

Effect of Loading and Support on the Activity and Selectivity of Partial Oxidation of Methane, I. Lee and K. Y. Simon Ng, Department of Chemical Engineering, Wayne State University, Detroit, Michigan 48202

The major component of our vast natural gas reserves is methane. Most of the methane produced nowadays is simply used as fuel, with only a small fraction used in the water-gas process. In order to utilize our gas reserves fully, it is desirable to turn methane into more valuable oxygenated products. Even though methane is a simple molecule, it is one of the most difficult hydrocarbons to oxygenate, due to its highly symmetric character.

A number of patents have been claimed on technologies for converting methane to methanol, but there is still no commercial oxidation process utilizing the direct oxidation mechanism. Recently, a considerable amount of research has been undertaken to identify a selective catalyst system. Two recent reviews by Pitchai and Klier (1) and by Foster (2) have summarized the research on partial oxidation reported in the literature. It is to be noted that most research work (3-8) has focused on evaluating the catalytic potential of different compounds, but the role of supports, the functions of promoters, and the effect of catalyst morphology have not been studied in detail. There are indications that catalyst morphology can have a significant impact on selectivities (1). Even though Liu et al. (4) used nitrous oxide and Pitchai et al. (1) used oxygen as oxidant, they both observed that low loading catalyst showed high selectivity. Catalyst morphology has been found to depend on the metal loading, method of preparation, support, and promoter addition (9). Based on the above literature survey, we have focused our efforts on searching for a selective catalyst through support interaction, and to understand the nature of active sites for partial oxidation of methane on different supported catalysts. In this paper, we report our findings in the activity and selectivity of molybdenum- and vanadium-based catalyst on silica, silica-titania, and titania support.

EXPERIMENTAL

Supports

Three types of catalyst supports were studied. The titania oxide was P-25

from Degussa, with a surface area of $50 \pm 5 \text{ m}^2/\text{g}$. The silica was from Kodak. Both supports were used as received, without further treatment. The 1:1 ratio of titania-silica mixed oxide support was made using the method of homogeneous coprecipitation. Sodium metasilicate was first dissolved in double-distilled water and acidified to pH 1 with hydrochloric acid. Equimolar of titanium tetrachloride was then added and followed by neutralization using urea. The mixture was then heated at $90 \text{ }^\circ\text{C}$ for 6 hours. The precipitate was filtered and washed with warm distilled water. The mixed oxide was dried at $120 \text{ }^\circ\text{C}$ for 24 hours, followed by calcination at $600 \text{ }^\circ\text{C}$ for 1 hour.

Catalyst

The catalysts were prepared by the conventional impregnation method. The molybdenum-based catalysts were prepared by dissolving the desired amount of ammonium heptamolybdate in double-distilled water, and the pH was adjusted to 10 using ammonium hydroxide. For vanadium-based catalysts, the desired amount of vanadium pentoxide was dissolved in an aqueous solution of oxalic acid. The solution was then impregnated on the support. The resulting mixture was stirred thoroughly and was dried at $120 \text{ }^\circ\text{C}$ for 2 hours, followed by calcination at $500 \text{ }^\circ\text{C}$ for 24 hours.

Reactor System

A 6mm I.D. quartz U-tube reactor, with a reduction of I.D to 2mm immediately following the catalyst bed, was used. The reactor design, which allows fast removal of products from the furnace, is intended to minimize the gas phase oxidation reactions. A K-type thermocouple with an Omega temperature controller was used to control the reactor temperature to $\pm 0.1 \text{ }^\circ\text{C}$. A typical of 0.1 g of catalyst was used. The catalyst was first heated at $500 \text{ }^\circ\text{C}$ in helium for 1 hour, and with CO in helium for another 30 minutes. The reactor temperature was then lowered to $400 \text{ }^\circ\text{C}$ for 30 minutes in helium, and was subsequently increased to the reaction temperature and the reactant gases introduced. Total gas flow rate is 8 c.c./minute unless stated otherwise. The compressed gases used -- methane

(99.99%), nitrous oxide (99.0%), oxygen (99.99%), helium (99.995%), hydrogen (99.9%), nitrogen (99.9985%), and carbon monoxide (99.9%) -- were from Air Products and were used as received. The mass flow rates of reactants were controlled by Tylan mass flow controllers to $\pm 1.0\%$. Water was introduced in form of steam using a Harvard syringe pump. The whole system is heat-traced with heating wire, and insulated to prevent possible condensation of products and reactants. The products were analyzed using an HP-5890A gas chromatograph equipped with TCD and FID detectors. A 20 ft. Hayesep A column and a 5 ft. Hayesep Q column were used to separate the products.

