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Selective Methane Oxidation Over Promoted Oxide Catalysts

Quarterly Report
March - May 1995

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Chunlei Shi
Qun Sun

August 1995

Work Performed Under Contract No.: DE-FG21-92MC29228

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Lehigh University
Bethlehem, Pennsylvania

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August 1995

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

Activation of methane at low temperature over modified palladium and platinum catalysts was studied to investigate the possible ways of developing metal catalysts for the oxidative conversion of methane to methanol and formaldehyde. This quarter, Ag-Pd/SiO_2, Fe-Pd/SiO_2, Fe-Pd/Al_2O_3, and Mo-Pt/SiO_2 catalysts were prepared and tested below 450°C at a pressure of 0.45 MPa with a reactant mixture of CH_4/air = 150/100 or 150/50 ml/min. The results showed that CO_2 and CO were the products over all the catalysts. Complete oxygen conversions were observed at temperatures of 335-350°C whether the 2 wt% Pd/SiO_2 catalyst was pretreated with N_2, air, or H_2/N_2 mixture, but no CO was detected when the catalyst was prereduced with the H_2/N_2 mixture. Methane conversions over 1 wt% Ag-0.1 wt% Pd/SiO_2, 1 wt% Fe-0.1 wt% Pd/SiO_2, 0.1 wt% Fe-0.1 wt% Pd/SiO_2, 0.1 wt% Fe-1 wt% Pd/SiO_2 and 0.1 wt% Fe-1 wt% Pd/Al_2O_3 catalysts were strongly suppressed compared to that observed over the 0.1 wt% Pd/SiO_2 catalyst. In the iron-modified palladium catalysts, the methane conversion decreased with an increase of the Fe/Pd ratio. Prereduced Fe-Pd/SiO_2 catalysts gave very high initial activities followed by subsequent low activities when the reactant mixture was CH_4/air = 150/100 ml/min. This initial high activity was suggested to result from iron oxidation upon exposure of the catalysts to the reactant mixture, which would release a large amount of thermal energy to make the catalyst bed overheated. It was observed that the 0.1 wt% Fe-1 wt% Pd/SiO_2 catalyst was more active than the 0.1 wt% Fe-1 wt% Pd/Al_2O_3 catalyst. This difference is attributed to the different interaction between the FePd clusters and the supports. Addition of Mo to the 2 wt% Pt/SiO_2 catalyst seemed slightly to increase the methane conversion. Compared to the 2 wt% Mo/SiO_2 catalyst, the 2 wt% Pt-2 wt% Mo/SiO_2 catalyst had much higher methane conversion. Double-bed experiments were also carried out by employing 0.02 g of a 2 wt% Pd/SiO_2 catalyst as the first bed followed by 0.1 g of a 1 wt% V_2O_5/SiO_2 catalyst as the second bed. The results showed that no methyl radicals were released into the gas phase from the palladium surface and then trapped on the surface of the V_2O_5/SiO_2 catalyst to produce oxygenates, and they also indicated that the V_2O_5/SiO_2 catalyst bed was almost inert below 390°C.

Attempts were also made to activate methane over Pd-modified SO_4^{2-}/ZrO_2 superacid catalysts. Six catalysts of ZrO_2, 5.4 wt% SO_4^{2-}/ZrO_2, 0.1 wt% Pd/ZrO_2 and Pd-SO_4^{2-}/ZrO_2 containing 0.01, 0.1 and 1.0 wt% Pd, were prepared and tested at a temperature range of 250-650°C and a pressure of 0.1 or 0.45 MPa. The preliminary results showed that the Pd-modified SO_4^{2-}/ZrO_2 was more active than the ZrO_2, SO_4^{2-}/ZrO_2 and Pd/ZrO_2

catalysts. The activity of the Pd-SO_4^{2-}/ZrO_2 catalysts markedly increased with an increase in Pd content. The main products observed over the ZrO_2, SO_4^{2-}/ZrO_2, and Pd-SO_4^{2-}/ZrO_2 catalysts were CO and CO_2 with C_2H_6 and C_2H_4 detected in small amounts. It seems that the acidity of the ZrO_2, SO_4^{2-}/ZrO_2 and Pd-SO_4^{2-}/ZrO_2 catalysts plays an important role in the formation of ethane and ethylene. The Pd/ZrO_2 catalyst did not yield ethane, possibly due to its weak acidic sites and its exposed Pd sites tend to catalyze the total oxidation of methane.

A third type of catalyst studied consisted of V_2O_5-SiO_2 xerogels. These catalysts contained 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 15.0, 20.0, and 25.0 wt% vanadia and were synthesized by a sol-gel process. They were investigated with regard to their structure and catalytic properties in partial oxidation of methane to methanol and formaldehyde. The BET surface areas showed the V_2O_5-SiO_2 xerogel with vanadia content up to 25.0 wt% still maintained high surface area. Crystalline V_2O_5 was not observed by X-ray powder diffraction (XRD) in the xerogels containing 1.0, 2.0 3.0 and 4.0 wt% vanadia, indicating that vanadia was finely dispersed within the silica matrix. However, the crystalline V_2O_5 phase could be detected by XRD when the vanadia content exceeded 5.0 wt%. The catalytic testing results showed that for a given methane conversion, the best selectivity to methanol was obtained in the range of 2.0-3.0 wt% vanadia content. The 2.0 wt% V_2O_5-SiO_2 catalyst gave the highest space time yield of methanol in the temperature range of 575-650°C. When the vanadia contents exceeded 15.0 wt%, the yields of methanol and formaldehyde decreased to very small amounts, even to zero. The decrease in the space time yields and selectivities of oxygenates with an increase in vanadia content may be attributed to the existence of the bulk-like vanadia, which catalyzes the secondary oxidation of oxygenates to carbon oxides. It was observed that deionized water and distilled water, which was fed as a reactant with CH_4 and air, gave different catalytic results. When deionized water was utilized, the conversion of methane was diminished with an increase of the space time yield and selectivity of formaldehyde but a decrease of the yield and selectivity of methanol. This difference may be caused by the impurities in the distilled water, which play a role in the partial oxidation of methane occurring both on the catalyst surface and in the gas phase, and further analyses are needed. Appropriate blank runs under our experimental conditions were also carried out. The results showed that the conversion of methane was negligible, smaller than 0.46 mol% up to 650°C at a pressure of 0.45 MPa with a space time yield of methanol less than 35.0 g/kg catal/hr and a space time yield of formaldehyde smaller than 183.5 g/kg catal/hr. As compared to the 2.0 wt% V_2O_5/SiO_2 catalyst prepared by impregnation, the 2.0 wt% V_2O_5-SiO_2 xerogel catalyst exhibited a lower methane conversion but higher selectivities to methanol and formaldehyde. The space time yield of methanol given by the 2.0 wt% V_2O_5-SiO_2 xerogel catalyst at 625-650°C is higher than that given by the supported 2.0 wt% V_2O_5/SiO_2 catalyst.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

OBJECTIVES OF THE RESEARCH

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

$$2CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons C_2H_6 + H_2O \tag{1}$$

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

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

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

$$CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons CH_3OH \tag{5}$$

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

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

Task 1. Maximizing Selective Methane Oxidation to C_2H_4 Products Over Promoted Sr/La_2O_3 Catalysts.
Task 2. Selective Methane Oxidation to Oxygenates.
Task 3. Catalyst Characterization and Optimization.

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

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

RESEARCH PROGRESS

Introduction

The partial oxidation of methane to methanol and formaldehyde over oxide catalysts proceeds at high temperature with only low selectivities. Better results can be expected by using catalysts capable of activating methane at mild conditions, but the low reactivity of methane makes this an extremely challenging task.

In recent years, activation of methane by transition metal complexes in solution under mild conditions has been reported (1-4). The metals that are active for this reaction include Ir, Pd, Pt, Co, Rh and Re. The most promising approach appears to be electrophilic activation by metal complexes in strong acid media. Periana et al. (5) found that methane could be oxidized by concentrated sulfuric acid at 180°C and 3.7 MPa to give a methane conversion of 50% and 85% selectivity to methyl bisulfate. The reaction is catalyzed by mercuric ions, Hg(II). However, these homogeneous reactions catalyzed by metal complexes have several disadvantages: (a) the high cost of separation of the products from the catalysts, (b) the disadvantage of processing huge liquid flows, and (c) the low solubility of methane in the solvents. To overcome the difficulties arising from homogeneous reactions, it would be desirable to develop heterogeneous catalysts capable of activating methane at low temperature.

