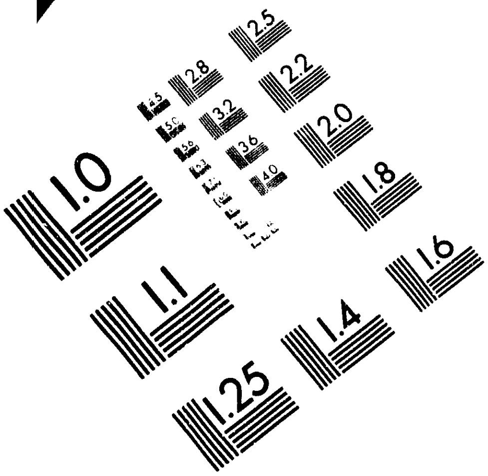

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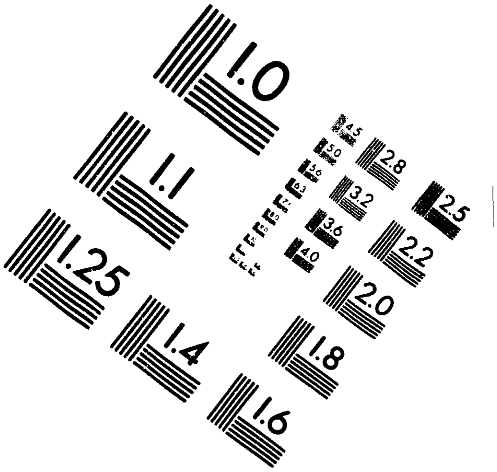

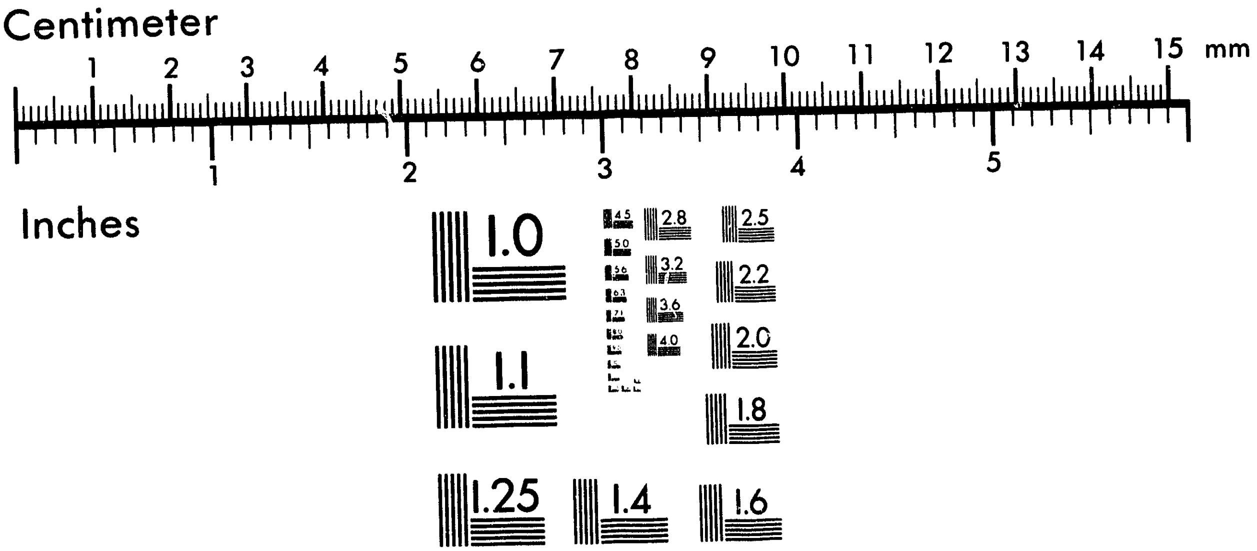

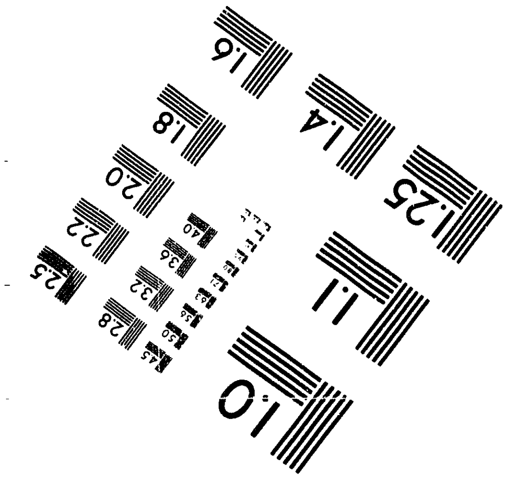

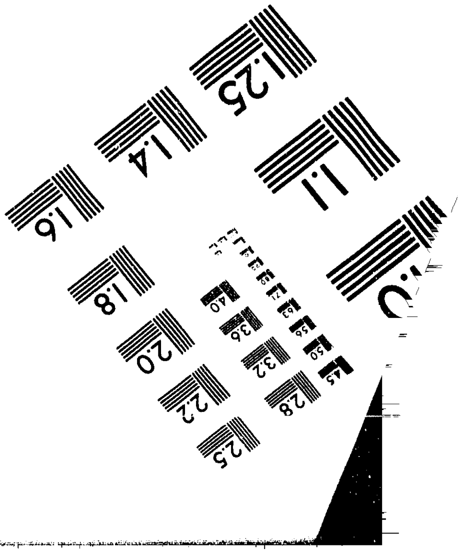

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SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

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SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

DISCLAIMER

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

Sulfate anion was used to modify the surface basicity of 1 wt% Sr/La_2O_3, and catalytic tests were carried out to probe the selective oxidation of methane to C_2 coupling products over these catalysts. Over a range of reaction temperatures of 500-700°C, most of the catalytic tests were carried out with a 1 wt% SO_4^{2-}/1 wt% Sr/La_2O_3 with a CH_4/air = 1/1 reactant mixture at 1 atm and with a gas hourly space velocity (GHSV) = 70,000 ℓ/kg catal/hr. The sulfated catalyst showed the largest improved catalytic effect at 500°C. Compared to the activity of the nonsulfated Sr/La_2O_3, the sulfated catalyst resulted in enhancement of the methane conversion, the C_2 selectivity, and the yield of C_2 products by factors of 1.7-2.0, 1.5-1.9, and 2.2-3.9, respectively.

At higher temperatures, the promoting effect of sulfate decreased, and at 650-700°C the sulfated and nonsulfated catalysts showed the same activity parameters. Subsequently decreasing the temperature from 700 to 500°C, the effect of sulfate was not detectable. It is probable that the sulfate was removed from the catalyst at higher temperatures (>600°C), especially when a reducing environment was produced because of the high oxygen conversion (>90%). Therefore, the originally sulfated catalyst, after testing at high temperatures, acted as a nonsulfated catalyst. However, it is demonstrated that an improved catalyst for selective oxidation of methane was produced by surface sulfate doping for utilization at milder reaction temperatures at and below 550°C.

The effect of sulfate content was studied at 500°C, CH_4/air = 1/1, and GHSV = 70,000 ℓ/kg catal/hr. From the catalysts containing 0.5, 1.0, 2.0, or 4.0 wt% SO_4^{2-} on Sr/La_2O_3, the 1.0 wt% $SO_4^{2-}/Sr/La_2O_3$ catalyst resulted in the largest activity in CH_4 conversion, C_2 selectivity, and C_2 yield. All of the sulfated catalysts exhibited higher activity parameters at 500°C than the nonsulfated Sr/La_2O_3.

In situ laser Raman spectroscopy was used to characterize the surface of sulfated and nonsulfated catalysts. Preliminary results indicate that the sulfate anion preferentially bonded to the Sr rather than to the La ions. The promoting effect of the acidic sulfate on the catalytic activity of basic Sr/La_2O_3 seems to be due to the inhibition of carbonate formation on the surface Sr ions.