RESULTS and DISCUSSION

Table 1 shows the conversion and selectivity of molybdenum-based catalysts with different loadings on the silica, silica-titania and titania supports using nitrous oxide as oxidant at 600 °C. On blank silica, there was a small conversion of 0.9% but no formaldehyde was observed. For the silica-supported molybdenum catalysts, both the 1% and 3% loading catalysts gave almost identical conversion (7.5%), indicating that the 3% catalyst may already contain bulk-like molybdenum species that are relatively inactive. The low loading catalyst gave a higher selectivity (42.7%) towards formaldehyde than the 3% catalyst (32.5%), which is consistent with the selectivity trends reported previously (3-5). Our results are comparable to the results of Liu et al. (14% conversion and 15% combined selectivity towards methanol and formaldehyde) and Khan et al. (2.6% conversion and 56% selectivity), taking into consideration of the conversion-selectivity relationship (7). However, the conversion-selectivity relationship is different when a different support is used. On a titania-silica support, the catalyst has a slightly higher conversion (10.2%), but the selectivity is much lower (7.2%). When supported on pure titania, the conversion of methane drops significantly, and no observable formaldehyde was detected. It is apparent from this result that on different supports, the nature of active sites is very different for partial oxidation. It is also suggested that silica plays an important role in the reaction mechanism, as evident from the fact

that mixed oxide support showed some selectivity.

Table 2 shows the effect of temperature on conversion and selectivity. For the blank silica using oxygen as oxidant, no conversion was observed at 500 °C. Conversion of 0.1% with 53.8% selectivity was observed for 600 °C, and conversion of 0.6% with 48% selectivity was observed for 650 °C. The 650 °C data was almost identical with Spencer's results (7). As we will see later, the selectivity is very different when water is added along with the reactants. When nitrous oxide was used as oxidant, a higher conversion (0.9%) was observed at 600 °C, indicating that nitrous oxide is a stronger oxidant compared to oxygen. Surprisingly, no formaldehyde was detected. For the 1.7% Mo/SiO₂ catalyst, the conversions are 0.9%, 2.3%, 7.5%, 34.6% at 500 °C, 550 °C, 600, and 650 °C respectively. The corresponding selectivities are 79.3%, 73.5%, 42.7% and 4.1%. There is a strong conversion-selectivity relationship, as reportedly previously. A similar temperature dependence was also observed for the TiSiO₂-supported catalyst. However, at comparable conversions, the selectivity is much lower compared to the silica-supported catalysts.

The performance of vanadia-based catalysts at 600 °C using nitrous oxide as oxidant was shown on Table 3. With 2% of vanadia on silica, a conversion of 31.5% and selectivity of 51.0% were observed. The yield was calculated to be 132.2 g/kgcat hr., which is significantly higher than yields reported in the literature. It should be noted that for pure silica the conversion was found to be only 0.9% and no formaldehyde could be detected. Unlike the molybdenum-based catalyst, a 15% selectivity towards formaldehyde was observed when supported on titania. Interestingly, no formaldehyde was observed for the TiSiO₂-supported catalyst, even though it showed a conversion similar to the titania-supported catalyst. It is apparent that the nature of the active site for vanadium-based catalysts is quite different from molybdenum-based catalysts, and that the effects of the support on the nature of the active site are not the same.

Table 4 shows the effect of temperature on conversion and selectivity on

vanadium-based catalysts. The conversion was found to increase, as expected, as a function of temperature; however, the selectivity did not show the same conversion-selectivity behavior as the molybdenum-based catalysts. The selectivity increases from 44% at 3% conversion (500 °C) to 51% at 31.5% conversion (600 °C). However, at 650 °C, only carbon oxides were detected. For TiSiO_2 -supported catalysts, no formaldehyde was detected for the temperature range (500-650 °C) tested. The titania-supported vanadium catalyst showed a 15% selectivity only at 600 °C, indicating that there is a narrow temperature range that can be used to produce formaldehyde.

The effect of water added as reactant and the effect of contact time on the conversion and selectivity is shown in Figures 1 and 2 for silica and vanadia-silica. The results are consistent with those reported in the literature. The conversion is generally lowered when water is added, with the exception of pure silica at 650 °C using oxygen as oxidant. The selectivity towards formaldehyde was generally improved. A more comprehensive study is continuing in this laboratory to elucidate the effect of water on product selectivity. When the contact time was reduced by 50%, the conversion was reduced from 13% to 7.5%, but the selectivity increased from 5.0% to 11.6%. With water added as reactant, a similar trend was observed. The conversion was reduced from 11.8% to 4.3% and the selectivity increased from 6.3% to 24.3%.

