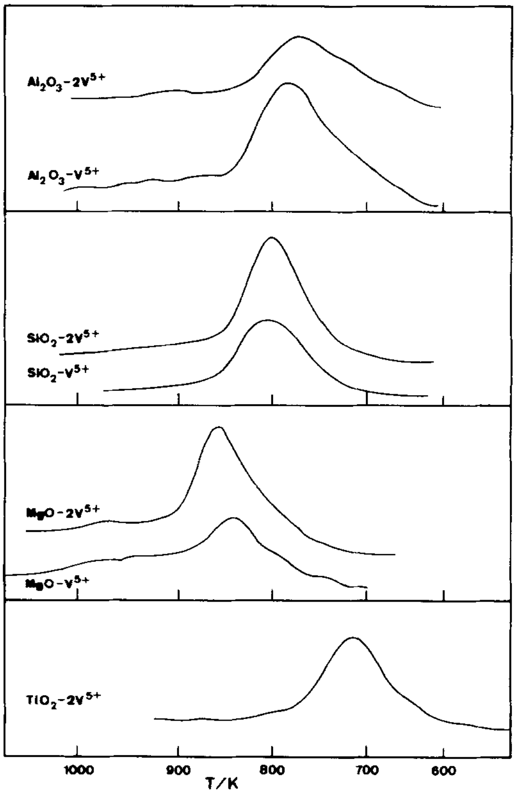


FIG. 1. Typical TPR profiles of supported V_2O_5 mono- and double layer catalysts. Conditions are given in the Experimental section.

The onset temperature of reduction, T_{on}, is a measure for the reducibility of the system. The following sequence can be given for T_{on} of the monolayer catalysts: $TiO_2 < Al_2O_3 < SiO_2 < MgO$. Second-layer impregnation did not significantly reduce the onset temperature, except for alumina-supported V_2O_5.

(*D*) *Catalytic Activity*

The oxidation of methanol and *n*-heptanol was investigated over the pure carriers, the monolayer and double layer catalysts. These reactants have been selected since they exemplify different chemical

TABLE 2

Onset Temperatures of Reduction, T_{on}, and Temperatures of Maximum Hydrogen Consumption, T_m, Obtained from TPR Profiles

Catalyst	T_{on} [K]	T_m [K]
Al_2O_3—V^{5+}	620 ± 5	780
Al_2O_3—$2V^{5+}$	610 ± 5	770
SiO_2—V^{5+}	635 ± 15	805
SiO_2—$2V^{5+}$	630 ± 15	800
MgO—V^{5+}	715 ± 15	840
MgO—$2V^{5+}$	715 ± 15	860
TiO_2—$2V^{5+}$	530 ± 5	715
V_2O_5[a]	920 960 985 1010	

[a] Four peaks, cf. Ref. (14).

properties. Observed reactions for methanol are the selective oxidation to formaldehyde, intermolecular dehydration forming dimethyl ether, and total oxidation to CO and CO_2. Reactions observed with *n*-heptanol are selective oxidation to *n*-heptanal, and inter- and intramolecular dehydration leading to *n*-heptene and di-*n*-heptyl ether, respectively.

Methanol oxidation. The results obtained for methanol oxidation are listed in Table 3. Note that on the supported systems, the product formation is given as a turnover frequency, whereas on the pure carriers the product distribution is specified in mol%.

Pure *alumina* exhibits a high selectivity for the formation of dimethyl ether, as expected from its acidic properties. Dimethyl ether formation decreases in the sequence $Al_2O_3 > Al_2O_3$—$V^{5+} > Al_2O_3$—$2V^{5+}$. The lower dehydration activity of the double layer catalyst is attributed to the significantly smaller OH group concentration on this catalyst (Table 1).

The pure *silica* support was practically inactive. However, the SiO_2-supported monolayer and double layer catalysts exhibited a very high selectivity to formaldehyde. Note that the activity of the double layer catalyst was smaller by almost an order of magnitude, as compared to the monolayer system.

Pure *magnesia* did not yield appreciable amounts of formaldehyde. However, it exhibited considerable activity for total oxidation and decomposition of methanol at higher temperatures. The MgO-supported monolayer and double layer catalysts produced formaldehyde with good selectivity.