The effects of total pressure and CH_4/O_2 ratio were studied at 600°C. At CH_4/O_2 = 5/1, using pure O_2 instead of air, the conversion of CH_4 and the yield of C_2 products increased only slightly, but the ethane and ethene selectivities showed larger increases at the expenses of CO and CO_2 selectivities. Upon changing the CH_4/O_2 ratio from 10/1 to 5/1 at 600°C, the ethene selectivity increased by a factor of *ca.* 4, while the CO selectivity decreased by a factor of *ca.* 3, which was not followed by the increase of CO_2. These data show that the formation of ethane and CO_2 are primary product, while ethylene and CO form *via* secondary reactions, in accordance with literature reports.

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_2 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, 1 atm total pressure). All the investigated process are catalytic, aiming at minimizing the difficult-to-control gas phase oxidation reactions.

$$2CH_4 + 1/2O_2 \rightleftarrows C_2H_6 + H_2O \tag{1}$$

$$2CH_4 + O_2 \rightleftarrows C_2H_4 + 2H_2O \tag{2}$$

$$2CH_4 + 2CO_2 \rightleftarrows C_2H_4 + 2CO + 2H_2O \tag{3}$$

$$CH_4 + O_2 \rightleftarrows CH_2O + H_2O \tag{4}$$

$$CH_4 + 1/2O_2 \rightleftarrows CH_3OH \tag{5}$$

Oxide catalysts are chosen for this research that are surface doped with small amount of acidic dopants. It is thought that, for example, the very basic Sr/La_2O_3 catalyst, which is active in the formations of methyl radical and therefore C_2 products, can be doped with some Lewis acidic oxides or other groups to increase further its activity and selectivity to C_2 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_2 Products Over Promoted Sr/La_2O_3 Catalysts.

Task 2. Selective Methane Oxidation to Oxygenates.

Task 3. Catalyst Characterization and Optimization.

Task 1 deals with the preparation, testing, and optimization of acidic promoted lanthana-based catalysts for the synthesis of C_2 hydrocarbons. 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 1 and 2.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

RESEARCH PROGRESS

PART 1. Oxidative Coupling of Methane Over Sulfate-Doped Sr/La_2O_3 Catalysts

1. Introduction

Methane is a significant component of natural gas. It is desirable to convert it to higher molecular weight products for transportation, storage, and for utilization as chemical feedstock. Although this desire is not a new topic in research, its importance increased significantly during the last decade. After the first publication concerning the catalytic coupling of methane in 1982 [1], many academic and industrial laboratories around the world have made intensive efforts to find commercial catalysts for methane conversion. Excellent reviews have appeared on this subject [2-11], and more than a hundred catalysts have been described to show more or less activity for oxidative transformation of CH_4. However, only a few of them are worthwhile to study in more detail.

The catalysts based on rare-earth oxides are among the most promising as they simultaneously present good selectivity to C_{2+} products, high activity, good stability at reaction conditions, and a relatively low cost. The strontium-doped La_2O_3 is one of the best known catalysts [12-14], which results in even a better catalytic performance than the pure oxide.

The catalytic features of the very basic Sr/La_2O_3 can be increased potentially by acidic doping, since it is believed that the formation of some surface carbonates is at least partially responsible for deactivation under some reaction conditions. On the analogy of earlier findings that sulfate ion strongly enhances the acidic properties of iron oxide [15], as well as alumina and titania [16], sulfate is used in our present study as an acidic surface dopant to improve the catalytic performance of the 1 wt% Sr/La_2O_3 catalyst.

2. Experimental

The 1 wt% Sr/La_2O_3 catalyst with a surface area of 6.5 m^2/g was obtained from Amoco Oil Co. under their Natural Gas University Research Program. The sulfated Sr/La_2O_3 catalysts were produced by the incipient wetness impregnation technique. The appropriate amount of $(NH_4)_2SO_4$ was dissolved in deionized water, the measured quantity of Sr/La_2O_3 was added, and the slurry was continuously stirred with a magnetic stirrer until dryness was achieved. This was followed by drying the solid overnight at 120°C and calcination in air at 600°C for 6 hr. Prior to catalytic testing, the samples were activated *in situ* under air (or O_2) flow at 500°C for 1 hr. The gases used in this study were zero grade purity and were used without further purification

Catalytic testing was carried out in the temperature range of 500-700°C in a fixed-bed continuous-flow 9 mm OD (7 mm ID) quartz reactor using 0.1000 g of catalyst. Reaction mixtures of CH_4/air = 1/1 and CH_4/O_2 = 5/1 and 10/1 were used at ambient pressure. The principal products analyzed by on-line sampling using gas chromatography were CO_2, C_2 (C_2H_6 + C_2H_4), C_3 (C_3H_8 + C_3H_6), CO, and H_2O. The carbon mass balance during the catalytic reaction was better than 95%.

The *in situ* laser Raman experiments were carried out in Dr. Israel E. Wachs' laboratory in Sinclair Lab. at Lehigh Unversity.

3. Results and Discussion

3.1. Effect of Temperature

The effect of temperature on the catalytic activity was studied with the 1 wt% SO_4^{2-} /1 wt% Sr/La_2O_3 catalyst. This sulfate-promoted catalyst, compared to the nonsulfated one, showed a large increase (by 75%) for methane conversion at 500°C **(Fig. 1)**. The extent of the promoting effect decreased with increasing temperature (T), and practically no effect after T >650°C was observed. Upon decreasing the temperature after the 700°C experiment, the former promoting effect was not observable even at 500°C. The C_{2+} selectivity **(Fig. 2)** and C_{2+} yield **(Fig. 3)** varied in a similar way. The % yield is defined as the product of the total C_2 selectivity [mol% ethane + ethene] and the total conversion of methane [mol%]. The presence of the sulfate anion caused a large promoting effect at 500°C, where the C_{2+} selectivity and C_{2+} yield increased from 32.2 to 45.1% and from 3.4 to 8.0%, respectively. However, the promotion irreversibly disappeared after T >650°C.

A new pretreatment of the tested catalyst in air at 500°C for one hour could not restore the former enhanced activity obtained at 500°C. One possible explanation of this instability is the high O_2 conversion (>85-90%) at the higher reaction temperatures, resulting in a reducing environment that transformed the sulfate to a volatile component. This would result in the loss of the acidic surface dopant.

3.2. Effect of Sulfate Concentration

The effect of sulfate content was examined at 500°C, CH_4/air = 1/1, $p_{(total)}$ = 1 atm, and GHSV = 70,000 ℓ/kg catal/hr. The content of sulfate added to the 1 wt% Sr/La_2O_3 varied as 0, 0.5, 1.0, 2.0 and 4.0 wt% of the total weight of catalyst. The 1 wt% SO_4^{2-}/1 wt% Sr/La_2O_3 showed the largest effects on the methane conversion **(Fig. 4)**, C_2 selectivity **(Fig. 5)**, and yield of C_2 products **(Fig. 6)**.

A working hypothesis is that the basic Sr/La_2O_3 promotes the formation of surface carbonate, which decreases the activity of the catalyst in oxidative methane coupling to C_2 products. The first step in the activation of CH_4, resulting in the formation of $\cdot CH_3$ radicals on the surface, probably needs negatively charged dioxygen [17,18] (designated as O_{II}) or monooxygen [19,20] species (designated as O_I), as shown in Equations 6-8.

