

"Kinetics and Mechanism of Methane
Oxidative Coupling over Samarium Oxide"

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Introduction

The direct conversion of methane to higher hydrocarbons is a promising process for the chemical utilization of methane, which is a major component of natural gas. Although many metal oxides (1,2) have proven to be active and selective for the direct conversion of methane to form C_2 hydrocarbons, there has been no general agreement on the mechanism of methane coupling. Lunsford and co-workers (3) studied the oxidative coupling of methane over Li/MgO and a series of rare earth oxide catalysts. Their results suggested that methyl radicals are formed during methane activation and the coupling of methyl radicals in the gas-phase is the major route for C_2 hydrocarbons formation. On the other hand, Carreiro and Baerns (4) and Asami *et al.* (5) studied the oxidative coupling of methane over lead oxo-salts and PbO/MgO catalysts, respectively. Their results suggested that ethane is formed from the coupling of adsorbed methyl radicals on the catalysts surface.

In addition, the types of oxygen species used for the activation of methane or for the subsequent reactions of activated methane are not very well defined. Lunsford and co-workers (3) suggested that O^- is responsible for the activation of methane and O^- and/or $O_2(g)$ are used for carbon oxides formation on Li/MgO catalysts. Otsuka and Nakajima (6) suggested that adsorbed O_2 is responsible for the activation of methane and $O_2(g)$ is responsible for the formation of carbon oxides over Sm_2O_3 .

Lo *et al.* (7) studied the adsorption of methanol, methyl iodide and methane over Sb_2O_4/SiO_2 using NMR spectroscopy. They observed the formation of methoxy species over the catalyst surface; this intermediate is the precursor for carbon dioxide formation.

The purpose of the present study is to use samarium oxide as a model catalyst to investigate the mechanism of methane coupling at atmospheric pressure using oxygen as the oxidant.

Experimental Procedure

Catalysts preparation

Samarium oxide (Sm_2O_3) catalysts were prepared from various samarium oxides and salts. Different calcination temperatures were employed also.

- (1) Hydrothermally (HT) treated samarium oxide was prepared by placing Sm_2O_3 (Aldrich 99.9%) in a beaker containing deionized water. Residues obtained after evaporation of the water were calcined at 800°C for 16 h and 800°C for 4 h.
- (2) Samarium oxide was heated to 1100°C for 22 h.
- (3) Samarium nitrate hexahydrate was calcined at 900°C for 1 h.

XRD was used to determine the phases present. Surface areas were determined from BET measurements using N_2 as the adsorbate at 77 K.

Reaction studies

Methane oxidation was studied using a laboratory scale fixed-bed reactor system which could be operated in either flow or pulse modes. The reactor consisted of a 7 mm ID and 19 mm length quartz tubes which act respectively as the pre-heating and catalytic zone of the reactor. The 7 mm ID tube was fused to a 6 mm OD, 1 mm ID capillary quartz tube in order to reduce the extent of post-catalytic reaction giving rise to combustion products.

Blank experiments were performed at a temperature range of 600°C to 775°C with quartz wool placed in the reactor. Catalytic tests and kinetic studies were performed using the flow mode of the reactor system at atmospheric pressure. 0.2 to 0.8 g of catalyst was used, and the flow rate ranged from 100 to 300 cc min^{-1} . Excess CH_4 was used in the reactant mixtures such that $\text{CH}_4/\text{O}_2 \geq 3$. Effluent gases were analyzed using an on-line gas chromatograph with a thermal conductivity detector. CO , O_2 , and CH_4 were analyzed using a molecular sieve 5A column and $\text{O}_2(\text{CO})$, CO_2 , CH_4 , C_2H_6 , C_2H_4 , and H_2O were analyzed using a Porapak Q column. Pulse experiments were performed using the pulse mode of the reactor system at a total flow rate of 25 cc min^{-1} with or without gas-phase oxygen. Pulse experiments using CH_3I or CH_3OH as reactants involved injection of either reactant at the reactor inlet.

Results and Discussion

The XRD powder patterns for the catalysts prepared in this study are shown in Figure 1. The catalyst prepared by hydrothermally treated Sm_2O_3 shows the presence of two phases, B (monoclinic structure) and C (cubic structure) phases (8,9). The C phase was the major component of this catalyst. The catalyst prepared by calcining Sm_2O_3 at 1100°C for 22 h shows the presence of the B phase only, and the catalyst prepared by calcining $\text{Sm}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 900°C for 1 h shows the presence of the C phase only. These results suggested that the phase composition of the catalyst is dependent on the salt used and the calcination temperature employed.

