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Reactivity of Supported Vanadium Oxide Catalysts: The Partial Oxidation of Methanol

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The partial oxidation of methanol was used to probe the reactivity of the surface vanadium oxide redox sites present in supported vanadium oxide catalysts. Formaldehyde was the main oxidation product for all the supported vanadium oxide catalysts operating under differential reactor conditions. The methanol oxidation turnover frequency (TOF) of the surface vanadium oxide phase varies by three orders of magnitude when the support is changed from ZrO_2/TiO_2 (10^0 s^{-1}) to SiO_2 (10^{-3}). The TOF of the surface vanadium oxide phase supported on Nb_2O_5 (10^{-1} s^{-1}) and Al_2O_3 (10^{-2} s^{-1}) have intermediate values with the surface vanadium oxide phase on Nb_2O_5 having a TOF very close to ZrO_2 or TiO_2. The TOF of the surface vanadium oxide phase on all the oxide supports is essentially independent of the vanadium oxide loading below monolayer coverage. The similar structures of the surface vanadium oxide phase on the different oxide supports as well as the independence of the TOF with respect to vanadium oxide surface coverage suggests that a structural difference is not responsible for the difference in reactivity of the various supported vanadium oxide catalysts. Similar activation energies are observed for all the supported vanadium oxide catalysts (19.6 ± 2.3 kcal/mol) which correspond to the C–H bond breaking of the surface methoxy species to form formaldehyde. The similar activation energies and different TOFs of the supported vanadium oxide catalysts with respect to the oxide support imply that the specific oxide support influences the Arrhenius pre-exponential factor. *In situ* Raman studies during methanol oxidation suggest that the pre-exponential factor is determined by the number of participating surface vanadium oxide sites. The importance of the activity per surface vanadium oxide site in determining the pre-exponential factor was not investigated and may also be significant. The TOF for methanol oxidation is not related to the terminal V═O bond strength, but appear to be related to the reducibility (T_{max}) of the supported vanadium oxide catalysts. It is proposed that the number of participating surface vanadium oxide sites is most probably related to the reducibility of the V–O–Support bond since this bridging bond strength controls the reducibility of the supported vanadium oxide catalysts. © 1994 Academic Press, Inc.

INTRODUCTION

Recent reviews outline the importance of supported vanadium oxide catalysts in several oxidation reactions (1, 2). These studies reveal that vanadium oxide supported on TiO_2 is a superior catalyst compared to vanadium oxide supported on Al_2O_3 or SiO_2 for several oxidation reactions. In addition to the role of the support, the vanadium oxide loading on a specific oxide support is also crucial in determining an active and selective catalyst. The active catalyst possesses a molecularly dispersed vanadium oxide phase which is usually more active and selective than bulk V_2O_5. This has led several investigations to relate the reactivity to the structural properties of the molecularly dispersed vanadium oxide phase (1, 3–18). These structure–reactivity relationships attributed the unique behavior of certain catalysts to various factors:

(a) stability of the surface vanadium oxide phase on TiO_2,
(b) structure of the surface vanadium oxide phase,
(c) strength and number of the V═O bonds,
(d) acidity of the surface vanadium oxide phase, and
(e) ease of reduction of the supported vanadium oxide catalysts.

These seemingly diverse reasons for the superior catalytic performance of some supported vanadium oxide catalysts suggests the lack of a fundamental understanding of the supported vanadium oxide catalysts. Thus, to elucidate the governing factors and develop a fundamental understanding of an effective catalyst it is necessary to conduct a systematic investigation involving the preparation, structural characterization, and reactivity of various supported vanadium oxide samples.

In an ongoing study, several supported vanadium oxide samples were prepared as a function of oxide support (Al_2O_3, TiO_2, ZrO_2, Nb_2O_5, and SiO_2) and vanadium oxide loading (19, 20). The physical characterization of the surface vanadium oxide species on different oxide supports was obtained using *in situ* Raman spectroscopy un-

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der dehydrated conditions. Dehydrated conditions were achieved by heating the catalysts to ~723 K in a stream of dry oxygen to remove the moisture present on the catalyst surface under ambient conditions. The maximum vanadium oxide loadings of stable molecularly dispersed vanadium oxide species were similar for the different oxide supports (Al_2O_3, TiO_2, Nb_2O_5, and ZrO_2), 11–14 μmol V^{+5}/m^2, with the exception of SiO_2, 1 μmol V^{+5}/m^2. Thus, the stability of the surface vanadium oxide phase is not only restricted to the TiO_2 support. The *in situ* Raman spectra of the supported vanadium oxide samples obtained under dehydrated conditions changes as a function of vanadium oxide loading and appears to suggest the presence of essentially two types of molecularly dispersed surface vanadium oxide species (corresponding to two distinct Raman features) on all the oxide supports. The relative ratio of these two species changes with coverage since one of the species is predominantly present at low coverages and the other species is present at high coverages (21–23). However, the relative ratio of the two species at a particular coverage is independent of oxide support, with the exception of SiO_2 (theoretical monolayer coverage could not be achieved) (19, 20).

This paper focuses on the reactivity of the surface vanadium oxide phase as a function of specific oxide support (Al_2O_3, SiO_2, Nb_2O_5, TiO_2, and ZrO_2) and vanadium oxide loading for the partial oxidation of methanol. The activity, selectivity, and activation energies of the methanol oxidation reaction for the supported vanadium oxide catalysts are obtained in order to determine the influence of the vanadium oxide loading and the specific oxide support. In addition, temperature programmed reduction experiments were carried out to determine the reducibility of the supported vanadium oxide samples. The fundamental factor(s) involved in determining the reactivity of the surface vanadium oxide phase are proposed.

