R.K. Grasselli and A.W. Sleight (Editors), *Structure-Activity and Selectivity Relationships in Heterogeneous Catalysis*
© 1991 Elsevier Science Publishers B.V., Amsterdam

MOLECULAR STRUCTURE-REACTIVITY RELATIONSHIPS OF SUPPORTED VANADIUM OXIDE CATALYSTS

G. Deo and I. E. Wachs
Zettlyemoyer Center for Surface Studies,
Department of Chemical Engineering,
Lehigh University, Bethlehem, PA 18015

ABSTRACT

The molecular structure of the surface vanadium oxide species present on different oxide supports (TiO_2, γ-Al_2O_3, and SiO_2) were determined by laser Raman spectroscopy and ^{51}V solid state NMR under hydrated and dehydrated conditions. The structure of the vanadium oxide species changes with dehydration and a four coordinated vanadium oxide species with a short terminal bond was present on all oxide supports considered. The reactivity of the supported vanadium oxide catalysts was determined via the methanol oxidation reaction. Correlation of the structure and reactivity data indicate the strength of the bridging, vanadium-oxygen-support, bond to be controlling the activity of these supported vanadium oxide catalysts. The effect of promoters/impurities on 1% V_2O_5/TiO_2 catalyst depends on their acid/base nature. Basic promoters titrate the vanadium oxide site and destroy the vanadium-oxygen-support bond of the parent 1% V_2O_5/TiO_2. Acidic promoters/impurities coordinate to the support and do not show any appreciable change to the structure, reactivity, and the vanadium-oxygen-support bond of the parent 1% V_2O_5/TiO_2.

INTRODUCTION

Supported vanadium oxide catalysts constitute an important class of oxidation catalysts which find a variety of uses in the petrochemical industry. Various studies have shown that supported vanadium oxide forms a two-dimensional metal oxide overlayer on the oxide supports which is structurally and catalytically different from bulk V_2O_5 [1-4]. The supported vanadium oxide phase is usually more active than bulk V_2O_5 during most oxidation reactions. The differences in catalytic activity of the various supported vanadium oxide catalysts have been attributed to the different structural modifications of the two-dimensional vanadium oxide overlayer. The structural modifications occur due to the vanadium oxide interaction with the surface of the oxide support. Furthermore, some researchers have attempted to correlate the activity of supported vanadium oxide catalysts, for some catalytic reactions, with the number of terminal V=O bond [5].

The present paper addresses this notion of structural differences for the supported vanadium oxide phase on different oxide supports (Al_2O_3, TiO_2 and SiO_2). The structural modifications of the supported vanadium oxide phase are studied using laser Raman spectroscopy and solid state ^{51}V NMR. The structure sensitive methanol oxidation reaction is used to probe the catalytic properties of the supported vanadium oxide phase. From these results it is possible to arrive at a conclusion regarding the structure-reactivity relationship of supported vanadium oxide catalysts.

EXPERIMENTAL

Support materials: The supports used in this study were TiO_2 (55 m^2/g) obtained from Degussa (P-25), γ-Al_2O_3 (180 m^2/g) obtained from Harshaw, and SiO_2 (300 m^2/g) Cab-o-sil.

Sample preparation: Vanadium tri-isopropoxide oxide (Alfa) was used as the precursor. The samples were made by incipient wetness impregnation of the precursor using methanol as the solvent. The impregnation was performed under a nitrogen atmosphere. The samples were then heated in nitrogen at 110 °C and finally calcined in oxygen at 500 °C. For the V_2O_5/TiO_2 samples the final calcination was done at 450 °C for 2 hrs. Details of the preparation technique have been outlined elsewhere [6]. To study the effect of promoters/impurities WO_3, Nb_2O_5, and K_2O were added, via incipient wetness impregnation of their respective precursors, to previously prepared 1% V_2O_5/TiO_2.

Laser Raman: The Raman spectra for the catalysts under ambient conditions were collected using low laser power, usually less than 20 mW. Laser induced dehydration studies were also carried out for some catalysts using higher laser powers, usually greater than 100 mW. Details of the Raman equipment have been described elsewhere [7].

NMR: Solid state ^{51}V NMR data were collected at room temperature using a General Electric Model GN-300 spectrometer. Details of the setup have been given elsewhere [4]. Dehydration experiments were performed at temperatures between 150 and 400 °C for 0.5-1 hour at 10^{-3} Torr in flame sealed containers. Within these limits the solid state ^{51}V NMR spectra showed little dependence on the dehydration conditions.

