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Conversion of Methyl Radicals to Methanol and Formaldehyde over Vanadium Oxide Catalysts

Sergei Pak, C. Edwin Smith, Michael P. Rosynek, and Jack H. Lunsford*

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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Methyl radicals, formed by the thermal decomposition of azomethane, react with V_2O_5 to form methoxide ions. Infrared results confirm the presence of methoxide ions, and ESR spectra demonstrate that the reaction involves the reduction of V^{5+} to V^{4+}. The methoxide ions may either decompose to formaldehyde or react with water or surface protons to form methanol. In temperature-programmed reaction experiments, both methanol and formaldehyde reached a maximum concentration in the gas phase at 200–250°C over V_2O_5, but over V_2O_5/SiO_2, the methanol and formaldehyde maxima were shifted to ca. 300 and 400°C, respectively. The production of CH_3OH at the lower temperature over V_2O_5/SiO_2 suggests that methoxide ions may react with water or surface protons to form methanol more quickly than they decompose to formaldehyde. Nevertheless, in continuous flow experiments at 300 and 500°C, formaldehyde was the principal oxygenated product because of the rapid oxidation of CH_3OH at this temperature, and, in the case of pure V_2O_5, the direct conversion of methoxide ions to formaldehyde appears to compete favorably with their reaction with water.

INTRODUCTION

There is an increasing body of evidence which suggests that $CH_3\cdot$ radicals are involved in the catalytic partial oxidation of CH_4. In the oxidative coupling of CH_4, the radicals emanate into the gas phase where they couple to form C_2H_6. Catalysts that are effective for this reaction are capable of generating $CH_3\cdot$ radicals, but they do not react further with the radicals (1). By contrast, other catalysts, such as MoO_3/SiO_2, react much more extensively with methyl radicals, and, under favorable conditions, CH_3OH and/or HCHO are the gas phase products (2). The latter reactions are believed to proceed through methoxide intermediates.

In order to study these secondary reactions of $CH_3\cdot$ radicals with metal oxides, independent of the more demanding radical generation step, we have chosen to produce the species by the thermal decomposition of azomethane, $CH_3N{=}NCH_3$, which decomposes cleanly to form $CH_3\cdot$ radicals and N_2. Sticking coefficients for $CH_3\cdot$ radicals reacting with several metal oxides have been measured (3), and the overall conversions of the radicals to HCHO and CH_3OH have been reported over MoO_3 and MoO_3/SiO_2 catalysts (2). Moreover, it was shown that H_2O reacted with a surface intermediate, presumably methoxide ions, to form CH_3OH at temperatures <300°C.

In the present study, the reactions of methyl radicals with V_2O_5 and V_2O_5/SiO_2 are compared with those previously reported for the molybdena catalysts. The V_2O_5 catalysts are of interest because they are considerably more active for the conversion of CH_4 to HCHO than are the MoO_3 catalysts (4). Moreover, with V_2O_5 we have been able to obtain infrared evidence for the formation of methoxide ions as a result of the reaction of $CH_3\cdot$ radicals with the catalyst. Emphasis has been placed on the products that are formed, rather than on the kinetics of $CH_3\cdot$ radical reactions.

EXPERIMENTAL

The vanadium oxide (99.9%, Alfa) used in these experiments had a surface area of 7.3 m^2/g. The V_2O_5/SiO_2 catalysts were prepared by the addition of Davison Grade 57 silica gel (330 m^2/g, 20–42 mesh size) to an aqueous solution of ammonium metavanadate (99.99%, Aldrich). The slurry was evaporated to dryness, and the catalysts were heated in air for 8 h at 550°C to decompose the ammonium vanadate. Supported catalysts were prepared with 0.6, 5.1, and 10.3 wt% V_2O_5. These supported catalysts had total surface areas of 340, 290, and 240 m^2/g, respectively. In addition, a pure MoO_3 catalyst was prepared by heating molybdenum(VI) oxalate (Climax molybdenum) in air from 115 to 300°C at a rate of 2°C/min. The sample was kept in air 1 h at 300°C. This process resulted in the formation of MoO_3 having a surface area of 17 m^2/g. The catalysts were treated *in situ* in 1.2 Torr of flowing O_2 for 1 h at 500°C.