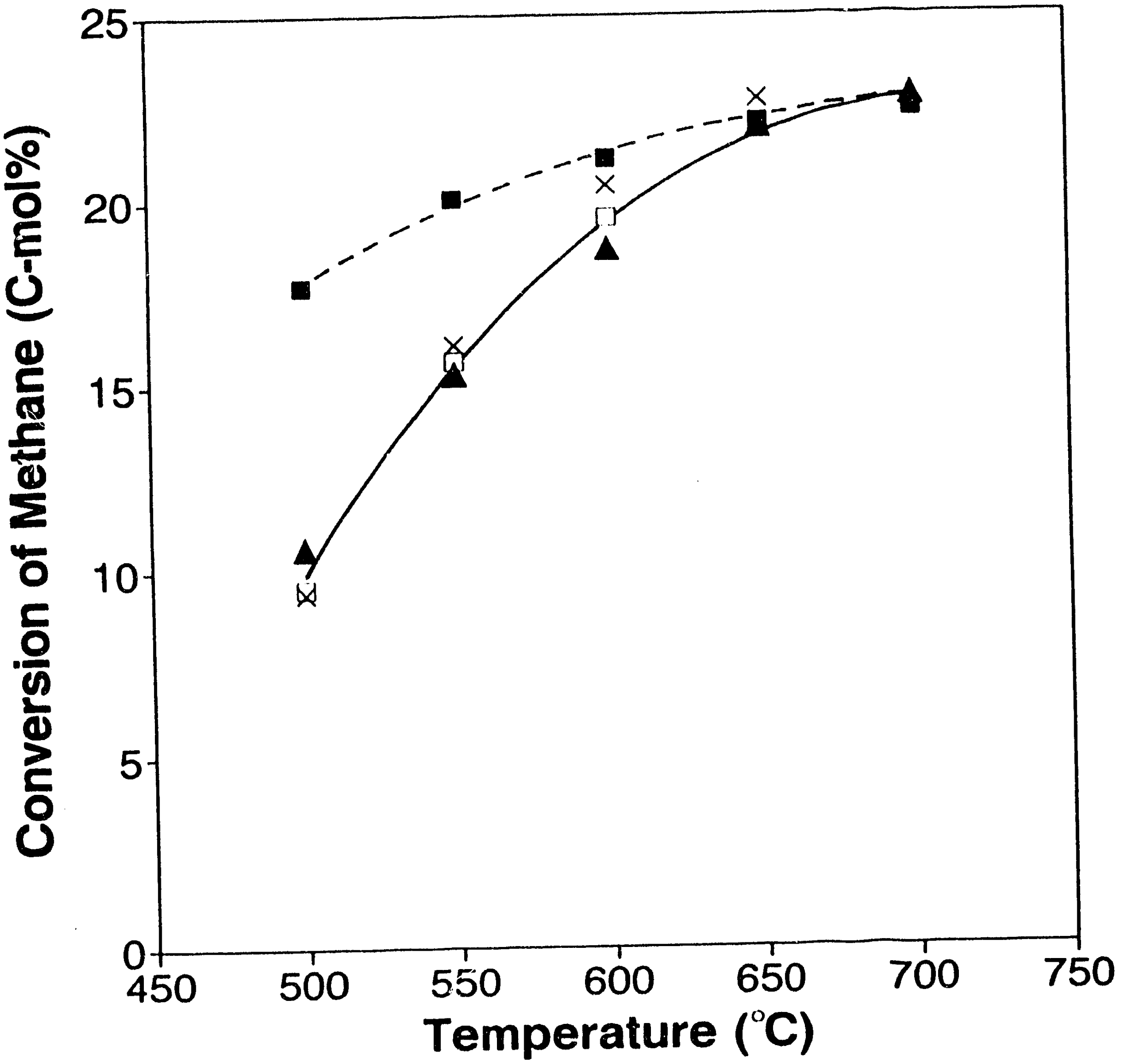

FIGURE 1

Effect of temperature on methane conversion in the range of 500-700°C. (a) 1 wt% Sr/La_2O_3 with increasing reaction temperature (▲), and then subsequently decreasing the reaction temperature stepwise from 700°C to 500°C (x); (b) 1 wt% SO_4^{2-}/1 wt% Sr/La_2O_3 with stepwise increasing reaction temperature (■), and then subsequent systematically decreasing the reaction temperature (□). Weight of catalyst = 0.1000 g; reactant mixture of CH_4/air = 1/1; total pressure = 1 atm; and GHSV = 70,000 ℓ/kg catal/hr.

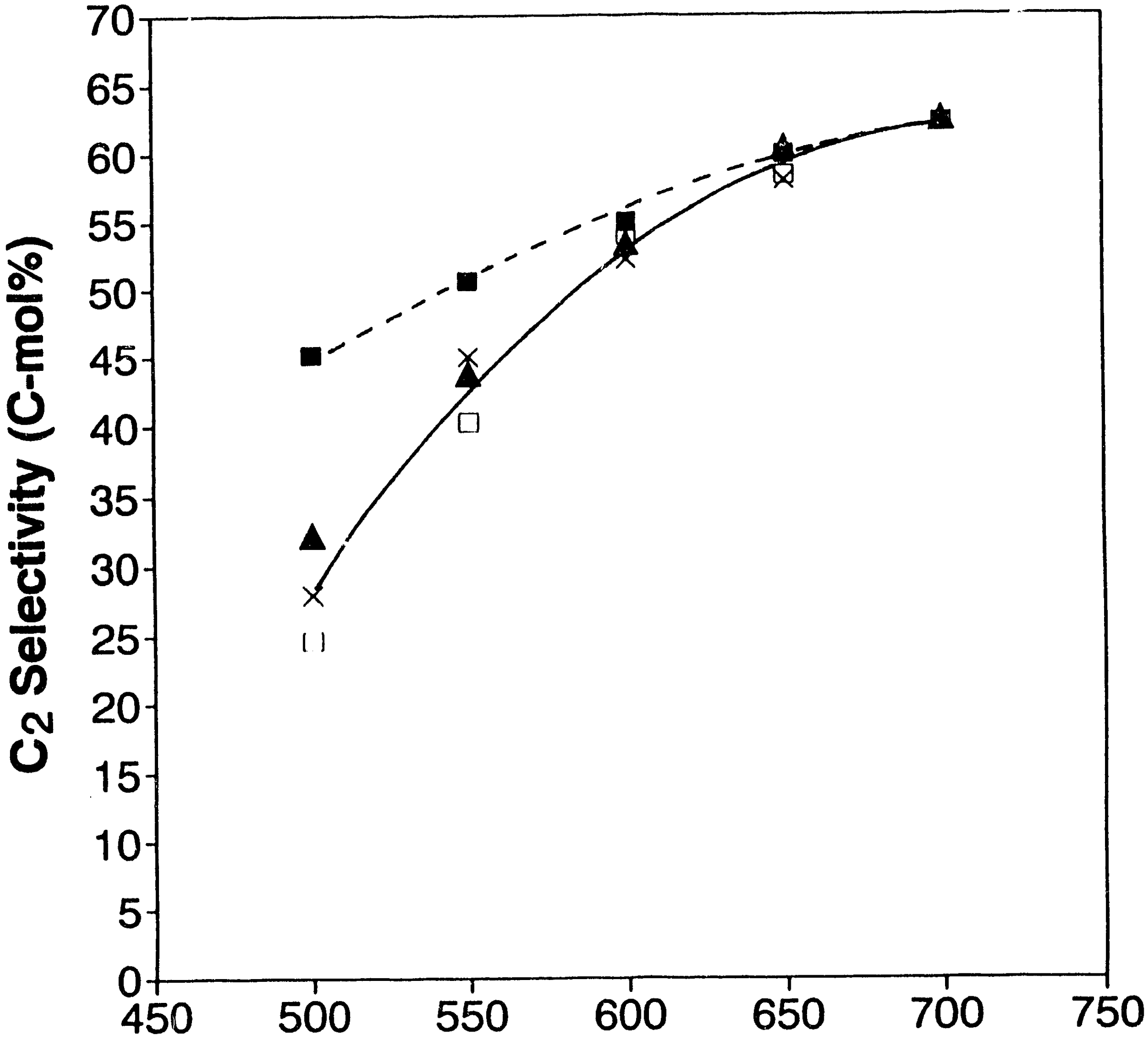

FIGURE 2

Effect of temperature on C_{2+} selectivity in the range of 500-700°C. (a) 1 wt% Sr/La_2O_3 catalyst with increasing reaction temperature (▲), and then with decreasing temperature (x); (b) 1 wt% $SO_4^{2-}/1$ wt% Sr/La_2O_3 catalyst with increasing temperature (■), followed by decreasing temperature (□). The experimental parameters are given in Fig. 1.