Catalytic studies: Methanol oxidation reaction was carried out in an isothermal fixed-bed differential reactor which was operated at atmospheric pressure and temperature of 230 °C. The mixture of methanol, oxygen, and helium were in the ratio 6/11/83 (molar %) and total flowrates of 25-100 sccm were employed in order to maintain $< 5\%$ conversion. The reactor was vertical and made of 6mm O.D. Pyrex glass. The catalyst was held at the middle of the tube between two layers of quartz wool. The gas flow was from the top to the bottom. Analysis of the product stream was performed using an on line gas chromatograph equipped with an FID and two TCD's. Due to the high activity of V_2O_5/TiO_2, γ-Al_2O_3, and V_2O_5/γ-Al_2O_3 these catalysts were diluted with SiO_2 to maintain conversions < 5%. For the catalytic runs, the activities and selectivities were reported as initial values. The activities for the different catalysts were converted to turnover numbers (t.o.n) which is defined as the moles of methanol converted per mole of surface vanadium atom per sec. For bulk V_2O_5 the area for a mole of $VO_{2.5}$ is known [1] and from the knowledge of the surface area of the bulk V_2O_5 material (~4 m^2/g) the t.o.n. can be determined.

RESULTS

1-20% V_2O_5/γ-Al_2O_3: The Laser Raman and ^{51}V solid state NMR spectra of these samples have been reported before. Under ambient conditions these catalysts are known to possess primarily four coordinated (metavanadate) structures at low loadings and six coordinated (decavanadate) structures at high loadings [4,6]. Dehydration of low vanadium oxide coverage catalysts (4% V_2O_5/γ-Al_2O_3) show vanadium oxide to be only four coordinated. Laser induced dehydration studies on these catalysts performed with the Raman spectrometer show the presence of a Raman band arising at ~1022 cm^{-1} which is assigned to a short terminal V=O bond. Previous *in situ* Raman studies show this terminal band to be at 1034 cm^{-1} [8].

1-8% V_2O_5/TiO_2 (Degussa): Laser Raman and ^{51}V solid state NMR spectra show that under ambient conditions four coordinated vanadium oxide structures form at low coverages which become primarily six coordinated at higher coverages similar to V_2O_5/γ-Al_2O_3 [4,9]. However, differing from vanadium oxide supported on γ-Al_2O_3 there is a preference for six coordinated vanadium oxide species on TiO_2. Dehydration of low vanadium oxide coverage V_2O_5/TiO_2 catalysts changes the vanadium oxide coordination from six to four, and the four coordinated species has a similar solid state ^{51}V NMR spectra as the dehydrated 4% V_2O_5/γ-Al_2O_3 catalyst [4]. Raman spectra of laser induced dehydrated V_2O_5/TiO_2 samples show the presence of a short V=O bond (Raman band at 1035 cm^{-1} [10]).

0.5-1.5% V_2O_5/SiO_2: From the Raman spectra of these catalysts no features of crystalline V_2O_5 were observed. Raman features of laser induced dehydrated samples show the presence of a terminal V=O band at 1033 cm^{-1}. Oyama et al. report the band position to be at 1042 cm^{-1} from *in situ* studies at 373 K after calcination of the V_2O_5/SiO_2 catalyst at 750 K [11]. Lischke et al. using uv-vis spectroscopy proposed the formation of tetrahedrally coordinated V^{5+} species upon dehydration [12].

Promoters/Impurities on 1% V_2O_5/TiO_2: The Raman spectra of

K_2O/1% V_2O_5/TiO_2, under ambient conditions, exhibit a shift of the terminal V=O band to lower wavenumbers compared to 1% V_2O_5/TiO_2. This indicates the abundance of tetrahedrally coordinated vanadium oxide species. The Raman spectra of dehydrated K_2O/1% V_2O_5/TiO_2 is stricking due to the absence of the ~1030 cm^{-1} band [13]. The Raman spectra of WO_3/1% V_2O_5/TiO_2 and Nb_2O_5/1% V_2O_5/TiO_2, under ambient conditions, exhibit a shift of the terminal V=O band to higher wavenumbers compared to 1% V_2O_5/TiO_2. This indicates a predominance of octahedrally coordinated vanadium oxide species. The Raman spectra of dehydrated WO_3/1% V_2O_5/TiO_2 and Nb_2O_5/1% V_2O_5/TiO_2 show the presence of a terminal V=O band at ~1030 cm^{-1} in addition to Raman bands of molecularly dispersed WO_3 and Nb_2O_5 [13,14].