The apparatus and the experimental procedures for the flow and the temperature-programmed surface reaction (TPSR) studies were essentially the same as those reported previously (2). Briefly, azomethane diluted in argon (1 : 10) was decomposed at 950°C in a 2-mm i.d. fused-quartz tube. The initial products of the decomposition reaction were mainly $CH_3\cdot$ radicals and N_2. It has been shown, using a matrix isolation electron spin resonance (MIESR) system,

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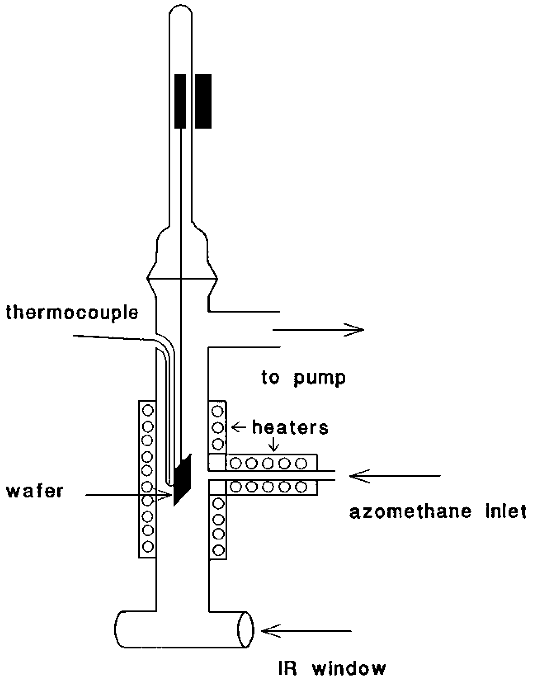

FIG. 1. Infrared cell.

that the flux of $CH_3\cdot$ radicals exiting the quartz tube was in good agreement with the amount of azomethane that was decomposed (5). The catalyst (100–200 mg) was placed about 15 mm above the point where the $CH_3\cdot$ radicals entered an 8-mm i.d. reactor. The radicals flowed into the catalyst bed at a rate of ca. $3 \times 10^{15}\ s^{-1}$, and the residence time over the catalyst was 0.001 s. When desired, O_2 could be added before the other gases passed through the catalyst bed. The pressure upstream from the catalyst bed was typically 35 mTorr. The stable products were analyzed using an INFICON Quadrex 200 quadrupole mass spectrometer. Selectivities were determined by the equation

$$S = \frac{x_i P_i}{\sum_i x_i P_i}, \qquad [1]$$

where P_i is the pressure of the respective product ($P_{C_2H_6}$, P_{HCHO}, P_{CH_3OH}, P_{CH_4}, and P_{CO_2}) and x_i is the number of carbon atoms in the molecule. When operating in the temperature-programmed surface reaction (TPSR) mode, 150 mg of oxidized catalyst was allowed to react with $CH_3\cdot$ radicals for 30 min at 150°C. After this period, the sample was cooled *in vacuo* to 50°C, and the temperature was then increased at a rate of 23°C/min.

The infrared experiments were carried out using a Perkin Elmer Model 1750 FT-IR spectrometer. The $CH_3\cdot$ radicals reacted with the catalyst, which was in the form of a semitransparent wafer. The infrared cell is depicted in Fig. 1. During reaction, the catalyst wafer was located about 15 mm from the source of the $CH_3\cdot$ radicals. The total pressure in the reactor was ca. 35 mTorr; the initial azomethane/argon ratio was 0.1. The temperatures of the catalyst and of the azomethane decomposition could be varied independently by using separate furnaces. The same cell was used to study the reaction of methanol with the catalyst. After reaction the wafer was lowered to a position such that it was in the infrared beam. The infrared windows were of KBr.

Electron spin resonance (ESR) spectra of the V_2O_5 catalyst were obtained using a Varian E6 spectrometer and a cell similar to that described previously (3). Spectra were recorded with the sample at 77 K.

RESULTS AND DISCUSSION

Flow experiments. Previous studies (2) of the reaction of $CH_3\cdot$ radicals using this system have shown that in an empty reactor at room temperature the primary hydrocarbon product (~95%) was C_2H_6, with a small amount (~4%) of CH_4 being formed. It can be calculated that ca. 66% of the $CH_3\cdot$ radicals couple *before* they reach the catalyst bed. The CH_4 may result from the reaction of $CH_3\cdot$ radicals with hydrogen on the metal walls of the vacuum system (6). We did not attempt to detect H_2; however, in related azomethane decomposition experiments, Smudde *et al.* (7) demonstrated that the molar ratio of $H_2/CH_3\cdot$ was only 0.14. When 150 mg of silica was introduced and the reactor was heated to 300°C, the results were similar to those obtained in the empty reactor, but at 500°C somewhat more CH_4 was formed, and in the presence of O_2 ($O_2/CH_3\cdot = 3.2$) the selectivities to HCHO and CO_2 were 4.2% and 3.2% respectively. At 500°C, the homogeneous reaction

$$CH_3\cdot + C_2H_6 \rightarrow CH_4 + C_2H_5\cdot \qquad [2]$$

may become significant.

