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**Selective Methane Oxidation Over
Promoted Oxide Catalysts**

**Quarterly Report
December 1993 - February 1994**

**Kamil Klier
Richard G. Herman
János Sárkány
Qun Sun**

April 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
Lehigh University
Bethlehem, Pennsylvania**

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SELECTIVE METHANE OXIDATION OVER PROMOTED OXIDE CATALYSTS

SUMMARY OF PROGRESS

A great deal of experimental research was carried out in previous quarters with sulfate-doped Sr/La₂O₃ catalysts that are very active for the oxidative coupling of methane, e.g. see quarterly technical progress reports 2-4 [1-3]. Data analysis has been continued, and the results are discussed further in this quarterly report. In addition to data analysis, a new postdoctoral research scientist has been employed this quarter to work on this research project, particularly in terms of developing catalysts and processes for switching the product selectivity away from C₂ hydrocarbons and to oxygenates.

Analysis of the catalytic testing data demonstrates that the 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ catalyst is stable at reaction temperatures below 600°C. Even after extensive testing in which reaction parameters such as gas hourly space velocity and temperature were systematically varied, the catalyst exhibited reproducible activity in terms of CH₄ conversion and selectivity to C₂ hydrocarbons.

It is shown that the La₂O₃, Sr/La₂O₃, and SO₄²⁻/Sr/La₂O₃ catalysts exhibit the same correlation between CH₄ conversion and C₂ hydrocarbon selectivity (i.e. as CH₄ conversion increases, the C₂ hydrocarbon selectivity increases) and in ethene/ethane selectivities (≈1/1, especially at higher conversions). This indicates that the mechanism for activating methane on the catalysts is probably the same for all the catalysts. The high C₂ selectivity at high CH₄ conversion appears to be due to the depletion of oxygen at high conversions, and this enhances the driving force toward partial oxidation products. At the same time, the lower levels of CO₂ produced decrease the poisoning effect of carbonate formation on the catalyst.

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 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/La_2O_3 catalyst that is active in the formation of methyl radicals, and therefore of C_2^+ products, can be doped with Lewis acidic oxides or other acidic groups to increase further its activity and selectivity to C_2 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 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 deals with the preparation, testing, and optimization of acidic promoted lanthana-based catalysts for the synthesis of C_2^+ 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

A great deal of experimental research was carried out in previous quarters with sulfate-doped $\text{Sr/La}_2\text{O}_3$ catalysts that are very active for the oxidative coupling of methane, e.g. see quarterly technical progress reports 2-4 [1-3]. Data analysis has been continued, and the results are discussed further in this quarterly report. In addition to data analysis, a new postdoctoral research scientist has been employed this quarter to work on this research project, particularly in terms of developing catalysts and processes for switching the product selectivity away from C_2 hydrocarbons and to oxygenates.

The experimental procedures used to dope the 1 wt% $\text{Sr/La}_2\text{O}_3$ catalyst, obtained from AMOCO Oil Co., with sulfate and to test it for activity and selectivity in converting methane to C_2 products have been described in our earlier reports [1-3].

DATA ANALYSIS AND DISCUSSION

Activity and Selectivity of the $\text{Sr/La}_2\text{O}_3$ -Based Catalysts

It was observed that doping the $\text{Sr/La}_2\text{O}_3$ catalyst with small amounts of sulfate greatly increased the catalytic activity of this catalyst, which already is one of the most active catalysts known for the oxidative coupling of methane. Indeed, the activity was approximately doubled by sulfate doping. Surprisingly, this pronounced promotion was evident at 500°C , as shown in Figure 1 (reproduced from [1] and [4]), which is much lower than the temperatures usually required to achieve oxidative coupling of methane, i.e. $700\text{--}750^\circ\text{C}$.

A large number of La_2O_3 , $\text{Sr/La}_2\text{O}_3$, and $\text{SO}_4^{2-}/\text{Sr/La}_2\text{O}_3$ catalysts were tested during this research. In each case, as the activity increased, the C_2^+ selectivity also increased (shown in Figure 2A). It was observed that at a methane conversion level of 20 mol%, corresponding to approximately complete depletion of the gas phase oxygen in tests with a reactant mixture of $\text{CH}_4/\text{air} = 1/1$, about 50% of the product consisted of C_2 hydrocarbons. As shown in Figure 2B, at the higher conversion levels of methane, the C_2 product was composed of about equal quantities of ethene and ethane, and it can be noted that the correlation in this figure is generated by a tight fit of the data points. These data were obtained over a range of space velocities (GHSV), which further supports the proposal, discussed later, that the conversion level of methane and the availability of oxygen control the product selectivity.

