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Characterization of Silica- and Alumina-Supported Vanadia Catalysts Using Temperature Programmed Reduction

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The nature of the vanadia–support interaction for silica and alumina-supported V_2O_5 catalysts was investigated using temperature programmed reduction (TPR), temperature programmed oxidation, and solid-state ^{51}V NMR. Solid-state ^{51}V NMR for the V_2O_5/SiO_2 catalysts indicated the presence of microcrystalline bulk-like vanadia species even at low vanadia loadings. Temperature programmed reduction of V_2O_5/SiO_2 exhibited multiple peaks. It is suggested that the low temperature peak is due to reduction of surface vanadia. This appears to be the case also for bulk V_2O_5. ^{51}V NMR indicated that bulk-like vanadia species are present for V_2O_5/Al_2O_3 catalysts only at high vanadia loadings. Vanadia was more highly dispersed on alumina than on silica as evidenced by NMR and TPR. The two lowest temperature TPR peaks appear to be related to the reduction of surface vanadia on V_2O_5/Al_2O_3. It was found that for V_2O_5/Al_2O_3 the average oxidation state of V after reduction to 900°C is consistent with the stoichiometry $V^{+5} \rightarrow V^{+4}$, whereas the V_2O_5/SiO_2 catalysts exhibited 70% reduction of the V_2O_5 to V_2O_3 as did bulk V_2O_5. The amount of surface vanadium as determined by TPR correlates reasonably to the amount of tetrahedral V found by NMR. It is concluded that TPR provides an excellent means by which vanadia dispersion can be estimated on supported vanadia catalysts.

INTRODUCTION

Supported and bulk vanadia catalysts are important catalysts for the partial oxidation of hydrocarbons (1–3). Supported vanadia catalysts, depending on the support used (Al_2O_3, SiO_2, MgO, TiO_2, etc.), have been found to have different activities and selectivities to the desired oxygenated hydrocarbon products (3, 4). Such differences are related to the nature of the catalyst–support interactions. It is known that the partial oxidation of hydrocarbons on oxide catalysts involves a redox mechanism in which the catalyst is partially reduced by the extraction of oxygen from the catalyst which in turn is replenished by gas-phase oxygen (5). The impact of the support or modifier on the redox potential of the catalyst can be used to help understand the differences seen in activity and selectivity.

There have been numerous reports on the nature of the catalyst–support interaction for vanadia on TiO_2 examined by a variety of techniques such as TPR (6–8), laser raman spectroscopy (6, 9–10), and solid-state NMR (11–14). Several researchers have also reported the nature of vanadia species on alumina supports by TPR (6, 8, 9, 15), laser Raman spectroscopy (16, 17), and solid-state NMR techniques (14, 18–20). The proposed vanadia species on alumina range from highly dispersed monomeric metavanadate species (16, 17) to mostly dimeric tetrahedral (8) and polymeric vanadia species (16, 17). It is evident that the reduction/oxidation behavior of these catalysts depend on the nature of the species on the support (8). However, no attempt has yet been made to clearly associate the temperature programmed reduction (TPR) peaks to the reduction of different surface/bulk species in these vanadia catalysts. Several studies have also reported on the nature of the vanadium species on silica supports by TPR (6, 8, 15) and by laser Raman spectroscopy (17, 20, 21). Controversy exists as to the reducibility of V_2O_5/SiO_2 catalysts (6, 8, 15). It is known that vanadia does not disperse well in SiO_2. In such a case, the estimation of dispersion of vanadia on silica supports is very important for comparison purposes. In order to estimate the dispersion of vanadia on silica supports, low temperature oxygen chemisorption has been carried out after partial reduction of the catalysts (22–24). However, erroneous dispersion values may result due to bulk reduction. Recently, Oyama *et al.* (21) have measured oxygen chemisorption at the same temperature (370°C) as used for mild reduction. This reportedly ensures that no bulk reduction occurs.

In this paper we report the results of an investigation of the V species in V_2O_5/SiO_2, and V_2O_5/Al_2O_3 catalysts using TPR and ^{51}V solid-state NMR techniques. We also present evidence showing the ability of TPR to distinguish between reduction of surface and bulk-like V species. Thus, the dispersion of vanadia was able to be estimated

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using TPR. This paper is part of a larger investigation on the partial oxidation of methane to oxygenates over silica- and alumina-supported catalysts, wherein the dispersion of vanadia has been found to influence the activity and selectivity of these catalysts (25).

EXPERIMENTAL

V_2O_5/SiO_2 and V_2O_5/Al_2O_3 catalysts were prepared by standard wet impregnation technique. The required amount of ammonium metavanadate (Aldrich, 99.99% purity) was dissolved in water and then slurried with either silica (nonporous, Cab-O-Sil M5, Cabot Corp.) or alumina (Vista Chemicals) while maintaining the pH of the solution at 10. The resulting mixture was evaporated to dryness and the powder further dried overnight at 100°C, followed by calcination at 550°C for 8 h. Catalysts having loadings of 1.5–25 wt% V_2O_5 were prepared. Bulk V_2O_5 was bought from Aldrich and used as received.

X-ray diffraction measurements of the supported and bulk vanadia catalysts were obtained with a General Electric No. 5 diffractometer using Cu$K\alpha$ radiation. The BET surface area measurements were carried out using N_2 physisorption at −196°C.

