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**Selective Methane Oxidation Over Promoted
Oxide Catalyst**

**Quarterly Report
September - November 1993**

**K. Klier
R. G. Herman
J. Sarkany
Q. Sun**

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**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880**

**By
Lehigh University
Department of Chemistry
7 Asa Drive, Sinclair Laboratory
Bethlehem, Pennsylvania 18015**

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SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

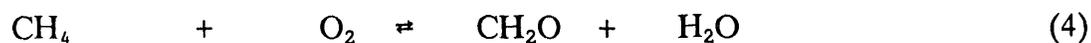
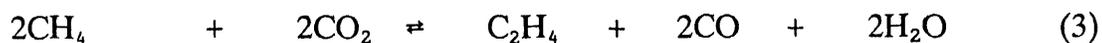
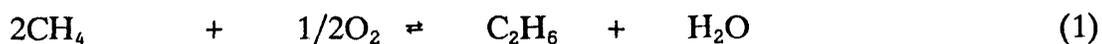
Dispersed metal oxide catalysts have been prepared and tested for the selective oxidation of methane. The catalysts were based on multivalent cations that were impregnated into a number of different oxide supports. These catalysts included $\text{MoO}_3/\text{SiO}_2$, $\text{V}_2\text{O}_5/\text{SiO}_2$, $\text{V}_2\text{O}_5/\text{MoO}_3/\text{SiO}_2$, $\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{SnO}_2/\text{SiO}_2$, and $\text{V}_2\text{O}_5/\text{SnO}_2$. Among the dispersed metal oxide catalysts studied this quarter, the most active catalyst was clearly the $\text{V}_2\text{O}_5/\text{SiO}_2$ catalyst. High surface area silica samples impregnated with 1-5 wt% V_2O_5 were found to be active catalysts with low selectivity toward CO_2 . Although CO was the major product, appreciable selectivities toward formaldehyde were also observed. Indeed, with the $\text{V}_2\text{O}_5/\text{SiO}_2$ catalysts, very high space time yields of formaldehyde of $> 1 \text{ kg CH}_2\text{O/kg catal/hr}$ could be obtained even though the conventional single pass %yields were $< 2\%$. These results were obtained at relatively high GHSV (70,000-280,000 $\ell/\text{kg catal/hr}$) but moderate temperatures (530-630°C).

Continued data analysis of the large amount of experimental data previously obtained with the sulfated $\text{Sr}/\text{La}_2\text{O}_3$ catalyst, i.e. 1 wt% $\text{SO}_4^{2-}/1 \text{ wt}\% \text{ Sr}/\text{La}_2\text{O}_3$ catalyst, which was shown to be highly active in the conversion of methane to C_2 products, is underway, and the results will be discussed further in a future quarterly report when the analysis is complete.

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

OBJECTIVES OF THE RESEARCH

The objective of this research is the selective oxidative coupling of methane to C₂ hydrocarbons (Equations 1-3) and oxygenates, in particular formaldehyde and methanol as represented by Equations 4 and 5. Air, oxygen, or carbon dioxide, rather than nitrous oxide will be utilized as the oxidizing gas at high gas hourly space velocity, but mild reaction conditions (500-700°C, 1 atm total pressure). All the investigated process are catalytic, aiming at minimizing difficult to control gas phase reactions.



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

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

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

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

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

RESEARCH PROGRESS

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

A great deal of experimental research was carried out in previous quarters with this very active catalyst, where the sulfate-doping was shown to increase both the activity and the selectivity of methane conversion to C₂ products. Continued data analysis is underway, and the results will be discussed further in a future quarterly report when the analysis is complete.

New Supported Catalysts for Conversion of Methane to Oxygenates

1. Introduction

The direct conversion of methane to oxygenates *via* controlled partial oxidation is a very challenging research area in fundamental heterogeneous catalysis. Many oxide catalyst systems have been investigated for this process, and a number of reviews have summarized the research that generally resulted in low activity catalysts [1,2]. One type of catalyst system that is most interesting is dispersed metal oxides on silica. Silica-supported V₂O₅ and MoO₃ have been studied extensively [3-6], and the V₂O₅/SiO₂ system was observed to produce formaldehyde from methane by using either N₂O [3,4] or molecular oxygen [5,6] as oxidants. It has been proposed that silica is the only effective support for the transition metal oxide catalysts for the selective conversion of methane to formaldehyde [7]. Indeed, it has been shown that silica itself can selectively produce formaldehyde from methane as well [8-10]. In either case, the reaction mechanisms are largely unknown, in part because of the lack of *in situ* analyses of the operating catalysts.