When 150 mg of V_2O_5 was present in the reactor, the results reported in Table 1 were obtained. It is apparent that those $CH_3\cdot$ radicals which had not coupled before reaching the catalyst bed were extensively converted to HCHO. The

TABLE 1

Product Distribution in the Reaction of Methyl Radicals over V_2O_5[a]

		Selectivities, %					
T, °C	$O_2/CH_3\cdot$	C_2H_6	HCHO	CH_3OH	CH_4	CO_2	ΔMB, %
300	0	63.4	25.0	7.0	3.1	1.5	23
	0.04	61.4	26.5	8.8	2.0	1.4	18
	2.26	51.5	36.5	8.8	0.8	2.4	18
500	0	54.9	35.6	4.2	2.7	2.6	21
	0.1	62.6	31.2	3.1	1.1	1.9	16
	1.4	51.8	43.9	0	0.7	3.5	17

[a] 155 mg of catalyst was used.

TABLE 2

Product Distribution in the Reaction of Methyl Radicals over MoO_3[a]

T,°C	$O_2/CH_3\cdot$	Selectivities,% C_2H_6	HCHO	CH_3OH	CH_4	CO_2	ΔMB,%
300	0	45.5	9.1	41.1	4.2	0	−5
	0.15	55.2	11.3	28.8	4.5	0.2	7
	2.25	46.0	16.5	16.5	3.2	0.2	2
500	0	50.2	34.5	8.0	4.8	2.5	7
	0.15	57.7	28.6	6.5	5.0	2.1	17
	0.8	55.6	30.0	7.6	4.7	2.1	20

[a] 208 mg of catalyst was used.

formation of formaldehyde is favored by higher temperatures and by the presence of O_2, but even in the absence of O_2, at short times on stream (see below) formaldehyde was the principal oxygenate. The major difference between the results given here for V_2O_5 and those reported previously for MoO_3 is the ratio of HCHO to CH_3OH in the products. With the V_2O_5 catalyst, considerably more HCHO was detected; however, it is difficult to compare specific activities because the surface areas of the two catalysts were so different (7.3 m^2/g for the V_2O_5 and 0.3 m^2/g for the previously used MoO_3). Moreover, the reactions were not carried out under differential conditions; i.e., a large fraction of the $CH_3\cdot$ radicals that did not couple reacted with the catalyst.

In order to have a better comparison of the reaction of $CH_3\cdot$ radicals over the two oxides, results also were obtained for the MoO_3 catalyst that had a surface area of 17 m^2/g, which was more comparable to the surface area of the V_2O_5 catalyst. The data of Table 2 show that a considerable amount of CH_3OH was produced over the higher surface area MoO_3, particularly at 300°C. A comparison of the results of Tables 1 and 2 suggests that either V_2O_5 is more active than MoO_3 in the partial oxidation of CH_3OH to HCHO, or, with V_2O_5, a direct pathway for the conversion of surface intermediates, e.g. methoxide ions, to HCHO is favored. With both V_2O_5 and MoO_3, the selectivity for CO_2 was small.

Experiments carried out with CH_3OH as the reagent confirm that V_2O_5 is indeed more active for its conversion to HCHO than is the high surface area MoO_3. When passing a mixture of CH_3OH in Ar, corresponding to 30% of $CH_3\cdot$ radicals in the flow experiments, the conversions were 80% at 300°C and 96% at 500°C over the V_2O_5 catalyst and 16% at 300°C and 81% at 500°C over the MoO_3 catalyst. The principal product over both catalysts was formaldehyde. Thus, if CH_3OH were produced from $CH_3\cdot$ radicals over the V_2O_5, it could be extensively converted to HCHO at 300°C.

The column labeled ΔMB in the tables refers to a deficit in the carbon mass balance, which is defined as the difference between the expected amount of carbon, based on the amount of azomethane decomposed, and the amount of carbon detected by the product analysis. Carbon monoxide was not included as a product because of the interference from the N_2 peak at 28 amu. A positive value of ΔMB, therefore, could reflect the presence of CO as a product, which is consistent with the larger values of ΔMB observed over MoO_3 at higher temperatures and larger $O_2/CH_3\cdot$ ratios. Errors in determining the amount of azomethane decomposed and the amounts of the products also may contribute significantly to ΔMB. For example, a 10% error in the amounts of $CH_3N{=}NCH_3$ reacted and the products could result in a value of 20% for ΔMB. An error of this magnitude in quantitative analysis by mass spectrometry is certainly reasonable (8).