Solid-state ^{51}V NMR spectra of model compounds (V_2O_5, NH_4VO_3) and the catalysts were obtained using a Bruker MSL 300 spectrometer. The wide-line NMR spectra were recorded at a frequency of 78.943 MHz using 2–3 μs radio frequency pulses with a repetition time of 10 s and 2 K data points. A spectral width of 125 kHz was used to acquire approximately 4000 scans for each sample. A line broadening factor of 500 Hz was applied prior to Fourier transform. The chemical shifts are reported relative to liquid $VOCl_3$.

Temperature programmed reduction was carried out in an AMI-1 system (Altamira Instruments). The catalyst samples (10–200 mg) were loaded in a quartz U-tube reactor and pretreated at 550°C for 2 h in flowing hydrocarbon-free, dry air in order to eliminate the moisture and to ensure complete oxidation. The temperature was then ramped linearly from 50 to 900°C at a constant rate of 5°C/min in a flow of 5% H_2 in Ar, and the H_2 consumption was monitored using a TCD. The calibration of the instrument was verified by reduction of CuO, which is known to reduce completely from Cu^{2+} to Cu^0 (26).

Temperature programmed oxidation of the reduced samples (from TPR) was carried out by ramping from 50 to 675°C in 2% O_2 in He. The oxygen consumption was also monitored using a TCD.

RESULTS AND DISCUSSION

XRD and BET Surface Area Measurements

The XRD pattern of bulk vanadia indicated the presence of crystalline V_2O_5. The XRD patterns of the V_2O_5/SiO_2 and V_2O_5/Al_2O_3 catalyst samples with up to 8.9 wt% loading did not show any vanadia peaks indicating that the vanadia was well dispersed with particle sizes less than 40 Å. For 25 wt% V_2O_5/Al_2O_3 and 25 wt% V_2O_5/SiO_2, however, peaks corresponding to crystalline V_2O_5 were observed. The BET surface areas for all the catalysts are listed in Table 1. The BET surface areas did not change appreciably upon impregnation of vanadia on SiO_2 or Al_2O_3.

TABLE 1

Physical Properties of the Catalysts Studied

Catalyst	S.A. (m^2/g)	V Structure seen by XRD
V_2O_5 (bulk)	30	V_2O_5
1.6% V_2O_5/SiO_2	150	ND
4.0% V_2O_5/SiO_2	145	ND
8.2% V_2O_5/SiO_2	135	ND
25.0% V_2O_5/SiO_2	120	V_2O_5
2.0% V_2O_5/Al_2O_3	205	ND
4.8% V_2O_5/Al_2O_3	200	ND
8.9% V_2O_5/Al_2O_3	190	ND
25.0% V_2O_5/Al_2O_3	160	V_2O_5

Note. ND, none detected.

^{51}V NMR

Bulk V_2O_5 and other model compounds. ^{51}V NMR spectra for the bulk and supported V_2O_5 catalysts were obtained in order to determine the nature of the vanadia species present. The ^{51}V isotope has a natural abundance of 99.76% but has a large magnetic moment due to quadrupolar interaction ($I = 7/2$). Thus, the spectra obtained are complicated by the presence of line broadening effects arising due to the second order quadrupolar effects and the chemical shift anisotropy. Eckert and Wachs (14) have demonstrated through field dependency experiments that ^{51}V spectra are dominated by the chemical shift anisotropy rather than second order quadrupolar effects at high fields (7.05 *T*). It has also been shown that generally only the central $\frac{1}{2} \rightarrow \frac{1}{2}$ is excited and by careful selection of the pulse length quantitatively reliable spectra can be obtained (14, 27–28).

The wide-line NMR spectra of model compounds (V_2O_5 and NH_4VO_3) were obtained in order to relate the nature of the vanadia species on the supports to the known structures of the model compounds (14, 18). Bulk V_2O_5 has a distorted octahedral symmetry (6-coordinated vanadium) and showed a wide-line chemical shift centered around −303 ppm. Ammonium metavanadate, on the other hand, has a tetrahedral geometry with a polymeric structure $[O\text{–}V(O_2)\text{–}]^{2-}$ (14) and exhibited a very broad spectrum with a major peak at −390 ppm and broad shoulders at −485 and −670 ppm. In general, the ^{51}V signal shifts increasingly downfield as the vanadium species becomes more polymeric in nature or as the number of oxygens attached to the vanadia increases (14, 18, 27–29).