Reduced transition metals (e. g. Pd, Pt, Rh, Re, Ir, Ni, W, Fe, Cu) could activate methane at mild conditions (6,7). Methane is dissociatively adsorbed on metal surfaces as the species CH_x ($x = 0\text{-}3$) when it is contacted with reduced transition metals above room temperature. In the presence of oxygen, methane is almost fully oxidized into CO_2 and H_2O. In recent years, a large number of studies, both experimental and theoretical, have been performed to focus on C-H activation of methane by transition metal clusters or single crystals (8-12). Among the above mentioned metals, palladium is considered to be the most promising potential candidate for the catalytic conversion of methane to coupling products and oxygenates under mild conditions. The palladium atom was found to be the atom with the second lowest activation barrier (16 kcal/mol) for breaking the C-H bond (9,12). The results of CH_4/D_2 and CH_4/CD_4 exchange showed that palladium mainly promotes the reversible activation of the single C-H bond, which was generally assumed for the coupling process and the formation of methanol (14-15). Fayet et al. (12) observed that the gas-phase reactions of methane with palladium clusters with up to 25 atoms showed strong variations depending on the size of palladium clusters. One of the most interesting results of that study was the finding that most palladium clusters were found to activate methane. In practice, a small quantities of HCHO was observed over palladium catalysts with the promotion of halogen-containing additives (16). However, industries have little interest in this process due to the potential pollution of halogen. Koenig (17) developed a process in which methane could be converted to methanol with 92% selectivity in aqueous $Fe_2(SO_4)_3$ solution at ambient temperature and pressures of 3-6 MPa using 0.6%Pd-Ag/C to activate methane. Experiments were carried out by Anderson et al. (18) on titanium and palladium membranes at around 120°C, which showed very low conversion of methane with coke as the main product. Another approach, by Wilson et al. (19), consisted in preparing stabilized phthalocyanine complexes that mimic oxygenase enzymes that are active at low temperature. By testing Pd complexes supported on MgO, they observed some ethane formation below 450°C. Based on the idea that if metal clusters are able to activate methane at low temperature, they could also be potential candidates for the catalytic conversion of methane to oxygenates by modification with ligands and/or with other metals via the formation of alloys. During this quarter, Ag-Pd/SiO_2, $Fe_2(SO_4)_3$-Pd/SiO_2, Fe-Pd/SiO_2, Fe-Pd/Al_2O_3 and Mo-Pt/SiO_2 catalysts were prepared and tested below 450°C at a pressure of 0.45 MPa, with the aim of studying possible ways to develop metal catalysts for the oxidative conversion of methane to oxygenates under mild conditions.

Superacids can also activate methane at low temperature. In 1967, Olah et al. (20) demonstrated that methane acts as a weak base and its C-H bond can be activated in superacid environment. Methane condensation catalyzed by 1:1 FSO_3H-SbF_5 at 140°C and atmospheric pressure was first reported in 1968 (21). It was suggested that methane was protonated in the superacid solution to the CH_5^+ ion, which then either underwent reversible deprotonation or lost hydrogen to form the extremely reactive CH_3^+, which then reacted with excess methane to start a polycondensation. Thermodynamically, the condensation of methane is not favorable except when the concurrent reduction of superacid occurs (2). However, the alkylation of methane by ethylene is favorable. Therefore, many studies have focused on the alkylation of methane by ethylene over homogeneous superacid solutions or solid superacid catalysts such as TaF_5, 1:1 TaF_5-AlF_3, and SbF_5 intercalated into graphite and SO_4^{2-}/ZrO_2 (22-24). In another respect, it was reported (25) that methane could be partially oxidized to methanol with maximum values of 77% selectivity, 8% conversion, and 3.4% yield at 250°C over a catalyst composed of solid superacid Cr^{3+}-Zr^{4+}-SO_4/silica gel containing a promoter of Cr_2O_3. This quarter, Pd-modified SO_4^{2-}/ZrO_2 catalysts were prepared and tested to probe the selective oxidation of methane at low temperature.

Among the numerous catalysts proposed for the partial oxidation of methane to formaldehyde, silica based systems are the more promising ones (7,26). V_2O_5 has been generally recognized as a good promoter of the silica support (27-30). Silica supported

V_2O_5 catalyst was found to be one of the most active and selective catalysts for partial methane oxidation by O_2 to formaldehyde (28,31,32). In our laboratory, a process including feeding steam and/or using double catalyst bed has been developed to obtain methanol over supported V_2O_5/SiO_2 catalysts at nearly ambient pressure (33). However, it is generally agreed that the interaction of the vanadia species with the silica support is relatively weak in catalysts prepared by impregnation of silica with a vanadium-containing precursor (34-36). As a result of the weak interaction, the immobilized vanadia species tend to agglomerate when exposed to higher temperature. This behavior resulted in deactivation of the V_2O_5/SiO_2 catalysts in partial methane oxidation. Baiker et al. (37) observed that finely dispersed vanadia species on silica could be stabilized in a silica matrix by employing a sol-gel process to prepare the catalysts. It was observed that in all mixed gel catalysts, the well-dispersed vanadia species were more stable at high temperature than those prepared by impregnation. During this quarter, V_2O_5-SiO_2 xerogels containing V_2O_5 content from 1.0 wt% to 25.0 wt% were prepared by the sol-gel precess and investigated with regard to their structure and catalytic properties in partial methane oxidation.

Experimental

Preparation of Catalysts

Catalysts consisting of 2 wt% Pd/SiO_2 and 2 wt% Ag-2 wt% Pd/SiO_2 were prepared by impregnating the SiO_2 support (Cabosil EH-5, surface area = 380 m^2/g) with $Pd(NO_3)_2$ and $AgNO_3$ solution of the appropriate concentrations followed by air drying overnight at 120°C and calcination at 450°C for 2 hr. The 1.8 wt% $Fe_2(SO_4)_3$-Ag-Pd/SiO_2 catalyst was obtained by impregnating the reduced 2 wt% Ag-2 wt% Pd/SiO_2 with $Fe_2(SO_4)_3$ solution with pH = 3 adjusted by adding 1 M nitric acid.

The 0.1 wt% Pd/SiO_2, 0.1 wt% Fe-0.1 wt% Pd/SiO_2, 1 wt% Fe-0.1 wt% Pd/SiO_2, 0.1 wt% Fe-1 wt% Pd/SiO_2, 0.1% Fe-1% Pd/Al_2O_3 and 1 wt% Ag-0.1 wt% Pd/SiO_2 catalysts were prepared by impregnating SiO_2 or Al_2O_3 (Aldrich, surface area 155 m^2/g) with $[Pd(OCOCH_3)_2]_3$, $Fe(OCOCH_3)_2$, and $AgOCOCH_3$ in acetone or acetone/water mixture and then drying at 120°C for 6 hr and 250°C for 2 hr. The catalysts prepared by using such organometallic compounds anchored to the surface of the supports have a much higher dispersion of metals after reduction than those by using inorganic salts (38).

A 2 wt% Mo/SiO_2 catalyst was obtained by heating a mixture of MoO_3 and SiO_2 at 550°C for 6 hr. A 2 wt% Pt-2 wt% Mo/SiO_2 catalyst was prepared from 2 wt% Mo/SiO_2 by aqueous impregnation with $H_2PtCl_6.6H_2O$ solution followed by drying at 120°C for 6 hr and calcination at 250°C for 2 hr.

Pure ZrO_2 was obtained by calcining $Zr(OH)_4$ at 550°C for 6 hr. The $Zr(OH)_4$ was obtained by the hydrolysis of $ZrOCl_2.8H_2O$ with aqueous NH_4OH solution followed by filtration and washing until no Cl ions were detected. Surface sulfating of $Zr(OH)_4$ was carried out by washing the previously dried material with 1 N H_2SO_4, followed by drying overnight and then calcining at 600°C for 3 hr. The Pd/ZrO_2 and Pd-SO_4^{2-}/ZrO_2 catalysts were prepared by impregnating ZrO_2 or SO_4^{2-}/ZrO_2 with $Pd[(OCOCH_3)_2]_3$/acetone solutions followed by drying at 120°C for 19 hr and calcination at 500°C for 2 hr.

The V_2O_5-SiO_2 xerogel was prepared by sol-gel synthesis with vanadium triisopropoxide oxide ($VO(OC_3H_7)_3$, Fisher) as precursor. The SiO_2 sol was first prepared by dissolving tetraethoxysilane ($Si(OC_2H_5)_4$, Fisher) in methanol (99.9%, Fisher) and combining it with a solution of deionized water and nitric acid (70%, Fisher), followed by stirring with a magnetic bar for 20 min for partial hydrolysis to occur. The SiO_2 sol was then mixed with vanadium triisopropoxide oxide diluted in methanol, after which the resulting transparent V_2O_5-SiO_2 sol was stirred for 15 min. Additional aqueous nitric acid was added to the V_2O_5-SiO_2 sol and a thick gel formed within 12 hr. The obtained gel was allowed to age at room temperature for an additional 10 hr. Subsequently, the V_2O_5-SiO_2 gel was dried at 50°C for 15 hr, at 120°C for 6 hr, and then calcined at 550°C for 4 hr. On the base of 1 mol of tetraethoxysilane, the following substances were used: 2.76 mol of methanol, 0.66 mol of nitric acid, 7.8 mol of water, and an appropriate amount of triisopropoxide oxide that gave V_2O_5 contents of 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 20.0 and 25.0 wt% in the final V_2O_5-SiO_2 xerogels. The synthesis of a 15.0 wt% V_2O_5-SiO_2 xerogel was different from the above xerogels in the amount of employed water and nitric acid. Only 4.0 mol of water and 0.0001 mol of nitric acid on the base of 1 mole of tetraethoxysilane was used for the preparation of 15.0 wt% V_2O_5-SiO_2 xerogel. The gel formed within 4 days.

