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Selective Methane Oxidation Over Promoted Oxide Catalysts

Quarterly Report
September - November 1994

Kamil Klier
Richard G. Herman
Chunlei Shi
Chuan-Bao Wang
Qun Sun

December 1994

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

MASTER

By
Lehigh University
Bethlehem, Pennsylvania

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Morgantown, West Virginia 26507-0880

By
Lehigh University
Zettlemoyer Center for Surface Studies and
Department of Chemistry
7 Asa Drive
Sinclair Laboratory
Bethlehem, Pennsylvania 18015

December 1994

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

Experimental research in the direct conversion of methane to methanol using a double bed reactor and with gaseous steam as cofeed with the CH_4/air reactant mixture continued during this quarter in order to improve the methanol space time yield. Work was carried out along several pathways that included a stability test of the second bed catalyst 1%V_2O_5/SiO_2 that yielded up to 100 g methanol/kg cat/hr and investigation of the effect of pressure on methanol yields. The stability of the double bed 1%$SO_4^{2-}/Sr/La_2O_3$ and 1%V_2O_5/SiO_2 catalyst system was tested at 600°C over a 72 hr period, and the results indicated a slow decrease in catalytic activity and methanol yield, possibly due to the loss of vanadium from the second bed.

Redox dopants such as Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu^{+} were put onto several metal oxide supports, including MgO, ZrO_2, Y_2O_3, and SiO_2, in an attempt to find better second bed catalysts. In most cases, this surface doping resulted in complete oxidation catalysts. However, a catalyst that was reasonably selective towards oxygenates was obtained when SiO_2 was used as the support and low quantities of Fe or Cu were utilized, i.e. the molar ratio of Si:Fe or Si:Cu was around 1000.

Attempts were also made to incorporate alkali ions into the catalysts to improve the surface hydrolyzability. K^+ ions were doped into a silica supported iron catalyst, and the catalytic results were compared with the undoped Fe/SiO_2 catalyst. An increased percentage of methanol in the total oxygenate product was observed, although the overall activity of the catalysts was nearly unaffected.

Experiments were carried out to examine the effect of pressure and temperature on the oxygenate productivity over a double-layered catalyst bed of 0.1 g 1 wt% $SO_4^{2-}/Sr/La_2O_3$ as the first bed and 0.1 g 1 wt% V_2O_5/SiO_2 as the second bed without H_2O cofeed in a glass-lined tubular down-flow reactor at pressures of 0.1-3.2 MPa (14.7-460 psig), temperatures of 450-500°C, and with a reactant flow rate having a ratio of CH_4/air = 150/50 ml/min. Reaction products observed were methanol, formaldehyde, carbon dioxide, acetylene, ethylene, and ethane. The overall activity of the catalyst increased at low pressures and high temperature. However, testing at low temperature and high pressure was found to favor methanol production, and a methanol space time yield obtained at 450°C and 3.2 MPa was 338 g/kg·hr.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

OBJECTIVES OF THE RESEARCH

The objective of this research is the selective oxidative coupling of methane to C_2 hydrocarbons (Equations 1-3) and oxygenates, in particular formaldehyde and methanol as represented by Equations 4 and 5. Air, oxygen, or carbon dioxide, rather than nitrous oxide will be utilized as the oxidizing gas at high gas hourly space velocity, but mild reaction conditions (500-700 °C, 1 atm total pressure). All the investigated 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_2 products, can be doped with some Lewis acidic oxides or other groups to increase further its activity and selectivity to C_2 products.

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

Task 1.	Maximizing Selective Methane Oxidation to C_2 Products Over Promoted Sr/La_2O_3 Catalysts.
Task 2.	Selective Methane Oxidation to Oxygenates.
Task 3.	Catalyst Characterization and Optimization.

