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Effect of Cesium Modification of Silica-Supported Vanadium Oxide Catalysts in Butane Oxidation

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The effect of Cs modification in the selective oxidation of butane at 520°C was studied over SiO_2-supported catalysts containing about 6 or 0.6 wt% vanadium atoms using a butane/oxygen/helium mixture of 4/8/88. Dehydrogenation products (unsaturated C_4's) and carbon oxides were the primary products. For the supported sample of high vanadium loading where a significant amount of vanadium existed as V_2O_5 crystallites under reaction conditions, Cs modification significantly increased the selectivity for dehydrogenation and decreased the extent of reduction of the vanadium oxide crystallites in the reaction mixture, but had only small effects on the activation energy or rate of reaction. Unsupported V_2O_5 catalysts modified by Cs at a Cs/V ratio of 0.023 also showed enhanced dehydrogenation selectivity, a lower degree of reduction at steady state, and a significantly different temperature-programmed reduction profile. Cs was found to be segregated on the surface of the crystallites. For the supported samples of low vanadium loading, Cs modification decreased the intensity of the Raman peak that was indicative of highly dispersed vanadia species and increased the activation energy of the reaction. These data were consistent with the picture that Cs modification enhanced the formation of vanadia clusters on the support.

INTRODUCTION

Selective oxidation of light alkanes to unsaturated hydrocarbons or oxygenated products is an attractive route to utilize these hydrocarbons. However, there are very few catalysts known that exhibit high selectivities. One of the most studied catalyst is vanadium oxide. In general, crystalline vanadium oxide is a nonselective catalyst. For example, in the oxidation of butane, the selectivity for dehydrogenation products is less than about 10% (1–3). The selectivity for partial oxidation products can be increased by suitable modification of the vanadium oxide. The most notable example is the modification by phosphorus (4). It has been shown that the formation of vanadyl pyrophosphate is accompanied by a significant increase in the selectivity for maleic anhydride in the oxidation of butane.

Modification of vanadium oxide with alkali and alkali earth metal ions has also been attempted. Modification with MgO resulted in the formation of vanadates such as Mg orthovanadate, Mg pyrovanadate, and Mg metavanadate (3, 5). Although these compounds are quite selective in the oxidative dehydrogenation of propane (6–9), Mg orthovanadate is much more selective in the dehydrogenation of butane than the others (10). Modification of vanadium oxide by transition metal oxides and lanthanide oxides has also been attempted, and the selectivity for dehydrogenation of butane can be correlated with the reducibility of the modifying cation (11, 12). The effect of alkali modification in the oxidation of ethane has also been studied (13).

There are relatively few detailed studies on the influence of modifiers on supported vanadium oxide in alkane oxidation. We have recently reported that the selectivity for oxidative dehydrogenation of butane on silica-supported vanadium oxide depends on the loading of vanadia: catalysts of low loadings in which the vanadia species exists as isolated vanadyl groups are much more selective than catalysts of high loadings in which the vanadia exists primarily as crystalline vanadium oxide (14). In view of the large difference in the selectivities over the two species of vanadia, it becomes interesting to investigate if they would be affected in different ways by modification with alkali metal ions. This paper reports the results of such an investigation in which cesium was used as the modifying ion.

EXPERIMENTAL

Catalyst Preparation

Davisil silica, grade 62 (250 m^2/g), was used for the supported samples. It was washed in acid to remove sodium and calcium impurities as described previously (14). The washed silica were found to contain <10 ppm Na, approximately 200 ppm Ca, and less than 100 ppm each of Ti, Al, Fe, and Zr. The vanadia-containing samples were prepared by impregnation by incipient wetness using

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a solution prepared from ammonium metavanadate (Johnson Matthey, 99.99%) and oxalic acid. Cesium modified samples were prepared by adding appropriate amounts of cesium nitrate (Aldrich, 99.99%) to the impregnation solution. After impregnation, the samples were dried in air at 100°C and then calcined at 550°C for 6 h.

Unsupported samples were prepared by dissolving appropriate amounts of ammonium metavanadate and cesium nitrate in deionized water at about 65°C. The solutions were evaporated to dryness while stirring until a wet paste was formed. It was then dried overnight at 100°C and calcined at 550°C for 6 h.

Reaction Studies

Reactions were conducted in a fused silica microreactor in a flow system. The apparatus and the conditions were the same as those described previously (14). Unless specified otherwise, a feed of $He/O_2/C_4H_{10}$ = 88/8/4 was used. The catalyst was packed between plugs of fused silica wool. Fused silica chips were added to dilute the higher loading samples to a bed height of approximately 1 cm. The remaining reactor volume was filled with the chips to quench gas-phase reactions. Without a catalyst, the butane conversion at 520°C was negligible. The silica support used also had negligible activity under the conditions used. The temperature of the catalyst was monitored with a thermocouple placed in the bed, and the product analysis was performed with gas chromatography using a combination of columns as described before (14).