Pure *titania* exhibited the highest selectivity to formaldehyde among all carriers, whereas no dimethyl ether production was observed. The titania-supported monolayer and double layer catalysts yielded only the total oxidation products CO and CO_2. This is ascribed to the high oxidation activity at the temperatures used. At temperatures below 470 K Roozeboom *et al.* (13) have observed high selectivity to formaldehyde on a V_2O_5 monolayer catalyst.

Note that the unsupported vanadium pentoxide exhibited a selectivity to formaldehyde which is comparable to the MgO-supported V_2O_5 layer catalysts, but lower than the one of the SiO_2-supported catalysts.

n-Heptanol oxidation. Results obtained with *n*-heptanol oxidation are summarized in Table 4. As observed with methanol oxidation, the dehydration activity of the alumina supported catalysts decreases in the sequence $Al_2O_3 > Al_2O_3$—$V^{5+} >$ Al_2O_3—$2V^{5+}$. This trend parallels the decrease of the OH group concentration (Table 1). The selectivity to *n*-heptanal shows the opposite sequence. Di-*n*-heptyl ether formation decreases from the monolayer to the double layer catalyst, resulting in a higher selectivity to *n*-heptanal.

Pure *silica* showed a selectivity to *n*-heptanal which was higher than those observed for the SiO_2 supported systems. Note the relatively large production of *n*-heptene on

TABLE 3

Methanol Oxidation over Pure Carriers and Supported Catalysts

Catalyst or carrier	Temperature [K]	Rates of product formation[a] $[ks]^{-1}$				Selectivity to formaldehyde [%]
		$H_2C{=}O$	$CH_3{-}O{-}CH_3$	CO	CO_2	
$Al_2O_3{-}V^{5+}$	523	1.4	19	0.3	0[b]	7
	538	1.5	20	0.8	0.1	7
$Al_2O_3{-}2V^{5+}$	553	0.4	12	0.5	0.1	3
	613	1.2	7	5	3	8
	633	0	0	20	7	0
Al_2O_3[c]	533	(0)	(80)	(1)	(0)	0
	613	(8)	(56)	(13)	(5)	10
$SiO_2{-}V^{5+}$	558	12	0	1	0	93
	583	28	1	2	0.1	90
	618	47	3	6	0.2	84
$SiO_2{-}2V^{5+}$	558	1.4	0	0.1	0	99
	633	4.8	0	0.1	1.5	75
SiO_2[c]	573	(2)	(Traces)	(1)	(Traces)	—
$MgO{-}V^{5+}$	548	2.1	0	1	0	72
	568	5.1	0	1	0.2	81
	588	7.4	1	1	0.5	76
	663	10	8	10	36	16
$MgO{-}2V^{5+}$	560	4.8	0	1	0.1	87
	583	7.8	3	0.8	0.6	63
	653	12	7	8	22	25
MgO[c]	553	(Traces)	(Traces)	(1)	(0.1)	0
	673	(1)	(8)	(33)	(54)	1
$TiO_2{-}V^{5+}$	543	0	0	21	2	0
	586	0	0	21	2	0
$TiO_2{-}2V^{5+}$	555	0	0	8	0.3	0
	573	0	0	8	0.2	0
	608	0	0	5	0.6	0
TiO_2[c]	569	(7)	(0)	(8)	(1)	44
	618	(12)	(0)	(38)	(7)	22
V_2O_5[c]	533	(76)	(7)	(12)	(5)	76
	573	(0)	(0)	(76)	(24)	0

[a] Rate is defined as moles of product formed per mole of V^{5+} ions and per ks.

[b] Means concentration beyond detection limit.

[c] Product distribution given as concentrations (mol%) in product mixture.

the monolayer catalyst, as compared to the double layer catalyst. This can be explained by the very low OH group concentration present in the double layer system.

Pure *magnesia* also shows a high activity for *n*-heptanal formation. Note that there is no pronounced difference between the product distributions of the supported systems and the pure carrier. MgO-containing catalysts were the most selective for heptanal production of all the catalysts investigated.

Pure *titania* exhibited a similar selectivity to *n*-heptanal as the titania-supported V_2O_5 systems. Note the markedly higher activity of the monolayer catalyst, as compared to the double layer catalyst.