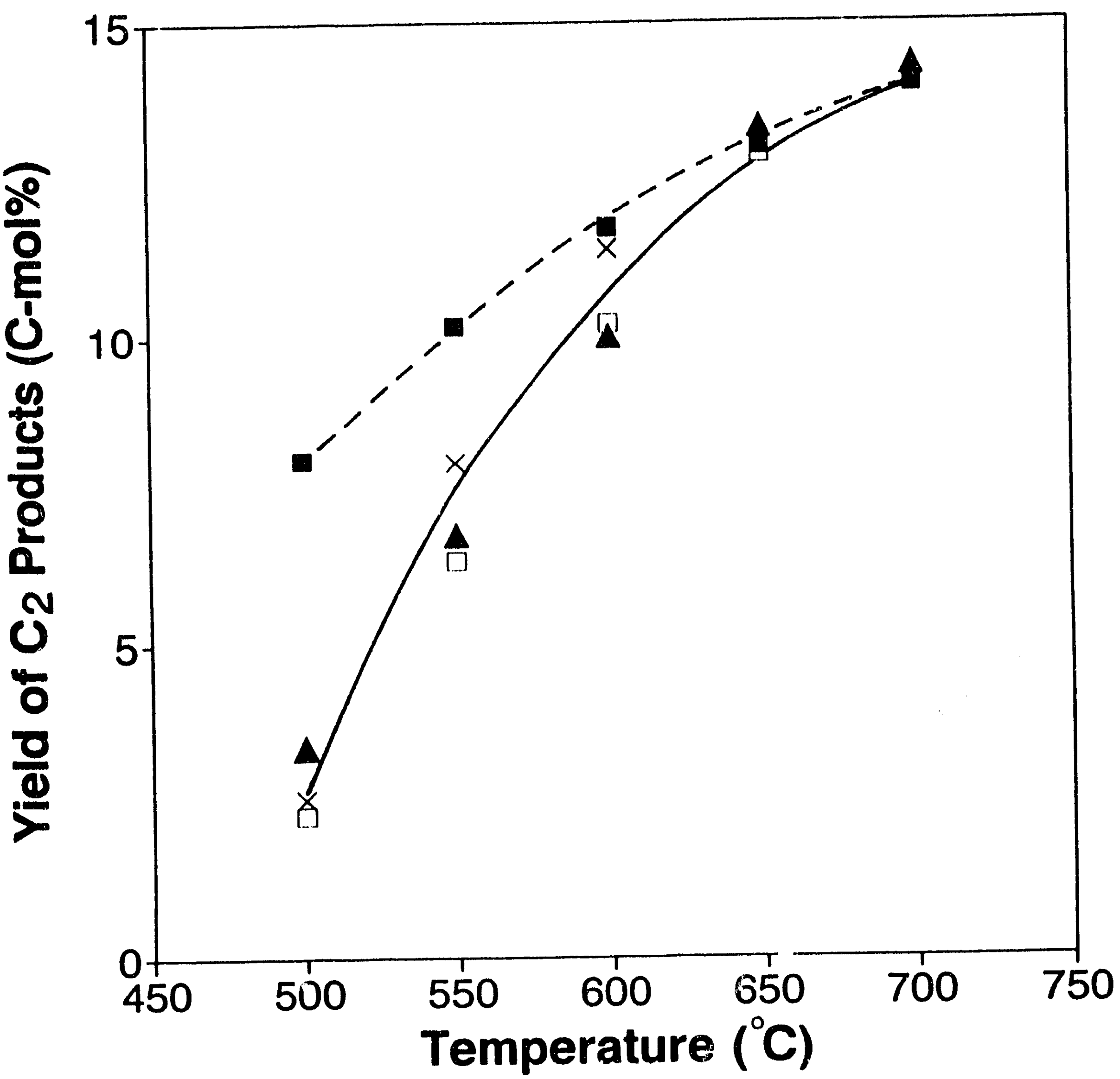

FIGURE 3

Effect of temperature on C_{2+} yield in the range of 500-700°C. (a) 1 wt% Sr/La_2O_3 with increasing reaction temperature (▲), and then with decreasing reaction temperature (x); (b) 1 wt% SO_4^{2-}/1 wt% Sr/La_2O_3 with increasing reaction temperature (■), and then with decreasing temperature (□). The experimental parameters are given in Fig. 1.

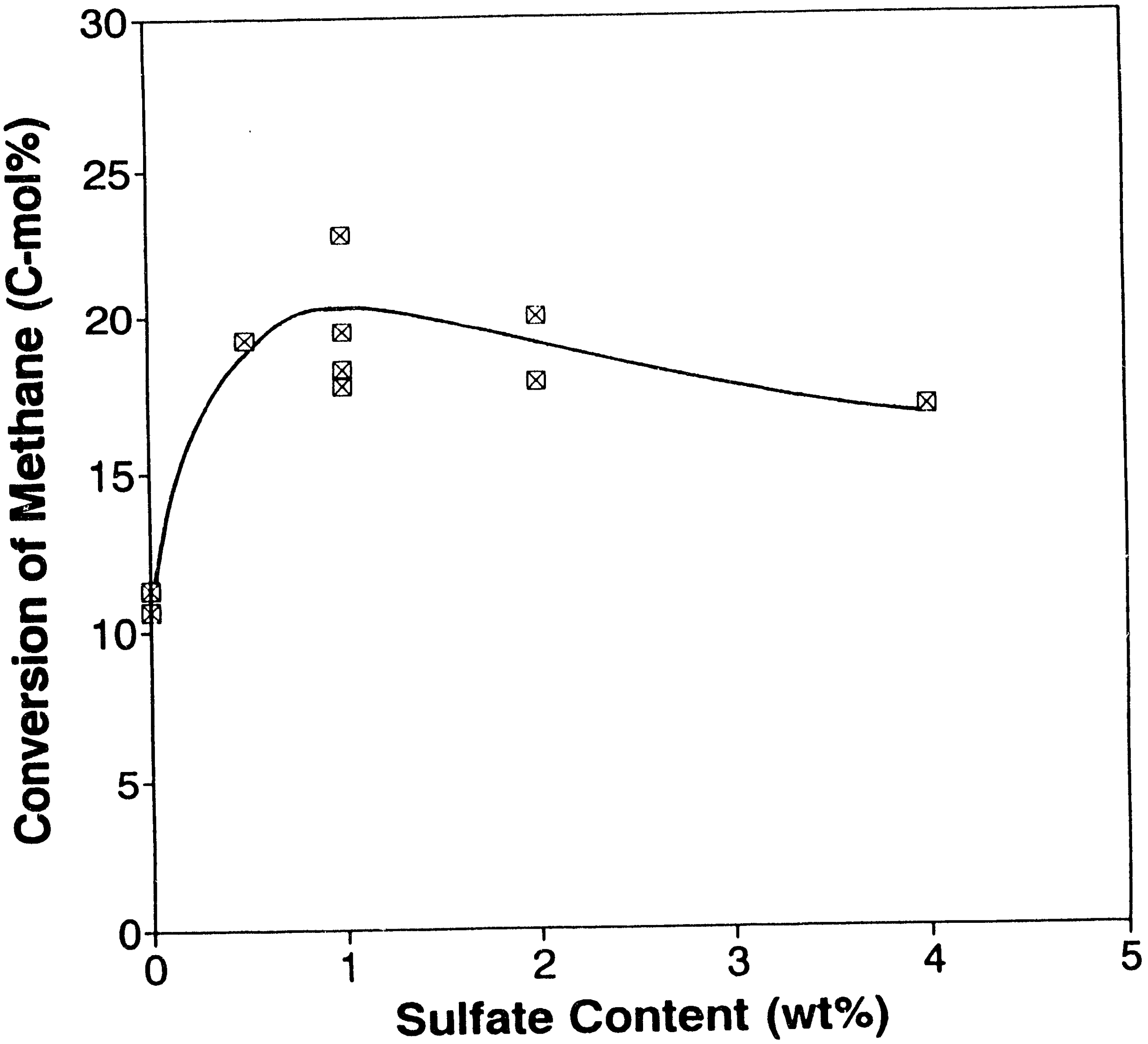

FIGURE 4

Effect of sulfate content on methane conversion at 500°C (☒) over the 1 wt% Sr/La_2O_3 catalyst (0.1000 g) with a CH_4/air = 1/1 reaction mixture at a total pressure of 1 atm and GHSV = 70,000 ℓ/kg catal/hr.