In this quarterly progress report, experimental results concerning the preparation and catalytic testing of V₂O₅-based catalysts on a number of supports are presented. The testing conditions used for the methane/air conversion are rather moderate reaction conditions (e.g. 630°C).

2. Experimental

Supports that were utilized included SiO₂, TiO₂, and SnO₂. The amorphous SiO₂ (Cabosil EH-5 with a surface area of 380 m²/g) was treated with water to make it more dense. TiO₂ was obtained from Degussa (P-25 with a surface area of 55 m²/g) and was used as received. SnO₂ (surface area = 20 m²/g) was made from tin(II) acetate (Aldrich) by hydrolysis with water, following by filtering, drying at ambient temperature, heating at 120°C overnight, and then calcining in air at 450°C for 6 hr.

The catalysts were prepared by the incipient wetness impregnation technique. The $\text{TiO}_2/\text{SiO}_2$ catalysts were prepared *via* a toluene solvent of titanium(IV) isopropoxide under a N_2 atmosphere, while the V_2O_5 -containing catalysts were prepared using a methanol solution of vanadium(VI) triisopropoxide oxide in a N_2 environment. $\text{SnO}_2/\text{SiO}_2$ samples were prepared from an aqueous solution of colloidal SnO_2 under ambient conditions. An aqueous solution of ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ from Matheson, Coleman, and Bell) was used for prepared the MoO_3 -containing catalysts. After impregnation, each catalyst was dried at room temperature, heated at 120°C overnight, and then calcined at 500°C for 4 hr in flowing air. The metal oxide loading levels on the oxide supports are calculated on the basis of %weight.

Catalytic testing was carried out in the temperature range of 400 - 630°C in a fixed-bed continuous-flow 9 mm OD (7 mm ID) quartz reactor, and usually 25-200 mg of catalyst was used for each test. A reaction mixture of $\text{CH}_4/\text{air} = 1.5/1.0$ was used at ambient pressure, and usually a total flow rate (GHSV) of $70,000 \text{ l/kg catal/hr}$ was used but a variety of flow rates were used with some of the catalysts. The principal products analyzed by on-line sampling using gas chromatography were CO_2 , C_2 ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$), CO , and H_2O . Formaldehyde was condensed from the exit stream with dual water scrubbers and then quantitatively determined by iodometric titration. The carbon mass balance during the catalytic reaction was usually better than 95%.

The BET surface areas of the catalysts used were measured by us with an instrument (Model Gemini-2360) from Micrometrics Instrumental Corporation. The weighed catalyst samples (50 to 70 mg) were pretreated in flowing N_2 at 250°C for a minimum of 2 hr, and the samples were then cooled in the flowing N_2 to room temperature. The surface area was measured with N_2 as adsorbate at liquid N_2 temperature (-196°C) using two test tubes (one sample and one reference tube) and the multipoint method. Before each measurement, the free volume was determined by He gas at liquid N_2 temperature.

3. Results and Discussion

The conventional steady-state catalytic partial oxidation of methane using air as the oxygen source was carried out with each catalyst at ambient pressure, and the observed conversions and product selectivities are summarized in Table 1. In general, high reactant space velocities, i.e. $70,000 \text{ l/kg catal/hr}$, were used to remove the synthesized products, in particular the formaldehyde, quickly from the heated reaction zone so that secondary oxidizing reactions would be inhibited. Under the reaction conditions employed here, it was shown that the effects on the methane conversion by the reactor and the silica support (by using the empty reactor and the pure Cabosil support) were negligible. For the SiO_2 and $\text{MoO}_3/\text{SiO}_2$ testing, accurate analyses of the products, other than formaldehyde, were very difficult because of the low methane conversion levels.