EXPERIMENTAL

Sample Preparation

The support materials used in this study are SiO_2, Al_2O_3, ZrO_2, TiO_2, and Nb_2O_5. All the oxide supports were calcined at 723–773 K and cooled to room temperature in air prior to impregnation with the vanadium oxide precursor. The source and surface area of the oxide supports after calcination are shown in Table 1. The vanadium oxide overlayers were prepared on the oxide support by the incipient wetness impregnation method. Vanadium triisopropoxide oxide (Alfa, 95–98% purity) was used as the vanadia precursor. The air and moisture sensitive nature of the alkoxide precursor required the preparation to be performed under a nitrogen environment and nonaqueous solutions. Solutions of known amounts of vanadium triisopropoxide oxide and methanol (Fisher-certified ACS, 99.9% pure), corresponding to incipient wetness impregnation volume and the final amount of vanadia required, were prepared in a glove box filled with nitrogen. The solutions of the vanadia precursor and methanol were then thoroughly mixed with the oxide support and dried at room temperature in the glove box for 16 hr. The impregnated samples were subsequently heated to 393 K in flowing nitrogen. The final calcination was performed in O_2 (Linde, 99.99% pure) at 723 K for vanadium oxide supported on ZrO_2, Nb_2O_5, and TiO_2, and at 773 K for vanadium oxide supported on Al_2O_3 and SiO_2. The ZrO_2, Nb_2O_5, and TiO_2 supported vanadium oxide catalysts were calcined at slightly lower temperatures than the Al_2O_3 and SiO_2 systems in order to assure that sintering of these less thermally stable oxide supports did not occur during the preparation step. All samples are reported as weight percent of V_2O_5 in the sample.

TABLE 1

Oxide Support Properties and Treatments

Oxide support	Supplier	Pretreatment temperature (K)	Surface area (m^2/g)
SiO_2	Cabot (Cab-O-Sil)	773	300
ZrO_2	Degussa	723	39
TiO_2	Degussa (P-25)	723	50
Nb_2O_5	NPC[a]	723	55
Al_2O_3	Harshaw (γ)	773	180

[a] Niobium Products Company.

Catalytic Studies

The methanol oxidation reaction was carried out in an isothermal fixed-bed differential downflow reactor operating at atmospheric pressure. A mixture of helium and oxygen from two mass flow controllers (Brooks) were bubbled through a methanol saturator cooled by flowing water from a cooler (Neslab RTE 110) to obtain a 6/13/81 (mole%) mixture of methanol/oxygen/helium and a flow rate of ~100 standard cubic centimeter per minute (sccm). The reactor was held vertical and made of 6-mm O.D. Pyrex glass. The catalysts were held at the middle of the tube between two layers of quartz wool. The outlet of the reactor to the gas chromatograph (GC) was heated at 393–403 K in order to avoid condensation of the products. The products were analyzed by an on-line GC (HP 5840) equipped with two TCDs and a FID, and two columns (Poropak R and Carbosieve SII) connected in parallel. Blank runs were performed on the Pyrex tube packed with quartz wool without any detectable conversions. Pretreatment of the catalyst samples were done at 573 K for ½ hr in a stream of oxygen + helium prior to each run. Catalytic runs were obtained for 3–4 hr, beginning 10 min after methanol flow through the reactor, on each catalyst sample at 473, 503, and 513 K (always in increasing order of temperature) to obtain the conversions, selectivity, and activation energy data. The amount of catalyst chosen (usually milligram amounts) was such that the methanol conversion was maintained below 20% in order to obtain differential reaction data, except for the V_2O_5/Al_2O_3 system, where higher conversions were used to obtain detectable amounts of partial oxidation products. Heat and mass transfer effects were considered using previously determined criteria (24). No heat and mass transfer limitations were indicated from the calculations using Weisz–Prater first-order criterion and a negligible temperature rise for an adiabatic reactor. The activity was calculated from the conversion and is the number of moles of methanol converted per hour per gram catalyst. The selectivity (%) of product X_i is calculated as 100× (number of moles methanol converted to product X_i)/(total number of moles of methanol converted). The activities for the different catalysts were converted to turnover frequency, TOF (s^{-1}), which is the moles of methanol converted per mole of surface vanadium atom per second. For the vanadium oxide supported on alumina samples only the partial oxidation products were used to determine the TOF of the surface vanadium oxide species because of the side reactions on the surface alumina acid sites.

Temperature Programmed Reduction Studies

A flow microbalance system (Cahn Model TG-131) was used to study the reduction characteristics of the supported vanadium oxide catalysts. The samples were first heated to 673 K in flowing helium (20 cm^3/min) and air (10 cm^3/min) mixture, and maintained at this temperature for 1 hr. This pretreatment removed the adsorbed moisture. The sample was then cooled to 313 K and then maintained at this temperature for $\frac{1}{2}$ hr, during which time the air stream was replaced by a 5% mixture of H_2 in helium (5 cm^3/min). The sample was then ramped at 20 K/min to a final temperature of 1273 K. Typically, various runs were carried out on a particular sample by decreasing the sample weight and observing when the reduction profile was similar, and, consequently, eliminating errors due to mass and heat transfer. The weight of the samples corresponding to 1–5 mg of V_2O_5 were used for the temperature programmed reduction (TPR) studies. The temperature was probed using a thermocouple (standard type K) placed ~0.62 cm below the sample basket. The weight of the sample was obtained as a function of time and for the reduction cycle the rate of change of sample weight per unit time was also obtained. This also provides the rate of change of sample weight per unit temperature change, dW/dT, since the ramp rate during the reduction cycle was linear. The temperature where the maximum value of dW/dT occurred was denoted as T_{max}.

TABLE 2

Experimental Monolayer of the Supported Vanadium Oxide Catalysts as a Function of Oxide Support

Oxide support	Surface area (m^2/g)	Experimental monolayer (wt.% V_2O_5)	Surface concentration (μmole V^{+5}/nm^2)
SiO_2	300	3[a]	1.1
ZrO_2	39	4	11.3
TiO_2	50	6	13.2
Nb_2O_5	55	7	14.0
Al_2O_3	180	20	12.2

[a] Bulk V_2O_5 crystals observed before monolayer achieved.

RESULTS

Determination of Experimental Monolayer

Studies using Raman spectroscopy on the various supported vanadium oxide samples determined the maximum V_2O_5 loading that can be accommodated on the different oxide supports as a molecularly dispersed species (19, 20), and are presented in Table 2. Examination of Table 2 reveals a similar surface concentration of the vanadium oxide species on the different supports (11–14 μmole V^{5+}/m^2), with the exception of SiO_2. For SiO_2, the experimental monolayer value was 1 μmole V^{5+}/m^2, one order of magnitude less than the expected monolayer value because of the preference of the surface hydroxyls on SiO_2 to form Si–O–Si linkages. Thus, all the oxide supports possess stable surface vanadium oxide overlayers under the present conditions. The surface of the supported vanadium oxide samples were analyzed by X-ray photoelectron spectroscopy and found to be free of impurities.

