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MOLECULAR DESIGN OF SUPPORTED METAL OXIDE CATALYSTS

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Abstract

This study demonstrates that molecular design of supported metal oxide catalysts is possible from molecular level information obtained from combined Raman spectroscopy and the methanol oxidation reaction. The important factors that influence the molecular design of the supported metal oxide catalysts are the specific oxide support (factor of $\sim 10^3$) and the specific surface metal oxide (factor of $\sim 10^1$). The synthesis method is not critical since it does not influence the surface metal oxide structure or reactivity. Calcination temperature is not important as long as moderate temperatures (350-500°C) are used.

1. INTRODUCTION

Many recent studies have demonstrated that two-dimensional transition metal oxide overlayers are formed when one metal oxide component (i.e., Re_2O_7, CrO_3, MoO_3, WO_3, V_2O_5, Nb_2O_5, etc.) is deposited on a second metal oxide substrate (i.e., Al_2O_3, TiO_2, SiO_2, etc.) [1]. The molecular structures and reactivity of these surface metal oxide species have been intensively investigated over the past decade because of the importance of these supported metal oxide materials in numerous catalytic applications [1,2]. The major structural information about these surface metal oxide species has been derived from Raman spectroscopy studies because of the molecular nature of this characterization method and its ability to discriminate between different metal oxide species that may simultaneously be present in the catalyst. Corresponding reactivity studies have demonstrated that these surface metal oxide species possess the active sites for many catalytic reactions. The fundamental information currently available about these oxide catalysts is beginning to allow us to molecularly design supported metal oxide catalysts. The molecular design of supported metal oxide catalysts requires that we specify the synthesis method, oxide support, catalyst composition, calcination temperature, location and structure of surface metal oxide species, as well as its reactivity. Consequently, the influence of each of the above parameters upon the catalytic properties of supported metal oxide catalysts needs to be examined. The present study primarily focuses on the molecular design aspects of supported vanadium oxide catalysts because these catalysts constitute a very important class of heterogeneous oxide catalysts. However, comparison with other supported metal oxide systems (MoO_3, Re_2O_7, and CrO_3) will also be made.

2. EXPERIMENTAL

The oxide supports employed in the present study were: TiO_2 (Degussa, ~55 m^2/g), Al_2O_3 (Harshaw, ~180 m^2/g), SiO_2 (Cabot, ~300 m^2/g), ZrO_2 (Degussa, ~39 m^2/g) and Nb_2O_5 (Niobium Products Co., ~50 m^2/g). Many different synthesis methods have been used to prepare supported metal oxide catalysts. In the case of supported vanadium oxide catalysts, the catalysts were prepared by vapor phase grafting with $VOCl_3$, nonaqueous impregnation (vanadium alkoxides), aqueous impregnation (vanadium oxalate), as well dry impregnation with crystalline V_2O_5 (spontaneous dispersion).

Supported chromium oxide (1% wt.), rhenium oxide (1% wt.) and molybdenum oxide (1% wt.) catalysts were prepared by the incipient-wetness impregnation method using an aqueous solution of chromium nitrate, $HReO_4$, and ammonium heptamolybdate, respectively.

The molecular structures of the supported metal oxide catalysts were characterized by laser Raman spectroscopy under *in situ* as well as ambient conditions. The laser Raman spectroscope consist of a Spectra Physics Ar^+ laser producing 1-100 mW of power measured at the sample. The scattered radiation was focussed into a Spex Triplemate spectrometer coupled to a Princeton Applied Research OMA III optical multichannel analyzer. About 100-200 mg of the pure catalysts were pelletized and used for obtaining the Raman spectra in the *in situ* mode. For ambient spectra 5-20 mg of catalysts was placed on a KBr backing.

The supported metal oxide catalysts were examined for their reactivity in the methanol oxidation reaction. The reactor was operated in the differential mode by keeping conversions below 8%. A methanol/oxygen/helium mixture of ~6/13/81 at 1 atm pressure was used as the reactant gas for all the data presented. The analysis was performed on an online gas chromatograph (GC) (HP 5840A) containing two columns (Poropak R and Carbosieve SII) and two detectors (FID and TCD). Reaction data at 230 °C are presented in the form of turnover number (TON) - defined as the number of moles of methanol converted per mole of vanadium atom per second. The reaction data for some catalysts were also obtained at 200, 240, 260 °C to calculate the activation energy and check for diffusional limitations in the reactor. No mass and heat transfer limitations were observed.

