

Effective and stable CeO₂-W-Mn/SiO₂ catalyst for methane oxidation to ethylene and ethane

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ABSTRACT

CeO₂-W-Mn/SiO₂ catalyst is found to be effective for the oxidative coupling of methane (OCM); ca. 30 % of C₂+ and 22 % of C₂H₄ yields have been obtained in single pass at 800 °C. During the 500 h continuous reaction, no significant decrease of activity and selectivity is observed.

Keywords: OCM, CeO₂-W-Mn/SiO₂, stability

1. Introduction

A number of strategies have been explored and developed for the conversion of methane to more useful chemicals and fuels.¹⁻⁶ But to date, no direct processes have progressed to a commercial stage due to generally small product yields operating in a single-pass mode. For the oxidative coupling of methane (OCM), as one of the more promising direct methods for the chemical utilization of methane, the conversions and selectivities obtainable are such that C₂+ (ethane + ethylene) yields are generally < 25%.⁷ Nevertheless, the strategic implications of being able to use natural gas as a feedstock continue to provide an incentive to develop the OCM process. The essential way is to explore effective and stable catalysts to improve C₂+ yields or, as an alternative, to enhance the ultimate C-efficiencies of methane conversion.

Here, CeO₂-Na₂WO₄-Mn/SiO₂ catalyst has been investigated for the OCM reaction and the results show that CeO₂-Na₂WO₄-Mn/SiO₂ has good stability and can obtain a high C₂ yield of OCM reaction.

2. Experimental

The CeO₂ modified 5% Na₂WO₄-2% Mn/SiO₂ catalysts were prepared by wet impregnation method. The catalysts were prepared on silica particles (40-55 Mesh) provided by Qindao Ocean Chemical Plant with a surface area of 156 m²/g. The catalysts were prepared by incipient wetness impregnation method with Mn(NO₃)₂, Na₂WO₄•2H₂O and Ce(NO₃)₃•6H₂O respectively. The impregnated silica particles were then evaporated to dryness overnight at 120 °C and calcinated in air at 850 °C for 8 hrs (the surface area of the resulting catalyst = 6.8 m²/g). Herein, the amounts of the various components were expressed in wt.%.

The catalytic runs were carried out in the integral mode using a fixed-bed vertical-flow reactor constructed from a quartz tube at ambient pressure. The fresh catalyst of 1.0 g was loaded in the reactor and the length of the catalyst bed was approximately 12 mm. Quartz chips were placed above and below the catalyst bed to preheat the reagents and also to decrease the free volume. In experiments, the reactant gases were co-fed into the reactor. At the reactor outlet a cold trap was used to remove water from the exit gas stream. Blank runs with quartz chips showed negligible conversion at the reaction conditions. The reaction products were then analyzed with an on-line gas chromatograph equipped with a TCD, using a Poropak Q column for the separation of CH₄, CO₂, C₂H₄, and C₂H₆, and a molecular-sieve 5A column for the separation of H₂, O₂, CH₄, and CO.

3. Results and discussion

The performance of CeO₂-Na₂WO₄-Mn/SiO₂ catalyst for the OCM reaction was examined by presence different diluents in reactant gases and the results were presented in Table 1. With addition of steam as diluent, obvious effect to increase CH₄ conversion and C₂+ selectivity for CeO₂-W-Mn/SiO₂ catalysts was observed. CH₄ conversion and C₂+ selectivity increased from 43.4 to 47.8 % and 47.5 to 61.8 %. As the results, at 800 °C, methane GHSV = 6667 ml·g⁻¹·h⁻¹, CH₄/O₂/H₂O = 2/1/5, C₂+ and C₂H₄ yields reached at 29.6 % and 21.6 % respectively. Because the deep oxidation of hydrocarbon was usually attribute to gas oxygen in OCM reaction, CO_x selectivity decreased with decreasing of O₂ conversion after the steam addition. A possible explanation is that steam can act as a gas phase radical trap, and can interrupt the chain reaction of methane combustion to CO_x, just as the case of a CaNiK catalyst.⁸

