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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

At 550°C, the 1 wt% SO_4^{2-} /1 wt% $\text{Sr/La}_2\text{O}_3$ catalyst, one of the most active catalyst for the selective conversion of methane at these moderate temperatures, showed a very good stability with a reactant mixture of $\text{CH}_4/\text{air} = 1/1$ with GHSV = 70,040 $\ell/\text{kg catal}/\text{hr}$. During a 25 hr catalytic test, the conversion of CH_4 and the C_2^+ selectivity did not change, indicating good stability of the catalyst. At the same time, the CO_2/CO ratio remained steady at about 2.2, but the C_2^-/C_2 ratio shifted slightly with time from 0.74 to 0.68. The oxidative coupling of CH_4 to C_2 -hydrocarbons was very sensitive at 550°C to the alteration of the CH_4/air reactant ratio at GHSV = 70,040 $\ell/\text{kg catal}/\text{hr}$. It was observed that the conversion of CH_4 , the C_2^+ selectivity, and the %yield of C_2^+ hydrocarbon products decreased very rapidly with increasing CH_4/air ratio from 1 to 3-4. At the largest CH_4/air ratio of 40.77 that was utilized, the CH_4 conversion was less than 0.5 C-mol%. The reverse process of decreasing the CH_4/air ratio from ≈ 40 to 1 showed nearly reversible catalytic performance, but some deactivation was apparent at the lowest reactant ratios. The 1 wt% SO_4^{2-} /1 wt% $\text{Sr/La}_2\text{O}_3$ catalyst used in the experiments in which the CH_4/air ratio was varied subsequently revealed a good stability in the CH_4 conversion level during testing at 550°C for 15 hr (GHSV = 70,040 $\ell/\text{kg catal}/\text{hr}$ and $\text{CH}_4/\text{air} = 1/1$). Indeed, the C_2^+ selectivity even increased by 3 to 4 C-mol%. Increasing the temperature from 550 to 600°C resulted in a further recovery of the activity of the partially deactivated catalyst.

It was shown that both the 1 wt% $\text{Sr/La}_2\text{O}_3$ and 1 wt% SO_4^{2-} /1 wt% $\text{Sr/La}_2\text{O}_3$ catalysts contained carbonate as prepared and before catalytic testing was carried out. During testing in which the temperature was increased from 500°C to 700°C and then back to 500°C, the amount of total carbonate increased in both catalysts. However, the sulfated sample showed a larger resistance against carbonate formation than the non-sulfated catalyst under the standard reaction conditions that were employed. Carbonate formation in the catalyst did occur when a low flow rate of the reactive gas mixture (GHSV = 5,400 $\ell/\text{kg catal}/\text{hr}$ and $\text{CH}_4/\text{air} = 1/1$) was utilized at 550°C, where the carbonate content for the sulfated catalyst increased by almost a factor of 3 compared with the catalyst tested at GHSV = 70,040 $\ell/\text{kg catal}/\text{hr}$ with $\text{CH}_4/\text{air} = 1/1$.

It was shown that pretreatments of the sulfated catalyst in air or He did not decrease the bulk sulfate concentration at even 800°C. After carrying out the methane oxidation reaction at 550°C with low reactant flow rate (decreasing GHSV from 70,000 to 5,400 $\ell/\text{kg catal}/\text{hr}$), the amount of sulfate in the 1 wt% SO_4^{2-} /1 wt% $\text{Sr/La}_2\text{O}_3$ catalyst had decreased slightly (≈ 7 wt%). However, the loss of sulfate was more than 60 wt% during a reaction sequence that reached a temperature of 700°C.

The sulfate doping increased the BET surface area of the $\text{Sr/La}_2\text{O}_3$ catalyst by more than 50%. The pretreatment of the 1 wt% SO_4^{2-} /1 wt% $\text{Sr/La}_2\text{O}_3$ catalyst in air or He at 800°C decreased the surface area only slightly. However, large losses of surface areas of both the non-sulfated and the sulfated catalysts when the methane oxidation reaction was carried out at 700°C.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

OBJECTIVES OF THE RESEARCH

The objective of this research is the selective oxidative coupling of methane to C₂ 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 difficult to control gas phase reactions.

Oxide catalysts are chosen for this research that are surface doped with small amounts of acidic dopants. It was proposed that, for example, the very basic Sr/La₂O₃ catalyst that is active in the formation of methyl radicals, and therefore of C₂⁺ products, can be doped with Lewis acidic oxides or other acidic groups to increase further its activity and selectivity to C₂ products.