Catalytic Testing

The above palladium and platinum catalysts (typically 0.10 g portions) were prereduced with pure H_2 at 250°C or 2% H_2 in N_2 at 450°C for 2 hr with a flow rate of 8.2 ml/min. Catalytic testing of palladium and platinum catalysts was carried out at a pressure of 0.45 MPa (due to the reaction system connecting to a back-pressure regulator) and in the temperature range of 150°C to 450°C with a CH_4/air reactant mixture typically having a ratio of 1.5/1.0 (typical flow rates = 150/100 ml/min). The superacid catalysts were pretreated in an air stream at 500°C for 1 hr prior to the reaction. Catalytic testing was carried out at a pressure of 0.45 MPa or atmospheric pressure with a ratio of CH_4/air = 150/100 ml/min. The V_2O_5-SiO_2 xerogel catalysts were pretreated at 550°C for 0.5 hr.

Catalytic testing was carried out with a reactant stream of CH_4/air/steam = 150/100/56 at a pressure of 0.45 MPa. Typically, 0.1 g catalyst was packed in a quartz reactor with quartz wool placed before and after the catalyst bed. The flow rates of methane and air were measured and controlled by mass-flow controllers (Brooks and Linde). The gases were preheated separately before entering the reactor. The exhaust gas lines from the reactor to the GC and from the GC to the ice trap were heated to 150°C to prevent condensation of the products.

The exhaust gas was analyzed by a Varian 3700 gas chromatograph with helium as a carrier gas at a pressure of ca. 0.14 MPa with a flow rate of 30 ml/min using a Porapak Q column (2 m length x1/8-in. o.d.) and a 5A zeolite column (2 m length x 1/8-in. o. d.) in parallel and a thermal conductivity detector. The condensable products were trapped by using an ice bath at 0°C and were separately analyzed by a Hewlett Packard 5970 MSD GC/MS instrument.

Characterization of Catalysts

All V_2O_5-SiO_2 xerogel catalysts were characterized by BET and XRD. BET surface area and pore volume were measured with a commercial Gemini 2360 unit using N_2 as adsorbent. XRD patterns were obtained with an APD1700 automated powder diffractometer using a Cu source. In XRD quantitative phase analysis, KCl was used as an inner standard. The peak areas for reflections $2\theta = 26.1°$ of V_2O_5 and $2\theta = 28.2°$ of KCl were measured to determine to the amount of crystalline V_2O_5 in the xerogels. Pure V_2O_5 was obtained by hydrolyzing $VO(OC_3H_7)_3$ in methanol followed by drying at 50°C for 10 hr, at 120°C for 6 hr, and calcining at 550°C for 6 hr.

Results and Discussion

Modified Palladium Catalysts

The results obtained for the partial oxidation of methane by air (CH_4/air = 150/100 ml/min) at temperatures of 150-450°C over a range of palladium catalysts are present in Table 1. The most striking catalytic feature is the oxidation of methane to CO_2, the deep oxidation product, under these reaction conditions.

Table 1. Methane conversion and product selectivities over 0.1 g Pd/SiO_2 and modified palladium catalysts (wt%) from CH_4/air = 150/100 ml/min (GHSV = 150,000 l/kg cat/hr). Catalyst testing was carried out at the temperature indicated and at a pressure of 0.45 MPa.

Catalyst	Temp. (°C)	CH_4 Conv. (mol%)	Selectivities (C mol%)	
			CO_2	CO
2% Pd/SiO_2[a]	200	0.0	0.0	0.0
	335	11.7	95.8	4.4
2% Pd/SiO_2[b]	350	9.6	99.7	0.3
	250	0.12	100	0.0
2% Pd/SiO_2[c]	200	0.0	0.0	0.0
	335	10.1	100	0.0
	450	10.1	100	0.0
2% Ag-2% Pd /SiO_2[b]	150	0.0	0.0	0.0
	250	0.0	0.0	0.0
	350	9.95	98.9	1.1
1.8% $Fe_2(SO_4)_3$- 2% Ag- 2% Pd/SiO_2[a]	350	0.07	100	0.0
	450	1.16	100	0.0
	525	10.8	91.0	9.0
1%Ag- 0.1% Pd/SiO_2[d]	250	0.0	0.0	0.0
	300	0.0	0.0	0.0
	350	0.7	100	0.0
	400	0.7	100	0.0
0.1% Pd/SiO_2[d]	250	0.2	100	0.0
	300	11.3	99.7	0.3
0.1% Fe- 0.1% Pd/SiO_2[e]	250	0.3	100	0.0
	300	0.1	100	0.0
0.1% Fe- 0.1% Pd/SiO_2[d]	300	0.4	100	0.0
	350	0.2	100	0.0
1% Fe- 0.1% Pd/SiO_2[d]	250	0.05	100	0.0
	350	0.2	100	0.0

[a]Pretreated at 300°C for 2 hr in a flow of N_2.
[b]Preoxidized at 600°C for 2 hr using air.
[c]Prereduced at 450°C for 2 hr using 2% H_2 in N_2 with a flow of 8.2 ml/min.
[d]Prereduced at 250°C for 2 hr by pure H_2 with a flow of 8.2 ml/min.
[e]Preoxidized at 250°C for 2 hr by air.

The methane oxidation reaction occurred at a temperature of 335-350°C with complete conversion of oxygen without regard to the manner in which the 2 wt% Pd/SiO_2 catalyst was pretreated with N_2, air, or H_2/N_2 mixture. The CO selectivities were 0% when the catalyst was prereduced with H_2/N_2 mixture, but CO was detected when the catalyst was not prereduced. It was previously suggested that the formation of CO results from methane oxidation by surface PdO species when the palladium catalyst had not been reduced before reaction (14).

A 2 wt% Ag-2 wt% Pd/SiO_2 catalyst operated at 350°C gave complete conversion of O_2 similar to that of the Pd/SiO_2, but a 1.1% CO selectivity was observed. However, for the 1 wt% Ag-0.1 wt% Pd/SiO_2 catalyst with a small amount of Pd and a large ratio of Ag/Pd, the methane conversion level decreased to 0.7 mol% at 350°C and 400°C. In this case, inactive silver metal was probably the predominant surface species although AgPd clusters were probably also present.

In Koenig's process (17), methane conversion to methanol was catalyzed by a Ag-Pd/C catalyst that was sprayed with a $Fe_2(SO_4)_3$ solution. During this quarter, a 1.8 wt% $Fe_2(SO_4)_3$-2 wt% Ag-2 wt% Pd/SiO_2 catalyst was prepared and tested. The result showed that methane conversion was strongly suppressed over this catalyst at 350-450°C compared to the 2 wt% Ag-2 wt% Pd/SiO_2 catalyst. At 525°C, the methane conversion was 10.8 mol% with 9.0% selectivity to CO. However, no methanol was observed under this conditions.

Past studies on methane conversion catalyzed by the methane monooxygenase (MMO) enzyme have shown that the oxygen activation and insertion chemistry of MMO occurs on the hydroxylase component, which contains dinuclear iron clusters (40-42). Based on the view that the iron clusters in the MMO are good oxygen activator sites and providers for selective methane conversion to methanol, iron could behave similarly when it is doped into palladium and platinum catalysts. Iron-modified palladium catalysts were prepared and tested for methane conversion, as shown in Tables 1 and 2. The results showed that the addition of iron strongly suppressed the level of methane conversion. At a given temperature, the methane conversion decreased with an increase of the Fe/Pd ratio (Table 2). It can also be seen that the 0.1 wt% Fe-1 wt% Pd/SiO_2 catalyst was more active than the 0.1 wt% Fe-1 wt% Pd/Al_2O_3 catalyst. This difference is attributed to the different interaction between the metal clusters and the supports. It was observed that the Fe-

Pd/SiO_2 catalysts prereduced by H_2 gave very high methane conversions for a short period at the beginning then followed by steady low methane conversions. However, the preoxidized catalyst didn't show this phenomenon. It is suggested that the initial high activity of the reduced catalysts resulted from iron oxidation upon exposure to the CH_4/air mixture, which would release a large amount of thermal energy to make the catalyst bed overheated. This was confirmed by the observations of the reactor temperature surpassing the preset temperatures at the beginning of the catalytic test for these experiments, and this effect was suppressed by reducing the oxidation potential of the reactant mixture by increasing the reactant ratio of CH_4/air to 150/50 ml/min.