Catalytic Studies: The main products of the methanol oxidation reaction are dimethyl ether, formaldehyde, methyl formate, methylal, CO and CO_2. Blank experiments without catalyst were performed to check the reactivity of the Pyrex tube and quartz wool. These experiments did not lead to any conversion taking place at the conditions considered. The t.o.n. gives a measure of the efficiency of each surface vanadium atom and the Raman/NMR characterization studies demonstrate that only atomically dispersed vanadium oxide was present in these samples.

Table 1 shows the activity and selectivity of the different support materials. It can be seen from this table that the activity of both TiO_2 and SiO_2 are low at these reaction conditions. The activity of γ-Al_2O_3, on the otherhand, is high and a 100% selectivity towards dimethyl ether is observed.

Table 1. Activity of Support Material for Methanol Oxidation Reaction (230 °C)

Support Material	Activity (mmole CH_3OH/g.cat./hr)	Selectivity (%) HCHO	CH_3OCH_3	CO/CO_2
SiO_2	1.0	---	---	100
Al_2O_3	100.0	---	100	---
TiO_2	2.3	9.5	90.5	---

Figure 1 shows the t.o.n. (multiplied by 1E+4) of 1% V_2O_5 dispersed on different oxide supports. The 1% V_2O_5/TiO_2 catalyst is the most active and the t.o.n. is 2-3 orders of magnitude greater than bulk V_2O_5, 1% V_2O_5/γ-Al_2O_3 and 1% V_2O_5/SiO_2. The activity of the 1% V_2O_5/γ-Al_2O_3 catalyst is mainly due to γ-Al_2O_3 which greatly overshadows the effect of supported vanadium oxide and only a trace amount of methylal is observed. The amount of methylal formed during the methanol oxidation of 1% V_2O_5/γ-Al_2O_3 was used to calculate the t.o.n. for this sample.

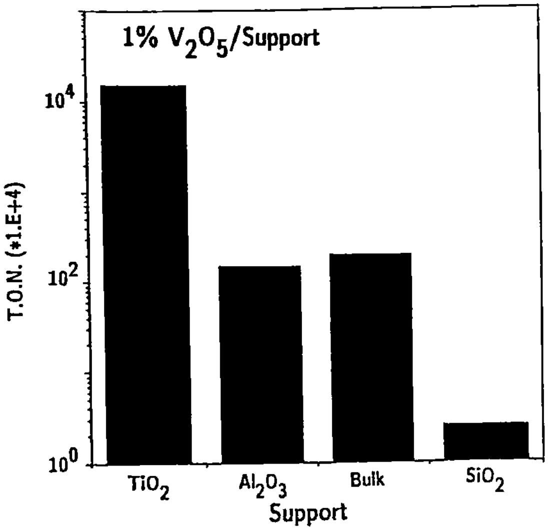


Fig. 1. Turnover Number for Methanol Oxidation Over Supported Vanadium Oxide Catalysts.

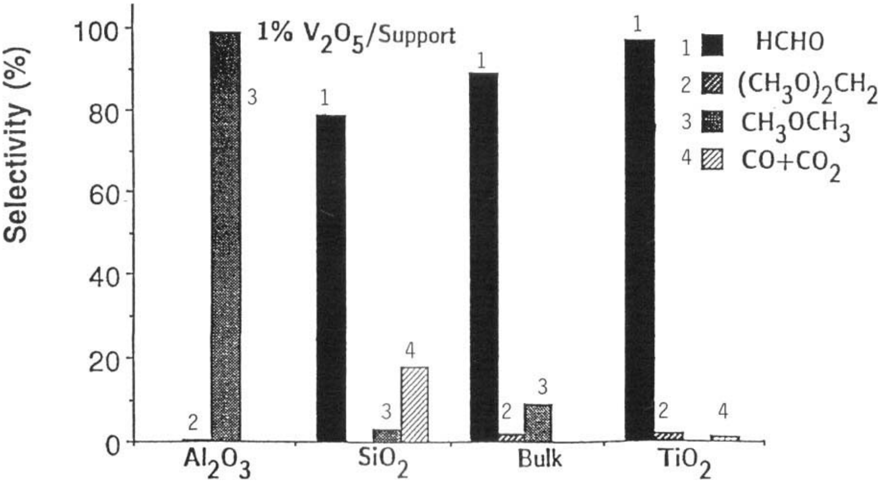


Fig. 2. Reaction Selectivities for Methanol Oxidation Over Supported Vanadium Oxide Catalysts.

