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Selective Methane Oxidation Over Promoted Oxide Catalysts

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CONTRACT INFORMATION

Contract Number	DE-FG21-92MC29228
Contractor	Lehigh University Zettlemoyer Center for Surface Studies and Department of Chemistry Bethlehem, PA 18015 (215) 758-3577 or 758-3486
Contractor Project Managers	Kamil Klier Richard G. Herman
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METC Project Manager	Rodney D. Malone
Period of Performance	September 8, 1992 to September 7, 1995

OBJECTIVES

The objective of this research is to selectively oxidize methane to C_2 hydrocarbons and to oxygenates, in particular formaldehyde and methanol, in high space time yields under milder reaction conditions than heretofore employed over industrially practical catalysts. In particular, air, carbon dioxide, or oxygen, rather than nitrous oxide, is being used as the oxidizing gas in a continuous flow reactor system and a wide range of reaction conditions, e.g. temperature, pressure, and gas hourly space velocity, is being explored to maximize the space time yields of the desired products. All of the investigated processes are catalytic and aimed at minimizing gas phase oxidation reactions.

BACKGROUND INFORMATION

Saturated linear hydrocarbons, particularly methane, are major components of natural gas and of the gas produced by certain gasifiers. While methane makes an excellent gaseous fuel, it is desirable to convert it to higher molecular weight products for transportation, storage, and for utilization as chemical feedstocks. The desired reactions are shown below for methane only:

$$CH_4 + 0.5\ O_2 \rightarrow CH_3OH \qquad [1]$$

$$CH_4 + O_2 \rightarrow CH_2O + H_2O \qquad [2]$$

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \qquad [3]$$

$$2CH_4 + 0.5\ O_2 \rightarrow C_2H_6 + H_2O. \qquad [4]$$

Another reaction of potential interest is

$$2CH_4 + 2CO_2 \rightarrow C_2H_4 + 2CO + 2H_2O. \quad [5]$$

After Keller and Bhasin described their catalytic research for methane coupling to form C_2 hydrocarbons in 1982 (1), many laboratories have been striving to develop efficient methane conversion catalysts and technologies. At present, there is no commercial technology for processes represented by Equations [1]-[5], despite the sizeable patent and open literature on this subject. Various aspects of the state of the art of methane oxidation, including early developments, have been reviewed by Foster in 1985 (2), Gesser et al. in 1985 (3), Pitchai and Klier in 1986 (4), Scurrell in 1987 (5), Lee and Oyama in 1988 (6), Hutchings et al. in 1989 (7), Amenomiya et al. in 1990 (8), Lunsford in 1990, 1991, and 1993 (9-11), Mackie in 1991 (12), Hamid and Moyes in 1991 (13), and Krylov in 1993 (14). Therefore, the literature will not be extensively reviewed here.

PROJECT DESCRIPTION

While the catalytic oxidative coupling paths [3] and [4] show considerable promise, it is evident from patent examples that the process conditions are still quite severe, in particular that the reaction temperatures of 650-800°C are still too high. Reactions leading to oxygenates (Equations [1] and [2]) are more difficult to conduct selectively, but they have been identified as being very desirable, particularly the oxidation to methanol (15). At the same time, the standard free energy of all the oxidations [1]-[4] is negative over a wide range of temperatures, establishing a thermodynamic driving force for these reactions even at room temperature should an effective catalyst be found. More practical considerations led us to seek a desirable temperature range of 350-650°C. The lower limit is based on experience with the dehydration of most oxide catalysts, which lose water at temperatures $\geq$350°C. The upper limit of 650°C is in the range of temperatures at which uncontrolled free radical reactions will occur and often will lower the selectivity by driving the oxidation process to CO and CO_2. Hence, it is desirable to investigate and develop catalysts that promote partial oxidations of methane to C_2^+ hydrocarbons, methanol, or formaldehyde in the temperature range of 350-650°C.

Oxide catalysts were chosen for this research that are surface doped with small amounts of acidic or redox dopants. It was proposed by us that, for example, the very basic Sr/La_2O_3 catalyst that is active in the formation of methyl radicals, and therefore of C_2^+ products (16,17), can be doped with acidic oxides or other acidic groups to increase further its activity and selectivity to C_2 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 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, i.e. formaldehyde and methanol. Task 3 involves characterization of the most promising catalysts so that optimization can be achieved under Tasks 1 and 2.

RESULTS

PART 1. Oxidative Coupling of Methane Over Sulfated-Doped SrO/La_2O_3 Catalysts

The basic 1 wt% SrO/La_2O_3 catalyst, with a surface area of 6.5 m^2/g has been shown to be a very active methane coupling catalyst (16,17). AMOCO Corp. has prepared a large batch of this catalyst for further investigation and has provided portions of this catalyst to us for catalytic testing. We demonstrated the reproducibility of this catalyst for the conversion of methane from a $CH_4/air = 1/1$ reactant mixture at 0.1 MPa (1 atm) and with gas hourly space velocity (GHSV) = 70,000 ℓ/kg catal/hr, wherein both the molar conversion of CH_4 and the %yield of C_2 products increased as the temperature was increased in the range of 500 to 675°C (18-20).

Experimental

In this program of research, the SrO/La_2O_3 catalyst was modified by surface doping with sulfate as described elsewhere (18-20). These $SO_4^{2-}/SrO/La_2O_3$ 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 SrO/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 unless stated otherwise. The gases used in this study were zero grade purity and were used without further purification

Catalytic testing was carried out in a fixed-bed continuous-flow 9 mm OD (7 mm ID) quartz reactor using 0.1000 g of catalyst. The reactor narrowed to 5 mm ID below the catalyst bed to speed the removal of reaction products from the hot reactor zone. The testing system had two independently controlled inlet gas lines, and a reactant mixtures of $CH_4/air = 1.0/1.0$ or $1.5/1.0$ were generally utilized at ambient pressure. The principal products analyzed by on-line sampling of the exit gas 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.