Analogous experiments were carried out over the V_2O_5/SiO_2 catalysts, in the absence and presence of O_2, and the results are given in Tables 3 and 4, respectively. For reference purposes, the results obtained over the MoO_3/SiO_2 catalyst, in the absence of O_2, are also included in Table 3. The selectivity to C_2H_6 is indicative of the reactivity of $CH_3\cdot$ radicals with the catalyst; i.e., lower selectivity to C_2H_6 results from greater reactivity of $CH_3\cdot$ radicals with the catalyst surface. One can conclude that even at a loading of 0.6% V_2O_5/SiO_2, the methyl radicals reacted at 300°C to form oxygenates, which is in contrast to the results on 6.6% MoO_3/SiO_2, for which 91.7% of the methyl radicals coupled to form C_2H_6. The differences in reactivities of the 5.1% V_2O_5/SiO_2 and 6.6% MoO_3/SiO_2 catalysts with $CH_3\cdot$ radicals and the product selectivities are less apparent at 500°C. At loadings of 0.6% and 5.1% V_2O_5/SiO_2, the principal oxygenate detected at 300°C was CH_3OH, rather than HCHO. This product distribution is different from that found with pure V_2O_5 and with the 10.3% V_2O_5/SiO_2 catalyst, for which HCHO was the main oxygenated product. Apparently, at

TABLE 3

Product Distribution in the Reaction of Methyl Radicals over MoO_3/SiO_2 and V_2O_5/SiO_2 Catalysts[a]

T,°C	Catalyst/ loading	Selectivities,% C_2H_6	HCHO	CH_3OH	CH_4	CO_2	ΔMB,%
300	MoO_3/SiO_2 6.6%	91.7	5.0	0	3.0	0.2	9
	V_2O_5/SiO_2						
	0.6%	75.9	4.2	11.3	8.1	0.5	27
	5.1%	81.5	4.0	8.3	9.3	0.5	30
	10.3%	76.1	12.7	6.3	4.4	0.6	17
500	MoO_3/SiO_2 6.6%	74.2	19.5	0.9	4.7	0.6	9
	V_2O_5/SiO_2						
	0.6%	77.3	8.1	1.8	10.9	0.8	17
	5.1%	77.5	15.9	0	4.9	1.6	12
	10.3%	76.3	19.1	0	3.3	1.2	18

[a] No O_2 was added to the $CH_3\cdot/Ar$ flow.

TABLE 4

Product Distribution in the Reaction of Methyl Radicals over 10.3% V_2O_5/SiO_2[a]

T,°C	O_2/CH_3	Selectivities,%					ΔMB,%
		C_2H_6	HCHO	CH_3OH	CH_4	CO_2	
200	0	82.6	5.4	5.6	6.1	0.3	45
	0.07	83.1	7.3	6.1	3.1	0.4	44
	0.45	73.7	14.6	8.9	2.1	0.6	37
	6.6	61.6	22.6	10.9	1.9	3.0	38
300	0	76.1	12.7	6.3	4.4	0.6	17
	0.08	72.4	16.1	8.5	2.0	0.9	35
	0.24	65.5	23.4	8.5	1.6	1.0	29
	4.68	55.4	29.3	11.4	1.1	2.7	28
500	0	76.3	19.1	0	3.3	1.2	18
	0.04	62.8	28.9	3.7	2.1	2.5	24
	0.95	56.0	36.3	5.2	0.6	1.9	24
	2.57	53.0	43.3	0	0.1	3.6	23

[a] 104 mg of catalyst was used.

the smaller loadings the V_2O_5/SiO_2 catalysts are less effective in the conversion of CH_3OH to HCHO.

In contrast to the results that were obtained under steady state conditions when O_2 was present, the catalysts were slowly reduced in the absence of O_2. The results reported in Table 3 were obtained after the catalysts had been exposed to the stream containing $CH_3\cdot$ radicals for approximately 3 min. Longer times on stream at 500°C resulted in a decrease in the HCHO selectivity and an increase in the CH_4 selectivity. For example, over the 10.3% V_2O_5/SiO_2 catalyst the HCHO selectivity decreased from 19 to 11% during 18 min on stream, while the CH_4 selectivity increased from 3 to 11% during the same period. Curiously, the C_2H_6 selectivity remained nearly constant. The decrease in HCHO selectivity is understandable since surface oxygen is involved in its formation. The increase in CH_4 formation may be attributed to reaction 1, but this also would result in a decrease in C_2H_6. As the surface becomes less reactive, more $CH_3\cdot$ radicals are free to couple and form C_2H_6. The net effect is that the C_2H_6 selectivity is essentially constant.