V_2O_5/SiO_2. The wide-line NMR spectra of the V_2O_5/SiO_2 catalysts are shown in Fig. 1 and the chemical shifts are tabulated in Table 2. It can be seen that the spectra predominantly exhibit two peaks at ca. −300 and −600 ppm. As the vanadia loading was increased the peak at −600 ppm decreased and by a loading of 8.2% a single peak at −300 ppm with a small shoulder at −580 ppm was observed. No attempt was made to obtain MAS-NMR spectra since a significant line narrowing is not expected by spinning the sample (14). Moreover, Eckert and Wachs (14) have shown that for V_2O_5/Al_2O_3 catalysts only one type of species could be identified by spinning the sample in spite of two peaks being seen in the wide-line spectrum. Attempts have been made previously to assign the peaks at various chemical shifts to known vanadium symmetries. For example, Wachs and co-workers (11–14) have attributed the peak at around −550 ± 30 ppm to a dimeric form of vanadium in tetrahedral symmetry on V_2O_5/Al_2O_3 catalysts. This is also seen from solution NMR at pH = 10, wherein a similar chemical shift was observed for a metavanadate species which is known to have a tetrahedral symmetry (29). The peak at −300 ppm has been attributed to a distorted octahedral crystalline vanadium species, as seen in the bulk V_2O_5 NMR, or to a surface polymeric vanadium species (14, 18). It is, however, rather difficult to distinguish between various tetrahedral symmetries, i.e., monomeric, dimeric, and even polymeric tetrahedral species. Based on the wide-line NMR spectra of reference compounds given in Ref. (14) it is expected that a monomeric species will exhibit a chemical shift more negative than −660 ppm, whereas a dimeric species should exhibit a chemical shift of −550 ± 30 ppm. The chemical shift for the tetrahedral peak for the V_2O_5/SiO_2 catalysts was around −600 ± 30 ppm. Since the peaks in wide-line NMR are very broad and errors may be involved due to line broadening and phasing, it is unclear whether this peak is due to monomeric or dimeric vanadium species. In any case, however, the presence of tetrahedral species is obvious. Thus, the V_2O_5/SiO_2 catalysts consisted of both tetrahedral V species as well as microcrystalline octahedral V species at very low vanadia loadings and predominantly of octahedral V species at high vanadia loadings. This is consistent with the observations reported earlier by laser Raman spectroscopy (17, 20, 21). Peak locations and assignments are given in Table 2.

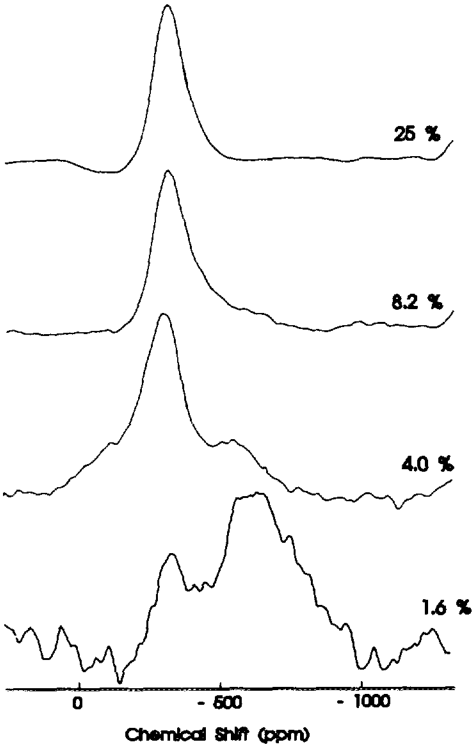

FIG. 1. Wide-line ^{51}V NMR spectra for V_2O_5/SiO_2 catalysts.

TABLE 2

^{51}V NMR Wide-line Chemical Shifts for the Peak Maxima Assigned to Octahedral and Tetrahedral Vanadium Species for Various Catalysts

Catalyst	Chemical shift (ppm)	
	Tetrahedral	Octahedral
V_2O_5	—	−303 ± 10
1.6% V_2O_5/SiO_2	−625 ± 30	−320
4.0% V_2O_5/SiO_2	−580	−302
8.2% V_2O_5/SiO_2	−580	−303
25% V_2O_5/SiO_2	—	−303
2.0% V_2O_5/Al_2O_3	−650	—
4.8% V_2O_5/Al_2O_3	−630	—
8.9% V_2O_5/Al_2O_3	−600	−295
25% V_2O_5/Al_2O_3	−570	−303

V_2O_5/Al_2O_3. The NMR spectra for the V_2O_5/Al_2O_3 catalysts are shown in Fig. 2. The peak at ca. −600 ppm dominated at low vanadia loadings, whereas a peak at −300 ppm appeared at loadings greater than 4.8%. For the 25% V_2O_5/Al_2O_3 catalyst the peak at −300 ppm became the dominant peak indicating the presence of octahedral V_2O_5. It should be noted that in wide-line ^{51}V NMR a surface polymeric vanadium species would exhibit a peak at a chemical shift similar to that for octahedral bulk V_2O_5 (14). However, it has been shown previously that the shielding tensor components for crystalline V_2O_5 and for polymeric surface species may be different resulting in different isotropic chemical shifts (14). Thus, the octahedral wide-line NMR signal observed in our studies is quite probably a combination of both a surface polymeric

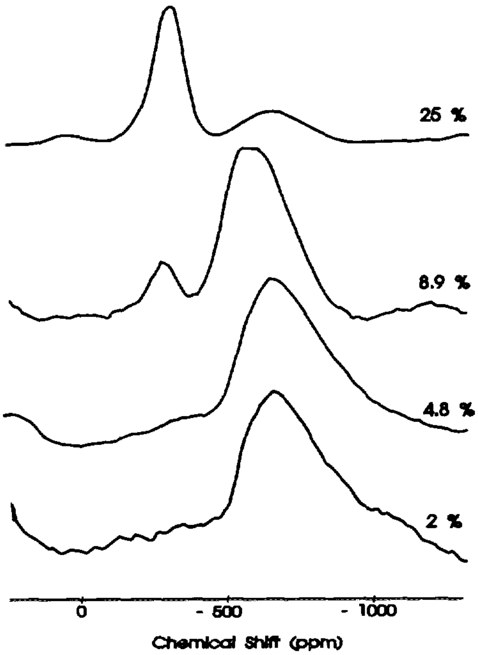

FIG. 2. Wide-line ^{51}V NMR spectra for V_2O_5/Al_2O_3 catalysts.

