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Selective oxidation of methane to formaldehyde and C_2 hydrocarbons over double layered Sr/La_2O_3 and MoO_3/SiO_2 catalyst bed

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A double layered catalyst bed of Sr/La_2O_3 followed by MoO_3/SiO_2 has been used to produce C_2 hydrocarbons and formaldehyde from a CH_4/air mixture with a formaldehyde space time yield of 187 g (kg cat)$^{-1}$ h^{-1}, which is significantly higher than those yields obtained with single bed catalysts or with mechanically mixed catalyst bed at ambient pressure and 630°C.

Keywords: Methane; oxidation coupling; formaldehyde; strontium/lanthanum oxide; hydrocarbons

1. Introduction

Due to abundant natural gas reserves, there has been an intense interest in converting methane, the major component of natural gas, to more valuable products consisting of C_2 hydrocarbons (C_2H_4, C_2H_6) [1] and oxygenates (CH_2O, CH_3OH) [2] via partial oxidation. The latter is a far more challenging goal for heterogeneous catalysis. Among the most active coupling catalysts so far are redox metal oxides, e.g., those of Sn, Pb, Sb, Bi, and Mn [3], alkali or alkaline earth promoted MnO_x/SiO_2 catalysts [4], and other alkali- or alkaline earth-doped metal oxides, such as Li/MgO, Li/Sm_2O_3, $LiNiO_2$, and Sr/La_2O_3 [1,5]. For the partial oxidation of CH_4 to oxygenates, the most selective catalysts are $FeMoO_4$ [6], those containing MoO_3 or V_2O_5 [7], and ternary Nb–Fe–B oxides [8]. The ZnO catalyst doubly doped with Cu and Fe was also found to be active for oxygenate production [9]. In this communication, we report the results for CH_4 oxidation over a double layered bed of the Sr/La_2O_3 coupling catalyst as the first layer followed by the very selective methane-to-oxygenates MoO_3/SiO_2 catalyst for cogeneration of C_2 hydrocarbons and formaldehyde at high yields.

It has been proposed by Liu et al. [10] that over MoO_3/SiO_2 catalysts, formaldehyde was produced by the decomposition of the surface methoxide species ($^-OCH_3$), which was formed by the reaction of the gas phase $^{\cdot}CH_3$ radicals and active surface oxygen. Mehandru et al. [11] used molecular orbital theory to suggest that methyl radicals can be trapped on the MoO_3 surface and subsequently undergo loss of hydrogen to form formaldehyde [12]. However, it was known that MoO_3/SiO_2 was not a very active catalyst for $^{\cdot}CH_3$ generation and the formaldehyde space time yield was quite low [2]. On the other hand, Sr/La_2O_3 is one of the best catalysts for the production of $^{\cdot}CH_3$ radicals and a poor catalyst for trapping the radicals on the surface [13]. Thus, a double layered catalyst bed with Sr/La_2O_3 closer to the reactor inlet to generate the $^{\cdot}CH_3$ radicals and the high surface area MoO_3/SiO_2 downflow of the first layer of the bed to trap the radicals was expected to yield formaldehyde with much higher space time yield than that from the individual catalysts, as is indeed shown in this paper. In a parallel reaction, the $^{\cdot}CH_3$ radicals also recombine in the gas phase to form C_2 hydrocarbons.

2. Experimental

The 1 wt% Sr/La_2O_3 catalyst with a surface area of 6.5 m^2/g was distributed by AMOCO Oil Co. under their Natural Gas University Research Program, and the C_2 productivities and activities for this catalyst have been reproduced in several laboratories. The 2 wt% MoO_3/SiO_2 catalyst was prepared by aqueous impregnation of Cabosil silica with ammonium heptamolybdate. After impregnation, the catalyst was partially dried at room temperature overnight, followed by drying overnight at 120°C and calcination at 500°C for 2 h under flowing dry air. This catalyst had a surface area of 280 m^2/g. Catalytic testing was carried out in the temperature range of 525–665°C in a fixed-bed continuous-flow 9 mm o.d. (7 mm i.d.) quartz reactor with 0.100–0.125 g of catalyst. A standard reactant mixture of CH_4–air (1.5 : 1) with a gas hourly space velocity (GHSV) of 70000 or 105000 dm^3 (STP) $(kg\ cat)^{-1}\ h^{-1}$ at ambient pressure was used. These reaction conditions, which are typical for oxidative coupling studies, were chosen because of the extremely high activity of the Sr/La_2O_3 catalyst. The principal products observed by on-line sampling using gas chromatography were CO_2, C_2 $(C_2H_6+C_2H_4)$, C_3 $(C_3H_8+C_3H_6)$, CO and H_2O. Formaldehyde was condensed with two water scrubbers and quantitatively determined by iodometric titration [14], which has been well established as a reliable method for determining small amounts of formaldehyde in aqueous solutions. In the present research, the carbon mass balance was always better than 90% and usually better than 95%.