Methanol Oxidation Results

V_2O_5/SiO_2. The reactivities for the methanol oxidation reaction at 503 K of 1–5% V_2O_5/SiO_2 samples are shown in Table 3 along with the reactivity of pure SiO_2 for reference. Pure SiO_2 produces CO_x (carbon monoxide + carbon dioxide) and trace amounts of dimethyl ether (DME) with very low activity. As vanadium oxide is deposited on SiO_2, formaldehyde (FA) and dimethoxy methane (DMM) are formed along with dimethyl ether and CO_x. No detectable change in the amount of dimethyl ether and CO_x is observed upon the addition of molecularly dispersed vanadium oxide species, which suggests that these products are still originating from the SiO_2 support. As the vanadium oxide loading is increased the catalyst activity (A_c) increases. Conversion of the activity data to turnover frequency (TOF), based on the oxidation products formed, reveals that the TOF varies from 1.6 ×

TABLE 3

Reactivity of V_2O_5/SiO_2 Samples as a Function of Vanadium Oxide Loading at 503 K

Sample	A_c $\left(\frac{\text{mole MeOH conv.}}{\text{g} \cdot \text{hr}}\right)$	TOF[a] ($\times 10^3$ s^{-1})	Selectivity (%)[b]				
			FA	MF	DMM	DME	CO_x
SiO_2	2.6×10^{-4}	—	—	—	—	15	85
0.5% V_2O_5/SiO_2	7.8×10^{-4}	2.6	66	—	—	17	17
1.0% V_2O_5/SiO_2	3.9×10^{-4}	3.9	72	—	—	20	8
1.5% V_2O_5/SiO_2	9.4×10^{-4}	1.6	83	—	—	14	3
2.5% V_2O_5/SiO_2	4.6×10^{-3}	4.2	60	—	28	7	2
3.0% V_2O_5/SiO_2	3.1×10^{-3}	2.3	45	—	41	12	2
5.0% V_2O_5/SiO_2	3.3×10^{-2}	15.1	88	—	2	8	2
10.0% V_2O_5/SiO_2	4.0×10^{-2}	10.0	86	—	8	6	—

[a] Turnover frequency for oxidation products (FA + DMM).

[b] FA, formaldehyde; MF, methyl formate; DMM, dimethoxy methane; DME, dimethyl ether; CO_x, CO + CO_2.

10^{-3} to 4.2×10^{-3} with no correlation between the vanadium oxide loading and the TOF, except for 5 and 10% V_2O_5/SiO_2. For the 5 and 10% V_2O_5/SiO_2 samples the monolayer coverage is exceeded since bulk V_2O_5 is observed in the Raman spectra (19, 20) and the TOF approaches the TOF of bulk V_2O_5 of 2.2×10^{-2} s^{-1} (25). For all the V_2O_5/SiO_2 samples studied, deposits of vanadium oxide were observed at the end of the reactor tube due to volatilization of the surface vanadium oxide phase in the methanol + oxygen environment. The reactor tube containing just the vanadium oxide deposits showed no methanol conversion.

V_2O_5/ZrO_2. The reactivities of a series of V_2O_5/ZrO_2 samples toward methanol oxidation at 503 K are shown in Table 4 along with the pure ZrO_2 support for reference. The ZrO_2 support possesses some methanol oxidation activity, and the main products are methyl formate (MF), dimethyl ether, and CO_x. Formaldehyde and dimethoxy methane in addition to MF, DME, and CO_x are formed as vanadium oxide is deposited on ZrO_2. The amount of methyl formate produced on the 0.5% V_2O_5/ZrO_2 sample is more than the amount that can be produced from the ZrO_2 surface alone. As the vanadium oxide loading is increased, the main products due to the surface vanadium oxide site are formaldehyde (80+ %) and small amounts of dimethoxy methane. The selectivity to methyl formate decreases with increasing vanadium oxide loading, and it appears that the oxide surface is responsible for the production of methyl formate (26). Even at monolayer coverages (4% V_2O_5/ZrO_2), small amounts of methyl formate are observed, which is probably associated with the exposed zirconia surface. The surface vanadium oxide species may also form methyl formate since higher conversion of methanol also produces methyl formate. Dimethyl ether and CO_x are produced in trace amounts for the V_2O_5/ZrO_2 samples. Consequently, the yield of formaldehyde (activity × formaldehyde selectivity) was used to calculate the turnover frequency for the surface vana-

TABLE 4

Reactivity of V_2O_5/ZrO_2 Samples as a Function of Vanadium Oxide Loading at 503 K

Sample	A_c $\left(\frac{\text{mole MeOH conv.}}{\text{hr} \cdot \text{g cat}}\right)$	TOF[a] (s^{-1})	Selectivity (%)				
			FA	MF	DMM	DME	CO_x
ZrO_2	0.02	—	—	86	—	Tr	14
0.5% V_2O_5/ZrO_2	0.58	1.6	54	40	—	Tr	4
1.0% V_2O_5/ZrO_2	1.58	3.3	82	17	—	Tr	1
2.0% V_2O_5/ZrO_2	1.94	2.2	89	9	1	Tr	Tr
3.0% V_2O_5/ZrO_2	2.28	1.8	92	7	Tr	Tr	Tr
4.0% V_2O_5/ZrO_2	2.92	1.7	92	7	Tr	Tr	Tr
5.0% V_2O_5/ZrO_2	3.42	1.6	94	5	Tr	Tr	Tr

[a] Based on amount of formaldehyde (FA) formed.