Table 2. Methane conversion and product selectivities over 0.1 g of iron-modified palladium catalysts with a ratio of CH_4/air = 150/50 ml/min (GHSV = 120,000 l/kg cat/hr). Catalyst testing was carried out at the temperatures indicated and at a pressure of 0.45 MPa.

Catal.	Temp. (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)			
			C_2H_4	C_2H_6	CO	CO_2
0.1 wt% Fe-0.1 wt% Pd /SiO_2[a]	250	0.03	0.0	0.0	0.0	100.0
	350	0.37	0.0	18.1	0.0	81.9
	400	4.80	0.0	0.0	0.0	100.0
0.1 wt% Fe-1 wt% Pd /SiO_2[a]	250	0.09	0.0	0.0	0.0	100.0
	350	5.34	0.0	0.0	0.0	100.0
	400	5.71	0.0	0.0	0.0	100.0
0.1 wt% Fe-1 wt% Pd /Al_2O_3[a]	250	0.25	0.0	0.0	0.0	100.0
	300	0.22	0.0	0.0	0.0	100.0
	350	0.32	0.0	0.0	0.0	100.0
	400	4.98	0.0	0.0	1.1	98.9
	500	5.32	0.0	0.0	0.0	100.0

[a] Prereduced at 250°C for 2 hr by pure H_2 with a flow of 8.2 ml/min.

Double-bed experiments were also carried out by using 0.02 g 2 wt% Pd/SiO_2 catalyst as the first bed followed by 0.1 g 1 wt% V_2O_5/SiO_2 catalyst as the second bed. Compared to the result of a single catalyst bed of 2 wt% Pd/SiO_2 (Table 1), higher CO selectivity was observed for the double catalyst bed (Table 3). Although the palladium catalyst can readily activate methane at low temperature, it can be remarked that there were no methyl radicals released in the gas phase and then trapped on the surface of the V_2O_5/SiO_2 catalyst. Instead, methane activation led to the final CO_x product by interaction with absorbed oxygen on the palladium surface. Addition of steam to the reactant mixture did not decrease the methane conversion level but did shift the product selectivity toward CO (Table 3). The result also indicated that the V_2O_5/SiO_2 bed was almost inert at 390°C or below.

Table 3. Methane conversion and product selectivities over a double catalyst bed of 0.02 g 2 wt% Pd/SiO_2 as the first bed and 0.1 g 1 wt% V_2O_5/SiO_2 as the second bed and with a ratio of CH_4/air = 150/100 ml/min (GHSV = 125,000 l/kg cat/hr) with or without feeding 56.0 ml/min steam. Catalyst testing was carried out at the temperatures indicated and at a pressure of 0.45 MPa.

Catalyst	Temp. (°C)	CH_4 Conv. (mol%)	Selectivities (C mol%)	
			CO_2	CO
D-Bed: 2 wt% Pd/ SiO_2 ||1 wt% V_2O_5/SiO_2	275	0.03	100	0.0
	390	10.2	95.2	4.8
	350, H_2O	11.1	89.6	10.4

Modified Platinum Catalysts

In addition to palladium, platinum is also one of the most active metals for methane activation. A platinum catalyst modified by molybdenum was prepared and tested. Contrary to iron, molybdenum in the 2 wt% Mo-2 wt% Pt/SiO_2 catalyst seemed to increase the methane conversion level, as shown in Table 4. For example, the methane conversion over the $Mo-Pt/SiO_2$ catalyst at 300°C was 1.05 mol%, whereas the conversion over the Pt/SiO_2 catalyst was 0.17 mol% CH_4 (Table 4). At 350°C, the CO selectivity for the $Mo-Pt/SiO_2$ catalyst reached 13.7 mol%. The 2 wt% Mo/SiO_2 gave a low methane conversion even at 450°C.

Table 4. Methane conversion and product selectivities over 0.1 g of molybdenum and platinum catalysts (wt%) with CH_4/air = 150/100 ml/min (GHSV = 150,000 l/kg cat/hr). Catalyst testing was carried out at the temperatures indicated and at a pressure of 0.45 MPa.

Catalyst	Temp. (°C)	CH_4 Conv. (mol%)	Selectivities (C mol%)	
			CO_2	CO
2% Pt/SiO_2[a]	200	0.0	0.0	0.0
	300	0.17	100	0.0
2% Mo/SiO_2[a]	200	0.0	0.0	0.0
	300	0.0	0.0	0.0
	450	0.16	100	0.0
2% Pt-2% Mo /SiO_2[a]	200	0.0	0.0	0.0
	300	1.05	100	0.0
	350	11.1	86.3	13.7

[a]Prereduced at 450°C for 2 hr using 2% H_2 in N_2 with a flow of 8.2 ml/min.

The above attempts to switch the selectivities to oxygenates by modifying palladium and platinum catalysts with silver, iron, and molybdenum did not succeed. The research work planned for the next step, aiming at developing metal catalysts for oxidative conversion of methane to oxygenates under mild conditions, includes: (a) continued preparation and catalyst testing of nanoscale Pd, Rh, or Pt alloys with other noble metals supported on different supports (e.g. SiO_2, Al_2O_3, ZrO_2, MgO, and glasses); (b) synthesis and catalyst testing of palladium (or platinum) and its bimetallic cluster complexes (i.e. molecular metal clusters); and (c) development of palladium and platinum complexes that would activate methane in solution and give high selectivity to methanol.

Pd-SO_4^{2-}/ZrO_2 Catalysts

Five catalysts, including 0.1 wt% Pd/ZrO_2, 5.4 wt% SO_4^{2-}/ZrO_2, 0.01 wt% Pd-SO_4^{2-}/ZrO_2, 0.1 wt% Pd-SO_4^{2-}/ZrO_2, and 1 wt% Pd-SO_4^{2-}/ZrO_2, were tested at a pressure of 0.45 MPa and temperatures between 250°C and 650°C with a reactant mixture of CH_4/air = 150/100 ml/min. The methane conversions, space time yields, and selectivities observed with the singly promoted 0.1 wt% Pd/ZrO_2 and the SO_4^{2-}/ZrO_2 catalysts are shown in Table 5A. It is noted that the sulfated zirconia was a very poor catalyst for activation of methane, while the Pd/ZrO_2 catalyst was active above 450°C.

Table 5A. Methane conversion, product yields and selectivities over 0.1 g of 0.1 wt% Pd/ZrO_2 and 5.4 wt% SO_4^{2-}/ZrO_2 catalysts with a ratio of CH_4/air = 150/100 ml/min (GHSV = 150,000 l/kg cat/hr). Catalyst testing was carried out at the temperatures (T) indicated and at a pressure of 0.45 MPa.

Catal.	T (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)					
			CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
0.1 wt% Pd/ ZrO_2	250	0.02	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	35.2 (100.0)
	350	0.17	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	270 (100.0)
	400	0.44	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	694 (100.0)
	450	12.00	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	6751 (56.4)	8215 (43.6)
	550	13.27	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	4919 (43.5)	1005 (56.5)
	650	16.67	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	16.9 (0.2)	1027 (70.5)	6765 (29.5)
5.4 wt% SO_4^{2-}/ ZrO_2	500	0.02	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	32.4 (100.0)
	550	0.02	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	26.8 (100.0)
	600	0.36	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	115 (59.3)	96.4 (26.6)	80.3 (14.1)
	650	1.34	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	76.0 (10.6)	984 (73.8)	326 (15.6)

The preliminary results obtained with the doubly promoted $Pd\text{-}SO_4^{2-}/ZrO_2$ catalysts showed that the 0.1% $Pd\text{-}SO_4^{2-}/ZrO_2$ catalyst (see Table 5B) was more active than the singly doped 0.1% Pd/ZrO_2 and SO_4^{2-}/ZrO_2 catalysts. For example, as shown in Tables 5A and 5B, the conversion of methane over 0.1% Pd/ZrO_2, SO_4^{2-}/ZrO_2, and 0.1% $Pd\text{-}SO_4^{2-}/ZrO_2$ at 400°C was 0.44, 0.0, and 13.84 mol%, respectively. With the increase of Pd content, the activities of $Pd\text{-}SO_4^{2-}/ZrO_2$ catalysts increased markedly, as seen from the fact that complete oxygen conversion occurred at 550°C for 0.01% $Pd\text{-}SO_4^{2-}/ZrO_2$, 400°C for 0.1% $Pd\text{-}SO_4^{2-}/ZrO_2$, and 350°C for 1% $Pd\text{-}SO_4^{2-}/ZrO_2$ (Table 5B). The products were

Table 5B. Methane conversion, product yields, and selectivities over 0.1 g of the Pd-SO_4^{2-}/ZrO_2 catalysts from CH_4/air = 150/100 ml/min (GHSV = 150,000 l/kg cat/hr). Catalyst testing was carried out at the temperatures (T) indicated and at a pressure of 0.45 MPa.