3. RESULTS AND DISCUSSION

It is well known that supported metal oxide catalysts possess surface metal oxide phases (see Figure 1) that are formed by the reaction of the deposited metal oxides with the surface hydroxyls of the high surface area oxide supports. Direct evidence for the titration of the surface hydroxyls (OH) by the deposited metal oxides is obtained from *in situ* infrared studies which reveal the sequential disappearance of the support OH bands during this process [3]. The consumption of surface hydroxyls can also be monitored by CO_2 chemisorption studies since CO_2 titrates the basic surface hydroxyls [3]. Both measurements, infrared spectroscopy of surface hydroxyls and chemisorption of CO_2 on the surface hydroxyls, provide a quantitative measure of the surface coverage of the metal oxide overlayer. Consequently, a necessary condition for the formation of surface metal oxide overlayers is the presence of reactive surface hydroxyls on the oxide support. Oxide supports such as Al_2O_3, TiO_2, ZrO_2, and Nb_2O_5 have a high surface density of reactive surface hydroxyls and tend to form a closed packed monolayer of the surface metal oxide phase, whereas, oxide supports such as SiO_2 which have a lower density of reactive surface hydroxyls do not form a closed packed monolayer of the surface metal oxide phase (see Table 1). Recent studies employing electrochemical methods [4] and non aqueous allyl preparation [5] have demonstrated that somewhat higher surface density on SiO_2 can be achieved with the special preparations, but still resulted in only a small fraction of a close-packed monolayer.

Table 1
Monolayer loading and surface density of some supported metal oxides as a function of oxide support

Oxide support	Surface area (m^2/g)	Monolayer loading (wt.%)				Surface density (wt.%/m^2)			
		V_2O_5	MoO_3	CrO_3	Re_2O_7	V_2O_5	MoO_3	CrO_3	Re_2O_7
Al_2O_3	180	20	18	13	17	.11	.10	.07	.09
TiO_2	55	6	6	--	5	.11	.11	--	.09
ZrO_2	39	4	3	--	5	.10	.08	--	.13
Nb_2O_5	55	6	4	4	--	.11	.07	.07	--
SiO_2	300	3	3	2	6.5	.01	.01	.01	.02

Thus, the surface hydroxyl chemistry controls the formation and location of the surface metal oxide species present in supported metal oxide catalysts.

The molecular structures of the surface metal oxide species present in the metal oxide overlayer are not well understood and the influence of surface coverage (catalyst composition), specific oxide support, preparation method, calcination temperature, and promoters need to be established. The Raman spectra of titania supported vanadia catalysts reveal the presence of three different vanadia species on the TiO_2 support under *in situ* conditions [6]. At low loadings, a single sharp band is present at ~1030 cm^{-1} which is due to an isolated tetrahedral coordinated surface vanadium oxide species containing one terminal V=O bond and three bridging V-O-Ti bonds [7]. At intermediate loadings, a second band is present at ~930 cm^{-1} which has been assigned to a polymerized, tetrahedral coordinated surface vanadium oxide species [7]. At high loadings, a third sharp band is present at 994 cm^{-1} due to crystalline V_2O_5 which indicates that the close-packed surface vanadium oxide monolayer has been formed and all the reactive surface hydroxyls consumed. Thus, the catalyst composition is a critical parameter since it influences the formation of different vanadium oxide structures.

The reactivity of the titania supported vanadium oxide catalysts was probed by the methanol oxidation reaction. The methanol oxidation reaction is very sensitive to the nature of surface sites present in oxide catalysts. Surface redox sites (sites that are capable of being reduced and oxidized) form primarily formaldehyde as well as methyl formate and dimethyl methane as the reaction products. Surface acid sites, Lewis as well as Bronsted, result in the formation of dimethyl ether. Surface basic sites yield CO/CO_2 as the reaction products [8]. The oxidation of methanol over the titania supported vanadia catalysts yielded formaldehyde exclusively, 98%+, as the reaction product. The titania support in the absence of surface vanadia yielded dimethyl ether and trace amounts of CO_2. The almost complete formation of formaldehyde demonstrates that the reactivity of the titania supported vanadia catalysts is due to the surface vanadia redox sites. The reactivity is measured as the turnover number (TON), the number of moles of methanol reacted per surface mole of vanadium atom per second, and is presented in Table 2 as a function of the vanadia loading. The TON increases somewhat with initial surface vanadium oxide coverage, and decreases at surface coverages approaching and exceeding monolayer coverage. Note that the TON of bulk V_2O_5 is two orders of magnitude less than the titania supported vanadia catalysts indicating that crystalline V_2O_5 is significantly less active than surface vanadia species. The slight increase in TON with the increase in surface coverage appears to be related to the presence of the polymerized surface vanadia species. Similar coverage effects were also observed for supported rhenium oxide [9], molybdenum oxide [10] and chromium oxide catalysts [11]. Thus, the reactivity of surface metal oxide species has a slight dependence on surface coverage (less than a factor of 10^1).