Catalyst Characterization

The concentrations of impurities and vanadium in the samples were analyzed by inductive plasma coupling spectroscopy, whereas the concentrations of cesium were by atomic absorption. Samples were labeled according to their compositions. The silica-supported vanadia samples were labeled αV in which α denoted the wt% of V. The Cs-modified supported samples were labeled αV/Csβ, in which β was the % Cs/V atomic ratio. The unsupported samples were labeled Csβ/V_2O_5. The sample used in this study are listed in Table 1. Supported samples containing 5.7 to 6.5 wt% V will be generally referred to as high loading, whereas those containing 0.58% V, as low loading.

Laser Raman spectra were collected using the 514.5-nm line of a Coherent INOVA 70-2 Ar ion laser and a beam intensity of 25 mW. About 0.2 g of powder sample was pressed into a wafer for analysis. For the fresh high loading samples, the wafer was pretreated by heating *in vacuo* at 520°C for 1 h and then in 1 atm O_2 for 0.5 h. The sample was cooled in O_2, and the spectra were collected at room temperature. For the low loading samples, the pretreatment was conducted at 600°C.

TABLE 1

Catalyst Compositions and Surface Areas

Sample	Composition (wt%) V	Composition (wt%) Cs	Cs/V[a]	Surface area (m^2/g)	H_2/V[b] in TPR
6.4V	6.4	0	0	150	0.80
5.7V	5.7	0	0	150	0.85
0.58V	0.58	0	0	230	0.55
5.7V/Cs2.3	5.7	0.34	0.023	160	0.8
0.58V/Cs2.3	0.58	0.034	0.023	240	—
0.58V/Cs23	0.58	0.34	0.23	260	0.7
V_2O_5	100	0	0	3.0	0.95
Cs1/V_2O_5	99.00	1.00	0.01	0.9	0.95
Cs2.3/V_2O_5	96.67	3.36	0.023	0.5	0.95

[a] Atomic ratio.

[b] Moles of H_2 consumed per mole of V ion in TPR experiments.

For the Raman spectrum of 5.7V/Cs2.3 that had been used for reaction, the catalyst (about 0.3 g) was first exposed to a reaction feed stream at a flow rate of 100 ml/min at 520°C for 5 h. The conversions of butane and oxygen were approximately 44 and 85%, respectively. Afterwards, the sample was cooled to room temperature in the reaction mixture. After exposure to air, it was treated *in vacuo* at 520°C for 1 h and then 1 atm of O_2 for 0.5 h, and cooled in O_2 to room temperature for spectra collection.

X-ray diffraction patterns were collected using a Rigaku diffractometer with Cu K_α radiation. The patterns of samples that had been used in reaction were collected in air after the samples were cooled to room temperature in the reaction mixture.

XPS analyses were preformed using a VG Scientific spectrometer using an Al K_α monochromatic X-ray source. The samples were supported on an indium foil. The surface compositions were calculated by dividing the peak areas by the sensitivity factors provided by the manufacturer, which were 1.2 for V $2p_{3/2}$ and 1.0 for Cs $3d_{5/2}$.

Temperature programmed reduction was conducted in a quartz tubular reactor using 10% H_2 in argon at a flow rate of about 60 ml/min and a heating rate of 5°C/min. The samples were pretreated in flowing O_2 (60 ml/min) at 500°C and cooled in O_2. The consumption of H_2 was measured using a thermal conductivity detector after removing the water formed with a molecular sieve trap.

RESULTS

Reaction Study

On all of the catalysts tested, the dominant products were dehydrogenation products (1-butene, *trans*-butene, *cis*-2-butene, and butadiene) and combustion products

TABLE 2

Representative Product Distributions in the Oxidation of Butane at 525°C

Sample	g cat.	Total flow[b]	Butane conv. (%)	Selectivities (%)[a]								
				1-But	*trans*-2-But	*cis*-2-But	BD	C_2/C_3	Oxy	CO	CO_2	TDS
6.4V	0.025	200	4.0	21	11	9	0	8	0	28	23	41
	0.15	100	20.0	6	3	3	0	1	0	56	31	12
5.7V	0.15	100	24.0	3	2	2	1	1	2	57	32	8
5.7V/Cs2.3	0.02	100	5.0	25	15	14	10	0	4	19	13	64
	0.1	100	22.0	14	9	7	5	2	5	33	24	35
0.58V	0.2	100	6.0	26	15	15	9	6	7	12	10	65
	0.5	100	20.0	22	10	10	8	9	10	15	16	50
0.58V/Cs2.3	0.2	100	7.8	21	14	12	8	6	11	15	13	55
0.58V/Cs23	0.324	100	5.1	29	19	17	9	3	4	9	10	74
V_2O_5	0.67	200	17.0	0	0	0	0	0	0	70	30	0
$Cs1/V_2O_5$	2.5	50	11.0	7	0	0	0	0	0	58	34	7
$Cs2.3/V_2O_5$	2.5	50	14.0	12	2	2	1	3	3	42	30	17

Note. Feed composition: $C_4H_{10}/O_2/He$ = 4/8/88.

