SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

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SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

Support effects on catalytic reactions, especially of highly exothermic oxidation reactions, can be very significant. Since we had shown that a $\text{MoO}_3/\text{SiO}_2$ catalyst, especially when used in a double bed configuration with a $\text{Sr}/\text{La}_2\text{O}_3$ catalyst, can selectively oxidize methane to formaldehyde, the role of the SiO_2 support was investigated. Therefore, partial oxidation of methane by oxygen to form formaldehyde, carbon oxides, and C_2 products (ethane and ethene) has been studied over silica catalyst supports (fumed Cabosil and Grace 636 silica gel) in the 630-780°C temperature range under ambient pressure. When relatively high gas hourly space velocities (GHSV) were utilized, the silica catalysts exhibit high space time yields (at low conversions) for methane partial oxidation to formaldehyde, and the C_2 hydrocarbons were found to be parallel products with formaldehyde. In general, the selectivities toward CO were high while those toward CO_2 were low.

Short residence times enhanced both the C_2 hydrocarbons and formaldehyde selectivities over the carbon oxides even within the differential reactor regime at 780°C. This suggests that the formaldehyde did not originate from methyl radicals, but rather from methoxy complexes formed upon the direct chemisorption of methane at the silica surface at high temperature. Very high formaldehyde space time yields (e.g. 812 g/kg catal/hr at the gas hourly space velocity = 560,000 $\ell(\text{NTP})/\text{kg catal/hr}$) could be obtained over the silica gel catalyst at 780°C with a methane/air mixture of 1.5/1. These yields greatly surpass those reported for silicas earlier, as well as those over many other catalysts. However, the methane conversion levels were <1% at the high GHSV where high space time yields were achieved.

Based on the present results obtained by a double catalyst bed experiment, the observations of product composition dependence on the variation of GHSV (i.e. gas residence time), and differences in apparent activation energies of formation of C_2H_6 and CH_2O , a reaction mechanism is proposed for the activation of methane over the silica surface. This mechanism can explain the observed product distribution patterns (specifically the parallel formation of formaldehyde and C_2 hydrocarbons).

Four catalytic tests of the 1 wt% $\text{Sr}/\text{La}_2\text{O}_3$ catalyst, as well as three tests of the 0.5 wt% $\text{Sb}/\text{Sr}/\text{La}_2\text{O}_3$ catalyst, were carried out with a $\text{CH}_4/\text{air} = 1/1$ reactant mixture at 1 atm and with GHSV = 70,000 $\ell/\text{kg catal/hr}$ over the range of temperatures of 500-700°C to check on reproducibility. It is shown that the $\text{Sr}/\text{La}_2\text{O}_3$ catalyst was reproducible and no deactivation was observed. Much more scatter in the activity data was observed with the $\text{Sb}/\text{Sr}/\text{La}_2\text{O}_3$ catalyst, and the catalyst appeared to exhibit deactivation upon decreasing the reaction temperature from the 700°C test. However, both of these catalysts were very active for the conversion of methane to C_2 products at temperatures as low as 500°C.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

OBJECTIVES OF THE RESEARCH

The objective of this research is to selectively oxidize methane to C₂ hydrocarbons (Equations 1-3) and to oxygenates, in particular formaldehyde and methanol as represented by Equations 4 and 5, in high space time yields under milder reaction conditions than heretofore employed over industrially practical catalysts. In particular, air, oxygen, or carbon dioxide, rather than nitrous oxide, will be utilized as the oxidizing gas and a wide range of reaction conditions, e.g. temperature, pressures up to 100 atm, and gas hourly space velocity, will be employed to maximize the space time yields of the desired products while minimizing the yield of carbon dioxide. All of the investigated processes are catalytic, aiming at minimizing difficult to control gas phase oxidation reactions.

The catalysts chosen for this research are based on oxide catalysts that are surface doped with small amounts of acidic dopants. An example of this type of catalyst to be investigated is basic Sr/La₂O₃ that is active for the conversion of methane to C₂ products. This catalyst will be surface doped with 0.5-2.0 wt% Lewis acid cations, which might also be coupled with a redox or a Lewis base function. An aim of this research is to develop catalysts that will activate methane at mild reaction temperatures and at the same time will enhance the ethene/ethane product ratio. The use of CO₂ rather than air or O₂ as the oxidant source will be explored to determine if the ethene/ethane ratio is enhanced while producing CO as the major by-product, as represented in Equation 3. It is expected that the catalysts developed in this research can be optimized to provide steady state space time yields of 3 kg C₂ products/kg catal/hr.