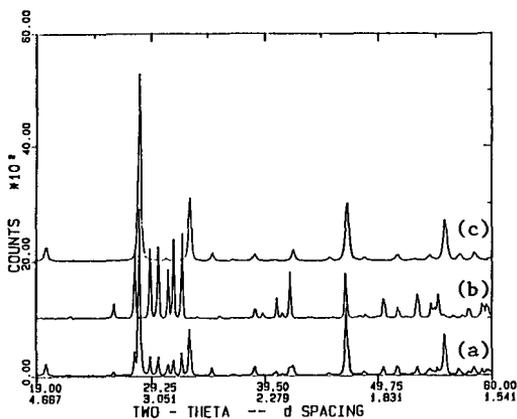


Figure 1. XRD powder patterns of samarium oxide prepared by (a) HT treatment of Sm_2O_3 (B and C phases), (b) Sm_2O_3 calcined at 1100°C for 22 h (B phase), (c) $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ calcined at 900°C for 1 h (C phase).

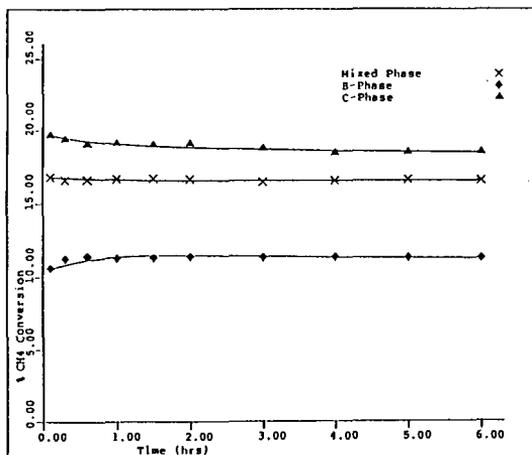


Figure 2. Time dependence on methane conversion over Sm_2O_3 catalysts prepared in this study at 750°C , $\text{CH}_4/\text{O}_2/\text{He} = 58/12/115$.

Blank experiments revealed that the conversion of methane was less than 1% with carbon oxides being the only products. This suggests that the reaction of methane over samarium oxide is surface initiated.

Table 1 shows the activity of methane coupling over untreated (used as obtained from Aldrich Chemical Co.) and hydrothermally treated Sm_2O_3 at steady state. The conversion of methane are practically the same for both catalysts. In addition, although the selectivity to CO is higher for the untreated catalyst, the total yield to carbon oxides and to C_2 hydrocarbons are constant for both catalysts. These data suggest that the two catalysts behave quite similar towards methane coupling. One possible explanation to this similarity is that the untreated catalyst has been on stream ($\text{CH}_4/\text{O}_2 = 3$) for several hours at 700°C . During this time period, the catalyst is continually exposed to water.

Figure 2 shows the conversion of methane over the three Sm_2O_3 catalysts prepared in the present study. Among the three catalysts tested, C-phase Sm_2O_3 is the most active and B-phase Sm_2O_3 is the least active for methane coupling. Figure 3 shows the selectivity to C_2 hydrocarbons over the three catalysts prepared. This figure shows that the HT-treated Sm_2O_3 catalyst gives the highest C_2 selectivity and B-phase Sm_2O_3 gives the lowest C_2 selectivity. In conclusion, C-phase Sm_2O_3 and HT-treated Sm_2O_3 catalysts show a similar C_2 yield for methane coupling. Since most methane coupling studies over Sm_2O_3 catalysts employ mixed phase Sm_2O_3 (B and C phases). The present study will employ HT-treated Sm_2O_3 , which consists of B and C phases, as the test catalyst for kinetic and mechanism study.

Figure 4 shows the effect of CH_4/O_2 ratio on methane conversion and product distribution for methane coupling over Sm_2O_3 at 750°C . High conversions of methane and high selectivity to carbon dioxide are obtained at low CH_4/O_2 ratios. On the other hand, high CH_4/O_2 ratios favor the formation of C_2H_6 in the expense of methane conversion.

Figure 5 shows the activity of methane coupling as a function of CH_4/O_2 time on stream over HT-treated Sm_2O_3 . No appreciable changes in either CH_4 conversion or product selectivities are observed after the catalyst has been used for 20 h. This suggests that the present Sm_2O_3 catalyst is much more stable than the other unpromoted low melting metal oxides (such as lead oxide) in which catalyst deactivation due to catalyst volatility is a serious problem.

Rate laws of the form:

$$\frac{d[\text{product}]}{dt} = k[\text{CH}_4]^m[\text{O}_2]^n$$

were determined for the formation of the principal products (CO , CO_2 and C_2H_6) in kinetic studies. Nonintegral reaction orders in both methane and oxygen were obtained for the formation of CO and C_2H_6 . These results suggest that the rate-determining step for C_2H_6 formation is the reaction between methane and adsorbed oxygen (0.9 order in CH_4 and 0.6 order in O_2

Table I. Activity of methane coupling over untreated and hydrothermally treated Sm_2O_3 at 700°C , $\text{CH}_4/\text{O}_2 = 3$.