The effect of oxidant for vanadium-based catalysts is summarized in Table 5. For pure silica, oxygen appears to be a better oxidant, with 82% selectivity (with water as reactant) as compared to nitrous oxide (0% selectivity). However, for the vanadia catalyst, N_2O is obviously a better oxidant than oxygen, especially at a higher reaction temperature (600 °C).

CONCLUSION

The nature of the support has a dramatic effect on the catalytic activities and selectivities of molybdenum- and vanadium-based catalysts. However, the extent of support influence is different for the two catalyst systems, suggesting different

levels of support interaction and possibly different reaction mechanisms. There is a distinct conversion-selectivity relationship for the Mo/SiO₂ catalyst. However, this is not observed with the V₂O₅/SiO₂ catalysts. Thus high conversion with reasonably high selectivity seems to be possible with the vanadium catalyst to produce a high yield. Addition of water reduces conversions but improves selectivities in most cases. Nitrous oxide is found to be a better oxidant for V₂O₅/SiO₂ catalyst. However, for blank silica, oxygen gives a high selectivity towards formaldehyde, which suggests that modified silica can be a promising approach to partial oxidation of methane.

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Table 1

Molybdenum - Based Catalyst at 600 °C

(W / F = 0.0125 g min / cc)

CH₄:N₂O:He = 1:4:2 Total flow rate = 8 cc/ min

Catalyst	Conversion	Selectivity (%)			Yield (g/kgcat hr) (HCHO)
		HCHO	CO	CO ₂	
SiO ₂	0.9	0	50.4	49.6	0
Mo/SiO ₂ (1.7%)	7.5	42.7	43.8	13.5	20.2
Mo/SiO ₂ (3%)	7.4	32.5	54.7	12.8	15.6
Mo/TiSiO ₂ (1.7%)	10.2	7.2	65.7	27.1	5.6
Mo/TiO ₂ (3%)	2.2	0	77.7	22.3	0
Mo/TiO ₂ (5%)	1.7	0	70.2	29.8	0

Table 2

Effect of Temperature on Conversion and Selectivity

(W/F = 0.0125 g min / cc)

CH₄:N₂O:He = 1:4:2 Total flow rate = 8 cc/ min

Catalyst	Oxidant	Temp(°C)	Conversion	Selectivity(%)			Yield (g/kgcat hr) HCHO
				HCHO	CO	CO ₂	
SiO ₂	O ₂	500	0	0	0	0	0
		600	0.1	58.3	24.1	17.6	1.3
		650	0.6	48.0	45.4	6.6	5.7
	N ₂ O	600	0.9	0	50.4	49.6	0
Mo/SiO ₂ (1.7%)	N ₂ O	500	0.9	79.3	10.5	10.2	3.9
		550	2.3	73.5	19.6	7.0	9.3
		600	7.5	42.7	43.8	13.5	20.2
		650	34.6	4.1	63.5	32.4	6.8
Mo/TiSiO ₂ (1.7%)	N ₂ O	550	3.7	0	83.9	16.1	0
		600	10.2	7.2	65.7	27.1	5.6
		650	20.6	1.1	56.5	42.4	1.2

Table 3

Vanadium - Based Catalyst at 600 °C

(W/F = 0.0125 g min / cc)

CH₄:N₂O:He = 1:4:2 Total flow rate = 8 cc / min

Loading(wt %)	Conversion	Selectivity (%)			Yield (HCHO) g/kgcat hr
		HCHO	CO	CO ₂	
SiO ₂	0.9	0	50.4	49.6	0
V ₂ O ₅ /SiO ₂ (2%)	31.5	51.0	35.4	13.6	132.2
V ₂ O ₅ /TiSiO ₂ (2%)	11.4	0	73.4	26.6	0
V ₂ O ₅ /TiO ₂ (2%)	13.7	15.0	34.0	51.0	15.8

Table 4

Effect of Temperature on Conversion and Selectivity

(W/F = 0.0125 g min / cc)