Table 2
The TON of V_2O_5/TiO_2 catalysts as a function of loading

wt.% V_2O_5/TiO_2	T.O.N. (sec^{-1})
0.5	1.0
1.0	1.9
1.8	4.4
2.5	8.4
4.5	2.2
5.0	1.7
bulk V_2O_5	0.022

Many research groups claim that the synthesis method is critical for forming metal oxide monolayers that possess specific structures and reactivities. To investigate this issue, a series of V_2O_5/TiO_2 catalysts were synthesized by different methods: equilibrium adsorption, vanadium oxalate, vanadium alkoxides and vanadium oxychloride grafting. The *in situ* Raman spectra of all these catalysts exhibit a sharp band at ~1030 cm^{-1} characteristic of the isolated surface vanadium oxide species. Thus, the synthesis method does not affect the final structure of the surface vanadium oxide species on titania. Similar conclusions were also found for molybdenum oxide supported on titania [12], silica [5], and alumina [5]. Reactivity studies with methanol oxidation exhibited essentially identical turnover numbers. Consequently, the preparation method is not a critical parameter since it does not influence the structure of the surface metal oxide species or its reactivity.

The nature of the supported metal oxide phase is influenced by the calcination temperature. Moderate calcination temperatures, 350-500 °C, are required to decompose the metal oxide precursors (oxalates, alkoxides, oxychlorides, etc.) to form the surface metal oxide species [13]. Insufficient calcination temperatures do not completely decompose the precursors and, consequently, do not react with the surface hydroxyls to form the surface metal oxide species. However, high calcination temperatures, greater than 600 °C, can result in shrinking of the surface area of the oxide support and decreasing the available surface area for the surface metal oxide species. Consequently, high calcination temperatures increase the surface coverage of the metal oxide species and, in severe cases, destroy the surface metal oxide phase and form crystalline V_2O_5 and eventually solid state solutions [13,14]. Thus, calcination temperature is an important parameter that controls the activation and deactivation of supported metal oxide catalysts. However, supported metal oxide catalysts are typically prepared by calcining at 400-500 °C which would eliminate problems with activation and deactivation.

A series of ~1% V_2O_5 catalysts were prepared in order to investigate the influence of different oxide supports upon the molecular structure and reactivity of the surface vanadium oxide species. The low loading catalysts were selected because at these surface coverages only the isolated surface vanadium oxide species is predominantly present on the different oxide supports and potential complication due to additional surface vanadium oxide species could be eliminated. The *in situ* Raman band due to the V=O bond was found to vary from 1015-1038 cm^{-1} as a function of the different oxide supports (see Table 3). The slight difference in band position is due to slightly different V=O bond lengths of the isolated surface vanadium oxide species on different oxide supports. The important point is that the Raman spectra reveal that the same surface vanadium oxide species are present on all the different oxide supports. The same conclusion is reached from solid state ^{51}V NMR studies of these catalysts [8]. Similar observations have also been made for supported molybdenum oxide [10], rhenium oxide [9,11], and chromium oxide [9,11]. Thus, the *in situ* surface metal oxide molecular structures are independent of the specific oxide support.

Table 3
In situ Raman band position for M=O terminal stretching vibration, as a function of oxide support for 1% supported metal oxide (M_xO_y) catalysts

Oxide Support	Raman Band for M=O terminal bond			
	V	Mo	Cr	Re
SiO_2	1038	978	985	1015
Nb_2O_5	1031	990	997	1008
TiO_2	1027	993	1009	1005
ZrO_2	1024	986	1010	990
Al_2O_3	1015	992	1002	1000

The reactivity of the surface vanadium oxide species on the different oxide supports was probed by the methanol oxidation reaction. For all the supported vanadium oxide catalysts, with the exception of alumina which possesses a high concentration of acid sites, the surface vanadia redox sites produced formaldehyde almost exclusively. On alumina, only a trace of formaldehyde was formed because the surface acid sites formed dimethyl ether. Thus, for the V_2O_5/Al_2O_3 system the formaldehyde produced was taken as representative of the reactivity of the surface vanadia redox sites. The reactivity of the surface vanadia species on different oxide supports was found to dramatically depend on the specific oxide support (a factor of 10^3). Similar trends were also observed for supported molybdenum oxide [10], rhenium oxide [11], and chromium oxide [11]. The specific oxide support is a critical parameter since it has such a profound effect on the reactivity of the surface metal oxide species.