Unsupported V_2O_5 exhibited a selectivity

TABLE 4

n-Heptanol Oxidation over Pure Carriers and Supported Catalysts at 573 K

Catalyst	Rate of product formation[a] [ks]$^{-1}$			Selectivity to *n*-heptanal [mol%]
	n-Heptene	*n*-Heptanal	di-*n*-Heptylether	
Al_2O_3—V^{5+}	9.3	1.3	0.8	12
Al_2O_3—$2V^{5+}$	4.0	3.0	0.1	42
Al_2O_3[b]	(31)	(4)	(3)	11
SiO_2—V^{5+}	5.5	3.4	0.5	37
SiO_2—$2V^{5+}$	0.8	2.1	0	72
SiO_2[b]	(1)	(6)	(0)	83
		5.7		
MgO—V^{5+}	0.3	5.1	0	95
MgO—$2V^{5+}$	0.5	(14)	0	91
MgO[b]	(1)		(0)	97
		8.4		
TiO_2—V^{5+}	5.9	2.3	0	59
TiO_2—$2V^{5+}$	1.8	(7)	0	56
TiO_2[b]	(5)		(0)	58
		(14)		
V_2O_5[b]	(3)		(0)	82

[a] Rate is defined as moles of product formed per mole of V^{5+} ions and per ks.

[b] Concentrations (mol%) in product mixture.

higher than 80% to *n*-heptanal. This selectivity was exceeded only by the magnesia-supported systems.

DISCUSSION

When interpreting the surface hydroxyl and vanadium concentrations given in Table 1 we should take into account that the number of OH groups measured on a given carrier depends on the calcination temperature. It can be assumed that the OH groups are the only species which react with the vanadyl alkoxide.

The most important results emerging from Table 1 are: (i) *alumina* and *silica* exhibit quantitative reaction of the surface hydroxyls with the alkoxide, i.e., one vanadium ion is immobilized per OH group present on the carrier. This can be considered to correspond to a completely developed monolayer. (ii) On *magnesia* and *titania* the abundant vanadyl species are doubly bound to the surface. With *magnesia* the balance of hydroxyl concentrations indicates that all OH groups on the carrier have reacted; with double bonding a monolayer coverage of vanadium corresponds to half the OH concentration found on the carrier. With *titania* part of the OH groups on the carrier were unreactive toward the alkoxide, and thus the coverage stays below one monolayer with first impregnation.

Further work will be necessary to assign the structure of the V_2O_5 layer(s) deposited during second impregnation. Following the argumentation presented above, it is plausible that with second impregnation the alkoxide reagent is mainly anchored on hydroxyls of the first V_2O_5 layer for alumina, silica, and magnesia supports. On titania some of the carrier hydroxyls react in the second impregnation step.

TPR profiles of all catalysts exhibited only one prominent maximum. This contrasts the behavior of bulk V_2O_5, where depending on the morphology three to four peaks were obtained in the TPR profiles (*14*). Single peaks in the TPR profiles were also observed for titania-supported monolayers of V_2O_5 by van Hengstum *et al.* (*15*). The appearance of only one peak in the TPR profiles of the supported monolayer catalysts does not decisively confirm that the reduction occurs in a single step. We should take into account the limited resolution of TPR measurements (*12*) performed on catalysts with low concentration of the reducible species, such as supported monolayer catalysts. In any case, it can be concluded that the supported monolayers of V_2O_5 exhibited a completely different reduction behavior than bulk V_2O_5.

Concerning the sequence given for the reducibility (T_{on}) of V_2O_5 supported on various carriers, it is interesting to compare the TPR results with ESR measurements performed on these systems. Recently, we have shown (*16*) that a measure for the vanadyl bond strength can be derived from the ESR parameters, and that this bond strength is consistent with the above conclusions on reducibilities derived from TPR measurements.

The method is based on a determination of tetragonal distortion in a local coordination octahedron of oxygen ligands surrounding the vanadium ions. From the principal values of the vanadium tensor, the ratio $\Delta g_{\|}/\Delta g_{\perp}$ is calculated which increases with a shortening of the vanadyl (V=O) bond, or with increasing distance between the central vanadium ion and the oxygen ligands in the basal plane (*16*). Both geometry changes correspond to a strengthening of the vanadyl bond. We have shown that for all catalyst systems discussed in this study, a decrease in $\Delta g_{\|}/\Delta g_{\perp}$ is paralleled by a decrease of the onset temperature of hydrogen consumption, T_{on}, measured by TPR (*16*). As discussed above, this corresponds to a catalyst that can be reduced more easily. We shall indicate below that both measures of reducibility are correlated with the partial oxidation selectivity of the catalysts.