Catal.	T (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)					
			CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
0.01 wt% Pd-SO_4^{2-}/ ZrO_2	400	0.13	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	211.1 (100.0)
	450	0.52	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	829.1 (100.0)
	500	6.36	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	15.4 (0.4)	84.5 (1.18)	11068 (98.4)
	550	9.61	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	154.4 (2.7)	2162.3 (20.4)	12782 (76.85)
	600	9.03	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	74.0 (1.4)	2711.3 (28.1)	10682 (70.5)
	650	10.6	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	173.3 (2.9)	5085.2 (45.7)	8999.6 (51.4)
0.1 wt% Pd-SO_4^{2-}/ ZrO_2	300	0.04	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	64.9 (100.0)
	350	0.29	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	62.5 (39.5)	280.6 (60.5)
	400	13.84	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	67.5 (0.9)	6949.8 (47.2)	12031 (52.0)
	500	10.89	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	36.5 (0.6)	4838 (44.8)	9263.6 (54.6)
	550	11.39	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	17.7 (0.3)	5698.6 (52.5)	8042.6 (47.2)

Table 5B (Continued). Methane conversion, product yields, and selectivities over 0.1 g of the Pd-SO_4^{2-}/ZrO_2 catalysts from CH_4/air = 150/100 ml/min (GHSV = 150,000 l/kg cat/hr). Catalyst testing was carried out at the temperatures (T) indicated and at a pressure of 0.45 MPa.

Catal.	T (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)					
			CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
1 wt% Pd-SO_4^{2-}/ ZrO_2	250	0.05	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	81.1 (100.0)
	300	1.79	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	58.2 (20.9)	317 (79.1)
	350	9.84	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	25.4 (0.5)	1433 (14.3)	1343 (85.2)
	400	9.90	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	100.5 (1.8)	1677 (16.4)	1313 (81.8)
	450	10.26	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	25.3 (0.5)	2582 (24.8)	1222 (74.7)
	550	12.11	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	51.0 (0.8)	5452 (46.1)	9878 (53.1)
	650	17.39	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	24.0 (0.3)	1118 (68.8)	7904 (31.0)

observed to be CO_2 and CO but with a small amount of C_2H_6 observed for SO_4^{2-}/ZrO_2 and Pd-SO_4^{2-}/ZrO_2 catalysts. The selectivity to CO fundamentally increased with an increase in temperature. The formation of C_2H_6 began to be observed at 600°C for SO_4^{2-}/ZrO_2, 500°C for 0.01% Pd-SO_4^{2-}/ZrO_2, 350°C for 0.1% Pd-SO_4^{2-}/ZrO_2 and 300°C for 1% Pd-SO_4^{2-}/ZrO_2. The SO_4^{2-}/ZrO_2 catalyst exhibited a higher selectivity for the formation of ethane than Pd-modified SO_4^{2-}/ZrO_2.

Table 6 gives the methane conversion and product selectivities observed over pure ZrO_2 and 0.01 wt% Pd-SO_4^{2-}/ZrO_2 catalysts at atmospheric pressure. The conversion of methane for the Pd-SO_4^{2-}/ZrO_2 catalyst was much lower than that obtained at 0.45 MPa pressure. For example, at 500°C the methane conversion at 0.45 MPa was 6.36 mol%, but at atmospheric pressure it was only 0.19 mol%. At higher pressure, both surface and gas phase reactions were greatly enhanced due to much longer residual time of the reactant mixture in the reactor. It was observed that the activity of the 0.01 wt% Pd-SO_4^{2-}/ZrO_2 catalyst at atmospheric pressure was also higher than that of the pure ZrO_2. Both of these catalysts yielded a small amount of C_2H_6 product. The CO selectivity for the 0.01 wt% Pd-SO_4^{2-}/ZrO_2 catalyst was smaller by almost an order of magnitude than that for ZrO_2 catalyst.

Table 6. Methane conversion, product yields, and selectivities over 0.1 g of ZrO_2 and 0.01 wt% Pd-SO_4^{2-}/ZrO_2 catalysts with a ratio of CH_4/air = 150/100 ml/min (GHSV = 150,000 l/kg cat/hr). Catalyst testing was carried out at the temperatures indicated and at 0.1 MPa.

Catal.	Temp. (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)			
			C_2H_4	C_2H_6	CO	CO_2
ZrO_2	500	0.10	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	168 (100.0)
	550	0.27	0.0 (0.0)	0.0 (0.0)	158 (57.6)	183 (42.4)
	600	0.66	0.0 (0.0)	0.0 (0.0)	826 (64.4)	719 (35.5)
	625	2.55	0.0 (0.0)	0.0 (0.0)	1725 (67.8)	1289 (32.2)
	650	3.40	0.0 (0.0)	31.7 (1.9)	2257 (71.0)	1359 (27.1)
0.01 wt% Pd-SO_4^{2-} /ZrO_2	500	0.19	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	311 (100.0)
	550	0.47	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	757 (100.0)
	600	3.28	22.0 (1.3)	39.2 (2.2)	219 (6.5)	4794 (90.0)

It seems that the acidity of ZrO_2, SO_4^{2-}/ZrO_2 and Pd-SO_4^{2-}/ZrO_2 catalysts plays an important role in formation of ethane and ethylene. Methane is first protonated on the surfaces of the catalysts to CH_5^+ which then loses hydrogen to form CH_3^+ that reacts with methane to produce ethane, as suggested by Olah et al. (21) mentioned above. The addition of Pd markedly enhanced the activity, but decreased the selectivity to ethane. The 0.1 wt% Pd/ZrO_2 did not yield ethane except for a trace amount being observed at 650°C.

There may be two reasons that make this catalyst different from other catalysts, i.e. (a) compared to SO_4^{2-}/ZrO_2 and Pd-SO_4^{2-}/ZrO_2 catalysts, the 0.1% Pd/ZrO_2 catalyst contains weaker acidic sites due to deficiency of sulfate, and (b) the Pd in the Pd-SO_4^{2-}/ZrO_2 catalyst is covered by S, as suggested by other researchers (43). Therefore, there is only a small concentration of exposed Pd that tends to catalyze the total oxidation of methane.

V_2O_5-SiO_2 Xerogel Catalysts

The BET surface areas and pore volumes of dried V_2O_5-SiO_2 xerogels containing 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 15.0, 20.0 and 25.0 wt% are listed in Table 7. The highest BET surface area was the 1.0 wt% V_2O_5-SiO_2 xerogel, although the xerogels containing vanadia contents up to 25.0 wt% still remained a very high surface area. In contrast, a drastic decrease in surface area was observed by Baiker et al. (37) with vanadia-silica mixed gels prepared by another method when the vanadia content was 20.0 wt%. Therefore, the present synthesis process produced V_2O_5-SiO_2 xerogels with higher surface area at higher vanadia content.

Table 7. Surface areas and pore volumes of dried V_2O_5-SiO_2 xerogel catalysts.

V_2O_5 Content (wt%)	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
1.0	509	0.36
2.0	384	0.27
3.0	383	0.27
5.0	447	0.32
10.0	451	0.32
15.0	338	0.24
20.0	267	0.19
25.0	368	0.26

X-Ray diffraction patterns of V_2O_5-SiO_2 xerogel catalysts are presented in Figure 1. The patterns of catalysts containing 1.0, 2.0, 3.0 and 4.0 wt% vanadia showed only a broad peak characteristic for amorphous silica. A small sharp peak of $2\theta = 31.0°$ was observed for 5.0 wt% V_2O_5-SiO_2 and several sharp reflections, such as $2\theta = 26.1°$ and $2\theta = 31.0°$, were observed for the catalysts with vanadia contents higher than 5.0 wt%. These sharp peaks were attributed to the existence of the crystalline V_2O_5 phase, which is well-recognized from the XRD pattern with a wide 2θ range for the 25.0 wt% V_2O_5-SiO_2 xerogel. Figure 2 gives a plot of the amount of crystalline V_2O_5, measured by XRD quantitative phase analysis, *vs* the total amount of V_2O_5 in the samples. From the plot, one can see that the straight line does not go through the origin but gives an intercept, corresponding to a critical dispersion capacity of V_2O_5 within the silica matrix at about 4.0 wt% vanadia in V_2O_5-SiO_2 xerogels. When the content of V_2O_5 is below the critical dispersion capacity, no crystalline V_2O_5 could be detected by XRD, indicating that V_2O_5 is finely dispersed within the matrix. This fine dispersion is predominantly a monolayer dispersion of V_2O_5 on the surfaces of the silica particles, as suggested and confirmed by other researchers for the V_2O_5/SiO_2 catalysts prepared by impregnation (35,36). However, it is possible that (a) there exists very small crystalline V_2O_5 within the silica matrix that can not be detected by XRD, and (b) a small fraction of vanadium ions is in the V^{4+} state immobilized in the three-dimensional matrix of silica, as observed in V_2O_5-SiO_2 gels by electron spin resonance (37). When the content of V_2O_5 exceeds this critical dispersion capacity, residual V_2O_5 will form its own crystalline phase mixed with the SiO_2 matrix. The amount of crystalline V_2O_5 increases with the total amount of V_2O_5.