It was shown in our prior research that by the use of appropriate reaction engineering concepts, the selectivity toward oxygenates could be enhanced. For example, this was achieved by coupling the methyl radical-producing Sr/La₂O₃ catalyst with an oxygenate-producing MoO₃/SiO₂ catalyst so that >100 g formaldehyde/kg catal/hr was produced at 630°C, in addition to a high yield of the C₂ hydrocarbons. This process and the ratio of the two catalysts in separate adjacent beds have not been optimized. It is proposed that at these mild temperatures, formation of methanol will be favored by increasing the pressure and perhaps by the addition of steam to the reactants. These process modifications will be

systematically examined so that a combination of catalyst and process optimization will yield efficient, stable, and selective methane conversion processes for either type of product, C₂ hydrocarbons or oxygenates.

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

- Task 1. Maximizing Selective Methane Oxidation to C₂ Products Over Promoted Sr/La₂O₃ Catalysts.
- Task 2. Selective Methane Oxidation to Oxygenates.
- Task 3. Catalyst Characterization and Optimization.

Task 1 deals with the preparation, testing, and optimization of acid promoted lanthana-based catalysts for the synthesis of C₂ hydrocarbons. Task 2 aims at the formation and optimization of promoted catalysts for the synthesis of oxygenates, in particular formaldehyde and methanol. Task 3 involves characterization of the most promising catalysts so that optimization can be achieved under Tasks 1 and 2.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

RESEARCH PROGRESS

PART 1. Methane Oxidation Over Silica

1. Introduction

There has been a great deal of research during the last decade into the catalytic partial oxidation reactions of methane to C₁ oxygenates (particularly methanol and formaldehyde). In many of these, silica has been used as a support for metal oxide catalysts for methane partial oxidation to oxygenates [1-8]. In addition, it has been also been shown that silica itself has discernible activities for methane oxidation to formaldehyde [5,7,9-13]. Kasztelan and Moffat [7] have shown that up to 4.5% of the methane co-fed with O₂ can be converted at 593°C at relatively high contact times, but selectivity to formaldehyde was poor (8%) and no formaldehyde was detected with N₂O as oxidant. In addition to using silica, Kastanas et al. [9] reported a detailed study on partial oxidation of methane over Vycor and on quartz walls of reactor tubing. In the temperature region employed (620-720°C), C₂ hydrocarbons were observed as coproducts. Parmaliana et al. [12] recently reported that precipitated and sol-gel silicas have higher activities than MoO₃ catalysts supported on silica (Cabosil and gel), and it was noted that high temperature treatment (1000°C) of the silica catalyst was very beneficial for methane conversion. However, there have been very few attempts to explore the reaction mechanism by which methane is activated over the silica surface to form formaldehyde and methyl radicals.

Recent studies in this laboratory have shown that a double bed catalyst configuration can greatly increase the yield of formaldehyde from a CH₄/air = 1.5/1 reactant mixture [14]. In particular, this was achieved over a double layered catalyst bed of Sr/La₂O₃ followed by MoO₃/SiO₂. Formaldehyde was formed at a significantly higher space time yield (187 g CH₂O/kg catal/hr) than that from the individual catalyst beds, as well as from a bed of the two mechanically mixed components. This indicated that the methyl radicals generated upstream over the Sr/La₂O₃ catalyst bed were trapped by the MoO₃/SiO₂ catalyst surface to produce formaldehyde. The reaction sequence can be partially explained with the following general scheme for methane-to-formaldehyde over the MoO₃/SiO₂ catalyst proposed by Liu et al. [3]:

