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In Situ Raman Spectroscopy during the Partial Oxidation of Methane to Formaldehyde over Supported Vanadium Oxide Catalysts

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Vanadia was found to be well dispersed and present as a two-dimensional overlayer when supported on SiO_2, TiO_2, SnO_2, 3 wt% TiO_2/SiO_2, 3 wt% MoO_3/SiO_2, and 3 wt% SnO_2/SiO_2. Partial oxidation of methane by oxygen formed formaldehyde most selectively over the V_2O_5/SiO_2 catalyst, but catalytic performance was strongly dependent on vanadia coverage and autocatalytic behavior was observed. At very low conversions, the formaldehyde activity increased linearly with vanadia coverage, indicating that isolated V^{5+} species were responsible for the active sites. No significant structural changes were revealed by *in situ* Raman spectroscopy for the V_2O_5/SiO_2 catalyst, which indicated that the fully oxidized surface sites were related to the high formaldehyde selectivity. This selectivity exhibited a maximum at 1 wt% V_2O_5 content, and the lower selectivities at higher loadings appeared to be due to the increasing Lewis acidity of the catalysts. Space–time yields of 0.1–1.4 kg CH_2O/kg cat/hr and selectivities of 2–78% are reported herein for the V_2O_5/SiO_2 catalysts. Deep oxidation products, CO and CO_2, were principally produced over the V_2O_5/TiO_2 and V_2O_5/SnO_2 catalysts. For the first time, *in situ* Raman analysis clearly showed that for these latter catalysts the surface vanadium(V) oxide species were partially reduced under the steady-state reaction conditions. The performance of the $V_2O_5/TiO_2/SiO_2$ catalyst was similar to that of the V_2O_5/TiO_2 catalyst, consistent with the earlier observation that vanadia was largely bound to the titania overlayer. It appears that formaldehyde selectivity decreased with increasing catalyst reducibility, but no direct correlation of catalyst activity with reducibility was observed. © 1997 Academic Press, Inc.

INTRODUCTION

The direct conversion of methane to methanol and formaldehyde *via* partial oxidation is still a very challenging research area in heterogeneous catalysis. Many catalysts have been investigated for this process and review articles are available in the literature (1, 2). Silica-supported V_2O_5 and MoO_3 have been studied extensively (3–6), and V_2O_5/SiO_2 was found to be one of the most active and selective catalysts for methane partial oxidation to formaldehyde by using either N_2O (3, 4) or molecular oxygen (5, 6) as oxidants. Besides steady-state catalytic tests, very few studies have focused on correlations between the catalyst structure and performance, as well as the nature of the active sites for methane partial oxidation.

It appears thus far that silica is the only effective support for transition metal oxide catalysts for the selective conversion of methane to formaldehyde (7). Silica itself was shown to be quite selective to formaldehyde production, but it was not very active (8–10). However, there is no explanation for the special property of the silica support in the open literature. Transition metal oxide catalysts on other oxide supports have not been studied extensively for the catalytic partial oxidation of methane to methanol and formaldehyde. The reaction mechanisms are largely unknown, partly because of the lack of *in situ* analysis of the catalyst surfaces under reaction conditions. Recently, Koranne *et al.* (11) employed a transient isotope technique to study the carbon pathways for the partial oxidation of methane over V_2O_5/SiO_2 catalysts. The surface residence times and concentrations of various intermediates were obtained and a hypothesis about the reaction pathways was proposed, namely that different types of "sites" involved in the formation of CH_2O, CO, and C_2H_6 may correspond to vanadium oxide species in different redox states.

The V_2O_5/SiO_2 catalyst has been extensively characterized by Raman spectroscopy (12, 13) and ^{51}V NMR spectroscopy (13, 14), as well as XANES/EXAFS (15). These studies revealed that under dehydrated conditions the V_2O_5/SiO_2 catalyst possesses a surface vanadium oxide species with an isolated mono–oxo tetrahedral vanadate structure. Similar surface vanadia structures were found over different catalyst supports such as TiO_2, Al_2O_3, and ZrO_2 (16), but polymeric tetrahedral vanadate structures were also present on these oxide supports. No *in situ* characterization studies have yet been undertaken under methane oxidation reaction conditions.

In the present study, single-component supported V_2O_5 systems (V_2O_5/SiO_2, V_2O_5/TiO_2, and V_2O_5/SnO_2) and mixed oxide systems ($V_2O_5/TiO_2/SiO_2$, $V_2O_5/SnO_2/SiO_2$, and $V_2O_5/MoO_3/SiO_2$) were tested for methane partial oxidation. The influence of vanadia loading and the specific

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oxide support were examined. *In situ* Raman spectra were recorded for the first time during the methane partial oxidation reaction over these catalysts, and correlations between the surface vanadia structures and their catalytic performances were made. Mechanistic insight into the activation of methane and the subsequent reaction for forming formaldehyde *via* partial oxidation over supported V_2O_5 catalysts is provided.

METHODS

Catalyst Preparation

Amorphous SiO_2 (Cab-O-Sil EH-5, surface area 380 m^2/g), treated with water to make it more dense, and TiO_2 (Degussa P-25 used as received, surface area 55 m^2/g) were utilized for making supported SiO_2 and TiO_2 catalysts. The SnO_2 support was made from tin(II) acetate (Aldrich). After hydrolyzing tin(II) acetate with water, the sample was dried at room temperature, further dried at 120°C overnight, and calcined in air at 450°C for 6 h. The resultant SnO_2 support had a surface area of 20 m^2/g. The incipient-wetness impregnation method with solutions of different precursors was used in preparing the supported catalysts for this study. A toluene solution of titanium(IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$) (Alfa) was used for making the TiO_2/SiO_2 samples. A methanol solution of vanadium(V) triisopropoxide oxide ($VO[i\text{-}OC_3H_7]_3$) (Alfa) was used for making supported vanadium oxide catalysts. The above preparations were performed inside a glove box under a nitrogen atmosphere to avoid preoxidation by atmospheric moisture. SnO_2/SiO_2 samples were prepared from an aqueous solution of colloidal tin(IV) oxide (Alfa, 18 wt%) under ambient conditions. An aqueous solution of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (obtained from Matheson, Coleman, and Bell), was used for the preparation of the supported molybdenum oxide catalysts. After impregnation, each catalyst was dried at room temperature at 120°C overnight and then calcined at 500°C for 4 h under flowing air. The metal oxide loadings on the oxide supports were calculated based on the weight percentage of the deposited metal oxides.