All of the V_2O_5-SiO_2 xerogels were tested for the selective oxidation of methane. Table 8 presented the conversion of methane, the space time yields, and the selectivities of products for the V_2O_5-SiO_2 xerogel catalysts containing 1.0, 2.0, 3.0, 5.0, 10.0, 20.0 and 25.0 wt% vanadia when using a reactant mixture of CH_4/air/steam = 150/100/56. For all catalysts, there were tendencies towards increasing the conversion of methane and the space time yields of methanol and formaldehyde but diminishing the selectivities to methanol and formaldehyde with an increase in reactor temperature. The conversion of methane at each temperature basically remained reasonable steady for each catalyst with different vanadia content except that 1.0 wt% V_2O_5-SiO_2 catalyst showed a very high methane conversion at 625°C and the 15.0 wt% V_2O_5-SiO_2 catalyst exhibited a very low methane conversion. The low activity of the 15.0 wt% V_2O_5-SiO_2 catalyst is probably due to its synthesis process, in which a smaller amount of deionized water and nitric acid was employed, as mentioned previously. For a given methane conversion, methanol selectivity exhibited the best result in the range of 2.0-3.0 wt% vanadia content and then decreased with an increase in V_2O_5 content. The 2 wt% V_2O_5-SiO_2 catalyst gave the highest space time yield of methanol at the temperature range of 575-650°C. It was observed that the tendencies in the relationships

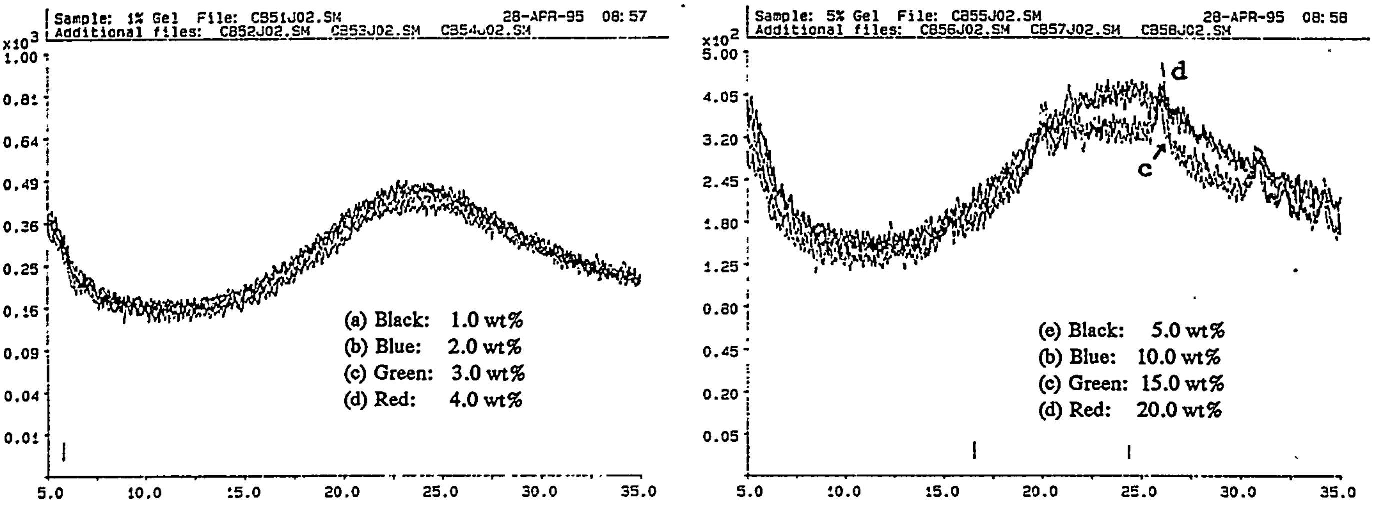

Figure 1. XRD patterns of V_2O_5-SiO_2 xerogels containing 1.0-20.0 wt% vanadia.

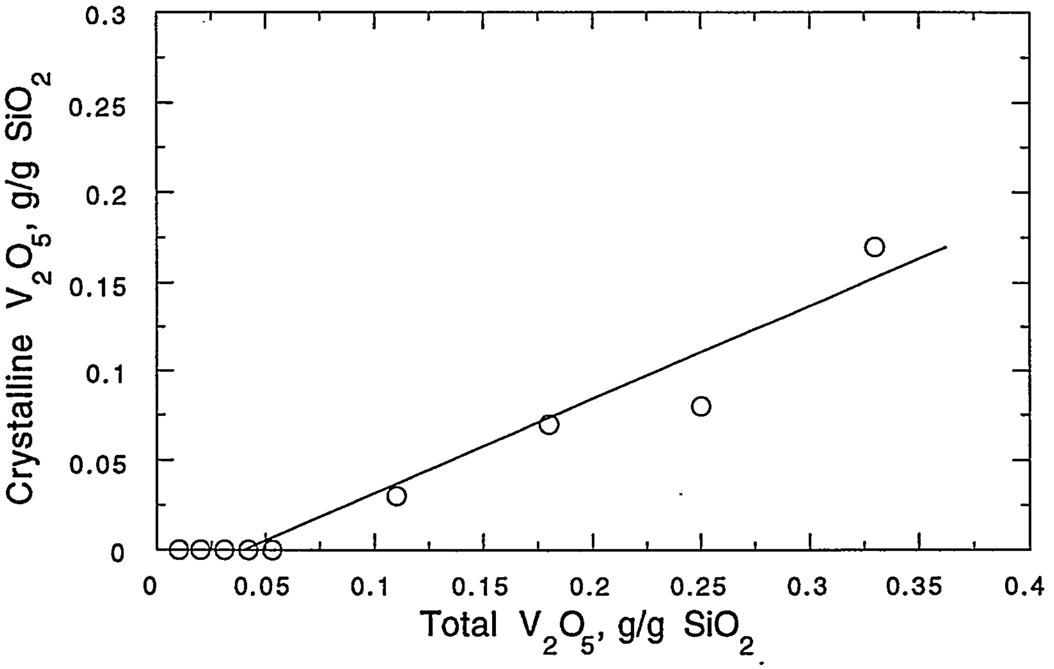

Figure 2. Amount of crystalline V_2O_5 *vs* total amount of V_2O_5 in the V_2O_5-SiO_2 xerogels.

TABLE 8. The conversion of methane and the space time yields and selectivities of products formed over 0.10 g V_2O_5-SiO_2 xerogel catalysts containing 1.0-25.0 wt % V_2O_5 The reactant stream was CH_4/air/steam (by feeding distilled water) = 150/100/56 ml/min with GHSV = 183,600 l/kg catal/hr. Catalyst testing was carried out at the temperatures (T) indicated and at a pressure of 0.45 MPa.

V_2O_5 (wt%)	T (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr Selectivities (C mol%)					
			CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
1.0	500	0.27	5.0 (1.6)	19.3 (6.8)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	382 (91.6)
	550	0.42	9.1 (1.9)	169 (37.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	409 (61.1)
	575	0.77	61.9 (8.1)	262 (36.6)	0.0 (0.0)	0.0 (0.0)	20.3 (3.0)	549 (52.3)
	600	4.25	92.7 (2.2)	456 (11.6)	86.8 (4.7)	302 (15.4)	1132 (30.9)	2031 (35.2)
	625	10.70	77.6 (0.7)	504 (4.9)	290 (6.0)	778 (15.1)	5420 (56.5)	2535 (16.8)
2.0	550	0.31	66.0 (19.7)	176 (56.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	112 (24.3)
	575	1.10	145 (12.4)	109 (10.0)	0.0 (0.0)	141 (25.8)	0.0 (0.0)	829 (51.8)
	600	2.00	154 (7.2)	253 (12.6)	0.0 (0.0)	206 (20.6)	671 (36.0)	691 (23.6)
	625	3.06	213 (6.7)	309 (12.9)	64.4 (4.7)	166 (11.2)	1266 (45.8)	812 (18.7)
	650	4.87	213 (4.3)	328 (7.1)	46.2 (2.1)	220 (9.5)	2728 (63.0)	957 (14.1)

TABLE 8 (Continued). The conversion of methane and the space time yields and selectivities of products formed over 0.10 g V_2O_5-SiO_2 xerogel catalysts containing 1.0-25.0 wt % V_2O_5 The reactant stream was CH_4/air/steam (by feeding distilled water) = 150/100/56 ml/min with GHSV = 183,600 l/kg catal/hr. Catalyst testing was carried out at the temperatures (T) indicated and at a pressure of 0.45 MPa.