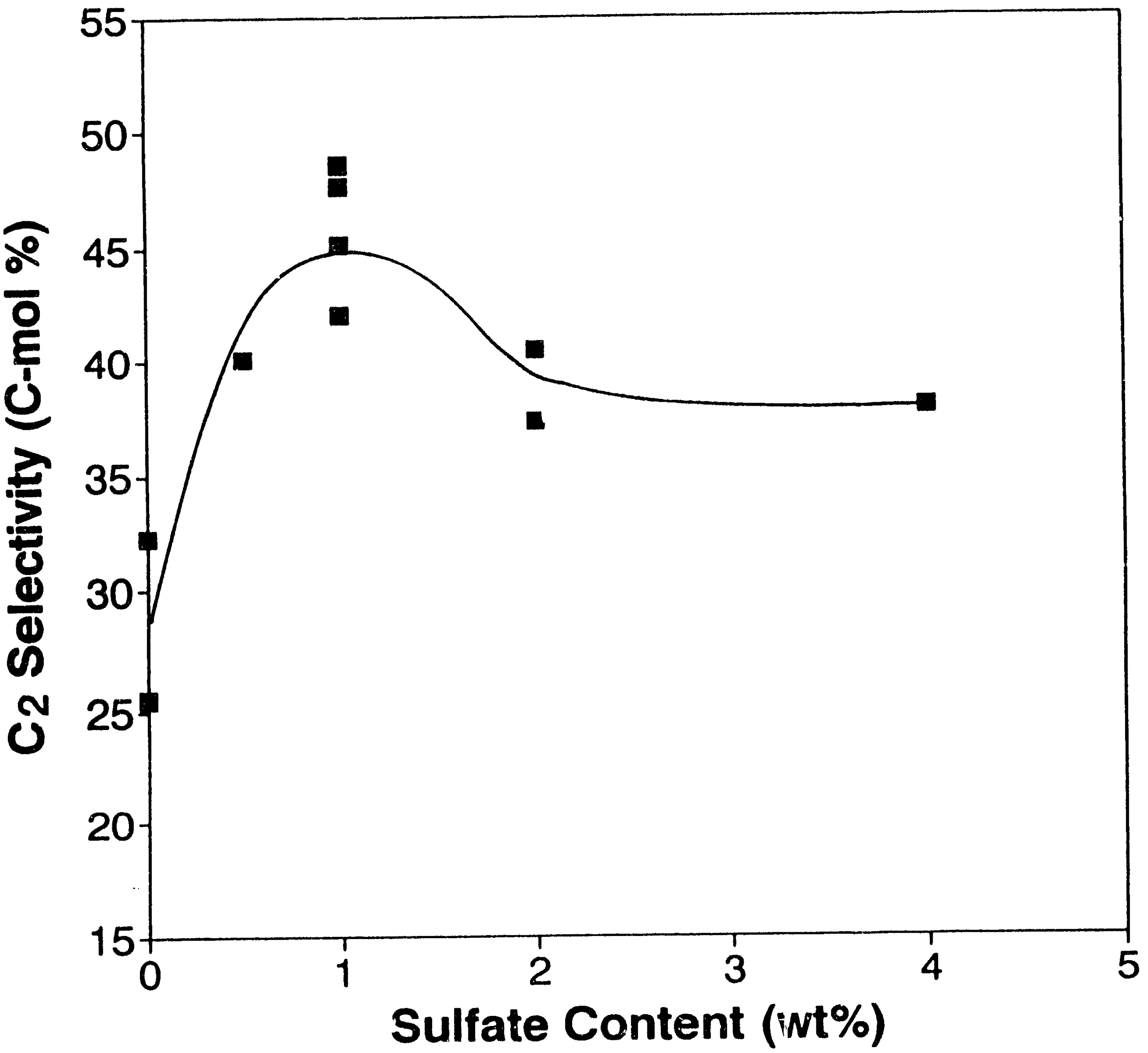

FIGURE 5

Effect of sulfate content on the C_{2+} selectivity at 500°C (■). The experimental parameters are given in Fig. 4.

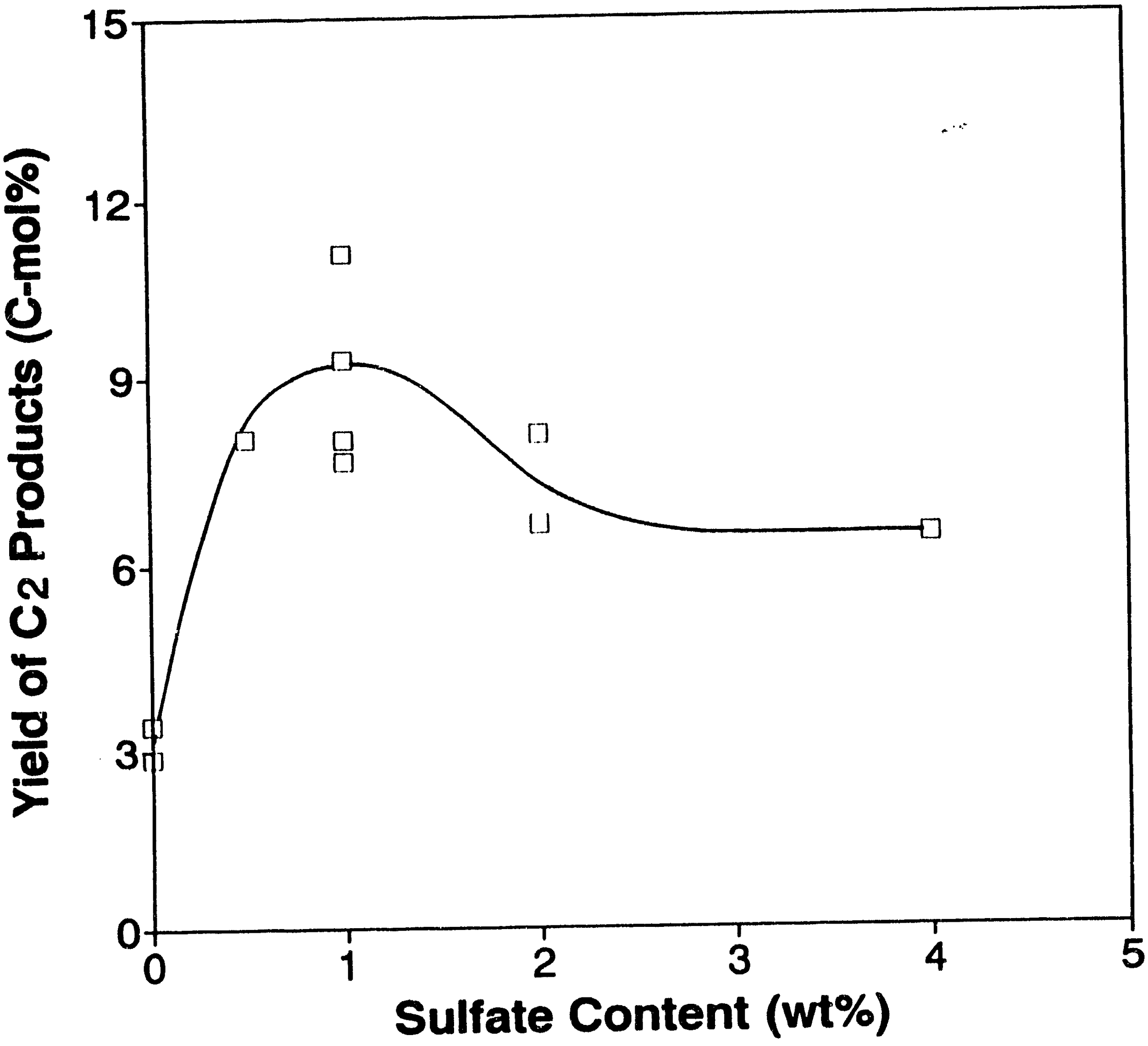

FIGURE 6

Effect of sulfate content on the C_{2+} yield at 500°C (□). The experimental parameters are given in Fig. 4.

$$CH_4 + O_2^- \rightleftarrows \bullet CH_3 + HO_2^- \qquad (6)$$

$$CH_4 + O_2^{2-} \rightleftarrows \bullet CH_3 + HO_2^{2-} \qquad (7)$$

$$CH_4 + O^- \rightleftarrows \bullet CH_3 + HO^- \qquad (8)$$

Carbon dioxide, as a by-product of methane oxidative coupling, may react with these oxygen species by the formation of surface carbonate, thus decreasing the number of active sites. It is probable that the doping of La_2O_3 with Sr changes the relative amounts of these active centers. It is possible that Sr as dopant increases the relative concentration of monoatomic surface species at the expense of diatomic ones resulting in larger C_2 selectivity. The poisoning effect of CO_2 on the monooxygen species should be smaller, hence the total methane conversion would also be larger.