Results

It was shown that approximately 1 wt% SO_4^{2-} doping produced the maximum increases in both the methane conversion level and the selectivity (C mol% basis) to C_2 products (18-20). It was also shown that the catalyst was stable in $CH_4/air = 1/1$ at 550°C for over 24 hr. At this temperature, the CH_4 conversion was ≈20 mol% (limited by the depletion of oxygen) and the selectivity was ≈50 C mol% to C_2 hydrocarbons and ≈50 C mol% to CO_x (18).

Further testing has been carried out and comparisons among the catalysts have been made. This has involved testing a large number of La_2O_3-based catalysts, both promoted, i.e. SrO/La_2O_3 and $SO_4^{2-}/SrO/La_2O_3$, and unpromoted La_2O_3. Each catalyst was tested at 500°C, and then the reaction temperature was sequentially increased to 700°C and then decreased stepwise back to 500°C. To generalize with respect to the effect of the dopants, (i) promoting the La_2O_3 catalyst with SrO approximately doubled the conversion of methane and the selectivity to C_2 hydrocarbons, and (ii) promoting the SrO/La_2O_3 catalyst with SO_4^{2-} approximately doubled the activity and C_2 selectivity again.

Figure 1 summarizes the experimental data and clearly shows that the selectivity

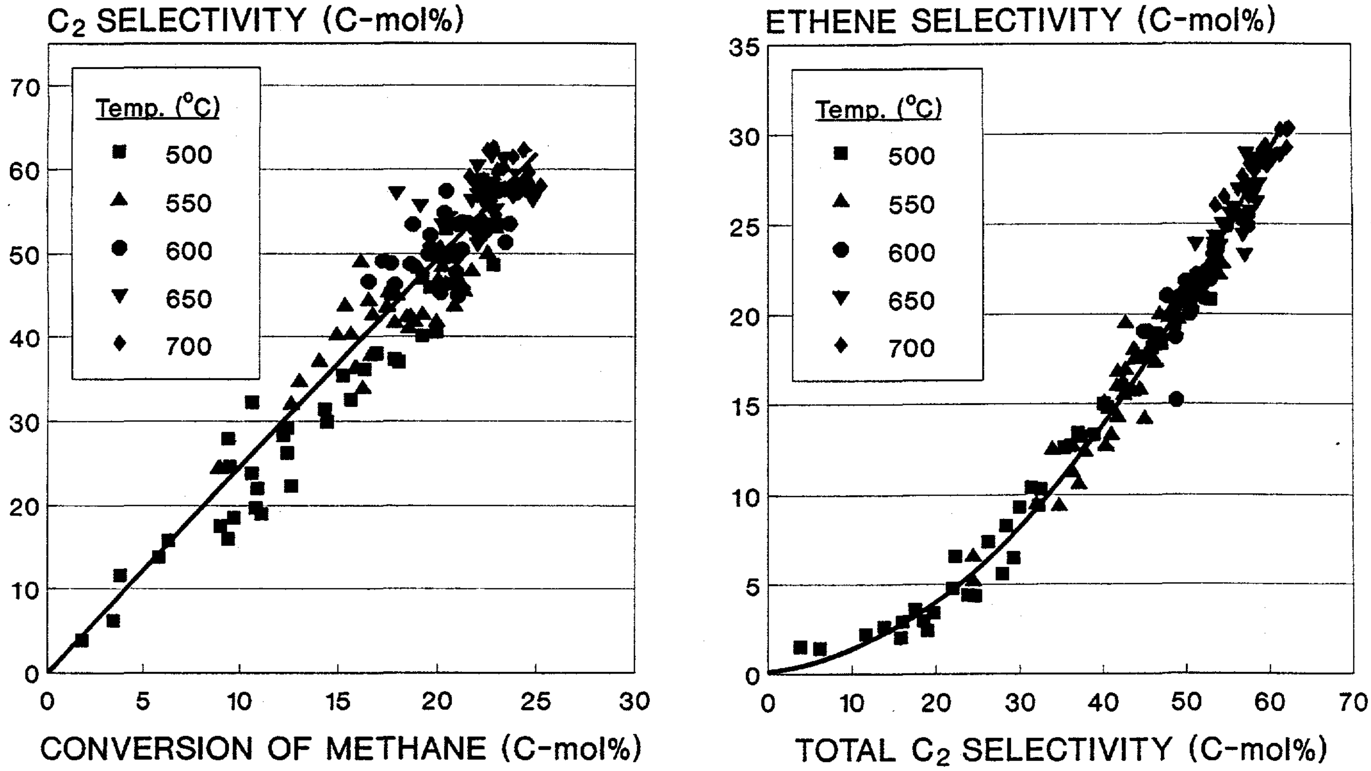

FIGURE 1. Correlations of the [A] C_2 Hydrocarbon Selectivity with Conversion of Methane and [B] Ethene Selectivity with the Total C_2 Hydrocarbon (Ethene + Ethane) Selectivity, where the Testing was carried out with a CH_4/air = 1/1 Reactant Mixture at 0.1 MPa and with GHSV = 70,000 ℓ/kg catal/hr. The Data Points Represent Steady State Experiments with La_2O_3, 1 wt% SrO/La_2O_3, and $SO_4^{2-}/SrO/La_2O_3$ Catalysts, where Sulfate Doping Levels of 1-4 wt% were Utilized. The Experiments were generally carried out by Stepwise Increasing the Reaction Temperature from 500°C to 700°C and then Stepwise Decreasing the Temperature back to 500°C.

toward formation of C_2 hydrocarbons is directly related to the level of conversion of the methane reactant, which is controlled by the reaction temperature and quantity of oxygen available. With respect to the synthesis of ethene relative to ethane, Figure 1 also shows that as the selectivity toward the C_2 hydrocarbons increased, the proportion of ethene formed increased significantly. For example, as the methane conversion approached 25%, ≈60 C mol% of the products were C_2 hydrocarbons, which exhibited a ethene/ethane molar ratio of 1/1.