The effects of O_2 and temperature are further evident from the results of Table 4. Generally, as the $O_2/CH_3\cdot$ ratio and the temperature were increased, the $HCHO/CH_3OH$ ratio increased and the conversion of $CH_3\cdot$ radicals to oxygenates increased. But even at 200°C and in the absence of O_2, the $CH_3\cdot$ radicals reacted to products other than C_2H_6. The surface intermediates formed from these reactions may be rather stable at 200°C, and they may not yield gas phase products. The net loss of carbon to these surface intermediates would give rise to the unusually large values of ΔMB.

In most respects, the results obtained for the 10.3% V_2O_5/SiO_2 and the pure V_2O_5 samples were very similar, although x-ray diffraction results showed no evidence that a V_2O_5 crystalline phase existed on the SiO_2 at this loading level. There is extensive Raman and NMR data which confirm that crystalline V_2O_5 is present on SiO_2 at a loading of ca. 10%, although there is disagreement as to whether the crystalline form exists at $\leq$3% V_2O_5 (9–11). The fact that crystalline material can be detected at the 10% level by Raman spectroscopy, but not by x-ray diffraction, suggests that the crystallites are small (<20 Å). In addition to the crystalline phase, vanadium is bound directly to SiO_2 as monomeric vanadyl species over a wide range of concentrations up to 10 wt%. The ratio of the monomeric to the crystalline form decreases with increasing loading (9).

TPSR experiments. TPSR results for the reaction of $CH_3\cdot$ radicals with V_2O_5 are shown in Fig. 2. In the absence of added water, the principal product was HCHO, which is consistent with the results obtained in the flow experiments. Since N_2 from the decomposition of azomethane was not present, it was possible in the TPSR experiments to determine the formation of CO. Only small amounts of CO and CO_2 were formed; therefore, the combined selectivities to HCHO and CH_3OH were large. The maximum in the HCHO peak was at 260°C. These results suggest that if $CH_3\cdot$ radicals could somehow be generated from CH_4 at low temperatures, it would be possible to convert them to CH_3OH and HCHO with a high selectivity.

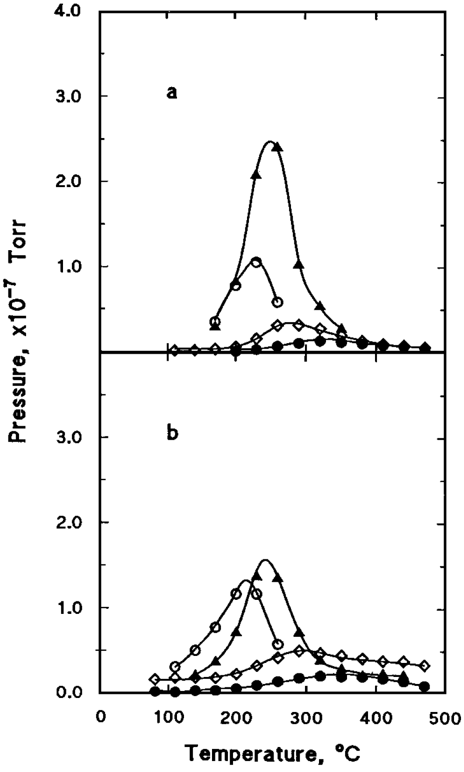

FIG. 2. TPSR results after reaction of 3 mTorr $CH_3\cdot$ radicals with V_2O_5 for 30 min at 150°C, followed by cooling to 50°C; (a) sample heated *in vacuo*, (b) sample heated in 9 mTorr H_2O: ○, CH_3OH; ▲, HCHO; ◇, CO; ●, CO_2.

Since the $CH_3\cdot$ radicals form methoxide ions on the V_2O_5 (see below), it was of interest to determine whether these ions would react with water to form CH_3OH. Upon heating the methylated sample in the presence of 9 mTorr H_2O, the results shown in Fig. 2b were obtained. It is evident that the CH_3OH peak area increased relative to the HCHO peak area; however, the effect of adding water was not as dramatic as that previously reported for the MoO_3/SiO_2 system (2). The extensive overlap of the CH_3OH and HCHO peaks suggests that methoxide ions may simultaneously convert to these two products or that the CH_3OH was rapidly converted to HCHO.

Analogous experiments were carried out on the V_2O_5/SiO_2 catalysts, and the results are shown in Fig. 3. Without added water, the TPSR maxima for CH_3OH and HCHO were shifted to higher temperatures. The shift in temperature may result, in part, from readsorption of CH_3OH and HCHO on the SiO_2. The maximum in the HCHO peak was at 405°C, and the CH_3OH peak was at 300°C. The separation between the maxima suggests that CH_3OH formed first, and that it was subsequently converted to HCHO only at somewhat higher temperatures. There may also exist a direct pathway for the conversion of methoxide ions to HCHO over the V_2O_5/SiO_2 catalyst.