[a] 1-but, 1-butene; *trans*-2-but, *trans*-2-butene; *cis*-2-but, *cis*-2-butene; BD, 1,3-butadiene; C_2/C_3, C_2 and C_3 hydrocarbons; oxy, oxygenates (including acetaldehyde, propionaldehyde, acetone, and maleic anhydride); TDS, total dehydrogenation selectivity (equal to sum of BD, 1-but, *trans*-2-but, and *cis*-2-but).

[b] Total flow rate, ml/min.

(CO and CO_2). Small amounts of other products were also observed, which included C_2 and C_3 hydrocarbons, acetone, acetaldehyde, propionaldehyde, and maleic anhydride. Table 2 lists the representative product distributions of the catalysts. In all experiments, there were substantial amounts of unused oxygen in the exit gas. The products observed for 6.4V, 5.7V, and 0.58V were similar to those reported previously (14). Figure 1 shows the selectivity to dehydrogenation products as a function of butane conversion for the complete set of experiments for the silica-supported samples. For clarity, the data taken from Ref. (14) for the catalysts without cesium are represented by the dotted and dashed lines. As reported before (14), the selectivity of the higher loading samples without cesium was lower and decreased more rapidly with increasing conversion. However, addition of a small amount of Cs (Cs/V = 0.023) to the high loading catalyst (5.8V/Cs2.3) made it much more selective for dehydrogenation. The selectivity approached those of the low loading samples. On the other hand, Cs modification of the low loading catalysts did not result in noticeable improvement in selectivity, whether the amount of Cs added corresponded to a Cs/V ratio of 0.023 or 0.23. Table 2 shows that an enhanced selectivity for dehydrogenation due to the addition of cesium was also observed with the unsupported samples.

Table 3 shows the kinetic parameters for the rate of consumption of butane. The activation energies were determined over the temperature range 500–540°C and using data at 5% butane conversion. Within experimental uncertainties, Cs did not change the activation energy on the high loading samples or the reaction rate per vanadium ion. Its effect on the activity of the low loading samples depended on the V/Cs ratio: little effect on the sample of a small Cs/V ratio of 0.023, but decreased the activity of the sample of a large Cs/V ratio of 0.23. The activation energy for the latter sample was significantly increased.

The reaction order in butane was determined using low conversion data at 520°C in the range 4–16% butane while keeping the oxygen concentration at 8%, and the order in oxygen in the range 8–32% while keeping the butane concentration at 4%. The results are shown in Table 3.

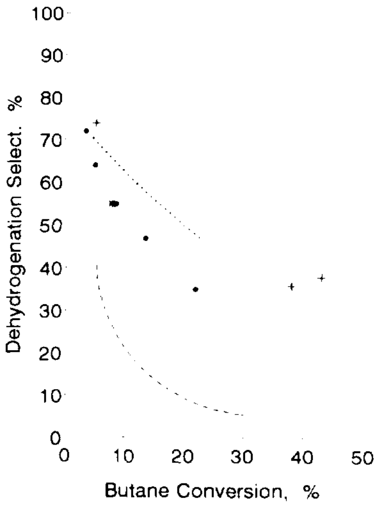

FIG. 1. Total dehydrogenation selectivity as a function of butane conversion at 520°C: (···) low loading without Cs; (---) high loading without Cs; (●) 5.7V/Cs2.3; (+) 0.58V/Cs2.3; (*) 0.58V/Cs23.

TABLE 3

Reaction Order and Activation Energy in Butane Oxidation

Sample	Rate[a,b] (mol/min-mol V)	E_{act}[a,c] (kJ/mol)	Reaction order[b]	
			Butane	Oxygen
6.4V	13 ± 3	164 ± 15	0.9 ± 0.1	0.3 ± 0.2
5.7V/Cs2.3	11 ± 3	155 ± 15	0.9 ± 0.1	0.5 ± 0.2
0.58V	16 ± 2	110 ± 15	1.0 ± 0.1	0.5 ± 0.1
0.58V/Cs2.3	19 ± 2	—	—	—
0.58V/Cs23	9 ± 1	174 ± 15	1.1 ± 0.1	0.6 ± 0.1

[a] Feed: $He/O_2/C_4$ = 88/8/4, determined for a butane conversion of 5%.