The origin of this support effect is either due to differences in the terminal M=0 bond or the bridging M-0-Support bond. Many publications have proposed that the terminal bond is responsible for catalysis and its activity is directly related to the M=0 bond strength. To investigate this, the reactivity was plotted against the Raman position of the M=0 bond (shorter bond corresponds to higher Raman position). The plot of TON versus Raman M=0 position for supported vanadium oxide, molybdenum oxide, rhenium oxide, and chromium oxide is presented in Figure 2. There does not appear to be any relationship between the catalyst reactivity and the terminal M=0 bond strength as was previously proposed. A more plausible conclusion is that the reactivity is related to the bridging M-0-Support bond since the oxide support has a very significant effect on the reactivity. This suggests that the reactivity should also be a function of the specific metal oxide species. Indeed, supported molybdenum oxide catalysts are about one order of magnitude less reactive than supported vanadia catalysts. The trend in reactivity with specific oxide support appears to be related to the surface reducibility of the oxide supports. The more reducible oxide supports (TiO_2, ZrO_2, and Nb_2O_5) always exhibit very high TON while the irreducible oxide supports (Al_2O_3 and SiO_2) always exhibit very low TON [15].

Additional information about the reactivity was obtained by determining the kinetic parameters during methanol oxidation for vanadia, molybdena, rhenia, and chromia on different oxide supports. For all these systems the activation energy is approximately the same, 18-22 kcal/mol. The activation energy corresponds to that expected for the breaking of the C-H bond of a surface methoxide intermediate, CH_3O_{ads}, and should be independent of the specific catalyst [16]. The pre-exponential factors, however, vary by orders of magnitude as the oxide support is varied. The difference in pre-exponential factors suggest that the number of active sites are responsible for the different TON. In calculating the TON we assume that all the surface vanadia species are participating in the reaction all the time. However, the different pre-exponential factor suggests that on less reducible oxide supports such as Al_2O_3 and SiO_2 only a small fraction of the surface vanadia species participate at a given time in the reaction, and that for reducible oxide supports such as TiO_2, ZrO_2, and Nb_2O_5 a significantly larger fraction of the surface vanadia species participate at a given time in the reaction. The different reactivities may also be due to different activity per active site. Experiments are currently in progress to quantify the number of active sites participating in the reaction at given time and their reactivity. Thus, the oxide supports control the reactivity of the surface metal oxide species.

Table 4
The TON for methanol oxidation reaction for various 1% supported metal oxide catalysts

Oxide Support	TON (sec^{-1})			
	V_2O_5	MoO_3	CrO_3	Re_2O_7
SiO_2	$2.0*10^{-3}$	$3.9*10^{-2}$ †	$1.6*10^{-1}$	$2.0*10^{-2}$ †
Al_2O_3	$2.0*10^{-2}$	--- ‡	$1.6*10^{-3}$	--- ‡
Nb_2O_5	$7.0*10^{-1}$	$3.2*10^{-2}$	$5.8*10^{-2}$	$1.2*10^{-2}$ †
TiO_2	$1.8*10^{0}$	$3.1*10^{-1}$	$3.0*10^{-1}$	$1.2*10^{0}$
ZrO_2	$2.3*10^{0}$	$9.2*10^{-2}$	$1.3*10^{0}$	$1.7*10^{-1}$

† metal oxide was found to be volatile and left deposits on tube
‡ no redox products observed due to activity of alumina support

Many publications have also claimed that the modification or structure of the oxide support is critical for obtaining a good catalyst [17]. To investigate this issue a series of V_2O_5/TiO_2 catalysts were prepared on different TiO_2 support structures (anatase, rutile, anatase+rutile, anatase+brookite, and B). *In situ* Raman characterization revealed that the same surface vanadia species were present on all the different titania supports with a band at 1024-1031 cm^{-1} for 1% V_2O_5/TiO_2. The reactivity of these different titania supported vanadia catalysts was probed with methanol oxidation and found to be identical with a TON of 2.1 ± 0.5 sec^{-1}. Thus, contrary to previous conclusions the structure or modification of the oxide support does not affect the surface metal oxide structure or the catalyst reactivity.