It was recently stated (21) that successful catalysts for the synthesis of C_2 hydrocarbons by the oxidative coupling of methane would meet the following criteria:

1. Have high catalytic activity,
2. Exhibit high selectivity to C_2 hydrocarbons,
3. Operate at a reaction temperature between 400 and 600°C, and
4. Have long-term stability under reaction conditions.

The 1 wt% $SO_4^{2-}/SrO/La_2O_3$ catalyst reported here meets these criteria.

PART 2. Methane Oxidation to Formaldehyde and Methanol Over Supported Oxide Catalysts.

Since many supported metal oxide catalysts being studied for selective oxidation of methane utilize silica as a support (4,8,22-31), including the Pd/SiO_2 catalyst investigated during the previous project (29), the reactivities and selectivities of two common silica supports (fumed Cabosil and Grace 636 silica gel) were determined. These results have been presented previously (18,32). It was found that the ability of the silicas to activate methane below 700°C was low. However, above 700°C, appreciable conversion of methane and oxygen was observed, and the principal oxidation products produced depended on the reaction temperature. For example, lower reaction temperatures favored selectivities toward CH_2O and CO, while higher temperatures, e.g. 780°C enhanced the formation of the C_2 hydrocarbons.

Part of the current research is directed to the direct synthesis of formaldehyde at lower reaction temperatures, e.g. 500-650°C, and this research is summarized here.

Experimental

The fumed silica (Cabosil EH-5) was obtained from Aldrich with a surface area of 380 m^2/g. TiO_2 was obtained from Degussa (designated as P-25) and had a surface area of 55 m^2/g. SnO_2 was also employed as a support and was made from tin(II) acetate from Aldrich by hydrolysis; after calcination at 450°C, its surface area was 20 m^2/g.

The doped catalysts were prepared by the incipient wetness impregnation technique. The TiO_2/SiO_2 catalysts were prepared *via* a toluene solvent of titanium(IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$) under a N_2 atmosphere, while the V_2O_5-containing catalysts were prepared using a methanol solution of vanadium(VI) triisopropoxide oxide ($VO[i\text{-}OC_3H_7]_3$) in a N_2 environment. SnO_2/SiO_2 samples were prepared from an aqueous solution of colloidal SnO_2 under ambient conditions. An aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ from Matheson, Coleman, and Bell) was used for prepared the MoO_3-containing catalysts. After impregnation, each catalyst was dried at room temperature, heated at 120°C overnight, and then calcined at 500°C for 4 hr in flowing air. The metal oxide loading levels on the oxide supports are calculated on the basis of %weight.

Catalytic testing was carried out in the temperature range of 400-630°C in a fixed-bed continuous-flow 9 mm OD (7 mm ID) quartz reactor, and usually 25-200 mg of catalyst was used for each test. A reaction mixture of $CH_4/air = 1.5/1.0$ was used at ambient pressure, and usually a total flow rate (GHSV) of 70,000 ℓ/kg catal/hr was used, but a series of flow rates were employed with some of the catalysts.

The principal products analyzed by on-line sampling of the exit gas 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. Condensable water-soluble products, i.e. formaldehyde in particular, were collected in two water-filled scrubbers in series, the first was kept at room temperature and the second at 0°C. Methanol was analyzed by combined GC and GC/MS methods. Formaldehyde was quantitatively determined by the modified Romijn's iodometric titration method (33). The carbon mass balance was always better than 90% and usually better than 95%.

Results

The conventional steady-state catalytic partial oxidation of methane using air as the oxygen source was carried out with each catalyst at ambient pressure, and the observed conversions and product selectivities for a set of reaction conditions are summarized in Table 1. The high reactant space velocity of 70,000 ℓ/kg catal/hr was used to remove the synthesized products, in particular the formaldehyde, quickly from the heated reaction zone so that secondary oxidizing reactions would be inhibited. Under the reaction conditions employed here, principally the use of reaction temperatures below 700°C, it was shown that the effects on the methane conversion by the reactor and the silica support (by using the empty reactor and the pure Cabosil support) were negligible. For the SiO_2 and MoO_3/SiO_2 testing, accurate analyses of the products, other than formaldehyde, were very difficult because of the low methane conversion levels.

Testing of the three materials used as catalyst supports demonstrated that the fumed SiO_2 exhibit low methane conversion activity. However, the only detectable product was formaldehyde, which resulted in the observed productivity of 24.3 g CH_2O/kg catal/hr. The titania was somewhat active for methane conversion, while the SnO_2 was very active. However, the latter two catalysts did not produce much formaldehyde, as shown in Table 1. Indeed, the TiO_2 catalyst produced predominantly CO, while the SnO_2 catalyst formed mainly CO_2.

Considering the silica-supported MoO_3, V_2O_5, TiO_2, and SnO_2 catalysts, it is clear from Table 1 that the 1 wt% V_2O_5/SiO_2 was by far the most active. In addition, an appreciable selectivity toward formaldehyde was obtained with this catalyst, which resulted in a very high formaldehyde productivity of 685 g CH_2O/kg catal/hr. At the same time, low selectivities toward CO_2 and C_2 hydrocarbons (HC) were observed. Adding 3 wt% MoO_3 to the 1 wt% V_2O_5/SiO_2 catalyst did not significantly alter the catalytic properties of the catalyst, as shown in Table 1, indicating that the MoO_3 did not cover the V_2O_5 nor influence its catalytic functioning. However, adding 3 wt% TiO_2 to the 1 wt% V_2O_5/SiO_2 catalyst greatly decreased the catalytic activity of the V_2O_5/SiO_2 catalyst but didn't alter the product selectivity.