The addition of sulfate to the Sr-doped La_2O_3 catalyst further increased the catalytic performance. The mechanistic effect of sulfate is not known at present. It may act on the surface (i) as an electron acceptor that decreases the electron density or/and the composition of the oxygen active sites, or/and (ii) as a simple blocking group that hinders the formation of poisoning surface carbonates.

Since the 1 wt% SO_4^{2-} content showed the largest promotional effect, and the sample with 0.5 wt% SO_4^{2-} exhibited somewhat higher activity and selectivity than the samples with 2.0 or 4.0 wt% SO_4^{2-}, it strongly suggests that the synergetic effect of sulfate is rather connected with Sr than La. Larger amounts of sulfate may block some active centers on both Sr and La. However, the desirable effect of sulfate in inhibiting the formation of poisoning carbonates should be larger than this undesirable blocking effect. This may be a reason why the 4 wt% SO_4^{2-}/1 wt% Sr/La_2O_3 showed still larger activity and selectivity than the nonsulfated 1 wt% Sr/La_2O_3.

3.3. Effect of Gas Composition

The effect of gas composition on the oxidative coupling of CH_4 to C_2 products was studied with 1 wt% Sr/La_2O_3 and 1 wt% SO_4^{2-}/1 wt%Sr/La_2O_3 at 600°C using pure oxygen instead of air (**Table 1**).

In the case of CH_4/air = 1/1, the CH_4/O_2 ratio was approximately 5/1. Using the same CH_4/O_2 ratio, but pure O_2 instead of air, the partial pressures of the reactant components were larger by a factor of 1.667. Although, the total conversion of CH_4 for the nonsulfated sample changed only slightly, the C_{2+} selectivity increased from 53.3 to 66.3 C-mol%, while the CO_x selectivity decreased from 45.9 to 33.2%. Very similar data were obtained for the sulfated catalyst (Table 1B). This may indicate that with CH_4/air, the formation of active oxygen species on the surface is fast enough at 600°C and at CH_4/O_2 = 5/1, but the formation of $\bullet CH_3$ radicals and subsequent recombination to C_2 products is slower compared with further reaction of oxygen species, i.e. before higher extent of burning to CO_x. In the case of pure oxygen (CH_4/O_2), there is no dilution by N_2 and the rate of recombination of $\bullet CH_3$ radicals relative to further oxidation might be faster, and this may be the reason why the yield of C_{2+} increased at the expence of the yield of CO_x.

TABLE 1

Effect of Gas Composition on the Oxidative Coupling of Methane (T=600°C)

(A) 1 wt% Sr/La_2O_3

Conditions	Conv. (%)		Product Selectivities (C-mol%)							Yield (%)	
	CH_4	O_2	CO_2	$C_2=$	C_2	C_3s	CO	C_{2+}	CO_x	C_{2+}	CO_x
CH_4:Air=1:1	18.7	78.7	34.5	23.8	29.6	0.77	11.4	53.4	45.9	10.0	8.58
CH_4:O_2= 5:1	19.2		28.3	30.1	36.2	0.49	4.9	66.3	33.2	12.7	6.37
CH_4:O_2=10:1	5.9		29.0	7.4	47.9	1.2	14.5	55.3	43.5	3.3	2.57

(B) 1 wt% SO_4^{2-}/1 wt% Sr/La_2O_3

CH_4:Air=1:1	21.2	87.9	35.9	23.6	30.1	0.9	9.5	53.7	45.4	11.4	9.62
CH_4:O_2= 5:1	18.3		30.0	26.6	38.4	0.5	4.6	65.0	34.6	11.9	6.33
CH_4:O_2=10:1	6.2		31.5	6.3	46.0	1.7	14.5	52.3	46.0	3.2	2.85

Experimental conditions: Temperature = 600°C; weight of catalyst = 0.1000 g; GHSV = 70,000 ℓ/kg catal/hr; $p_{(total)}$ = 1 atm.

Partial pressures:

(i)	CH_4:Air = 1:1	p(CH_4)	0.500 atm	(380.0 Torr)
		p(O_2)	0.100 atm	(76.0 Torr)
(ii)	CH_4:O_2 = 5:1	p(CH_4)	0.833 atm	(633.3 Torr)
		p(O_2)	0.167 atm	(126.7 Torr)
(iii)	CH_4:O_2 = 10:1	p(CH_4)	0.909 atm	(690.9 Torr)
		p(O_2)	0.091 atm	(69.1 Torr)

Note: The partial pressures of CH_4 and O_2 were 1.667 times larger in experiment (ii) than in experiment (i).

Increasing the CH_4/O_2 ratio from 5/1 to 10/1 resulted in a decrease of the total CH_4 conversion from 19.2 to 5.9% for the 1 wt% Sr/La_2O_3 catalyst and from 18.3 to 6.2 % over the 1 wt% SO_4^{2-}-promoted 1 wt% Sr/La_2O_3 catalyst. According to these data, it is not surprising that the C_{2+} selectivity decreased while the CO_x selectivity increased. Although the yields of both C_{2+} and CO_x decreased at $CH_4/O_2 = 10/1$ (Table 1), the decrease was much larger for the C_2 products than for CO_x. It is probable that with decreasing oxygen pressure the concentration of monooxygen species (O_I) decreased much more than that of the dioxygen species (O_{II}). If O_I is responsible for the formation of $\bullet CH_3$ radicals and O_{II} for the deeper oxidation, the larger decrease in the yield of C_{2+} products is explained.

PART 2. *In Situ* Raman Study of Methane Activation over the Sr/La_2O_3 Catalysts

In situ laser Raman spectroscopy was used for the first time on these Sr/La_2O_3 systems to explore the mechanism for the promoting effect of the sulfate on the Sr/La_2O_3 catalysts for methane activation. It is known that the surface carbonates play important roles for the partial oxidation of methane over strong basic metal oxide catalysts [21, 22]. It has been reported that carbon dioxide, produced as a by-product during the coupling reaction, rapidly poisons the SrO catalyst by forming the $SrCO_3$ [23]. When it was added to the reaction mixture, carbon dioxide strongly inhibited the $\bullet CH_3$ radical production over the Sr/La_2O_3 catalyst [24]. However, the surface species on these catalysts have never been monitored by *in situ* spectroscopic techniques under the coupling reaction condition employed with these catalysts.