Catalyst Testing

The catalytic testing was carried out in a fixed-bed continuous flow quartz reactor (9 mm o.d., 7 mm i.d.) in the temperature range 400–630°C. Usually 25 to 200 mg of catalyst was used. A standard reactant mixture of methane and air (1.5/1.0 volume ratio) was used at ambient pressure, where the flow rates of the methane (Air Products and Chemicals, Inc.; ultra high purity grade) and air (JWS Technologies; zero grade) were controlled by calibrated Linde mass flowmeters. The principal products analyzed by online sampling *via* an automated heated sampling valve using a Hewlett Packard (HP) 5890 Series II gas chromatograph (GC) were CO_2, C_2 hydrocarbons ($C_2H_6 + C_2H_4$), CO, and H_2O. The GC was equipped with two TCD detectors and Poraplot Q and molecular sieve 13 Å capillary columns, and it was coupled to an HP 3396 Series II recorder/integrator and a PC data station using ChromPerfect chromatographic software. Each analysis was carried out using temperature programming in the 50–150°C range using a 10°C/min temperature ramp. Formaldehyde was condensed from the exit stream with dual water scrubbers and quantitatively determined by iodometric titration (17). In the present research, the carbon balance between methane consumed and CH_2O, CO, CO_2, and C_2 hydrocarbons produced was always better than 90% and usually better than 95%.

In Situ Raman Spectroscopy

The *in situ* Raman spectrometer system consisted of a quartz cell and sample holder (schematically shown in Fig. 1), a triple-grating spectrometer (Spex, model 1877), a photodiode array detector (EG&G, Princeton Applied Research, model 1420), and an argon ion laser (Spectra-Physics, model 165). The sample holder was made from a metal alloy, and a 100–200 mg sample disc was held by the cap of the sample holder. The sample holder was mounted onto a ceramic shaft and was rotated by a DC motor at a speed of 1000–2000 rpm. The quartz cell containing the sample holder assembly, Fig. 1, was surrounded by a cylindrical heating coil that was used to heat the sample at a controlled temperature, which was monitored by an internal thermocouple. The quartz cell was capable of operating up to 600°C, and the reaction gas was introduced into the cell at a rate of 100–300 ml/min at atmospheric pressure.

The 514.5 nm line of the Ar^+ laser, with 10–100 mW of power, was focused on the sample disc in a right-angle scattering geometry. An ellipsoid mirror collected and reflected the scattered light into the filter stage of the spectrometer

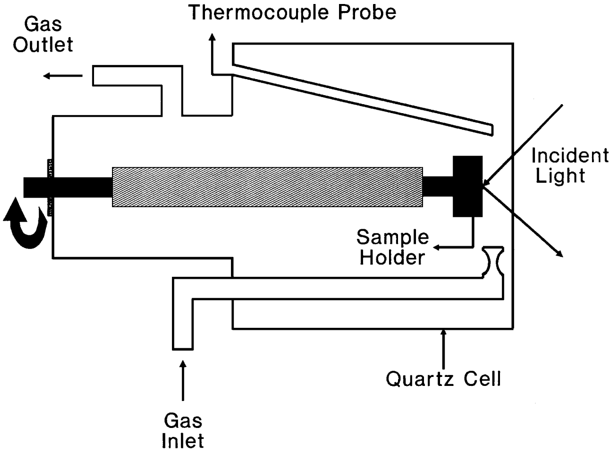

FIG. 1. Schematically representation of the *in situ* cell used to obtain the Raman spectra of catalyst samples being tested for the selective oxidation of methane under continuous flow conditions.

to reject the elastically scattered component. The resulting filtered light, consisting primarily of the Raman component of the scattered light, was collected with an EG&G intensified photodiode array detector that was coupled to the spectrometer and was thermoelectrically cooled to −35°C. The photodiode array detector was scanned with an EG&G optical multichannel analyzer (model OMA III 1463). The Raman spectra under reaction conditions were initially obtained by the following procedures: the Raman spectra of the dehydrated samples were collected after heating the sample to 500°C in a flow of pure oxygen gas (Linde Specialty Grade, 99.99% purity) for 30 min. A flowing gas mixture of CH_4/O_2 (10/1 vol%) was then introduced into the cell and the Raman spectra were collected again upon reaching steady state reaction conditions. After the above treatments, the sample was further sequentially treated with pure oxygen gas and pure methane gas at 500°C for 1 h in each case. The Raman spectra were recorded in the 100–1200 cm^{-1} region with an overall resolution of better than 1 cm^{-1}.

RESULTS

Raman Studies of Dehydrated Catalysts

The Raman spectra of the dehydrated SiO_2 support and the silica-supported MoO_3, V_2O_5, and V_2O_5/MoO_3 catalysts are shown in Fig. 2. The SiO_2 support possessed Raman features at ~450 and ~800 cm^{-1} (Si–O–Si siloxane linkages), ~600 and ~487 cm^{-1} (three- and fourfold siloxane rings), ~970 cm^{-1} (surface silanol groups), and a very weak band at ~1050 cm^{-1} (the antisymmetric mode of the siloxane linkages) (18, 19). Upon impregnation of the SiO_2 support with 3% MoO_3 and 1% V_2O_5, strong Raman bands appeared at ~986 and ~1037 cm^{-1} that are characteristic of a surface molybdenum oxide species possessing a highly distorted MoO_5 structure and a surface vanadium oxide species possessing a tetrahedral VO_4 structure, respectively (13, 20–22). For the 1 wt% V_2O_5/3 wt% MoO_3/SiO_2 sample, the surface vanadium oxide (Raman band at ~1037 cm^{-1}) and surface molybdenum oxide (Raman band at ~986 cm^{-1}) species coexist as isolated species on the SiO_2 support.

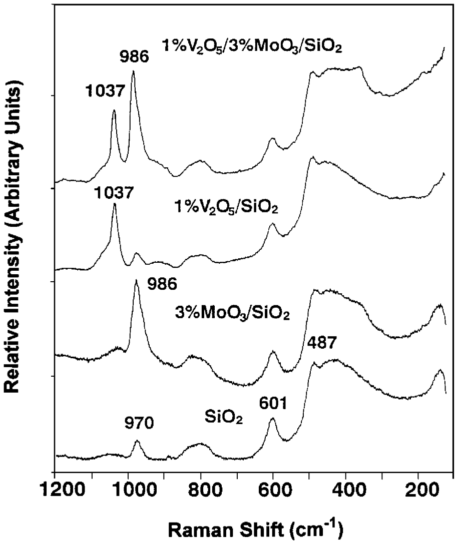

FIG. 2. Raman spectra of SiO_2, 3% MoO_3/SiO_2, 1% V_2O_5/SiO_2, and 1% V_2O_5/3% MoO_3/SiO_2 under dehydration conditions of 250°C in flowing O_2.

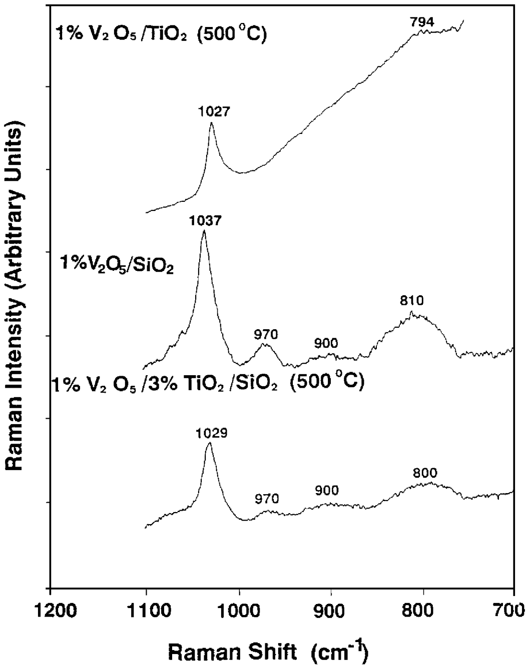

FIG. 3. Raman spectra of 1% V_2O_5/TiO_2, 1% V_2O_5/SiO_2, and 1% V_2O_5/3% TiO_2/SiO_2 catalysts dehydrated at 500°C.