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

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

RESEARCH PROGRESS

Introduction

In direct conversion of methane to methanol and formaldehyde, research described in the current literature (1,2) has focused on developing a single catalyst that would be capable of both activating methane and generating methanol. In order to circumvent the difficulty of trying to accomplish two tasks using one catalyst, a different approach has been adopted in this research by using a double-layered catalyst bed. This provides for separate optimization of the two catalysts in the double-layered catalyst bed and greatly broadens the choices for the catalysts. In high-pressure direct conversion of methane to oxygenates, previous research by others (2-5) had focused on examining the relationship between operating pressure, reaction temperature, residence time, and methane conversion/selectivity in noncatalytic or single-bed catalytic operation. In this quarter, work has been done to improve the methanol yield over the double-bed catalyst system of a $1\%SO_4^{2-}/Sr/La_2O_3$ catalyst followed by a $1\%V_2O_5/SiO_2$ catalyst by increasing the total reaction pressure for the catalytic reaction. In addition, a new group of catalysts involving Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu^{+} were synthesized and tested in an attempt to find better second bed catalysts.

Experimental

A 1 wt% Sr/La_2O_3 catalyst was first prepared following procedure described in (6,7). The catalyst was then impregnated with an aqueous $(NH_4)_2SO_4$ solution by stirring on a magnetic hot plate at 60°C until nearly dry and then drying the solid at 140°C overnight. The resulting catalyst was calcined at 600°C for 6 hr. The silica-supported 1 wt% V_2O_5 catalyst was prepared by using methanol solution of vanadium(V) triisopropoxide oxide ($VO[i\text{-}OC_3H_7]_3$) and amorphous silica (Cabosil EH-5, surface area = 380 m^2/g). The silica supported iron and copper catalysts were prepared by aqueous impregnation of iron(II) acetate or copper(II) acetate with the pH adjusted to 3-4 by adding an appropriate amount of acetic acid. Typically, an appropriate amount of previously prepared iron(II) acetate or copper(II) acetate aqueous solution was further diluted with deionized water. Dry MgO, ZrO_2, Y_2O_3, or amorphous SiO_2 was then added to the solution at about 60°C under vigorous stirring until a thick paste was formed, which was then dried at 140°C overnight and calcined at 600°C for six hr.

Under ambient pressure conditions, catalytic testing was carried out in varying temperature ranges, e.g. 550-650°C, and the gas hourly space velocity (GHSV) of the CH_4/air reactant mixture was 153,000 ℓ/kg cat·hr. Steam cofeeding was achieved by pumping distilled water into the top of the preheater section of the reactor with an ISCO liquid metering pump (Model 314). The water was vaporized to steam that was well-mixed with the CH_4/air = 1.5 reagent gases before contact with the catalyst beds. The rate of steam cofeeding was controlled at 19.6 ml/min by the metering pump, and all the tubing leading into and out of the reactor was heated at *ca.* 150°C. This setup enabled the feeding of steam at up to several hundred torr in the reagent gas mixture in ambient pressure tests.

The high pressure reactor consisted of a close-fitting Pyrex tube with an inner diameter of 4 mm inserted into a vertically mounted stainless steel (6 mm o.d. x 201 mm), of which the central 155 mm was heated by an electrical heater. In the middle of the heated zone, 5.8 mm of the downflow reactor was packed with an upper bed of 0.1 g 1 wt% $SO_4^{2-}/Sr/La_2O_3$ catalyst followed by 0.1 g 1 wt% V_2O_5/SiO_2 catalyst supported on quartz wool. 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, where they mixed. The pressure could be set to a designated value by a back-pressure regulator. The exhaust gas lines from the reactor to the GC and from the GC to the cold trap were heated to 150°C to prevent condensation of the products. The reactant mixture consisted of CH_4/air flow at rates of 150/50 ml/min, respectively. The pressure range was from ambient pressure (0.1 MPa) to 3.2 MPa (14.7-460 psig), and the temperature range was 450-500°C. Noncatalytic testing was carried out with the same experimental parameters.

Two catalyst testing reactor units were utilized, and these had different computer-interfaced analytical systems. In the high pressure reactor testing system, 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 x 1/8-in. o.d.) and a 5A zeolite column (2 m length x 1/8-in. o.d.) in parallel and a thermal conductivity detector. In the atmospheric pressure reactor testing system, the feed and product gases were analyzed by using a Hewlett Packard 5890 gas chromatograph with a molecular sieve 13X column and a Chrompack Model 7550 PoraPLOT Q fused silica capillary column in parallel and TCD detectors. With both testing systems, the liquid products, methanol and formaldehyde, were trapped by using an ice bath at 0°C and were separately analyzed by a Hewlett Packard 5970 MSD GC/MS instrument.