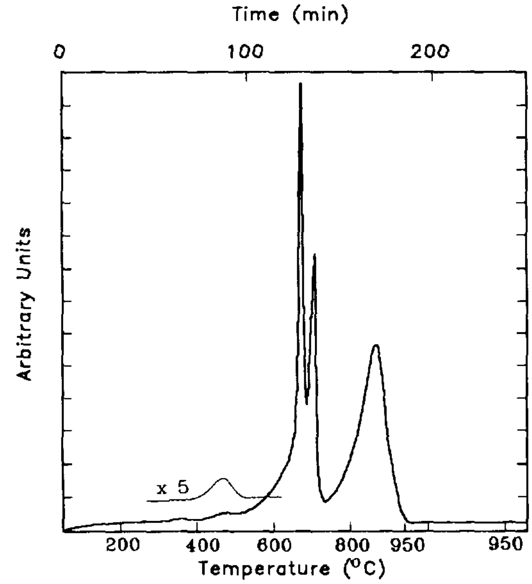

FIG. 3. TPR profile for bulk V_2O_5.

species and the bulk crystalline V_2O_5 species detected by XRD. Thus, the V_2O_5/Al_2O_3 catalysts possessed predominantly a tetrahedral V species at lower vanadia loadings with octahedral V species appearing only at high loadings. This is consistent with the observations made earlier by laser Raman and ^{51}V NMR studies (14, 16–18).

Temperature Programmed Reduction/Oxidation

Bulk V_2O_5. The temperature programmed reduction profile for bulk V_2O_5 is shown in Fig. 3. It was found that bulk V_2O_5 exhibited multiple major reduction peaks when treated in 5% H_2-in-Ar up to 900°C. The peak locations are listed in Table 3 (P_2, P_3, P_4). Bosch *et al.* (30) have reported a similar observation, and they have attributed this phenomenon to the reduction sequence

$$V_2O_5 \rightarrow V_6O_{13} \rightarrow V_2O_4 \rightarrow V_2O_3.$$

In addition to the major peaks that can be attributed to the reduction sequence described above, a small reduction peak (P_1) at 460°C was observed, which is also shown on a different scale in Fig. 3. Repeated experiments with different sample sizes and heating rates have proven the reproducibility of this peak. It is likely that the low temperature peak for bulk V_2O_5 was ignored due to its low intensity in the earlier study by Bosch *et al.* (30).

Table 3 shows the average oxidation state of V after H_2 reduction up to 900°C. It was found that the average oxidation state of V after reduction was 3.6, indicating 72% reduction of V_2O_5 to V_2O_3. The degree of reduction was also verified using smaller sample sizes (10–15 mg) and lower heating rates (2–3°C/min). It should be noted that the level of impurities as well as the method of preparation of vanadia may play an important role in determining the reducibility of vanadia, which is probably the cause for the differences seen in the degree of reduction and reduction profiles observed by various researchers in kinetic experiments such as this. In addition, the partial pressure of H_2 used would also affect the degree of reduction. For example, Roozeboom *et al.* (6) have observed only a single reduction peak in their reduction studies, in contrast to the multiple reduction peaks seen here and by Bosch *et al.* (30).

V_2O_5/SiO_2 catalysts. Figure 4 shows the temperature programmed reduction profiles for the V_2O_5/SiO_2 cata-

TABLE 3

Summary of Temperature Programmed Reduction Results

Catalyst	Temperature of major TPR Peaks (°C)				Average oxidation state of V after H_2 Reduction to 900°C
	P_1	P_2	P_3	P_4	
1.6% V_2O_5/SiO_2	460	540	580	—	3.2
4.0% V_2O_5/SiO_2	460	545	580	—	3.2
8.2% V_2O_5/SiO_2	460	550	590	—	3.6
25% V_2O_5/SiO_2	460	580	630	—	3.6
V_2O_5 (bulk)	460	661	698	860	3.6
2.0% V_2O_5/Al_2O_3	440	525	—	—	3.9
4.8% V_2O_5/Al_2O_3	445	500	—	—	3.8
8.9% V_2O_5/Al_2O_3	440	485	640	—	3.8
25% V_2O_5/Al_2O_3	(440)	500	640	—	3.8

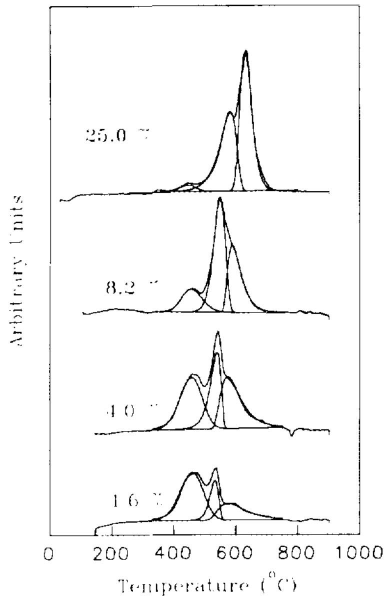

FIG. 4. TPR profiles for V_2O_5/SiO_2 catalysts.