The Raman spectra of the surface vanadium oxide species on dehydrated TiO_2, SiO_2, and 3% TiO_2/SiO_2 are presented in Fig. 3. The Raman peak position of 1029 cm^{-1} for the 1% V_2O_5/3% TiO_2/SiO_2 sample strongly suggests that the vanadium oxide species were largely associated with the titania surface layer and additional details can be found in a previous publication (23). The Raman spectra of dehydrated SnO_2, 1% V_2O_5/SnO_2, and 1% V_2O_5/3% SnO_2/SiO_2 are presented in Fig. 4. The SnO_2 as a support possessed a strong Raman band at 622 cm^{-1} that was characteristic of the symmetric stretching mode of an octahedral SnO_6 structure. The weak and broad Raman bands in the 650–800 cm^{-1} and 200–600 cm^{-1} region are characteristic of asymmetric modes of the octahedral SnO_6 structure and the bending modes of the Sn–O–Sn linkages. Upon doping of 1% V_2O_5 onto the SnO_2, additional Raman bands appeared at ~1027 and ~900 cm^{-1}, which are characteristic of surface vanadium oxide species possessing monomeric VO_4 and polymeric $[VO_3]_n$ structures, respectively. The additional new Raman band at ~830 cm^{-1} is probably due to the formation of a V_x–Sn_y–O_z compound (24, 25). For the

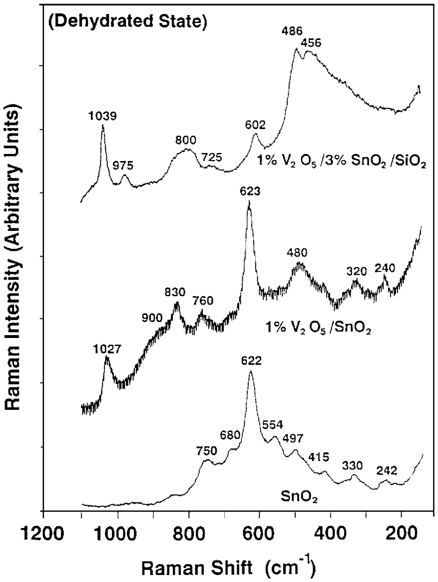

FIG. 4. Raman spectra of dehydrated SnO_2 (450°C), 1% V_2O_5/SnO_2 (500°C), and 1% V_2O_5/3% SnO_2/SiO_2 (500°C) catalysts.

1 wt% V_2O_5/3 wt% SnO_2/SiO_2 catalyst sample, SnO_2 apparently formed a surface tin oxide overlayer on the SiO_2 support as suggested by the absence of any Raman features of bulk SnO_2, and vanadium oxide formed an isolated surface VO_4 species with a terminal V=O bond that gave rise to the peak at ~1039 cm^{-1} (13).

Catalytic Activities and Selectivities

The study of catalytic partial oxidation of methane by molecular oxygen was conducted in a flow reactor at ambient pressure. The methane conversions and product selectivities are summarized in Table 1. In general, very high reactant gas hourly space velocities (GHSV) were used so that the formaldehyde product could be removed effectively from the reaction zone without being further oxidized. At the reaction conditions employed in the present study, the contributions from the empty reactor and even from the pure silica support (Cab-O-Sil) were negligible for methane conversion. For the SiO_2 and MoO_3/SiO_2 catalyst, accurate analysis of the products other than formaldehyde was very difficult since methane conversions were extremely low. Over the V_2O_5/SiO_2 catalysts, very high formaldehyde space–time yields (STY > 1 kg CH_2O/kg cat · h) could be obtained even though the single pass percentage yields (CH_4 conversion% × %CH_2O selectivity) were still quite low (<2%).

Methane conversions as a function of contact time over the 1.0 and 3.0% V_2O_5/SiO_2 catalysts are shown in Fig. 5. The data for the 1.0% V_2O_5/SiO_2 catalyst were obtained at 630°C, while those for the 3.0% V_2O_5/SiO_2 catalyst were obtained at 580°C because of the much higher activity of the 3% V_2O_5 catalyst. Figure 6 represents formaldehyde selectivities as a function of methane conversion over four catalysts with different V_2O_5 loadings. For the 1.0% V_2O_5/SiO_2 catalyst, data were collected at three different temperatures. Formaldehyde selectivity as a function of the vanadia loading over the silica support at a constant methane conversion level of ≈1 mol% is shown in Fig. 7.

Using a 2 wt% V_2O_5/SiO_2 catalyst, the activation energy for conversion of methane to products was determined in the temperature range of 555 to 630°C. The methane conversion was limited to 1–2% by varying the GHSV between

TABLE 1

Methane Oxidation by Air (CH_4/Air = 1.5/1.0) over Supported Metal Oxide Catalysts

Catalysts	GHSV (L/kg cat · h)	Temp. (°C)	Conv. (CH_4%)	STY(CH_2O) (g/kg cat · h)	Selectivities(C-mol%)			
					CH_2O	C_2's	CO	CO_2
SiO_2[a]	70,000	630	0.05	24.3	100.0	—	—	—
2% MoO_3/SiO_2	70,000	630	0.08	37.9	100.0	—	—	—
1% V_2O_5/SiO_2	70,000	630	9.52	684.9	15.7	1.7	76.4	6.3
5% V_2O_5/SiO_2	280,000	630	5.60	1,440.0	13.5	0.2	81.3	4.3
1% V_2O_5/3% MoO_3/SiO_2	70,000	630	8.47	675.2	16.6	2.0	73.5	7.9
TiO_2	70,000	630	1.55	17.6	2.3	—	94.0	3.6
1% V_2O_5/TiO_2[b]	70,000	630	0.82	14.0	3.3	1.2	73.0	22.5
1% V_2O_5/3% TiO_2/SiO_2	70,000	630	1.07	101.3	18.6	—	76.6	4.8
1% $V_2O_5/SiO_2/TiO_2$[c]	70,000	630	6.50	9.1	0.6	—	92.7	6.7
SnO_2	70,000	530	8.10	2.3	0.1	—	8.9	90.4
1% V_2O_5/SnO_2[d]	70,000	530	7.60	—	—	—	13.4	83.6
1% V_2O_5/3% SnO_2/SiO_2	35,000	630	2.00	17.8	3.9	—	77.2	18.9

[a] SiO_2 fumed Cab-O-Sil.

[b] TiO_2 as a support.

[c] Double bed experiment using 50 mg 1% V_2O_5/SiO_2 followed by 50 mg TiO_2.