Results and Discussion

The Stability of the Double-Bed Catalysts

It was worthwhile to investigate the stability of the double bed catalyst pair of $1\%SO_4^{2-}/Sr/La_2O_3||1\%V_2O_5/SiO_2$, which previously had given the highest methanol space time yield (nearly 100 g/kg cat·hr at 600°C) (8), as a function of time on stream at ambient pressure (0.1 MPa). As shown in Table 1, deactivation of the double bed catalyst system was observed. Although the overall methane conversion decreased by 29% over a period of 72 hr, the space time yield of methanol decreased by 52% over the same period.

This deactivation is possibly due to the gradual loss of vanadium from the second bed, and this loss might be enhanced by the presence of steam in the reactant mixture. However, it is surprising to note that the space time yields of HCHO over the same time period hardly changed, and, in fact, the HCHO selectivity increased during the test. If vanadium was lost during the test, this result indicates that the formation of HCHO was not very sensitive to changes in the vanadium content on the catalyst, at least not within the range of vanadium content change of the experiment. These results might also indicate that higher vanadium content in the second bed catalyst might favor methanol formation more than HCHO formation. Double bed experiments with catalysts of various vanadium contents are currently under way in our laboratory in order vertify this and to maximize methanol yields over this catalyst.

Silica Supported Fe and Cu Catalysts

An inherent problem with the V_2O_5/SiO_2 catalysts is the apparent gradual and irreversible loss of vanadium from the bulk of the catalyst, particularly when H_2O is added in the feed. This adversely affects the activity of the second catalyst bed and is undesirable from an engineering prospective. Kobayashi *et al.* (9) recently investigated partial oxidation of methane over silica-supported copper, manganese, and iron catalysts and reported considerable rates for the synthesis of oxygenates. Work in our laboratory with Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu^{1+} doped catalysts continued during this quarter, and the effect of supports in these catalysts on oxygenate production was investigated. Fe^{3+}/Fe^{2+} or Cu^{2+}/Cu^{+} was supported on MgO, ZrO_2, Y_2O_3, and SiO_2, and these catalysts with loadings of 1 mol% and 0.1 mol% were prepared. With the exception of silica-supported catalysts, all of the others tended to give complete oxidation products at 600°C, as shown in Table 2. Since the SiO_2 catalysts appeared to be the most promising, the research focus was placed on the silica-supported iron- and copper-containing catalysts.

TABLE 1. The conversions of methane and the space time yields of products formed over double bed catalysts with gaseous steam as cofeed. The first bed contained the 0.10 g 1%SO_4^{2-}/Sr/La_2O_3 catalyst and the second bed consisted of 0.10 g 1%V_2O_5/SiO_2. The reactant mixture consisted of CH_4/air/steam = 1.5/1.0/0.2 with GHSV = 153,000 ℓ/kg catal/hr. The reaction temperature was 600°C and the pressure was 0.1 MPa.

Time on stream,	CH_4 Conv.,	Space Time Yields, g/kg cat·hr (Selectivities, mol%)					CH_3OH /HCHO Molar Ratio
hr	mol%	C_2 HC	HCHO	CH_3OH	CO	CO_2	
2	14.4	2875 (39.7)	820 (5.5)	97.9 (0.6)	2688 (19.2)	7697 (35.0)	0.11
5	14.2	3427 (48.0)	771 (5.2)	91.6 (0.6)	2510 (18.2)	6077 (28.0)	0.11
11	13.1	3214 (48.8)	764 (5.6)	86.0 (0.6)	2479 (19.5)	5111 (25.6)	0.11
26	12.2	2876 (46.9)	854 (6.7)	70.6 (0.5)	1964 (16.6)	5416 (29.3)	0.07
29	11.4	2435 (42.5)	819 (6.9)	66.0 (0.5)	2170 (19.6)	5312 (30.5)	0.07
47	11.1	2498 (44.7)	786 (6.8)	60.4 (0.5)	1822 (16.8)	5266 (31.1)	0.07
58	10.6	2273 (42.6)	729 (6.6)	57.0 (0.5)	1962 (19.1)	5054 (31.2)	0.07
72	10.2	2194 (42.8)	741 (7.0)	46.7 (0.4)	1875 (18.9)	4816 (30.9)	0.06

TABLE 2. The conversions of methane and the space time yields and molar selectivities of products formed over a single bed of 0.10 g of the iron- or copper-doped catalysts. The reactant stream was CH_4/air/steam = 1.5/1.0/0.2 with GHSV = 153,000 ℓ/kg catal/hr. The reaction temperature was 625°C and the pressure was 0.1 MPa.