Finally, Table 1 shows that supporting 1 wt% V_2O_5 on titania did not result in an active catalyst for methane conversion to formaldehyde. Supporting the V_2O_5 on SnO_2 did result in an active methane conversion catalyst (note the lower temperature of 530°C), but the predominant product was CO_2, as was observed for all SnO_2-containing catalysts tested under these reaction conditions.

<u>V_2O_5/SiO_2 Catalysts</u>. Selected data for V_2O_5/SiO_2 catalysts having three different doping levels of V_2O_5 are given in Table 2. Under the given reaction conditions, the silica support was quite inactive. The 3 wt% V_2O_5/SiO_2 catalyst was appreciably more active that the 1 wt% V_2O_5/SiO_2 catalyst, as indicated by the lower reaction temperature of 580°C used with the former catalyst. Table 2 shows that decreasing the contact time (doubling the GHSV in two steps) of the reactant mixture over the 3.0 wt% V_2O_5/SiO_2 catalyst at 580°C lower the methane conversion level but increased the space time yield of formaldehyde. Finally, increasing the dopant level to 5 wt% and increasing the reaction temperature to 630°C increased the methane conversion and increased the productivity of formaldehyde to 1.44 kg CH_2O/kg catal/hr. This increase was more of reflection of the higher reaction temperature than of the higher doping level because under comparable reaction conditions, it was shown that the 5 wt% V_2O_5/SiO_2 catalyst

TABLE 1. Methane Oxidation by Air From a CH_4/Air = 1.5/1.0 Reactant Mixture at 630°C (except as noted) and 0.1 MPa with GHSV = 70,000 ℓ/kg catal/hr Over SiO_2, TiO_2, and SnO_2 Supports and Supported Catalysts. In Addition to Methane Conversion, the Space Time Yield (STY) of Formaldehyde is Given, as well as the Selectivities (S) of the Products.

Catalyst	CH_4 Conv. (mol%)	CH_2O STY (g/kg/hr)	S CH_2O	S C_2 HC	S CO	S CO_2
SiO_2 = (F)	0.05	24.3	100	--	--	--
TiO_2	1.55	17.6	2.3	--	94.0	3.6
SnO_2 (530°C)	8.10	2.3	0.1	--	8.9	90.4
2% MoO_3/(F)	0.08	37.9	100	--	--	--
1% V_2O_5/(F)	9.52	685	15.7	1.7	76.4	6.3
3% TiO_2/(F)	0.31	27.6	17.8	--	71.1	11.1
3% SnO_2/(F)	1.60	8.8	1.1	13.7	8.7	76.3
1% V_2O_5/ 3% MoO_3/(F)	8.47	675	16.6	2.0	73.5	7.9
1% V_2O_5/ 3% TiO_2/(F)	1.07	101	18.6	--	76.6	4.8
1% V_2O_5/TiO_2	0.82	14.0	3.3	1.2	73.0	22.5
1% V_2O_5/SnO_2 (530°C)	7.60	--	--	--	13.4	83.6

exhibited lower activity than did the 3 wt% V_2O_5-doped catalyst.

The V_2O_5/SiO_2 catalysts were studied further to probe the activity of these catalysts as a function of vanadia doping level. This study was conducted so that the methane conversion level could be express in terms of turnover number (TON) per active site under differential conditions at constant temperature and pressure. Thus, the level of CH_4 conversion was maintained at a low and rather constant level for all of the catalysts tested by controlling the flow rates (GHSV) of the reactants.

The results are shown in Table 3 for V_2O_5/SiO_2 catalysts containing from 0.25 to 5.00 wt% V_2O_5. It is seen that a rather constant TON was obtained with these catalysts. This indicates that methane activation and conversion is a unimolecular reaction that requires only one active site.

TABLE 2. Methane Oxidation by Air From a CH_4/Air = 1.5/1.0 Reactant Mixture Over Different V_2O_5/SiO_2 Catalysts at 0.1 MPa. In Addition to Methane Conversion, the Space Time Yield (STY) of Formaldehyde is Given.

Catalyst	GHSV (ℓ/kg/hr)	Temp. (°C)	CH_4 Conv.[‡] (mol%)	CH_2O STY[*] (g/kg/hr)
SiO_2 = (F)	70,000	630	0.05	24.3
1% V_2O_5/(F)	70,000	630	9.52	685
3% V_2O_5/(F)	70,000	580	10.04	614
3% V_2O_5/(F)	140,000	580	6.86	1,022
3% V_2O_5/(F)	280,000	580	2.67	1,220
5% V_2O_5/(F)	280,000	630	5.60	1,440

[‡] Methane conversion is limited by the availability of oxygen.

[*] The C-mol% selectivities did not vary appreciably as the space time yields varied over the V_2O_5/SiO_2 catalysts, i.e. 13.5-16.6% CH_2O and 76.4-81.3% CO, with the remainder predominantly CO_2.

TABLE 3. Methane Conversion Turnover Numbers (TON) for Methane Oxidation by Air (CH_4/Air = 1.5/1.0) Over V_2O_5/SiO_2 Catalysts at 580°C and 0.1 MPa.

V_2O_5 Loading (wt%)	0.25	1.00	2.00	3.00	5.00
GHSV (ℓ/kg/hr)	16,200	70,000	140,000	350,000	280,000
CH_4 Conv.[‡] (mol%)	1.7	1.0	1.1	0.8	1.1
TON ($10^{-2}s^{-1}$)	6.8	4.5	5.0	5.9	3.8

[‡] Methane conversion was maintained at a relatively constant moderate value by variation of the reactant flow rate in order to compare the experimental TON as a function of promoter loading.

