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Selective Methane Oxidation over Promoted Oxide Catalysts

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SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

Series of catalysts consisting of MoO_3, V_2O_5, TiO_2, and SnO_2 impregnated onto oxide supports consisting of SiO_2 (Cab-O-Sil), TiO_2, or SnO_2 were previously prepared and tested for the selective oxidation of methane to oxygenates, and it was found that the V_2O_5/SiO_2 catalyst was the most active and most selective toward the formation of formaldehyde [1]. These catalysts have been characterized by laser Raman spectroscopy after dehydration and during the methane oxidation reaction with a $CH_4/O_2 = 10/1$ reaction mixture at 500°C in a continuous flow *in situ* reaction cell.

With the V_2O_5/SiO_2 catalyst (the most active catalyst among those studied), no significant structural changes were revealed by *in situ* Raman analyses, indicating that the fully oxidized surface sites were related to the high formaldehyde selectivity. Over the V_2O_5/TiO_2 and V_2O_5/SnO_2 catalysts, CO and CO_2 were the principal products produced by oxidation of methane. 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 reductibility was observed.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

OBJECTIVES OF THE RESEARCH

The objective of this research is the selective oxidative coupling of methane to C_2H_4 hydrocarbons (Equations 1-3) and oxygenates, in particular formaldehyde and methanol as represented by Equations 4 and 5. Air, oxygen, or carbon dioxide, rather than nitrous oxide will be utilized as the oxidizing gas at high gas hourly space velocity, but mild reaction conditions (500-700 °C, 0.1 MPa total pressure). All the investigated processes are catalytic, aiming at minimizing gas phase reactions that are difficult to control.

$$\begin{array}{cccccccccl}
2CH_4 & + & \frac{1}{2}O_2 & \rightleftharpoons & C_2H_6 & + & H_2O & & & (1) \\
2CH_4 & + & O_2 & \rightleftharpoons & C_2H_4 & + & 2H_2O & & & (2) \\
2CH_4 & + & 2CO_2 & \rightleftharpoons & C_2H_4 & + & 2CO & + & 2H_2O & (3) \\
CH_4 & + & O_2 & \rightleftharpoons & CH_2O & + & H_2O & & & (4) \\
CH_4 & + & \frac{1}{2}O_2 & \rightleftharpoons & CH_3OH & & & & & (5)
\end{array}$$

Oxide catalysts have been chosen for this research that are surface doped with small amount of acidic dopants. It was thought that, for example, the very basic Sr/La_2O_3 catalyst which is active in the formation of methyl radicals and therefore C_2H_4 products, can be doped with some Lewis acidic oxides or other groups to increase further its activity and selectivity to C_2H_4 products.

The research to be carried out under U.S. DOE-METC contract is divided into the following three tasks:

Task 1. Maximizing Selective Methane Oxidation to C_2H_4 Products Over Promoted Sr/La_2O_3 Catalysts.

Task 2. Selective Methane Oxidation to Oxygenates.

Task 3. Catalyst Characterization and Optimization.

Task 1 dealt with the preparation, testing, and optimization of acidic promoted lanthana-based catalysts for the synthesis of C_2H_4 hydrocarbons and is essentially completed. Task 2 aims at the formation and optimization of promoted catalysts for the synthesis of oxygenates, in particular formaldehyde and methanol. Task 3 involves characterization of the most promising catalysts so that optimization can be achieved under Task 2.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

RESEARCH PROGRESS

This research project is directed toward the direct selective oxidation of methane to oxygenates. Many supported metal oxides have been reported to exhibit some activity for the synthesis of oxygenates such as formaldehyde and methanol from methane, but most of these oxides produced oxygenates with only marginal yields and often required high pressure [2,3]. In the present work, series of catalysts consisting of MoO_3, V_2O_5, TiO_2, and SnO_2 impregnated onto oxide supports consisting of SiO_2 (Cab-O-Sil), TiO_2, or SnO_2 that were previously prepared and tested for the selective oxidation of methane to oxygenates were tested and examined in an *in situ* laser Raman reaction cell.

These catalysts were previously tested in a continuous flow fixed bed catalyst testing system in the temperature range of 400-630°C with a CH_4/air = 1.5/1.0 reactant mixture at ambient pressure as described in a previous quarterly technical progress report [1]. Table 1 is reproduced from that report and gives the observed conversions of methane, the space time yields of formaldehyde, and the product selectivities.