2. Experimental

Fumed silica (Cabosil) and silica gel (Grace 636 gel) obtained from Aldrich with surface areas of 385 and 480 m²/g, respectively, have been used in this research. A 2 wt% MoO₃/SiO₂ catalyst was prepared by aqueous impregnation of Cabosil silica with

ammonium heptamolybdate. After impregnation, the catalyst was partially dried at room temperature overnight, followed by drying overnight at 120°C and calcination at 500°C for 2 hr under flowing dry air. This catalyst had a surface area of 280 m²/g. The 1 wt% Sr/La₂O₃ catalyst with a surface area of 6.5 m²/g was used as distributed by AMOCO Oil Co. under their Natural Gas University Research Program. The ≈0.5 wt% Sb/Sr/La₂O₃ catalyst was prepared by aqueous impregnation of the Sr/La₂O₃ catalyst with SbCl₃. After drying with stirring for 30 hr at ≈100°C, samples were calcined at 600°C for 20 hr. Prior to catalytic testing, the samples were typically activated *in situ* under He flow at 700°C for 3 hr.

Catalytic testing was carried out in the temperature range of 500-780°C in a fixed-bed continuous-flow 9 mm OD (7 mm ID) quartz reactor using 0.100-0.125 g of catalyst. A standard reactant mixture of CH₄/air (1.5/1) was used under ambient pressure. The principal products analyzed by on-line sampling using gas chromatography were CO₂, C₂ (C₂H₆ + C₂H₄), C₃ (C₃H₈ + C₃H₆), CO and H₂O. Formaldehyde was condensed from the exit stream with two water scrubbers and quantitatively determined by iodometric titration [15], which has been well-established as a reliable method for determining small amounts of formaldehyde in aqueous solutions. In the present research, the carbon mass balance was always better than 90% and usually better than 95%.

3. Results and Discussion

The methane conversions over the silica catalysts at 730°C, and comparison studies of the double bed catalysts of Sr/La₂O₃ followed downstream by silica catalysts, are listed in Table 1. Because of the high space velocities employed, blank tests with the empty reactor have shown that contributions from reactor wall and gas phase reactions were negligible. Table 1 shows that the silica supports alone indeed have significant activities for methane partial oxidation to formaldehyde, and the formaldehyde space time yield (267 g/kg catal/hr) obtained here with the silica gel is among the highest yields reported to-date [16]. The silica gel is several times more active than the fumed silica under the same reaction conditions.

It was pointed out earlier by Parmaliana et al. [12] that the controlling effect by the silica support on the activity of the silica-supported oxide catalysts should be studied more thoroughly. This is evident in the case of the MoO₃/SiO₂ system, which has methane conversion levels comparable to those of the silica supports alone [5]. Apparently, the support contributes significantly to the overall methane conversion. However, the product distributions obtained from the MoO₃/SiO₂ catalyst and that from the silica support are quite different [3-5,9]. The main selectivity difference lies in the considerable amounts of C₂ hydrocarbons formed over the silica catalyst. On the other hand, over the MoO₃/SiO₂ catalyst it has been well-established that the major products are formaldehyde and carbon oxides when oxygen was used as oxidant, with negligible C₂ hydrocarbon product [5]. The reason for this is that the surface MoO₃ species are capable of trapping the methyl radicals (Equation 6) and convert them into formaldehyde before they recombine to form C₂ hydrocarbons in the gas phase. A very high sticking coefficient for the methyl radical over the MoO₃/SiO₂ catalyst surface has been reported by Tong and Lunsford [17].

Table 1 Methane conversion, formaldehyde space time yields, and product selectivities over the SiO₂(Cabosil and Grace 636 gel) catalysts and the dual bed catalysts of Sr/La₂O₃ followed by SiO₂ with CH₄-Air (1.5:1) reactant at ambient pressure and 730°C and gas hourly space velocity = 70,000 l/kgcat.h.

	SiO ₂ (0.100g)						Sr/La ₂ O ₃ (0.025g)/SiO ₂ (0.100g)					
	CH ₄ Conv. ^a			Selectivities ^c			CH ₄ Conv. ^a			Selectivities ^c		
				CH ₂ O	C ₂	C ₃				CH ₂ O	C ₂	C ₃
	Yield ^b	CH ₂ O	Yield ^b	CH ₂ O	Yield ^b	CH ₂ O	Yield ^b	CH ₂ O	Yield ^b	CH ₂ O	Yield ^b	CH ₂ O
Cabosil	0.31	75.7	46.0	39.1	-	14.9	-	20.5	29.5	0.3	61.2	4.0
Gel	1.36	267.0	38.8	11.4	-	8.0	41.4	19.1	-	-	69.3	2.4

^a Total methane conversion, mol%. ^b Space time yield of formaldehyde, (g/kgcat.h). ^c Selectivities are given in carbon atom%.