The reactivity (t.o.n.) of the supported vanadium oxide catalysts exhibit the following trend:

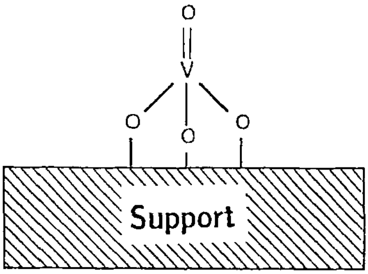
$$1\%\ V_2O_5/TiO_2 > V_2O_5 \sim 1\%\ V_2O_5/\gamma\text{-}Al_2O_3 > 1\%\ V_2O_5/SiO_2.$$

Figure 2 shows the selectivity of the different catalysts. 1% V_2O_5/TiO_2 shows an 98% selectivity towards HCHO. On the otherhand the selectivities towards HCHO was 89% for bulk V_2O_5 and 79% for 1% V_2O_5/SiO_2. For the 1% V_2O_5/Al_2O_3 a high selectivity towards CH_3OCH_3 was observed which is typical of the support (γ-Al_2O_3). Other oxidation products were produced in minor amounts.

The reactivity 1% V_2O_5/TiO_2 during the methanol oxidation reaction is dramatically reduced with the addition of K_2O. Compared to 1% V_2O_5/TiO_2, the activity of 4% K_2O/1% V_2O_5/TiO_2 decreases by orders of magnitude. The reactivity of WO_3/1% V_2O_5/TiO_2 and Nb_2O_5/1% V_2O_5/TiO_2, on the other hand, are similar to 1% V_2O_5/TiO_2 catalyst.

DISCUSSION AND CONCLUSION

The Raman spectroscopy and solid state ^{51}V NMR studies reveal that at low vanadium oxide loadings the supported vanadium oxide phase is present as a two-dimensional metal oxide overlayer on the surface of the oxide support (100% dispersion). Under *in situ* conditions, where the oxide surfaces are dehydrated, the surface vanadium oxide phases possess tetrahedral coordination on all the oxide supports (Al_2O_3, TiO_2, and SiO_2). The ^{51}V NMR line shapes indicates the presence of a highly symmetric species [4] and the Raman signal at ~1030 cm^{-1} indicates an extremely short V=O bond. These results suggest the formation of the following surface vanadium oxide species on the different oxide supports:



Thus, the molecular structure of the supported vanadium oxide phase is independent of the specific oxide support at low vanadium oxide loadings and the Raman band at ~1030 cm^{-1} is very indicative of this structure.

The reactivity of this highly distorted, tetrahedral surface vanadium oxide species, however, is markedly dependent on the specific oxide support to which it is anchored. The combined structural characterization and catalytic studies suggest that the bridging oxygens, V-O-S (S=support), are responsible for the vast differences in catalytic activities since the terminal V=O bonds are not significantly influenced by the nature of the oxide support and possess Raman bands at ~ 1030 cm^{-1}. Under the chosen reaction conditions of an excess oxygen partial pressure the rate determining step is the extraction of oxygen from the surface vanadium oxide species. The influence of the oxide support on the rate of oxygen removal from the V-O-S bond would be expected to exert its greatest influence on the overall reaction rate. Indeed, this is exactly what is observed and the overall reaction rate correlates with the ease of oxygen removal from the different oxide supports since titania is significantly easier to reduce than alumina and silica [15].

The addition of promoters/impurities to 1% V_2O_5/TiO_2 has a pronounced effect on its structure and reactivity. Basic promoters/impurities titrate the surface vanadium oxide species and coordinate with the surface vanadium oxide species in 1% V_2O_5/TiO_2. This is evident from the absence of the ~1030 cm^{-1} band in the dehydrated Raman spectra of K_2O/1% V_2O_5/TiO_2. As a result, the vanadium-oxygen-support bond is destroyed and the activity of K_2O/1% V_2O_5/TiO_2 is reduced dramatically. Acidic promoters/impurities on 1% V_2O_5/TiO_2 coordinate directly to the TiO_2 support without drastically influencing the vanadium oxide four coordinated species. The direct coordination to the support of acidic promoters on 1% V_2O_5/TiO_2 catalysts is evident as the ~1030 cm^{-1} Raman band remains unaltered for the WO_3/1% V_2O_5/TiO_2 and Nb_2O_5/1% V_2O_5/TiO_2 catalysts. Hence, no appreciable change occurs to the vanadium-oxygen-support bond of these acidic promoted catalysts and the acitivity remains similar to 1% V_2O_5/TiO_2.