3. Results and discussion

Table 1 gives the results for the catalytic oxidation of methane over the single MoO_3/SiO_2 catalyst and the double layered Sr/La_2O_3 followed by the MoO_3/SiO_2 catalyst bed. The conversions of methane over the MoO_3/SiO_2 catalyst were low throughout the temperature range used in this experiment. The product was almost exclusively formaldehyde at those conversion levels. Both methane conversion and formaldehyde space time yield increased dramatically when a small amount of Sr/La_2O_3 was placed upstream from the MoO_3/SiO_2 catalyst. The formaldehyde yield obtained at 630°C was 129 g (kg cat)$^{-1}$ h^{-1}, which is more than three times that of the MoO_3/SiO_2 catalyst at the same reaction conditions. Even though this is an encouraging formaldehyde space time yield, the formaldehyde yield expressed as the product of methane conversion times selectivity is still quite low. The formaldehyde selectivity as well as the yield can be improved by changing the reaction conditions, such as increasing the space velocity (table 2). The higher space velocity drives more methyl radicals from the Sr/La_2O_3 layer to the following MoO_3/SiO_2 layer,

Table 1
Methane conversion, formaldehyde space time yields, and product selectivities over the MoO_3/SiO_2 and double layered Sr/La_2O_3 followed by MoO_3/SiO_2 catalyst with CH_4–air (1.5:1) reactant at ambient pressure and gas hourly space velocity = 70000 dm^3 (kg cat)$^{-1}$ h^{-1}

T (°C)	CH_4 conv. [a]	CH_2O yield [b]	Selectivities [c]				
			CH_2O	C_2	C_3	CO_2	CO
2 wt% MoO_3/SiO_2 (0.100 g)							
525	< 0.01	2.1	100	–	–	–	–
560	< 0.01	4.4	100	–	–	–	–
595	0.02	10.8	100	–	–	–	–
630	0.08	37.9	100	–	–	–	–
665	0.24	39.7	31.5	63.0	–	5.5	–
double bed 1 wt% Sr/La_2O_3 (0.025 g)/2 wt% MoO_3/SiO_2 (0.100 g)							
525	0.4	2.3	1.0	11.5	–	74.0	13.5
560	3.1	18.8	1.3	14.1	0.9	51.0	32.8
595	5.4	62.1	2.4	23.3	2.3	43.1	28.9
630	8.2	129.0	3.3	38.7	1.2	33.5	23.2
665	11.3	52.4	1.0	50.5	2.9	27.4	18.3

[a] Total methane conversion, mol%.
[b] Space time yield of formaldehyde, g (kg cat)$^{-1}$ h^{-1}.
[c] Selectivities are given in carbon atom%.

Table 2
Methane conversion, formaldehyde space time yields, and product selectivities over the double layered Sr/La_2O_3 (0.025 g) followed by MoO_3/SiO_2 (0.100 g) catalyst and the mixed catalyst (same composition) with CH_4–air (1.5 : 1) reactant at ambient pressure, 630°C and gas hourly space velocity = 105 000 dm^3 (kg cat)$^{-1}$ h^{-1}

	CH_4 conv. [a]	CH_2O yield [b]	Selectivities [c]				
			CH_2O	C_2	C_3	CO_2	CO
double bed	6.7	186.7	4.1	41.3	0.6	36.7	17.4
mixed bed	9.2	2.1	< 0.1	39.0	0.8	36.8	23.4

[a] Total methane conversion, mol%.
[b] Space time yield of formaldehyde, g (kg cat)$^{-1}$ h^{-1}.
[c] Selectivities are given in carbon atom%.

therefore increases the formaldehyde yield. The highest formaldehyde space time yield obtained in the present study was 187 g (kg cat)$^{-1}$ h^{-1} at 630°C and gas hourly space velocity of 105 000 dm^3 (STP) (kg cat)$^{-1}$ h^{-1}. In addition to formaldehyde, C_2 and C_3 hydrocarbons were also produced. The temperature of 630°C for formaldehyde production is 120°C lower than that utilized to obtain a significant formaldehyde yield of 76 g (kg cat)$^{-1}$ h^{-1} with the earlier investigated Cu–Fe–ZnO catalyst [9].