Experimental

The *in situ* Raman spectrometer system consisted of a quartz cell and sample holder, 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 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 in a well. 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 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 one hr in each case. The Raman spectra were recorded in the 100-1200 cm^{-1} region with overall resolution 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 Figure 1. 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 four-fold siloxane rings), ~970 cm^{-1} (surface silanol groups), and a very weak band at ~1050 cm^{-1} (the antisymmetric mode of the siloxane linkages) [4,5]. Upon impregnation of 3% MoO_3 and 1% V_2O_5 on the SiO_2 support, strong Raman bands appeared at ~986 and ~1037 cm^{-1} that are characteristic of the surface molybdenum oxide species possessing a highly distorted MoO_5 structure and the surface vanadium oxide species possessing a tetrahedral VO_4 structure, respectively [6-9]. For the fully dehydrated 1 wt% V_2O_5/3 wt% MoO_3/SiO_2 catalyst, 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.

The Raman spectra of the surface vanadium oxide species on dehydrated TiO_2, SiO_2, and 3% TiO_2/SiO_2 are presented in Figure 2. 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 [10]. 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 Figure 3. 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 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 $[VO_3]_n$ structure, 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 [11,12]. For the 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 isolated surface VO_4 species with a terminal V=O bond that gave rise to the peak at ~1039 cm^{-1} [6]

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 Figures 4-7. The background due to the SnO_2 support was subtracted from the 1.0% V_2O_5/SnO_2 sample in Figure 6. 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 [11,12]. Under methane oxidation reaction conditions, Raman intensities of the surface vanadium oxide species decreased in the V_2O_5/TiO_2 (Figure 5) and V_2O_5/SnO_2 (Figure 6) 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 (Figure 4) and $V_2O_5/TiO_2/SiO_2$ (Figure 7) catalyst systems. In the case of subjecting the SnO_2-supported catalyst to only flowing methane, reduction resulted in a reduced surface V(IV) phase characterized by a weak and broad band at 855 cm^{-1} (cf. Figure 6). The original surface vanadium(V) oxide species was restored by flowing pure oxygen into the cell and reoxidizing the reduced surface vanadium phase (as evidenced by Figure 6).

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Table 1. Methane oxidation by air (CH_4/Air = 1.5/1) over supported metal oxide catalysts.

Catalysts	GHSV (L/kgcat.hr)	Temp. (°C)	Conv. (CH_4%)	STY(CH_2O) (g/kgcat.hr)	Selectivities(C-mol%)				Yield(CH_2O)[a] (%)
					CH_2O	C_2's	CO	CO_2	
SiO_2(F)[b]	70,000	630	0.05	24.3	100.0	-	-	-	0.05
2%MoO_3/(F)	70,000	630	0.08	37.9	100.0	-	-	-	0.08
1%V_2O_5/(F)	70,000	630	9.52	684.9	15.7	1.7	76.4	6.3	1.49
3%V_2O_5/(F)	140,000	580	6.86	1,022.0	16.6	0.2	76.8	6.3	1.14
5%V_2O_5/(F)	280,000	630	5.60	1,440.0	13.5	0.2	81.3	4.3	0.76
1%V_2O_5/3%MoO_3/(F)	70,000	630	8.47	675.2	16.6	2.0	73.5	7.9	1.41
TiO_2	70,000	630	1.55	17.6	2.3	-	94.0	3.6	0.03
3%TiO_2/(F)	70,000	630	0.31	27.6	17.8	-	71.1	11.1	0.05
1%V_2O_5/TiO_2[c]	70,000	630	0.82	14.0	3.3	1.2	73.0	22.5	0.03
1%V_2O_5/3%TiO_2/(F)	70,000	630	1.07	101.3	18.6	-	76.6	4.8	0.20
3%V_2O_5/3%TiO_2/(F)	70,000	630	2.30	150.0	12.5	-	82.2	5.3	0.30
SnO_2	70,000	530	8.10	2.3	0.1	-	8.9	90.4	0.05
3%SnO_2/(F)	70,000	630	1.60	8.8	1.1	13.7	8.7	76.3	0.02
1%V_2O_5/SnO_2[d]	70,000	530	7.60	-	-	-	13.4	83.6	-
1%V_2O_5/3%SnO_2/(F)	35,000	630	2.00	17.8	3.9	-	77.2	18.9	0.08

[a] Yield(CH_2O) = Conversion(CH_4%) × Selectivity(CH_2O%), [b] SiO_2(fumed cabosil), [c] TiO_2 as support, [d] SnO_2 as support.

CAPTIONS OF THE FIGURES

Figure 1. 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.

Figure 2. 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.

Figure 3. 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.

Figure 4. *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.

Figure 5. *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.

Figure 6. *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.

Figure 7. *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.