$\text{V}_2\text{O}_5/\text{SiO}_2$ Catalysts. The methane conversion levels as a function of the contact time over the 1.0 wt% and 3.0 wt% $\text{V}_2\text{O}_5/\text{SiO}_2$ catalysts, obtained at 630°C and 580°C , respectively, are shown in Figure 1. It was evident that the 3 wt% catalyst was much more active than the 1 wt% catalyst. The oxidation of methane is a highly exothermic reaction,

and in the low contact time region shown in Figure 1, the conversions of methane exceeded the linear reaction rate increase with increasing contact time, as expected for a differential reactor conversion. Thus, an autocatalytic reaction is indicated. At longer contact times, diffusion limitations caused the conversion of methane to decrease. Two factors that could be contributing to the autocatalytic reactions are the following:

- (i) formation of hot spots by the exothermic reaction that would further accelerate the reaction, and
- (ii) initiation of gas phase free radical chain reactions by surface reactions.

The selectivities toward formaldehyde as a function of methane conversion levels for four V_2O_5/SiO_2 catalysts with different loading levels are shown in Figure 2. For the 1.0 wt% catalyst, experimental data were collected at three different temperatures. This figure shows that formaldehyde selectivity was very sensitive to the methane conversion level, as well as the coverage of the support by V_2O_5 . It is seen that the formaldehyde selectivity had an inverse relationship with methane conversion and that a loading level of 1 wt% gave the best selectivity for formaldehyde. With the highly active 1.0 wt% V_2O_5/SiO_2 catalyst, the selectivity/conversion relationship was independent of reaction temperature over the range utilized in this study.

MoO_3/SiO_2 and $V_2O_5/MoO_3/SiO_2$ Catalysts. Both of these catalysts were tested at 630°C and with GHSV = 70,000 ℓ/kg catal/hr. The data in Table 1 shows that the 2 wt% MoO_3/SiO_2 catalyst exhibited an activity that was very similar to that of the fumed silica support by itself. On the other hand, the 1 wt% $V_2O_5/MoO_3/SiO_2$ catalyst exhibited a rather high conversion level of methane, and the space time yield and product selectivity was approximately the same as observed for the 1 wt% V_2O_5/SiO_2 catalyst. This tends to support the proposal that the V_2O_5 - and MoO_3 -derived surface species are distinct and coexisting on the surface of the silica without strong interactions. In addition, the catalytic activity is mostly due to the surface vanadium oxide species.

V_2O_5/TiO_2 and $V_2O_5/TiO_2/SiO_2$ Catalysts. Catalytic testing studies showed that the TiO_2 -containing catalysts, with TiO_2 as a support or as a surface component, possessed low activity for the oxidative conversion of methane. TiO_2 by itself did show some activity, 1.55 mol% CH_4 conversion, and exhibited the higher selectivity for CO and the lowest selectivity for CO_2 among the catalysts of this type prepared and studied to-date. The activity and the CH_2O space time yield of TiO_2/SiO_2 catalysts increased as V_2O_5 was dispersed on the surface. However, the activities and space time yields were significantly less than those observed with non-titanium-containing V_2O_5/SiO_2 catalysts, as shown in Table 1. The trends indicate that the V_2O_5 is dispersed on surface of the TiO_2/SiO_2 catalyst.

V_2O_5/SnO_2 and $V_2O_5/SnO_2/SiO_2$ Catalysts. The SnO_2 support by itself was found to be a very active catalyst, but the product was principally CO_2 . Table 1 shows that the temperature was lowered from the usual 630°C to 530°C to have the activity in the range of the V_2O_5/SiO_2 catalysts. Similarly, the activity of the 1 wt% V_2O_5/SnO_2 catalyst was very high and the reaction temperature utilized was also lowered to 530°C. However, in contrast to the V_2O_5/SiO_2 catalysts, no formaldehyde was formed over this catalyst and the principal

product was CO₂. Using SnO₂ as a surface layer between the silica support and the V₂O₅ overlayer decreased the activity of the catalyst as compared to the V₂O₅/SiO₂ catalysts, as indicated in Table 1. However, the selectivities of these two catalysts were similar, i.e. CO was the principal product, not CO₂ as for the other SnO₂-containing catalysts.