TABLE 5

Reactivity of V_2O_5/TiO_2 Samples as a Function of Vanadium Oxide Loading at 503 K

Sample	A_c $\left(\frac{\text{mole MeOH conv.}}{\text{g} \cdot \text{hr}}\right)$	TOF[a] (s^{-1})	Selectivity (%)				
			FA	MF	DMM	DME	CO_x
TiO_2	0.002	—	—	—	—	91	9
1.0% V_2O_5/TiO_2	0.81	2.0	99+	—	—	Tr	—
2.0% V_2O_5/TiO_2	2.1	2.7	97	—	2	Tr	Tr
3.0% V_2O_5/TiO_2	1.94	1.6	98	—	1	Tr	Tr
4.0% V_2O_5/TiO_2	2.30	1.5	97	—	2	Tr	—
5.0% V_2O_5/TiO_2	2.54	1.3	95	—	5	Tr	—
6.0% V_2O_5/TiO_2	2.71	1.1	99	—	1	Tr	Tr
7.0% V_2O_5/TiO_2	3.23	1.2	99	—	1	Tr	Tr

[a] Based on amount of formaldehyde (FA) formed.

dium oxide species, since it appears that methyl formate is primarily produced from the ZrO_2 support. The TOF for the 0.5 to 4% V_2O_5/ZrO_2 samples vary within the limits of 1.6 and 3.3 s^{-1}. For slightly above-monolayer coverages (5% V_2O_5/ZrO_2), no appreciable change was observed in the TOF. The TOF of crystalline V_2O_5 is two orders of magnitude lower than the TOF of surface vanadium oxide species supported on zirconia (25) and, consequently, the TOF is dominated by the molecularly dispersed vanadium oxide species. Unlike the V_2O_5/SiO_2 system no deposits of vanadium oxide were found on the end of the reactor tube.

V_2O_5/TiO_2. The reactivities of various V_2O_5/TiO_2 samples toward methanol oxidation at 503 K are shown in Table 5. The pure TiO_2 support is included for reference. The TiO_2 support produces dimethyl ether and small amounts of CO_x. As vanadium oxide is deposited on the TiO_2 support, the activity increases by two orders of magnitude with the predominant formation of formaldehyde (95+ %). Small amounts of dimethoxy methane arising from surface vanadium oxide redox sites are also observed without any apparent trend. Trace amounts of dimethyl ether and CO_x from the TiO_2 support are also observed for the V_2O_5/TiO_2 catalysts. The formaldehyde yield was used to calculate the TOF of the surface vanadium oxide sites. The TOF of the 1–6% V_2O_5/TiO_2 varies from 1.1 to 2.7 s^{-1}. No appreciable change in TOF for slightly above monolayer loadings (7% V_2O_5/TiO_2) is observed. Even at monolayer coverages, 6% V_2O_5/TiO_2, trace amounts of dimethyl ether and CO_x are produced, suggesting the presence of some exposed TiO_2 surface. No deposits of vanadium oxide were found on the end of the reactor tube for all the V_2O_5/TiO_2 catalysts studied.

V_2O_5/Nb_2O_5. The reactivity for methanol oxidation of a series of V_2O_5/Nb_2O_5 samples at 503 K is shown in Table 6 along with the Nb_2O_5 support for reference. The Nb_2O_5 support produces dimethyl ether. As vanadium oxide is deposited on the Nb_2O_5 support, the activity increases by an order of magnitude, and partial oxidation products of formaldehyde and dimethoxy methane are predominantly formed. Dimethyl ether formation due to the exposed Nb_2O_5 surface is also observed in very small amounts. As the vanadium oxide loading is increased the

TABLE 6

Reactivity of V_2O_5/Nb_2O_5 Samples as a Function of Vanadium Oxide Loading at 503 K

Sample	A_c $\left(\frac{\text{mole MeOH conv.}}{\text{g} \cdot \text{hr}}\right)$	TOF[a] (s^{-1})	Selectivity (%)				
			FA	MF	DMM	DME	CO_x
Nb_2O_5	0.01	—	—	—	—	100	—
1% V_2O_5/Nb_2O_5	0.36	0.8	91	—	1	8	—
2% V_2O_5/Nb_2O_5	0.99	1.2	97	—	1	2	—
3% V_2O_5/Nb_2O_5	1.55	1.2	97	—	2	1	—
4% V_2O_5/Nb_2O_5	1.25	0.8	96	—	3	1	—
6% V_2O_5/Nb_2O_5	1.10	0.4	95	—	2	2	Tr

[a] Based on amount of formaldehyde (FA) formed.

TABLE 7

Reactivity of V_2O_5/Al_2O_3 Samples as a Function of Vanadium Oxide Loading at 503 K

Sample	A_c $\left(\frac{\text{mole MeOH conv.}}{\text{g} \cdot \text{hr}}\right)$	TOF[a] ($\times 10^2$ s^{-1})	Selectivity (%)				
			FA	MF	DMM	DME	CO_x
Al_2O_3	3.70	—	—	—	—	100	—
1% V_2O_5/Al_2O_3	2.69	3.6	<1	—	—	99	—
3% V_2O_5/Al_2O_3	1.89	4.0	2	—	—	97	Tr
10% V_2O_5/Al_2O_3	0.69	8.1	16	—	Tr	84	—
15% V_2O_5/Al_2O_3	0.52	9.3	22	—	1	77	—
20% V_2O_5/Al_2O_3	0.49	6.8	46	—	3	50	1

[a] Based on oxidation products (FA + DMM) formed.

activity passes through a maxima for the 3% V_2O_5/Nb_2O_5 and then decreases somewhat on approaching monolayer coverage. Similar changes in activity for the V_2O_5/Nb_2O_5 system were also observed for vanadium oxide supported on high surface area Nb_2O_5 (~100 m^2/g) (27). Compound formation of a small part of the surface vanadium oxide species cannot be excluded (19, 20). Irrespective of this anomalous behavior, the variation of TOF for formaldehyde formation is between 0.4 and 1.4 s^{-1}. The V_2O_5/Nb_2O_5 system is essentially selective toward formaldehyde (91–97%). Even near monolayer coverages (7% V_2O_5/Nb_2O_5), small amounts of dimethyl ether are detected, which is indicative of exposed niobia acid sites. No deposits of vanadium oxide were found on the end of the reactor tube for the V_2O_5/Nb_2O_5 catalysts studied.