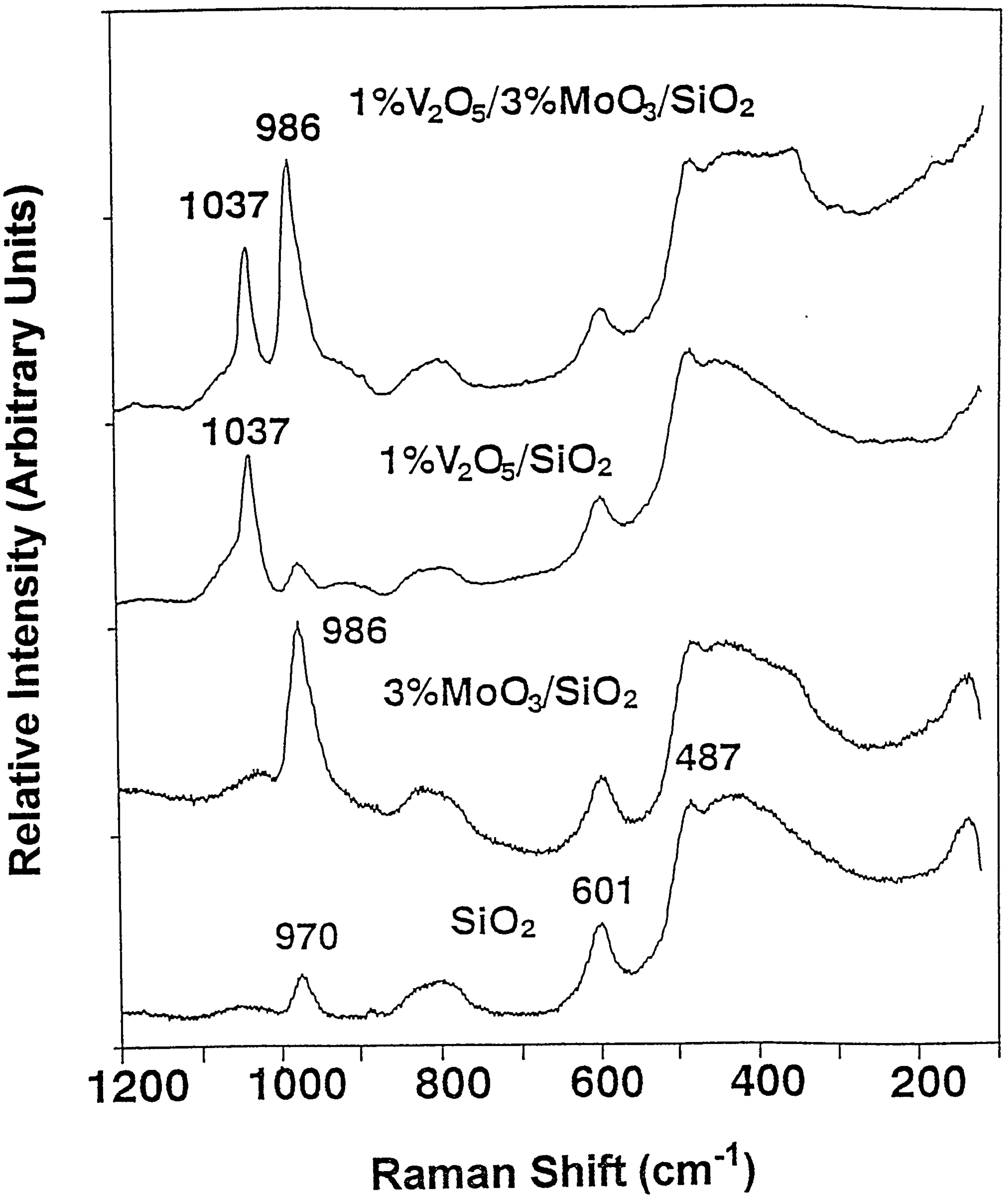