lysts. The peak locations are summarized in Table 3. Three peaks could be identified from the profiles: a low temperature peak (P_1) at 460°C, an intermediate temperature peak (P_2) at 540–580°C, and a high temperature peak (P_3) at 580–630°C. Each of the original profiles was deconvoluted into three log-normal peaks using a curve-fitting software. The choice of number and shape of the peaks to be fitted to each of the original profiles was not entirely arbitrary. Various combinations of shape and number of peaks were tried to obtain the best fit, and it was found that such combination yielded the minimum error. It should be noted, however, that there is no physical significance to the exact shape of the deconvoluted signals. The area percents of the TPR peaks are summarized in Table 4.

The average oxidation state of V in the V_2O_5/SiO_2 catalysts after various TPR peaks was calculated from the amount of H_2 consumed and is listed in Table 4. It was found that this average oxidation state of vanadium on V_2O_5/SiO_2 after TPR to 900°C ranged from 3.2 to 3.6. After TPR, the reduced samples were reoxidized by temperature programmed oxidation (TPO) with a mixture of 2% O_2 in He, and the oxygen consumption was monitored using a TCD. The oxidation experiments for the supported V_2O_5/SiO_2 samples also exhibited multiple peaks (see Table 5). Any inference about the relationship of these peaks to the original structure of vanadia on the supports, however, has to be treated with caution since the programmed reduction treatment up to 900°C may have induced structural changes in the catalysts. The real purpose of TPO was to verify the stoichiometry observed for reduction. The amount of oxygen consumed was calculated from the TPO profile and is reported in Table 5. The average oxidation state of TPR-reduced V (estimated from the amount of O_2 consumed during TPO assuming that all the V was reoxidized back to V_2O_5) is also listed in Table 5 for comparison purposes. It can be seen that the average oxidation state of TPR-reduced V obtained from the oxygen consumption during TPO is between 3.4 and 3.8. This is in close agreement with the average oxidation state of V obtained during TPR (see Table 3) and suggests that there was, on average ca. 70% reduction of V_2O_5 to V_2O_3.

It should be noted that Roozeboom *et al.* (6) have reported complete reduction of silica-supported V_2O_5 to V_2O_3. On the other hand, Haber *et al.* (8) have shown by volumetric reduction studies of V_2O_5/SiO_2 catalysts at 500°C that one H_2 molecule is consumed per two vana-

TABLE 4

Analysis of TPR Peaks for Various Vanadia Catalysts

	Percent area of TPR peaks				Average oxidation state of V after various TPR peaks			
Catalyst	P_1	P_2	P_3	P_4	P_1	P_2	P_3	P_4
1.6% V_2O_5/SiO_2	60	18	22	—	3.9	3.6	3.2	—
4.0% V_2O_5/SiO_2	38	30	32	—	4.3	3.8	3.2	—
8.2% V_2O_5/SiO_2	17	49	34	—	4.8	4.0	3.6	—
25% V_2O_5/SiO_2	5	43	52	—	4.9	4.3	3.6	—
V_2O_5 (bulk)	3	33	22	45	4.95	4.5	4.2	3.6
2.0% V_2O_5/Al_2O_3	55	45	—	—	4.4	3.9	—	—
4.8% V_2O_5/Al_2O_3	37	63	—	—	4.5	3.8	—	—
8.9% V_2O_5/Al_2O_3	48	39	13	—	4.4	4.0	3.9	—
25% V_2O_5/Al_2O_3	(incl. in P_2)	51	49	—	—	4.4	3.9	—
Average oxidation state of V	V_2O_5 → +5	V_6O_{13} → +4.33	VO_2 → +4	V_2O_3 +3				

TABLE 5

Summary of Temperature Programmed Oxidation Results

Catalyst	Temperature of TPO peaks (°C)		Moles of O_2 consumed/mol of V_2O_5	Average oxidation state of V oxidized back to V_2O_5
	LT	HT		
1.6% V_2O_5/SiO_2	313	433	0.8 ± 0.1	3.4 ± 0.1
4.0% V_2O_5/SiO_2	314	451	0.7	3.6
8.2% V_2O_5/SiO_2	317	451	0.6	3.8
25.0% V_2O_5/SiO_2	323	450	0.6	3.8
V_2O_5 (bulk)	—	610	0.5	4.0
2.0% V_2O_5/Al_2O_3	—	560	0.5	4.0
4.8% V_2O_5/Al_2O_3	—	560	0.6	3.8
8.9% V_2O_5/Al_2O_3	—	560	0.6	3.8
25.0% V_2O_5/Al_2O_3	—	570	0.5	4.0

dium atoms (i.e., reduction to VO_2). Recently, Nag and Massoth (15) have found using a gravimetric method that H_2 reduction for 6 h at 500°C resulted in 70% reduction of silica-supported V_2O_5 to V_2O_3. Our results are thus in agreement with these observations of Nag and Massoth (15).