CH₄:N₂O:He = 1:4:2 Total flow rate = 8 cc / min

Catalyst	Temp (°C)	Conversion	Selectivity (%)			Yield (HCHO) (g/kgcat hr)
			HCHO	CO	CO ₂	
V ₂ O ₅ /SiO ₂ (2 %)	500	3.0	44.0	43.4	12.6	9.7
	600	31.5	51.0	35.4	13.6	132.2
	650	42.8	0	62.8	37.2	0
V ₂ O ₅ /TiSiO ₂ (2 %)	500	2.3	0	76.9	23.1	0
	600	11.4	0	73.4	26.6	0
	650	25.6	0	53.7	46.3	0
V ₂ O ₅ /TiO ₂ (2 %)	500	1.3	0	71.7	28.3	0
	600	13.7	15.0	34.0	51.0	15.8
	650	24.2	0	27.4	72.6	0

Table 5

Effect of Oxidant

(W / F = 0.0125 g min / cc)

CH₄:N₂O:He = 1:4:2 , CH₄:O₂:He = 4:1:2 Total flow rate = 8 cc/min

Loading (Wt %)	Temp (°C)	Oxidant	Conversion	Selectivity(%)			Yield(HCHO) g/kg cat hr
				HCHO	CO	CO ₂	
SiO ₂	600	O ₂	0.1	58.3	24.1	17.6	1.3
	600	N ₂ O	0.9	0	50.4	49.6	0
V ₂ O ₅ /SiO ₂ (2 %)	500	O ₂	0.2	38.5	42.5	19.0	1.4
	500	N ₂ O	3.0	44.0	43.4	12.6	9.7
	600	O ₂	13.0	5.0	69.1	25.9	14.4
	600	N ₂ O	31.5	51.0	35.5	13.5	132.2

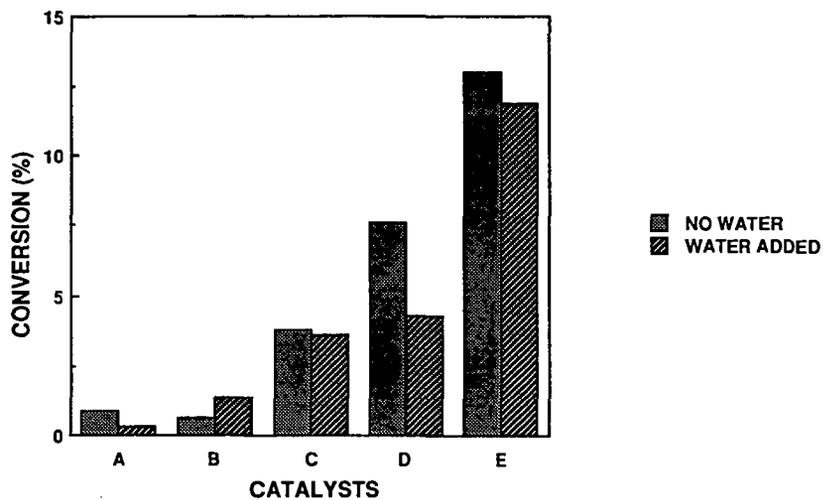


FIGURE 1. EFFECT OF WATER ON CONVERSION

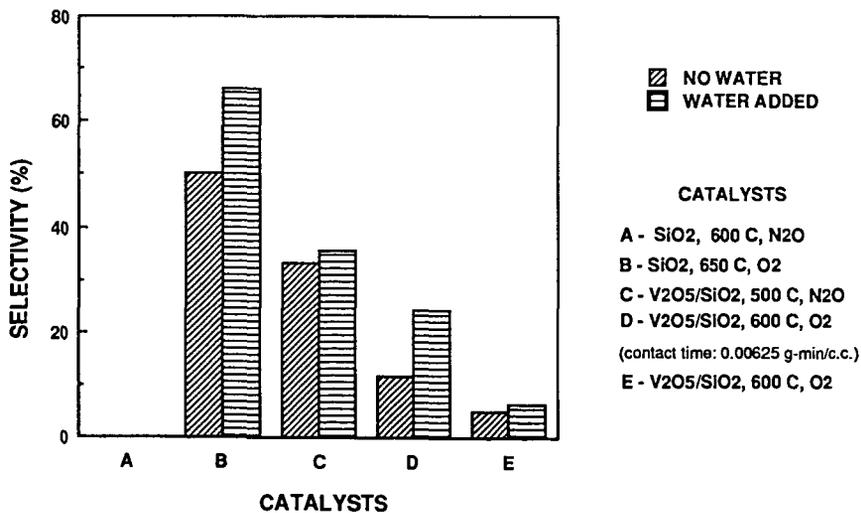


FIGURE 2. EFFECT OF WATER ON FORMALDEHYDE SELECTIVITY

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