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

- Task 1. Maximizing Selective Methane Oxidation to C₂⁺ Products Over Promoted Sr/La₂O₃ 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 C₂⁺ 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 Tasks 1 and 2.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

RESEARCH PROGRESS

Oxidative Coupling of Methane Over Sulfate-Doped Sr/La₂O₃ Catalysts

1. Introduction

The desire to convert CH₄ catalytically to more valuable products is not a new topic in research, and its importance has increased very much in the last decade. After the first publication centered on the catalytic coupling of methane in 1982 [1], many academic and industrial laboratories around the world have been investigating the selective oxidation of methane to find a commercial catalyst for methane conversion to C₂ products.

Excellent reviews have appeared on this subject [2-11], and more than a hundred catalysts that exhibit activity for the oxidative transformation of CH₄ to hydrocarbons or to oxygenates have been described. This number is still growing, but 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 high activity, selectivity to C₂⁺ hydrocarbon products, good stability at reaction conditions, and a relatively low cost. The strontium-doped La₂O₃ is one of the best known catalysts [12-14], which results in even a better catalytic performance than the pure oxide.

It was found earlier in this research project that the catalytic features of the very basic Sr/La₂O₃ catalyst were improved by surface doping with sulfate. It was found by us that a 1 wt% sulfate content, initially doped onto the 1 wt% Sr/La₂O₃ catalyst, yielded the best catalytic performance when using a CH₄/air = 1/1 reactant mixture at 1 atm and with a gas hourly space velocity (GHSV) = 70,000 l/kg catal/hr [15]. It was subsequently observed that a decrease in the total flow rate of the reactant CH₄/air = 1/1 gas mixture at 550°C caused a large decrease in the CH₄ conversion and C₂⁺ selectivity [16]. It has been suggested that the by-product CO₂ may cause such deactivation [16-20].

In this quarterly progress report, experimental results concerning the (a) stability of the 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ catalyst at moderate reaction conditions (e.g. 550°C), (b) effect of the CH₄/air ratio on the catalytic performance, (c) chemical analysis of the bulk carbonate and sulfate, and (d) BET surface areas of the catalysts used in this study (both 1 wt% Sr/La₂O₃ and 1 wt% SO₄²⁻/Sr/La₂O₃) are reported.

2. Experimental

The 1 wt% Sr/La₂O₃ catalyst was obtained from Amoco Oil Co. under their Natural Gas University Research Program. The 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ catalyst was produced by the incipient wetness impregnation technique. The appropriate amount of (NH₄)₂SO₄ was dissolved in deionized water, the measured quantity of Sr/La₂O₃ was added,

and the slurry was continuously stirred at ambient temperature with a magnetic stirrer until dryness was achieved. This was followed by drying the solid at 120°C overnight and then calcination in air at 600°C for 6 hr. Prior to catalytic testing, the samples were activated *in situ* under air flow at 500°C for 1 hr (standard pretreatment), or at 800°C in air or He (new pretreatments). The gases used in this study were zero grade purity and were used without any 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. Generally, a reaction mixture of CH₄/air = 1/1 was used at ambient pressure and at high total flow rate (GHSV = 70,000 l/kg catal/hr). In other experiments, the gas composition in terms of the CH₄/air ratio was varied while the total flow rate was kept constant, i.e. GHSV = 70,040 l/kg catal/hr. The principal products analyzed by on-line sampling using gas chromatography were CO₂, C₂ (C₂H₆ + C₂H₄), C₃ (C₃H₈ + C₃H₆), CO, and H₂O. The carbon mass balance during the catalytic reaction was better than 95%.

The BET surface areas of the catalysts used were measured by us with an instrument (Model Gemini-2360) from Micrometrics Instrumental Corporation. The weighed catalyst samples (50 to 70 mg) were pretreated in flowing N₂ at 250°C for a minimum of 2 hr, and the samples were then cooled in the flowing N₂ to room temperature. The surface area was measured with N₂ as adsorbate at liquid N₂ temperature (-196°C) using two test tubes (one sample and one reference tube) and the multipoint method. Before each measurement, the free volume was determined by He gas at liquid N₂ temperature.

The chemical analyses for sulfate and carbonate were made by Galbraith Laboratories, Inc.