Catalysts	% CH_4 Conversion	% Selectivity			
		CO	CO_2	C_2H_4	C_2H_6
Untreated Sm_2O_3	21.9	17.1	38.0	20.9	24.0
HT treated Sm_2O_3	21.2	11.7	46.2	19.9	22.2

Table II. Product distribution of methane coupling over Sm_2O_3 as a function of the # of the pulse at 800°C , $\text{O}_2/\text{CH}_4/\text{He} = 2-0/5-7/130$ with 0.4 g of catalyst.

# of pulse	Rate of product formation ($\mu\text{mole}/\text{min g}$)			
	CO	CO_2	C_2H_6	C_2H_4
1	17.2	101.1	6.8	14.6
2	19.7	90.9	6.7	14.0
3	17.2	87.7	6.4	13.8
4 ^a	--	--	--	--
5	10.7	79.9	4.5	13.1
6	9.8	56.4	3.8	11.0
7	13.5	42.2	3.2	11.0
8	23.2	38.9	2.7	10.6
9	24.9	37.2	2.2	8.9
10	21.4	27.9	3.0	8.9
reoxidation, 11 (20 cc) ^b	22.2	104.8	6.9	13.3
reoxidation, 12 (10 cc)	21.5	70.9	7.2	13.1
reoxidation, 13 (5 cc)	20.9	46.9	6.8	9.1

^aMolecular sieve 5A column was used to analyze the products formed from this pulse experiment to determine whether all O_2 are consumed during this pulse. It was found that all O_2 are consumed during all pulse experiments.

^bReoxidation was done by passing O_2 pulses through the catalyst until no O_2 uptake has taken place, the value in the parenthesis reflects the flow rate of oxygen used during pulse exit.

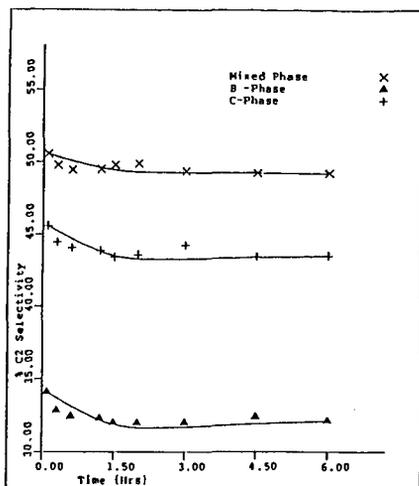


Figure 3. Time dependence on C₂ hydrocarbons selectivity over Sm₂O₃ catalysts prepared in this study at 750°C, CH₄/O₂/He = 2³ 58/12/115.

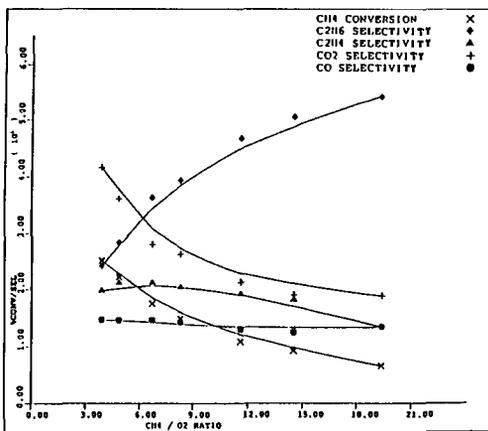


Figure 4. Effect of CH₄/O₂ ratio on methane coupling over HT treated Sm₂O₃ (B + C phases) at 750°C, total flow = 174 cc min⁻¹.

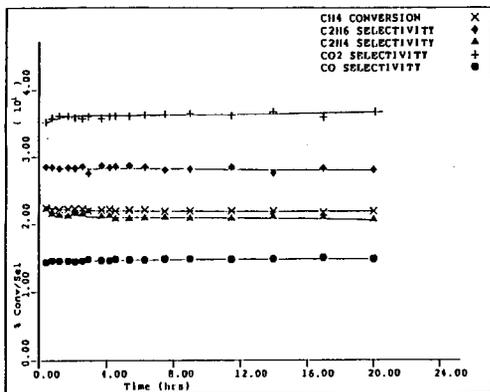


Figure 5. Time dependence on methane coupling over HT treated Sm_2O_3 (B + C phases) at 750°C , $\text{CH}_4/\text{O}_2/\text{He} = 58/12/115$.