[b] For consumption of butane at 520°C.

[c] For consumption of butane over 500–540°C.

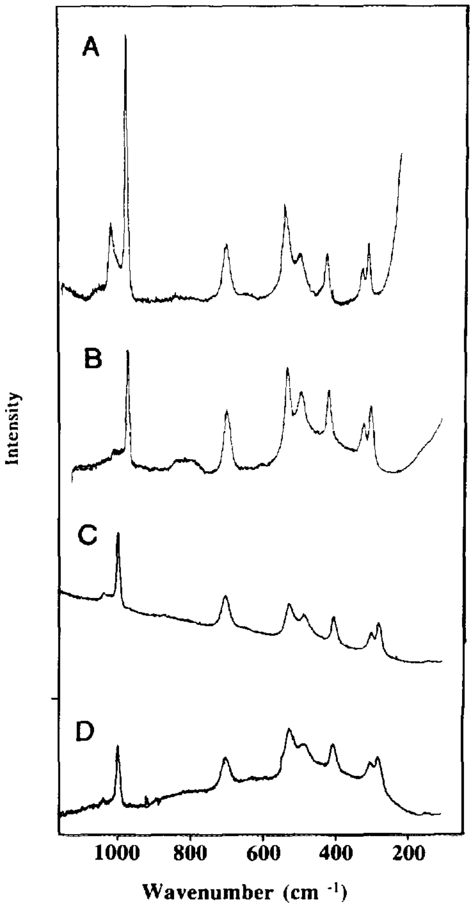

FIG. 2. Raman spectra of high loading V/SiO_2 catalysts: (A) 6.4V, (B) 6.4V used and reoxidized, (C) 5.7V/Cs2.3, and (D) 5.7V/Cs2.3 used and reoxidized.

Within experimental uncertainties, all samples, high or low loadings of vanadium and with or without Cs, showed first order in butane. Likewise, the order in oxygen was 0.5 for all samples. However, there might be a trend that the orders were lower for the high loading samples than the low loading samples. The product distributions in these experiments were unchanged, except for the low loading sample without Cs (sample 0.58V) when the butane concentration was changed. For this sample at about 7% butane conversion, the total dehydrogenation selectivity decreased from 66 to 41% as the butane concentration in the feed increased from 4 to 16%, while the oxygenate products increased from 8 to 30%.

Characterization

The colors of some of the samples changed after reaction. Before reaction, samples 6.4V and 5.7V/Cs2.3 were deep orange. After reaction at butane conversions higher than 5%, and 6.4V sample was very dark green. The original color could be restored after treatment in a flow of He and O_2 at 520°C. However, the color of the 5.7V/Cs2.3 sample remained unchanged after reaction at lower conversions, and turned dark green only as the conversion increased. The low loading samples, with or without cesium modification, were light yellow before reaction and white immediately after reaction, but returned to their original colors on exposure to air. The unsupported samples containing Cs retained their original orange-brown color after reaction, but the unsupported V_2O_5 sample turned black after reaction from the original light orange color.

The structure of the catalysts were characterized by laser Raman spectroscopy and X-ray diffraction. The Raman spectra of the high loading samples are shown in Fig. 2. As reported previously, the 6.4V catalyst showed the presence of the 1040-cm^{-1} peak indicative of dispersed vanadia, and the peaks at 998, 703, 526, 480, 404, 304, and 284 cm^{-1} indicative of V_2O_5 crystallites. The spectrum of 5.7V/Cs2.3 showed only the spectrum of V_2O_5 crystallites. This was consistent with the idea that Cs neutralized any acid sites on silica and that on basic surfaces, polyvanadates were deposited, which on calcination resulted in V_2O_5 crystallites (15). Cs modification did not cause any shift of these peaks, which could be understood with the fact that the Raman peaks of V_2O_5 were primarily due to vibrations in the bulk of the crystallite and the amount of Cs added was small (Cs/V = 0.023). The spectrum of 6.4V after being used and then treated in O_2 showed larger peaks of V_2O_5 relative to the dispersed species, but that of 5.7V/Cs2.3 did not show significant changes. For the unsupported V_2O_5 sample, no change in the Raman spectra was observed on addition of the small amounts of Cs.