3. Results and Discussion

3.1. Stability Test

The 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃, determined by us to be one of the most active catalyst for oxidative coupling of CH₄ to C₂-hydrocarbons [15], was used in the stability test. The sample was pretreated with the standard method at 500°C in air (GHSV ≈ 35,000 l/kg catal/hr) for 1 hr. The methane conversion reaction was then carried out at 550°C in the gas mixture of CH₄/air = 1/1 (GHSV = 70,040 l/kg catal/hr), and the catalyst showed a very good stability (Figure 1). During the entire 25 hr experiment, the conversion of CH₄ was around 20 C-mol% with a C₂⁺ selectivity of 50 C-mol% and a yield of 10 mol/kg catal/hr of C₂⁺ hydrocarbons. The C₂⁺/C₂ and CO₂/CO ratios also remained quite stable. The CO₂/CO ratio remained steady at ≈ 2.2. The calculated average of C₂⁺/C₂ ratio was 0.71, but this ratio shifted in time from an initial value of 0.74 to 0.68. This might also be reflected in the O₂ conversion, which after a short initial period of increasing, decreased (after 4 hr) in time by a few C-mol% (curve d in Figure 1).

FIGURE 1

Stability test at 550°C with the 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ catalyst: (a) CH₄ conversion (■); (b) C₂⁺ product selectivity (□); (c) yield of C₂⁺ hydrocarbon products (▲); (d) conversion of oxygen (⊠); and (e) CO_x selectivity (+). Weight of the catalyst = 0.1000 g; reaction mixture of CH₄/air = 1/1; total pressure = 1 atm; and GHSV (gas hourly space velocity) = 70,040 l/kg catal/hr.

3.2. Effect of CH₄/Air Ratio

3.2.1. Conversion of Methane

While GHSV was kept constant (70,040 l/kg catal/hr) at the reaction temperature of 550°C, the CH₄/air ratio was increased stepwise from 1.01 to 40.77, which caused the conversion of methane to decreased significantly from ≈15 to less than 0.5 C-mol% (Figure 2). The drop in the activity was especially large upon increasing the CH₄/air ratio from 1 to ≈3, which yielded about a 4.5-fold decrease in the conversion of methane.

During the reverse process of decreasing the CH₄/air ratio, the CH₄ conversion increased in basically a reversible manner, as shown by curve b in Figure 2, although some deactivation was observed at low reactant ratios. This approximate reversibility is in marked contrast with the results obtained in the prior experiments where the flow rate (GHSV) was systematically decreased from 70,175 to 5,388 l/kg catal/hr and then stepwise increased back to the original value while maintaining the CH₄/air reactant ratio at a constant value of 1 (see Figure 5 in Reference [16]). In that case, deactivation of at least 20-25% was observed at all flow rates [16], while in the current experiment the CH₄ conversion exhibited much less deactivation.

3.2.2. C₂⁺ Selectivity

The C₂⁺ selectivity decreased very rapidly from ≈32 to 13 C-mol% as the CH₄/air ratio was increased from 1.01 to 3.45 (Figure 3). However, it was very surprising that as the CH₄/air ratio was further increased to 40.77, the C₂⁺ selectivity reversed and increased quite linearly to over 50 C-mol%. It is noted here that as the CH₄/air ratio increased, the methane conversion decreased, as shown in Figure 2, and the concentrations of both the C₂ and CO_x products were quite small. This resulted in greatly error in the gas chromatographic product analyses, but the lack of appreciable scatter in the selectivity plots tend to provide some confidence in the analyses.

The stepwise decrease in the CH₄/air reactant ratio resulted in rather reversible behavior, but at the lowest ratios there was some loss of C₂⁺ selectivity. As shown in Figure 3, the final C₂ selectivity obtained with CH₄/air = 1.01 was ≈85% of the initially observed selectivity with the fresh catalyst.