Second bed Catalyst	CH_4 Conv.,	Space Time Yields, g/kg cat·hr (Selectivities, mol%)					CH_3OH/HCHO Molar Ratio
	mol%	C_2 HC	HCHO	CH_3OH	CO	CO_2	
Fe/MgO (Si:Mg=100)	5.8	48 (1.1)	0 (0)	0 (0)	499 (8.5)	8066 (90.4)	-
Fe/MgO (Si:Mg=1000)	4.4	38 (0.8)	0 (0)	0 (0)	300 (8.0)	6177 (91.2)	-
Fe/SiO_2 (Si:Fe=100)	3.4	0 (0)	11 (0.3)	0 (0)	1542 (46.4)	2793 (53.4)	0
Fe/SiO_2 (Si:Fe=500)	3.1	0 (0)	18 (0.6)	0 (0)	1498 (49.3)	2390 (50.1)	0
Fe/SiO_2 (Si:Fe=1000)	1.4	0 (0)	217 (14.8)	18.2 (1.2)	874 (63.7)	436 (20.2)	0.08
Fe/SiO_2 (Si:Fe=2000)	1.5	0 (0)	278 (17.7)	19.6 (1.2)	821 (55.9)	584 (25.3)	0.07
Cu/SiO_2 (Si:Cu=100)	2.8	0 (0)	0 (0)	0 (0)	985 (35.9)	2761 (64.1)	-
Cu/SiO_2 (Si:Cu=1000)	1.5	0 (0)	176 (11.2)	16.2 (1.0)	782 (53.2)	798 (34.6)	0.09
Cu/SiO_2 (Si:Cu=2000)	1.5	0 (0)	185 (11.8)	18.2 (1.1)	744 (50.6)	843 36.5)	0.09
Fe/ZrO_2 (Zr:Fe=1000)	4.6	0 (0)	0 (0)	0 (0)	1088 (24.2)	5369 (75.8)	-
Fe/Y_2O_3 (Y:Fe=1000)	4.9	0 (0)	0 (0)	0 (0)	1204 (25.1)	5649 (74.9)	-
Pure SiO_2 support	0.09	0 (0)	37 (44.1)	0 (0)	0 (0)	69 (55.9)	0

The experiments with the Fe- and Cu-containing SiO_2-based catalysts were repeated but with these catalysts as the second catalyst bed in the reactor. In this case, the first bed, located immediately above the second bed, consisted of the 1 wt% $SO_4^{2-}/Sr/La_2O_3$ catalyst. The double bed experimental results are shown in Table 3. As indicated in Table 2, the Fe/SiO_2 catalysts almost completely oxidized methane to CO_2/CO, especially when the Si:Fe atomic ratio was relatively low, e.g. 100. As shown in Table 3, the double catalyst bed configuration gave much higher conversion levels of methane. The second bed catalyst with a Si:Fe atomic ratio of 100 was quite non-selective, and it almost completely oxidized the methyl radicals and/or hydrocarbons generated from the first bed to produce carbon oxides at 625°C. However, as the Si:Fe atomic ratio increased to 500, the space time yields for C_2 hydrocarbons nearly doubled, and there was a considerable increase in the production of oxygenates. When the Si:Fe atomic ratio was increased to 1000, the C_2 production jumped five times, signifying that there had been a significant shift of selectivity away from carbon oxides. More importantly, the space time yields for oxygenates jumped from 0.7 to 29 g/kg cat·hr for methanol and from 9 to 270 g/kg cat·hr for HCHO. This was caused by a reduced iron concentration on the surface due to the lower iron loading in the catalyst, indicating the involvement of iron in the catalytic reaction. When the Si:Fe atomic ratio was further increased to 2000, the oxygenate productivities slightly decreased. Calculations based on the catalyst surface area showed that this loading level was much less than a monolayer coverage of the metal ions on the silica surface; monolayer coverage of the SiO_2 by FeO would correspond to a Si:Fe atomic ratio of 0.56.