The reactivity of the distorted, tetrahedral surface vanadium oxide species appears to strongly depend on the strength of the vanadium-oxygen-support bond and correlates with the ease of oxygen removal from the oxide support. This conclusion is contrary to previous investigations on supported vanadium oxide catalysts which speculate that the vast differences in catalytic activities were due to the different vanadium oxide structures present in such catalysts and also to the strength and abundance of the terminal V=O bond.

ACKNOWLEDGMENT

We would like to thank Dr. H. Eckert for the helpful discussions. This study has been supported by the National Science Foundation grant # CBT-8810714

REFERENCES

1. (a) F. Roozeboom, T. Fransen, P. Mars, and P. J. Gellings,

Z. anorg. allg. Chem., 449 (1979) 25.
(b) F. Roozeboom, M. C. Mittelmeijer-Hazeleger, J. A. Moulijn, J. Medema, V. H. J. de Beer, and P. J. Gellings, J. Phys. Chem. 84 (1980) 2783.
(c) G. C. Bond, J. Sarkany, and G. D. Parfitt, J. Catal., 57 (1979) 476.
(d) G. C. Bond and K. Brukman, Faraday Disc., 72 (1981) 235.

2. (a) R. Y. Saleh, I. E. Wachs, S. S. Chan, and C. C. Chersich, J. Catal., 98 (1986) 102.
(b) I. E. Wachs, R. Y. Saleh, S. S. Chan, and C. C. Chersich, Appl. Catal., 15 (1985) 339.
3. (a) J. Haber, A. Kozlowska, and R. Kozlowski, J. Catal., 102 (1986) 52.
(b) H. Miyata, K. Fujii, T. Ono, Y. Kubokawa, J. Chem. Soc. Faraday Trans., 1, 83 (1987) 675.
(c) G. Bergeret, P. Gallezot, K. V. R. Chary, B. Rama Rao, and V. S. Subrahmanyam, Appl. Catal., 40 (1988) 191.
(d) J. Haber, A. Kozlowska, and R. Kozlowski, Proc. 9th Intl. Congr. Catal., (1988) 1481.
4. (a) H. Eckert, and I. E. Wachs, Mat. Res. Soc. Symp. Proc., 111 (1988) 459.
(b) H. Eckert, and I. E. Wachs, J. Phys. Chem., 93 (1989) 6796.
5. A. Miyamoto, Y. Yamazaki, M. Inomata, Y. Murakami, J. Phys. Chem., 85 (1981) 2366.
6. G. Deo, F. D. Hardcastle, M. Richards, and I. E. Wachs, Preprints Petrol. Chem. Div., ACS 34(3) (1989) 529.
7. I. E. Wachs, F. D. Hardcastle, and S. S. Chan, Mat. Res. Soc. Symp. Proc., 111 (1988) 353.
8. S. S. Chan, I. E. Wachs, L. L. Murrell, L. Wang, and W. K. Hall, J. Phys. Chem., 88 (1984) 5831.
9. J. M. Jehng, F. D. Hardcastle, and I. E. Wachs, Solid State Ionics, 32/33 (1989) 904.
10. C. Cristiani, P. Forzatti, and G. Busca, J. Catal., 116 (1989) 586.
11. S. T. Oyama, G. T. Went, K. B. Lewis, A. T. Bell, and G. A. Somarjai, J. Phys. Chem., 93 (1989) 6786.
12. G. Lischke, W. Hanke, H. -G. Jerschkewitz, and G. Ohlmann, J. Catal., 91 (1985) 54.
13. G. Deo and I. E. Wachs, unpublished results.
14. M. A. Vuurman, A. M. Hirt, and I. E. Wachs, to be submitted to J. Phys. Chem.
15. Y. Moro-oka, Y. Morikawa, and A. Ozaki, J. Catal., 7 (1967) 23.