3.2.3. CO_x Selectivity

The CO_x selectivity as the CH₄/air reactant ratio was varied showed a mirror image of the C₂⁺ selectivity, as shown in Figure 4. The CO_x selectivity increased from 66.5 to 82.6 C-mol% as the CH₄/air ratio was increased from 1.01 to 3.24. As the reactant ratio was increased further, the CO_x selectivity decreased until the end of the first part of the experiment (CH₄/air = 40.77). In the reverse process when the CH₄/air ratio was decreased, a similar reversibility was obtained for the CO_x selectivity (curve b in Figure 4) as that observed for the C₂⁺ selectivity. At the end of this test (CH₄/air = 1.01), the CO_x

Effect of CH_4/air reactant ratio on the conversion of CH_4 at 550°C over the $1 \text{ wt}\% \text{SO}_4^{2-}/1 \text{ wt}\% \text{Sr}/\text{La}_2\text{O}_3$ catalyst (0.1000 g) with a constant GHSV = $70,040 \text{ h/kg catal/hr}$ at a total pressure of 1 atm , and with (a) increasing ($\blacksquare$, solid line) and (b) decreasing ($\square$, dashed line) CH_4/air reactant ratio. The CH_4/air ratio was changed stepwise from 1.01 to 40.77 and then the procedure was reversed.

FIGURE 2

FIGURE 3

Effect of CH_4/air reactant ratio on the C_2^+ selectivity at 550°C over the 1 wt% $\text{SO}_4^{2-}/1$ wt% $\text{Sr}/\text{La}_2\text{O}_3$ catalyst at a constant GHSV = 70,040 $\ell/\text{kg catal}/\text{hr}$ at a total pressure of 1 atm, and with (a) increasing (■, solid line) and (b) decreasing (□, dashed line) CH_4/air reactant ratio. The CH_4/air ratio was first increased stepwise from 1.01 to 40.77, and then the procedure was reversed.

FIGURE 4

Effect of CH_4/air ratio on the CO_x selectivity at 550°C over the 1 wt% $\text{SO}_4^{2-}/1$ wt% $\text{Sr}/\text{La}_2\text{O}_3$ catalyst at a constant GHSV = 70,040 $\ell/\text{kg catal}/\text{hr}$ at a total pressure of 1 atm, and with (a) increasing (■, solid line) and (b) decreasing (□, dashed line) CH_4/air reactant ratio. The CH_4/air ratio was changed in a stepwise from 1.01 to 40.77 and then the procedure was reversed.

selectivity was 71.54 C-mol%, i.e. $\approx 8\%$ larger than at the beginning of the test.

3.2.4. Yield of C_2^+ Products

The %yield of the C_2^+ products decreased very rapidly with increasing CH_4 /air ratio, as shown by curve a in Figure 5, and this is a reflection of the conversion level of CH_4 (see Figure 2). While the CH_4 /air ratio increased from 1.01 to 3.24, the %yield of CH_4 decreased by more than a factor of 10 (from 4.81 to 0.45 C-mol%). When the CH_4 /air ratio reached its largest experimental value (40.77), the methane %yield was only 0.25 C-mol%.

During the reverse process of decreasing the CH_4 /air ratio at 550°C, the productivity of the catalyst was nearly reversibility, as indicated by curve b in Figure 5. However, some deactivation was evident at low reactant ratios, e.g. at the final ratio of CH_4 /air = 1.01, the %yield of CH_4 was $\approx 72\%$ of the original value.

3.3. Stability of Used Catalyst

The 1 wt% SO_4^{2-} /1 wt% Sr/La₂O₃ catalyst used in the experiments described above was monitored for stability by continuing to carry out the catalytic testing at 550°C with the CH_4 /air = 1.01 reactant mixture with GHSV = 70,040 ℓ /kg catal/hr. During the experimental time period (15 hr), the activity data revealed a very good stability (Figure 6). As shown during the 15 hr test, the CH_4 conversion did not change. However, the C_2^+ selectivity increased, while the CO_x selectivity decreased, by 3-4 C-mol%. The %yield of C_2^+ products increased by 0.3 to 0.4 C-mol%.

3.4. Effect of Temperature on Reactivation

3.4.1. Increase of Reaction Temperature

After the experiments were completed in which the CH_4 /air ratio was varied, the reaction temperature was increased stepwise at the original experimental conditions (GHSV = 70,040 ℓ /kg catal/hr, CH_4 /air = 1.01). By increasing the temperature from 550 to 600°C, the conversion of CH_4 (Figure 7) and the C_2^+ selectivity (Figure 8) increased gradually, without any sudden increase, while the CO_x selectivity steadily decreased (Figure 9). The %yield of C_2 products (Figure 10) showed also a smooth increase as the temperature was increased because both the activity and selectivity had increased.