It is reasonable to speculate that the active center, which possibly involves the redox pair Fe^{3+}/Fe^{2+}, is efficient in abstracting additional hydrogen atoms from the methyl intermediates only when it is in close proximity to another center of the same kind. Therefore, when the iron loading was reduced, thus reducing the surface iron concentration, the reaction along the pathway leading to complete oxidation was decreased. The catalytic behavior was similar for the Cu/SiO_2 catalysts, except that at a Si:Cu atomic ratio of 2000 the space time yields for oxygenates slightly increased. More studies are needed to understand the role of iron and copper on the surface of the silica catalysts in guiding the mechanism of methane conversion toward methanol and formaldehyde.

Potassium-Modified Iron Supported on Silica Catalysts

Assuming the formation of methanol is through the hydrolysis of surface methoxide species, incorporating alkali ions into the catalysts may improve the hydrolysis reaction. The ease of surface-held methoxide hydrolysis is expected to follow the order alkali > alkaline earth >> covalent surface compound. Potassium ions were incorporated into Fe/SiO_2 catalysts *via* aqueous impregnation, and catalytic testing results were compared with those

TABLE 3. The conversions of methane and the space time yields of products formed over double bed catalysts at ambient pressure with gaseous steam as cofeed. The first bed contained the 0.10 g 1%SO_4^{2-}/Sr/La_2O_3 catalyst and the second bed consisted of 0.10 g iron or copper doped catalyst. The reactant stream was CH_4/air/steam = 1.5/1.0/0.2 with GHSV = 153,000 ℓ/kg catal/ hr. The reaction temperature was 625°C and the pressure was 0.1 MPa.

Second bed Catalyst	CH_4 Conv.,	Space Time Yields, g/kg cat·hr (Selectivities, mol%)					CH_3OH /HCHO Molar Ratio
	mol%	C_2 HC	HCHO	CH_3OH	CO	CO_2	
Fe/SiO_2 (Si:Fe=100)	15.6	754 (9.6)	9 (0.1)	0.7 (0.0)	2376 (15.6)	17916 (74.8)	0
Fe/SiO_2 (Si:Fe=500)	15.1	1363 (17.8)	57 (0.4)	7.4 (0.0)	1675 (11.4)	16322 (70.4)	0
Fe/SiO_2 (Si:Fe=1000)	15.7	3878 (48.8)	269 (1.6)	29.0 (0.2)	984 (6.4)	10343 (42.9)	0.13
Fe/SiO_2 (Si:Fe=2000)	15.2	3619 (47.1)	174 (1.1)	21.8 (0.1)	1217 (8.2)	10158 (43.8)	0.09
Cu/SiO_2 (Si:Cu=100)	14.7	1147 (15.4)	15 (0.1)	1.1 (0.0)	1984 (13.8)	15958 (70.7)	0
Cu/SiO_2 (Si:Cu=1000)	14.3	3451 (47.7)	143 (1.0)	18.6 (0.1)	1547 (11.1)	8817 (40.2)	0.10
Cu/SiO_2 (Si:Cu=2000)	14.6	3692 (50.0)	169 (1.1)	20.4 (0.1)	1472 (10.3)	8624 (38.5)	0.09
Pure SiO_2 support	16.3	3917 (48.7)	16 (0.1)	1.2 (0.0)	1088 (7.0)	10796 (44.2)	0

obtained with the K$^+$-free catalyst. As shown by the comparison in Table 4, in the temperature range of 575-625°C after incorporating K$^+$, the space time yields of the oxygenates, methanol and formaldehyde, tended to decrease slightly while overall methane conversion tended to increase slightly (or as at 600°C, it remained the same). However, the methanol-to-formaldehyde molar ratio increased, particularly at 575°C. At this reaction temperature, the selectivity toward the partially oxidized products was increased by doping the catalyst with potassium. These observations are instructive, and experiments are currently under way to incorporate alkali ions into V_2O_5/SiO_2 catalysts in order to increase the CH_3OH selectivity and space time yields even higher.