There have been a large number of reports in the literature of studies investigating the nature of vanadia on the supports using reduction experiments (6–9, 15). For V_2O_5/SiO_2 catalysts, Roozeboom *et al.* (6) have attributed a peak at 430°C to a surface phase and another at 430–510°C to crystalline V_2O_5. It is expected that at a lower temperature a surface-type (probably tetrahedral) species would be reduced, whereas at a higher temperature a more polymeric or bulk-like vanadia would be reduced. Thus, for our catalysts, such an assignment would mean that bulk-like vanadia existed even at low vanadium loadings. The NMR spectra confirm the presence of microcrystalline bulk vanadium species even at low loadings of vanadia on SiO_2.

It is expected that as the vanadia species becomes more bulk-like, i.e., the particle size increases with an increase in loading, the vanadia becomes more difficult to reduce due to bulk diffusion limitations resulting in a shift in the TPR peaks to higher temperatures. However, the low temperature peak (P_1) did not shift significantly to higher temperatures with an increase in the vanadia loading. This peak position was similar even for bulk V_2O_5. This suggests that this peak can be attributed to the reduction of a surface species. It is important to note that if the peaks were assigned to stages in reduction then the average oxidation state after every TPR peak (or the percent reduction) would be constant for all vanadia loadings. However, from Table 4 it can be seen that the average oxidation state after the first peak changes with vanadia loading indicating that this peak cannot be assigned as one of the stages in reduction of V_2O_5. The assignment of low temperature peak to a surface species was also reported by Bond and Tahir (3) for TiO_2-supported vanadia catalysts.

In contrast to peak P_1, peaks P_2 and P_3 were found to shift to higher temperatures as the loading was increased from 1.6 to 25 wt% V_2O_5 (see Table 3), suggesting increased particle size of microcrystalline vanadia with loading. This is consistent with the XRD pattern seen for 25% V_2O_5/SiO_2 wherein crystalline V_2O_5 having crystallites >4 nm were detected. In accordance with this trend, the reduction of bulk V_2O_5 occurred at much higher temperatures than silica-supported vanadia due to increased diffusional limitations in bulk V_2O_5 (see Figs. 3 and 4, and Table 3). For the V_2O_5/SiO_2 catalysts, the assignment of the individual peaks P_2 and P_3 either to reduction of a particular type of bulk-like species or to different stages of reduction of bulk-like vanadia is rather difficult. It is likely that each of these peaks P_2 and P_3 may in fact be a combination of reduction peaks corresponding to various reduction states of "bulk-like" vanadia on the silica support.

V_2O_5/Al_2O_3. Figure 5 shows the TPR profiles for the V_2O_5/Al_2O_3 catalysts. Overlapping multiple reduction peaks (P_1 and P_2; see Table 3) were seen for the 2% V_2O_5/Al_2O_3 catalyst. At higher loadings, however, these peaks appear to merge into a single peak at 500°C. As the loading increased to 8.9% vanadia, a new peak (P_3) appeared at 640°C. For the 25% V_2O_5/Al_2O_3 catalyst the peak at 640°C was very distinct. Deconvolution of these profiles into multiple peaks is also shown in Fig. 5. The temperatures corresponding to these peaks P_1, P_2, and P_3 are listed in Table 3. Attempts were made again to fit more than three peaks. However, multiple peaks were not force fitted to the observed profiles. For example, only two peaks could

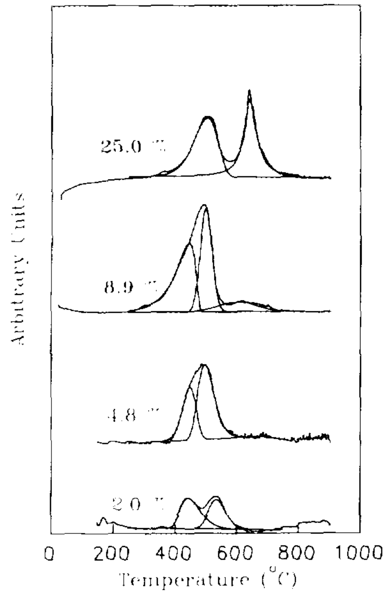

FIG. 5. TPR profiles for V_2O_5/Al_2O_3 catalysts.

be fitted for the 25% V_2O_5/Al_2O_3 catalyst instead of the expected three peaks. The area percent of the TPR peaks is summarized in Table 4.

The oxidation state of the vanadium after various TPR peaks was calculated from the amount of H_2 consumed and is consistent with the overall reduction of $V^{+5} \rightarrow V^{+4}$ corresponding to 0.5 H_2/V (see Table 4). TPO was performed for TPR-reduced catalysts in order to verify the reduction stoichiometry obtained from TPR and the results are summarized in Table 5. Haber *et al.* (8) found that 0.75 H_2/V was consumed during volumetric reduction of V_2O_5/Al_2O_3 catalysts at 500°C. They attributed this consumption to the removal of one oxygen from the dimeric V–O–V linkage and the formation of an -OH bond. This results in the formation of $V_2O_3(OH)$ rather than V_2O_3. If one hydrogen atom were assumed to remain during reduction in the form of -OH group, then the oxygen consumption would be 0.75 O/V corresponding to the oxidation of $V_2O_3(OH)$ to V_2O_5 as shown in the equation

$$V_2O_3\text{-}OH + 0.75\,O_2 \rightarrow V_2O_5 + 0.5\,H_2O.$$

Within the accuracy of our TPO experiments, only 0.5 O/V was consumed, which is consistent with our TPR results. Recently Nag and Massoth (15) have also reported a reduction stoichiometry of $V^{+5} \rightarrow V^{+4}$ for V_2O_5/Al_2O_3 catalysts by gravimetric reduction experiments.