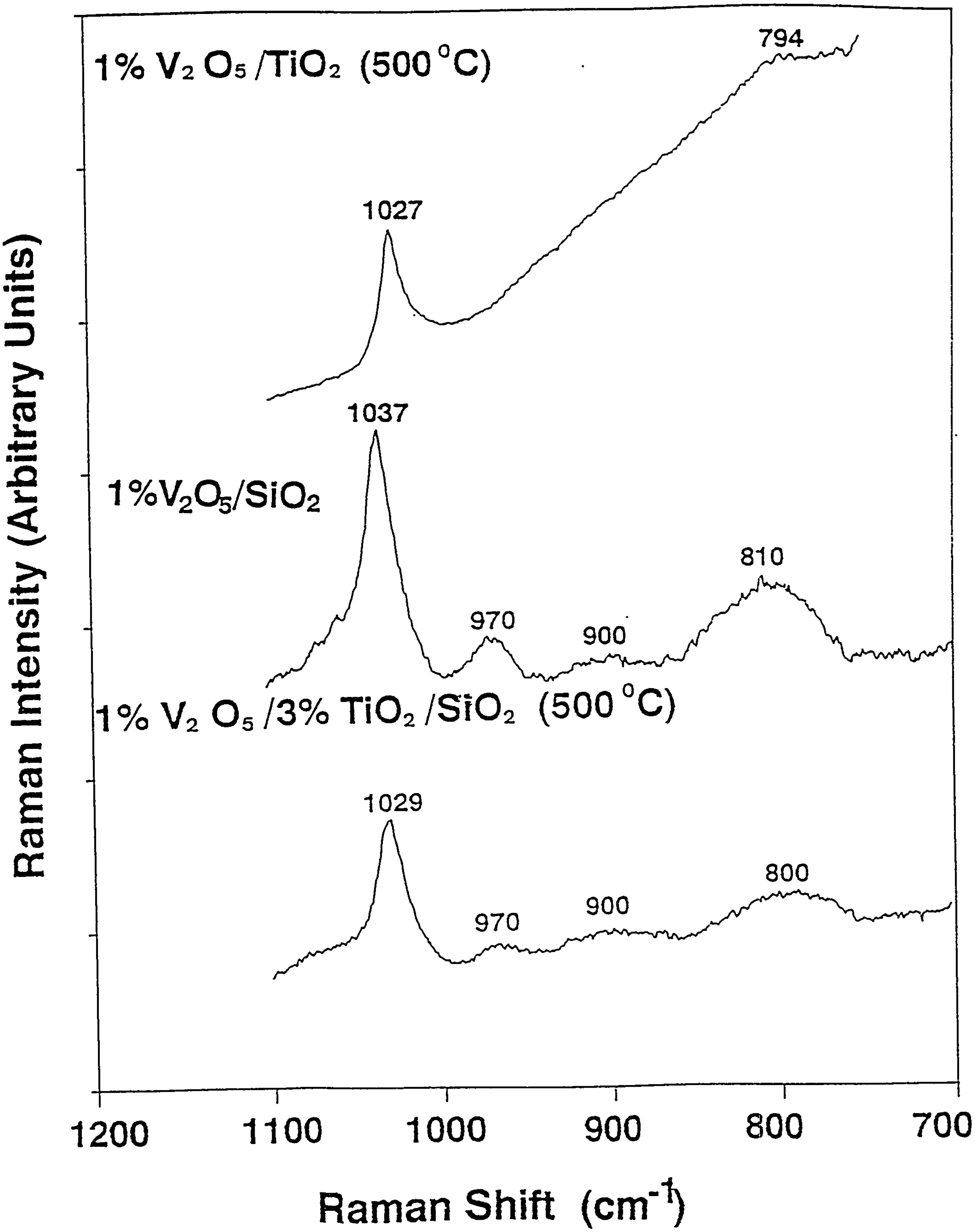