4. CONCLUSIONS

The above discussion demonstrates that it is possible to molecularly design supported metal oxide catalysts with the assistance of molecular characterization methods such as Raman spectroscopy. The formation and location of the surface metal oxide species are controlled by the surface hydroxyl chemistry, and the surface metal oxide species are located in the outermost layer of the catalysts as an overlayer. The catalyst composition is a critical parameter since it affects the presence of different metal oxide species (isolated surface species, polymerized surface species, and crystalline phases), and the reactivity, TON, also varies somewhat with surface metal oxide coverage. The preparation method is not a critical parameter since it does not influence the structure or reactivity of the surface metal oxide species. Calcination temperature is an important parameter that controls activation and deactivation of supported metal oxide catalysts, but calcination temperature is not critical if moderate temperatures, 350-450 °C, are used. The specific oxide support is a critical parameter since it dramatically affects the reactivity of the surface metal oxide species, but the structure of the oxide support has no effect on the surface metal oxide structure and reactivity. In summary, the critical parameters that affect the catalytic properties are the specific oxide support (factor of 10^3) and catalyst composition or surface metal oxide coverage (factor of 10^1).

5. ACKNOWLEDGEMENT

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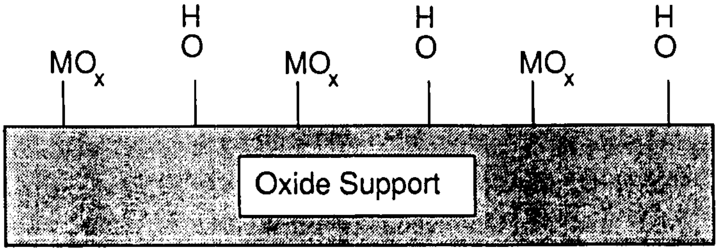

Figure 1 Surface Metal Oxide (MO_x) are formed by Titration of Surface Hydroxyls (OH) on Oxide Supports

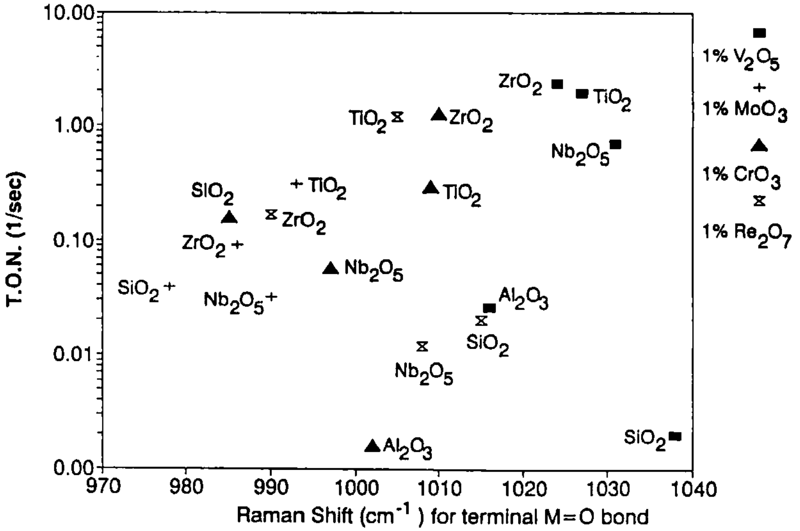

Figure 2 The plot of TON of the various supported metal oxides versus the *in situ* Raman band position of the terminal M=O stretch. The Raman band position is related to the M=O bond strength.

DISCUSSION

Q: U. S. Ozkan (USA)

I have a comment and a question. My comment is that we have compared the two phases of the titania support in selective catalytic reduction of NO over vanadia catalysts. We were able to identify polymeric vanadate species on both phases of the titania support. We did not see more differences between the catalytic activity of the vanadia species found on the two different support materials.

My question is: How did you calculate the turnover frequency (or turnover number, TON) for bulk V_2O_5 ? Could you describe it in detail ?

A: I. E. Wachs

Thank you for your comment regarding the similar properties of anatase and rutile supported vanadia catalysts for the selective catalytic reduction of NO_x.

To calculate the TON for V_2O_5 the surface of crystalline, V_2O_5 was assumed to have the same structure as the bulk, i.e., the area covered by a $VO_{2.5}$ unit was 1.03 nm. In addition, with the two up-two down arrangement of V_2O_5 bulk structure, only half of the area of the bulk of V_2O_5 was considered as active. Based on this assumption the number of active vanadium units could be calculated and, consequently, the TON could be obtained.