In the previous study of methane activation over the double layered catalysts of Sr/La₂O₃ followed by MoO₃/SiO₂, a significant promotional effect of the Sr/La₂O₃ catalyst on formaldehyde generation was observed [14]. The Sr/La₂O₃, which is one of the most active and selective methane oxidative coupling catalysts [18,19], has been shown to be an excellent methyl radical producer [20,21]. The Sr/La₂O₃ catalyst produces C₂ and C₃ hydrocarbons and carbon oxides but not formaldehyde [18,19]. With a small amount of the Sr/La₂O₃ (0.025g) upstream of the MoO₃/SiO₂ (0.100g) catalyst, the formaldehyde production rate was increased about 4-fold over that of the MoO₃/SiO₂ catalyst alone under the same reaction conditions [14]. However, the data in Table 1 clearly show that the Sr/La₂O₃ combined with silica in a double bed configuration did not promote the formaldehyde production. Indeed, the product selectivity was switched from formaldehyde to the hydrocarbon products. This indicates that the silica surface cannot effectively trap the methyl radicals generated by the Sr/La₂O₃ catalyst and convert the radicals to formaldehyde like the MoO₃/SiO₂ catalyst. The facts that (i) silica itself does produce formaldehyde as one of the major products at low methane conversions and (ii) the Sr/La₂O₃ catalyst produces methyl radicals without formaldehyde formation suggest that the formaldehyde generated over the silica surface does not originate from methyl radicals.

The effective activation energies determined in the present study corroborate the difference in reaction mechanisms for C₂ hydrocarbons and formaldehyde. The overall activation energies for methane conversion were 34 and 47 kcal/mol over Cabosil and silica gel catalysts, respectively (Table 2), while the apparent activation energies for formaldehyde formation were 26 kcal/mol over Cabosil and 41 kcal/mol over the silica gel. If formaldehyde were formed in the gas phase by the reaction of methyl radicals and oxygen, the overall activation energy for formaldehyde formation would be at least equal to that of methane conversion. However, the apparent activation energies for formaldehyde formation are appreciably less than that observed for methane conversion. This suggests that the formaldehyde is formed by a surface reaction over the silica catalysts. The apparent activation energies should include terms for surface reactions, which could give the lower

Table 2 Catalyst surface areas (before and after the catalytic test) and the apparent activation energies for methane conversion and C₂ and formaldehyde formation over silica catalysts.

Catalyst	Surface area (m ² /g) before/after	Apparent Activation energy (kcal/mol)(±5)			Temperature range (°C)
		CH ₄	C ₂ H ₆	CH ₂ O	
Cabosil	385/365	34	57	26	630-780
Silica gel	480/260	47	68	41	630-780

value observed. On the other hand, the C₂ hydrocarbon formation proceeds in many cases *via* gas phase methyl radical coupling [20,21]. The apparent activation energy for C₂ products are 57 kcal/mol over the Cabosil and 68 kcal/mol over the silica gel catalyst. These values are much higher than the activation energies for methane conversion, which implies that the methyl radical desorption processes are difficult ones.

To attain a better understanding of the silica system for methane oxidation, the methane conversion and the product selectivities were determined over a wide range of the flow rate. In this experiment, a constant reaction temperature of 780°C was utilized with the silica gel catalyst. The methane conversions, the yields of formaldehyde, and the product selectivities are given in Table 3. Figure 1 shows the methane conversion and formaldehyde space time yield as a function of the contact time of the reactants. It is apparent that several data points at short contact times were obtained in the differential reactor regime [22], where there is no diffusion limitation and the methane conversion increased linearly with the contact time. In Figure 2, the product selectivities are plotted

Table 3. Methane conversion, formaldehyde space time yields, and product selectivities over the pure SiO₂ gel catalyst with CH₄-Air (1.5:1) reactant at 780°C and ambient pressure and different gas hourly space velocities (GHSV).