1%V_2O_5/3%MoO_3/SiO_2
986
1037
1037
1%V_2O_5/SiO_2
986
3%MoO_3/SiO_2
487
601
970
SiO_2
Relative Intensity (Arbitrary Units)
1200
1000
800
600
400
200
Raman Shift (cm^{-1})

FIGURE 1



1% V2 O5 /TiO2 (500 °C)
794
1027
1037
1%V2O5/SiO2
810
970
900
1% V2 O5 /3% TiO2 /SiO2 (500 °C)
1029
800
970
900
Raman Intensity (Arbitrary Units)
1200
1100
1000
900
800
700
Raman Shift (cm-1)

FIGURE 2

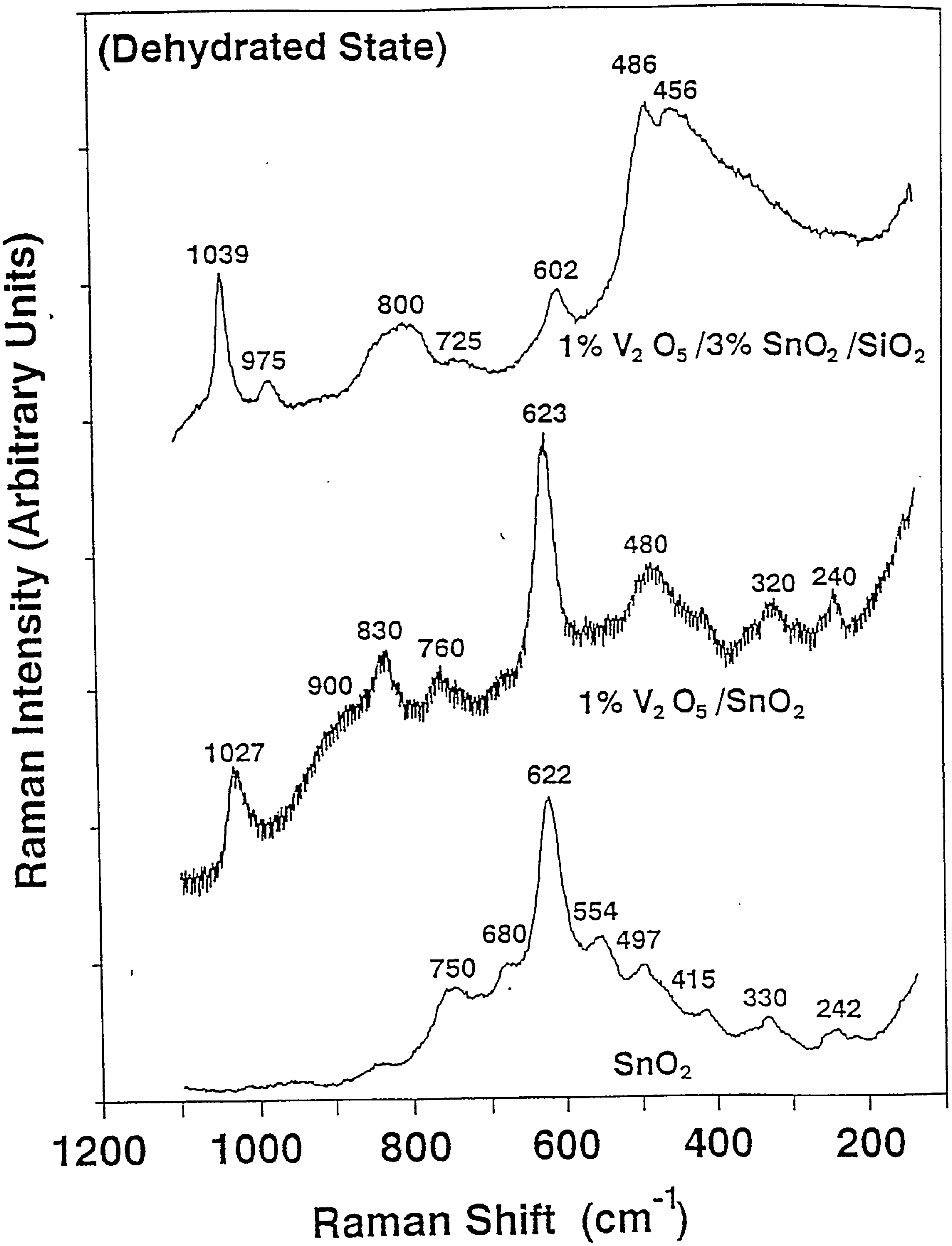

(Dehydrated State)
486
456
1039
602
800
975
725
1% V_2O_5 /3% SnO_2 /SiO_2
623
480
320
240
830
760
900
1% V_2O_5 /SnO_2
1027
622
554
680
497
750
415
330
242
SnO_2
Raman Intensity (Arbitrary Units)
1200
1000
800
600
400
200
Raman Shift (cm^{-1})