Q: F. Solymosi (Hungary)

Your paper contained many interesting data. I have a little problem with your last conclusion, namely that the catalytic behavior of V_2O_5 was completely independent of the structure, preparation, and pretreatment of the TiO_2 support. We know that the properties and reactivity of TiO_2 can be strongly influenced by those factors. Therefore, I would rather prefer to say that in the oxidation of methanol the properties of TiO_2 support do not play an important role. This could be different for other reactions.

A: I. E. Wachs

The reason that many researchers have claimed that the type of TiO_2 support is critical is because they have been using commercial titania pigments that are usually contaminated with K, P, Al, and Si on the surface. We have carefully compared different titania phases that were synthesized in the laboratory and had relatively clean titania surfaces (as determined by XPS). Such clean titania samples show no difference between the type of titania support.

These findings are not limited to methanol oxidation since they have been observed for much more complex reactions (see comments of Professor Trifiro for o-xylene oxidation and Professor Ozkan for selective catalytic reduction of NO_x).

Q: A. K. Datye (USA

Your results show that changing the support can increase the reactivity of the dispersed oxide by 3 orders of magnitude. It is indeed remarkable that the structure of the dispersed oxide as seen by Raman spectroscopy is not affected by the support. For comparison, it would help if you provide data on the reactivity of the corresponding bulk oxides, also as a turnover number.

A: I. E. Wachs

We have also measured the turnover number for bulk crystalline V_2O_5 and found it to be $2.2x10^{-2}$ s^{-1}, which is two orders of magnitude less than for V_2O_5/ZrO_2 and one order of magnitude more than V_2O_5/SiO_2. It is not possible to measure the TON for Re_2O_7/CrO_3 phases because they are not thermally stable and volatilize/phase transform at the conditions of the oxidation reaction. We have recently measured the TON for bulk MoO_3, and found it to be $\sim10^{-2}$ s^{-1}.

Q: F. Trifiro (Italy)

For some years now we have investigated the catalytic behavior of V-TiO_2 (either rutile or anatase) for oxidation of o-xylene to phthalic anhydride and ammoxidation of xylenes and toluenes. We have found very slight differences between the two types of support. I confirm the results of Professor Wachs concerning the TiO_2 as support for V_2O_5.

A: I. E. Wachs

Thank you for your comments regarding the similar catalytic properties of vanadia supported on anatase and rutile for the oxidation/ammoxidation of o-xylene and butenes.

Q: Y. Iwasawa (Japan)

I agree with the question of Professor Solymosi. Different surface structures have been reported from different preparation methods (see pp.503,515,529). My question is concerned with an increase in the TON for methanol oxidation as a function of Mo content on support. Could you make some comment on the meaning of this ?

A: I. E. Wachs

The papers that typically claim different surface metal oxide structures usually do not extensively characterize their samples and do not compare different preparations side by side (especially important in such studies is to maintain the same metal oxide loading). I would be happy to characterize samples from other laboratories by Raman spectroscopy to confirm this conclusion.

Our recent data show that the TON for the MoO_3/TiO_2 catalysts vary from $2x10^{-1}$ to $4x10^{-1}$ s^{-1}, and the apparent increase in the TON is minor.

Q: J. G. van Ommen (The Netherlands)

The fact that you find the same behavior for V_2O_5 on TiO_2 rutile and anatase is very surprising. Why is the type of support so important and not the structure ?

My question is: can you exclude that the anatase you use is not covered with a surface layer of rutile ? If this is the case (or anatase covering rutile, which is not to be expected) you should find the same results for V_2O_5 activity in MeOH oxidation and V_2O_5 reduction.

An other remark: old results also from our group show that careful washing of K and P containing sample gives clean anatase and/or rutile surfaces,which show different behavior in MeOH oxidation, reduction (TPR) and especially in toluene oxidation. This cannot be explained by the presence of surface contaminations ?

A: I. E. Wachs

The reason that different support types (Al_2O_3, TiO_2, SiO_2, etc.) affect the catalytic properties of vanadium oxide monolayers is that the support is a ligand that controls the ease of oxygen removal from the V-O-S (S=support) band. However, this is a local phenomenon that does not depend on long range order (anatase or rutile). Consequently, only the support type (Al_2O_3, TiO_2, SiO_2, etc.) is critical.

This is a very interesting question. Raman spectroscopy is much more sensitive to anatase compared to rutile and, thus, we should be able to detect an anatase overlayer on rutile (which is probable at mild calcination temperatures when rutile is not formed). The reverse situation is more difficult since a rutile overlayer will not be readily detected by Raman spectroscopy. We plan to attempt such a synthesis to address this question, but I feel that the titania overlayers will not adopt the bulk structures because of epitaxial growth.