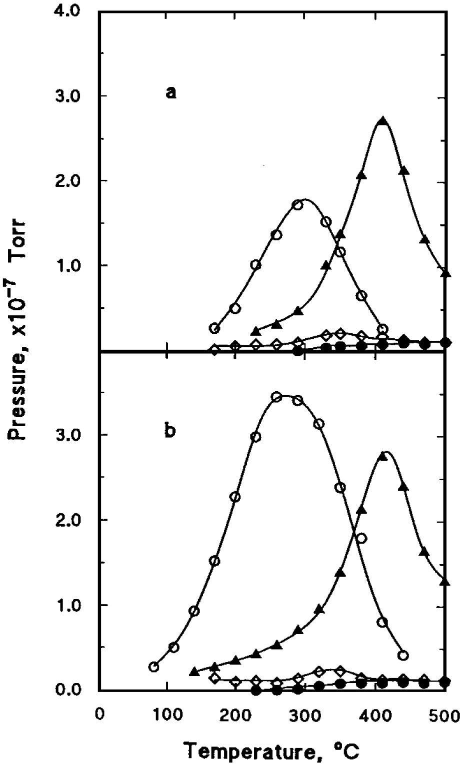

FIG. 3. TPSR results after reaction of 3 mTorr $CH_3\cdot$ radicals with 5.1% V_2O_5/SiO_2 for 30 min at 150°C followed by cooling to 50°C; (a) sample heated *in vacuo*, (b) sample heated in 7 mTorr H_2O: ○, CH_3OH; ▲, HCHO; ◇, CO; ●, CO_2.

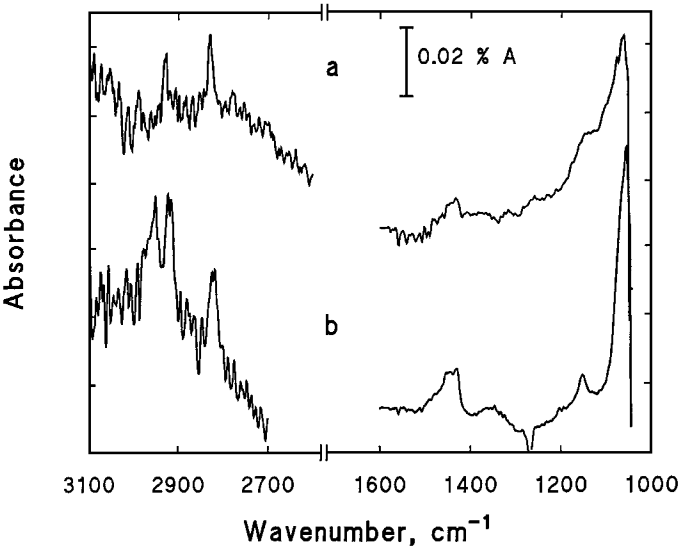

FIG. 4. IR spectra of V_2O_5 catalyst after exposure of the sample to (a) 3 mTorr $CH_3\cdot$ radicals at 30°C and (b) 90 mTorr CH_3OH at 25°C.

The addition of water during the TPSR caused a substantial increase in the amount of CH_3OH relative to the amount of HCHO. The increase in the amount of CH_3OH is most apparent at the lower temperatures. At ca. 200°C and in the presence of H_2O, the ratio of $CH_3OH/HCHO$ was ca. 5. The shape of the CH_3OH peaks for the V_2O_5 and the V_2O_5/SiO_2 catalysts is similar, which is expected if the same surface intermediate gives rise to the product.

Infrared evidence for methoxide ions. Methoxide ions are believed to be intermediates in the partial oxidation of CH_3OH to HCHO, over both MoO_3 and V_2O_5 catalysts (12, 13). The most direct evidence for the involvement of methoxide ions comes from the infrared spectra of the oxide catalysts following reaction with CH_3OH. Similarly, we have proposed that $CH_3\cdot$ radicals react with metal oxides having reducible cations according to reaction 3 (3):

$$CH_3\cdot + M^{n+1}O^{2-} \rightarrow M^{n+}(OCH_3)^-. \qquad [3]$$

Following the reaction of $CH_3\cdot$ radicals with CeO_2 at 25°C, there was infrared evidence for methoxide ions on the surface (3).

The infrared spectrum following the reaction of $CH_3\cdot$ radicals with V_2O_5 at 30°C is shown in spectrum a of Fig. 4. For reference purposes the spectrum obtained by reacting 90 mTorr CH_3OH with V_2O_5 at 25°C is given also (spectrum b). The signal-to-noise ratio is rather poor because of the low surface area of the V_2O_5 and the small amount of the reagent that was added to the oxide. Nevertheless, distinct bands are evident, which may be used to identify the species present on the surface. The bands observed in this study are compared in Table 5 with those reported by other investigators for CH_3OH adsorbed on V_2O_5 (13) and SiO_2 (14) and for CH_3OH in the liquid phase (15).