GHSV (l/kgcat.h)	CH ₄ Conv. ^a	CH ₂ O Yield ^b	Selectivities ^c				
			CH ₂ O	C ₂ ^d	C ₂	CO ₂	CO
35,000	5.96	147.5	9.8	6.2	13.3	11.5	59.2
52,500	4.95	234.3	13.5	5.0	13.0	8.9	59.6
70,000	3.96	307.0	15.0	4.6	14.4	7.3	58.7
105,000	3.09	352.3	14.9	3.9	15.9	5.5	59.8
140,000	2.65	344.7	13.2	4.3	17.5	5.5	59.5
210,000	1.59	487.0	19.1	7.9	22.6	3.7	48.8
280,000	1.20	549.2	21.2	7.9	25.2	3.7	41.5
420,000	1.00	726.2	23.3	7.4	27.9	2.8	38.6
560,000	0.68	812.8	28.0	7.2	31.6	3.2	30.0

^a Total methane conversion, mol%. ^b Space time yield of formaldehyde, (g/kg.cat.h). ^c Selectivities are given in carbon atom%, ^d C₂[•] = C₂H₄.

FIGURE 1

Methane conversion (●) and formaldehyde space time yield (○) as a function of the contact time for methane activation over Grace 636 silica gel at ambient pressure and 780°C with $CH_4/air = 1.5/1$. W is the weight of catalyst (g) and F is the flow rate of the CH_4/air mixture in ml(STP) per second. Thus, W/F is proportional to the contact time.

FIGURE 2

Methane Activation over SiO_2 (Grace 636)

Product selectivity as a function of the methane conversion for the same set of data as in Figure 1.

against the methane conversion for the same set of data. It appears that the C_2H_6 and formaldehyde products that exhibit parallel behavior (decreasing with increasing methane conversion) are primary products, while the carbon oxides are secondary products. Similar product distribution patterns has also been observed by Kastanas et al. [9] with an empty quartz reactor.

Parmaliana et al. [12] previously noticed that silica gel had higher activity for methane oxidation than fumed silica, in agreement with the present results. Silica gel is known to have a higher sodium level than Cabosil due to the different preparation methods employed. However, only a slight effect on activities was found for the acid washed silica gels, with much lower sodium contents, compared to those of the unwashed ones [5,12]. In the present research, it was noticed that the product distribution for methane oxidation over silica catalysts depended on the reaction temperature, in addition to the level of methane conversion that has been demonstrated to affect the product selectivity. Data shown in Table 4 were obtained after designing the reaction conditions (CH_4 /air mixture flow rates and temperatures) so that the methane conversions were at a comparable level. It is evident that the overall selectivity to CO and CO_2 did not vary considerably with the reaction temperature at relatively constant methane conversions. On the other hand, low reaction temperatures clearly favored the formation of formaldehyde over the C_2 hydrocarbons, and vice versa at high temperatures. This is attributed to the significantly lower apparent activation energy for CH_2O generation compared to that for C_2 formation.

Table 4 Methane conversion, formaldehyde space time yields, and product selectivities over the pure SiO_2 gel catalyst with CH_4 -Air (1.5:1) reactant at ambient pressure and different reaction temperature and gas hourly space velocities (GHSV).

Temp. (°C)	GHSV (l/kgcat.h)	CH_4 Conv. ^a	CH_2O Yield ^b	Selectivities ^c			
				CH_2O	C_2	CO_2	CO
630	8,000	0.91	25.8	49.0	4.6	6.8	39.7
680	17,500	1.53	77.7	40.2	6.4	5.0	48.3
730	70,000	1.36	267.0	38.8	11.4	8.4	41.4
780	280,000	1.20	549.2	21.2	33.1	3.7	41.5

^a Total methane conversion, mol%. ^b Space time yield of formaldehyde, (g/kg.cat.h). ^c Selectivities are given in carbon atom%.