The Raman spectra of the low loading samples are shown in Fig. 3. As previously reported, the 0.58V sample showed only a peak at 1040 cm^{-1} due to the dispersed vanadia species commonly assigned to $(Si\text{–}O\text{–})_3\ V{=}O$ (16, 17) and features of the support. Addition of Cs did not result in new observable peaks. Instead, the 1040-

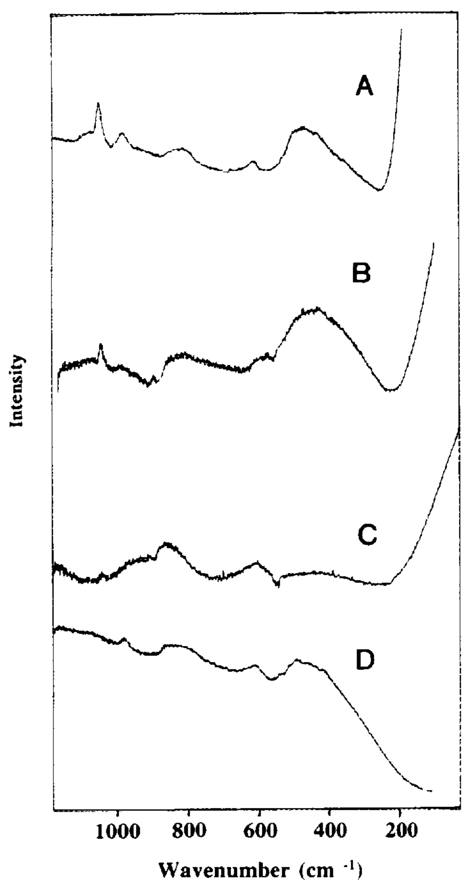

FIG. 3. Raman spectra of low loading V/SiO_2 samples: (A) 0.58V, (B) 0.58V/Cs2.3, (C) 0.58V/Cs23, and (D) silica.

cm^{-1} peak decreased in intensity. The decrease was larger for 0.58V/Cs23 than for 0.58V/Cs2.3.

The X-ray diffraction patterns of unsupported catalysts modified with Cs are shown in Fig. 4. In addition to peaks of V_2O_5, small peaks due to CsV_3O_8 and $Cs_xV_2O_5$ were also detected. The patterns of samples after reaction were essentially the same. No peaks of vanadia of lower valencies could be detected. This was consistent with the absence of color change of these samples. Thus, at steady state, these samples were mostly in the fully oxidized state.

The X-ray diffraction patterns of 6.4V and 5.7V/Cs2.3 are shown in Fig. 5. Before reaction, only peaks of V_2O_5 could be detected. If the samples were examined after reaction immediately upon removal from the reactor, the 6.4V sample showed peaks of V_2O_4, whereas the 5.7V/Cs2.3 sample showed peaks of both $VO_2 \cdot H_2O$ and V_2O_5. This implied that the Cs-modified sample maintained a higher average oxidation state at steady state than the unmodified sample, consistent with the lesser degree of color change mentioned earlier. Treatment of these samples in O_2 removed the V_2O_4 peaks.

Cs 3d signals could be detected by XPS on the unsupported samples. From the intensities of the Cs 3*d* and V 2*p* peaks, the ratio of surface Cs to V were 0.5 and 0.55 for samples $Cs1/V_2O_5$ and $Cs2.3/V_2O_5$, respectively. No useful XPS signals could be obtained for the supported samples.

Figure 6 shows the TPR profiles of various samples. The profile of V_2O_5 (curve 6A) showed two broad peaks that consisted of a number of overlapping peaks. This behavior is similar to that observed by Roozeboom *et al.* (18). Addition of 2.3% Cs changed the profile significantly (curve 6B). Reduction of $Cs2.3/V_2O_5$ proceeded in three well separated regions, each accounted for about one-third of the total H_2 consumption. Curves 6C, 6D, and 6E are for the high loading supported samples. They showed a prominent peak which was at about 535°C for samples without Cs, and about 545°C for the one with Cs. They also showed a shoulder on the high temperature side that was more prominent for the Cs-containing sample and the higher loading 6.4V sample than the 5.7V sample. The low loading sample 0.58V also showed only one reduction peak at about 490°C, which was shifted to a higher temperature of about 505°C after Cs modification (curves 6F and 6G).