Effects of Reaction Parameters and Stability of the $\text{SO}_4^{2-}/\text{Sr/La}_2\text{O}_3$ Catalyst

Experimental data have been obtained as functions of variations in reaction parameters such as temperature, methane/air reactant ratio, and residence time of the reactants over the catalyst [2,3]. These data have now been further analyzed, and some of the more significant observations are discussed here.

In one particular fairly long-term experiment with the 1 wt% SO_4^{2-} / 1 wt% $\text{Sr/La}_2\text{O}_3$ catalyst, the gas hourly space velocity (GHSV) of the reactant mixture was sequentially decreased and then increased while maintaining a constant temperature, which was following by increasing and then decreasing the reaction temperature while a constant GHSV was maintained. In the first part of this experiment at a constant temperature of 550°C with $\text{CH}_4/\text{air} = 1/1$, it was observed that decreasing the GHSV of the reactant from $\approx 70,000$ $\ell/\text{kg catal/hr}$ to 5,400 $\ell/\text{kg catal/hr}$ resulted in lost of activity (to $\approx 8\%$ CH_4 conversion) and selectivity (to 1 C-mol% C_2), as shown in Figure 3. This observation is contrary to the usual expectation that the conversion should increase with increasing residence time. Upon returning to the original reaction conditions, only $\approx 50\%$ of the activity and selectivity was recovered.

At this point in the experiment, the GHSV was maintained constant at 70,175 $\ell/\text{kg catal/hr}$ and the reaction temperature was increased in small increments to 600°C. As shown in Figure 3, as the temperature was increased from 550 to 585°C, the methane conversion level increased gradually without any significant change in the C_2 hydrocarbon selectivity. However, a sudden jump in both activity and C_2 selectivity was observed as the temperature passed through 585°C. At 590-600°C, the methane conversion level was limited by the depletion of available oxygen, and the activity and selectivity were quite constant at these higher reaction temperatures. Upon subsequently decreasing the temperature from 600°C to the 550°C temperature used to initiate the testing of this catalyst, it was observed that the activity and C_2 selectivity were reproduced, as shown in Figure 3. Thus, no deactivation of this catalyst occurred during this testing sequence, where each testing condition was maintained at steady state for at least 2-4 hr.

These changes in activity and selectivity as functions of reaction conditions appear to be interrelated to the partial pressure of CO_2 over the catalyst. The partial pressure of CO_2 is controlled by the extent of the conversion of CH_4 to products, i.e. C_2 hydrocarbons, CH_2O , CO , and CO_2 , and by the quantity of O_2 available for oxidation reactions. If the supply of reactive oxygen is limited, the formation of partial oxidation products will be enhanced. If the surface area of the catalyst is maintained and if the surface of the catalyst is not poisoned or blocked by surface species, high catalytic activity will be observed.

It is now being established by a number of research groups that basic catalysts are susceptible to carbonate formation on the catalysts and that this carbonate layer can directly affect the resultant catalytic properties. This appears to be surface poisoning by blockage of the active sites, which can be reversed at least under some reaction conditions by decomposition of the carbonate. This appears to be the case here where increasing the reaction temperature to 585°C led to decomposition of surface carbonate and regeneration of the activity of the catalyst, which was accompanied by reaction and depletion of oxygen that resulted in enhanced production of partial oxidation products (C_2 hydrocarbons) and a lower production of CO_2 , resulting in lower carbonate build-up on the catalyst that would suppress the methane conversion activity.

References:

- [1] Klier, K., Herman, R. G., Sárkány, J., and Sun, Q., Quarterly Technical Progress Report DOE/MC/29228-2 (March 1993).
- [2] Klier, K., Herman, R. G., Sárkány, J., and Sun, Q., Quarterly Technical Progress Report DOE/MC/29228-3 (June 1993).
- [3] Klier, K., Herman, R. G., Sárkány, J., and Sun, Q., Quarterly Technical Progress Report DOE/MC/29228-4 (September 1993).
- [4] Sárkány, J., Sun, Q., Herman, R. G., and Klier, K., Preprints, Div. Pet. Chem., ACS., 39(2), 226, (1994).

FIGURE 1

CONVERSION OF METHANE
FROM $\text{CH}_4/\text{AIR} = 1/1$ AT 1 ATM,
GHSV = 70,000 l/kg catal/hr

FIGURE 2. Correlation of (A) the C₂ Selectivity with the Conversion of Methane to Products and (B) the Ethene Selectivity with the Total C₂ Selectivity for the La₂O₃, Sr/La₂O₃, and SO₄²⁻-doped Sr/La₂O₃ Catalysts.

FIGURE 3. Sequences of determining (A) the activity in terms of conversion of methane to products and (B) the C₂ selectivity of the 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ catalyst as the reactant GHSV was varied at 550°C and then reaction temperature was varied at constant GHSV = 70,175 l/kg cat/hr.

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