[d] SnO_2 as a support.

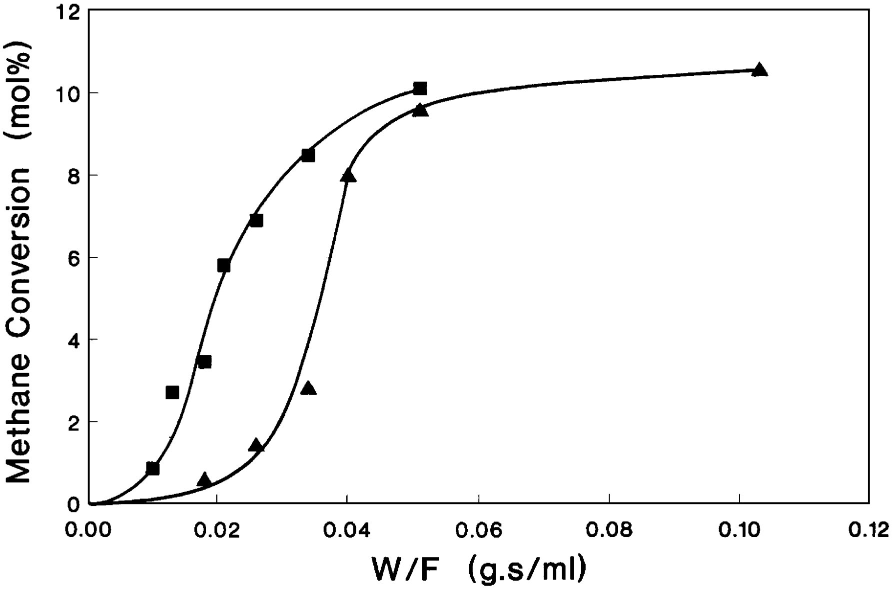

FIG. 5. Conversions of methane to products as a function of the reactant contact time over 1 wt% V_2O_5/SiO_2 (▲, 630°C) and 3 wt% V_2O_5/SiO_2 (■, 580°C) catalysts from a reactant mixture of CH_4/air = 1.5/1.0 (volume ratio).

65,000 and 350,000 L/kg cat · h as the reaction temperature was progressively increased. The resultant Arrhenius plot obtained with this catalyst is shown in Fig. 8.

In Situ Raman Studies

The Raman spectra of 1% V_2O_5 supported on SiO_2, TiO_2, SnO_2, and 3% TiO_2/SiO_2 were recorded during methane oxidation at 500°C, utilizing the procedures described in the Methods section, and are shown in Figs. 9–12. The background due to the SnO_2 support was subtracted from the 1.0% V_2O_5/SnO_2 sample in Fig. 11. Upon oxygen gas treatment, dehydrated surface monomeric VO_4 species with a Raman band in the 1027–1034 cm^{-1} region were predominantly present on all the samples, and the surface polymeric $[VO_3]_n$ species with a broader Raman band at ~900 cm^{-1} were primarily present on the SnO_2 support. An additional Raman band at ~830 cm^{-1} appeared only in the V_2O_5/SnO_2 system, indicating the formation of a V_x–Sn_y–O_z compound mentioned earlier (24, 25). Under methane oxidation reaction conditions, Raman intensities

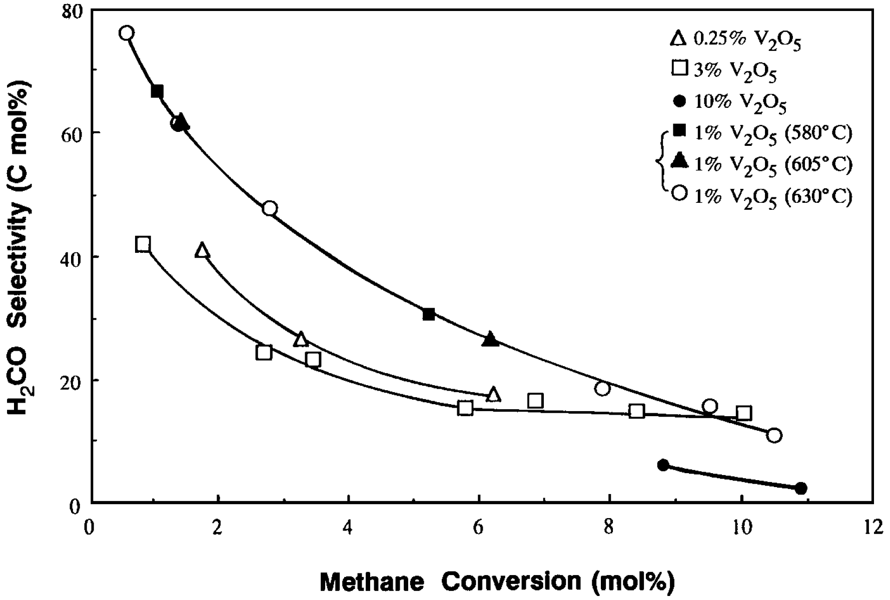

FIG. 6. Formaldehyde selectivity vs methane conversion from CH_4/air = 1.5/1.0 (volume ratio) over different V_2O_5/SiO_2 catalysts, at 580°C except as noted.

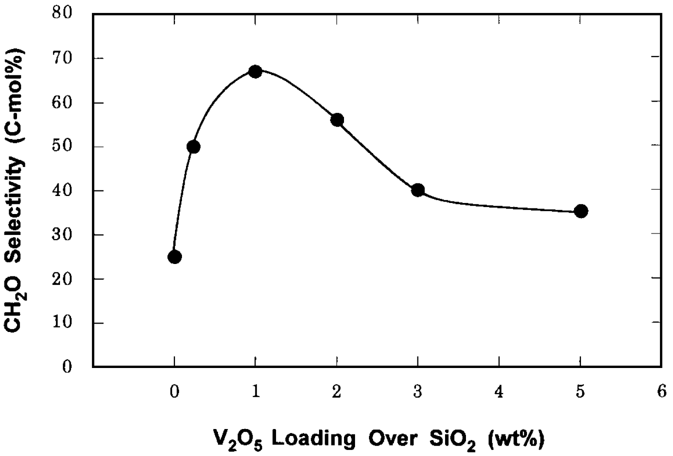

FIG. 7. Formaldehyde selectivity as a function of the V_2O_5 loading of the silica support at a methane conversion level of $\approx$1 mol% from a CH_4/air = 1.5/1.0 volume ratio reactant mixture.

of the surface vanadium oxide species decreased in the V_2O_5/TiO_2 (Fig. 10) and V_2O_5/SnO_2 (Fig. 11) systems due to the reduction of the surface vanadium oxide species under the reducing methane oxidation environment, but no significant changes were observed in the V_2O_5/SiO_2 (Fig. 9) and $V_2O_5/TiO_2/SiO_2$ (Fig. 12) catalyst systems. In the case of the SnO_2-supported catalyst, reduction resulted in a reduced surface V(IV) phase characterized by a weak and broad band at 855 cm^{-1} (cf. Fig. 11). The original surface vanadium(V) oxide species was restored by flowing pure oxygen into the cell and reoxidizing the reduced surface vanadium phase (Fig. 11).