Again, these gradual changes in the catalytic features are in distinct contrast with those obtained earlier in this research project when the at CH_4 /air = 1/1 reactant flow rate was systematically varied, i.e. see Figures 9-12 in Reference [16]. This may be attributed to different treatment of the catalyst and a much larger reversibility at the present conditions.

FIGURE 5

Effect of CH_4/air ratio on the C_2^+ yield at 550°C over the 1 wt% $\text{SO}_4^{2-}/1$ wt% $\text{Sr/La}_2\text{O}_3$ catalyst at a constant GHSV = 70,040 $\ell/\text{kg catal}/\text{hr}$ at a total pressure of 1 atm, and with (a) increasing ($\blacksquare$, solid line) and (b) decreasing ($\square$, dashed line) CH_4/air reactant ratio. The CH_4/air ratio was changed in a stepwisely from 1.01 to 40.77 and then the procedure was reversed.

FIGURE 6

Second stability test at 550°C with the 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ catalyst after the experiments of (1) the variation (increase and decrease) of CH₄/air ratio at 550°C (see Figures 2-5) and (2) the subsequent variation (increase and decrease) of temperature from 550 to 600°C and then back to 500°C (see Figures 7-10): (a) CH₄ conversion (■); (b) C₂⁺ product selectivity (□); (c) yield of C₂⁺ hydrocarbon products (+); (d) conversion of oxygen (▲); and (e) CO_x selectivity (⊠). The weight of the catalyst = 0.1000 g; reaction mixture of CH₄/air = 1/1; total pressure = 1 atm; and GHSV (gas hourly space velocity) = 70,040 l/kg catal/hr.

FIGURE 7

Effect of temperature on the conversion of CH_4 over the used partially deactivated 1 wt% SO_4^{2-} /1 wt% $\text{Sr/La}_2\text{O}_3$ catalyst (0.1000 g) with $\text{CH}_4/\text{air} = 1/1$ reaction mixture at a total pressure of 1 atm and GHSV = 70,040 $\ell/\text{kg catal}/\text{hr}$. The reaction temperature was increased stepwise from 550 to 600°C (■, solid line), and then the temperature was stepwise decreased to 500°C (□, dashed line).

FIGURE 8

Effect of temperature on the C_2^+ selectivity over the 1 wt% SO_4^{2-} /1 wt% Sr/La_2O_3 catalyst with $CH_4/air = 1/1$ reaction mixture at a total pressure of 1 atm and GHSV = 70,040 ℓ/kg catal/hr, where the reaction temperature was increased stepwise from 550 to 600°C (■, solid line), and then it was decreased to 500°C (□, dashed line).

FIGURE 9

Effect of temperature on the CO_x selectivity over the 1 wt% SO_4^{2-} /1 wt% $\text{Sr/La}_2\text{O}_3$ catalyst with $\text{CH}_4/\text{air} = 1/1$ reaction mixture at a total pressure of 1 atm and GHSV = 70,040 ℓ/kg catal/hr. The reaction temperature was increased stepwise from 550 to 600°C (■, solid line), and then it was decreased to 500°C (□, dashed line).

FIGURE 10

Effect of temperature on the %yield of C₂⁺ hydrocarbon products over the 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ catalyst with CH₄/air = 1/1 reaction mixture at a total pressure of 1 atm and GHSV = 70,040 l/kg catal/hr. The reaction temperature was increased stepwise from 550 to 600°C (■, solid line), and then it was decreased to 500°C (□, dashed line).

3.4.2. Decrease of Reaction Temperature

The reaction temperature was gradually decreased from 600 to 500°C while keeping the other reaction parameters constant, as indicated above when the temperature was increased. In the first stage of the experiment, where the temperature was decreased from 600 to 580-585°C, the conversion of CH₄, surprisingly did not decrease (Figure 7). Indeed, the C₂⁺ selectivity (Figure 8) and yield of C₂⁺ products (Figure 10) even showed small increases, while the CO_x selectivity (Figure 9) decreased.

Further decrease in the temperature varied the catalytic features in the usual expected directions, i.e. the conversion of CH₄, the C₂⁺ selectivity and the % yield of C₂⁺ products decreased while the CO_x selectivity increased gradually (Figures 7 to 10). The small hysteresis observed during the cycle of the variation of the temperature showed that the surface was active and fairly selective to C₂ hydrocarbons between 550°C and 600°C, and decreasing the temperature from 600°C to 550°C resulted in a slight more active and selective catalyst. However, below a reaction temperature in the 530-540°C range, the catalytic performance decreased significantly, and this might be due to the build-up of carbonates on the surface of the catalyst at these lower temperatures.