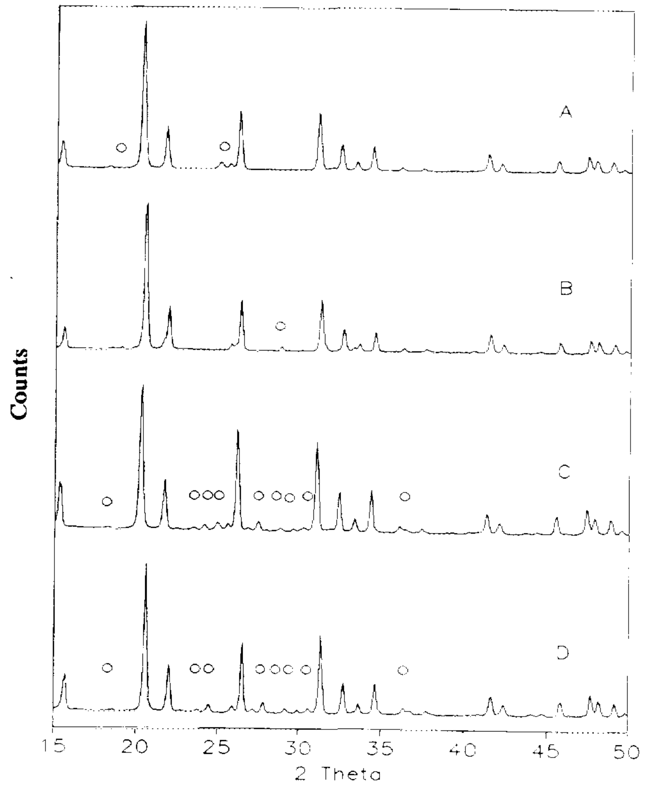

FIG. 4. X-ray diffraction pattern of unsupported samples: (A) $Cs1/V_2O_5$, (B) $Cs1/V_2O_5$ used, (C) $Cs2.3/V_2O_5$, and (D) $Cs2.31/V_2O_5$ used; (O) CsV_3O_8 or $Cs_xV_2O_5$.

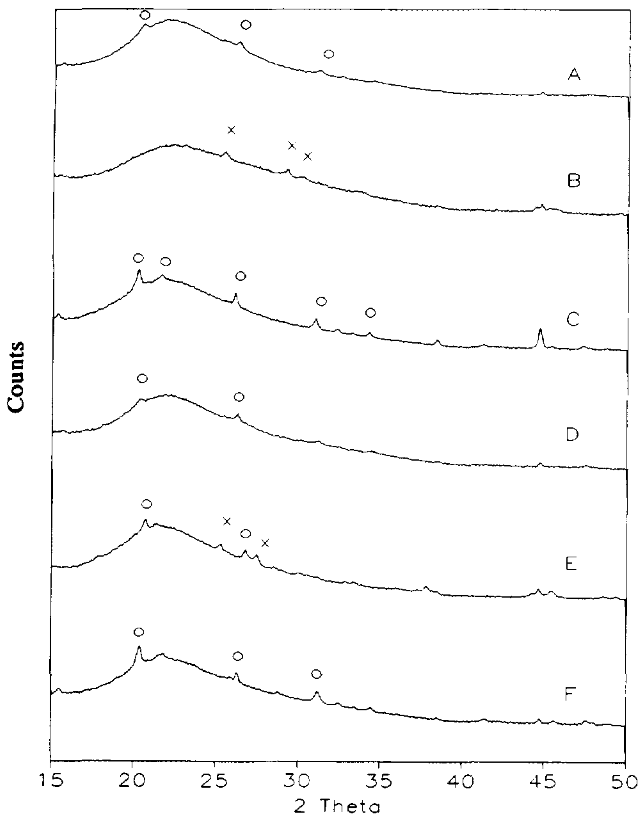

FIG. 5. X-ray diffraction pattern of high loading V/SiO$_2$ samples: (A) 6.4V, (B) 6.4V used, (C) 6.4V used and reoxidized, (D) 5.7V/Cs2.3, (E) 5.7V/Cs2.3 used, and (F) 5.7V/Cs2.3 used and reoxidized; (O) V$_2$O$_5$ and (×) VO$_2$.

From the amount of H$_2$ consumed in TPR (Table 1), the extent of reduction of the V ions could be estimated. Within experimental error, the V ions in the unsupported samples were reduced from V^{5+} to V^{3+}. Reduction of the V ions in the supported samples was less severe and the addition of Cs to these samples did not significantly affect the extent of reduction.

DISCUSSION

The results of this investigation show that the effect of Cs depends on the nature of the vanadium oxide species. It is different for the unsupported samples and the supported samples of different loadings. Thus, these samples will be discussed separately.