DISCUSSION

V_2O_5/SiO_2 Catalyst

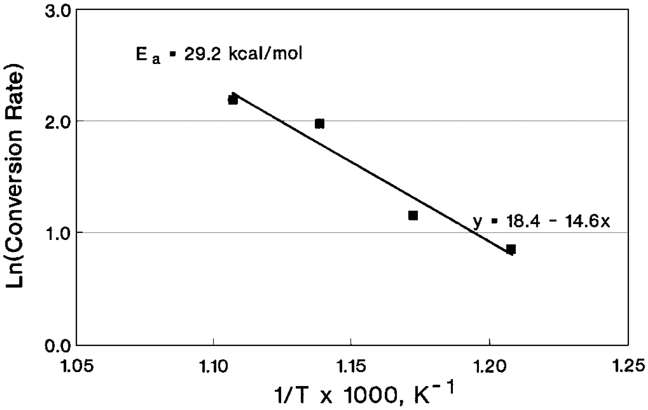

FIG. 8. Arrhenius plot for methane conversion to products over a 2 wt% V_2O_5/SiO_2 catalyst using a CH_4/air = 1.5/1.0 volume ratio reactant mixture.

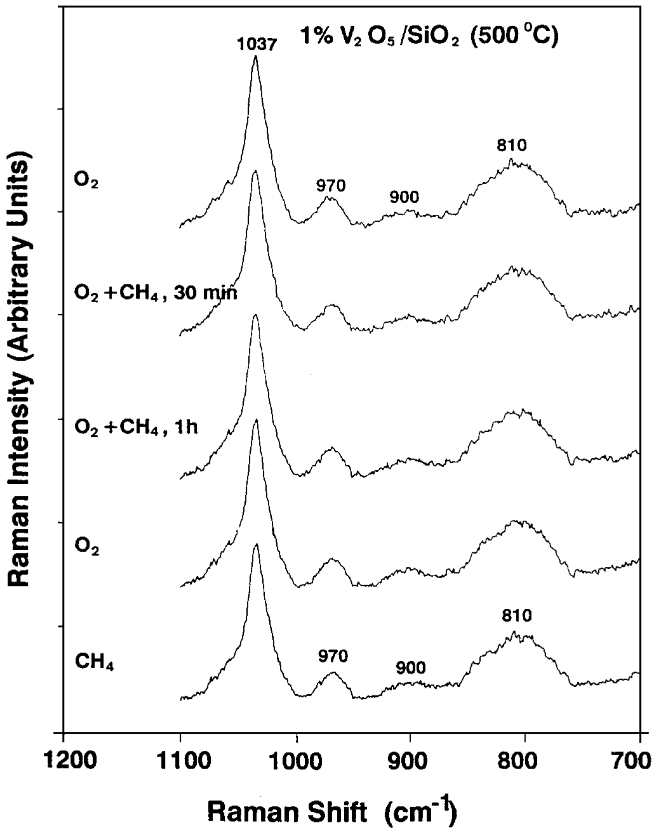

FIG. 9. *In situ* Raman spectra of the 1% V_2O_5/SiO_2 catalyst obtained after sequential treatments at 500°C in flowing O_2, CH_4/O_2 (10/1) reactant mixture, and CH_4.

Partial oxidation of methane to formaldehyde over V_2O_5/SiO_2 catalysts has recently been studied by several groups (3–6, 26–28). Spencer and Pereira (6) reported very high activity for their V_2O_5/SiO_2 catalyst for methane activation compared with their MoO_3/SiO_2 catalyst and proposed a sequential reaction pathway ($CH_4 \rightarrow CH_2O \rightarrow CO \rightarrow CO_2$). Kennedy and co-workers (26) evaluated the effect of V_2O_5 loading in the range 1.8–7.2 wt% V_2O_5. The high activity of the V_2O_5/SiO_2 catalyst relative to the MoO_3/SiO_2 catalyst was interpreted by Parmaliana *et al.* (27) in terms of the higher density of reduced sites and stabilization of the reduced vanadium ions.

Partial oxidations of methane are highly exothermic reactions (1). At high reaction temperatures, homogeneous gas phase reactions also contribute significantly to the overall partial oxidation reactions once the reactions are initiated over the catalyst surface (29). The methane conversions as a function of the contact times over the V_2O_5/SiO_2 catalysts at two V_2O_5 loadings are shown in Fig. 5. At contact times below 0.04 s, methane conversion exceeded the linear increase with increasing contact time expected for a differential reactor, which indicates that autocatalytic reactions occurred. At longer contact times, diffusion limitations caused the methane conversion to decrease. This autocatalytic property of methane partial oxidation over the V_2O_5/SiO_2 catalyst has not been explicitly noted in previous studies. There are two factors that could contribute to the autocatalytic behavior: (i) a hot spot may be able to form in the catalyst bed during the reaction and accelerate further the surface reactions due to the high exothermic nature of the partial oxidations or (ii) the gas phase free radical chain reaction could be initiated on the surface.

The presence of autocatalytic reactions makes it difficult to precisely determine the turnover frequency (TOF; methane molecules reacted/vanadium atom/s) for methane activation over the V_2O_5/SiO_2 catalysts. Nevertheless, based on the fact that surface vanadium oxide species are molecularly dispersed and isolated over the SiO_2 support for loadings with less than 10% V_2O_5, the TOF of methane conversion was estimated by using the data obtained at methane conversions of less than 2% (as shown in Table 2).Data in Table 2 indicate that the TOF for methane conversion did not change significantly as the V_2O_5 loading was increased from 0.25 to 5.0%. This suggests that methane activation only needs one type of active site, which increased linearly with the V_2O_5 content in the range studied here. Figure 6 shows that formaldehyde selectivity was very sensitive to the methane conversion level, which is well recognized in the literature (1, 6), and is also very sensitive to the V_2O_5 loadings. On the other hand, the selectivity was rather insensitive to the reaction temperature, at least within the temperature range 580–630°C. Koranne *et al.* (11) also reported a universal curve showing decreasing formaldehyde selectivity as the methane conversion increased in the 550–660°C temperature region where methane conversion rather than temperature was the primary factor for controlling selectivity.