4. Conclusions

Among the dispersed metal oxide catalysts studied this quarter, the most active catalyst was clearly the V₂O₅/SiO₂ catalyst. High surface area silica impregnated with 1-5 wt% V₂O₅ were found to be active catalysts with low selectivity toward CO₂. Although CO was the major product, appreciable selectivities toward formaldehyde were also observed. Indeed, with the V₂O₅/SiO₂ catalysts, very high space time yields of formaldehyde of > 1 kg CH₂O/kg catal/hr) could be obtained even though the conventional single pass %yields were < 2%. These results were obtained at relatively high GHSV (70,000-280,000 l/kg catal/hr) but moderate temperatures (530-630°C).

5. References

1. Pitchai, R., and Klier, K., *Catal. Rev.-Sci. Eng.* **28** (1986) 13.
2. Brown, M. J., and Parkyns, N. D., *Catal. Today*, **8** (1991) 305.
3. Liu, H.-F., Liu, R.-S., Liew, K. Y., Johnson, R. E., and Lunsford, J. H., *J. Am. Chem. Soc.*, **106** (1984).
4. Zhen, K. J., Mark, C. H., Lewis, K. B., and Somorjai, G. A., *J. Catal.*, **94** (1985) 501.
5. Spencer, N. D., *J. Catal.*, **109** (1988) 187.
6. Spencer, N. D., and Pereira, C. J., *J. Catal.*, **116** (1989) 399.
7. Kasztelan, S., and Moffat, J. B., *J. Chem. Soc., Chem. Commun.* (1987) 1663.
8. Kastanas, G. N., Tsigdinos, G. A., and Schwank, J., *Appl. Catal.*, **44** (1988) 33.
9. Parmaliana, A., Frusteri, F., Miceli, D., Mwzzapica, A., Scurrrell, M. S., and Giordano, N., *Appl. Catal.*, **78** (1991) L7.
10. Sun., Q., Herman, R. G., and Klier, K., *Catal. Lett.*, **16** (1992) 251.

Table 1. Methane oxidation by air (CH₄/Air = 1.5/1) over supported metal oxide catalysts.

Catalysts	GHSV (L/kgcat.hr)	Temp. (°C)	Conv. (CH ₄ %)	STY(CH ₂ O) (g/kgcat.hr)	Selectivities(C-mol%)				Yield(CH ₂ O) ^a (%)
					CH ₂ O	C ₂ 's	CO	CO ₂	
SiO ₂ (F) ^b	70,000	630	0.05	24.3	100.0	-	-	-	0.05
2%MoO ₃ (F)	70,000	630	0.08	37.9	100.0	-	-	-	0.08
1%V ₂ O ₅ (F)	70,000	630	9.52	684.9	15.7	1.7	76.4	6.3	1.49
3%V ₂ O ₅ (F)	140,000	580	6.86	1,022.0	16.6	0.2	76.8	6.3	1.14
5%V ₂ O ₅ (F)	280,000	630	5.60	1,440.0	13.5	0.2	81.3	4.3	0.76
1%V ₂ O ₅ /3%MoO ₃ (F)	70,000	630	8.47	675.2	16.6	2.0	73.5	7.9	1.41
TiO ₂	70,000	630	1.55	17.6	2.3	-	94.0	3.6	0.03
3%TiO ₂ (F)	70,000	630	0.31	27.6	17.8	-	71.1	11.1	0.05
1%V ₂ O ₅ /TiO ₂ ^c	70,000	630	0.82	14.0	3.3	1.2	73.0	22.5	0.03
1%V ₂ O ₅ /3%TiO ₂ (F)	70,000	630	1.07	101.3	18.6	-	76.6	4.8	0.20
3%V ₂ O ₅ /3%TiO ₂ (F)	70,000	630	2.30	150.0	12.5	-	82.2	5.3	0.30
SnO ₂	70,000	530	8.10	2.3	0.1	-	8.9	90.4	0.05
3%SnO ₂ (F)	70,000	630	1.60	8.8	1.1	13.7	8.7	76.3	0.02
1%V ₂ O ₅ /SnO ₂ ^d	70,000	530	7.60	-	-	-	13.4	83.6	-
1%V ₂ O ₅ /3%SnO ₂ (F)	35,000	630	2.00	17.8	3.9	-	77.2	18.9	0.08

^a Yield(CH₂O) = Conversion(CH₄%) × Selectivity(CH₂O%), ^b SiO₂(fumed cabosil), ^c TiO₂ as support, ^d SnO₂ as support.