He and N₂ as diluents were also investigated to compare with steam for the OCM reaction over CeO₂-W-Mn/SiO₂ catalyst. The comparative results of different diluents at the same reaction condition were listed in Table 1. The

addition of He and N₂, to some extent, resulted in higher C₂⁺ selectivity and lower CO_x selectivity. This can be explained by the fact that the formation of ethylene and ethane are of a lower reaction order than the production of carbon oxides.⁹ However, generally speaking, the positive functions of He and N₂ were inferior to that of steam. Because of He and N₂ were much inerte than steam under OCM reaction conditions, it was expectable that the addition of steam to the gas feed had taken out thermal by reaction because H₂O has higher thermal capacity. Moreover, an important incentive for the use of steam as diluent is that almost all of the steam will condense in the quench step following the catalytic reactor and will not have to be handled in the downstream compression and separation systems.

Table 1. Comparison of catalytic performances of CeO₂-W-Mn/SiO₂ catalyst for OCM reaction with addition of different diluents.¹

Diluents	Conversion. %		Selectivity %				Yield %	
	O ₂	CH ₄	C ₂ ⁺	C ₂ H ₄	CO ₂	CO	C ₂	C ₂ H ₄
No diluent	99.3	43.4	47.5	33.2	34.9	17.5	20.6	14.4
Steam	96.6	47.8	61.8	45.1	19.4	18.8	29.6	21.6
He	99.9	46.1	54.0	37.5	32.5	13.5	24.9	17.3
N ₂	99.6	43.2	53.3	36.6	29.5	17.2	23.0	15.8

¹Reaction conditions: methane GHSV=6667 ml •g⁻¹•h⁻¹, CH₄/O₂/diluent =2 /1/5, T=800 °C

Table 2 shows the influence of varying ratio of CH₄/O₂ for OCM reaction over CeO₂-W-Mn/SiO₂ catalysts at 800 °C, methane GHSV = 6667 ml•g⁻¹•h⁻¹, steam/CH₄ = 2.5/1. With the increase of CH₄/O₂ ratio, C₂ selectivity increased and CO_x selectivity decreased, accompanying that CH₄ and O₂ conversions decreased sharply. It suggested that gas phase oxygen played a key role in the oxidation of methane and C₂ hydrocarbons to CO_x. At a CH₄/O₂ of 4, the C₂⁺ selectivity increased to 74.4% with 30.0% CH₄ conversion, which is desirable from the practical viewpoint. Although a higher CH₄/O₂ was beneficial to high C₂⁺ selectivity, C₂⁺ yield was dropped by the decrease of CH₄ conversion. Achieved the highest yield was at the point of nearly total exhaustion of the oxygen supply. This observation agrees with experimental observations reported by a number of researchers.^{10,11}

With steam as diluent for OCM reaction, one could easily consider that the steam would accelerate the loss of active phases during long reaction period and

hence be deleterious to the stability of catalyst. So a 500h stability test over CeO₂-W-Mn/SiO₂ catalyst has been carried out in a 10ml fixed-bed quartz reactor. As described above, lower CH₄/O₂ can obtained high yield of C₂+ hydrocarbon but also decrease the C₂ selectivity. So, in long-term stability test, the reaction conditions were chosen with 800°C, methane GHSV = 6667 ml·g⁻¹·h⁻¹ and CH₄/O₂/H₂O = 4/1/4.

Table 2. The effect of CH₄/O₂ ratio for OCM reaction over Ce-W-Mn/SiO₂ catalyst¹

CH ₄ /O ₂	Conversion. %		Selectivity %				Yield %	
	O ₂	CH ₄	C ₂ +	C ₂ H ₄	CO ₂	CO	C ₂	C ₂ H ₄
2	96.6	47.8	61.8	45.1	19.4	18.8	29.6	21.6
4	83.2	30.0	74.4	47.6	12.4	13.2	22.3	14.3
6	51.5	22.2	75.6	43.6	11.4	13.0	16.8	9.7