Unsupported Samples

On the unsupported samples, Cs modification results in lower catalytic activity but higher dehydrogenation selectivity, and lower extent of reduction of vanadium oxide crystallites under reaction conditions. It has a very significant effect on the reduction behavior of the sample by H$_2$, and it results in the formation of detectable Cs vanadate compounds (CsV$_3$O$_8$ and Cs$_x$V$_2$O$_5$). Since the amounts of Cs in the samples corresponded to a Cs/V atomic ratio of 2.3% or lower, the amounts of such compounds are small. It is interesting that such small amounts of Cs cause such noticeable effect on the chemical properties of the samples. It appears that the significant effect of Cs is due to its segregation to the surface of the V$_2$O$_{5-x}$ crystallites as detected by XPS and its effect on the mobility of lattice oxygen in the crystallites. As shown by the changes in the TPR profiles (curves 6A and 6B), the onset temperature is higher on the Cs-containing sample, which suggests the Cs hinders the ability of the sample to activate hydrogen. Furthermore, the reduction of the Cs-containing sample from V^{5+} to V^{3+} proceeds in three well defined stages, which, from the stoichiometry of reduction, corresponds to the following conversions: $V_2O_5 \rightarrow V_6O_{13} \rightarrow V_7O_{13} \rightarrow V_2O_3$. The sharp reduction peaks corresponding to each transformation suggests that once the transformation is started, it converts one compound to another rapidly. It also suggests that the Cs-modified vanadium oxide crystallites prefer to be in one form or another of these intermediate oxides instead of an assembly of domains of different oxides. Thus, Cs increases the activation barrier for the initiation of transformation of these intermediate oxides, which implies an increase in the barrier for the lattice to undergo small extents of

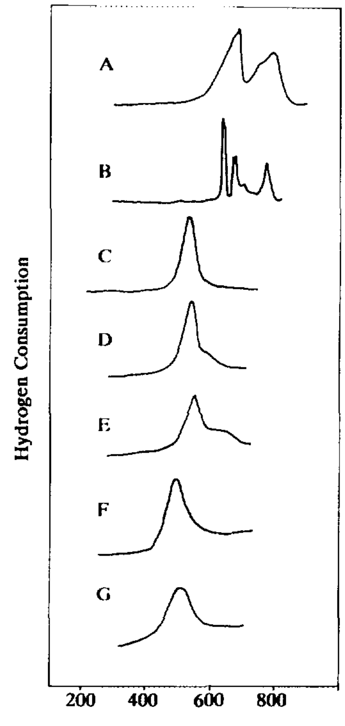

FIG. 6. Temperature programmed reduction profiles of (A) V$_2$O$_5$, (B) Cs2.3/V$_2$O$_5$, (C) 5.7V, (D) 6.4V, (E) 5.7V/Cs2.3, (F) 0.58V, and (G) 0.58V/Cs23; 10% H$_2$ in argon; 5°C/min.

reduction. In contrast, for the sample without Cs, the broad peaks in its TPR profile suggest that reduction of the vanadium oxide crystallites proceeds gradually and readily. That is, the lattice can undergo redox readily. Increased resistance to reduction by hydrocarbons due to alkali metal modification has also been reported by Martin *et al.* (19).

It has been proposed that modification of a vanadia catalyst resulting in an increase in resistance to reduction would lead to higher selectivity in butane oxidation (3, 11, 12, 19). Indeed, a correlation has been observed between the selectivity for dehydrogenation and the heat of reoxidation of alumina-supported vanadia catalyst (20). Thus, the increase in selectivity for dehydrogenation on Cs modified unsupported samples can be due to the increased difficulty of the sample to undergo redox cycles. On the other hand, the kinetic data observed in this study show a half-order dependence in the reaction rate on oxygen partial pressure on all catalysts with or without Cs. Coupled with the discussion above on changes in reducibility, this suggests that Cs affects both the rates of reduction and reoxidation of the catalyst to the same extent, resulting in little change in the overall kinetics. This is different from Mg modification of vanadia. In that case, Mg orthovanadate is formed and the rate of oxidation of butane shows a zeroth-order dependence in oxygen pressure (22).

Supported Higher Loading Samples: 6.4V, 5.7V, and 5.7V/Cs2.3

On sample 5.7V, modification by a small amount of Cs (Cs/V = 0.023) significantly increases the dehydrogenation selectivity, increases the portion of sample that reduces at the higher temperature shoulder in the TPR profile, and greatly suppresses the formation of isolated vanadyl species such that only crystalline V_2O_5 are detected by Raman spectroscopy. On the other hand, the activity per vanadium ion or the activation energy are not affected.

The size of the high-temperature shoulder in the TPR profile relative to the peak at 535–545°C can be correlated with the relative intensities of the Raman peaks for V_2O_5 crystallites versus highly dispersed vanadyl species in these samples. Thus, this shoulder is likely due to reduction of small V_2O_5 crystallites, equivalent to the higher temperature portion of the TPR profile of unsupported V_2O_5 but shifted to a lower temperature due to the much smaller crystallite size of V_2O_5 in these samples. If this is correct, it implies that on the Cs-modified sample, there is still a significant amount of dispersed vanadyl species present that are not detected by Raman spectroscopy because their Raman scattering cross section is much lower than that of V_2O_5 crystallites.