The surface of the extracted TiO_2 [1] still did contain impurities of P_2O_5 and K_2O as determined by X-ray fluorescence. In addition, the surface concentration is important, not the bulk concentration of these impurities as shown by X-ray fluorescence. For this reason it appears that the surface of these vanadia-titania catalysts still contain the impurities.

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Q: A. Andersson (Sweden)

1) In the case of vanadia on anatase, you have observed two Raman bands at 1030 and 930 cm^{-1} which you assign to isolated and polymerized vanadia species, respectively. Have you considered the possibility that the two bands can be from differing species on different surface planes of titania ?

2) You have found the same vanadia species to be present on the various polymorphs of titania. In our laboratory we have found similar spectral features as you have for vanadia on anatase. However, for vanadia on TiO_2(B) we observed a Raman band at 970 cm^{-1}. Also, we found the monolayer on anatase to give 50% selectivity for benzaldehyde formation in toluene oxidation. The monolayer our TiO_2(B) gave only combustion. Even though vanadia can be in tetrahedral coordination on both supports, the V-O bond lenghts angles most differs. Can you comment on this ?

A: I. E. Wachs

1) I do not think these two Raman bands are due to different surface planes of titania because they are observed on other oxide supports as well. The same surface species are essentially formed on all oxide supports.

2) We have observed the 1030 cm^{-1} Raman band shift to 970 cm^{-1} upon addition of small amounts of K to V_2O_5/TiO_2. Since TiO_2(B) is made from a potassium titanate precursor, it may be possible that some residual K is present which would alter the spectral and catalytic properties of your TiO_2(B) catalysts.

Q: W. K. Jozwiak (Poland)

I like very much your generalizing approach trying to put some order in so complicated matter of the heterogeneous catalysis. Even with the most unfavorable starting materials (such as mechanical mixture of α-Cr_2O_3 and SiO_2 (also Al_2O_3 or MgO) we have been able to obtain the effective ethylene polymerization catalyst. Thus, the process of chromium redispersion (confirmed by XRD and TPR methods) takes place in the oxidative atmosphere above 500 ^{0}C. Probably the crucial role is played by the support hydroxyl groups, governing the sort of equilibrium sintering $\rightleftarrows$ redispersion between surface and bulk oxide phases. Do you suppose that such behavior may be common among your oxide/support systems ?

A: I. E. Wachs

The spreading of metal oxides onto supports have been demonstrated in the literature for many oxide systems (MoO_3, V_2O_5, WO_3, etc.). These oxides are all mobile at elevated temperatures and spontaneously diffuse over oxide surfaces of supports (silica is somewhat of an exception because of the low concentration of reactive surface hydroxyls). Thus, oxides with low melting temperature will have sufficient mobility to spontaneously disperse over oxide supports.

Q: D. Wang (China)

Your work demonstrated the importance of surface hydroxyl groups in the preparation of supported metal oxides. Is there any difference in hydroxyl groups (1) of any one support, and (2) of different supports ?

A: I. E. Wachs

The hydroxyl groups of oxide supports depend on the support type (Al_2O_3, TiO_2, SiO_2, etc.) and usually several different hydroxyls are present on the same support. A very detailed article on surface hydroxyls has recently been written [2]

[2] H.-P. Boehm and H. Knözinger in "*Catalysis Science and Technology*", (Eds.: J. R. Anderson and M. Boudart), 1983, **Vol. 4**, Chap. 2

Q: J. M. Thomas (United Kingdom)

In describing the preparation of your surface overlayers you emphasized, not unnaturally, that it is the OH concentration of the exterior surface of the support that is all important. One wonders, therefore, whether you have considered taking several of the minerals that have constitutional OH in their structures as supports. Perhaps kaolinite, with nice flat surfaces such in OH groups, is not stable enough. But what of the oxy-hydroxides (e.g. CrOOH) which would give you the added advantage of being able to graft one functional group in a justaposed manner to another (transition metal) functional group. This would then enable you to produce bifunctional, surface-modified catalysts.

A: I. E. Wachs

I agree with you that it should be possible to react the surface hydroxyls of minerals with metal oxide overlayers. I am currently not aware of any such studies.

Q: H. L. Krauss (Germany)

I wonder how you got good catalytic properties in the Cr/SiO_2 system at such moderate activation temperatures as 350-500 ^{0}C. Many of our results, in fact all, show that activation temperatures of >600 ^{0}C, preferentially 800 ^{0}C, are to be applied to get good catalysts in cases when a reduction of the chromium species is a crucial step in the preparation of the active catalytic species.