V_2O_5/Al_2O_3. Table 7 shows the reactivity of the V_2O_5/Al_2O_3 samples toward methanol oxidation at 503 K along with the Al_2O_3 support as reference. The Al_2O_3 support is very active for the dehydration of methanol to dimethyl ether. As vanadium oxide is deposited on the Al_2O_3 support, partial oxidation products are observed and the total activity decreases, which suggests that the dehydration of methanol on the alumina sites is more active than the partial oxidation of methanol on the vanadium oxide sites. The selectivity of methanol conversion to formaldehyde increases noticeably with increasing vanadium oxide loading. A small increase in dimethoxy methane is also observed as the vanadium oxide loading is increased. In addition, the dimethyl ether formed from the Al_2O_3 support decreases nonlinearly with the increase in vanadium oxide loading, indicating a selective titration of surface acidic Al_2O_3 sites. This is not surprising since surface vanadium oxide is known to selectively titrate the alumina surface (28). Even at monolayer coverages of vanadium oxide (20% V_2O_5/Al_2O_3) dimethyl ether is observed, which corresponds to 15–20% of the Al_2O_3 surface being exposed. The amount of oxidation products (FA + DMM) were used to calculate the TOF since the surface vanadium oxide is responsible for the redox sites. The TOF of the 1–20% V_2O_5/Al_2O_3 samples varies within the limits of 3.6×10^{-2} to 9.3×10^{-2} s^{-1}. A significant error may be involved in calculating the TOF for the 1 and 3% V_2O_5/Al_2O_3 due to the low selectivities for these samples to formaldehyde over the surface vanadium oxide sites and the large conversions of methanol to dimethyl ether over the exposed alumina sites. No deposits of vanadium oxide were found on the end of the reactor tube for the V_2O_5/Al_2O_3 catalysts studied.

Activation Energy for Methanol Oxidation

The activation energies for the series V_2O_5/TiO_2 catalysts were obtained from the amount of formaldehyde formed at 473, 503, and 513 K, and are tabulated in Table 8. The results in Table 8 reveal that the activation energies for the V_2O_5/TiO_2 series are independent of surface coverage with a somewhat lower value at low vanadium oxide loading. The activation energy of formaldehyde formation for vanadium oxide supported on Al_2O_3, SiO_2, Nb_2O_5, and ZrO_2 samples was also obtained, and is plotted in Fig. 1, along with the V_2O_5/TiO_2 samples, as a function of coverage. The vanadium oxide coverage is defined as the ratio of the wt.% V_2O_5 to the experimental monolayer

TABLE 8

Activation Energy for Monolayer and Submonolayer V_2O_5/TiO_2 Samples

x% V_2O_5/TiO_2	Activation energy (kcal/mole)
1	16.5
3	20.6
4	19.8
5	20.5
6	21.7

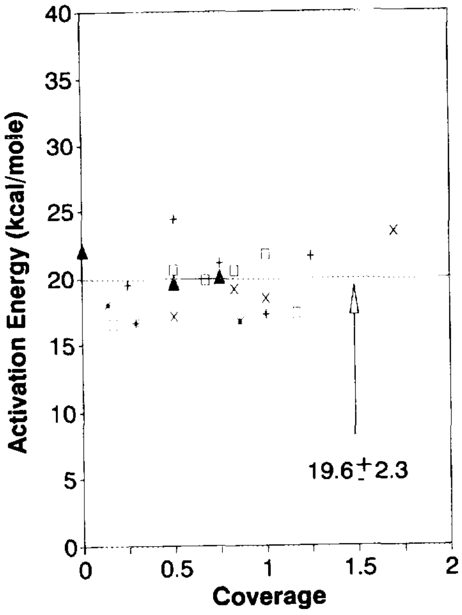

FIG. 1. The activation energy for formaldehyde formation for the different supported vanadium oxide catalysts. (×) V_2O_5/SiO_2; (*) V_2O_5/Nb_2O_5; (□) V_2O_5/TiO_2; (+) V_2O_5/ZrO_2; (▲) V_2O_5/Al_2O_3.

value of V_2O_5 on the different supports from Table 2. The activation energy of the various supported vanadium oxide catalysts is approximately constant at 19.6 kcal/mole, with a standard deviation of 2.3. This activation energy is similar to the 84 to 95 kJ/mole (20 to 23 ± 0.5 kcal/mole) obtained for methanol oxidation to formaldehyde over unsupported vanadium oxide (29).

Temperature Programmed Reduction Results

Temperature programmed reduction experiments were also performed for the series of supported vanadium oxide samples (V_2O_5/ZrO_2 and V_2O_5/TiO_2), and the T_{max} temperature is approximately constant for the monolayer and submonolayer vanadium oxide catalysts. Similar conclusions were obtained by Bond *et al.* (30). The TPR experiments for monolayer supported vanadium oxide samples are plotted in Fig. 2, with the exception of the V_2O_5/Nb_2O_5 sample. For the V_2O_5/Nb_2O_5 sample a distinct T_{max} peak was not observed in the TPR experiments, and additional experiments are underway to obtain a well-defined T_{max}. The T_{max} value of the supported vanadium oxide catalysts is observed to be a strong function of the oxide support as shown in Fig. 2. Vanadium oxide supported on SiO_2 has the highest T_{max} value (1047 K), and vanadium oxide supported on ZrO_2 has the lowest (873 K). These T_{max} values are very different from the values obtained by Roozeboom *et al.* (16–18) and are apparently due to the different experimental apparatus and conditions used for the TPR studies.

The T_{max} temperature is plotted versus the respective TOFs in Fig. 3 (semi-log plot). The TOF of the respective supported vanadium oxide catalysts are inversely related to the T_{max} temperature as shown in Fig. 3. The V_2O_5/ZrO_2 sample, which has the highest TOF, has the lowest T_{max} value, and the V_2O_5/SiO_2 sample, which has the lowest TOF, has the highest T_{max} value. The line drawn in Fig. 3 is meant to illustrate that the oxidation activity is

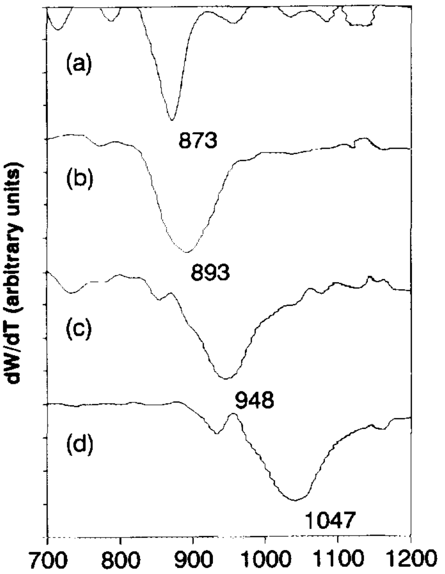

FIG. 2. Temperature programmed reduction profiles for monolayer (a) V_2O_5/ZrO_2, (b) V_2O_5/TiO_2, (c) V_2O_5/Al_2O_3, and (d) V_2O_5/SiO_2 catalysts.