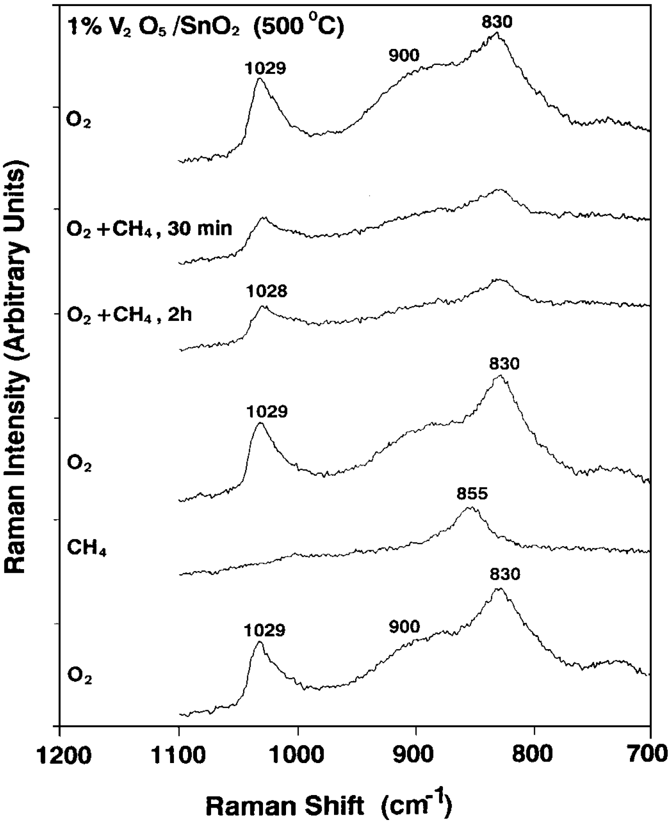

FIG. 11. *In situ* Raman spectra of the 1% V_2O_5/SnO_2 catalyst obtained after sequential treatments at 500°C in flowing O_2, CH_4/O_2 (10/1) reactant mixture, and CH_4.

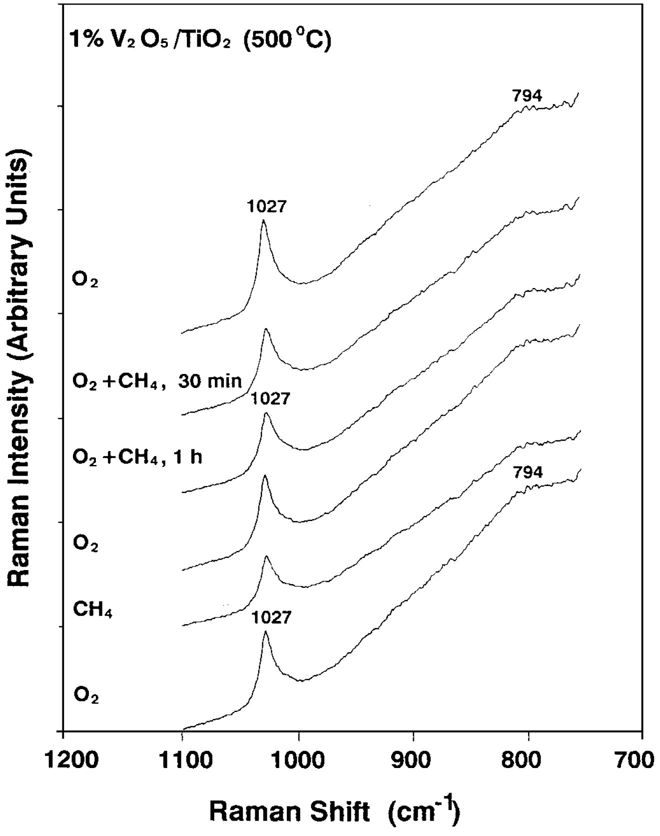

FIG. 10. *In situ* Raman spectra of the 1% V_2O_5/TiO_2 catalyst obtained after sequential treatments at 500°C in flowing O_2, CH_4/O_2 (10/1) reactant mixture, and CH_4.

The effective activation energy for methane conversion over the 2% V_2O_5/SiO_2 catalyst was measured by carefully varying the flow rate and controlling the methane conversion levels to <2% at different temperatures. The value determined here (Fig. 8) was 29.2 kcal/mol. This value of the apparent activation energy strongly indicates that the reaction was initiated by surface reactions. Interestingly,

TABLE 2

The Turnover Frequencies (TOF) of Methane Conversion over V_2O_5/SiO_2 Catalysts at 580°C

V_2O_5 loadings (wt%)	0.25	1.00	2.00	3.00	5.00
GHSV (L/kg cat · h)	16,200	70,000	140,000	350,000	280,000
CH_4 conversion (%)	1.7	1.0	1.1	0.8	1.1
TOF (10^{-2} s^{-1})	6.8	4.5	5.0	5.9	3.8

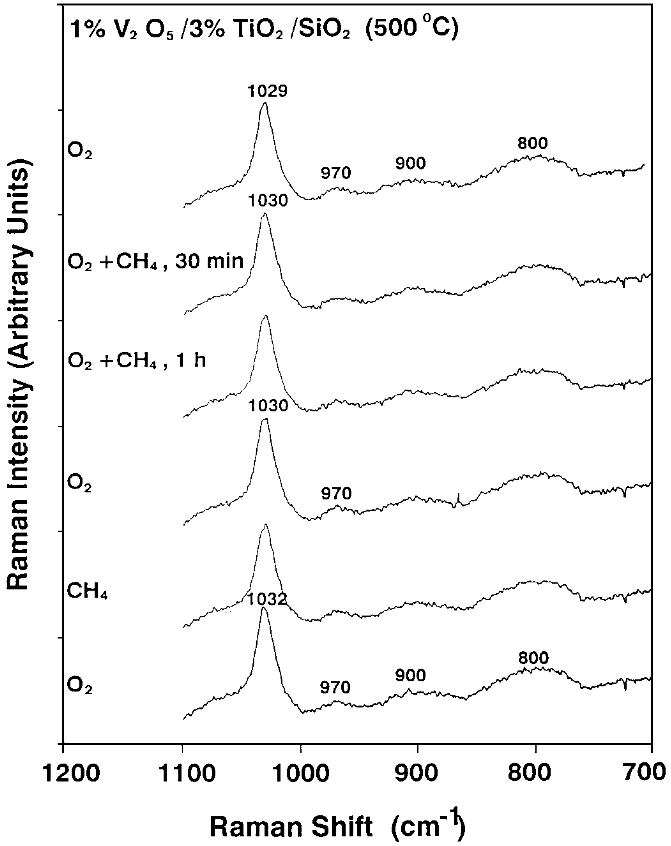

FIG. 12. *In situ* Raman spectra of 1% V_2O_5/3% TiO_2/SiO_2 catalyst obtained after sequential treatments at 500°C in flowing O_2, CH_4/O_2 (10/1) reactant mixture, and CH_4.

Fig. 7 indicates the presence of an optimum V_2O_5 loading for methane partial oxidation to formaldehyde over the V_2O_5/SiO_2 catalysts: over the range investigated, 1% V_2O_5 yielded the highest formaldehyde selectivity at constant methane conversion level. The *in situ* Raman spectra obtained under the reaction conditions (Fig. 9) show that the pentavalent vanadium oxide moieties were the predominant species on the silica support, and even under a pure flowing methane atmosphere there was no observable reduction of the surface vanadium(V) oxide species. Generally, the V=O stretching vibration frequency appears in the 950–1000 cm^{-1} region for the monomeric oxovanadium(IV) complexes (30). Upon reduction from the V(V) state to a lower oxidation state, the 1035 cm^{-1} V=O band intensity should be reduced in the Raman spectrum (see Figs. 10 and 11 for V_2O_5/TiO_2 and V_2O_5/SnO_2, respectively). The lack of significant reduction of the 1035 cm^{-1} band with the SiO_2-supported catalyst does not imply that the surface vanadium does not undergo a redox cycle, e.g., between V(V) and V(IV), but it does mean that the dynamic redox potential of vanadium in V_2O_5/SiO_2 is shifted toward V(V) compared to the other systems studied, V_2O_5/TiO_2 and V_2O_5/SnO_2, under otherwise identical reaction conditions. It, therefore, appears that stability of pentavalent vanadia is a key factor controlling the selectivity of methane oxidation to formaldehyde.

