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**Selective Methane Oxidation Over
Promoted Oxide Catalysts**

**Quarterly Report
March - May 1994**

**Kamil Klier
Richard G. Herman
Chunlei Shi
Qun Sun**

June 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

By
Zettlemoyer Center for Surface Studies and
Department of Chemistry
Lehigh University
Bethlehem, Pennsylvania

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June 1994

SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

Experimental work aiming at developing active catalysts for selective oxidation of methane to methanol was started in this quarter. Some of the experiments used a double catalyst bed design and with H_2O as cofeed. The first catalyst bed, which serves as CH_3 radical generator, was chosen to be 1 wt% $\text{SO}_4^{2-}/\text{Sr}/\text{La}_2\text{O}_3$, as this catalyst exhibits remarkable activity and selectivity at lower temperature (500°C - 550°C). A few transition metal oxides were used as the second catalyst bed to react with CH_3 to form $\text{CH}_3\text{O}\cdot\text{M}^+$ species, which was then hydrolyzed to form CH_3OH .

As part of the preparatory work, the effect of H_2O feeding on the activity and selectivity of the 1 wt% $\text{SO}_4^{2-}/\text{Sr}/\text{La}_2\text{O}_3$ catalyst was studied. It was found that in the presence of 90 Torr of H_2O , the activity of the $\text{SO}_4^{2-}/\text{Sr}/\text{La}_2\text{O}_3$ catalyst decreased to the activity level that was seen at a reaction temperature roughly 50°C lower without the presence of H_2O . The partial pressure of H_2O was also studied as a variable, and it was found that there was a maximum H_2O content of the reactant before a significant decrease in activity was observed. In addition, the reactor was also redesigned so as to minimize the further oxidation of CH_3OH while it exited the catalyst bed by using a capillary quartz tube at the exit.

It was found that unsupported metal oxides ZrO_2 , Y_2O_3 , SrO , Fe_2O_3 , MnO_2 , Cr_2O_3 , CaO , and MgO did not produce CH_3OH between 430°C and 600°C when used as the only catalysts, while MoO_3 supported on silica produced CH_3OH in the temperature range of 430°C - 480°C under the current single-bed reactor configuration. However, when the double-bed configuration was used with the 1 wt% $\text{SO}_4^{2-}/\text{Sr}/\text{La}_2\text{O}_3$ as the first methyl radical generating catalyst bed, CH_3OH was observed when ZrO_2 and Y_2O_3 were used as the second bed catalysts. Preliminary quantitative analysis showed that the ability of producing CH_3OH was in the order of unsupported $\text{Y}_2\text{O}_3 > \text{unsupported ZrO}_2 > \text{MoO}_3$ on silica. For all of these cases, the CH_3OH space time yield was within a dozen grams per kilogram catalyst per hour.

Using the double-bed reactor design, experiments were carried out to study the ability of the ion pair $\text{Fe}^{3+}/\text{Fe}^{2+}$ to oxidize CH_3 radicals to form surface methoxide species by analyzing the production of CH_3OH . ZrO_2 was used as the support. Preliminary results showed marginal enhancement of CH_3OH production by the ion pair $\text{Fe}^{3+}/\text{Fe}^{2+}$ supported on ZrO_2 .

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 gas phase reactions that are difficult to control.

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/La₂O₃ catalyst which is active in the formation of methyl radicals and therefore C₂ products, can be doped with some Lewis acidic oxides or other groups to increase further its activity and selectivity to C₂ 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 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 CH₂O and CH₃OH. 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

Experimental

The 1% $\text{SO}_4^{2-}/\text{Sr}/\text{La}_2\text{O}_3$ was prepared under Task 1 as designated in earlier progress report. The unsupported metal oxides ZrO_2 , Y_2O_3 , SrO , Fe_2O_3 , MnO_2 , Cr_2O_3 , CaO , and MgO were obtained from Aldrich and were calcined at 600°C for 6 hr and sieved into 20/40 mesh particles. The $\text{Fe}^{3+}/\text{ZrO}_2$ catalyst was prepared by wet impregnation of the ZrO_2 by equal molar of $\text{Fe}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ (prepared by dissolving Fe_3O_4 with HNO_3) at 50°C under constant stirring until dry and the solid was calcined at 750°C for 6 hr.