TABLE 5

Infrared Bands of Methoxide Ions and Methanol

CH_3/V_2O_5 (this study) (cm^{-1})	CH_3OH/V_2O_5 (Busca, 13) (cm^{-1})	CH_3OH/V_2O_5 (this study) (cm^{-1})	CH_3OH/SiO_2 (Clark *et al.*, 14) (cm^{-1})	$CH_3OH(\ell)$ (15) (cm^{-1})	Assignment
			3003	3000	CH_3OH, ν_{CH}
		2950	2956	2950	CH_3OH, ν_{CH}
2930	2930				CH_3O^-, ν_{CH}
		2920	2921		CH_3OH, ν_{CH}
			2848	2845	CH_3OH, ν_{CH}
2830	2830				CH_3O^-, ν_{CH}
		2820			CH_3O^-, ν_{CH}
		1480	1470	1475	CH_3OH, δ_{CH}
		1450	1451	1454	CH_3OH, δ_{CH}
1445	1448				CH_3O^-, δ_{CH}
1430	1435	1430			CH_3O^-, δ_{CH}
	1380	1350	1366		CH_3OH, δ_{OH}
1150	1155	1150		1115	CH_3OH, CH_3O^-, r_{CH_3}
				1160	
1065	1070	1060		1040	CH_3OH, CH_3O^-, ν_{CO}

The bands in spectrum a at 2930, 2830, 1445, 1430, 1150, and 1065 cm^{-1} are in good agreement with those that Busca (13) assigned to methoxide ions. Although the C–O stretching band at 1065 cm^{-1} is present as a shoulder on a strong band due to a lattice mode of V_2O_5, difference spectra provide convincing evidence for its existence. This band is significant because it confirms that $CH_3\cdot$ radicals reacted with the surface to form a new species (i.e., methoxide ions) that contain a C–O bond. The methoxide ions on V_2O_5 may either decompose to yield HCHO or they may react with water to produce CH_3OH. By analogy, we have previously shown that $MoO(OCH_3)_4$ reacts with water to form CH_3OH (16).

Spectrum b indicates that, following adsorption of methanol on V_2O_5, the molecularly adsorbed species was mainly present on the surface. This conclusion is based on the good agreement between the bands at 2950, 2920, 1480, and 1350 cm^{-1} and similar bands for physically adsorbed CH_3OH on SiO_2 and for liquid CH_3OH as reported in Table 5. The band at 3000 cm^{-1} is relatively weak in the references cited. Bands at 2820 and 1430 cm^{-1} in spectrum b may indicate that methoxide ions also were present; however, the expected band at 2930 cm^{-1} is not apparent. This band might be masked by the band at 2920 cm^{-1}. Alternatively, the expected band at 2848 cm^{-1} for CH_3OH may be shifted to 2820 cm^{-1} when the molecule is adsorbed on V_2O_5. It is not clear why methoxide ions were the dominant species in the work of Busca (13) when CH_3OH was added to V_2O_5; whereas, molecularly adsorbed CH_3OH was the dominant species in this study. His sample was a fumed V_2O_5 having a surface area of 18 m^2/g.

ESR evidence for the reduction of V^{5+} by $CH_3\cdot$ radicals. In support of reaction 3, it was previously demonstrated that $CH_3\cdot$ radicals reacted with 2 wt% MoO_3/SiO_2 at 25°C and reduced Mo^{6+} to Mo^{5+} (3). The Mo^{5+} ions were detected by their characteristic ESR spectrum. Analogous results were obtained using the pure V_2O_5 sample, and the spectra are shown in Fig. 5. It is very difficult to obtain completely stoichiometric V_2O_5, as is evident from spectrum a, which is attributed to the presence of a small amount of paramagnetic V^{4+}. This sample had been pretreated in 200 mTorr of O_2 at 350°C and cooled in O_2 to 25°C. A sample that had first been oxidized and then exposed to 20 mTorr C_2H_6