MoO_3/SiO_2 and $V_2O_5/MoO_3/SiO_2$ Catalysts

The MoO_3/SiO_2 catalyst system has been studied extensively for methane partial oxidation to formaldehyde, and it was found to be much less active than the V_2O_5/SiO_2 catalyst (1, 6, 31). Banares *et al.* (31) have studied the effect of alkali metal cations on the structure and performance of MoO_3/SiO_2 catalysts for partial oxidations of methane and methanol. It was concluded that alkali metal cations caused a decrease in the number of isolated Mo species possessing one terminal Mo=O bond by the formation of alkali–molybdate compounds, and consequently the activity for methane oxidation to formaldehyde was reduced. The data in Table 1 clearly indicate that the 2% MoO_3/SiO_2 catalyst had an activity similar to that of the pure fumed silica support and was significantly less active than the V_2O_5/SiO_2 catalyst. The 1% V_2O_5/SiO_2 and 1% V_2O_5/3% MoO_3/SiO_2 catalysts exhibited almost identical catalytic activities and product selectivities for methane partial oxidation to formaldehyde. This indicates that V_2O_5 and MoO_3 were isolated species coexisting over the SiO_2 support without strong interactions and the catalytic activity was dominated by the surface vanadium oxide species. This conclusion is corroborated by the structural information obtained from Raman spectroscopy that showed no interaction between the two transition metal oxides (Fig. 2).

V_2O_5/TiO_2 and $V_2O_5/TiO_2/SiO_2$ Catalysts

Partial oxidation of methane over V_2O_5/TiO_2 had not been previously studied extensively and no studies have been reported for the mixed oxides and $V_2O_5/TiO_2/SiO_2$ in the literature. These catalyst systems have been well-characterized by *in situ* Raman and other spectroscopic techniques (23). Analogous to the V_2O_5/SiO_2 catalyst, the V_2O_5/TiO_2 catalyst was found to possess well dispersed surface vanadia species over the TiO_2 support for low loadings. In the case of the TiO_2/SiO_2 catalyst, a surface titania overlayer was found to be present on the surface of the SiO_2 support (23). For the multicomponent 1% V_2O_5/3% TiO_2/SiO_2 catalyst, Raman studies suggested that V_2O_5 was principally bonded to the TiO_2 overlayer. Partial oxidation of methanol to formaldehyde was studied over these catalysts (23), and the TOFs over 1% V_2O_5/TiO_2 and 1% V_2O_5/3% TiO_2/SiO_2 catalysts were found to be three and two orders of magnitude higher, respectively, than that observed over the 1% V_2O_5/SiO_2 catalyst. However, data in Table 1 reveal that for methane oxidation, the 1% V_2O_5/SiO_2 catalyst was much more active than the 1% V_2O_5/TiO_2 catalyst. Under the same reaction conditions, the methane conversion over the V_2O_5/SiO_2 catalyst was about one order of magnitude higher than that over the V_2O_5/TiO_2. This suggests a different reaction mechanism for the partial oxidation of methane compared to methanol oxidation.

It is interesting that the catalytic performance of the 1% V_2O_5/TiO_2 and the 1% V_2O_5/3% TiO_2/SiO_2 catalysts for methane oxidation are very similar, except that the 1% V_2O_5/3% TiO_2/SiO_2 catalyst exhibited a higher selectivity for formaldehyde production. These results are consistent with the structural information that the vanadia overlayer is coordinated to the titania overlayer, which results in behavior similar to the V_2O_5/TiO_2 catalyst. *In situ* Raman spectra for V_2O_5/TiO_2 (Fig. 10) indicate that the surface vanadium(V) oxides were appreciably reduced (30%) under the reaction conditions employed. The reduced surface vanadium oxide species do not exhibit the 1027 cm^{-1} Raman band attributed to the stretching mode of the terminal V=O bond of vanadium(V) oxide and resulted in the intensity reduction of this Raman band. These reduced species were reoxidized to the vanadium(V) oxide under a pure oxygen environment at elevated temperature (here shown for 500°C reoxidation). There is evidence that a significant amount of reduced vanadium oxide species coexisted with the V(V) species under the steady-state reaction condition. *In situ* Raman spectra of the 1% V_2O_5/3% TiO_2/SiO_2 system (Fig. 12) suggest that the surface V_2O_5 species were quite stable under reaction conditions, as in the case of the 1% V_2O_5/SiO_2 catalyst, and remain fully oxidized. One striking observation (Table 1) was that the catalytic activities of the V_2O_5/TiO_2 catalyst and the bare TiO_2 support were very similar. However, the product selectivity patterns were quite different for these two systems. While methane oxidation over TiO_2 produced CO almost exclusively, a significant amount of CO_2 was produced over the V_2O_5/TiO_2 catalyst as well. In the absence of detailed mechanistic information, one can only suggest at this point that coupled redox systems, e.g., V(IV)/V(V)‖Ti(IV)/Ti(III), may be responsible for the deep oxidation properties of the V_2O_5/TiO_2 catalyst.

V_2O_5/SnO_2 and $V_2O_5/SnO_2/SiO_2$ Catalysts

The V_2O_5/SnO_2 catalyst has previously been shown to be very active for methanol partial oxidation (32). Data in Table 1 show that the catalytic activity for methane activation was extremely high for 1% V_2O_5/SnO_2; however, it only produces deep oxidation products CO_x, and predominantly CO_2. *In situ* Raman study demonstrated (Fig. 11) that the V_2O_5 species were largely reduced (55%) under the methane oxidation reaction conditions employed here. Similar to the V_2O_5/TiO_2 catalyst, coupled redox systems of V(IV)/V(V)‖Sn(IV)/Sn(II) could be promoting deep oxidation of methane to CO_2. However, for the 1% V_2O_5/3% SnO_2/SiO_2 catalyst, the catalytic activity for the methane oxidation was low and even lower than that of the 1% V_2O_5/SiO_2 catalyst (Table 1). Dispersed vanadium(V) oxide species on the SiO_2 surface were suggested by the presence of the Raman band corresponding to the stretching vibration of the terminal V=O bond at 1039 cm^{-1} (Fig. 4). However, the catalytic results suggested a poisoning effect of the SnO_2 overlayer, which might have eliminated some of the active surface vanadia species on SiO_2 and reduced the catalytic activity. It is interesting to note that over the mixed 1% V_2O_5/3% SnO_2/SiO_2 catalyst, the predominant product was CO instead of CO_2 as observed over the V_2O_5/SnO_2 catalyst. It is possible that CO was mainly formed *via* decomposition of the primary formaldehyde product accelerated by the supported SnO_2 overlayer on the SiO_2 surface.