V_2O_5 (wt%)	T (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr Selectivities (C mol%)					
			CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
3.0	500	0.03	2.8 (7.9)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	44.0 92.2)
	550	0.28	66.5 (20.8)	176 (58.8)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	89.2 (20.3)
	575	0.75	108 (12.3)	448 (54.4)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	403 (33.3)
	600	1.15	99.9 (7.5)	542 (43.3)	0.0 (0.0)	0.0 (0.0)	425 (36.4)	235 (12.8)
	625	1.57	155 (8.5)	560 (32.8)	0.0 (0.0)	0.0 (0.0)	670 (42.1)	416 (16.6)
	650	1.91	181 (8.2)	533 (25.8)	0.0 (0.0)	0.0 (0.0)	966 (50.1)	483 (15.9)
5.0	500	0.08	11.0 (11.9)	35.6 (41.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	59.8 (47.1)
	550	0.10	21.3 (18.1)	41.0 (37.2)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	72.3 (44.7)
	575	1.25	19.9 (1.4)	150 (11.4)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	1685 (87.2)
	600	1.67	50.9 (2.8)	301 (17.9)	0.0 (0.0)	0.0 (0.0)	0.0 0.0)	1959(79.3)
	625	2.07	51.0 (2.3)	357 (17.0)	56.1 (5.7)	185 (17.6)	145 (7.4)	1535 (49.9)

TABLE 8 (Continued). The conversion of methane and the space time yields and selectivities of products formed over 0.10 g V_2O_5-SiO_2 xerogel catalysts containing 1.0-25.0 wt % V_2O_5 The reactant stream was CH_4/air/steam (by feeding distilled water) = 150/100/56 ml/min with GHSV = 183,600 l/kg catal/hr. Catalyst testing was carried out at the temperatures (T) indicated and at a pressure of 0.45 MPa.

V_2O_5 (wt%)	T (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr Selectivities (C mol%)					
			CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
10.0	500	0.04	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	66.4 (100.0)
	575	1.05	52.4 (4.7)	154 (14.7)	0.0 (0.0)	0.0 (0.0)	128 (13.1)	1035 (67.5)
	600	1.24	51.4 (3.9)	349 (28.2)	0.0 (0.0)	0.0 (0.0)	47.3 (4.1)	1160 (63.8)
	625	1.50	76.6 (4.7)	495 (32.2)	0.0 (0.0)	139 (12.3)	46.8 (3.3)	1077 (47.6)
	650	1.19	103 (8.1)	183 (15.4)	0.0 (0.0)	95.7 (16.1)	93.2 (8.4)	909 (52.1)
15.0	500	0.02	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	24.2 (100.0)
	550	0.09	7.0 (6.8)	21.0 (21.9)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	100 (71.3)
	575	0.25	11.3 (4.0)	29.5 (11.2)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	327 (84.8)
	600	0.31	14.7 (4.1)	34.0 (14.3)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	280 (80.0)
	625	0.32	11.3 (0.5)	30.0 (1.4)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	494 (98.2)
	650	0.34	18.7 (4.7)	21.4 (5.8)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	488 (89.5)

TABLE 8 (Continued). The conversion of methane and the space time yields and selectivities of products formed over 0.10 g V_2O_5-SiO_2 xerogel catalysts containing 1.0-25.0 wt % V_2O_5 The reactant stream was CH_4/air/steam (by feeding distilled water) = 150/100/56 ml/min with GHSV = 183,600 l/kg catal/hr. Catalyst testing was carried out at the temperatures (T) indicated and at a pressure of 0.45 MPa.

V_2O_5 (wt%)	T (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr Selectivities (C mol%)					
			CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
20.0	500	0.02	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	23.8 (100.0)
	550	0.04	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	49.7 (100.0)
	575	0.09	0.0 (0.0)	10.5 (10.7)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	128 (89.3)
	600	0.35	0.0 (0.0)	12.0 (3.3)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	516 (96.7)
	625	3.2	0.0 (0.0)	16.7 (0.6)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	4222 (99.4)
	650	4.26	2.8 (0.1)	15.2 (0.4)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	6437 (99.6)
25.0	500	0.00	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	550	0.11	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	175 (100.0)
	575	0.0	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	600	2.28	2.9 (0.1)	161.3 (6.6)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	3349 (93.3)
	625	2.60	3.1 (0.1)	224.8 (8.5)	0.0 (0.0)	0.0 (0.0)	36.8 (1.5)	3496 (89.2)
	650	3.43	11.7 (0.3)	144.5 (4.2)	0.0 (0.0)	0.0 (0.0)	935.2 (29.1)	3358 (66.4)

between the yield and selectivity of formaldehyde and the vanadia content are in agreement with those observed by other researchers for silica-supported vanadia catalysts (30,44-46). When the vanadia content exceeded 15.0 wt%, the selectivities and space time yields of methanol and formaldehyde fell to very small values or even to zero.

The difference in the yields and selectivities of oxygenates with V_2O_5 content is attributed to the changes in the structure of vanadia. It is well-known that the partial oxidation of hydrocarbons on oxide catalysts involves a redox mechanism in which the catalyst is partially reduced by the hydrocarbon and then reoxidized by gas-phase oxygen (47-49) to form oxygenated products. At low V_2O_5 content, vanadia is present on the silica support in the form of tetrahedral surface V species, as confirmed by ^{51} V NMR, laser Raman spectroscopy, and TPR (30,50,51). Thus, it was suggested that the tetrahedral surface V species is an active site for methane oxidation on the supported V_2O_5/SiO_2 catalysts (45).

As mentioned above, vanadia in the V_2O_5-SiO_2 xerogels containing low vanadia contents is also well-dispersed within or on the silica matrix, likely as a surface V species. It is expected that the structure and behavior of vanadia in the xerogel catalysts during partial oxidation of methane to methanol are similar to that of vanadia in the supported V_2O_5/SiO_2 catalysts prepared by impregnation. Methane is first activated by the surface V species to form a surface methoxy intermediate, which is then hydrolyzed by water to produce methanol. The bridging oxygens of the surface VO_n species can possibly play a direct role in the partial oxidation of methane because these oxygens are more labile than terminal oxygens once the surface V species is reduced (52).

The space time yields and selectivities of oxygenates should increase with an increase in vanadia content at a low vanadia content because more dispersed vanadia can provide more active sites. On the other hand, the amount of bulk-like vanadia also increased with V_2O_5 content. It is known that vanadia does not disperse well on the surface of a silica support. As shown in Figure 2, the crystalline V_2O_5 phase could be observed by XRD in the 5.0 wt% V_2O_5-SiO_2 xerogel. In fact, it is quite possible that microcrystalline vanadia is present in the xerogels containing 3.0 and 4.0 wt% vanadia content. Solid-state ^{51}V NMR studies of supported V_2O_5/SiO_2 catalysts indicated the presence of microcrystalline vanadia species even at very low vanadia loadings, such as in a 1.6 wt% catalyst (51). The bulk-like vanadia of the crystalline V_2O_5 has an octahedral structure, which is suggested as an active site for further oxidation of formaldehyde to CO and CO_2 (48). It was also observed that pure V_2O_5 showed a much higher activity for partial oxidation of methanol than the 1.0 wt% supported V_2O_5/SiO_2 catalyst (53). The turnover frequency of methanol oxidation catalyzed by pure V_2O_5 was ten times greater than that catalyzed by the 1.0 wt% supported

V_2O_5/SiO_2 catalyst. Therefore, the decreases in methanol and formaldehyde selectivities with an increase in vanadia content may be attributed to the further oxidation of oxygenates on bulk-like vanadia. ^{51}V NMR and TPR experiments will by carried out to determine whether V_2O_5 microcrystals are present in the 3.0 and 4.0 wt% V_2O_5-SiO_2 xerogel catalysts.

The results presented in Table 9 were obtained by feeding deionized water instead of distilled water and keeping other parameters unchanged. From Table 9 it could be seen that the conversion of methane and the yield and selectivity of methanol were diminished, whereas the yield and selectivity of formaldehyde was enhanced when deionized water was fed (shown in Table 8), compared to the results by feeding distilled water. The distilled water was obtained from a tap to which distilled water is conducted by a long steel pipe, and it is possible that it contained some impure ions. It is reasonable to assume that these impure ions would influence the partial oxidation of methane to oxygenates occurring both on the catalyst surface and in the gas phase and would result in changes in the conversion and selectivity. More studies are needed to understand the enhancing effect of methanol and the diminishing effect of formaldehyde when distilled water was fed to the reactant steam.

TABLE 9. The conversion of methane and the space time yields and selectivities of products formed over 0.10 g V_2O_5-SiO_2 xerogel catalysts containing 2.0, 5.0 and 15.0 wt% V_2O_5. The reactant stream was CH_4/air/steam (by feeding deionized water) = 150/100/56 ml/min with GHSV = 183,600 l/kg catal/hr. Catalyst testing was carried out at the temperatures indicated and at a pressure of 0.45 MPa.