The nature of the vanadium species on the V_2O_5/Al_2O_3 catalysts is different from that on the V_2O_5/SiO_2 catalysts. As described earlier, the NMR results indicated that only tetrahedrally coordinated species are present at low loadings and bulk-like V_2O_5 is formed only at higher loadings. Like V_2O_5/SiO_2, peak P_1 for the V_2O_5/Al_2O_3 catalysts did not change with an increase in the vanadia loading. However, unlike V_2O_5/SiO_2, peak P_2 for the V_2O_5/Al_2O_3 catalysts did not shift in position with an increase in the vanadia loading. This suggests that both the low temperature peaks, P_1 and P_2, in the TPR profiles should be assigned to surface species. The existence of monomeric and dimeric surface vanadia on alumina is well known (14, 19). It is likely that the vanadia species becomes more polymeric in nature with an increase in vanadia loading resulting in the merging of the low temperature peaks. However, from our TPR and NMR data it is not possible to attribute a particular surface structure to the first two low temperature TPR peaks. In any case, the vanadia seems to be more dispersed on the alumina than on the silica support.

The 8.9 and 25% V_2O_5/Al_2O_3 catalysts exhibited a distinct peak at 640°C corresponding to a bulk-like vanadia species. Such a bulk-like species was also detected by NMR. The presence of large (>4 nm) crystals of bulk vanadia on the 25% V_2O_5/Al_2O_3 catalyst was also evident from XRD. Back calculating the maximum vanadia loading at which no crystalline V_2O_5 would be present from the first two TPR peaks for the 25% V_2O_5/Al_2O_3 catalyst gives a value of ca. 13% V_2O_5/Al_2O_3. Assuming a V–V bond distance of 3.4 Å, a monolayer of vanadia on alumina would correspond to ca. 14% vanadia. This may mean that vanadia preferentially spreads on the alumina surface, up to monolayer coverage, before the formation of bulk-like vanadia as suggested by Wachs (31).

The extent of reduction for V_2O_5/SiO_2 was found to be higher than for V_2O_5/Al_2O_3. It is suggested that this is due to differences in the structure of the VO_x species and in the oxide–oxide interactions for V_2O_5 on SiO_2 and Al_2O_3. It would appear that the V^{+4} oxidation state is stabilized on Al_2O_3 probably due to removal of an oxygen from a V–O–V linkage in a dimeric surface vanadia species as has been previously hypothesized by Nag and Massoth (15) and Haber *et al.* (8). However, for V_2O_5/SiO_2 catalysts the presence of bulk-like vanadia results in reduction stoichiometries similar to reduction of bulk V_2O_5.

Estimation of Dispersion

Determination of the dispersion of an oxide on another oxide is not easy. In general, low temperature oxygen chemisorption after partial hydrogen reduction has been used to estimate the dispersion of supported oxides (22–24). However, erroneous dispersion values may result due to bulk reduction. Recently Oyama *et al.* (21) have pointed out that oxygen chemisorption at the same temperature as used for mild reduction is a better method for the estimation of dispersion. They have obtained a measure of the vanadia dispersion for V_2O_5/SiO_2 after reduction in pure H_2 at 370°C in a static system followed by oxygen chemisorption at the same temperature. They concluded from the reduction of bulk V_2O_5 at various temperatures that at 370°C only surface reduction occurs, whereas above 370°C bulk reduction of V_2O_5 takes place in the time frame of the procedure.

As discussed earlier, the NMR results for V_2O_5/SiO_2 catalysts have indicated the existence of both tetrahedral and microcrystalline V species even at low loadings. The area percent of the tetrahedral peak, defined as the ratio of the tetrahedral peak area to the total peak area is listed in Table 6. It can be seen that the area percent decreased with an increase in vanadia content. In the discussion above we have also shown that for the V_2O_5/SiO_2 catalysts the low temperature peak can be unambiguously assigned to the reduction of a surface species. Thus an estimation dispersion of vanadia for the V_2O_5/SiO_2 catalysts can be made from the area of the low temperature TPR peak, P_1, divided by the total area under the TPR profile. The dispersion values estimated by TPR are also listed in Table 6. It can be seen that the dispersion estimated by TPR follows the same trend as the area percent tetrahedral peak found by NMR.

Recently, we have reported on surface kinetics of the partial oxidation of methane over 1.6% V_2O_5/SiO_2 using steady-state isotopic transient kinetic analysis (SSITKA) (32). This technique enabled the determination of the total number of surface intermediates and the surface coverages without disturbing the steady state of the system. Based on the total number of surface intermediates at 600°C, the dispersion of vanadia was obtained assuming one intermediate adsorbed per V_2O_5 surface unit (see Table 6). It can be seen that this value is in agreement with the dispersion estimated using TPR and NMR. Obviously, the assumption of the stoichiometry is somewhat arbitrary; however, as an additional indication of dispersion, this result adds additional verification of our conclusions.