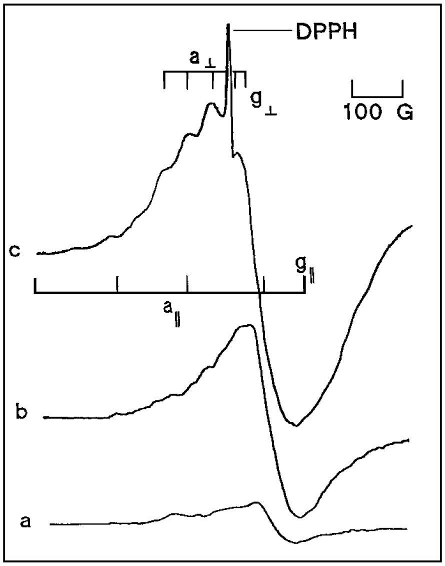

FIG. 5. ESR spectra of V_2O_5 catalyst after exposure of sample to (a) 200 mTorr O_2 at 350°C for 30 min, followed by cooling in O_2 to 25°C, (b) 20 mTorr C_2H_6 at 25°C for 30 min, and (c) 1 mTorr $CH_3\cdot$ radicals at 25°C for 30 min.

was even further reduced, as indicated by the greater amplitude of spectrum b. The 20 mTorr is more than an order of magnitude greater than the pressure of C_2H_6 that might be expected during the exposure of the oxidized V_2O_5 sample to $CH_3\cdot$ radicals. Most significantly, the amplitude of the ESR spectrum was the largest when the oxidized sample was exposed to 1 mTorr of $CH_3\cdot$ radicals for 30 min at 25°C (spectrum c).

The vanadium in V_2O_5 is present in a highly distorted octahedron, with one oxygen ion being close to and one being very far from the metal ion (17). Thus, if V^{4+} were formed by the reduction of V^{5+}, without removal of an oxygen atom, one would expect an anisotropic ESR signal, with sets of eight hyperfine lines. Normally, V_2O_5 exhibits a single broad line at $g = 1.98$ (18, 19); however, a careful study by Boesman and Gillis (20) of Mo-doped V_2O_5 single crystals revealed well resolved vanadium hyperfine structure that was attributed to V^{4+} at lattice sites in the crystal. The spectrum of Mo-doped V_2O_5 was characterized by $g_x = 1.905$, $g_y = 1.981$, and $g_z = 1.977$ with $a_x = 158.5$ G, $a_y = 52.8$ G, and $a_z = 50.8$ G. It should be noted that the principal components of the g and a tensors indicate nearly axial symmetry. In the polycrystalline spectrum of Fig. 5c, the most evident hyperfine lines are attributed to the $a_\perp$ components, and the four low-field lines are indicated above the spectrum. The values of $g_\perp = 1.98$ and $a_\perp = 49$ G are in good agreement with the parameters reported by Boesman and Gillis. There is less certainty about the parallel components, although values of $g_\parallel = 1.93$ and $a_\parallel = 151$ G appear to be consistent with spectrum c and the results obtained with the Mo-doped V_2O_5 single crystal. No inflection was detected at the position of the lowest field hyperfine lines, but this may reflect the fact that the outer components of the polycrystalline spectrum are lower in amplitude. The value of $g_\parallel = 1.93$ is significantly greater than the value of $g_x = 1.905$, and this difference suggests that the crystal field gradient at the V^{4+} center in the polycrystalline V_2O_5 is larger than the gradient in the single crystal, perhaps because of surface effects.

CONCLUSIONS

Both $CH_3\cdot$ radicals and CH_3OH react with V_2O_5 to form surface methoxide ions. These ions may decompose to yield HCHO or they may react with protons, derived from H_2O or hydroxyl groups on silica, to form CH_3OH according to the following scheme:

$$\mathrm{CH_3OH} \underset{+\mathrm{H^+}}{\overset{-\mathrm{H^+}}{\rightleftarrows}} \mathrm{CH_3O_s^-} \rightarrow \mathrm{HCHO} + \mathrm{OH_s^-}. \qquad [4]$$

The methoxide ions also serve as intermediates in the partial oxidation of CH_3OH to HCHO. Under flow conditions, $CH_3\cdot$ radicals react over supported and unsupported V_2O_5 at temperatures greater than 300°C to form mainly formaldehyde as the oxygenated product. Since water was present in the system and methanol is readily converted to formaldehyde over these catalysts, it is difficult to determine whether CH_3OH was an initial product. The larger $CH_3OH/HCHO$ ratios observed for the V_2O_5/SiO_2 catalysts, particularly at smaller loadings, may result from the reaction of surface protons (i.e., hydroxyl groups) with methoxide ions that are stabilized at the V–O–Si interfaces. TPSR results over V_2O_5/SiO_2 suggest that CH_3OH was formed at a lower temperature than HCHO and therefore is an intermediate product, but over pure V_2O_5 and the 10.3% V_2O_5/SiO_2 catalyst, HCHO may be formed directly from methoxide ions. In any event, CH_3OH and HCHO have a common intermediate; namely, methoxide ions. Most significantly, it is possible to convert $CH_3\cdot$ radicals to HCHO under relatively mild conditions, and, except for the coupling reaction, the selectivity to HCHO is large.

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