Fig. 7 shows the ambient Raman spectra of the 1% Sr/La_2O_3, 1% $SO_4^{2-}/Sr/La_2O_3$ and 2% $SO_4^{2-}/Sr/La_2O_3$ catalysts between the 100-1400 cm^{-1} regions. Raman bands below 500 cm^{-1} are due to the lattice vibrations, and they will not be discussed in this report. However, the strong band at 405 cm^{-1} was used to normalize the intensities of Raman spectra. Raman spectra of the standard synthetic compounds $SrCO_3$ and $La_2(CO_3)_3$ were recorded. The breathing mode (ν_1) [25] of the $SrCO_3$ was observed at 1070 cm^{-1} and the bending mode (ν_3) was at 741 cm^{-1}, while those for the $La_2(CO_3)_3$ were observed at 1087 cm^{-1}(ν_1) and 699 cm^{-1}(ν_3), respectively. According to these standard spectra, the 1087 cm^{-1} and 1068 cm^{-1} Raman bands in Fig. 7 were assigned to the ν_1 breathing modes of the $La_2(CO_3)_3$ and $SrCO_3$, respectively. The 992 cm^{-1} band was assigned to the breathing mode (ν_1) of the strontium and lanthanum sulfates, based on their standard Raman spectra that are not shown here. These Raman band frequencies indicate that the carbonates and sulfates formed over these catalyst surfaces are bulk compounds [25] rather than the surface species with a double C=O bond or a double S=O bond, in which cases higher frequency Raman bands (>1300 cm^{-1}) should be observed.

Fig. 8 depicted the Raman spectra of the above three catalysts taken at 500°C with flowing air (flow rate ~ 100 ml/min) (Fig. 8A-8C) and with flowing air and methane (CH_4/air ~ 1.2, total flow rate ~ 120 ml/min) (Fig. 8A'-8C') in the 600-1400 cm^{-1} region. From Fig. 8A-8C, it appears that surface sulfates inhibited the overall formation of the carbonates. In particular, it appears that $SrCO_3$ was preferentially inhibited since the relative intensity of the $SrCO_3$ ν_1 band compared with the $La_2(CO_3)_3$ ν_1 band decreased more upon sulfate treatment. In accord, Aika and Aono [23] have observed much lower

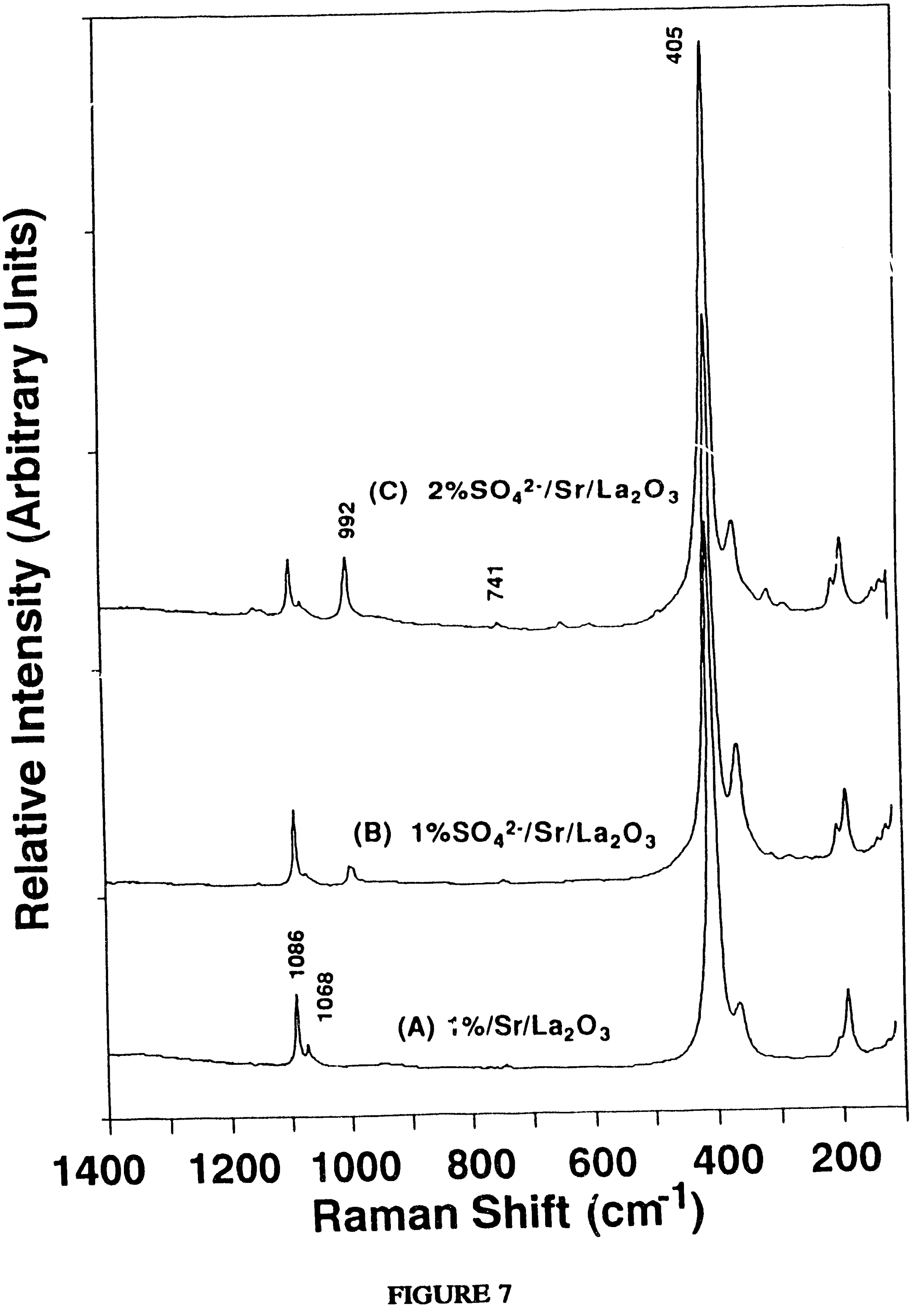

FIGURE 7

Laser Raman spectra of the 1% Sr/La_2O_3, 1% $SO_4^{2-}/Sr/La_2O_3$, and 2% $SO_4^{2-}/Sr/La_2O_3$ catalysts under ambient conditions.