FIGURE 1
METHANE CONVERSION OVER V_2O_5/SiO_2

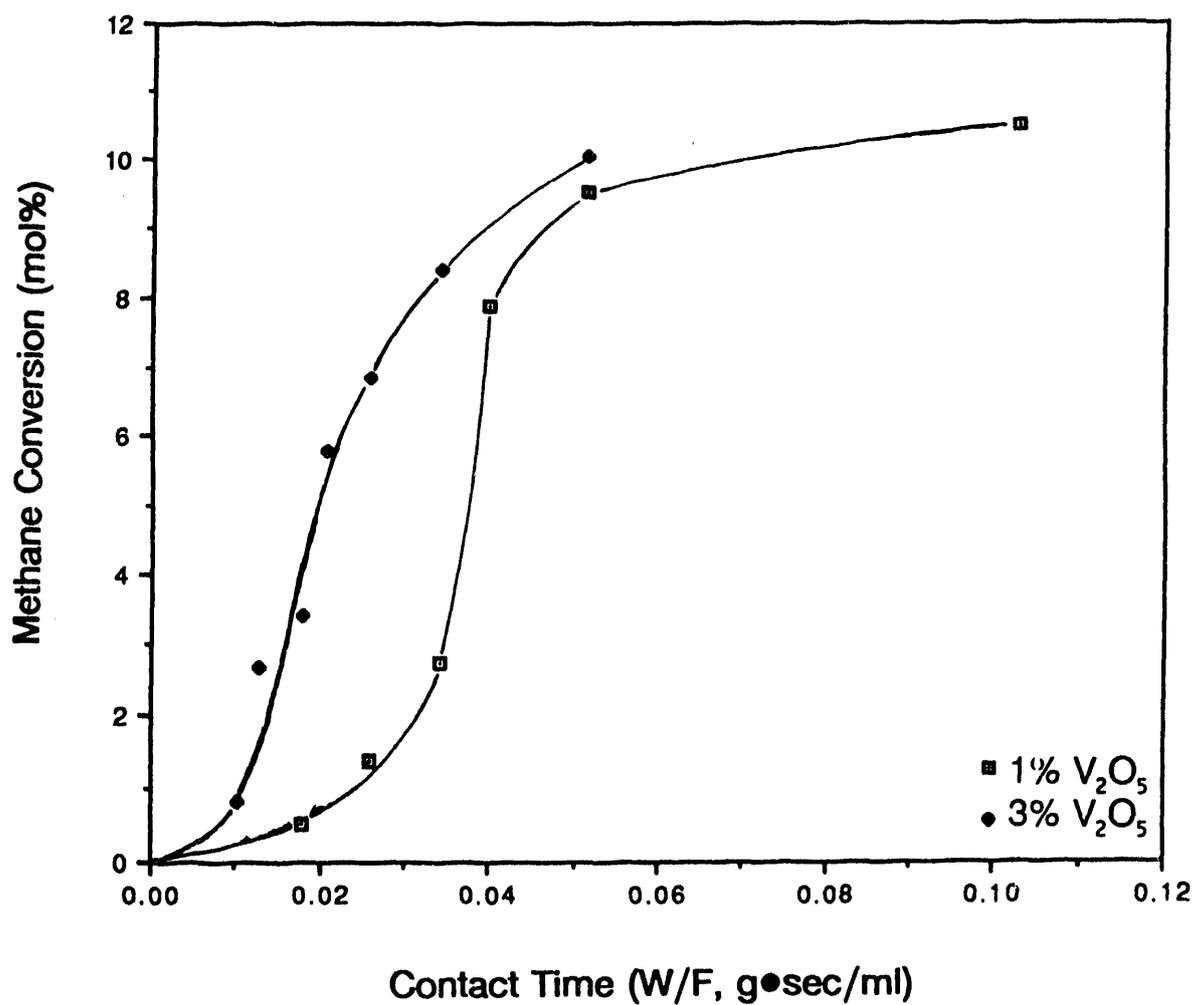
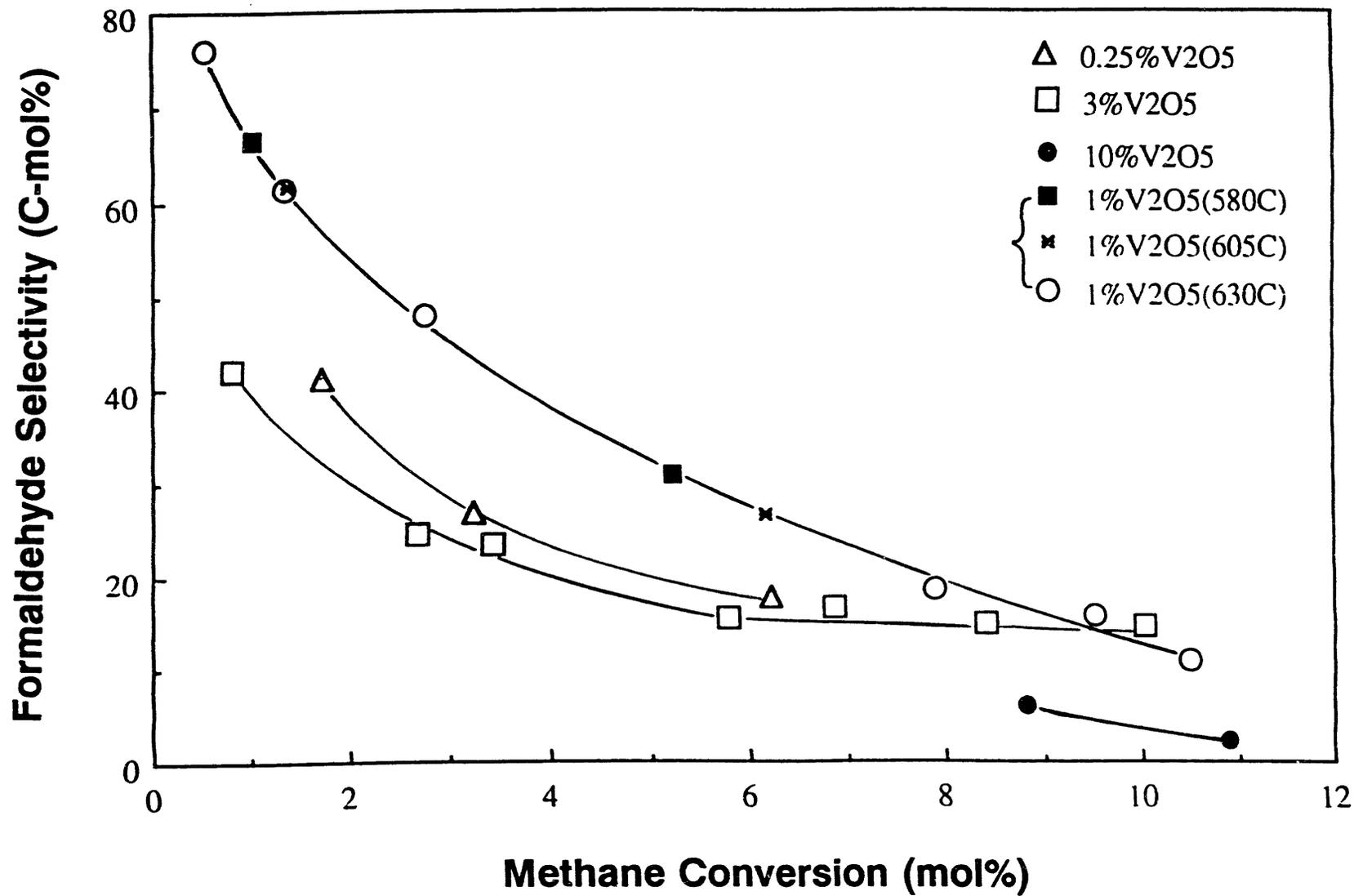


FIGURE 2
METHANE CONVERSION OVER V_2O_5/SiO_2



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