The experiments were carried out both in the absence and presence of H_2O . The typical temperature range was $400\text{--}600^\circ\text{C}$ and the gas hourly space velocity (GHSV) was 20,000 - 100,000 L/kg.cat.hr. The analyses of the feed and product gases were done by using a Hewlett Packard 5890 gas chromatograph with a molecular sieve column and a capillary column in parallel and TCD detectors. The liquid products CH_3OH and HCHO were trapped at 0°C and analyzed by a Hewlett Packard 5970 MSD detector.

Results and Discussion

Effect of H_2O feeding on the activity of the first bed catalyst

As it was usually observed that cofeeding H_2O significantly affected activities and selectivities of many oxidative coupling catalysts, it was necessary to study the effect of H_2O cofeeding on the performance of the first bed catalyst, the 1% $\text{SO}_4^{2-}/\text{Sr}/\text{La}_2\text{O}_3$, particularly under conditions where CH_3OH was to be produced. The information obtained was to be used to optimize the ability of the first bed to generate CH_3 radicals. Experiments were carried out at 1 atm over 0.10 g of the 1% $\text{SO}_4^{2-}/\text{Sr}/\text{La}_2\text{O}_3$ catalyst at a methane-to-air ratio of 1:1, a total flow rate of 120 cc/min, and a fixed

Figure 1 Effect of H_2O feed on the activity of $\text{SO}_4^{2-}/\text{Sr}/\text{La}_2\text{O}_3$ as a function of temperature.

H₂O partial pressure of 90 Torr.

As shown in Figure 1, within the entire range of temperature, the activity of the catalyst in the presence of the cofeed water decreased to the level that was seen at temperatures 50°C to 70°C lower than the activities observed before the water was added to the reagents. This behavior is expected because the presence of H₂O or hydroxyls on the surface would interfere with the methane activation process and, as a result, fewer CH₃ radicals were generated. The selectivity was observed to be slightly higher (<10%) if compared at the same level of conversion. These observations were consistent with fact that the generation of CH₃ radicals occurs on the surface while the coupling of CH₃ radicals occurs in the gas phase. The higher C₂ selectivity can be explained by interference with the secondary reaction of C₂ on the surface.

In order to find the optimum partial pressure for H₂O cofeeding with minimum sacrifice in activity, a series of H₂O partial pressures was employed and the activity measured. Results are plotted in Figure 2. It is evident from this figure that the maximum partial pressure of H₂O that can be employed in a double-bed experiment without significant decrease in activity is around 20 Torr under the chosen conditions. The use of the maximum H₂O partial pressure may be necessary depending on the nature of the second bed.

CH₃OH production over metal oxides using a single bed reactor

Experiments were carried out to test the background production of CH₃OH by the 1% SO₄²⁻/Sr/La₂O₃ catalyst in the single-bed reactor, which was to be used as the first bed catalyst. The tests were carried out under typical double-bed experimental condition and the results are shown in Figure 3. It can be seen that the production of CH₃OH by the 1% SO₄²⁻/Sr/La₂O₃ catalyst was nearly at a constant low level of about 1 g/kg.cat/hr in the temperature range employed.

As the first step for the double bed experiment, metal oxides such as MoO₃, ZrO₂, Y₂O₃, SrO; Fe₂O₃, MnO₂, Cr₂O₃, CaO, and MgO that were to be used as the second

CH₄ Conversion As a Function of H₂O Partial Pressure

Figure 2 CH₄ conversion as a function of H₂O partial pressure.

Figure 3 Background production of CH₃OH by 1% SO₄²⁻/Sr/La₂O₃ catalyst.

bed catalysts were tested for CH₃OH production in the single bed reactor. Since MoO₃ was unstable under the reaction temperatures studied, it was put on silica support. Results showed that except for MoO₃ supported on silica, which produced only a small amount of CH₃OH in temperature range of 430-480°C with H₂O as cofeed (≈ 1 g/kg · cat · hr), none of the metal oxides produced detectable CH₃OH in the temperature range of 400-600°C. The experiments were carried out both with and without H₂O as cofeed.

CH₃OH production over metal oxides using double bed reactor

The experiments on CH₃OH production by double-layered catalyst beds were started in this quarter, and the studies have concentrated on using Y₂O₃ and ZrO₂ as the second bed, particularly ZrO₂. Variables such as temperature and H₂O partial pressure were explored, and a set of typical results are shown in Table I.