V_2O_5 (wt%)	Temp. (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)					
			CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
2.0	550	0.05	8.9 (15.0)	34.1 (61.5)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	19.1 (23.5)
	575	0.71	86.0 (10.6)	588 (77.3)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	135 (12.1)
	600	1.60	166 (9.2)	1042 (61.3)	0.0 (0.0)	0.0 (0.0)	281 (17.7)	295 (11.8)
	625	2.67	164 (5.6)	1311 (47.4)	0.0 (0.0)	0.0 (0.0)	986 (38.2)	361 (8.9)
	650	3.14	164 (4.6)	1307 (39.4)	0.0 (0.0)	0.0 (0.0)	1541 (49.8)	299 (6.2)

TABLE 9 (Continued). The conversion of methane and the space time yields and selectivities of products formed over 0.10 g V_2O_5-SiO_2 xerogel catalysts containing 2.0, 5.0 and 15.0 wt% V_2O_5. The reactant stream was CH_4/air/steam (by feeding deionized water) = 150/100/56 ml/min with GHSV = 183,600 l/kg catal/hr. Catalyst testing was carried out at the temperatures indicated and at a pressure of 0.45 MPa.

V_2O_5 (wt%)	Temp. (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)					
			CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
5.0	525	0.08	0.0 (0.0)	66.0 (76.8)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	29.2 (23.2)
	550	0.17	20.4 (10.9)	73.3 (41.8)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	122 (47.3)
	575	0.90	31.4 (3.2)	213 (23.2)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	990 (73.6)
	600	1.49	23 (1.4)	502 (33.3)	0.0 (0.0)	0.0 (0.0)	278 (19.8)	1004 (45.5)
	625	1.60	17.6 (1.0)	384 (24.0)	0.0 (0.0)	0.0 (0.0)	109 (7.3)	1581 (67.58)
	650	1.87	13.1 (0.7)	544 (29.0)	0.0 (0.0)	0.0 (0.0)	85.4 (4.9)	1798 (65.4)
15.0	525	0.04	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	64.9 (100.0)
	550	0.11	0.0 (0.0)	64.6 (53.7)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	76.6 (46.3)
	575	0.24	0.0 (0.0)	85.0 (33.8)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	229 (66.2)
	600	0.40	0.0 (0.0)	92.3 (21.7)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	459 (78.3)
	625	0.47	0.0 (0.0)	95.0 (18.6)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	571 (81.4)
	650	0.48	0.0 (0.0)	102 (19.5)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	580 (80.5)

Table 10 reported the catalytic data of appropriate blank runs under our experimental conditions. The results show that the conversion of methane was negligible, smaller than 0.46 mol% up to the temperature of 650°C, while the space time yields of methanol and formaldehyde were less than 35.0 and 183 g/kg catal/hr, respectively. These results demonstrate the positive influence of the V_2O_5-SiO_2 xerogel catalysts in the partial oxidation of methane to oxygenates. However, it is still uncertain of the importance of the contribution of gas phase reaction to the production of oxygenates over V_2O_5-SiO_2 catalysts because the methyl radicals generated on the catalyst surface can leave the catalyst surface and undergo gas phase reactions forming methanol and formaldehyde.

TABLE 10. The conversion of methane and the space time yields* and selectivities of products formed [A] over a quartz wool bed and [B] in a blank reactor from CH_4/air/steam (from deionized water) = 150/100/56 ml/min with GHSV = 183,600 l/kg catal/hr. Testing was carried out at 0.45 MPa at the temperatures (T) indicated.

	T (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)					
			CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
[A]	550	0.00	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	600	0.13	3.4 (2.3)	131 (95.1)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	5.3 (2.6)
	625	0.05	3.2 (5.9)	40.1 (79.4)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	10.8 (14.6)
	650	0.46	21.8 (4.2)	152 (31.3)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	13.3 (1.89)
[B]	550	0.00	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	600	0.13	7.0 (4.8)	124 (89.9)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	10.7 (5.3)
	625	0.20	20.0 (8.8)	184 (86.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	16.2 (5.2)
	650	0.13	35.0 (24.1)	92.6 (67.9)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	16.0 (8.0)

*Here, the same dimensional unit was utilized as was used for the previous testing in order to compare the product productivities with those obtained over a catalyst bed.

Table 11 gives the catalytic results over the 2.0 wt% V_2O_5/SiO_2 catalyst prepared by impregnation under the same experimental conditions as used in the catalytic testing of the 2.0 wt% V_2O_5-SiO_2 xerogel catalyst (Table 9). As can be seen from Table 9 and Table 11, the methane conversion for the V_2O_5-SiO_2 xerogel catalyst was lower than that for the supported V_2O_5/SiO_2 catalyst. At 600°C and higher, C_2 hydrocarbons were produced over the impregnated V_2O_5/SiO_2 catalyst but were not observed over the xerogel catalyst. It is especially noted the methanol and formaldehyde selectivities for the V_2O_5-SiO_2 xerogel catalyst were much higher than that for the supported V_2O_5/SiO_2 catalyst. The interesting thing is that the space time yield of methanol for the V_2O_5-SiO_2 xerogel catalyst at 600-650°C was higher than that for the supported V_2O_5/SiO_2 catalyst. These results suggest that the active sites of the V_2O_5-SiO_2 xerogel catalyst for production of methanol are probably more stable at higher temperature than that of the supported V_2O_5-SiO_2 catalyst. A similar result was observed in the selective reduction of nitric oxide with ammonia over mixed V_2O_5-SiO_2 gel catalyst (37). A long term catalytic testing will be carried out next quarter to investigate the stability of the V_2O_5-SiO_2 xerogel catalysts.

TABLE 11. The conversion of methane and the space time yields and selectivities of products formed over 0.10 g 2.0 wt%V_2O_5/SiO_2 catalyst prepared by impregnation. The reactant stream was CH_4/air/steam (by feeding deionized water) = 150/100/56 ml/min with GHSV = 183,600 l/kg catal/hr. Catalyst testing was carried out at the temperatures indicated and at a pressure of 0.45 MPa.

Temp. (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)					
		CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
550	0.31	18.7 (5.0)	282 (80.4)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	74.9 (14.6)
575	0.57	73.0 (11.5)	505 (84.6)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	34.6 (4.0)
600	7.62	152 (2.0)	1170 (16.4)	36.8 (1.1)	70.4 (2.0)	4651 (69.7)	938 (8.9)
625	9.05	140 (1.6)	1652 919.7)	135 (3.5)	145 (3.5)	4970 (63.6)	1015 (8.3)
650	9.86	116 (1.2)	1340 (14.8)	184 (4.4)	261 (5.8)	5419 (64.2)	1273 (9.6)

The methane conversion and product selectivities of the 2.0 wt% V_2O_5-SiO_2 xerogel catalyst with a 0.30 g loading in the reactor, but employing the same reactant flow rates (in ml/min) as utilized in the previous experiments, are shown in Table 12. As compared to the results obtained with a 0.10 g loading of the catalyst (Table 9), the 0.30 g loading exhibited a much higher methane conversion with an enhancing selectivity to CO, but much lower space time yields and selectivities of methanol and formaldehyde. Two factors affect the changes in the methane conversion, product yields, and selectivities when a large amount of the catalyst is loaded in the reactor. One is an increase of the thickness of the catalyst bed, which will cause an increase in methane conversion but a decrease in oxygenate selectivities due to the secondary oxidation of oxygenates. Another factor is that the decrease of GHSV makes a negative contribution to the space time yields of oxygenates.

TABLE 12. The conversion of methane and the space time yields and selectivities of products formed over 0.30 g 2.0 wt% V_2O_5-SiO_2 xerogel catalyst. The reactant stream was CH_4/air/steam (by feeding distilled water) = 150/100/56 ml/min with GHSV = 61,200 l/kg catal/hr. Catalyst testing was carried out at the temperatures indicated and at a pressure of 0.45 MPa.

Temp. (°C)	CH_4 Conv. (mol%)	Space Time Yield, g/kg cat/hr (Selectivities, C mol%)					
		CH_3OH	HCHO	C_2H_4	C_2H_6	CO	CO_2
550	2.80	18.1 (1.5)	62.0 (5.5)	0.0 (0.0)	0.0 (0.0)	954 (90.3)	50.2 (3.0)
575	8.94	63.1 (2.3)	221 (8.4)	0.0 (0.0)	6.0 (0.5)	1896 (77.3)	447 (11.6)
600	10.21	63.7 (2.1)	343 (11.9)	3.6 (0.3)	18.8 (1.3)	1949 (72.3)	518 (12.2)
650	11.00	71.3 (2.1)	276 (8.8)	47.0 (3.2)	152.6 (9.7)	2048 (69.8)	298 (6.5)

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