3.5. Chemical Analysis and BET Area

The amount of bulk carbonate and sulfate in these catalysts were analysed (a) before the reaction, (b) after the pretreatments at 800°C in air or He; (c) after a regular methane coupling reaction when the temperature was increased from 500 to 700°C and decreased back to 500°C (GHSV = 70,000 l/kg catal/hr, CH₄/air = 1/1); and (d) after a special reaction at 550°C with decreasing flow rate (GHSV decreased from 70,000 to 5,400 l/kg catal/hr), but with constant CH₄/air (1/1) ratio. Some relevant data obtained from the bulk chemical analysis for carbonate and sulfate are given in Table 1.

3.5.1 Carbonate

Carbonate existed after the preparation of both catalysts, as indicated in Table 1 (A) for both the 1 wt% Sr/La₂O₃ and 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ samples, with 3.30 and 4.35 wt% carbonate, respectively. After a regular oxidative methane coupling experiment was carried out using the temperature testing sequence of 500 → 700 → 500°C, the amount of carbonate increased (Table 1 (C)). However, the 1 wt% SO₄²⁻ sample contained less carbonate than the non-sulfated Sr/La₂O₃ (5.35 and 7.50 wt%, respectively). This might indicate that the sulfate somehow protected the catalyst from the larger build-up of carbonate.

When the total flow rate was decreased at 550°C from 70,000 to 5,400 l/kg catal/hr (CH₄/air = 1/1) and then the reaction was stopped, the amount of carbonate was 15.35 wt% (Table 1 (D)), which was almost three times larger than after a regular reaction. This unambiguously revealed that the deactivation caused by the low flow rate at 550°C [16] was due to the large amount of carbonate in the catalyst, in a good accordance with the

Table 1
Chemical Analysis of Sr/La₂O₃-Based Catalysts

Sample	Sulfate (wt%)	Carbonate (wt%)	BET Area (m ² g ⁻¹)
(A) Before Reaction			
1 wt% Sr/La ₂ O ₃	—	3.30	10.36
1 wt% SO ₄ ²⁻ /Sr/La ₂ O ₃	0.93	4.35	16.17
(B) Pretreatment only at 800°C (for 1 hr in Air or He); no reaction			
1 wt% SO ₄ ²⁻ /Sr/La ₂ O ₃ (Air)	0.96	—	15.18
1 wt% SO ₄ ²⁻ /Sr/La ₂ C ₃ (He)	0.93	—	13.15
(C) After Reaction (500 → 700 → 500°C; GHSV = 70,000 ℓ kg⁻¹hr⁻¹; CH₄/Air = 1/1)			
1 wt% Sr/La ₂ O ₃		7.50	7.03
1 wt% SO ₄ ²⁻ /Sr/La ₂ O ₃	0.36	5.35	8.20
(D) After Special Reaction at 550°C with Low GHSV (70,000 → 5,400 ℓ kg⁻¹hr⁻¹; CH₄/Air = 1/1)			
1 wt% SO ₄ ²⁻ /Sr/La ₂ O ₃	0.87	15.35	

- Notes: (1) The chemical analysis of sulfate and carbonate contents of the catalysts were carried out by Galbraith Laboratories, Inc. (Knoxville, TN 37950-1610, P.O.Box 51610);
- (2) The BET areas were measured by us with an instrument (Model Gemini-2360) from Micrometrics Instrumental Corporation (Norcross, GA 30093-1877, 1 Micrometrics Drive).

literature [17-20]. The decomposition of the carbonate was not complete at 550°C when the gas flow rate was restored to 70,000 ℓ /kg catal/hr, but apparently complete decomposition was only achieved at higher reaction temperatures, e.g. 580°C [16].

3.5.2. Sulfate

The 1 wt% Sr/La₂O₃ catalyst that was sulfated nominally with 1 wt% sulfate was shown to contain 0.93 wt% SO₄²⁻ by chemical analysis (Table 1 (A)). This catalyst had been prepared by impregnation and drying, followed by calcination at 600°C in air for 4 hr. Analyses of samples that were pretreated at 800°C in air or He for 1 hr confirmed that these high temperature pretreatments did not result in loss of sulfate (Table 1 (B)).