FIGURE 3

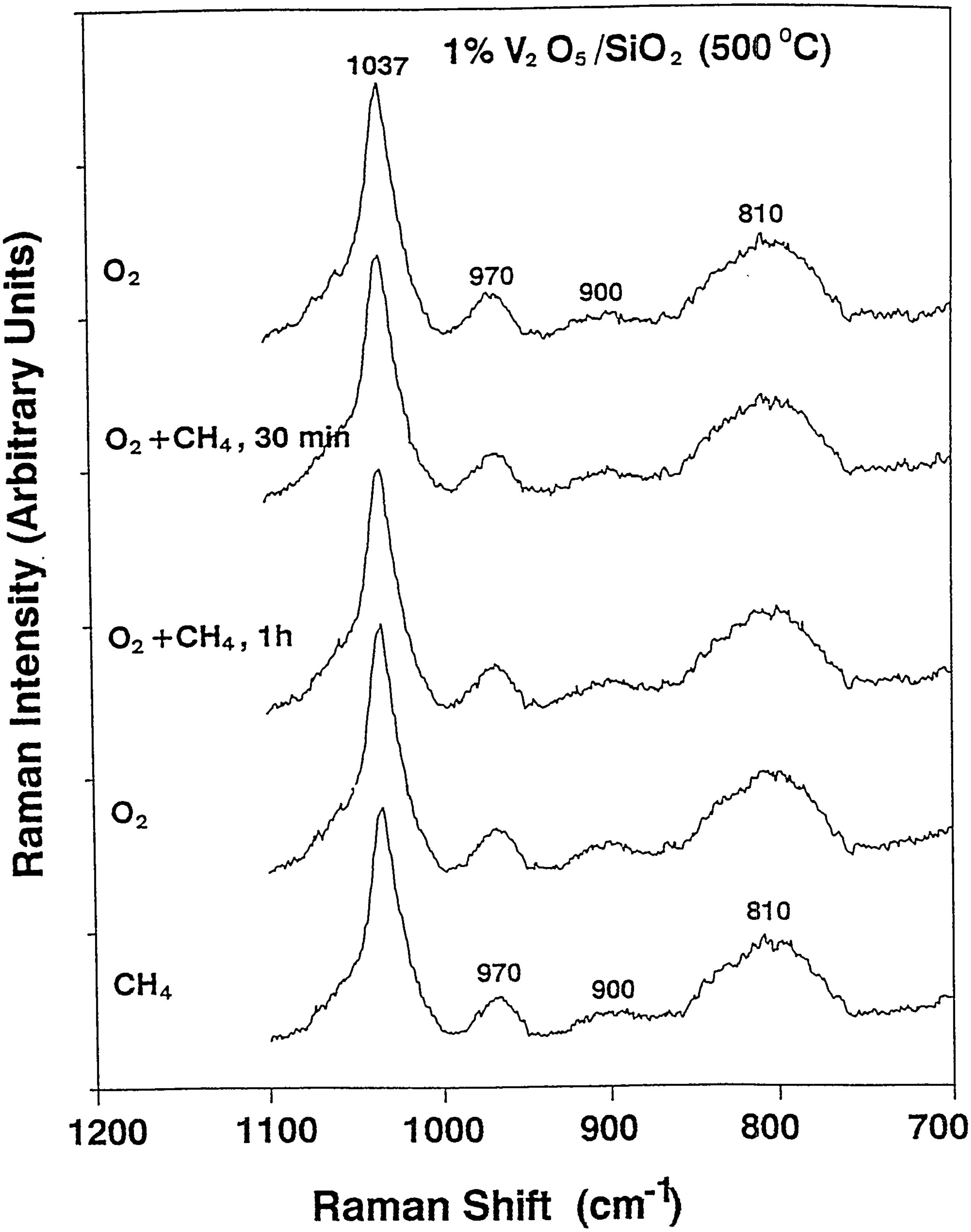
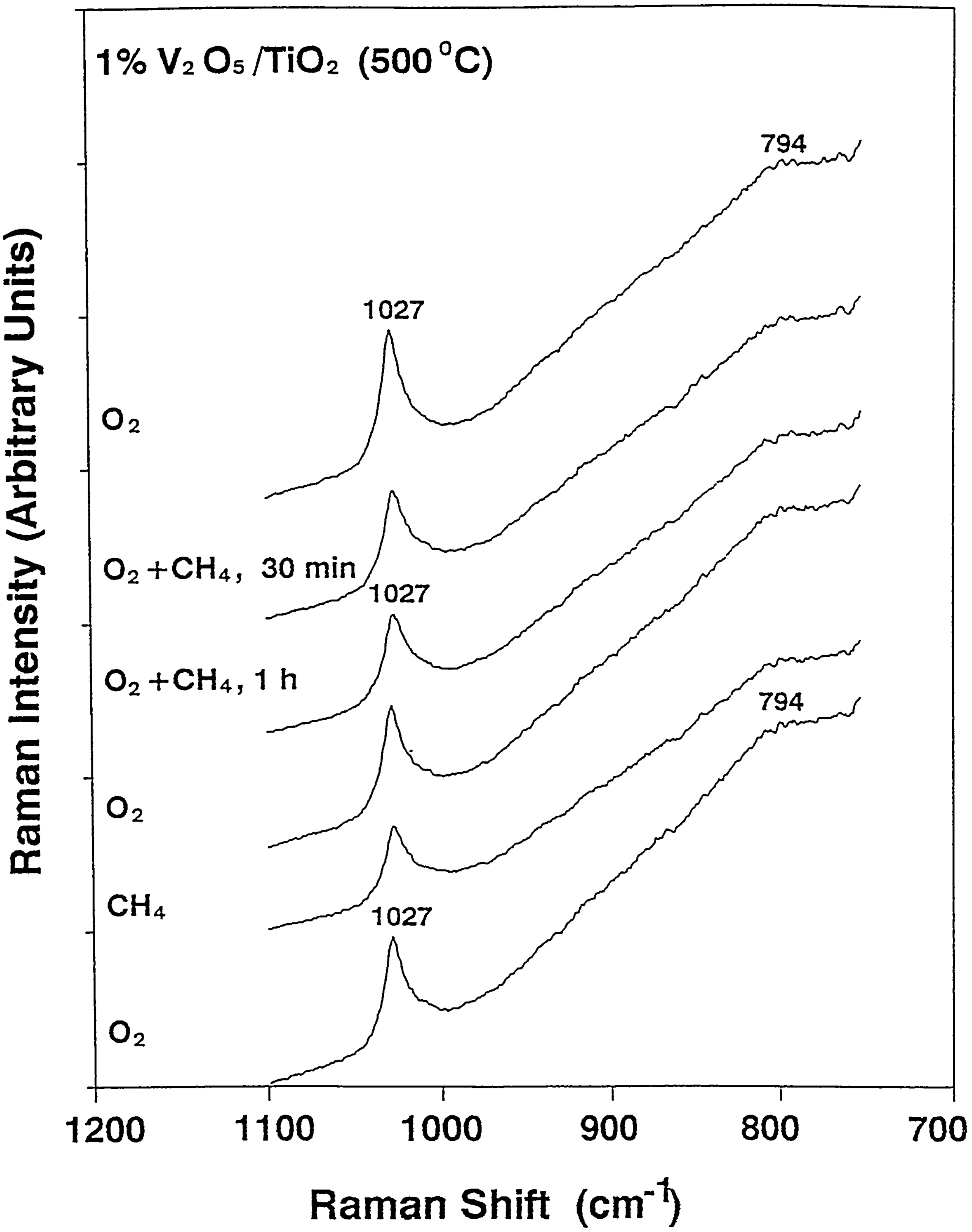