In the research field of selective partial oxidation of hydrocarbons, it is always essential to identify the nature of the active sites that determine the catalytic activity and the product selectivities. For propylene oxidation, Sachtler and De Boer (33) correlated the catalytic selectivity with the catalyst reducibility. They found that the higher the reducibility of the catalysts was, the higher the activity and the lower the selectivity. Bielanski and Haber (34) explained the selectivity patterns by postulating that lattice oxygen (nucleophilic) was responsible for partial oxidation, while adsorbed ionic or radical oxygen species (electrophilic) caused total oxidation.

Recently, Koranne *et al.* (11) proposed reaction pathways for methane oxidation over V_2O_5/SiO_2 catalysts based on isotope transient kinetic studies and suggested three types of active sites: S1, a site with high oxygen insertion and H-abstraction capabilities; S2, a site with intermediate oxygen insertion and H-abstracting capabilities; and S3, a site with low oxygen insertion capability and with high H-abstraction capability. They have further suggested (11) that these sites may merely be the same “site” but in different oxidation states. it would be very interesting to provide experimental evidence for characterizing the nature of these active sites and to determine how they vary with catalyst composition and reaction conditions.

The present Raman study provides some fundamental details about the properties of the active sites for methane activation and product selectivity. For the V_2O_5/SiO_2 catalyst in the dehydrated state, the vanadium(V) oxide is bound to the SiO_2 surface *via* V–O–Si bridging bonds and possesses a terminal V=O double bond. These bridging and double bonded oxygen functionalities can be viewed as surface lattice oxygens (nucleophilic) (34). The bond order of the V=O bond was found to vary only by a very small amount over different supports (12). Therefore, the V=O bond is not likely to be responsible for the activity differences observed for V_2O_5 over different catalyst supports. Furthermore, *in situ* Raman study has shown that the V=O bond is very stable under the reaction conditions in the case of V_2O_5/SiO_2. Consequently, it is reasonable to argue that the terminal V=O bond is not the active center for activating the methane molecule.

However, the catalytic data certainly showed that the methane oxidation activity was a direct result of the V_2O_5 loading and was dependent on the specific oxide support. The bridging oxygen (V–O–Support, e.g., V–O–Si) bond strength is expected to vary with the support and could be responsible for the differences observed for the V_2O_5 catalysts on different supports. These bridging bonds could be one of the determining factors for the initial activity of the catalysts for the methane activation. Once the methane conversion proceeds, some vanadium(V) oxide species will be reduced to the lower oxidation states and provide the sites for oxygen adsorption to form undesirable electrophilic oxygen species (34). The population of these reduced species should depend on the catalyst support. The present *in situ* Raman studies clearly show that these reduced species are not favored over the SiO_2 surface and are much more prevalent over the TiO_2 and SnO_2 supports under the reaction conditions employed. The stability trend of the reduced vanadium oxides over these catalysts is $V_2O_x/SnO_2 > V_2O_x/TiO_2 > V_2O_x/SiO_2$ (where $x < 5$). This catalyst reducibility trend correlates quite well with the CO_2 selectivity trend and in the reverse order to that of the formaldehyde selectivity. Upon increasing methane conversion, formaldehyde selectivity decreased and CO selectivity increased monotonically over the V_2O_5/SiO_2 catalysts. It is evident that the CO mostly arises from the decomposition of formaldehyde by further H-abstraction. On the other hand, there is no simple correlation between the selectivities to CO and CO_2, which indicates that these two carbon oxides could be formed through two parallel reaction pathways instead of the sequential reactions $CH_2O \rightarrow CO \rightarrow CO_2$.

A different pathway needs to be invoked over pure SiO_2, which also produced formaldehyde as well as C_2 hydrocarbons at low methane conversions and elevated temperatures. A parallel reaction pathway for formaldehyde and C_2 hydrocarbon production was previously proposed (10). Unlike the V_2O_5/SiO_2 and MoO_3/SiO_2 catalysts that were capable of converting the methyl radical to formaldehyde instead of C_2 hydrocarbons, over the SiO_2 surface methyl radicals once formed are most likely to couple in the gas phase to produce ethane. In a recent dual catalyst bed study, it was demonstrated that methyl radicals generated by a first SrO/La_2O_3 catalyst bed could be converted to formaldehyde over a second bed consisting of MoO_3/SiO_2 (35). In fact, at very low methane conversions (i.e., <1%), the selectivities to formaldehyde were previously reported to approach 100% over MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts (5, 6). This agrees with the selectivities shown in Table 1 for very low conversions of methane over SiO_2 and MoO_3/SiO_2 catalysts.

A very unique property of the SiO_2 support is its low surface acidity. In comparison with other common supports like TiO_2, γ-Al_2O_3, and ZrO_2 that all have quite high densities of surface Lewis acid sites, pure SiO_2 is almost free of Lewis acid sites (36). This could be another underlying cause of the major differences between SiO_2 and TiO_2 supports, giving rise to the relatively higher selectivity for formaldehyde over pure SiO_2 and SiO_2-supported catalysts, while the Lewis acid sites on TiO_2 promote the formation of CO. In a double-bed experiment performed by Spencer (5) where a MoO_3/SiO_2 catalyst bed was followed by γ-Al_2O_3, it was noted that the formaldehyde produced by the upstream MoO_3/SiO_2 catalyst was decomposed by the downstream γ-Al_2O_3. The current double bed experiment with an upstream V_2O_5/SiO_2 bed followed by a TiO_2 bed (Table 1) has also shown that TiO_2 is very active for decomposing formaldehyde to carbon monoxide. This is probably due to the Lewis acidity of the TiO_2 surface.

CONCLUSIONS

The present study indicates that silica is the best support for the multivalent V_2O_5 catalyst for partial oxidation of methane to formaldehyde. Very high space time yields of formaldehyde (>1 kg CH_2O/kg cat · h) have been achieved with the 1% V_2O_5/SiO_2 catalyst. Methane activation over this catalyst only needed a single active site whose concentration increased linearly with the V_2O_5 loadings up to at least 5 wt%. *In situ* Raman spectra have shown that methane alone could not reduce the surface vanadia species and methane conversion required the simultaneous presence of oxygen. This suggests that methane was activated by active sites on the silica surface created upon the dispersion of vanadium(V) oxide. The *in situ* Raman studies strongly suggest that V=O is not the active site for the initial activation of the methane molecule. TiO_2-based catalysts produced mostly CO, while the very active SnO_2-supported catalysts formed almost exclusively CO_2. It is evident that, under reaction conditions, TiO_2- and SnO_2-supported catalysts were largely reduced by the reactant mixture and favored the deep oxidation of methane. There is no simple correlation of the catalyst activity with the reducibility of the supported vanadia catalysts studied. However, the CO_2 selectivity tended to increase with the increasing reducibility of the catalysts.

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