In addition to causing agglomeration of the vanadia species to V_2O_5 crystallites due to neutralization of the small amount of acid sites on silica, Cs modification also makes the V_2O_5 crystallites less reducible under reaction conditions, as evident by the lack of color change of the sample after reaction. Thus, some of the Cs ions are also associated with the V_2O_5 crystallites and affect their reducibility and thus their catalytic properties in a similar manner as in the unsupported samples. However, the reason why the change in the selectivity on the supported V_2O_5 crystallites is much larger than on the unsupported ones is not fully understood.

Supported Lower Loading Samples: 0.58V, 0.58V/Cs2.3, and 0.58V/Cs23

The effects of Cs on the low loading samples are more obvious when the Cs/V ratio is 23 than 2.3. On the sample with a Cs/V ratio of 23, the major catalytic effects of Cs addition are an increase in activation energy to a value similar to that observed on the high loading sample and a decrease in activity per vanadium. The TPR peak is shifted to a higher temperature. The change in the catalytic behavior can be explained assuming that Cs causes agglomeration of the vanadia. Because of the low loading of vanadia, such agglomeration only results in polymeric clusters of VO_x which are not easily observable by Raman spectroscopy. However, their chemical properties resemble those of V_2O_5. Thus the activation energy becomes similar to Cs-modified V_2O_5 catalysts. The activity decreases because fewer vanadium is at the surface due to agglomeration. Since the selectivity for dehydrogenation over Cs-modified V_2O_5 catalysts with small V_2O_5 crystallites (such as in 5.7V/Cs2.3) is also high, the observable changes in the selectivity is small.

It is also possible that on these samples, the effect is not due to agglomeration of vanadia species but due to Cs modifying the properties of the dispersed vanadia species ($(\mathrm{Si{-}O{-}})_3\ \mathrm{V{=}O}$). Such species is highly selective for dehydrogenation of butane because it contains only a small number of oxygen ions (14). If Cs coordinates to it, it can affect the properties of the V–O bonds. It has been shown by infrared spectroscopy that alkali ions lowers the vibrational frequency of the V=O bond (23). This may be due to direct interaction of Cs^+ with the V=O bond, or to changes in the net charge on the ions induced by Cs^+ through the bridging oxygen, as suggested by CNDO calculation of a VO_4 cluster (24). Lowering of the vibrational frequency of this bond is also observed on K^+-modified low loading V_2O_5/TiO_2, which are less active in methanol oxidation than the unmodified sample (25). These changes should affect the interaction of the species with butane, resulting in a change in the activation energy. However, such coordination of $(\mathrm{Si{-}O{-}})_3\ \mathrm{V{=}O}$ by Cs would not change the number of oxygen ions in the species, and thus the selectivity for dehydrogenation is unchanged.

Unfortunately, there is insufficient evidence to distinguish these two possibilities. The only spectroscopic information from Raman scattering about this sample, which shows that the intensity of the V=O stretch of the dispersed species is decreased by Cs modification, can be interpreted by either possibility. Although the TPR profiles of these catalysts do not show a high temperature shoulder and suggests that crystallites of V_2O_5 are absent, there is no information on the TPR profile of polyvanadate clusters on silica support.

In spite of absence of direct experimental evidence, the lack of changes of color of the low loading samples or their Raman spectra after reaction suggests that the vanadia species in these samples remain primarily in the fully oxidized state under reaction conditions. If so, the half-order dependence of the rate of reaction on oxygen for these samples cannot be due to a slow rate of reoxidation of reduced vanadia species. It could be that for the highly dispersed vanadia species, dissociatively adsorbed oxygen plays an important role in the activation of butane. However, more experimental evidence is needed to better understand this system.

CONCLUSION

The effect of Cs on the oxidation of butane on vanadium oxide catalysts depended on whether the vanadium oxide was supported or not, and on the loading of vanadium oxide on the support. Modification by Cs of unsupported V_2O_5 and high loading silica-supported samples containing primarily V_2O_5 crystallites resulted in increases in dehydrogenation selectivity in the oxidation of butane and resistance to reduction of the crystallites under reaction conditions, but little change in the activation energy or the order of reaction in butane and oxygen. Cs was found to segregate on the surface of V_2O_5 crystallites. These were interpreted with the model that Cs form a vanadate layer on the surface where the VO_x units become isolated. Such isolated VO_x units were more selective for dehydrogenation.

On the other hand, on the low loading silica-supported samples where vanadia was present as highly dispersed species, modification by Cs resulted in a decrease in the intensity of the V=O vibrational band and an increase in the activation energy. There were no obvious changes in the dehydrogenation selectivity or the extent of reduction of the sample under reaction conditions. This was consistent with the picture that Cs caused agglomeration of vanadia species to form aggregates that had catalytic properties similar to Cs-modified V_2O_5. However, it was also possible that Cs affected the vanadium–oxygen bonds in the dispersed vanadia species and thus the reaction. The data were insufficient to distinguish the two possibilities.

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