1% V_2O_5/SiO_2 (500 °C)
1037
810
970
900
O_2
O_2 +CH_4, 30 min
O_2 +CH_4, 1h
O_2
CH_4
810
970
900
Raman Intensity (Arbitrary Units)
1200
1100
1000
900
800
700
Raman Shift (cm^{-1})

FIGURE 4



1% V2O5/TiO2 (500 °C)
794
1027
O2
O2 +CH4, 30 min
1027
O2 +CH4, 1 h
O2
794
CH4
1027
O2
Raman Intensity (Arbitrary Units)
1200
1100
1000
900
800
700
Raman Shift (cm-1)

FIGURE 5

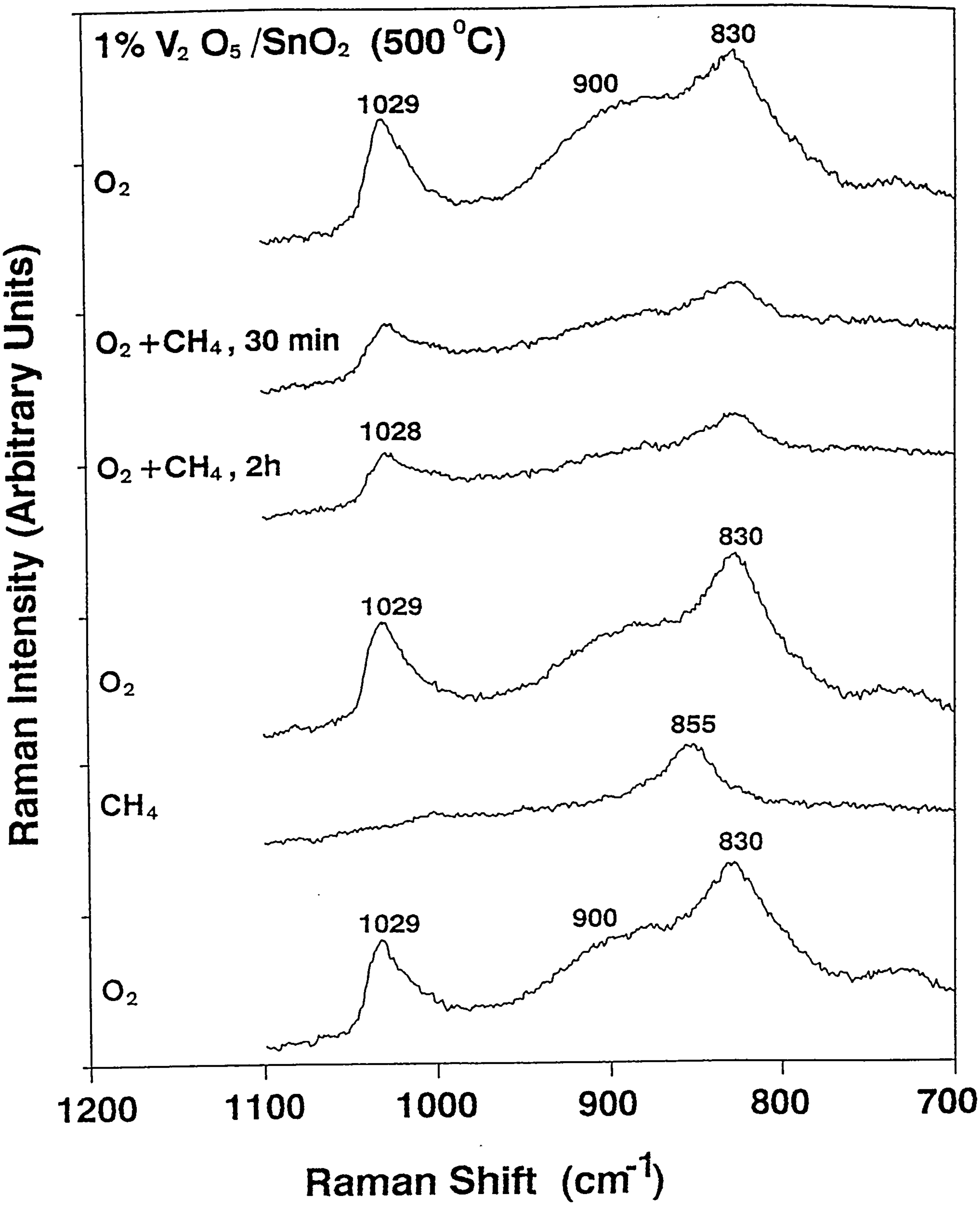

1% V₂ O₅ /SnO₂ (500 °C)
O₂
1029
900
830
O₂ +CH₄, 30 min
O₂ +CH₄, 2h
1028
O₂
1029
830
CH₄
855
O₂
1029
900
830
Raman Intensity (Arbitrary Units)
1200
1100
1000
900
800
700
Raman Shift (cm⁻¹)