4. Conclusions

Silicas that are utilized as supports for oxide catalysts being investigated for methane activation and conversion to C_2 products (ethane and ethene), or especially to selective oxidation products such as formaldehyde, exhibit catalytic activity without the presence of surface-held promoters. It was shown that the silicas have high selectivities toward partial oxidation products, and the space time yields of formaldehyde are very high under optimum reaction conditions, e.g. low temperatures, and low conversions. It was also shown that readsorption of methyl radicals on the silica surface was highly unlikely to occur, in contrast to MoO_3/SiO_2 catalysts, and once desorption of the methyl radicals occurs, coupling in the gas phase is the dominant reaction.

This investigation indicates that there are two different, possibly parallel, mechanistic pathways for the conversion of surface activated methane into formaldehyde and C_2 products over silica. Although not discussed in detail here, the first involves conversion of surface methoxy species into formaldehyde and the second involves desorption of surface-held methyl groups as gas phase methyl radicals. These two pathways have different apparent activation energies that are reflected in the temperature dependence observed in the product selectivity trends.

PART 2. Methane Oxidation Over Sr/La_2O_3 and $Sb/Sr/La_2O_3$ Catalysts

To determine the degree of reproducibility of catalyst testing of the AMOCO Oil Co. Sr/La_2O_3 catalyst and its thermal stability, three different researchers tested four different portions of the catalyst as a function of temperature. For these tests, a reactant mixture consisting of $CH_4/air = 1/1$ was utilized at 1 atm and with a GHSV = 70,000 $\ell / kg \text{ catal/hr}$. The observed steady state conversions of methane as the temperature was varied are shown in Figure 3. In this figure, the open data points were obtained while increasing the temperature, while the solid data points were obtained while the temperature was decreased in a stepwise manner. The conversion at 500°C is very sensitive to the reaction temperature since the methane oxidation reaction, once initiated, is highly exothermic. Thus, the data points indicated for 500°C but with $\approx 10-13\%$ conversion could actually be for a somewhat higher temperature than 500°C.

The % yields of C_2 products as a function of temperature under these reaction conditions, i.e. $CH_4/air = 1/1$ at 1 atm and with GHSV = 70,000 $\ell / kg \text{ catal/hr}$, are shown in Figure 4. The % yield is defined as the product of the total C_2 selectivity (mol% ethane + ethene) and the total conversion of methane (mol%). Once again, the data indicates that the Sr/La_2O_3 catalyst is quite reproducible and stable.

The Sb-surface doped Sr/La_2O_3 catalyst was also tested in a similar manner by three different investigators under the same reaction conditions as employed for the Sr/La_2O_3 catalyst. The conversion levels of methane observed over this catalyst that contained ≈ 0.5 wt% Sb are shown in Figure 5. Again, the open symbols represent data points that were obtained while increasing the reaction temperatures and the solid data points were obtained upon stepwise decreasing the temperature. With this catalyst, there is appreciably more

FIGURE 3
CONVERSION OF METHANE OVER Sr/La₂O₃
 CH₄/air = 1/1, 1 atm,
 GHSV = 70,000 l/kg catal/hr

FIGURE 4
YIELD OF C₂ PRODUCTS OVER Sr/La₂O₃
 CH₄/air = 1/1, 1 atm,
 GHSV = 70,000 l/kg catal/hr

FIGURE 5
CONVERSION OF METHANE OVER Sb/Sr/La₂O₃
 $\text{CH}_4/\text{air} = 1/1, 1 \text{ atm},$
 $\text{GHSV} = 70,000 \text{ l/kg catal/hr}$

scatter in the activity data, and additional testing of this catalyst will be carried out. In addition, an apparent deactivation of the catalyst is observed upon decreasing the temperature. Characterization of the catalysts needs to be carried out to determine the cause of this deactivation. The scatter and activity trends are also followed by the % yields of the C₂ products.

It is notable in Figures 3-5 that methane is activated and converted to products over the Sr/La₂O₃-based catalysts at temperatures as low as 500°C. This contrasts with the typical steam reforming reaction of methane over Ni-based catalysts that is carried out at ≈850°C. At temperatures higher than 550°C under the reaction conditions employed here, over 70% of the oxygen is consumed. Thus, at the higher temperatures studied, the conversion level of methane is limited by the availability of the oxygen reactant.

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