Concerning the distorted octahedral geometry used in the analysis of the ESR results, it should be noted that the stoichiometries of reactions (1)–(3) are not intended to imply a statement on the coordination geometry. Using laser Raman spectroscopy, Roozeboom *et al.* (*17*) have found distorted vanadate octahedra for a preparation starting from aqueous solution of ammonium metavanadate. Kozlowski *et al.* (*18*) have studied the coordination of vanadium in monolayer catalysts prepared by impregnation of TiO_2 with $VOCl_3$. Their X-ray adsorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) investigations revealed the presence of two terminal and two bridging oxygen ligands. The authors interpret their results in terms of an irregular coordination octahedron, with two ligands at larger distances that are not detected by the EXAFS and XANES measurements.

In the discussion of the oxygen bond strength, it has been advocated (*19, 20*), that catalysts which are easily reduced exhibit high activities but low selectivities in partial oxidation reactions. A higher value of T_{on} (Table 2) indicates more tightly bound oxygen, and thus higher partial oxidation selectivity. This concept is supported by the sequence found for the selectivities to formaldehyde in methanol oxidation, i.e., $SiO_2 > MgO > Al_2O_3 > TiO_2$. Note that the low value of T_{on} observed for TiO_2—$2V^{5+}$ results in a very high total oxidation activity. However, selective oxidation to formaldehyde has been observed at considerably lower temperatures, i.e., in the range 420–470 K (*13*).

Finally it is interesting to compare the product distribution obtained for methanol and *n*-heptanol oxidation at temperatures around 570 K. Some of the supported catalysts clearly show a bifunctional character, since they contain both acidic sites (OH groups) and oxidizing sites (V=O). The bifunctional activity is most prominent with the SiO_2- and TiO_2-supported V_2O_5 systems for heptanol oxidation. To a lesser extent it was also observed with Al_2O_3-supported V_2O_5 for both reactions.

The activity and selectivity behavior is markedly different in methanol and heptanol oxidation, both for pure carriers and supported catalysts. On all *pure carriers n*-heptanol oxidation yielded appreciable amounts of *n*-heptanal. In contrast, with methanol marked formaldehyde formation occurred on TiO_2 only. Dehydration was most prominent with Al_2O_3 for both reactions.

From the monolayer catalysts, SiO_2—V^{5+} was most active and selective for formaldehyde formation, whereas for *n*-heptanal formation MgO—V^{5+} was found to be most selective. TiO_2—V^{5+} yielded only total oxidation products for methanol at the temperatures investigated. For heptanol oxidation TiO_2—V^{5+} was the most active catalyst of all systems studied, but exhibited similar activity for dehydration and oxidation.

Second-layer impregnation did not lead to enhanced activity and selectivity for methanol oxidation. In contrast, second-layer impregnation was found to increase the selectivity to *n*-heptanal, by a factor of 3 for Al_2O_3, and a factor of 2 for SiO_2.

CONCLUSIONS

The reaction of vanadyl triisobutoxide with surface OH groups was introduced as a powerful technique to immobilize uniform monolayers of V_2O_5 onto oxidic carriers. The OH groups present in the monolayer catalyst can be utilized further for the second-layer impregnation. On *alumina* and *silica* the vanadyl species are singly bound to the carrier surface and quantitative transformation of the OH groups has been confirmed. On *magnesia* and *titania* the abundant vanadyl species are doubly bound to the carrier surface. On *titania* some of the carrier hydroxyl groups did not react under the conditions used. The catalytic properties of such monolayers are strongly influenced by the support material.

The high specificity of the impregnation method may allow to tailor the bifunctional character of catalysts containing acidic and oxidizing sites. The importance of the bifunctional properties of such catalysts for the product distribution has been demonstrated using methanol and *n*-heptanol oxidation. In general, impregnation of the acidic carriers with V^{5+} layers led to an increase of the oxidizing character of the catalyst, whereas the dehydration activity was lowered. The activity for total oxidation of methanol parallels the reducibility, as derived from TPR and ESR measurements. The selectivity to formaldehyde shows an antiparallel tendency. No similar correlation was established for the *n*-heptanol oxidation.

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