(i) Effects of Temperature

As indicated by the second and third rows in Table I, there is a decrease of CH₃OH production with increasing temperature. This can be explained by the fact that at higher temperature, CH₃OH oxidation to secondary products becomes more important.

(ii) Effects of H₂O Cofeed

An important concept was that the CH₃ radicals trapped on the surface could be hydrolyzed to form CH₃OH when H₂O was present. As shown by the second and last rows in Table I, there was a slight decrease in CH₃OH production when H₂O was not used as a cofeed. However, a better experiment to investigate the role of H₂O would be at very low CH₄ conversion because at higher conversions the amount of H₂O produced by the reaction can not be neglected. To achieve that goal, a single-bed of the less active 1% MoO₃/SiO₂ catalyst was used. Results obtained are shown by the fifth and sixth rows in Table I, and it is evident that H₂O cofeeding was instrumental in CH₃OH production even over the single-bed 1% MoO₃/SiO₂ catalyst.

Table I CH₃OH Production over Double-bed Catalysts

Row No.	First bed ^a	Second bed ^a	P(H ₂ O) Torr ^b	Temp. °C	CH ₄ Conv. %	C ₂ Sel. %	CH ₃ OH STY g/kg.cat.hr ^c
1	SO ₄ ²⁻ /Sr/La ₂ O ₃	Y ₂ O ₃	40	600	12.7	45.5	3.0
2	SO ₄ ²⁻ /Sr/La ₂ O ₃	ZrO ₂	40	550	11.5	40.8	2.0
3	SO ₄ ²⁻ /Sr/La ₂ O ₃	ZrO ₂	40	600	13.4	38.8	1.6
4	MoO ₃ /SiO ₂	-	100	480	0.1	0	0.3
5	MoO ₃ /SiO ₂	-	100	430	0.1	0	1.1
6	MoO ₃ /SiO ₂	-	0	430	0	0	0
7	-	ZrO ₂	80	600	0.2	0.5	0.2
8	SO ₄ ²⁻ /Sr/La ₂ O ₃	SrO	40	550	10.2	37.8	0.4
9	SO ₄ ²⁻ /Sr/La ₂ O ₃	ZrO ₂	0	550	13.9	36.4	1.6

^a Typical bed sizes: first bed = 0.10 g, second bed = 0.20 g.

^b H₂O partial pressures shown are those in the feed.

^c CH₃OH space time yield (STY) was obtained by trapping and analyzing liquid products.

(iii) Comparison of Results Over Unsupported Y₂O₃ and ZrO₂

As shown by the first and third rows in Table I, there was an observed increase of CH₃OH production when the second bed metal oxide was switched from ZrO₂ to Y₂O₃ under identical conditions. However, under the same conditions, when the second bed was SrO, there was essentially no CH₃OH detected. At the present stage, it is not clear how these results should be explained. Obviously, more experimental work is needed before these results can be understood.

Study of supported Fe³⁺/Fe²⁺ catalysts

As shown in Figure 4, using the double-bed reactor design, experiments were carried out to study the ability of the ion pair Fe²⁺/Fe³⁺ to oxidize CH₃ radical to form surface CH₃O·M⁺ species, with subsequent the production of CH₃OH. Literature data indicate that ion pairs Fe³⁺/Fe²⁺ and Cu⁺/Cu²⁺ are excellent redox systems for oxidizing CH₃ radicals to surface methoxides. However, neither of them were studied in a double-bed setting. Experiments were carried out in this quarter to dope Fe²⁺/Fe³⁺ into ZrO₂ by wet impregnation of ZrO₂ with Fe(NO₃)₂/Fe(NO₃)₃ and calcining at 750°C. The idea was to see if the ion pair could function

Comparison of ZrO_2 and $\text{Fe}^{3+}/\text{ZrO}_2$ as the Second Bed

Figure 4 Comparison of ZrO_2 and $\text{Fe}^{3+}/\text{ZrO}_2$ as the second-bed catalyst.

as promoter to ZrO_2 , or alternatively, if ZrO_2 could function as a good support for the redox pair $\text{Fe}^{2+}/\text{Fe}^{3+}$. Preliminary results as indicated in Figure 4 showed enhancement of CH_3OH production by the ion pair $\text{Fe}^{3+}/\text{Fe}^{2+}$ supported on ZrO_2 . This indicated that the redox system of $\text{Fe}^{3+}/\text{Fe}^{2+}$ may have come into play for generation of CH_3OH .

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