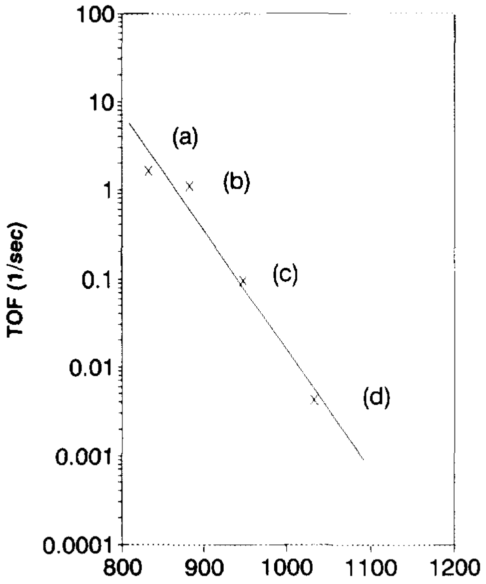

FIG. 3. Semi-log plot of TOF versus the T_{max} temperature for monolayer (a) V_2O_5/ZrO_2, (b) V_2O_5/TiO_2, (c) V_2O_5/Al_2O_3, and (d) V_2O_5/SiO_2 catalysts.

inversely related to the T_{max} temperature and is not curve fitted. The T_{max} temperature determines the ease of reduction or oxygen removal from the catalyst (16).

DISCUSSION

The partial oxidation of methanol (CH_3OH) was used to probe the reactivity of the surface vanadium oxide redox sites. Methanol chemisorbs on supported vanadium oxide catalysts as a surface methoxy (CH_3O) species (31, 32). This methoxy species can react via various reaction pathways to form formaldehyde, methyl formate, dimethoxy methane, dimethyl ether, carbon monoxide, and carbon dioxide. The type of reaction pathway taken by the surface methoxy species depends on the nature of the sites present on the catalyst surface (e.g., redox, acid, or basic). On redox sites, the partial oxidation products are formaldehyde, methyl formate, and dimethoxy methane. Acid sites dehydrate methanol to form dimethyl ether, and basic sites oxidize methanol to formate, which decomposes to CO/CO_2. Further oxidation of the partial oxidation and dehydration products also forms carbon oxides. Details of the various surface intermediates and reaction pathways can be found elsewhere (26, 31–35).

Comparison of the activity and selectivity of the pure oxide supports with those of the supported vanadium oxide catalysts (Tables 3–7) shows that the amount of partial oxidation products (formaldehyde, methyl formate, and dimethoxy methane) increases as vanadium oxide is deposited on the oxide supports. The formation of partial oxidation products with increasing vanadium oxide loading reveals that the surface vanadium oxide species form redox sites on these oxide supports. Furthermore, the formation of formaldehyde as the main reaction product indicates the similar reaction pathway during methanol oxidation over the surface vanadium oxide phases on different oxide supports. The predominant formation of formaldehyde by the surface vanadium oxide redox sites allows for the direct comparison of the reactivity of the different supported vanadium oxide catalysts without having to deal with the complexities of different reaction pathways.

Examination of the TOF of the different low loading supported vanadium oxide samples in Tables 3–7 indicates three orders of magnitude change as a function of the specific oxide support. The TOF of 0.5% V_2O_5/SiO_2 is 2.6×10^{-3} s^{-1} and the TOF of 0.5% V_2O_5/ZrO_2 is 1.6×10^0 s^{-1}. The dramatic influence of the specific oxide support on the catalytic activity of the different low loading supported vanadium oxide catalysts is at first surprising since there is no significant structural difference in the surface vanadium oxide species (19, 20, 25). Similar conclusions were also reached for methanol oxidation over low coverages of supported MoO_3, CrO_3, and Re_2O_7 samples, where it was observed that the structure of the supported metal oxide species is essentially independent of the oxide support, but the reactivity is a strong function of the specific oxide support used to support these metal oxides (36). Thus, the reactivity (TOF) for methanol oxidation over the supported vanadium oxide catalysts, which varies by three orders of magnitude with the specific oxide support, is not related to the structural differences of the surface vanadium oxide phase.

The strong dependence of the reactivity (TOF) on the specific oxide support of the supported vanadium oxide catalysts is common for all vanadium oxide coverages since no appreciable change in TOF is observed as a function of vanadium oxide loading (see Tables 3–7). The small variation of the TOF for the supported vanadium oxide samples as a function of vanadium oxide loading does not follow any particular trend and is attributed to experimental error. These observations suggest that either the partial oxidation of methanol is structure insensitive or only a single surface vanadium oxide species is present for all monolayer and submonolayer supported vanadium oxide catalysts.

The presence of only a single surface vanadium oxide species on a specific oxide support as a function of vanadium oxide coverage is not confirmed by physical characterization studies since the *in situ* Raman spectra of these samples obtained under dehydrated conditions exhibit changes with surface vanadium oxide coverage (19–23). The changes in the Raman spectra with surface vanadium oxide coverage are independent of the oxide support (19, 20), and the Raman bands are assigned to isolated (low and high coverage) and polymeric (high coverage) vanadium oxide species (21–23). Therefore, all the surface vanadium oxide species behave similarly toward methanol oxidation under the present reaction conditions. This suggests that the methanol oxidation reaction takes place on a single surface redox site (structure insensitive), and is consistent with the observation that the dramatic influence of the oxide support on the reactivity (TOF) during methanol oxidation is present at all vanadium oxide coverages. Similar conclusions regarding the requirement of only one vanadium site for the methanol oxidation reaction have also been made for vanadium-containing Keggin units (37).