TABLE 6

Dispersion of Vanadia Estimated by Various Techniques

Catalyst	Fractional tetrahedral peak area (%)[a]	Dispersion estimated by TPR (%)	Dispersion estimated otherwise
V_2O_5	—	3	4.5[b]
1.6% V_2O_5/SiO_2	68	60	66[c]
4.0% V_2O_5/SiO_2	18	38	
8.2% V_2O_5/SiO_2	<5	17	
25% V_2O_5/SiO_2	<1	5	
2.0% V_2O_5/Al_2O_3	100	100	
4.8% V_2O_5/Al_2O_3	100	100	
8.9% V_2O_5/Al_2O_3	82	85	
25% V_2O_5/Al_2O_3	27	51	

[a] Fractional tetrahedral NMR peak area = area of tetrahedral peak/total area.

[b] Dispersion estimated by BET.

[c] Dispersion estimated by SSITKA; based on the number of surface carbon intermediates estimated from SSITKA during methane oxidation at 600°C assuming one surface intermediate per V_2O_5 molecule.

The average particle size from the X-ray line broadening for the 25% V_2O_5/SiO_2 was estimated to be 175 Å. The expected dispersion of vanadia calculated from this average particle size assuming a 0.201 nm^2 area/V_2O_5 unit was found to be 12 (±4) %. However, the dispersion estimated by TPR for the 25% V_2O_5/SiO_2 was 6% (see Table 6). It should be noted that the dispersion calculated by XRD is approximate since only particles larger than ca. 4 nm can detected by XRD. Also,the estimation of the line broadening is considerably affected by the amorphous SiO_2 background.

The dispersion of vanadia in bulk V_2O_5 based on a BET surface area of 30 m^2/g for bulk V_2O_5 and an area of 0.201 nm^2/surface V_2O_5 group was calculated to be 4.5% and is also listed in Table 6. This is agreement with the dispersion of vanadia in bulk V_2O_5 estimated by TPR.

The area percent of the tetrahedral peak calculated from NMR for the V_2O_5/Al_2O_3 catalysts is listed in Table 6. As in the case with V_2O_5/SiO_2 catalysts, the area percent decreased with an increase in vanadia loading. Likewise, for the V_2O_5/Al_2O_3 catalysts we have shown that the first two reduction peaks can be attributed to the reduction of surface vanadia. Thus for the V_2O_5/Al_2O_3 catalysts an estimation of the dispersion of vanadia can be made from the area for the first two TPR peaks divided by the total area under the TPR profile. The calculated dispersion values for the V_2O_5/Al_2O_3 catalysts are also listed in Table 6. This is in reasonable agreement with the area percent tetrahedral peak found by NMR.

Thus it can be concluded that TPR can also be used as a technique to estimate the dispersion of supported vanadia as well as, probably, other supported oxides. Such a technique for estimation of dispersion eliminates the ambiguity in the stoichiometry of oxygen chemisorption, i.e., the stoichiometry of O/V, to be used in calculation of dispersion. In the method of Oyama *et al.* (21) the temperature for reduction and then reoxidation has to be found out by trial and error. The estimation of dispersion by TPR overcomes this problem. However, this method also has some limitations. The assignment of peaks to the reduction of surface versus bulk species is not possible in all cases by TPR alone. Prior knowledge of such an assignment is necessary or at least useful. Obviously, investigation of a series of weight loadings of a supported oxide provides a means for identifying to a certain extent which peaks are due to reduction of subsurface species (those which move to higher temperatures due to an increase in particle size). Of course, if average particle size does not change over a wide range of loadings, this means of identification is not valid. The TPR technique also involves an assumption that both the surface and the bulk species are reduced to the same extent. Such an assumption is valid provided the heating rate is sufficiently slow and TPR is allowed to proceed to high enough temperatures to ensure similar reduction of the bulk and the surface species.

CONCLUSIONS

The nature of V_2O_5/SiO_2 and V_2O_5/Al_2O_3 catalysts was investigated using solid-state ^{51}V NMR, TPR, and TPO techniques. Solid-state ^{51}V NMR for V_2O_5/SiO_2 catalysts indicated the presence of microcrystalline vanadia species even at very low vanadia loadings. The TPR profiles for V_2O_5/SiO_2 indicated multiple peaks of which the low temperature peak can be assigned to the reduction of surface vanadia. This appeared to be the case also for the bulk V_2O_5. The NMR spectra of the V_2O_5/Al_2O_3 catalysts indicated the presence of tetrahedral vanadia species at low loadings. At high loadings a polymeric or bulk-like species also appeared. TPR results for V_2O_5/Al_2O_3 catalysts exhibited multiple peaks. In this case, the first two peaks can be assigned to reduction of surface vanadia. It was shown that an estimate of the dispersion of vanadia in V_2O_5/SiO_2 and V_2O_5/Al_2O_3 catalysts can be obtained using TPR. This correlates reasonably well with the amount of tetrahedral V found by NMR, the dispersion estimated by SSITKA, and the dispersion based on BET surface area. This method was found to overcome the limitation of over reduction in the low temperature O_2 chemisorption method which is commonly employed in the estimation for dispersion in supported oxide systems.

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