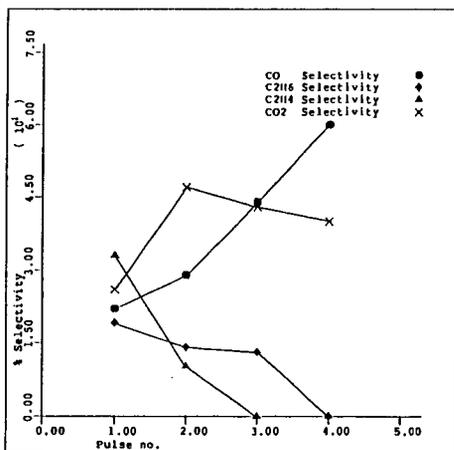


Figure 6. Product distribution in pulsed conversion of methane over HT treated Sm_2O_3 at 800°C in the absence of oxygen. Pulse size = 0.5 mL , $\text{CH}_4/\text{He} = 57/130$.

for a CH_4/O_2 ratio ranging from 4.5 to 18). Rate dependences for CO_2 formation were first order in oxygen and a negative order in methane. This suggests that gas-phase oxygen or adsorbed molecular oxygen (or both) are used for CO_2 formation. In addition, the inhibition effect of CH_4 , as indicated by the negative order, may be one reason why a 93% selectivity to C_2 hydrocarbons is obtained at very high CH_4/O_2 ratios, i.e., $\text{CH}_4/\text{O}_2 = 45$ (2).

The types of oxygen used for methane activation as well as the subsequent reactions of activated methane was investigated by using the pulse reaction studies. Figure 6 shows the product distribution obtained for the pulse reaction with CH_4 as the only reactant. Consecutive CH_4 pulses led to an immediate decrease in the formation of both C_2H_6 and C_2H_4 . No C_2H_4 is observed after the second pulse and no C_2H_6 is observed after three pulses. The total amount of oxygen used for the formation of oxygenates during the first three pulses is less than one monolayer of oxygen (assuming an oxygen packing density of 1×10^{19} atoms/ m^2). This suggests that only surface oxygen species are used for the formation of C_2 hydrocarbons. This result is in good agreement with the kinetic data in which the rate-determining step for C_2H_6 formation is found to be the reaction between gaseous methane and adsorbed monoatomic oxygen. This also suggests that the mobility of bulk oxygen to the surface is slow compared with the rate of C_2H_6 formation.

Table II provides the product distribution for the pulse experiments performed by co-feeding methane and oxygen ($\text{CH}_4/\text{O}_2/\text{He} = 5.7/2/13$) to the reactor. Despite the fact that a high O_2/CH_4 ratio was used, the rate of products formation declined as the pulse experiment progressed. This suggests that adsorbed oxygen species is involved in the formation of products. If only gas-phase oxygen were required we would expect to observe a constant rate of product formation.

The results also show that the decrease in the rate of CO_2 formation is much faster than the rate of the replenishment of oxygen species on the surface of the catalyst. This result is in good agreement with the kinetic data in which the rate of CO_2 formation is reoxidation limited.

The rate of formation of C_2H_6 and C_2H_4 also decreased as the pulse number increased, but to a lesser extent compared to the decrease in the rate of CO_2 formation. However, when the catalyst is reoxidized with O_2 prior to CH_4/O_2 pulses, the rate of C_2H_6 formation is independent to the partial pressure of oxygen in the reactant (pulses #11 to 13). This indicates that the catalyst is partially reduced at steady state since a partial dependency on O_2 partial pressure is observed in kinetic studies.

In addition, since the replenishment of oxygen species for CO_2 formation is slow and is the rate-determining step for CO_2 formation, suppression in this replenishment of oxygen species may lead to an increase in C_2 yield. This also explains why a 93% in C_2 selectivity is obtained by Otsuka et al. (2) when $\text{CH}_4/\text{O}_2 = 45$ was used. In such experiments, replenishment of surface oxygen for CO_2 formation is suppressed.

It is generally accepted that the breaking of a C-H bond of methane is the rate-determining step in methane coupling. As a result, methyl radical or radical-like intermediates are formed. The details on the subsequent steps of these intermediates are not very clear yet. The use of methanol or methyl iodide as reactants, in conjunction with the pulse technique, has permitted the subsequent steps following methane activation to be probed. The major products formed from methanol and methyl iodide are methane, carbon dioxide and carbon monoxide. Less than 10% of C₂ hydrocarbons are formed in both reactions. These results suggest that methoxy species is a common intermediate formed from both methanol and methyl iodide, as well as methane. This methoxy species will form either carbon oxides or methane, plus ethane in cases where methane is the reactant, depending on the availability of surface oxygen. Since less than 10% of C₂ hydrocarbon are formed, it seems reasonable to conclude that the coupling of gas-phase methyl radical is a major pathway for ethane formation during methane coupling.

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