To learn more about the kinetics of methanol oxidation over supported vanadium oxide catalysts the activation energy was determined. Methanol oxidation over the supported vanadium oxide catalysts exhibits an activation energy (19.6 ± 2.3 kcal/mole) that is essentially independent of the specific oxide support and vanadium oxide loading. The 19.6 ± 2.3 kcal/mole activation energy for formaldehyde formation over the various supported vanadium oxide catalysts is typical of C–H bond breaking of the surface methoxide species during its conversion to formaldehyde (38–40). The similar activation energy is particularly helpful in the analysis of the rate expression for methanol oxidation. The rate expression for the oxidation of methanol for low conversions can be put into power law form as (41)

$$R = k_1 (p_{\mathrm{CH_3OH}})^m (p_{\mathrm{O_2}})^n, \qquad [1]$$

where R is the reaction rate, k_1 is the rate constant, p_i is the partial pressure of the reactant i, and m and n are exponents of the power law expression.

Under differential reactor conditions,

$$N_f = \frac{\Delta x}{\Delta \mathrm{V}} = R, \qquad [2]$$

where N_f is the partial oxidation turnover frequency, Δx is the number of moles of methanol converted to partial oxidation products per unit time, and ΔV is the number of moles of vanadium atom.

In the present study the partial pressures of methanol and oxygen are constant since identical reaction conditions were used, and N_f for the different supported vanadium oxide catalysts is directly proportional to k_1. The three orders of magnitude change in N_f for the supported vanadium oxide catalysts correlates to a three orders of magnitude change in k_1. Furthermore, k_1 is related to the activation energy and pre-exponential factor by the Arrhenius equation

$$k_1 = A_{\mathrm{catalyst}} \exp\left(-\frac{E}{RT}\right), \qquad [3]$$

where A_{catalyst} is the pre-exponential factor for catalyst, E is the activation energy, R is the gas constant, and T is the temperature of reaction.

The similar activation energies for methanol oxidation over the surface vanadium oxide species directly imply (using Eqs. [1], [2], and [3]) that changes in the turnover frequency, N_f, of the different supported vanadium oxide catalysts are due to the differences in the pre-exponential factor (A_{catalyst}). The pre-exponential factor is made up of different parameters which include the structure, the number of active sites, and the activity per site. Since the methanol oxidation reaction over the supported vanadium oxide catalysts is structure insensitive (see discussion above) the pre-exponential factor depends on the number of active sites and/or the activity per site.

In situ Raman characterization of supported vanadium oxide catalysts during methanol oxidation was undertaken to obtain additional insight into the importance of the number of active sites and/or the activity per site in determining the pre-exponential factor. During methanol oxidation over the 1% V_2O_5/SiO_2 catalyst no appreciable change in the Raman spectrum is observed under *in situ* reaction conditions. However, for the 1% V_2O_5/ZrO_2, 1% V_2O_5/TiO_2, and 1% V_2O_5/Nb_2O_5 catalysts a substantial decrease of the 1016–1040 cm^{-1} Raman band (typical of the molecularly dispersed surface vanadium oxide species) is observed during methanol oxidation. These studies indicate that a different number of active sites are participating in the reaction on the different supported vanadium oxide catalysts under steady-state conditions. The number of active sites on V_2O_5/ZrO_2, V_2O_5/TiO_2, and V_2O_5/Nb_2O_5 catalysts is significantly greater than the number of active sites on the V_2O_5/SiO_2 catalyst. This difference in the number of active sites gives rise to the difference in the pre-exponential factor for the different supported vanadium oxide catalysts. Thus, the reactivity for methanol oxidation reaction over supported vanadium oxide samples is controlled by the pre-exponential factor, which is determined by the number of active sites on the catalyst, V_2O_5/ZrO_2 and V_2O_5/TiO_2 having the greatest number of active sites and V_2O_5/SiO_2 having the least number of active sites of the supported vanadium oxide catalysts used in this study. Relating the differences in TOF to the differences in the number of active sites for these supported vanadium oxide catalysts, however, does not exclude the importance of the activity per site, which may also differ. Additional studies are required to clarify the importance of the activity per site, perhaps similar to the differences in entropy of the chemisorbed species as proposed for butane oxidation over V_2O_5/SiO_2 catalysts (42). A constant activity per site would imply that the number of active sites is the only parameter controlling the TOF for methanol oxidation.

The strength of the terminal V=O bond has been proposed to be one of the factors controlling the reactivity of vanadium oxide catalysts (7, 8, 43, 44). The validity of this proposal was investigated in the present study by relating results from Raman spectroscopy to the TOFs of methanol oxidation. The position of the Raman band of the terminal V=O bond is directly related to the V=O bond strength (45), and a stronger V=O bond gives rise to a higher Raman band position. The Raman band positions of the terminal V=O bond of the various supported vanadium oxide samples determined previously (19, 20) are tabulated with the TOFs for methanol oxidation in Table 9. Comparison of the TOFs and Raman band positions in Table 9 reveals that the TOFs are not related to the surface vanadium oxide Raman band positions on the different supported vanadium oxide samples. Consequently, the TOF is not related to the terminal V=O bond strength. Since the terminal V=O bond strength is not related to the TOF it follows, from Fig. 3, that the V=O bond strength is also not related to the $T_{\max}$ temperature. Therefore, the claims in the literature that the strength

TABLE 9

The TOF and Raman Shift of the V=O Terminal Bond for Low and Near Monolayer Coverages of Supported Vanadium Oxide Samples

	Low coverage		Near monolayer coverage	
V_2O_5 on oxide support	Raman band[a] of V=O (cm^{-1})	TOF (s^{-1})	Raman band[a] of V=O (cm^{-1})	TOF (s^{-1})
SiO_2	1039	2.6×10^{-3}	—[b]	—[b]
Al_2O_3	1016	3.6×10^{-2}	1026	6.8×10^{-2}
Nb_2O_5	1031	9.0×10^{-1}	1033	4.5×10^{-1}
TiO_2	1027	2.0×10^{0}	1030	1.1×10^{0}
ZrO_2	1023	1.6×10^{0}	1030	1.8×10^{0}

[a] From Refs. (19, 20).

[b] Theoretical monolayer not reached.

of the terminal V=O bond controls the reactivity and reducibility of supported vanadium oxide catalysts are not supported by the current observations, and, by elimination, the vanadium–oxygen–support (V–O–S) bridging bond appears to be controlling the reactivity and reducibility of supported vanadium oxide catalysts.