TABLE 4. The conversion levels of methane, the space time yields, and molar selectivities of products formed over 0.10 g Fe/SiO_2 and K-modified Fe/SiO_2 catalysts at ambient pressure. The reactant stream was CH_4/air/steam = 1.5/1.0/0.2 with GHSV = 153,000 ℓ/kg catal/hr.

Second Bed Catalyst	Temp., °C	CH_4 Conv., mol%	Space Time Yields, g/kg cat·hr (Selectivities, mol%)					MeOH/ HCHO Molar Ratio
			C_2 HC	HCHO	CH_3OH	CO	CO_2	
Fe/SiO_2 (Si:Fe = 2000:1)	575	0.8	0 (0)	9 (1.1)	1.1 (0.1)	321 (41.0)	711 (57.8)	0.09
	600	1.2	11 (1.8)	42 (3.3)	6.0 (0.4)	512 (43.6)	939 (50.8)	0.12
	625	1.5	45 (5.9)	137 (8.7)	19.6 (1.2)	670 (45.7)	889 (38.5)	0.14
K/ Fe/SiO_2 (Si:Fe:K = 2000:1:1)	575	1.0	0 (0)	29 (2.8)	8 (0.7)	420 (42.8)	826 (53.7)	0.25
	600	1.2	10 (1.6)	32 (2.5)	5.9 (0.4)	584 (49.7)	845 (45.7)	0.16
	625	1.6	52 (6.4)	103 (6.1)	16.6 (0.9)	698 (44.5)	1034 (42.0)	0.15

Effect of Pressure on the Space Time Yields of Oxygenates

The reaction pressure was varied over a wide range to determine the effect on the productivity of methanol and formaldehyde. The pressure dependences of the space time yields for these two oxygenates at 450°C and 500°C are shown in Figure 1. As is to be expected, the methanol space time yield increased with increasing reaction pressure. It reached 338 g/kg cat·hr at 450°C and 460 psig (3.2 MPa). However, upon increasing the reaction temperature to 500°C, the methanol space time yield decreased significantly, i.e. the methanol space time yield dropped sharply from 338 g/kg cat·hr at 450°C to 143 g/kg cat·hr at 500°C. This is apparently due to the fact that methanol is more readily oxidized than formaldehyde at higher temperatures. Compared to the previous results (8) obtained at ambient pressure and temperatures ranging from 575°C to 650°C, it was observed that the ratio of formaldehyde/methanol at pressures of 300-460 psig (2.1-3.2 MPa) and temperatures of 450-500°C decreased. For example, the HCHO/CH_3OH ratio was 14 at ambient pressure and 650°C, while it was only 2.3 at 460 psig and 500°C.