Effect of Steam in the Reactant Mixture. Based on the proposal by us (4,32) and others (22,34) that it is the methoxy intermediate that gives rise to formaldehyde, it was thought that hydrolysis of this intermediate should result in the formation of methanol. Therefore, experiments were carried out in which water was injected into the reactant gas stream just above the perheater section of the reactor. The preheater section of the reactor was filled with Pyrex beads, and in this section the water was vaporized into steam and mixed with the CH_4/air reactants as they were heated to the reaction temperature before reaching the catalyst.

Since the 1 wt% V_2O_5/SiO_2 catalyst was an active catalyst and produced a high space time yield of formaldehyde, it was utilized in this study. The first experiments involved injecting a small steady state quantity of steam into the reactant mixture and determining the effect of temperature on the productivity of the selectively formed oxygenates. The results are summarized in Figure 2, where it is shown that an appreciable space time yield of methanol was formed at temperatures higher than 600°C, e.g. ≈60 g CH_3OH/kg catal/hr at 625°C. At the same time, high productivity of formaldehyde was also observed. Therefore, the presence of steam over the catalyst did enhance the formation of methanol.

Conclusions

Among the dispersed metal oxide catalysts studied for the selective oxidation of methane, the most active catalyst was clearly V_2O_5/SiO_2. These high surface area silica-based catalysts impregnated with 1-5 wt% V_2O_5 were also found to exhibit low selectivities toward CO_2. Although CO was the major product, appreciable selectivities toward formaldehyde were also observed. Indeed, with the V_2O_5/SiO_2 catalysts, very high space time yields of formaldehyde of >1 kg CH_2O/kg catal/hr) could be obtained even though the conventional single pass %yields were <2%. These results were obtained at relatively high GHSV (70,000-280,000 ℓ/kg catal/hr) but moderate temperatures (530-630°C). Utilizing steam in the CH_4/air reactant mixture led to the formation of methanol over the V_2O_5/SiO_2 catalyst in the same GHSV and temperature ranges.

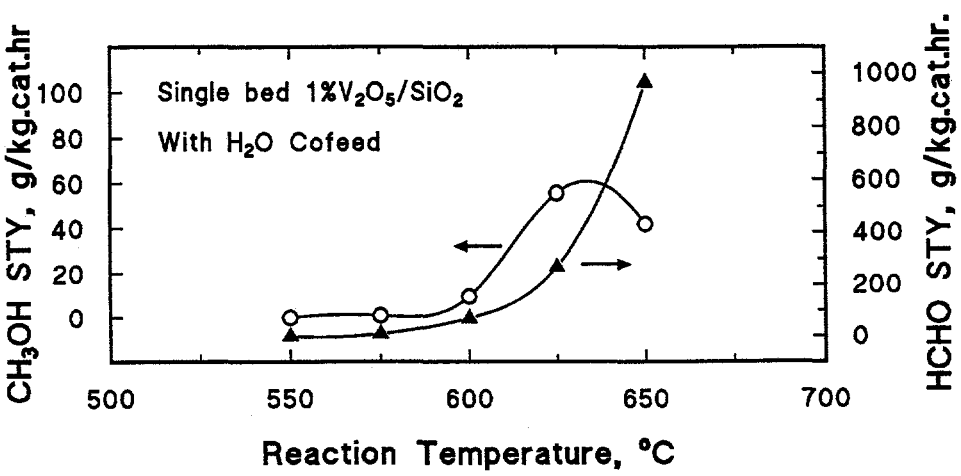

FIGURE 2. Space Time Yields of Methanol and Formaldehyde Over 0.1 g of 1 wt% V_2O_5/SiO_2 Catalyst at 0.1 MPa. The Reactant Mixture Consisted of CH_4/Air/Steam = 140/96/20 with GHSV = 153,600 ℓ/kg catal/hr.

PART 3. Formation of Methanol and Formaldehyde From Methane Over Double Bed Catalysts

Since we have developed (i) a very active catalyst for the synthesis of C_2 hydrocarbons from methane, which arise from methyl radicals generated by the catalyst [See PART 1], (ii) a very active catalyst for the synthesis of formaldehyde from methane [see PART 2], and (iii) a process of using steam in the reactant CH_4/air mixture that led to the formation of a significant quantity of methanol [see PART 2], a reaction system combining these three technological advances was devised and tested for increasing the formation of methanol as a direct product formed *via* selective oxidation of methane.

This reactor system utilizes a double catalyst bed and is based on the concepts of

(i) the first catalyst bed of SO_4^{2-}/SrO/La_2O_3 generates methyl radicals,

(ii) the second catalyst bed traps the methyl radicals to form surface-held methoxy species, and

(iii) the steam in the reactant mixture hydrolyzes the methoxy intermediates to form methanol.

This reaction system is shown schematically in Figure 3.

While the first catalyst always consisted of the methyl radical generating SO_4^{2-}/SrO/La_2O_3 catalyst, a wide variety of unsupported and supported catalysts was tested as the second bed catalyst. Initial testing was carried out using equal quantities of the two catalysts (0.1 g of each) in each test. The total gas flow rate of GHSV = 72,000 ℓ/kg catal/hr is relative to the total quantity (mass) of the two catalysts present in the reactor. The methanol space time yields of some of these oxides are indicated in Figure 4, where the Mo, V, Cr, and Re oxides were prepared as silica-supported catalysts. As shown here, the most active catalyst and the catalyst that produced the most methanol under these reaction conditions was the 1 wt% V_2O_5/SiO_2 catalyst. Therefore, we continued our studies with this catalyst.