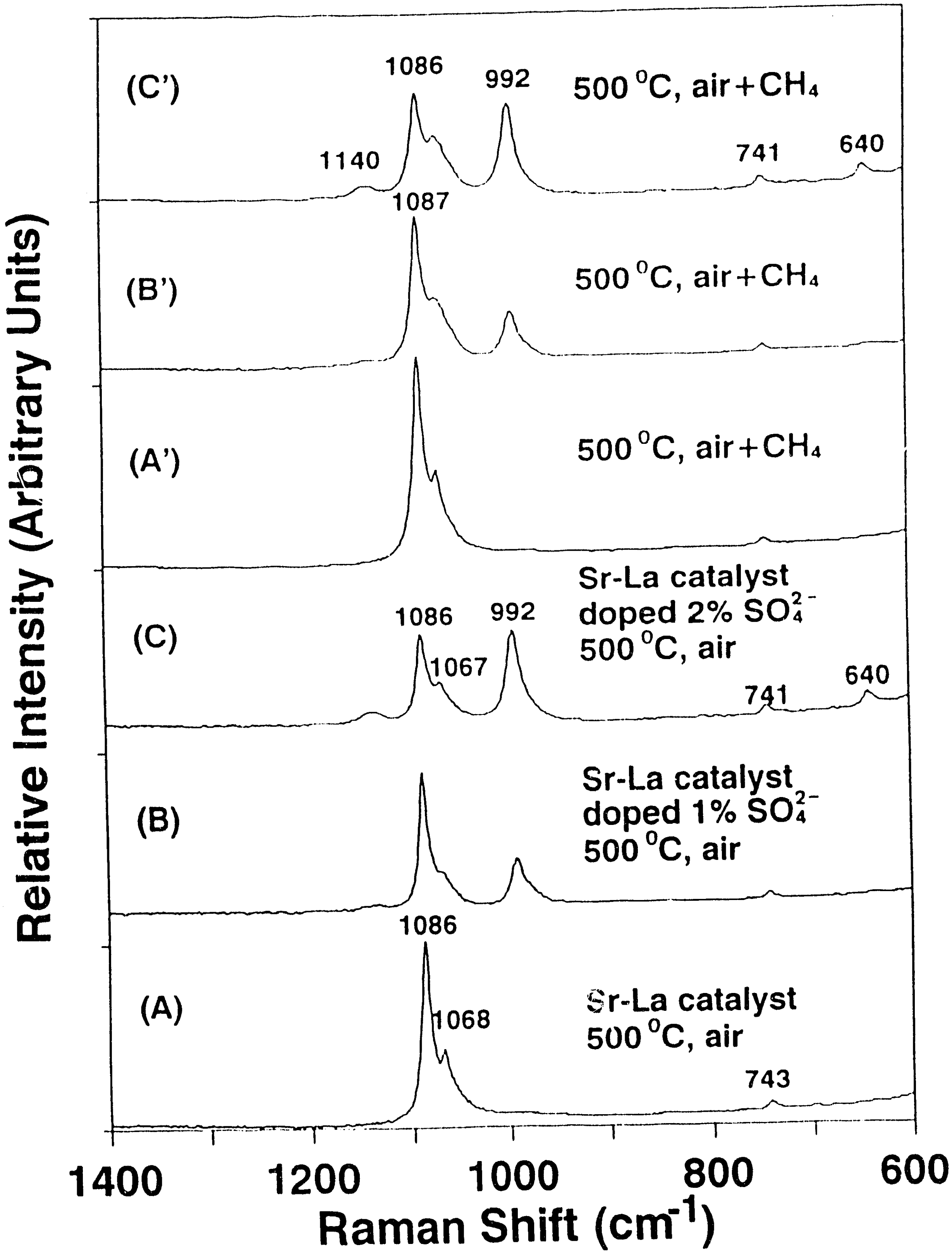

FIGURE 8

In situ laser Raman spectra of the 1% Sr/La_2O_3, 1% SO_4^{2-}/Sr/La_2O_3, and 2% SO_4^{2-}/Sr/La_2O_3 catalysts at 500°C with flowing air (A-C) and with flowing methane and air (A'-C').

activity for $SrCO_3$ as compared with SrO for the activation of methane. The inhibition of $SrCO_3$ formation by surface sulfate could be directly contributing to the promoting effect of sulfate on the Sr/La_2O_3 catalysts for methane coupling reactions at the low temperature regions.

Spectra A'-C'in Fig. 8 were recorded under the reaction conditions ~30 min after the introduction of the reaction mixture. These *in situ* spectra suggest that sulfates remained on the catalyst surfaces during the coupling reactions and more carbonates were formed in comparison to those in Fig. 8A-8C. Fig. 9 shows the difference spectra between the spectral sets A'-A, B'-B and C'-C in Fig. 8 correspondingly. Fig. 9 indicates that the carbonates formed during the coupling reactions are different for the Sr/La_2O_3 and the sulfated catalysts. For the Sr/La_2O_3 catalyst, it appears that $La_2(CO_3)_3$ was the only carbonate produced. On the other hand, for the sulfate-promoted catalysts, it is evident that $SrCO_3$ or other forms of carbonates were also formed in addition to the formation of the $La_2(CO_3)_3$.

The assignment of the broad band at 1062 cm^{-1} is uncertain, but there are at least two possibilities. One origin of this band could be $SrCO_3$, where sulfate may have been preferentially bonded to SrO but subsequently partially depleted under the overall reducing environment during the oxygen-consuming reactions, as perhaps evidenced by the negative peak at ~995 cm^{-1} in Fig. 9 by spectrum C'-C. The partial removal of the $SrSO_4$ surface species (loss of SO_4^{2-}) could have contributed to increased $SrCO_3$ formation during the reactions. However, these surface reactions resulting in change in surface composition should lead to rapid deactivation of the sulfated catalysts, which was not observed. A second possibility might be that the 1062 cm^{-1} band arises from the formation of another type of lanthanum carbonate, where it would be a more stable form and could benefit the methane oxidative coupling reactions [21]. Sulfate may be able to promote the formation of this type of carbonate while inhibiting $SrCO_3$ formation, and thus promoting the catalytic performance of the Sr/La_2O_3 catalysts. Further *in situ* spectroscopy studies are under way to gain a better understanding of the surface chemistry involved in enhancement of methane activation, as well as retardation of methane activation and conversion, over Sr/La_2O_3 catalysts.

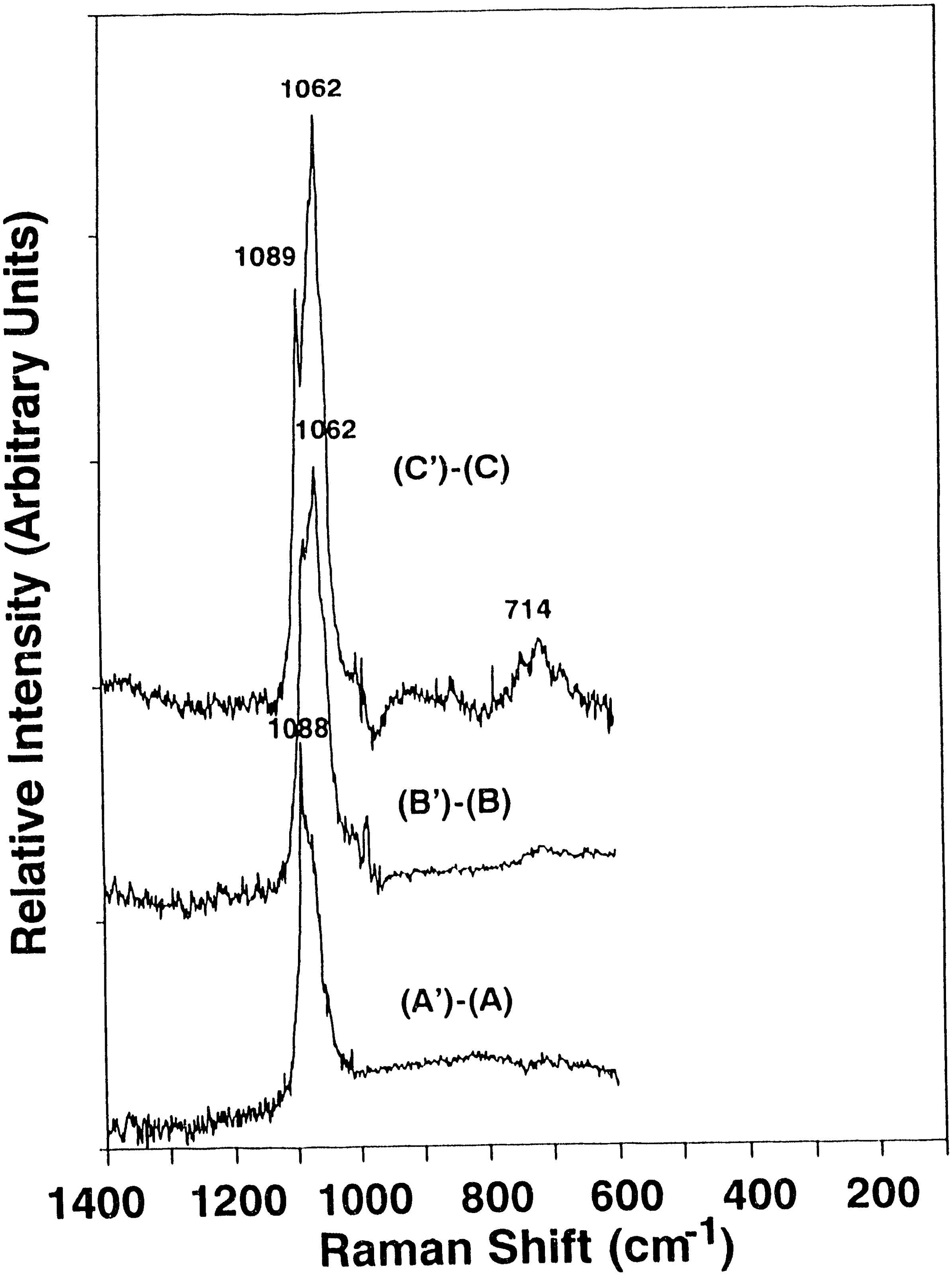

FIGURE 9

The corresponding difference Raman spectra of A'-A, B'-B, and C'-C, where the individual spectra were shown in Fig. 8.

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