¹Reaction conditions: methane GHSV=6667 ml·g⁻¹·h⁻¹, steam/O₂=2.5/1, T=800 °C

Figure. 1 shows that, during 500h period continuous reaction without recharging the catalyst, CeO₂-W-Mn/SiO₂ catalyst remained fairly stable for OCM reaction. The C₂+ selectivity was stabilized at about 70% and the best CH₄ conversion reached 30-31% during the initial several days. The decrease of C₂ and C₂H₄ yield was mainly due to the methane conversion decreased slightly. It was interesting that the CO selectivity increased with time on stream. The sum of C₂+ and CO selectivity remained at 95%, and the CO₂ selectivity decreased from 10% to 5% at 500 h on stream. Unexpectedly H₂ began to form after 116h and the yield of H₂ maintained in the range of 3.2-4.8% on stream. H₂ can be formed via many of possible pathways. H₂ produced with the increase of CO selectivity and the decrease of CO₂ selectivity, which indicated that water-gas shift reaction was not a major pathway for the production of H₂. By the analysis of product distribution, the H₂: CO ratios lay in between about 0.4 to 1, which suggested that hydrogen was probably produced mainly via CO₂ reforming reactions or partial oxidation reactions, but steam reforming reactions was not important. Among methane, ethane and ethylene, it is generally known that methane is much less reactive than the others and the reactivity of ethane is comparable to that of ethylene^{12,13}. Therefore, the major reactions for the production of H₂ over Ce-W-Mn/SiO₂ catalyst can be said to be the CO₂ reforming and partial oxidation of ethane and ethylene. This explanation can be exactly consistent with the results shown in Fig. 1 that the production of H₂ was

accompanied with the decreases of C₂ and CO₂ selectivity and the increase of CO selectivity. Although the addition of steam improved the performance of Ce-W-Mn/SiO₂ for OCM reaction, one could easily consider that the steam would accelerate the loss of active phases during long reaction period and hence be deleterious to the stability of catalyst.

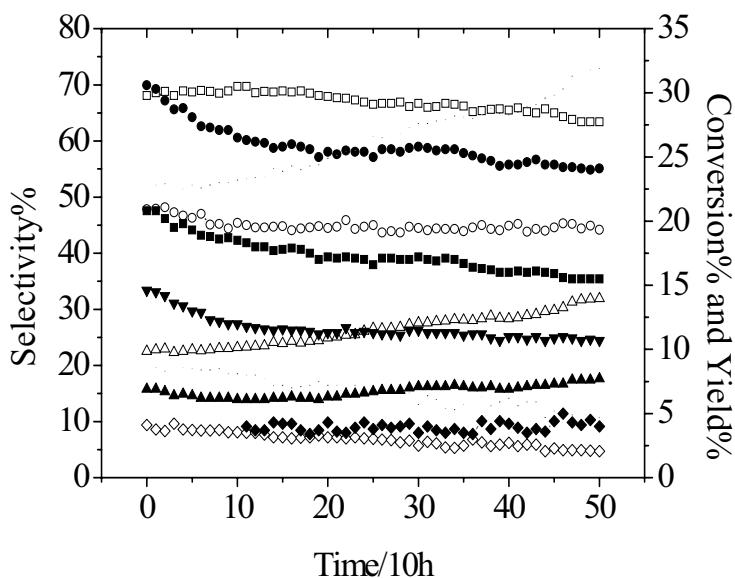


Figure. 1. 500h stability test over 10 ml CeO_2 -W-Mn/SiO₂ catalyst at methane GHSV=6667 ml · g⁻¹ · h⁻¹, CH₄/O₂/steam=4/1/4, T=800 °C. Conversion: (●) CH₄; Selectivity: (□) C₂+, (○) C₂H₄, (◇) CO₂, (Δ) CO; Yield: (●) C₂, (■) C₂H₄; (▼) CO₂, (▲) CO, (◆) H₂.

4. Conclusion

In summary, CeO_2 -W-Mn/SiO₂ catalyst has been found to exhibit not only excellent catalytic performance for the oxidative coupling of methane but also excellent stability in long-term reaction. The best C₂ and C₂H₄ yields reached at nearly 30 % and 22 % in single pass respectively. Nevertheless, further work is in progress to elucidate the nature of CeO_2 -W-Mn/SiO₂ catalyst through catalyst characterization and carry out reaction on larger experimental scales.

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