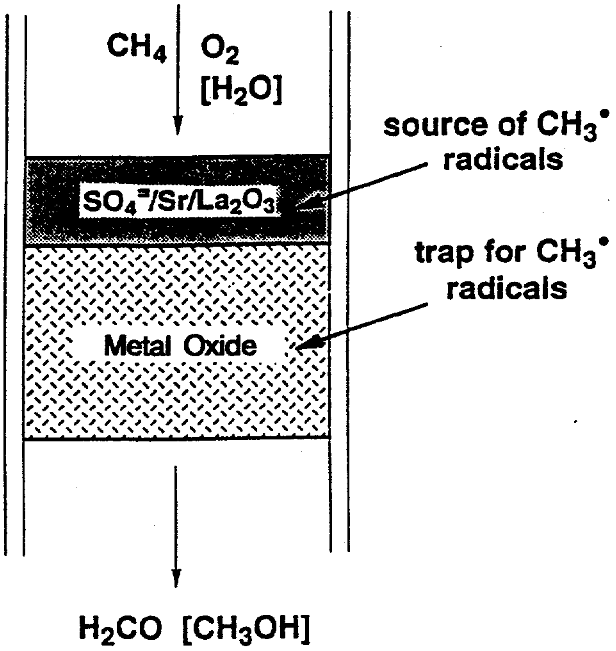

FIGURE 3. A Schematic Representation of the Double Bed Catalyst System Used to Convert Methane to Methanol.

Using the 1 wt% V_2O_5/SiO_2 catalyst as the second bed catalyst and the SO_4^{2-}/SrO/La_2O_3 catalyst as the first bed catalyst, catalytic testing was carried out in the <u>absence of steam</u> in the reactant gas mixture. The resultant catalytic data are shown in Table 4 as a function of the reaction temperature employed. In all cases, high conversion levels of methane were obtained, which was limited by

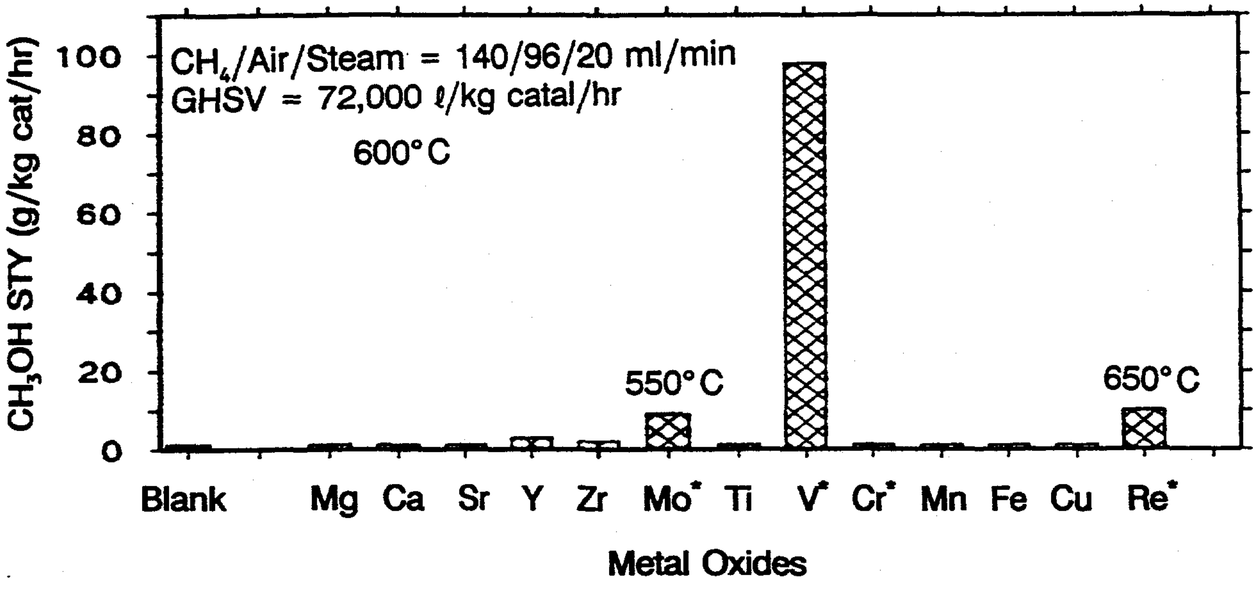

FIGURE 4. Methanol Space Time Yields (STY) Obtained From a CH_4/Air/Steam Reactant Mixture Over Double Bed Catalysts. The First Catalyst Bed Consisted of 0.1 g $SO_4^{2-}/SrO/La_2O_3$ and the Second Bed Consisted of 0.1 g of the Metal Oxide Catalysts. *Represents Silica-Supported Catalysts.

the availability of oxygen, but distinct differences in selectivities were observed as the temperature was increased from 550°C to 650°C. It is evident that as the reaction temperature was increased, the productivities of all products increased except for CO_2. In contrast to the single bed testing of the V_2O_5/SiO_2 catalyst where no C_2 hydrocarbons were generally observed in the product mixture, the double bed catalyst system produced significantly quantities of C_2 hydrocarbons. This is a reflection of the first bed catalyst consisting of $SO_4^{2-}/SrO/La_2O_3$, which generated methyl radicals that were coupled in the gas phase to form the C_2 hydrocarbons.

As the reaction temperature was increased stepwise, the methane conversion level gradually increased to a rather constant level of ≈15%, as shown in Table 4. At the same time, the oxygen conversion level followed the same increasing pattern, i.e. increasing from ≈67% to ≈88 mol% as the reaction temperature was increased.