However, catalytic testing of the sulfated Sr/La₂O₃ at 550°C for methane conversion at various flow rates (GHSV from 70,000 to 5,400 ℓ /kg catal/hr) with a CH₄/air = 1/1 reactant mixture did decrease somewhat the sulfate content (to 0.87 wt% as shown in Table 1 (D)). This decrease in sulfate content was much larger (down to 0.36 wt% sulfate) when the catalytic reaction was probed by using a temperature sequence that involved the higher temperatures of 700°C, as shown in Table 1 (C). At 700°C, the O₂ conversion level was generally 90-92%, and hence the reductive environment and/or the water formed in the oxidative coupling of methane might be the reason(s) of the loss of sulfate that corresponded to more than 60% of the original content.

3.5.3. BET Area

Doping of the 1 wt% Sr/La₂O₃ catalyst with 1 wt% sulfate increased the initial BET area of from 10.36 to 16.17 m²/g (Table 1 (A)). The pretreatments at 800°C in air or He caused some loss of surface area (15.18 and 13.15 m²/g, respectively) (Table 1 (B)). Large decreases were obtained for both the 1 wt% Sr/La₂O₃ and 1 wt% SO₄/Sr/La₂O₃ catalysts after the methane conversion reaction was carried out at 700°C (7.03 and 8.20 m²/g, respectively), as shown in Table 1 (C).

Further investigations are necessary to determine whether the loss of surface area takes place already at the beginning of the methane oxidation reaction at 500°C, only at higher temperatures, or only in a reductive-type environment under high conversion conditions when the reactant oxygen is basically depleted, and whether the loss of surface area is accompanied by the loss of sulfate.

4. References

- [1] G.E. Keller and M.M. Bhasin, *J. Catal.* **73** (1982) 9.
- [2] N.R. Foster, *Appl. Catal.* **19** (1985) 1.
- [3] H.D. Gesser, N.R. Hunter, and C.B. Prakash, *Chem. Rev.* **85** (1985) 235.
- [4] R. Pitchai and K. Klier, *Catal. Rev.-Sci. Eng.* **28** (1986) 13.
- [5] M.S. Scurrrell, *Appl. Catal.* **32** (1987) 1.
- [6] J.S. Lee and S.T. Oyama, *Catal. Rev.-Sci. Eng.* **30** (1988) 249.
- [7] G.H. Hutchings, M.S. Scurrrell, and J.R. Woodhouse, *Chem. Soc. Rev.* **18** (1989) 251.
- [8] J.H. Lunsford, *Catal. Today* **6** (1990) 235.
- [9] Y. Amenomiya, V.I. Birss, M. Goledzinowski, J. Galuska, and A.R. Sanger, *Catal. Rev.-Sci. Eng.* **32** (1990) 163.
- [10] J.C. Mackie, *Catal. Rev.-Sci. Eng.* **33** (1991) 169.
- [11] J.H. Lunsford, in "Studies in Surface Science and Catalysis", Vol. 61: "Natural Gas Conversion" (A. Holmen, K.-J. Jens and S. Kolboe, Eds), Elsevier, New York, 1991, p. 3.
- [12] H.B.A. Hamid and R.B. Moyes, *Catal. Today* **10** (1991) 267.
- [13] J.M. Deboy and R.F. Hicks, *J. Catal.* **113** (1988) 517; *J. Chem. Soc., Chem. Commun.* (1988) 982.
- [14] T. LeVan, M. Che, and J.-M. Tatibouet, *Catal. Lett.* **14** (1992) 321.
- [15] K. Klier, R.G. Herman, J. Sárkány, and Q. Sun, *Quarterly Technical Progress Report DOE/MC/29288-2*, March 1993.
- [16] K. Klier, R.G. Herman, J. Sárkány, and Q. Sun, *Quarterly Technical Progress Report DOE/MC/29288-3*, June 1993.
- [17] R.P. Taylor and G.L. Schrader, *Ind. Eng. Chem. Res.* **30** (1991) 1016.
- [18] S.J. Conway, J.A. Greig, and G.M. Thomas, *Appl. Catal. A*, **86** (1992) 199.
- [19] K.I. Aika and K. Aono, *J. Chem. Soc., Faraday Trans.*, **87** (1991) 1273.
- [20] M.-T. Xu and J.H. Lunsford, *Catal. Lett.*, **11** (1991) 295.

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