The results shown in table 1 demonstrate the promotional effect on the conversion of methane and formaldehyde formation by using the combined catalytic bed. Under the relatively mild reaction conditions employed, methane was predominantly activated by the Sr/La_2O_3 catalyst layer, while the MoO_3/SiO_2 catalyst was responsible for the production of formaldehyde because of its high surface area and relatively high reactivity towards $^{\cdot}CH_3$ radicals [15]. Some catalyst deactivation was observed with the dual bed configuration, and the formaldehyde space time yield decreased about 20% after 24 h of reaction at 630°C.

To gain a better understanding of the reactions involved, similar experiments were also performed with a single bed containing well mixed Sr/La_2O_3 and MoO_3/SiO_2 catalysts. The results are given in table 2, which shows that the formaldehyde space time yield is much lower than that observed with the MoO_3/SiO_2 catalyst or the double bed Sr/La_2O_3–MoO_3/SiO_2 system (table 1). Even though formaldehyde could be formed over the mixed bed catalyst, it would react in the $^{\cdot}CH_3$ radical rich environment to form CO. At the same time, depletion of the $^{\cdot}CH_3$ radicals would reduce the C_2 hydrocarbon yields [16], as was observed experimentally (table 2). The pure Sr/La_2O_3 catalyst was tested at ambient pressure, 630°C and gas hourly space velocity of 70 000 dm^3 (STP) (kg cat)$^{-1}$ h^{-1}, and there was no detectable amount of formaldehyde observed in the products. Comparison tests for methane activation over the pure SiO_2 (Cabosil) support and over a double layered bed of Sr/La_2O_3 followed by

Table 3
Methane conversion, formaldehyde space time yields, and product selectivities over the pure SiO_2 (Cabosil) catalyst and the double layered Sr/La_2O_3 (0.025 g) followed by SiO_2 (Cabosil) (0.100 g) catalyst with CH_4–air (1.5 : 1) reactant at ambient pressure, 630°C and gas hourly space velocity = 70000 dm^3 (kg cat)$^{-1}$ h^{-1}

	CH_4 conv. [a]	CH_2O yield [b]	Selectivities [c]				
			CH_2O	C_2	C_3	CO_2	CO
SiO_2 (Cabosil)	0.05	24.3	≈ 100	–	–	–	–
double bed	15.00	12.5	0.2	52.3	1.0	26.0	20.5

[a] Total methane conversion, mol%.

[b] Space time yield of formaldehyde, g (kg cat)$^{-1}$ h^{-1}.

[c] Selectivities are given in carbon atom%.

the unpromoted SiO_2 support were also performed under the same conditions as that of pure Sr/La_2O_3 experiment (table 3). It is evident that the SiO_2 support had a somewhat lower activity, and formaldehyde yield, for methane oxidation than that of the supported MoO_3/SiO_2 catalyst (table 1) under the reaction conditions employed. With the $(Sr/La_2O_3)/SiO_2$ double bed system (table 3), much lower formaldehyde selectivity and yield were observed than with the $(Sr/La_2O_3)/(MoO_3/SiO_2)$ double catalyst bed (table 1). Thus, the pure SiO_2 support could not effectively trap the $^{\cdot}CH_3$ radicals and convert them to formaldehyde. There is no detectable amount of formaldehyde and no methane conversion has been observed in the blank test with the reactor filled with quartz wool under the reaction conditions employed in the SiO_2 test.

4. Conclusions

The configuration of the dual component catalyst bed, consisting of Sr/La_2O_3 followed by MoO_3/SiO_2, is critical in its functioning for the selective oxidation of methane to formaldehyde. These experiments support the proposal that the formation of formaldehyde occurs on the MoO_3/SiO_2 catalyst surface rather than in the gas phase.

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