FIGURE 6

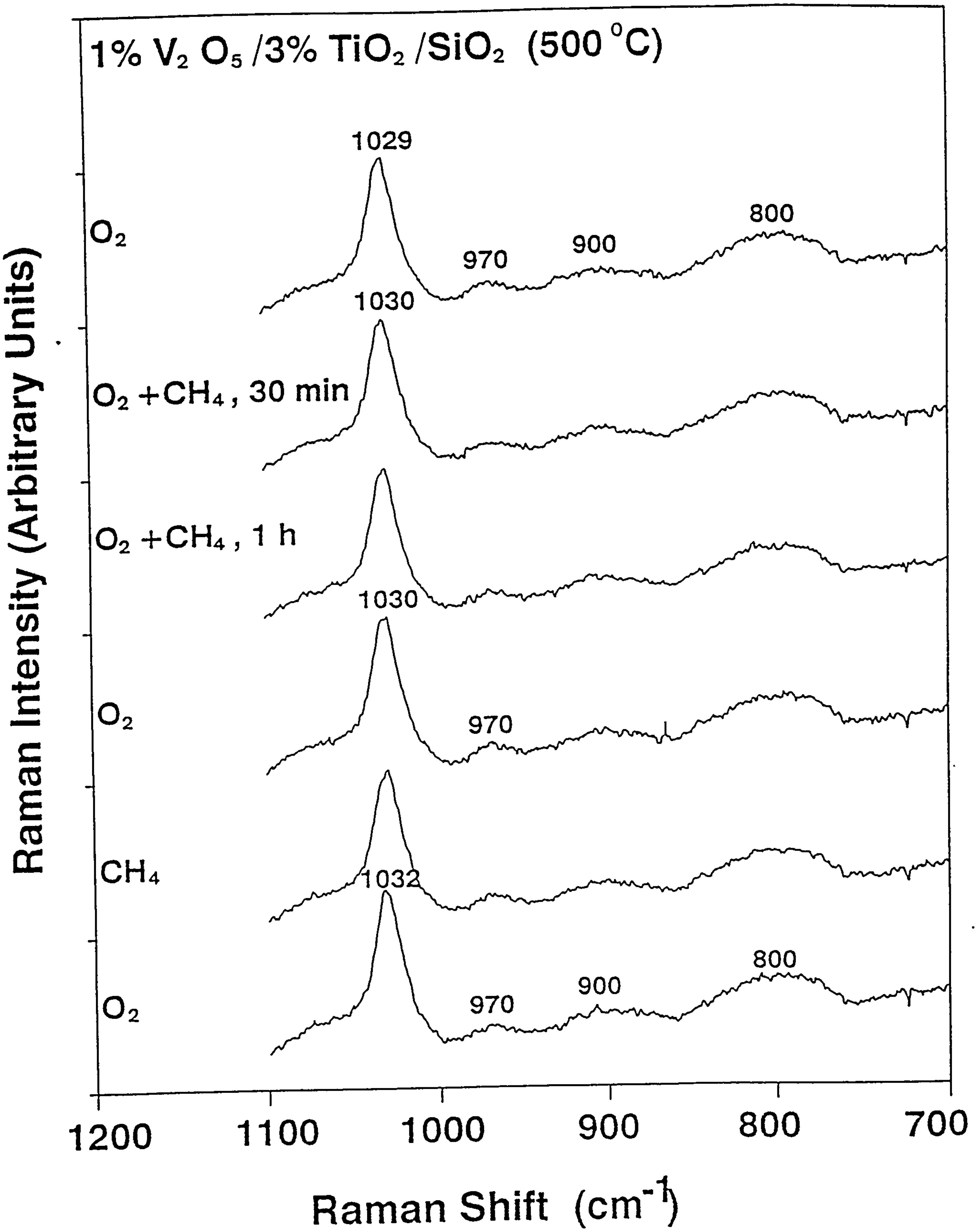

1% V_2O_5/3% TiO_2/SiO_2 (500 °C)
Raman Intensity (Arbitrary Units)
O_2
1029
970
900
800
O_2 + CH_4, 30 min
1030
O_2 + CH_4, 1 h
1030
O_2
970
CH_4
1032
O_2
970
900
800
1200
1100
1000
900
800
700
Raman Shift (cm^{-1})

FIGURE 7