Using fresh portions of the two catalysts, testing was carried out under the same reaction contitions but with the presence of steam in the reactant gas mixture. As indicated in Table 5, the space time yields of both methanol and formaldehyde were significant even at a reaction temperature of 550°C, a temperature at which the single bed V_2O_5/SiO_2 catalyst was inactive, as shown Figure 2. Indeed, the productivity of methanol from the double bed reactor reached a maximum of over 100 g/kg catal/hr at 600°C, and the productivity of formaldehyde reached over 1000 g/kg catal/hr at 625 and 650°C. From a comparison of Tables 4 and 5, it can be seen that injection of water into the reactant gas stream apparently retarded the conversion of methane to products to a small degree at the lower temperatures. However, the inhibition was not evident at

TABLE 4. The methane conversion and space time yields (STY) of products formed over the double catalyst bed <u>in the absence of steam</u>, where the first bed contained the $SO_4^{2-}/SrO/La_2O_3$ catalyst and the second bed consisted of 1 wt% V_2O_5/SiO_2. The bed of each catalyst was 0.10 g and the reactant mixture was steam-free CH_4/air ≈ 1.5/1 with GHSV = 141,000 ℓ/kg catal/hr relative to each catalyst and 70,500 ℓ/kg catal/hr for the double catalyst bed.

Temp. (°C)	Conv. (mol%)	STY (g/kg.hr)				
		C_2 HC	HCHO	CH_3OH	CO	CO_2
550	13.8	1575	167	16.8	2980	11275
575	14.5	1946	247	21.4	3586	10100
600	15.2	2720	434	38.9	3951	8165
625	15.5	3025	746	39.5	4232	6895
650	15.1	3577	940	48.0	4234	4491

TABLE 5. The conversion of methane and the space time yields (STY) of products formed over double bed catalysts <u>in the presence of steam</u>. The first bed contained the 1 wt% $SO_4^{2-}/SrO/La_2O_3$ catalyst and the second bed consisted 1 wt% V_2O_5/SiO_2. In each case, the bed of each catalyst was 0.10 g and the reactant stream was CH_4/air/steam ≈ 1.5/1.0/0.2, with GHSV = 153,000 ℓ/kg catal/hr relative to each catalyst bed and 76,500 ℓ/kg catal/hr for the double catalyst bed.

Temp. (°C)	Conv. (mol%)	STY (g/kg.hr)				
		C_2 HC	HCHO	CH_3OH	CO	CO_2
550	11.1	1438	210	31.4	2574	8136
575	11.9	1782	576	70.2	3228	6661
600	12.8	2690	739	104.5	3537	4687
625	15.3	3303	1082	86.4	3815	5842
650	14.8	3614	1248	89.1	3876	3967

625°C. Although not given, the conversions of the oxygen reactant corresponding to the data in Table 5 increased from ≈67% to ≈88 mol% as the temperature was increased from 500 to 650°C.

Comparison of the data in Tables 4 and 5 also demonstrates that much higher productivities of the HCHO and CH_3OH oxygenates were obtained in the presence of steam in the reactant gas mixture (Table 5). Therefore, the presence of steam is necessary in order to achieve high productivities of methanol. This is demonstrated graphically in Figures 5A and 5B, where the space time yields of methanol and formaldehyde are shown for the testing in the absence of steam and in the presence of steam, respectively, in the CH_4/air ≈ 1.5/1.0 reactant gas mixture.

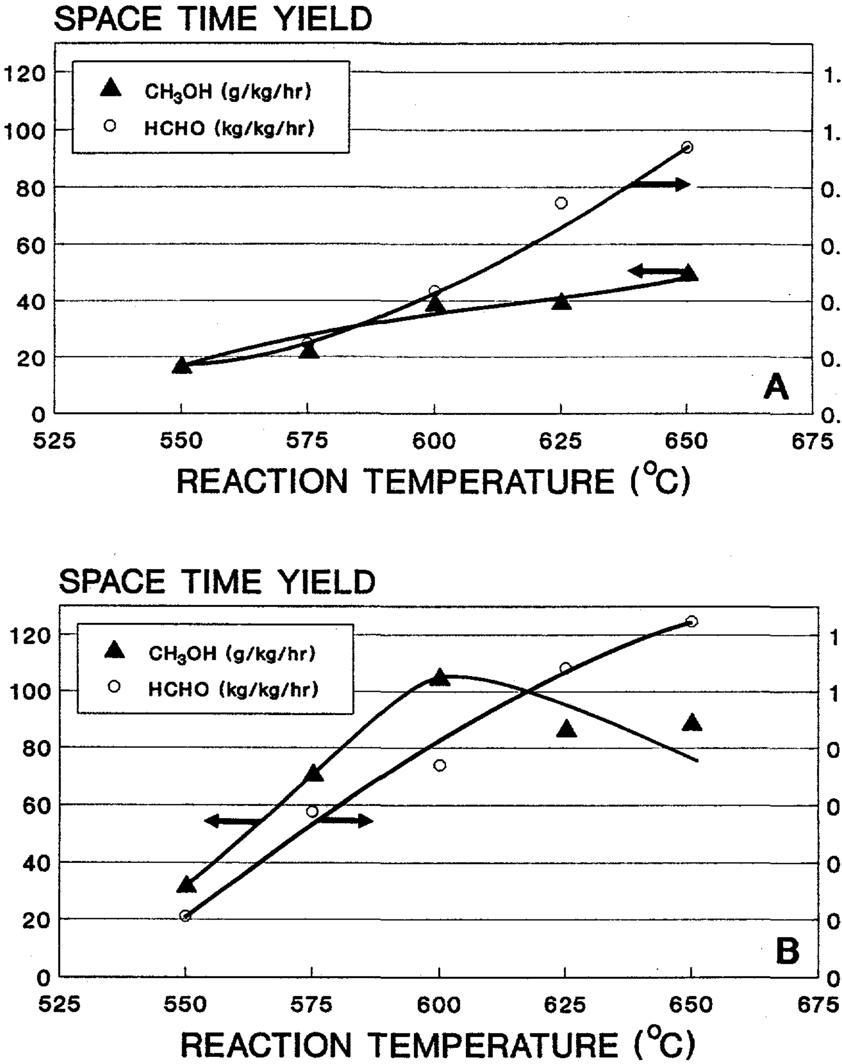

FIGURE 5. The Space Time Yields of Methanol and Formaldehyde Over the Double Bed $SO_4^{2-}/SrO/La_2O_3||V_2O_5/SiO_2$ Catalyst System with a CH_4/Air Reactant Mixture Flowing at a Rate of 140/96 ml/min, Respectively, that [A] Contained No Steam or [B] Contained Steam Flowing at a Rate of 20 ml/min. See Tables 4 and 5 for Additional Details.