In addition to the TOF being related to the pre-exponential factor, Fig. 3 shows that the TOFs of the supported vanadium oxide catalysts are also related to the T_{max} temperatures from TPR experiments. A decrease in the T_{max} temperature results in an increase in TOF. Furthermore, the T_{max} temperature depends on the reducibility of the oxide supports. The TiO_2 and Nb_2O_5 supports are reducible oxides, and ZrO_2 is known to reduce at the surface (46, 47). The Al_2O_3 and SiO_2 supports, however, are not easily reducible. Relating the reduction behaviors of the oxide support and the supported vanadium oxide catalysts suggests that the reduction process takes place at the V–O–S bond and that a higher T_{max} temperature is most probably due to a greater V–O–S bond strength. Consequently, the independence of the terminal V=O bond strength and the dependence of the reduction characteristics with the TOF suggest that the TOF for methanol oxidation over supported vanadium oxide catalysts is most probably related to the V–O–S bond strength. It should be noted that the variations in the V–O–S bond strength are indirectly inferred, and a direct method to experimentally determine the V–O–S bond strength is yet to be found.

Relating the reduction characteristics and the pre-exponential factor during methanol oxidation suggests that the strength of the V–O–S bond determines the number of active sites present on the particular supported vanadium oxide catalyst (assuming the activity per site is constant). For example, the V–O–Zr bond strength is weaker (lower T_{max}) than the V–O–Si bond strength (higher T_{max}), which gives rise to the larger number of active sites at steady-state conditions and greater TOF of the V_2O_5/ZrO_2 catalysts compared to the V_2O_5/SiO_2 catalysts. The controlling effect of the V–O–S bond in the oxidation activity is also observed in the $V_2O_5/TiO_2/SiO_2$ system where the inactive V–O–Si bonds are modified by the presence of the surface titania phase (48). The importance of the bridging bond (M_1–O–Support) in determining the reactivity of a specific catalyst suggests that the reactivity should also be a function of the specific supported metal oxide species (i.e., of M_1). Indeed, the TOF for the MoO_3/TiO_2 catalyst (containing Mo–O–Ti bridging bonds) is an order of magnitude less reactive than the V_2O_5/TiO_2 catalyst (containing V–O–Ti bridging bonds) (36). Thus, knowledge of the V–O–Support bond strength (or M_1–O–Support bond strength) and, hence, the number of active sites is one of the fundamental criteria determining the oxidation activity of supported metal oxide catalysts. Furthermore, the presence of only surface reduction of the ZrO_2 support (46, 47) suggests the reactivity is controlled by the surface reduction process only and the contribution of bulk reduction can be neglected for this study.

In summary, the present results suggest that the differences in the catalytic behavior of supported vanadium oxide catalysts is not related to structural difference or the terminal V=O bond strengths, but is primarily determined by the number of active sites. The number of active sites of the supported vanadium oxide catalysts controls the oxidation activity of these catalysts and is reflected in the different pre-exponential factors. The activity per site may also be important in determining the pre-exponential factor, but this information is currently not available. It is proposed that the fundamental factor controlling the reactivity is the strength of the V–O–Support bond. Current theoretical efforts should provide more insight into the fundamental aspect of this important catalytic phenomenon (49).

The influence of the specific oxide support on the reactivity of the surface vanadium oxide phase is also found during the oxidation of carbon monoxide (9, 17), *o*-xylene [3], buta-1,3-diene (11), but-1-ene (11), furan (12), and benzene (13), and during the selective catalytic reduction of NO_x (50). The similar dependence on the oxide support for methanol oxidation and the partial oxidation activity of these molecules suggests a common governing factor controlling the reactivity of these reactions. This implies that the oxidation of methanol can be used as an effective chemical probe of the reactivity of the surface vanadium oxide redox species. Thus, conclusions based on the effect of the oxide support on the oxidation of methanol should also apply to other redox reactions involving supported vanadium oxide catalysts. Care must be taken, however, in generalizing all of these results involving catalytic oxidation reaction since other factors might also be important for certain reactions. For example, as the surface vanadium oxide coverage increases there is a decrease in the surface concentration of hydroxyls and exposed support sites, and an increase in the surface Brønsted acid sites is also observed (28, 51). The relative importance of these factors for different oxidation reactions needs to be established, and this is the goal of ongoing research in our laboratory.

CONCLUSIONS

Methanol was used to determine the redox activity of the surface vanadium oxide species as a function of oxide supports and vanadium oxide loading. The methanol partial oxidation activity over the supported vanadium oxide species increases as a function of vanadium oxide loading for submonolayer and monolayer catalysts. Formaldehyde is the main partial oxidation product formed by the surface vanadium oxide redox sites under differential reactor conditions. The TOF does not depend on the vanadium oxide loading for the monolayer and submonolayer supported vanadium oxide samples and is structure insensitive. No relationship exists between the terminal V=O bond strength and TOF or reducibility. However, the TOF is a strong function of the specific oxide support used for supporting the surface vanadium oxide species. The TOF for V_2O_5/ZrO_2 and V_2O_5/TiO_2 catalysts are three orders of magnitude greater than the TOF for the V_2O_5/SiO_2 catalysts. The activation energy for formaldehyde formation on the different supported vanadium oxide catalysts is 19.3 ± 2.3 kcal/mole, independent of the vanadium oxide loading and oxide support, and corresponds to the C–H bond breaking of the surface methoxy intermediate. The similar activation energies and different TOFs indicate that the pre-exponential factor of the different supported vanadium oxide catalysts is determined by the specific oxide support. *In situ* Raman studies during methanol oxidation suggest that the pre-exponential factor is determined by the number of participating surface vanadium oxide sites. The activity per vanadium oxide site may also play a role in determining the pre-exponential factor, but such information is currently not available. The TOF is directly related to the T_{max} temperature from TPR experiments. The above suggests that the reactivity of the supported vanadium oxide catalysts most probably depends upon the V–O–Support bond strength. Thus, the reactivity of the surface vanadium oxide phase is determined by the specific oxide support and is

(a) not related to the stability of the surface vanadium oxide phase,

(b) not related to the structure of the surface vanadium oxide phase,

(c) not related to the terminal V=O bond strength, but is related to the ease of reduction of the supported vanadium oxide catalysts. The strength of the V–O–Support bond appears to determine the number of participating surface vanadium oxide sites and, consequently, the pre-exponential factor.

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