A: I. E. Wachs

The methanol oxidation reaction is a unimolecular reaction involving only the active surface site (surface chromate species). However, the types of reactions that you are referring to are bimolecular reactions, which apparently are inhibited by surface hydroxyls adjacent to the active surface site, and elevated calcination temperatures are required to remove these hydroxyls from the silica surface. A detailed discussion of the comparison between methanol oxidation and ethylene polymerization over CrO_3/SiO_2 catalysts can be found recently [3].

[3] D. S. Kim, K. Segawa, T. S. Ya and I. E. Wachs, *J. Catal.*, **136**, 539 (1992).

Q: E. Bordes (France)

You mentioned that by Raman spectroscopy on V-oxides you see a slight difference in V=O band position, corresponding to slight difference in bond length. These differences should be reflected also in catalytic reactivities. I wonder if the reaction with methanol is not too much simple. V-based catalysts have the capability to cyclize molecules. If you used butane, for example, do not you think that the reactivities would be more differentiated, and particularly the selectivities in various products.

A: I. E. Wachs

It has been reported in the literature by many authors that the V=O bond length controls the catalytic activity. However, there was not direct proof of this assumption. We have, for the first time, measured the V=O bond lengths by Raman spectroscopy and find that it does not correlate with catalytic activity. This is not surprising since the V-O-S (S=support) bond is critical in determining the catalytic activity.

The results are not unique to methanol oxidation since we have also found a similar activity trend for butene oxidation. An examination of the literature data for o-xylene oxidation, a significantly more complex molecule, also shows similar activity trend. Thus, the reactivity results for methanol oxidation appear to be quite general.

Q: H. H. Kung (USA)

This was a very nice paper. My question is to ask for you comment as to the possibility that while spectroscopy sees the majority species, the reaction is catalyzed by some minority species. For example, a 1 wt% and a 2 wt% V_2O_5/SiO_2 may be indistinguishable with Raman spectroscopy, yet they are somewhat different catalytically in butane oxidation.

Also what is your view on the possibility that in hydrocarbon oxidation reactions, the water that is produced results in a constant partial pressure of water that causes migration of the surface species ? Thus the catalyst is in a different state than the one characterized structurally.

A: I. E. Wachs

Thank you for your nice comment. It is true that not all the surface species may simultaneously be participating catalytically, but that they may be taking turns performing the catalysis. Furthermore, we find that the same surface metal oxide species are found on all oxide supports because they have a preferred coordination to oxide support surfaces. Thus, it is very unlikely that there is some unusual coordination that is not detected spectroscopically and is responsible for the catalytic behavior. In addition, doping the supported vanadium oxide catalysts with potassium results in change in the Raman spectra and a corresponding change in the methanol oxidation TON suggesting that the active sites are indeed being probed by Raman spectroscopy.

Your results with butane oxidation reflect the complexity of this reactant which may simultaneously be interacting with the surface vanadia species and surface hydroxyls. In such a situation, increasing the vanadia coverage does not affect the vanadia structure (as long as all the vanadia is dispersed), but decreases the surface hydroxyl concentration which is beneficial.

Q: L. Dixit (India)

Your Raman spectral observations on titania supported vanadia catalysts reveal that there exist three different vanadia species on a TiO_2 support. The observation of a single sharp band (at low loading) that is present at 1030 cm^{-1} is due to isolated tetrahedrally coordinated surface vanadium oxide species containing one terminal V=O bond and three bridging V-O-Ti bonds. This is true. However, the assignment of bands at moderate and high loadings of vanadia, which appear at 930 cm^{-1} and 994 cm^{-1}, respectively to polymerised tetrahedrally coordinated surface vanadium oxide species and crystalline V_2O_5 may be mixed.

I would like to know whether structure-dependent position of bands of different vanadium oxide precursors compatible with V=O bond length variations are also compatible in terms of their intensities? Do you have any intensity data of bands in terms of their structures ?

A: I. E. Wachs

The Raman bands at 930 and 994 cm^{-1} are not related since the 930 cm^{-1} band precedes the appearance of the 994 cm^{-1} band due to crystalline V_2O_5. Furthermore, crystalline V_2O_5 does not possess a band in this region.

The different Raman band positions are directly related to the vanadium-oxygen bond lengths [4]. We have no relative intensity data at present, but the bands at higher wavenumbers should be slightly stronger due to the increased electron density of the vanadium-oxygen bonds.

[4] Hardcastle and I. E. Wachs, *J. Phys. Chem.*, **95**, 5031 (1991)