Directions for Optimization. There are several directions in which this reaction system can be optimized. These include optimization of the amount of steam in the reactant gas mixture, the relative sizes of the two catalyst beds, reconfiguration of the reactor so that the primary products are removed from the hot reactor zone (which can be balanced with the gas hourly space velocity), pressure at which the reaction is carried out, and surface areas of the two catalysts.

With the double bed catalyst system, it has been found that the relative sizes of the two catalyst beds are important. With 1 wt% Re_2O_7/SiO_2 as the second bed, it has been found that the highest space time yield of methanol was obtained when the first $SO_4^{2-}/SrO/La_2O_3$ catalyst bed was half the weight of the second oxide catalyst bed. These studies are being continued.

Utilizing a V_2O_5/SiO_2 catalyst in a single bed, an example of the optimization procedure is examining the effect of increased partial pressure of steam. It has been determined that the amount of steam in the reactant gas mixture is an important variable that affects the conversion of methane, as well as the selectivities of the products. A demonstration of this is shown in Tables 6A and 6B. As the quantity of steam in the reactant mixture was increased to very large proportions, the methane conversion decreased. However, at the same time the selectivities toward CO and CO_2 decreased while those toward CH_3OH and CH_2O increased significantly. This was reflected in the higher space time yields obtained for methanol and formaldehyde. Indeed, the space time yields of methanol obtained when the reactant gas mixture consisted of approximately $CH_4/air/steam \approx 1.5/1/1$ and 1.5/1/1.5 are perhaps the highest ever obtained for a catalytic process under steady state conditions.

Further optimization studies with both single bed and with double bed catalyst reaction systems are being carried out so that the product selectivity is shifted further toward methanol and/or formaldehyde and that the space time yields of these oxygenates are increased to even higher levels.

OVERALL SUMMARY CONCLUSIONS

Principal accomplishments have been achieved in all three areas of selective catalytic oxidation of methane that have been pursued in this research project. These accomplishments are centered on the development of catalyst systems that produce high space time yields of C_2 hydrocarbon products, formaldehyde, and methanol from methane/air mixtures at moderate temperatures and at ambient pressure. The accomplishments can be summarized as the following:

- the $SO_4^{2-}/SrO/La_2O_3$ catalyst developed here has been further optimized to produce 2 kg of $\underline{C_2\text{ hydrocarbons}}$/kg catalyst/hr at 550°C,
- V_2O_5/SiO_2 catalysts have been prepared that produce up to 1.5 kg formaldehyde/kg catalyst/hr at 630°C with low CO_2 selectivities, and
- a novel dual bed catalyst system has been designed and tested that produces over 100 g methanol/kg catalyst/hr at 600°C.

Further optimization, especially of the methanol synthesis catalyst system, needs to be carried out with these stable oxide catalysts.

TABLE 6A. The Methane Conversions Observed Over a 2 wt% V_2O_5/SiO_2 (0.1 g) at 0.1 MPa Pressure From a Reactant Mixture Consisting of CH_4/Air/Steam = 140/95/variable ml/min.

Catalyst Test	Steam (ml/min)	GHSV (ℓ/kg/hr)	Temp (°C)	%CH_4 Conv.
c	40	165,000	600	11.1
h	80	189,000	600	6.30
i	80	189,000	625	8.90
k	160	237,000	625	4.43

TABLE 6B. The Methane Conversions, Space Time Yields (STY) of Methanol and Formaldehyde, and the Product Selectivities Observed Over a 2 wt% V_2O_5/SiO_2 (0.1 g) at 0.1 MPa Pressure From CH_4/Air/Steam = 140/95/variable ml/min.

Test	Steam	STY (g/kg cat/hr)		Selectivities (C-mol%)			
No.	(ml/min)	CH_3OH	HCHO	CH_3OH	HCHO	CO	CO_2
c	40	72.0	795.2	0.7	8.0	81.9	9.4
h	80	181.4	795.1	2.9	23.8	76.4	6.9
i	80	211.4	1241.9	2.5	15.4	74.9	7.2
k	160	276.4	1281.6	6.1	30.3	54.9	8.7

FUTURE WORK

Our research will proceed according to our Year 3 work plan, as described in the **PROJECT DESCRIPTION.** We have finished work under Task 1 with the acid promoted SrO/La_2O_3 catalyst that we have shown to be a very active and selective catalyst for the oxidative coupling of methane to ethane and ethene under moderate reaction conditions.

Under Task 2, the objective is to direct methane conversion to the selective formation of oxygenates, especially methanol and formaldehyde. This has involved studying new catalysts and determining the influence of reaction conditions, such as reactant flow rate and gas phase additives such as steam, on enhancing the selectivity toward oxygenates. Catalysts that exhibit high productivities of formaldehyde and of methanol have been developed. During the remainder of this project, our efforts will be directed toward further improvement in the selectivity of methanol formation directly from methane. Research under Task 3, which involves catalyst characterization and optimization of these very promising catalysts, is being continued in order to obtain the best industrially practical catalysts for the synthesis of oxygenates from methane.

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