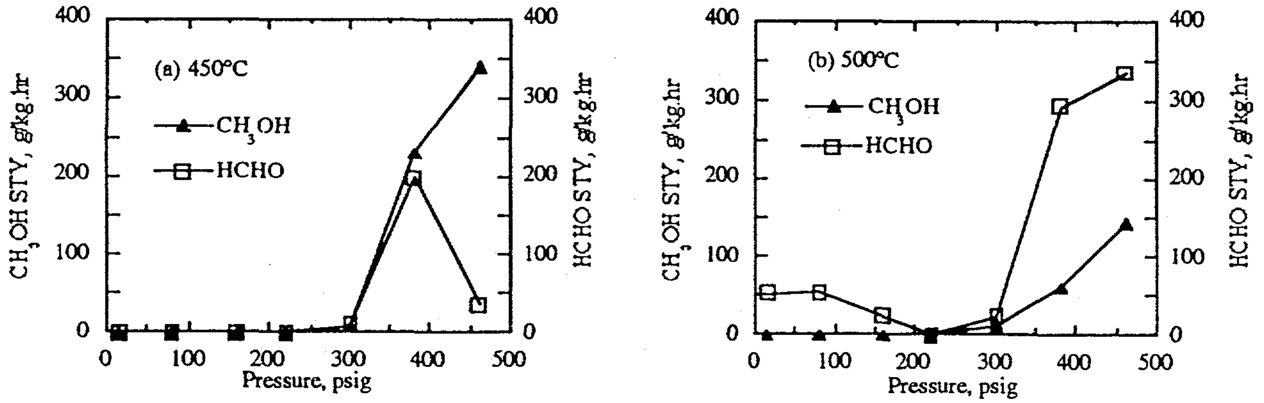

Figure 1. Effects of total reaction pressure on the methanol and formaldehyde space time yields (STY) over a double-layered catalyst bed of 0.10 g 1 wt% $SO_4^{2-}/Sr/La_2O_3$ as the first bed and 0.10 g 1 wt% V_2O_5/SiO_2 as the second bed with a ratio of CH_4/air = 150/50 ml/min.

The above 450°C experiment was rerun but with no catalyst in the reactor. With this empty reactor, the results of the pressure dependence on the productivity of the oxygenates, methanol and formaldehyde, in the noncatalytic operation are shown in Figure 2. In these experiments, it should be pointed out that it is difficult to compare the results of the methanol and formaldehyde space time yields obtained in a noncatalytic operation with those obtained by using double-layered catalysts because the heated zone was much larger then the volume occupied by the bed size of the double bed catalysts.

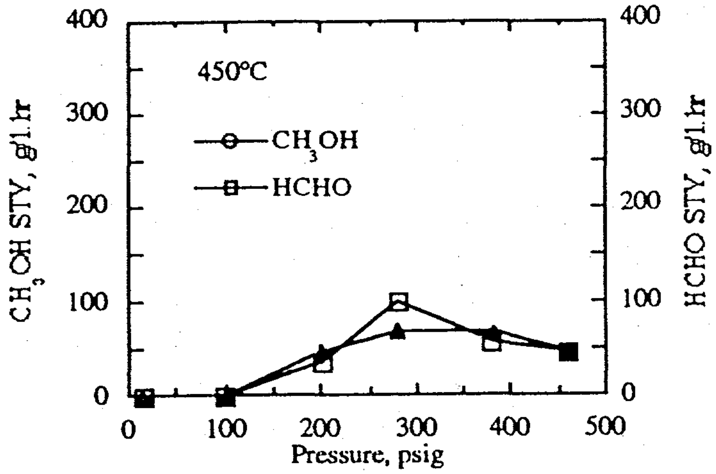

Figure 2. Effects of reaction pressure on the methanol and formaldehyde space time yields in a noncatalytic operation with a reactant ratio of CH_4/air = 150/50 ml/min.

The role of the double bed catalysts at higher pressures needs to be classified further. However, at lower pressures, the importance of the catalyst bed is certainly noted. For example, at ambient pressure and 500°C, the methane conversion increased from 0.06 mol% in a noncatalytic operation to 4.50 mol% in the presence of the double-layered catalyst bed (Table 5). This result is consistent with the catalyst's increasing importance at low pressures and elevated temperatures currently being developed for oxidative coupling of methane, as well as for partial oxidation of methane to formaldehyde.

Table 5. Methane conversion, formaldehyde space time yield (STY), and product selectivities (not considering CO) for noncatalytic operation and over a double-layered catalyst bed of 0.10 g 1 wt% $SO_4^{2-}/Sr/La_2O_3$ as the first bed and 0.10 g 1 wt% V_2O_5/SiO_2 as the second bed with a reactant ratio of CH_4/air = 150/50 ml/min. Testing was carried out at ambient pressure and with a total flow rate of GHSV = 153,000 ℓ/kg catal/hr.

	Temp., °C	CH_4 Conv.,[a] mol%	HCHO STY	Selectivities, C mol%			
				HCHO	CH_3OH	CO_2	C_2
Non-catal.	450	0.00	0.0	0.0	0.0	0.0	0.0
	500	0.06	2.4[b]	79.6	0.0	20.4	0.0
Catal.	450	0.09	0.0	0.0	0.0	100	0.0
	500	4.50	52.6[c]	2.2	0.0	76.7	21.1

[a] CO has not been considered in calculation of CH_4 conversion due to the unsatisfactory separation of CO and CH_4 with the present 5A zeolite column.

[b] Space time yield, g/ℓ heated reactor·hr

[c] Space time yield, g/kg cat·hr

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